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Establishing a Rigid Strongly π -donating Bisphosphinimide Ligand Framework to Demonstrate
Reversible Four-Electron Oxidative Addition of an N=N Double Bond at a Single Chromium
Center

By

Paul Rathke

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

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Professor Jonathan Rittle, Chair

Professor Polly Arnold

Professor Alexander Katz

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Abstract

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Doctor of Philosophy in Chemistry

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Professor Jonathan Rittle, Chair

Chapter 1 Introduction

Chapter 2 Isocyanide Activation by Phosphinimide-Ligated Cr(II) Centers

This report describes the synthesis and reactivity of a heteroleptic phosphinimide/phosphinimine Cr(II) complex HL'CrAdHMDS, which was obtained by incomplete protonolysis of Cr(HMDS)₂(THF)₂ in the presence of the bisphosphinimine pro-ligand H₂L'Ad. Addition of common ligands such as N-heterocyclic carbenes and isocyanides displaces the remaining HMDS ligand concomitant with complete deprotonation of the phosphinimine pro-ligand furnishing three- and four-coordinated complexes respectively. The resulting tetrahedral chromium(II) bis(isocyanide) species was found to adopt an unusual $S = 1$ spin state at room temperature. Under certain reaction conditions, one coordinated isocyanide ligand was found to insert into a chromium-phosphinimide bond. The described compounds are characterized by single-crystal X-ray diffraction and solution-phase spectroscopy and the mechanism for isocyanide insertion was investigated by DFT calculations.

Chapter 3 Four-Electron Oxidative Addition of an N=N Double Bond at a Chromium Metallocyclopropene

This report describes the synthesis of a pseudo-tetrahedral chromium alkyne complex supported by a bidentate phosphinimide ligand and its reactivity with azobenzene. Characterization of the former by structural and computational methods reveals an unprecedented extent of alkyne activation by a formal chromium(II) center, suggesting that this complex is best described as a chromium(IV)-metallocyclopropene. Exposure of this compound to an azobenzene derivative results in the formation of a chromium(VI) diimido complex, which constitutes a rare 4-electron oxidative addition of an N=N double bond. The isolation of a chromium(IV)-hydrazido

intermediate enabled mechanistic investigations of this challenging bond cleavage process. This work substantiates the notion that terminal phosphinimide ligands can engender first-row transition metal ions with exceptional reactivity.

Chapter 4 Two-electron reactivity between Phthalazines and a Chromium Metallocyclopropene

This report describes the diverging reactivity of two N=N double bond containing phthalazines, namely 5,8-difluorophthalazine and 1,4-diphenylphthalazine, with a bisphosphinimide chromium metallocyclopropene acting as a masked chromium(II) synthon originally envisioned to demonstrate reversible N=N bond cleavage across a single metal center. Addition of 5,8-difluorophthalazine to the chromium synthon did not result in N=N bond cleavage, instead an imino-pinacol coupling of two equivalents of phthalazine atop the chromium center was observed. The desired cleavage was observed when 1,4-diphenylphthalazine, featuring a different substitution pattern to prevent dimerization, was used. Crystallographic structure determination revealed that both 1,4-diphenylphthalazine reacts in a two-electron process forming a bisketimide. Utilizing benzil as a trapping reagent the imino-pinacol coupling of 5,8-difluorophthalazine could be reversed under thermodynamic control.

Chapter 5 Demonstrating Reversible N=N-Bond Cleavage Across a Single Chromium Center

Oxidative addition and reductive elimination of single bonds are fundamental organometallic reactions paramount to numerous catalytic applications of transition metal complexes, however an analogous examples involving double of this reactions featuring the formation and cleavage of double bonds are exceedingly rare individually and a reversible example remains unknown. Discovery of such processes would greatly enhance the toolkit available to organometallic chemists for the development of new catalytic processes. This report describes the reactivity of the N=N double bond containing heterocycle, 2,9-difluorobenzo[c]cinnoline with a bisphosphinimide chromium metallocyclopropene acting as a masked chromium(II) synthon, demonstrating reversible four-electron N=N bond cleavage across a single metal center. Addition of 2,9-difluorobenzo[c]cinnoline to the bisphosphinimide chromium metallocyclopropene lead to the formation of an intermediate, which features 2,9-difluorobenzo[c]cinnoline weakly bound to the chromium center. This intermediate can be converted to the corresponding N-N cleaved product under thermodynamic control in first order. Crystallographic structure determination and spectroscopic analysis revealed that 2,9-difluorobenzo[c]cinnoline reacts in a four-electron process forming the chromium(VI) bisimido complex. Utilizing benzil as a trapping reagent, 2,9-difluorobenzo[c]cinnoline can be displaced from the intermediate and in conjunction with green light the 4-electron oxidative addition of 2,9-difluorobenzo[c]cinnoline could be reversed under photochemical conditions respectively, demonstrating a reversible 4-electron cleavage of a N=N double bond across a single transition metal center.

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Chapter 1 Introduction

Fundamental research into elementary organometallic reactions lies at the forefront of new catalytic processes. For example, the reversible addition of dihydrogen^{1,2} and dioxygen³ by Vaska's complex⁴ ($\text{IrCl}(\text{CO})[\text{PPh}_3]_2$), described following its first report in 1961, helped to establish the concepts of two-electron oxidative addition, oxidative ligation as well as reductive elimination—seminal concepts, which lie at the core of countless catalytic reactions, featuring prominently across contemporary organometallic chemistry (Figure 1-1).

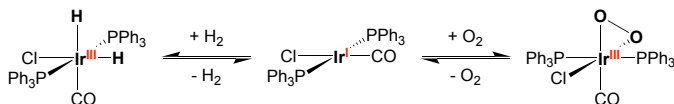


Figure 1-1 Reversible oxidative addition of dihydrogen and reversible oxidative ligation of dioxygen by Vaska's complex

One might naturally ask a deceptively simple question, related to this system: Can this two-electron reactivity encompassing oxidative addition and reductive elimination of non-polar bonds be translated to four-electron processes making and breaking double bonds instead of single bonds across a single transition metal center, ideally in a reversible fashion. Four-electron oxidative addition reactions—wherein a metal center inserts into a double bond—remain rare and the respective reductive elimination process is unknown, which indicated that this problem is best approached from the oxidative addition angle. This area was pioneered by the Mayer group, who utilized a tungsten(II) complex ($\text{WCl}_2(\text{PMe}_2\text{Ph})_4$) that was found to react with cumulated double bonds ($\text{E}=\text{C}=\text{E}'$) in a two-electron process to form tungsten(IV) complexes ($\text{WCl}_2(\text{E})(\text{C}\equiv\text{E}')(\text{PR}_3)_2$).⁵ The former compound was later shown to react with cyclopentanone to form a tungsten(VI)(oxo)(alkylidene) complex $\text{W}(\text{O})(=\text{CR}_2)\text{Cl}_2(\text{PR}_3)_2$, which constitutes the first documented example of a 4-electron oxidative addition.⁶ With regard to nonpolar double bonds, reactions of this class are limited to the four electron reductive cleavage of oxygen^{7–11} and the oxidative addition of $\text{N}=\text{N}$ bonds in azo compounds. Examples of this reaction, mainly involve highly reduced tungsten and uranium complexes.^{12–23} These metals are particularly predisposed to this type of reaction due to their large number of available valence electrons in low oxidation states as well as strong metal ligand bonds in high oxidation states mediated by the large radial extent of their frontier orbitals. However, this in turn renders the return reaction out of reach. At the core of this thesis lies the assumption that if this oxidative reactivity could be translated to chromium²⁴—a 3d metal featuring the same number of valence electrons and one that is significantly more conducive to reductive elimination—the reaction can be rendered reversible.

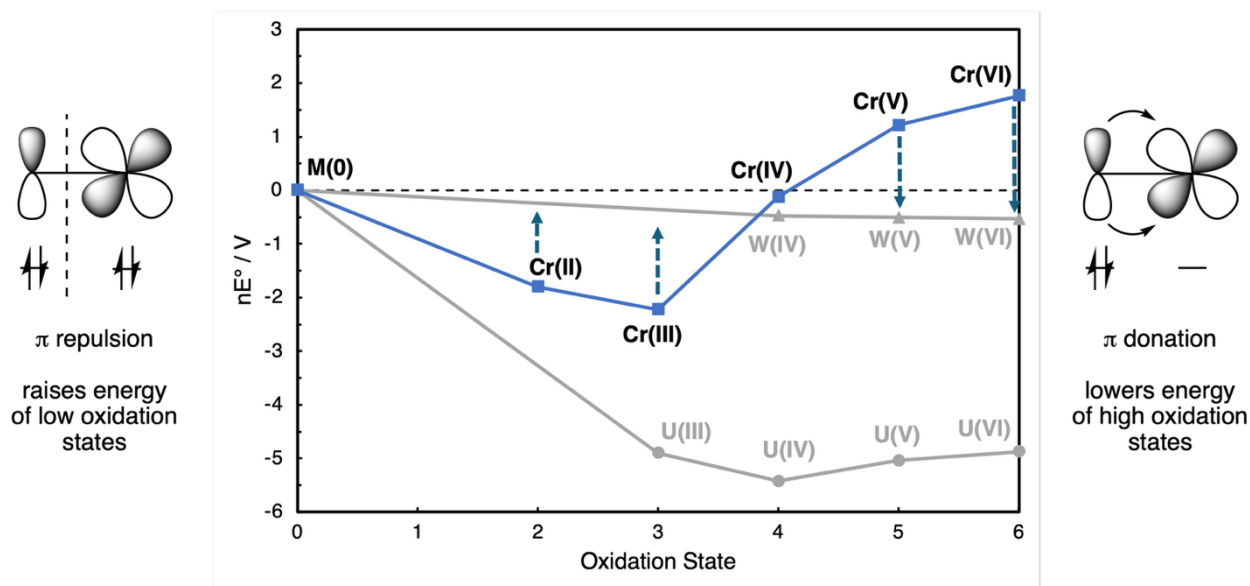


Figure 1-2 Relative stability of the oxidation states of chromium in relation to tungsten and uranium, illustrated by a pH=0 Frost diagram and anticipated effect of applying a highly π -donating ligand framework

However, chromium complexes featuring traditional ligands are not reducing enough to enable the forward reaction, which necessitated the development for a rigid, sterically encumbering and highly π -donating bis phosphinimide ligand framework in order to shift the relative energy of the various oxidation states closer to tungsten (Figure 1-2). Chapter 2 of this thesis outlines the development of this ligand system as well as intricacies in its metalation with chromium, followed by Chapter 3, which demonstrates that this ligand system indeed enables the four-electron oxidative addition of diazines on a single chromium center. Unfortunately, the resulting bis imido proved to be stable to enable the return reaction which led to the investigation of N=N-bond containing heterocycles as potential substrates. Chapter 4 describes the reactivity with phthalazines, which reacted in undesirable two-electron processes, but led to the development of a trapping method that formed the basis for Chapter 5, which ultimately answers the question posed above, not only demonstrating the first four-electron reductive elimination but also reversible oxidative addition of the N=N-bond in 2,9-difluorobenzo[c]cinnoline.

Chapter 2 Isocyanide Activation by Phosphinimide-Ligated Cr(II) Centers

Introduction

Isocyanide ligands are deployed throughout organometallic chemistry as building blocks for novel materials, essential components of radiopharmaceuticals,²⁵ and serve as isoelectronic CO surrogates with tunable steric properties.²⁶ Due to their strong Lewis basicity and moderate π -acidity they strongly interact with a variety of transition metal centers and commonly act as spectator ligands.²⁷ However, they also represent an important class of reactive C1 fragments and prominently feature as substrates for multicomponent reactions, such as the Ugi reaction,²⁸ and transition metal-catalyzed insertion reactions,²⁹ which almost exclusively employ precious 4d-transition metals such as Palladium and Ruthenium.³⁰ There is a widespread interest in replacing organometallic catalysts featuring 4d and 5d transition metals with analogues containing earth-abundant first row transition metals. Since these metals often operate via divergent reaction mechanisms from their heavier congeners^{31–34} their continued investigation is attractive from a standpoint of reaction discovery.

Analogous to their heavier Group VI congeners, most reported chromium isocyanide complexes adopt low spin states, octahedral geometries and are of low-valent nature.³⁵ The coordinated isocyanide ligands in these complexes are typically unreactive, but can undergo photoinduced ligand dissociation. Recently it has been reported that related complexes featuring chelating bisisocyanide ligands are competent photo reductants.³⁶ Salient reports of reactivity of Cr-CNR species (Scheme 1A) include isocyanide oligomerization by metal-metal bonded Chromium complexes,³⁷ isocyanide insertion into Cr-based Fischer carbenes,³⁸ and C-C coupling of cis-oriented CNR ligands upon acid exposure.³⁹ High valent chromium complexes rarely coordinate isocyanides, owing to their low d electron counts that preclude traditional π -backbonding interactions and certain chromium(VI) alkyl⁴⁰ and aryl⁴¹ complexes insert isocyanides generating η^2 -iminoacyl complexes instead. There is also report of carbodiimide formation stemming from the reaction of a Cr(IV) bis alkoxy imido complexes with isocyanides, with limited mechanistic rational.⁴²

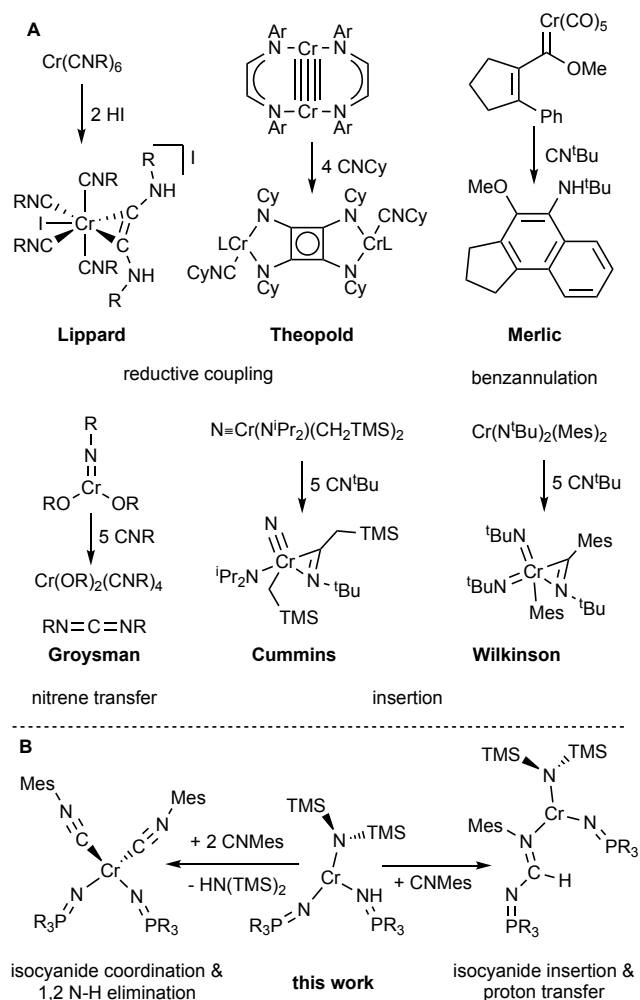


Figure 2-1 (A) Overview of isocyanide transformations mediated by molecular chromium complexes. (B) Work presented in this report.

In an effort to access low-to-mid valent chromium isocyanide complexes, we utilized a previously reported, sterically encumbering bis phosphinimide ligand framework, L'Ad.⁴³ We and others have demonstrated that phosphinimide ligands serve to stabilize a variety of metal ions in unusual oxidation states^{44,45} and spin states.⁴⁶ Furthermore we demonstrated that this specific ligand framework has exceptional ability to activate organic substrates when ligated to chromium.⁴³ We hypothesize that the strongly π -donating nature of the phosphinimides dramatically raises the energy of the Cr d-electrons which enables this atypical reactivity. Herein, we sought to investigate the reactivity of a bis-phosphinimide chromium fragment with isocyanides (Figure 2-1B), in anticipation that the mismatch between π -donating phosphinimide ligands and π -accepting isocyanides would result in unusual electronic structures and reactivity, demonstrating that an intermediate spin Cr(II) bis isocyanide can be accessed which features labile isocyanide ligands and unique insertion reactivity.

Results and Discussion

Previously, we reported Cr derivatives of the bis(phosphinimine) proligand, $\text{H}_2\text{L}^{\text{Ad}}$, and identified $\text{L}^{\text{Ad}}\text{Cr}(\text{TMSCTMS})^{43}$ as a useful Cr(II) synthon. Seeking alternative metal complexes of this ligand, we investigated the reaction of $\text{H}_2\text{L}^{\text{Ad}}$ with $\text{Cr}(\text{HMDS})_2(\text{THF})_2^{47}$ as this metal precursor has been successfully employed for the synthesis of a range of Chromium complexes.^{24,48,49}

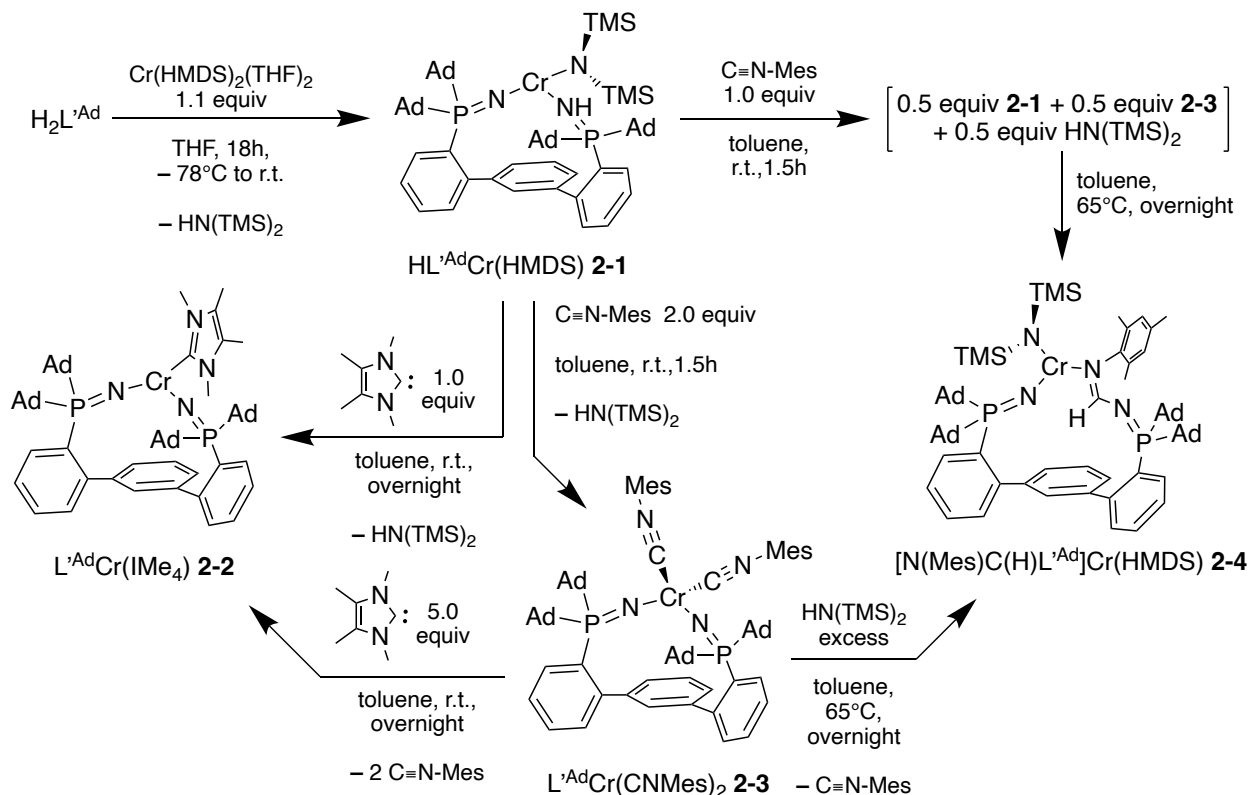


Figure 2-2 Synthesis of $\text{HL}^{\text{Ad}}\text{Cr}(\text{HMDS})$ **1**, $\text{L}^{\text{Ad}}\text{Cr}(\text{IMe}_4)$ **2**, $\text{L}^{\text{Ad}}\text{Cr}(\text{CNMe})_2$ **3** and $[\text{N}(\text{Mes})\text{C}(\text{H})\text{L}^{\text{Ad}}]\text{Cr}(\text{HMDS})$ **4**.

The reaction of $\text{H}_2\text{L}^{\text{Ad}}$ with 1.1 equivalents of $\text{Cr}(\text{HMDS})_2(\text{THF})_2$ in THF at -78°C (Scheme 2) followed by warming to room temperature resulted in the loss of the ^{31}P NMR signal associated with $\text{H}_2\text{L}^{\text{Ad}}$ while two broad, paramagnetically-shifted features at 44.9 and 37.1 ppm appeared in the ^1H NMR. The solution phase magnetic moment of **1** ($m_{\text{eff}} = 4.8 \text{ mB}$) was found to be consistent with a high spin, $S = 2$ chromium(II) center. However, the IR spectrum of the isolated material revealed a broad peak in the region between 3100 cm^{-1} and 3450 cm^{-1} ascribed to a $\nu(\text{N-H})$ oscillator, suggestive of an incomplete protonolysis reaction. This notion was corroborated by crystallography, which revealed the reaction product as $\text{HL}^{\text{Ad}}\text{Cr}(\text{HMDS})$ **2-1** (Figure 2-3). The crystal structure of **2-1** features a significantly distorted trigonal planar chromium center bound to both arms of the pro-ligand in addition to an HMDS ligand. The significant distortion from trigonal geometry appears to be the result of the chromium center being displaced towards the phosphinimide arm and steric interactions between the TMS groups and the

adamantyl groups of the ligand. A trigonal planar d^4 metal center is expected to be subject to a pseudo-Jahn Teller distortion owing to an $^5E'$ ground state in D_{3h} geometry that is afforded considerable stabilization upon splitting into $^5A_1$ and $^5B_2$ states on descent of symmetry to C_{2v} .⁵⁰ In this context, it is noteworthy that most, low-coordinate $S = 2$ Cr(II) derivatives adopt square planar geometries.⁵¹

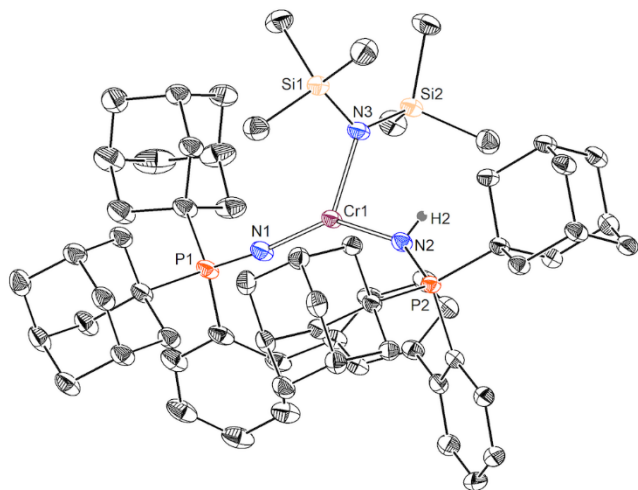


Figure 2-3 Crystal structure of HL'AdCr(HMDS) **2-1** with ellipsoids shown at 50% probability. Hydrogen atoms bound to carbon atoms have been omitted for clarity. Selected bond distances (Å), Cr1-N1 1.8913(14), Cr1-N2 2.0955(15), Cr1-N3 2.0553(15), N1-P1 1.543

Inspection of the Cr-N(P) distances ($d(\text{Cr1-N1}) = 1.8913(14)$ and $d(\text{Cr1-N2}) = 2.0955(15)$ Å) suggested that the N2 atom remained protonated and the corresponding H-atom (H2) was located in the Fourier difference map and freely refined. The Cr-NP interaction featured a more linear phosphinimide chromium linkage ($\angle \text{P1-N1-Cr} = 169.5(1)^\circ$), compared to a more bent phosphinimine chromium linkage ($\angle \text{P-N-Cr} = 151.51(8)^\circ$) in the Cr-N(H)P interaction. The N-atom of the HMDS ligand is found at a distance of 2.0553(15) Å from the Cr center which matches distances observed in other neutral Chromium(II) bis-HMDS complexes.⁴⁷ We hypothesized that the incomplete protonolysis of $\text{H}_2\text{L}'^{\text{Ad}}$ with $\text{Cr}(\text{HMDS})_2(\text{THF})_2$ might stem from the high energy nature of the desired, “naked” $\text{L}'^{\text{Ad}}\text{Cr}$ species, and that this species must rapidly recombine with $\text{HN}(\text{TMS})_2$ to afford the thermodynamic product, **2-1**.

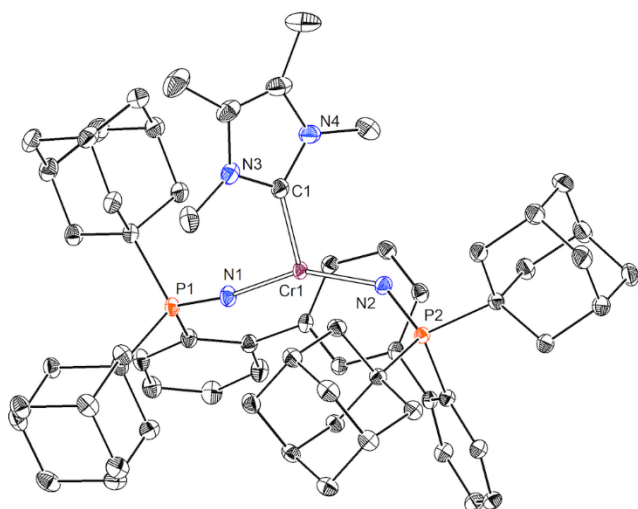


Figure 2-4 Crystal structure of L'AdCr(Ime₄) 2-2 with ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity. Selected bond distances (Å), Cr1-N1 1.9117(11), Cr1-N2 1.9345(11), Cr1-C1 2.0587(13).

To test whether such an equilibration process was operative, we sought to capture L'^{Ad}Cr *in situ* via the reaction of HL'^{Ad}Cr(HMDS) with s-donor ligands such as N-heterocyclic-carbenes and isocyanides (Scheme 1) and induce α -H abstraction. These abstraction reactions are well documented in chromium alkyl complexes *en route* to alkylidenes⁵² and related to b-⁵³ and g-H abstractions⁵⁴ reported for chromium amides. Addition of 1 equivalent of tetramethyl-imidazolin-2-ylidene (Ime₄) to **2-1** resulted in the rapid loss of its associated ¹H NMR peaks, the formation of HN(TMS)₂, and a new, $S = 2$ ($m_{\text{eff}} = 5.0$ m_B) paramagnetic species characterized by ¹H NMR peaks at 37.7 and 14.7 ppm. FTIR analysis of the resultant product revealed no absorption features ascribable to $\nu(\text{N-H})$ vibrations, suggesting that coordination of Ime₄ to the chromium center served to activate the remaining acidic proton on HL'^{Ad}Cr(HMDS) to afford the bisphosphinimide carbene complex, L'^{Ad}Cr(Ime₄) (**2-2**). The crystal structure of **2-2** confirmed the presence of two deprotonated phosphinimide ligands and a Cr-coordinated Ime₄ ligand (Figure 2-4). The Cr center was found to adopt a distorted T-shaped coordination geometry in which both phosphinimide nitrogen chromium distances are below 2 Å at 1.9117(11) and 1.9345(11) Å. The chromium carbene distance of 2.0587(13) is marginally shorter than the ones observed in the only other reported chromium Ime₄ complex [CpCr(Ime₄)₂]Cp.⁵⁵

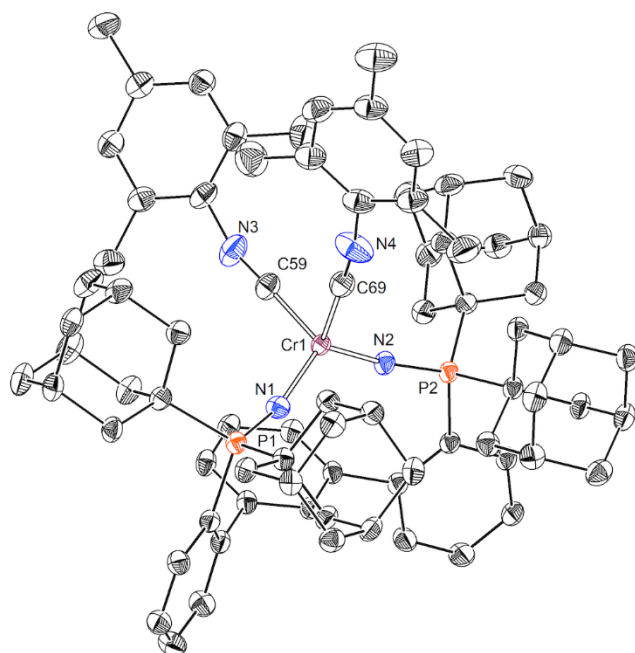


Figure 2-5 Crystal structure of L'AdCr(CNMe)s2 2-3 with ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity. Selected bond distances (Å), Cr1-N1 1.8256(18), Cr1-N2 1.8196(17), Cr1-C59 1.855(2), Cr1-C69 1.876(2) Å.

In contrast to the straightforward reactivity with IMe_4 , the combination of **2-1** and mesityl isocyanide (MesNC) furnishes different products depending on the reaction conditions. Addition of a single equivalent of the latter to **2-1** at room temperature results in a mixture of **2-1** and a new paramagnetic species as judged by ^1H NMR spectroscopy (Figure 2-10). The FTIR spectrum obtained on this mixture (Figure 2-11) revealed two strong absorption bands at 1850 and 1990 cm^{-1} , that would be consistent with the formation of a bis(isocyanide)chromium. It is noteworthy that the IR stretches associated with these aryl-isocyanide groups are considerably lower than values observed for the “ T_{1u} ”-like vibrations associated with octahedral Cr(II) and Cr(I) binary chromium aryl-isocyanide complexes at $\sim 2150\text{ cm}^{-1}$ and $\sim 2060\text{ cm}^{-1}$ respectively and fall into the region of Cr(0) complexes at $\sim 1975\text{ cm}^{-1}$,⁵⁶ suggesting that the newly formed Cr complex contains a highly electron-donating metal center.

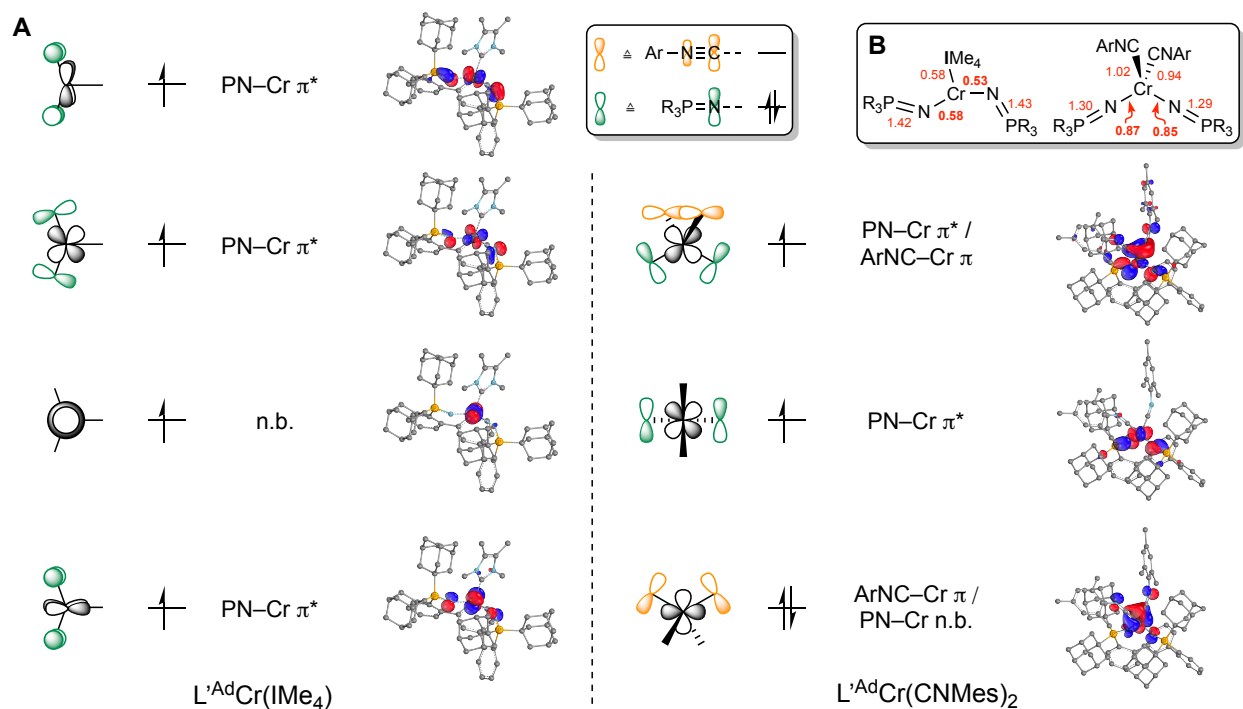


Figure 2-6 (A) Frontier orbitals of **2-2** and **2-3** obtained by DFT calculations at the B3LYP/TZVPP-SVP/D3BJ level of theory drawn at contour values of 65%. Hydrogen atoms removed for clarity. Grey, orange and green orbitals correspond to Cr d-orbitals, the isocyanide LUMOs and the phosphinimide HOMOs respectively. (B) Selected Wiberg bond indexes obtained from these calculations.

The addition of 2.0 equiv of MesNC to either **2-1** or $L^{Ad}Cr(TMSCCTMS)^{43}$ produced the same ^1H NMR spectral features and resulted in the isolation of the bis-isocyanide complex $L^{Ad}Cr(CNMe_5)_2$ **2-3** in 62 % or 76% yield, respectively. **2-3** features a distorted tetrahedral ($t_4'=0.86$) chromium center bound to two isocyanide ligands in addition to both arms of the ligand (Figure 2-5). The short Cr-NP distances (1.8256(18) and 1.8196(17) Å) reflect deprotonated phosphinimide ligands, but these distances are substantially shorter than those found in **2-2**. Unlike **2-2**, complex **2-3** was found to adopt an intermediate ($S = 1$) spin state in solution, as determined by Evans' method ($m_{eff} = 2.7 \mu_B$) and this lower spin state is likely the cause for the shorter Cr-NP distances. The isocyanide ligands are bound at distances of 1.855(2) and 1.876(2) Å in line with $Me_2Si(\eta^5-C_5Me_4)(\eta^3-C_5Me_3(H)(=CH_2))Cr(CNXyl)_2$,⁵⁷ the only Cr(II) bis-isocyanide example reported in the literature. DFT calculations (B3LYP/TZVPP-SVP/D3BJ) were performed on the optimized geometries of **2-2** and **2-3** to rationalize the observed spin state and Cr-NP bond length differences. Inspection of the occupied Cr d-orbital based frontier orbitals (Figure 2-6A) reveals 3 p^* Cr-NP anti-bonding interaction in addition to a non-bonding orbital that resembles the Cr $3d_z^2$ orbital for **2-2**. In contrast **2-3** features a doubly occupied, frontier orbital that is non-bonding with respect of the phosphinimides and stabilized by a bonding interaction with the isocyanides' unfilled π -symmetry orbitals. Consequently, only two orbitals with Cr-NP π^* character are singly-occupied, resulting in an increased Cr-NP bond order that is supported by the computed Wiberg bond indexes

(Figure 2-6B) and rationalizes the short bond lengths found in the crystal structure. The IR and ^1H NMR spectra of isolated $\text{L}^{\text{Ad}}\text{Cr}(\text{CNMes})_2$ **2-3** match those features found in the mixture obtained following the addition of a single isocyanide ligand to **2-1**, suggesting that addition of one equivalent of CNMes to **2-1** leads to a 1:1 mixture of **2-1** and **2-3** (Figure 2-2). In an effort to elucidate whether these two species are in equilibrium, we sought to perturb the distribution of these two species by the addition of excess hexamethyldisilazane. While no reaction was observed following incubation of these mixtures at room temperature overnight, gentle heating at 65°C overnight resulted in the consumption of **2-1** and **2-3** concomitant with formation of a new paramagnetic species (Figure 2-10).

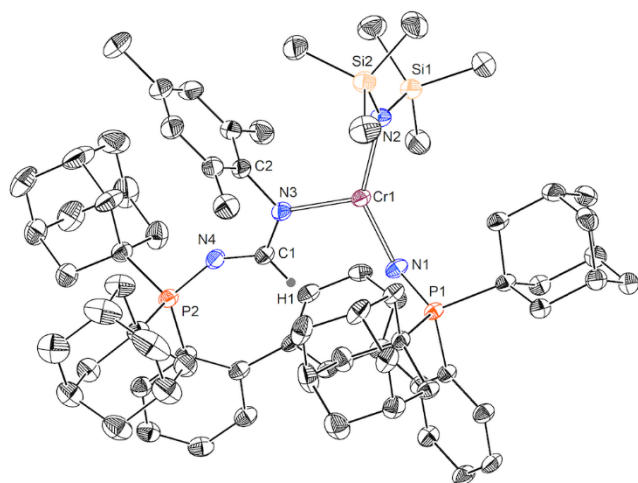


Figure 2-7 Crystal structure of $[\text{N}(\text{Mes})\text{C}(\text{H})\text{L}'^{\text{Ad}}]\text{Cr}(\text{HMDS})$ **2-4** with ellipsoids shown at 50% probability. Hydrogen atoms on adamantyl groups and the base of the ligand removed for clarity. See Figure 6 for selected bond distances.

These observations suggest that the 1,2 N-H elimination is not reversible at room temperature and attempts to overcome thermal barriers unlocks further reactivity. The resultant product is characterized by no vibrations ascribable to isocyanide stretches and a strong FTIR feature at 1526 cm^{-1} (Figure 2-11).

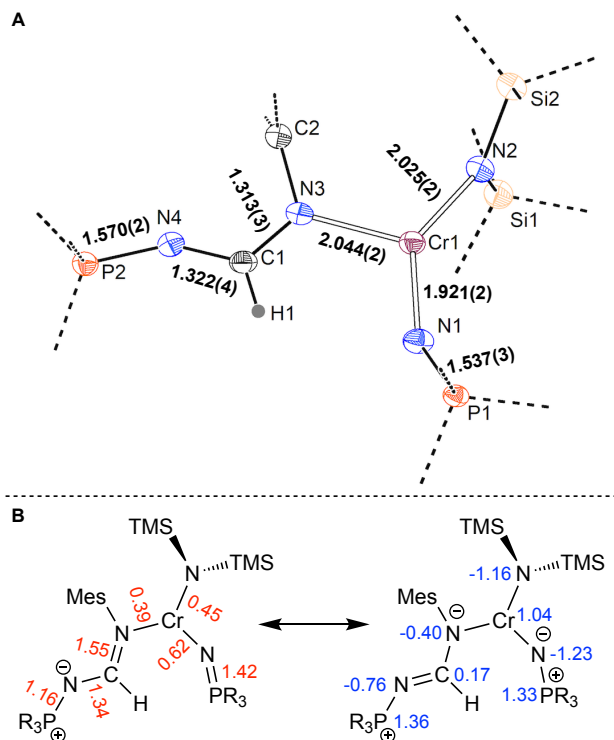


Figure 2-8 (A) Selected bond distances of [N(Mes)CHL'Ad]Cr(HMDS) **2-4** (Å). (B) Resonance structures best describing the bonding in **4**. Wiberg bond indices associated with individual bonds in red. NPA charges associated with individual atoms in blue.

This species has been identified crystallographically as [N(Mes)=C(H)L'Ad]Cr(HMDS) **2-4** (Figure 2-7). This complex can also be obtained by heating mixtures of the **1** with 1.0 eq. of MesNC or **2-3** with excess hexamethyldisilazane at 65°C for 19 h (Figure 2-2). The crystal structure of **2-4** reveals a distorted trigonal planar chromium center ($S(\angle \text{Cr}) = 359.7^\circ$) ligated by an HMDS ligand, one phosphinimide arm and a moiety resulting from an apparent insertion of MesNC into the second phosphinimide arm. The absence of a counterion in the crystal suggests that this structure formally consists of mesityl isocyanide, doubly deprotonated L'Ad, HMDS- and a proton, with the chromium center being coordinated in an X_2L -type fashion. The fate of the proton was ascertained by close inspection of the Fourier difference map, which displays a notable peak in electron density adjacent to the carbon (C1) derived from the inserted isocyanide ligand. A chromium phosphinimide bond distance of 1.921(2) Å as well as C(H)-N bond distances comparable to organic N,N'-diarylformimidamides⁵⁸ at 1.322(4) and 1.313(3) Å (Figure 2-8A) are consistent with this picture. The solution-phase magnetic moment of **2-4** (4.0 μ_B) is most consistent with a high spin $S = 2$ chromium(II) center. The high spin assignment is supported by DFT calculations (B3LYP/TZVPP-SVP/D3BJ) and a corresponding frequency calculation performed on an optimized geometry based on the crystal structure of **2-4** was found to faithfully reproduce the prominent FTIR feature at 1526 cm^{-1} associated with the asymmetric stretching mode of the formimidamide fragment (Figure 2-12). The closest reported structural analogue of the formimidamide fragment

are N-phosphanylformamidines⁵⁹ which are related by exchange of one alkyl group from the phosphorous to the distant nitrogen.

Wavefunction analysis of **2-4** is consistent with the multiple bond character between the phosphorus and the formimidamide nitrogen being reduced by delocalization of the negative charge over the formimidamide compared to the canonical phosphinimide (Figure 6B). This delocalization is more pronounced compared to the related N-Phosphanylformamidines. Noticeably, the N-P bond order of the inserted fragment is lower than that of the bis isocyanido product **2-3** (Figure 2-8B). The increased stabilization of the negative charge on the phosphinimide via resonance between the formimidamide fragment is our preferred rationale for the thermodynamic stability of **2-4** compared to **2-3**.

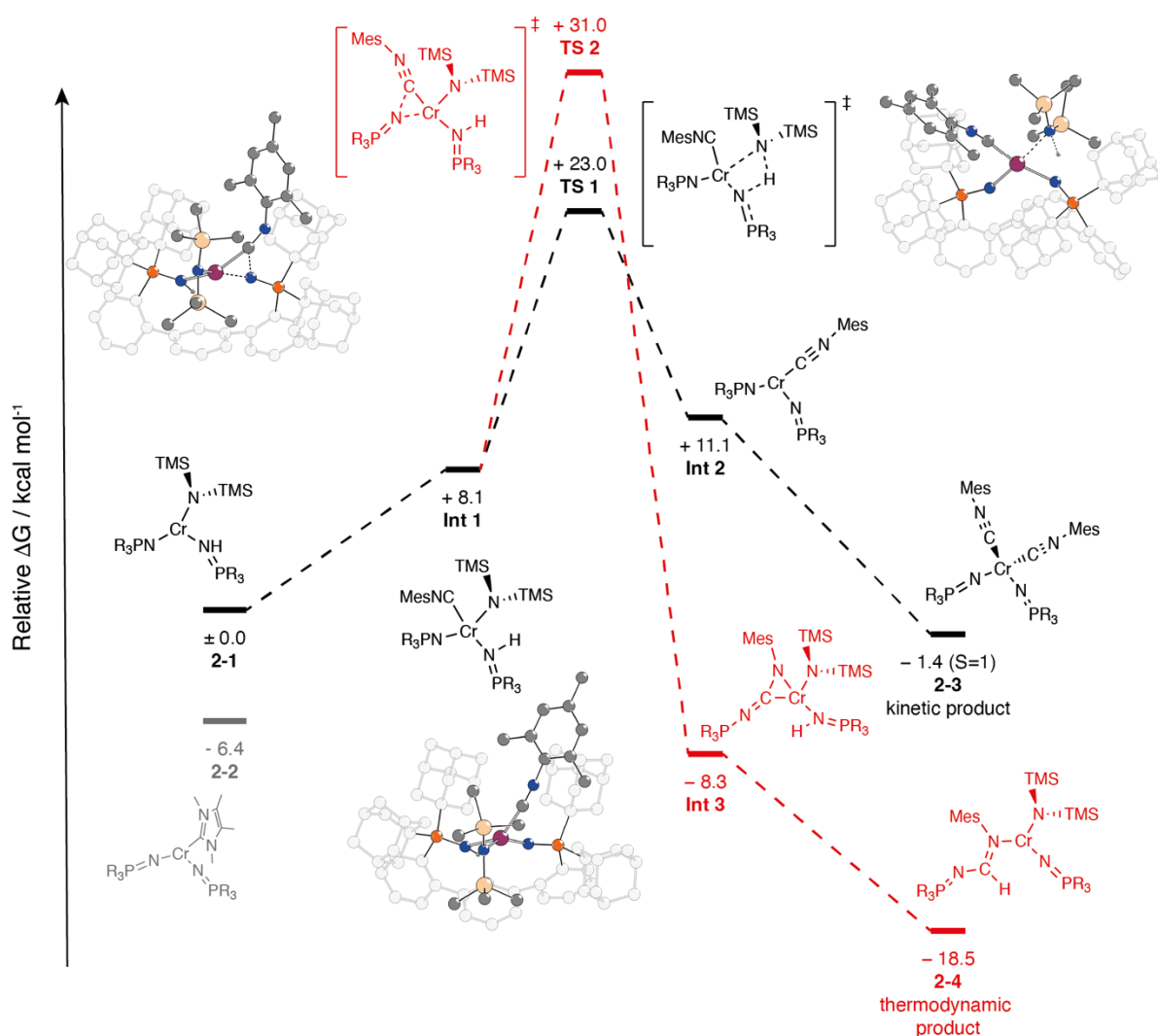


Figure 2-9 Reaction coordinate obtained for the formation of $L^{Ad}Cr(CNMe)_2$ **2-3** and $[N(Me)=CHL'Ad]Cr(HMDS)$ **2-4** obtained by DFT calculations.

While isocyanide insertions into hydrides, alkyls and amides are common in early transition metals and lanthanides,⁶⁰ examples involving chromium complexes are rare.^{40,41} Accordingly, we sought to elucidate the mechanism for the formation of **2-4**. The observation that **2-3** can serve as a viable starting material to form **2-4** at 65 °C and contrasting lack of reactivity with HN(TMS)₂ at room temperature suggests a certain degree of reversibility in the isocyanide binding at 65 °C. Since it is highly unlikely that an HMDS and two CNMes groups simultaneously associate with the chromium center due to the substantial steric bulk associated with the adamantyl groups, we presume that exchange proceeds through a dissociative mechanism (I_d or D).^{61,62} The possibility of ligand exchange in **2-3** is further corroborated by addition of 5.0 eq. of IMe₄ to **2-3** at room temperature which resulted in the complete dissociation of the isocyanides and quantitative formation of L'^{Ad}Cr(IMe₄) as judged by ¹H NMR spectroscopy (Figure 2-13).

Attempts to observe this dissociation by heating a toluene solution of **2-3** in the absence of other reagents at 90 °C overnight results in the formation of free isocyanide as judged by IR spectroscopy (Figure 2-14) and an unidentified mixture paramagnetic species in the ¹H NMR spectrum. Notably addition of excess HN(TMS)₂ to this species does not regenerate any known complexes and provides evidence against mechanistic hypotheses that involve isocyanide insertion in the absence of HN(TMS)₂. We therefore propose the mechanism shown in Figure 2-9. We postulate that at room temperature the conversion of **2-1** to **2-3** proceeds initially by coordination of MesNC to HLCrHMDS to form the 4-coordinate intermediate **2-Int1**, which can reversibly lose HN(TMS)₂ and generate a mono isocyanide intermediate **2-Int2**, which is intercepted by a second isocyanide to form the kinetic bis(isocyanide) product **2-3**. When these reactions are conducted at higher temperatures, the isocyanide ligand in **2-Int1** may insert between the phosphinimide and the chromium center, which eventually leads to the formation of the thermodynamic product **2-4** following proton transfer by way of **2-Int3**.

Computational investigation of this mechanism by DFT qualitatively reproduces the experimental observations and mechanistic hypotheses (Figure 2-9). Addition of MesNC to **2-1** is not prevented by the steric bulk of the adamantyl groups and leads to **2-Int1** which optimizes to a distorted square planar geometry at a relative ΔG of + 8.1 kcal/mol. Notably, attempts to optimize **2-Int1** with the proton being placed on the HMDS nitrogen instead of the phosphinimide nitrogen lead to HN(TMS)₂ dissociation, suggesting that HN(TMS)₂ loss occurs in a concerted manner analogous to reversible 1,2 C-H additions reported for early transition metal imido complexes.⁶³ The corresponding transition state could be located at $\Delta G^\ddagger$ + 14.9 kcal/mol relative to **2-Int1**. Addition of a second MesNC to the resulting **2-Int2** affords **2-4** with an overall ΔG_r of -1.4 kcal/mol, which is likely an underestimation since B3LYP artificially favors higher spin states due to its hybrid nature.⁶⁴ Isocyanide insertion from **2-Int1** occurs with a significantly higher transition state energy of $\Delta G^\ddagger$ 22.9 kcal/mol relative to **2-Int1**. This barrier is also considerably

higher compared to isocyanide insertions into group 4 amide bonds,⁶⁵ but **2-4** is afforded with a drastically more exergonic ΔG_r of -18.5 kcal/mol representing the thermodynamic product.

Conclusion

In summary, chromium phosphinimide phosphinimine complex $\text{HL}^{\text{'Ad}}\text{Cr}(\text{HMDS})$ **2-1** has been prepared by an arrested protonolysis of pro-ligand $\text{H}_2\text{L}^{\text{'Ad}}$ with $\text{Cr}(\text{HMDS})_2(\text{THF})_2$. Complete deprotonation of the pro-ligand could be effected by inducing 1,2 N-H elimination by addition of sigma donor ligands such as carbenes and isocyanides affording $\text{L}^{\text{'Ad}}\text{Cr}(\text{IME}_4)$ **2-2** and $\text{L}^{\text{'Ad}}\text{Cr}(\text{CNMe}_5)_2$ **2-3**. The latter features an unusual intermediate spin state and represents a kinetic product. Heating of the reaction mixtures leads to the formation of the thermodynamic product $[\text{N}(\text{Mes})\text{CHL}^{\text{'Ad}}]\text{Cr}(\text{HMDS})$ **2-4** which results from isocyanide insertion and subsequent proton transfer—reactions that are traditionally associated with high oxidation state chromium complexes.

Supporting Information

General Considerations

All reactions were performed at room temperature in a N_2 -filled glovebox or by employing standard Schlenk techniques unless otherwise stated. Glassware was oven-dried at 150 °C for at least 2 h prior to use and allowed to cool under a vacuum. All reagents were used as received unless otherwise stated. Anhydrous pentane, diethyl ether, benzene, toluene, THF and acetonitrile were purified by sparging with nitrogen for 30 min and then passing under nitrogen pressure through a column of activated A2 alumina. NMR solvents were purchased from Cambridge Isotope Laboratories. C_6D_6 and toluene- d_8 were degassed by three freeze–pump–thaw cycles and dried over freshly activated 3 Å molecular sieves for 24 h prior to use. The following compounds were synthesized according to published procedures: $\text{H}_2\text{L}^{\text{'Ad}}$,⁴³ IME_4 ,⁶⁶ CNMe_5 ,⁶⁷ $\text{Cr}(\text{HMDS})_2(\text{THF})_2$,⁵³ $\text{L}^{\text{'Ad}}\text{Cr}(\text{btmsa})$ ⁴³

X-ray Crystallography

XRD studies were performed at the University of California, Berkeley College of Chemistry Small Molecule X-ray Crystallography Facility (CheXray) or at beamline 12.2.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory.

For studies performed at ChexRay, crystals were mounted on a Kapton loop under Paratone oil. Data was collected on a Rigaku XtalLAB P200 (Cu K_α radiation) equipped with a MicroMax-007 HF microfocus rotating anode and a Pilatus 200 K hybrid pixel array detector at 100 K under a stream of N_2 . Data collection, integration, and scaling were carried out using the CrysAlisPro⁶⁸ software package.

For studies performed at the Advanced Light Source, crystals were mounted on a MiTeGen loop under Paratone oil. Data was collected on a Bruker D85 three-circle diffractometer with a PHOTON II CCD area detector using silicon monochromated synchrotron radiation ($\lambda = 0.7288 \text{ \AA}$). Bruker APEX2 software⁶⁹ was used for data collection. Bruker SAINT⁷⁰ and SADABS⁷¹ software packages were utilized for data reduction and absorption correction, respectively.

Structures were solved using SHELXT⁷² and refined against F^2 on all data by full matrix least-squared with SHELXL⁷³ using OLEX 2 Version 1.5⁷⁴ crystallographic software. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms bonded to carbon atoms of the adamantyl groups as well as the terphenyl anchor were placed in idealized positions and refined using a riding model all other hydrogen atoms were refined against peaks in the Fourier difference map and freely refined.

Infrared Spectroscopy

FTIR measurements were carried out on a Thermo Scientific Nicolet iS20 spectrometer utilizing KBr pellets.

Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on Bruker or Joel 400 MHz instruments. ^1H chemical shifts are reported in ppm relative to tetramethylsilane (TMS) at 0.00 ppm using residual solvent peaks as internal standards.⁷⁵ The widths of paramagnetic peaks at half maximum (FWHM) are reported in the experimental section. Solution phase magnetic measurements were performed using Evans' method.⁷⁶

UV/visible Spectroscopy

UV/visible measurements were taken on a Hewlett-Packard 8453 UV/visible spectrophotometer using 1 cm quartz cells sealed with a Teflon stopcock.

Elemental Analysis

Elemental analyses were performed at the University of California, Berkeley College of Chemistry Microanalytical Facility using a PerkinElmer 2400 Series II combustion analyzer. It should be noted that the isocyanide-based compounds $\text{L}^{\text{Ad}}\text{Cr}(\text{CNMes})_2$ **3** and $[\text{N}(\text{Mes})\text{CHL}^{\text{Ad}}]\text{Cr}(\text{HMDS})$ **4** analyzed consistently low in carbon over multiple runs. We

attribute this to the exceeding air sensitivity as well as isocyanide lability of these compounds. Representative results are given below for these compounds.⁷⁷

Figures supporting the main text

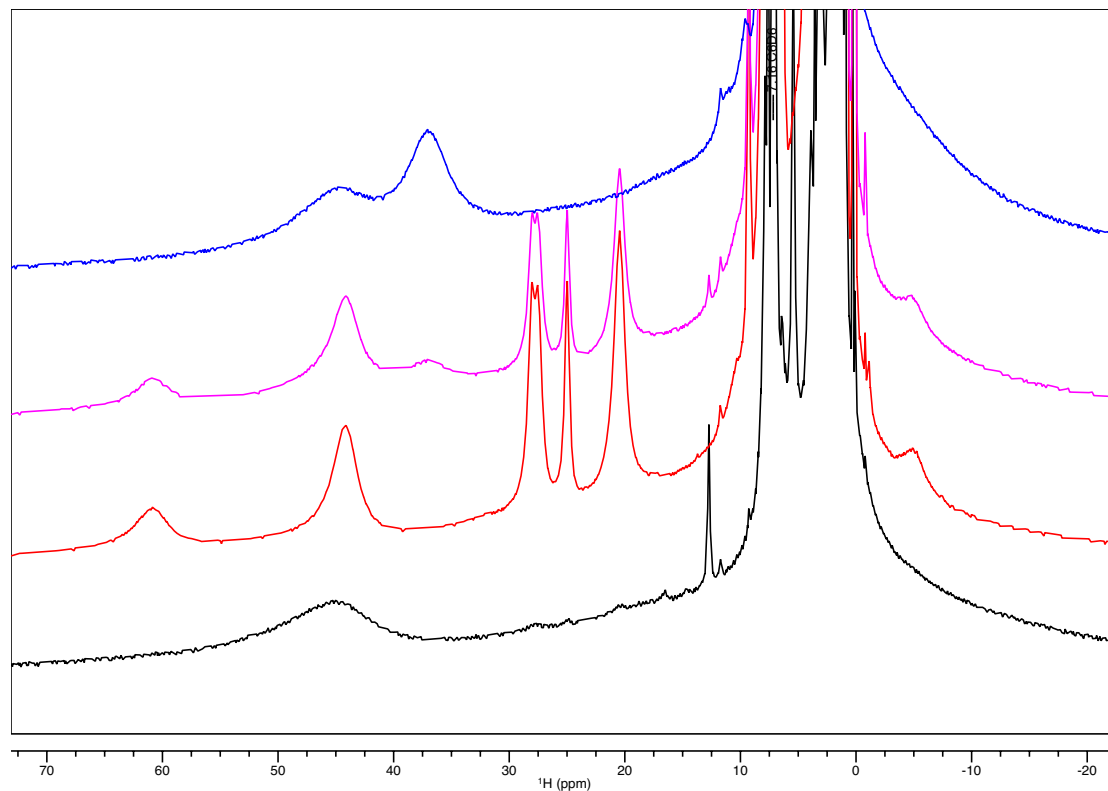


Figure 2-10 ^1H NMR spectrum (400 MHz) of $\text{HL}^{*\text{Ad}}\text{Cr}(\text{HMDS})$ 2-1 recorded in C_6D_6 at 298 K (blue). ^1H NMR spectrum (400 MHz) obtained of an equimolar mixture of $\text{HL}^{*\text{Ad}}\text{Cr}(\text{HMDS})$ 2-1 and mesityl isocyanide recorded in C_6D_6 at 298 K (magenta). ^1H NMR spectrum (400 MHz) of $\text{L}^{*\text{Ad}}\text{Cr}(\text{CNMe})_2$ 2-2 recorded in C_6D_6 at 298 K (red). ^1H NMR spectrum (400 MHz) obtained after heating an equimolar mixture of $\text{HL}^{*\text{Ad}}\text{Cr}(\text{HMDS})$ 2-1 and mesityl isocyanide at 338 K for 19 h recorded in C_6D_6 at 298 K (black).

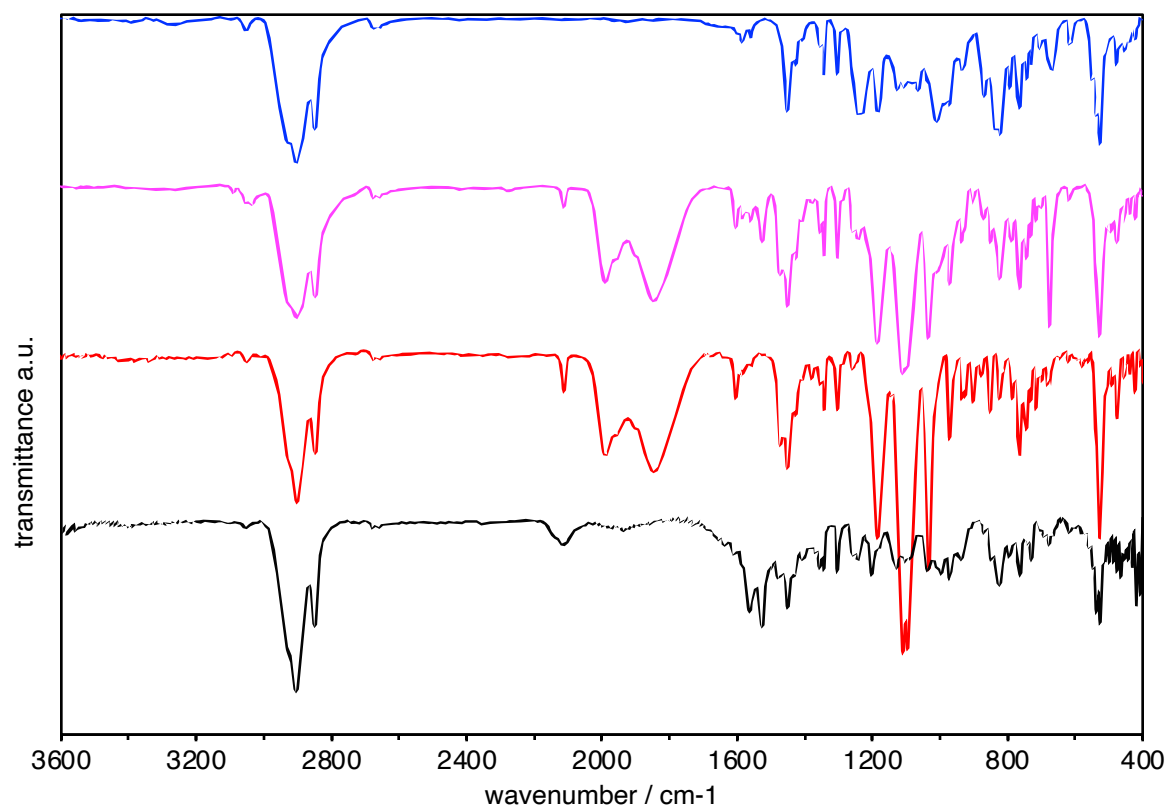


Figure 2-11 FTIR spectrum of $\text{HL}^{\text{AdCr}}(\text{HMDS})$ 2-1 (blue). FTIR spectrum obtained of an equimolar mixture of $\text{HL}^{\text{AdCr}}(\text{HMDS})$ 2-1 and mesityl isocyanide (magenta). FTIR spectrum of $\text{L}^{\text{AdCr}}(\text{CNMe})_2$ 2-2 (red). FTIR spectrum obtained after heating an equimolar mixture of $\text{HL}^{\text{AdCr}}(\text{HMDS})$ 2-1 and mesityl isocyanide at 338 K for 19 h (black).

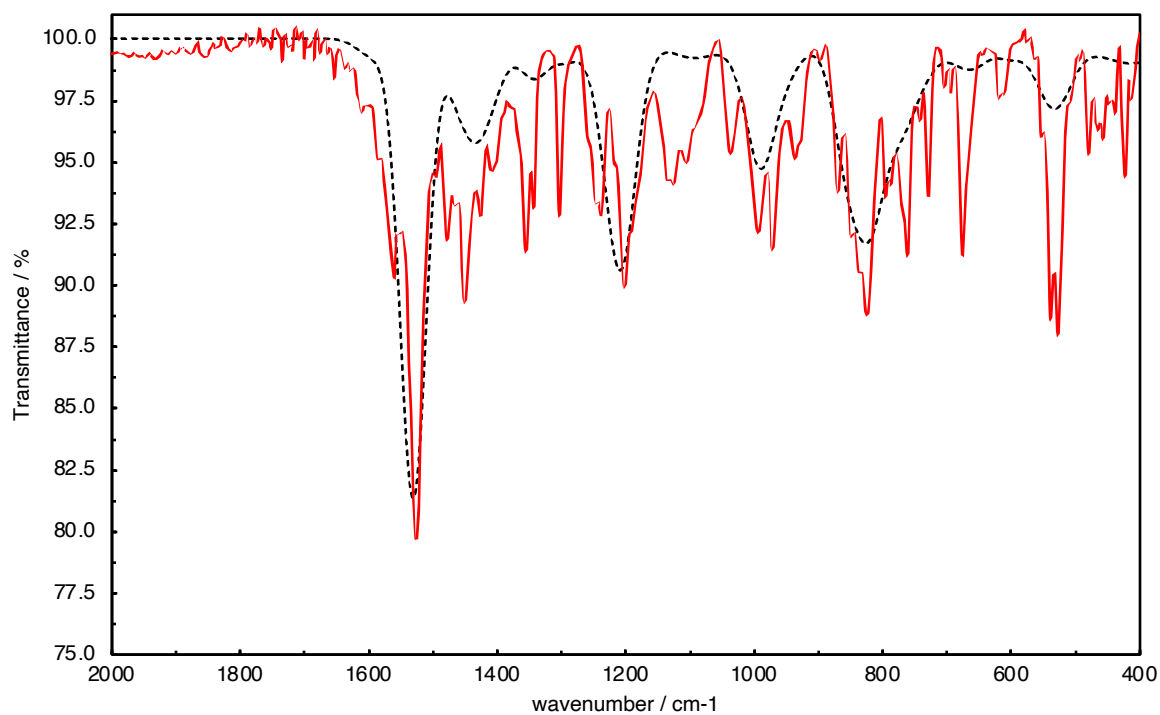


Figure 2-12 FTIR spectrum of $[\text{N}(\text{Mes})\text{CHL}^{\text{Ad}}]\text{Cr}(\text{HMDS})$ 2-4 (red). Calculated IR spectrum obtained from a numerical frequency calculation following geometrical optimization of $[\text{N}(\text{Mes})\text{CHL}^{\text{Ad}}]\text{Cr}(\text{HMDS})$ (S=2) (B3LYP/TZVPP-SVP, D3BJ dispersion correction) (dashed black).

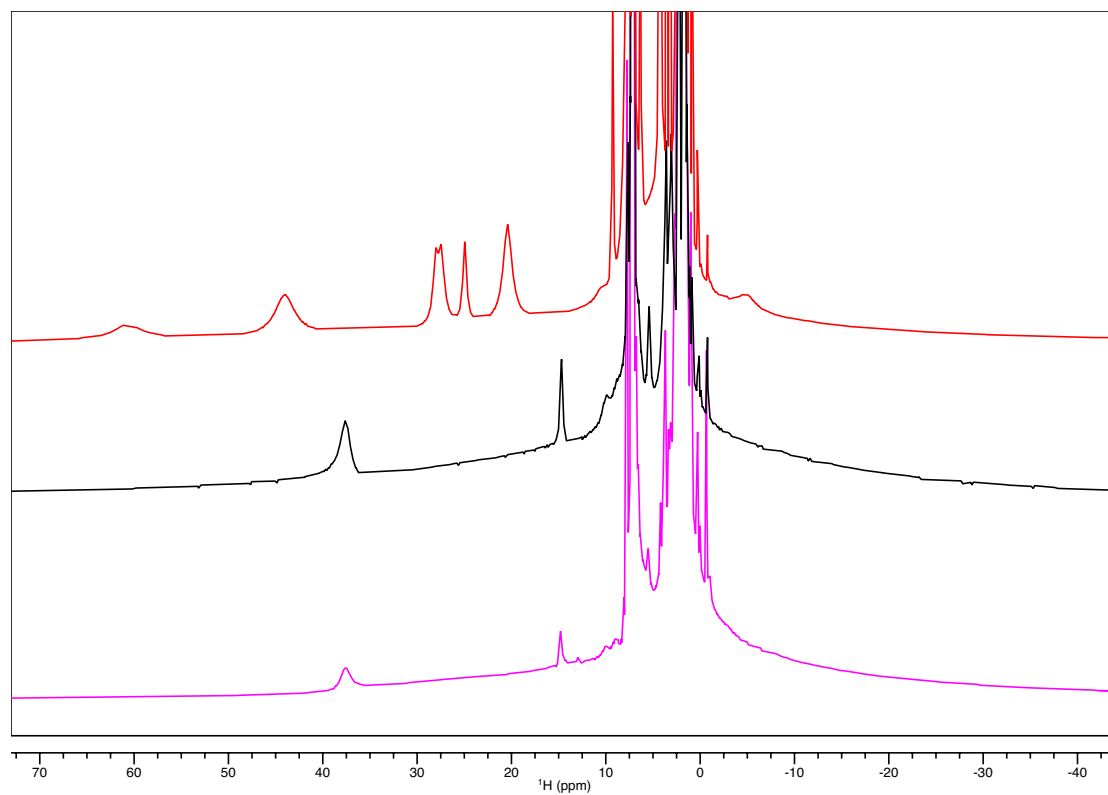


Figure 2-13 ^1H NMR spectrum (400 MHz) of $\text{L}'\text{AdCr}(\text{CNMe}_s)_2$ 2-3 recorded in C_6D_6 at 298 K (red). ^1H NMR spectrum (400 MHz) of $\text{L}'\text{AdCr}(\text{IME}_4)$ 2-2 recorded in C_6D_6 at 298 K (black). ^1H NMR spectrum (400 MHz) obtained after stirring $\text{L}'\text{AdCr}(\text{CNMe}_s)_2$ 2-3 with 5 equivalents of IME_4 at room temperature overnight.

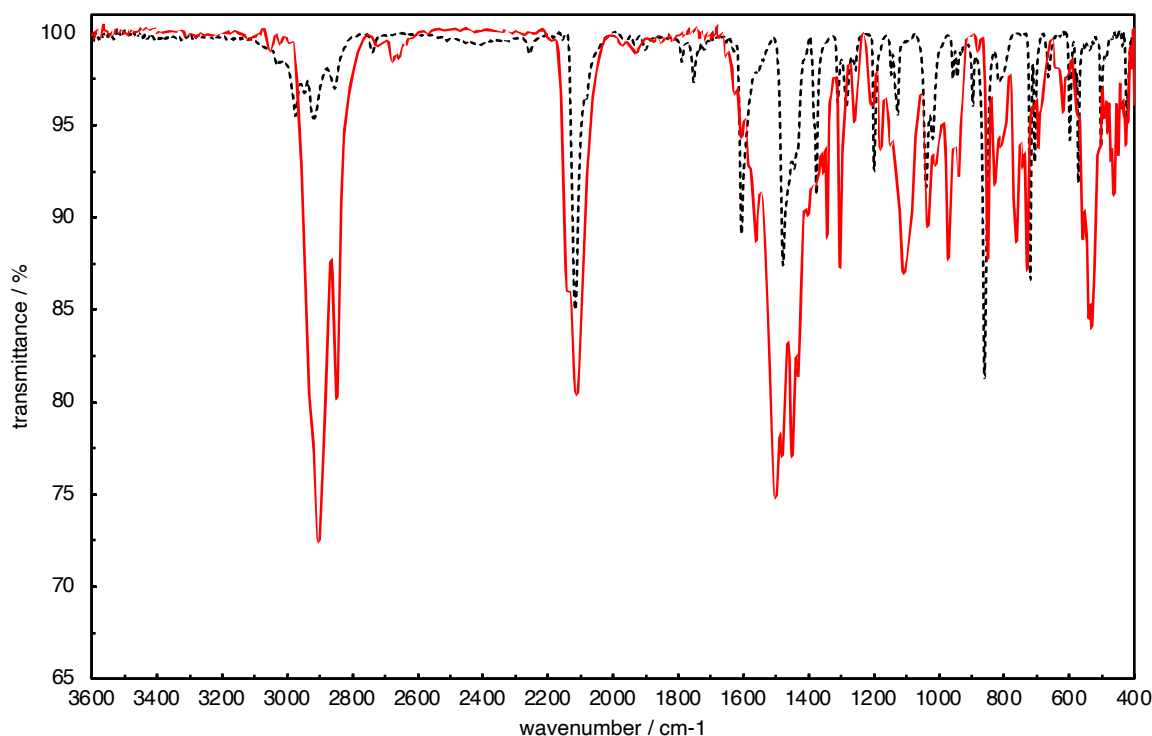
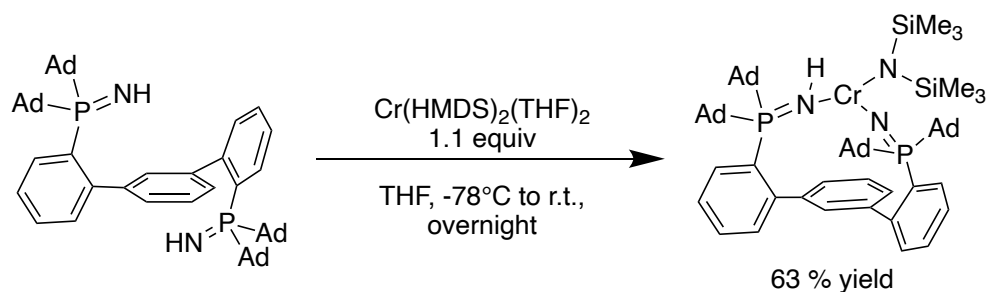


Figure 2-14 FTIR spectrum of the mixture obtained after heating $L'^{Ad}Cr(CNMes)_2$ 2-3 at 95°C overnight (red). IR spectrum of MesNC (dashed black).

Synthetic procedures

Synthesis of $HL'^{Ad}Cr(HMDS)$ 2-1

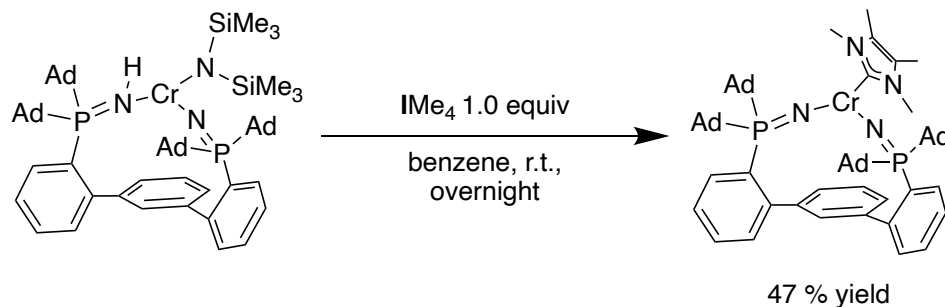


A solution of $Cr(HMDS)_2(THF)_2$ (0.639 mmol, 330 mg, 1.1 eq.) in THF (25 mL) was added dropwise to a solution of $H_2L'^{Ad}$ (0.581 mmol, 500 mg, 1.0 eq.) in THF (90 mL) precooled to -78 °C. The resulting dark orange solution was stirred and allowed to warm to room temperature over a course of 18 h. Subsequently, the solvent was removed *in vacuo*, the residue washed with pentane (15 mL) and reextracted into THF (5 mL). Removal of the solvent afforded the title compound as an orange powder (0.372 mmol, 394 mg, 63% yield). $C_{64}H_{91}CrN_3P_2Si_2$ (1072.6 g/mol). ^1H NMR (400 MHz, C_6D_6) δ 44.91 ($Dn_{1/2}$ = 2020 Hz), 37.10 (1490 Hz). IR ν_{max}/cm^{-1} 2903, 1451, 1241, 1183, 1008, 823, 527. UV-vis $\lambda_{max}(THF)/nm$ 275inf ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 10180), 325inf (4500), 400inf (1080).

Anal. calcd. for $C_{64}H_{91}CrN_3P_2Si_2$: C, 71.67; H, 8.55; N, 3.92. Found: C 71.52, H 8.56, N 3.69. μ_{eff} (C_6D_6 , 293 K, 400MHz): $4.8 \mu_B$.

Single crystals suitable for X-ray diffraction were grown by vapor diffusion of Et_2O into a saturated benzene solution.

Synthesis of $L'^{Ad}CrIME_4$ **2-2**

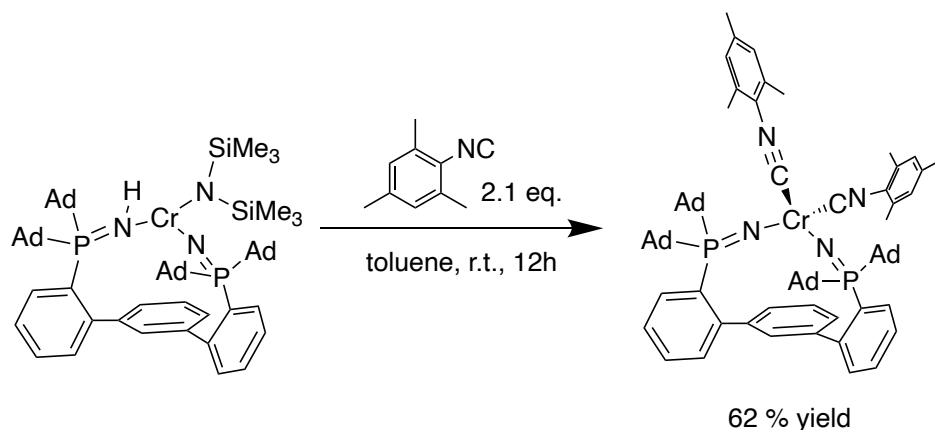


A 0.1 mol/L solution of IME_4 (0.071 mmol, 0.71 ml, 1.0 eq.) in toluene was added to a solution of $HL'^{Ad}Cr(HMDS)$ (0.071 mmol, 75 mg, 1.0 eq.) in benzene (10 mL). The resulting mixture was stirred for 18 h during which the color gradually changed from orange to olive green. Subsequently, all volatiles were removed *in vacuo* leaving an olive green powder that was washed with Et_2O (5 mL). The ether washing was set aside and the residue redissolved in benzene and lyophilized to afford the title compound as an olive green powder (0.033 mmol, 34 mg, 47% yield). $C_{65}H_{84}CrN_4P_2$ (1035.4 g/mol). ^1H NMR (400 MHz, C_6D_6) δ 37.70 ($Dn_{1/2} = 590$ Hz), 14.70 (120 Hz). IR ν_{max}/cm^{-1} 2901, 1451, 1190, 1090, 1030, 763, 676, 527. UV-vis $\lambda_{\text{max}}(THF)/nm$ 400inf ($\epsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 1770). Anal. calcd. for $C_{65}H_{84}CrN_4P_2$: C, 75.41; H, 8.18; N, 5.4. Found: C, 75.26; H, 8.54; N, 5.14. μ_{eff} (C_6D_6 , 298 K, 400MHz): $5.0 \mu_B$.

Single crystals suitable for X-ray diffraction were grown by storing the ether fraction at room temperature overnight.

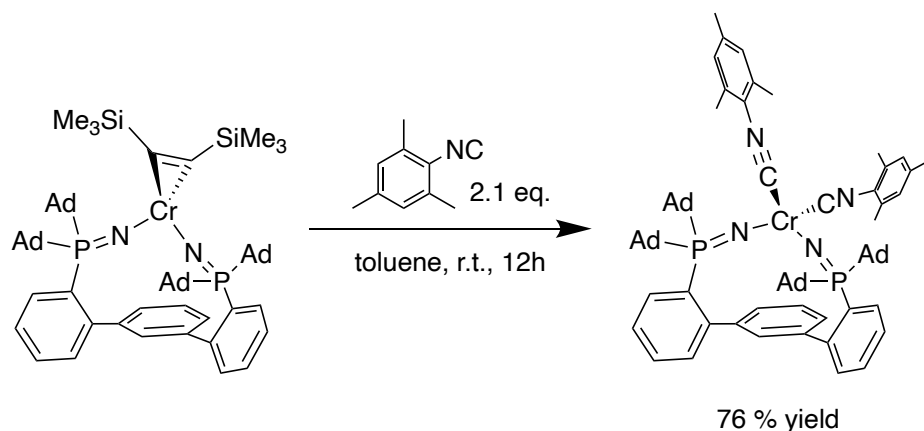
Synthesis of $L'^{Ad}Cr(CNMe)_2$ **2-3**

Method A – Reaction between $HL'^{Ad}Cr(HMDS)$ **2-1** and $MesNC$



A solution of mesityl isocyanide (0.124 mmol, 18.1 mg, 2.1 eq.) in toluene (1.5 mL) was added to a solution of $\text{HL}'^{\text{Ad}}\text{Cr}(\text{HMDS})$ (0.059 mmol, 63 mg, 1.0 eq.) in toluene (3.5 mL). Upon mixing, an instant color change from brown orange to dark maroon was observed. The resulting mixture was stirred for 12 h at room temperature and the solvent was subsequently removed *in vacuo* leaving a maroon film. Addition of pentane (5 mL) to this film resulted in a maroon suspension. The solids were separated by filtration and subsequently extracted into THF (6 mL). The pentane washings were set aside. Removal of the solvent from the THF fraction resulted in the formation of a maroon film which was subsequently triturated with Et_2O (2 mL). Removal of all volatiles *in vacuo* afforded the title compound as a maroon powder (0.037 mmol, 44 mg, 62% yield)

Method B – Reaction of $\text{L}'^{\text{Ad}}\text{Cr}(\text{h}^2\text{-TMSC}\equiv\text{CTMS})$ and MesNC



A solution of mesityl isocyanide (0.205 mmol, 30.0 mg, 2.1 eq.) in toluene (2.5 mL) was added to a solution of $\text{L}'^{\text{Ad}}\text{Cr}(\text{h}^2\text{-TMSC}\equiv\text{CTMS})$ (0.098 mmol, 100 mg, 1.0 eq.) in toluene (7.5 mL). Upon mixing an instant color change from crimson to dark maroon was observed. The resulting mixture was stirred for 12 h at room temperature and the solvent was subsequently removed *in vacuo* leaving a maroon film. Addition of pentane (10 mL) to this film resulted in a maroon suspension. The solids were separated by filtration and subsequently extracted into THF (10 mL). The pentane washings were set aside. Removal

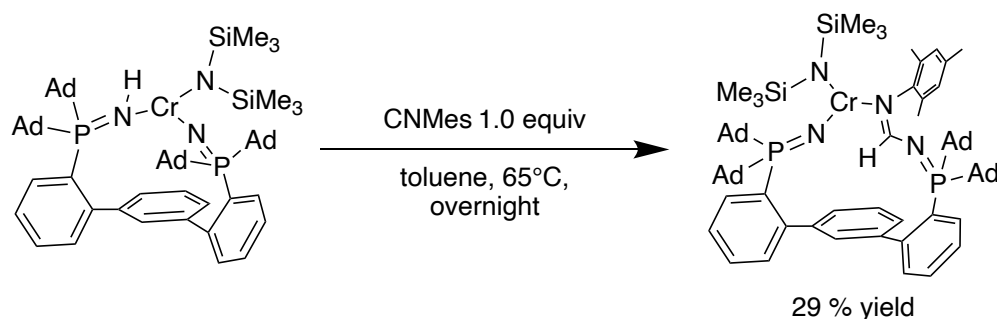
of the solvent from the THF fraction resulted in the formation of a maroon film which was triturated with Et₂O (2.5 mL). Removal of all volatiles *in vacuo* afforded the title compound as a maroon powder (0.074 mmol, 89 mg, 76% yield).

C₇₈H₉₄CrN₄P₂ (1201.6 g/mol). ¹H NMR (400 MHz, C₆D₆) δ 60.84 (Dn_{1/2} = 1560 Hz), 44.03 (1110 Hz), 28.03 (300 Hz), 27.44 (300 Hz), 24.97 (180 Hz), 20.42 (460 Hz), 9.27 (50 Hz), -4.88 (870 Hz). IR n_{max}/cm⁻¹ 2901, 1988 (CN), 1848 (CN), 1451, 1189, 1110, 1032, 527. UV-vis λ_{max}(THF)/nm 317inf (ε/dm³ mol⁻¹ 16840), 386 (11070), 537sh (4820). Anal. calcd. for C₇₈H₉₄CrN₄P₂: C, 77.97; H, 7.89; N, 4.66. Found: C, 76.74; H, 7.95; N, 4.32. μ_{eff} (C₆D₆, 298 K, 400MHz): 2.7 μ_B.

Single crystals suitable for X-ray diffraction were grown by storing the pentane fraction at room temperature for two days.

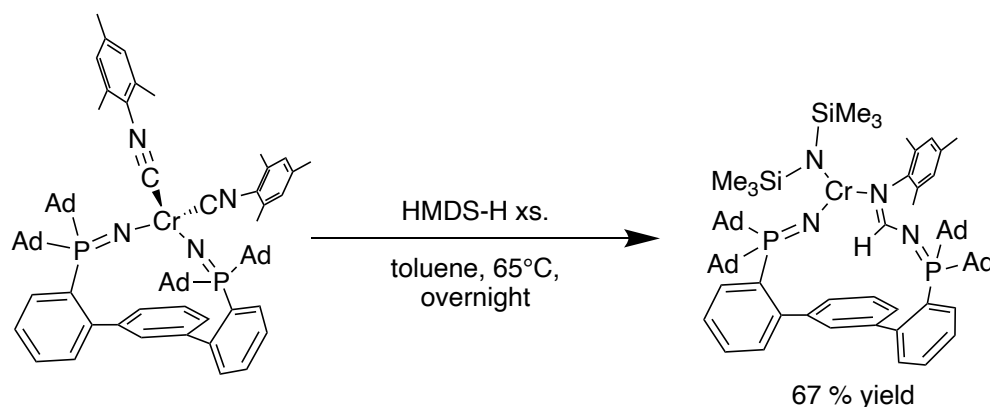
Synthesis of [N(Mes)CHL'^{Ad}]Cr(HMDS) **2-4**

Method A – Reaction of HL'^{Ad}CrHMDS **2-1** and MesNC



A mixture of mesityl isocyanide (0.071 mmol, 10.3 mg, 1.0 eq.) and HL'^{Ad}Cr(HMDS) (0.071 mmol, 75 mg, 1.0 eq.) was dissolved in toluene (5 mL) and transferred to a Schlenk flask sealed with a Teflon pin. The resulting maroon solution was removed from the glovebox and placed into an oil bath preheated to 65 °C. The temperature of the oil bath should be carefully controlled as temperatures over 70 °C initiate substantial decomposition of the Cr-containing materials. After stirring for 19 h, the resulting brown solution was allowed to cool to room temperature, brought back into the glovebox and the solvent removed was *in vacuo* leaving a brown film. Addition of pentane (3 mL) resulted in the formation of a brown suspension and the solids were separated by filtration and subsequently washed with pentane (3 x 2 mL) until the washings became colorless. Extraction into benzene (5 mL) and subsequent lyophilization afforded the title compound as a brown fluffy powder (0.0209 mmol, 25.4 mg, 29% yield).

Method B – Reaction of L'^{Ad}Cr(CNMes)₂ **2-3** and HMDS-H



$L'^{Ad}Cr(CNMe)_2$ (0.042 mmol, 50 mg, 1.0 eq.) was dissolved in toluene (10 mL), hexamethyldisilazane (0.42 mmol, 0.09 mL, 10.0 eq.) was added via syringe and the resulting solution was transferred to a Schlenk flask sealed with a Teflon pin. The resulting maroon solution was removed from the glovebox and placed into an oil bath preheated to 65 °C. The temperature of the oil bath should be carefully controlled as temperatures over 70°C initiates substantial decomposition of the Cr-containing materials. After being stirred for 19 h at that temperature, the resulting brown solution was allowed to cool to room temperature, brought back into the glovebox and the solvent removed *in vacuo* leaving a brown film. Addition of pentane (4 mL) resulted in the formation of a brown suspension and the solids were separated by filtration and subsequently washed with pentane (3 x 2 mL) until the washings became colorless. Extraction into THF (5 mL) and subsequent removal of volatiles *in vacuo* afforded the title compound as a brown powder (0.0280 mmol, 34.1 mg, 67.3% yield).

$C_{74}H_{102}CrN_4P_2Si_2$ (1217.8 g/mol). ^1H NMR (400 MHz, C_6D_6) δ 45.62 ($D_{n1/2} = 2650$ Hz), 12.73 (80 Hz). IR ν_{max}/cm^{-1} 2904, 1526 (NC(H)N), 1201, 994, 972, 825, 527. UV-vis $\lambda_{max}(THF)/nm$ 275inf ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 12980), 325sh (4210). Anal. calcd. for $C_{74}H_{102}CrN_4P_2Si_2$: C, 72.99; H, 8.44; N, 4.60. Found: C, 69.16; H, 7.68; N, 4.40. μ_{eff} (C_6D_6 , 298 K, 400MHz): 4.0 μ_B .

X-ray Crystallography

Compound	HL ^{1Ad} Cr ₂ (HMDS) 2-1	L ^{1Ad} Cr ₂ (IMe ₄) 2-2	L ^{1Ad} Cr ₂ (CNMes) ₂ 2-3	[N(Me ₃)CHL ^{1Ad}]Cr ₂ (HMDS) 2-4
CCDC Deposition Number				
Empirical formula	C ₇₀ H ₆₇ CrN ₃ P ₂ Si ₂	C ₆₉ H ₆₄ CrN ₃ OP ₂	C ₈₃ H ₁₀₆ CrN ₄ P ₂	C ₈₄ H ₁₂₆ CrN ₄ P ₂ Si ₂
Formula weight	1150.62	1109.42	1273.65	1362.00
Temperature/K	100.15	100	100	100
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	P2 ₁ /c	P-1	P-1	P-1
a/Å	17.2200(2)	12.5702(12)	13.0040(12)	12.4354(11)
b/Å	19.1644(2)	14.2751(13)	13.4906(12)	14.9919(14)
c/Å	19.6121(2)	17.2724(16)	19.9105(18)	21.3042(18)
α/°	90	72.810(3)	94.193(4)	99.529(4)
β/°	108.3130(10)	83.457(4)	97.241(4)	105.887(4)
γ/°	90	89.402(4)	96.460(4)	90.357(4)
Volume/Å ³	6144.42(12)	2940.8(5)	3429.5(5)	3761.8(6)
Z	4	2	2	2
ρ _{calc} g/cm ³	1.244	1.253	1.233	1.202
μ/mm ⁻¹	2.726	0.315	0.278	0.290
F(000)	2480.0	1196.0	1372.0	1480.0
Crystal size/mm ³	0.182 × 0.11 × 0.091	0.3 × 0.1 × 0.05	0.05 × 0.05 × 0.03	0.1 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)
2θ range for data collection/°	6.618 to 157.856	3.346 to 69.804	3.262 to 69.872	2.828 to 54.194
Index ranges	-21 ≤ h ≤ 21, -24 ≤ k ≤ 18, -24 ≤ l ≤ 24	-19 ≤ h ≤ 19, -21 ≤ k ≤ 22, -27 ≤ l ≤ 27	-20 ≤ h ≤ 20, -21 ≤ k ≤ 21, -31 ≤ l ≤ 31	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -26 ≤ l ≤ 26
Reflections collected	69007	161501	175341	136395
Independent reflections	12990	23611	27673	15387
Data/restraints/parameters	[R _{int} = 0.0330, R _{sigma} = 0.0236] 12990/0/744	[R _{int} = 0.0750, R _{sigma} = 0.0511] 23611/0/700	[R _{int} = 0.0889, R _{sigma} = 0.0821] 27673/69/901	[R _{int} = 0.0838, R _{sigma} = 0.0481] 15387/50/951
Goodness-of-fit on F ²	1.079	1.058	1.034	1.026
Final R indexes [I > 2σ (I)]	R ₁ = 0.0381, wR ₂ = 0.0991	R ₁ = 0.0469, wR ₂ = 0.1178	R ₁ = 0.0667, wR ₂ = 0.1643	R ₁ = 0.0530, wR ₂ = 0.1333
Final R indexes [all data]	R ₁ = 0.0420, wR ₂ = 0.1019	R ₁ = 0.0641, wR ₂ = 0.1270	R ₁ = 0.1233, wR ₂ = 0.1927	R ₁ = 0.0727, wR ₂ = 0.1443
Largest diff. peak/hole / e Å ⁻³	0.45/-0.52	0.57/-0.77	1.54/-0.83	0.93/-0.70

FT-IR Spectroscopy

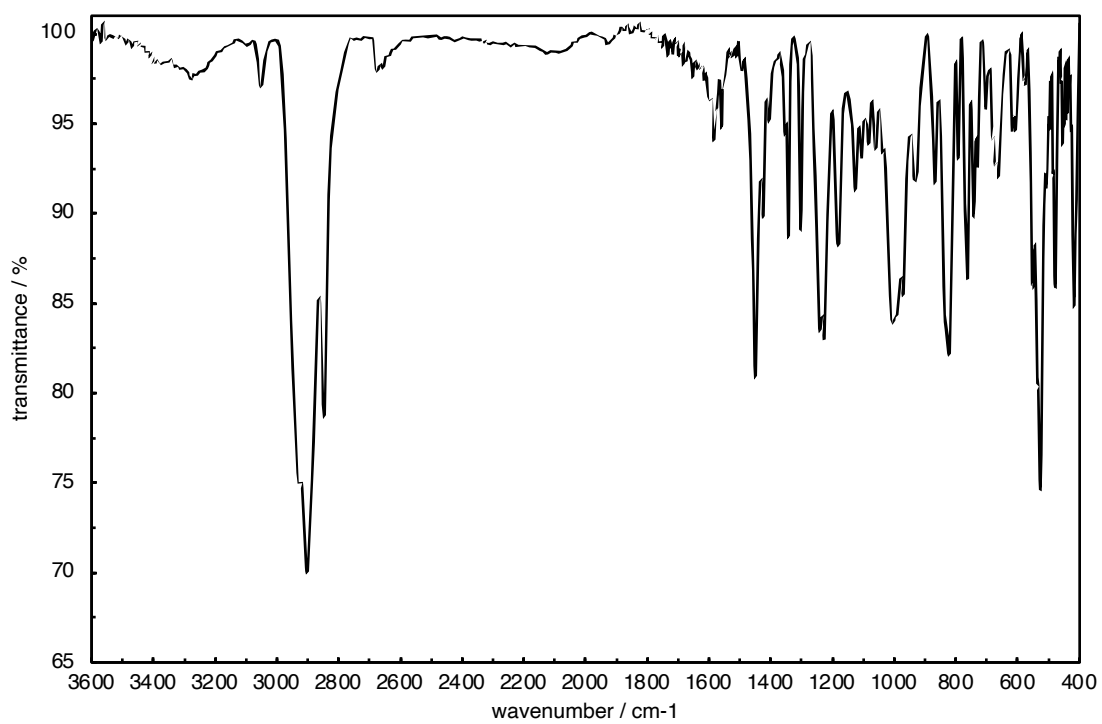


Figure 2-15 FTIR spectrum of HL¹AdCr(HMDS) **2-1** (KBr pellet).

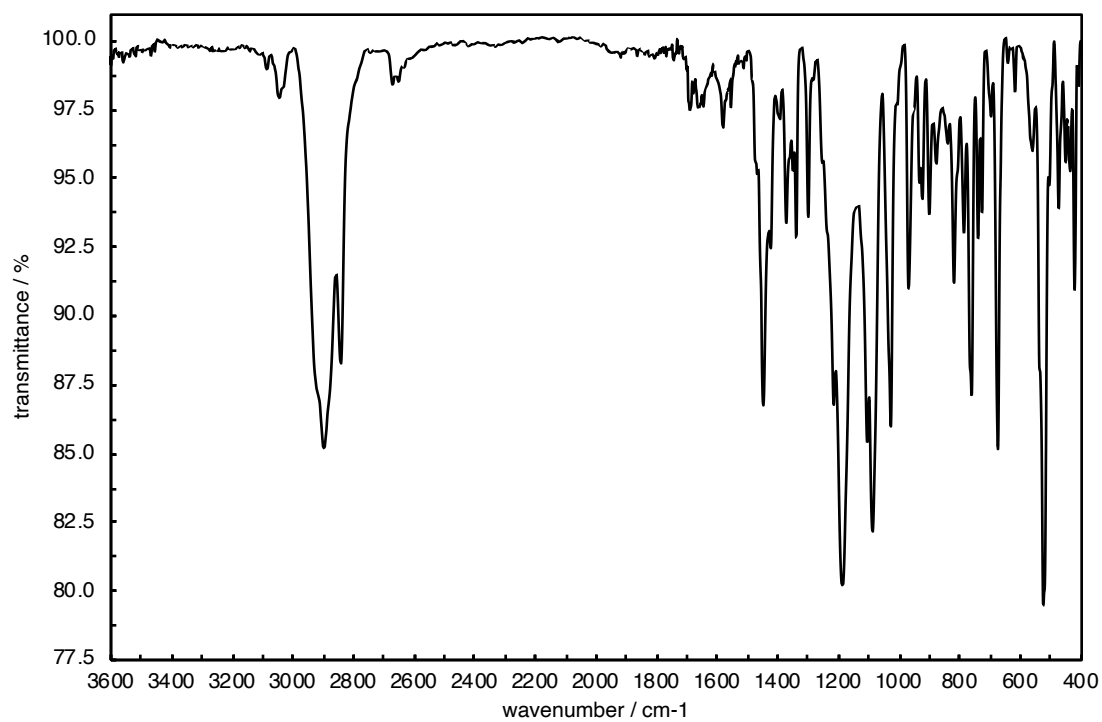


Figure 2-16 FTIR spectrum of L'AdCr(IMe4) 2-2 (KBr pellet).

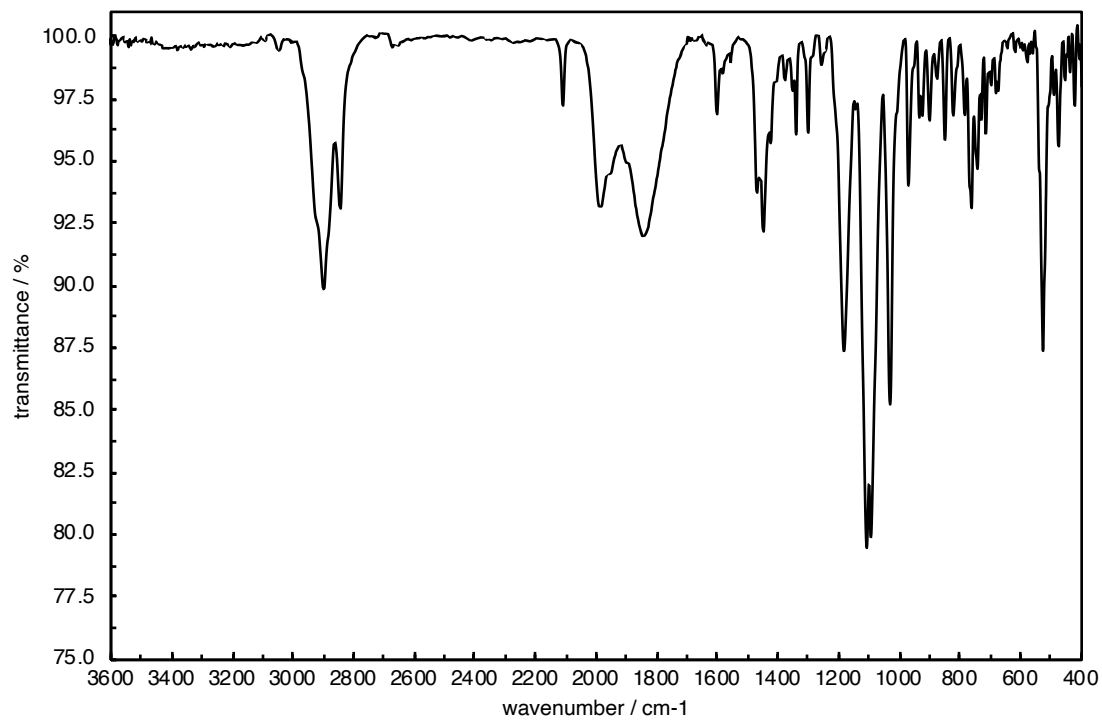


Figure 2-17 FTIR spectrum of L'AdCr(CNMeS)₂ 2-3 (KBr pellet).

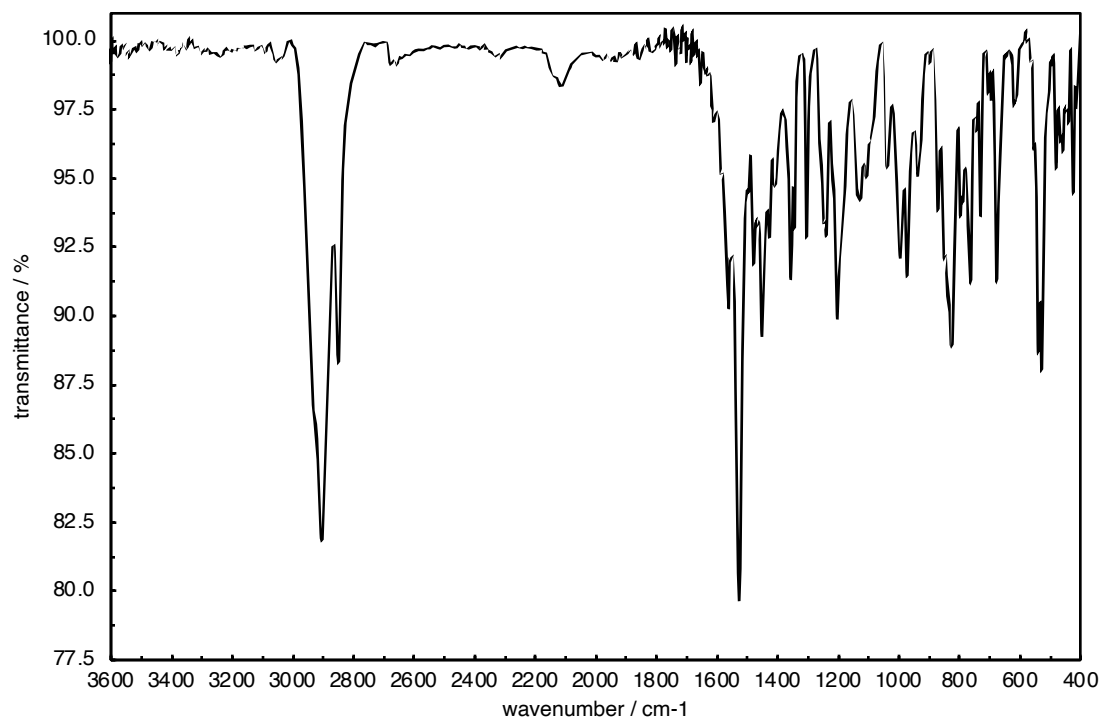


Figure 2-18 FTIR spectrum of [N(Mes)CHL'Ad]Cr(HMDS) 2-4 (KBr pellet).

NMR spectroscopy

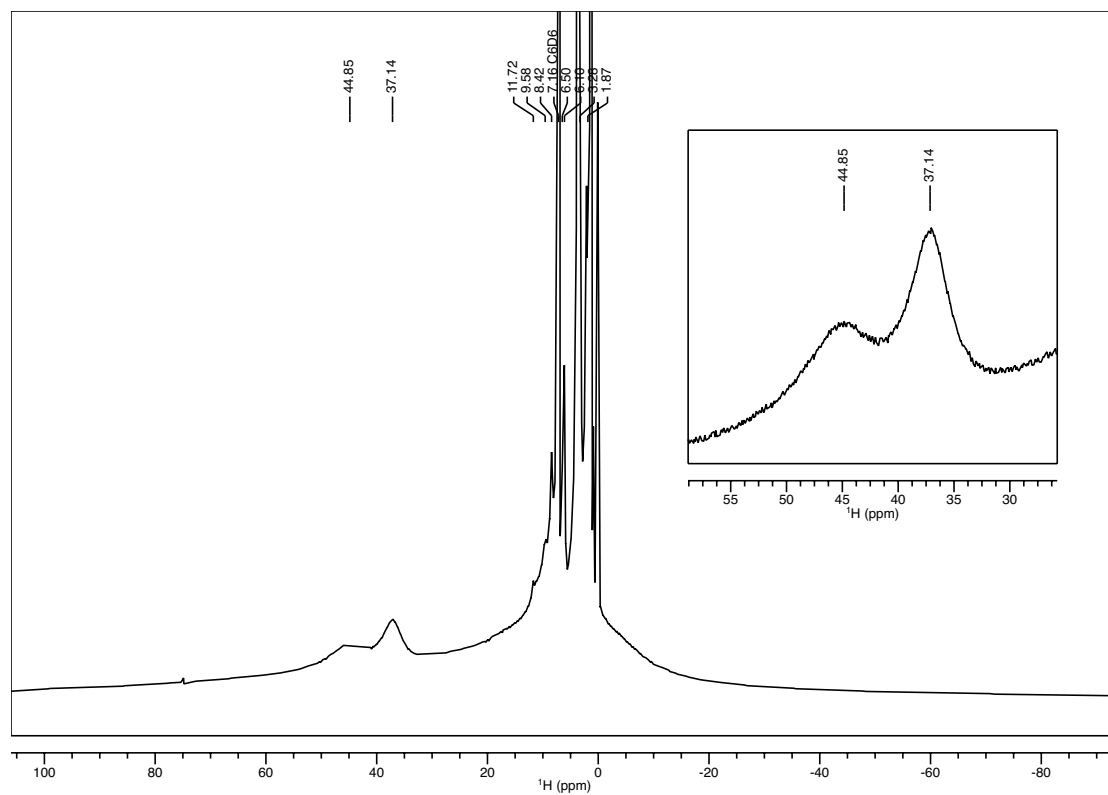


Figure 2-19 ^1H NMR spectrum (400 MHz) of $\text{HL}'\text{AdCr}(\text{HMDS})$ **2-1** recorded in C_6D_6 at 298 K.

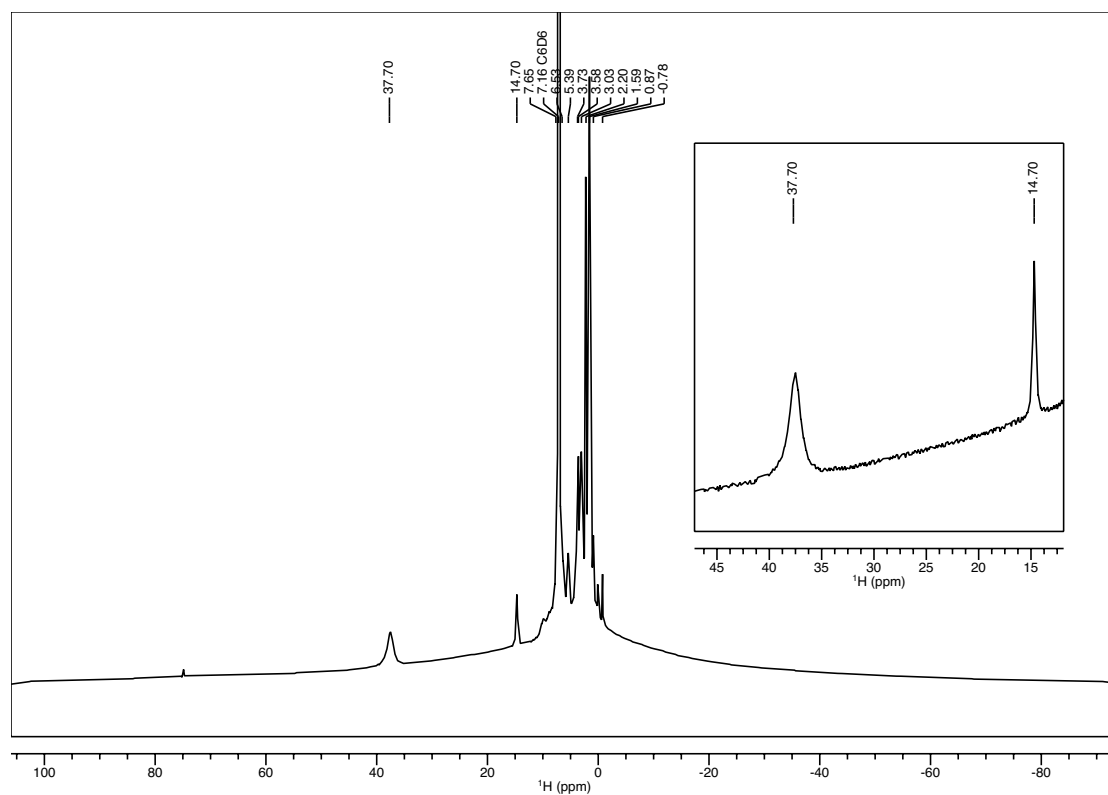


Figure 2-20 ^1H NMR spectrum (400 MHz) of $\text{L}'\text{AdCr}(\text{IME}_4)$ **2-2** recorded in C_6D_6 at 298 K.

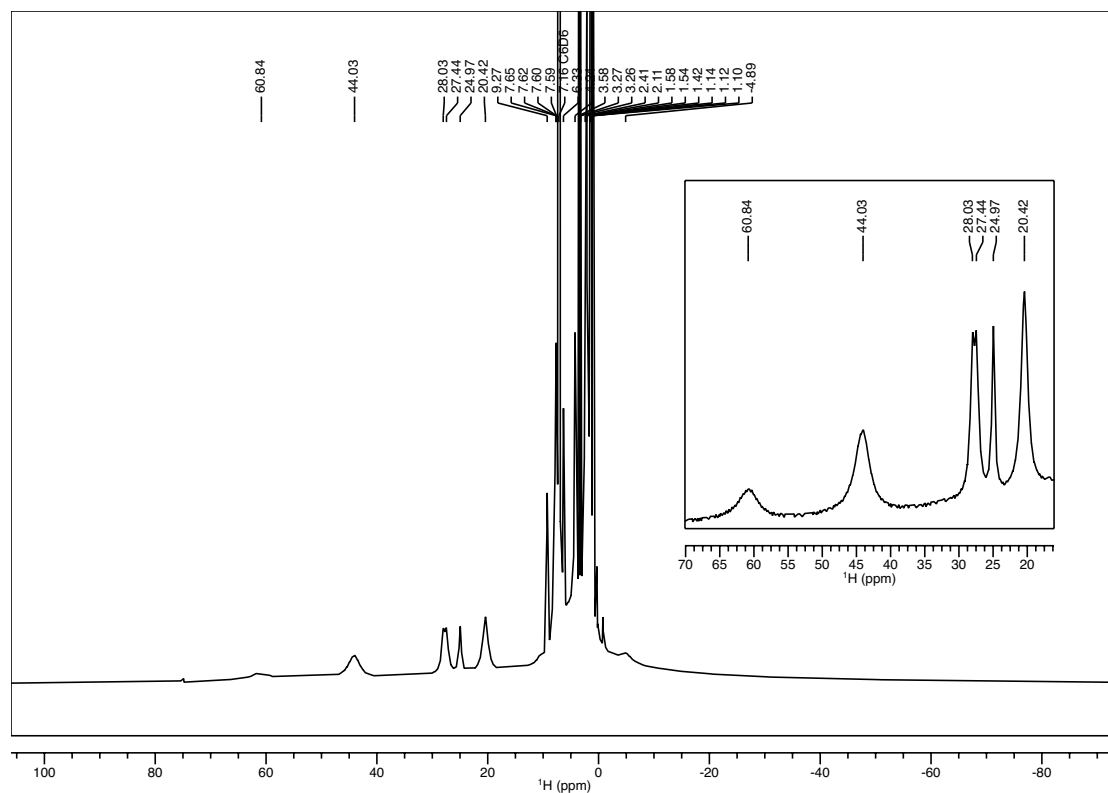


Figure 2-21 ^1H NMR spectrum (400 MHz) of $\text{L}'\text{AdCr}(\text{CNMe})_2$ **2-3** recorded in C_6D_6 at 298 K.

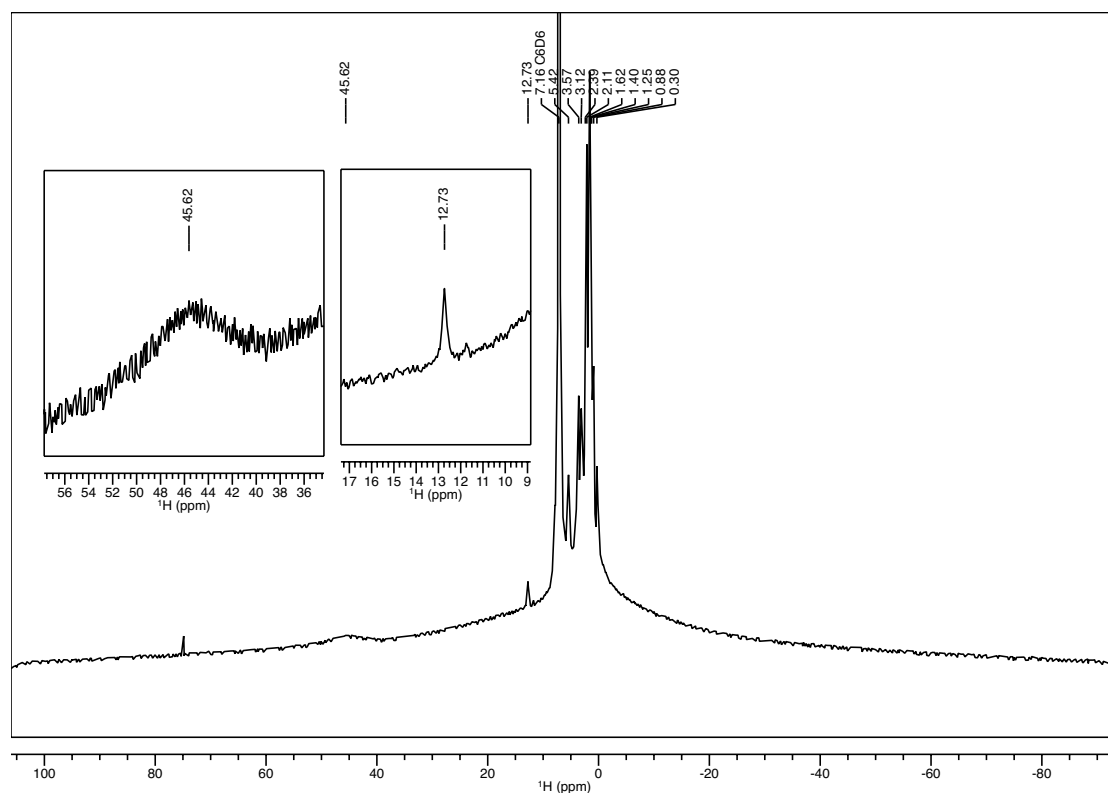


Figure 2-22 ^1H NMR spectrum (400 MHz) of $[\text{N}(\text{Me})\text{CHL}'\text{Ad}]\text{Cr}(\text{HMDS})$ **2-4** recorded in C_6D_6 at 298 K.

UV/visible Spectroscopy

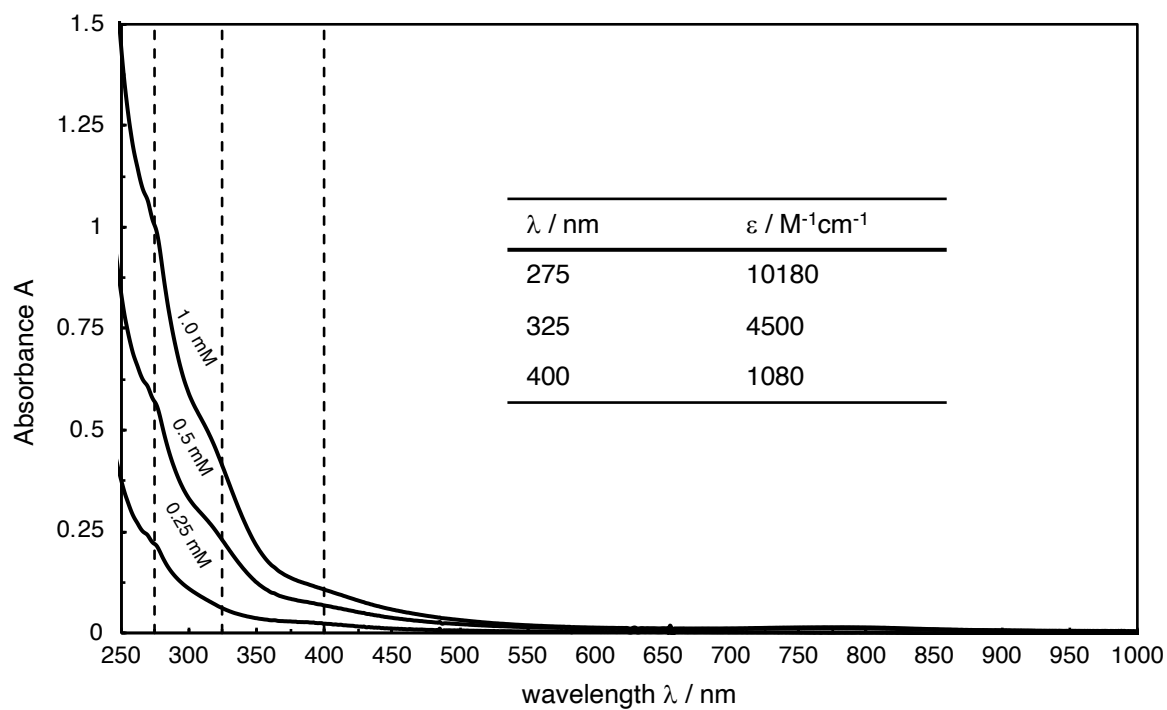


Figure 2-23 UV/visible spectrum of HL¹AdCr(HMDS) **2-1** at various concentrations in THF recorded at 298 K.

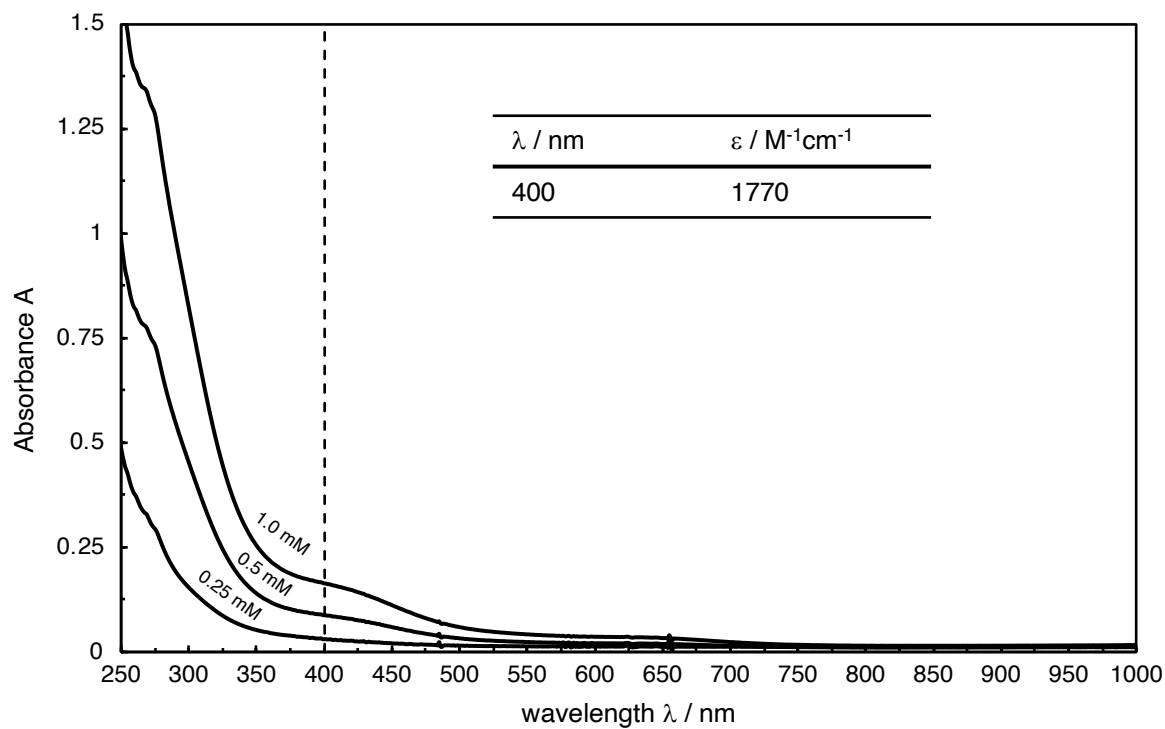


Figure 2-24 UV/visible spectrum of L¹AdCr(Ime₄) **2-2** at various concentrations in THF recorded at 298 K.

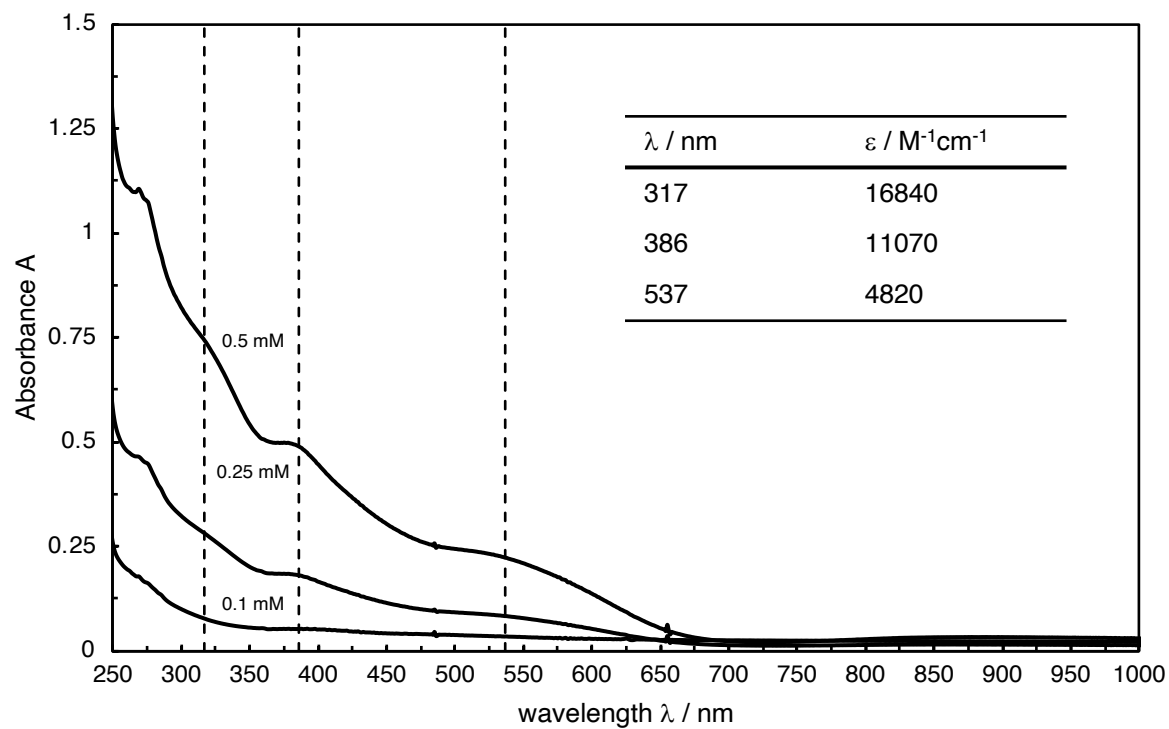


Figure 2-25 UV/visible spectrum of $L^1AdCr(CNMe)_2$ **2-3** at various concentrations in THF recorded at 298 K.

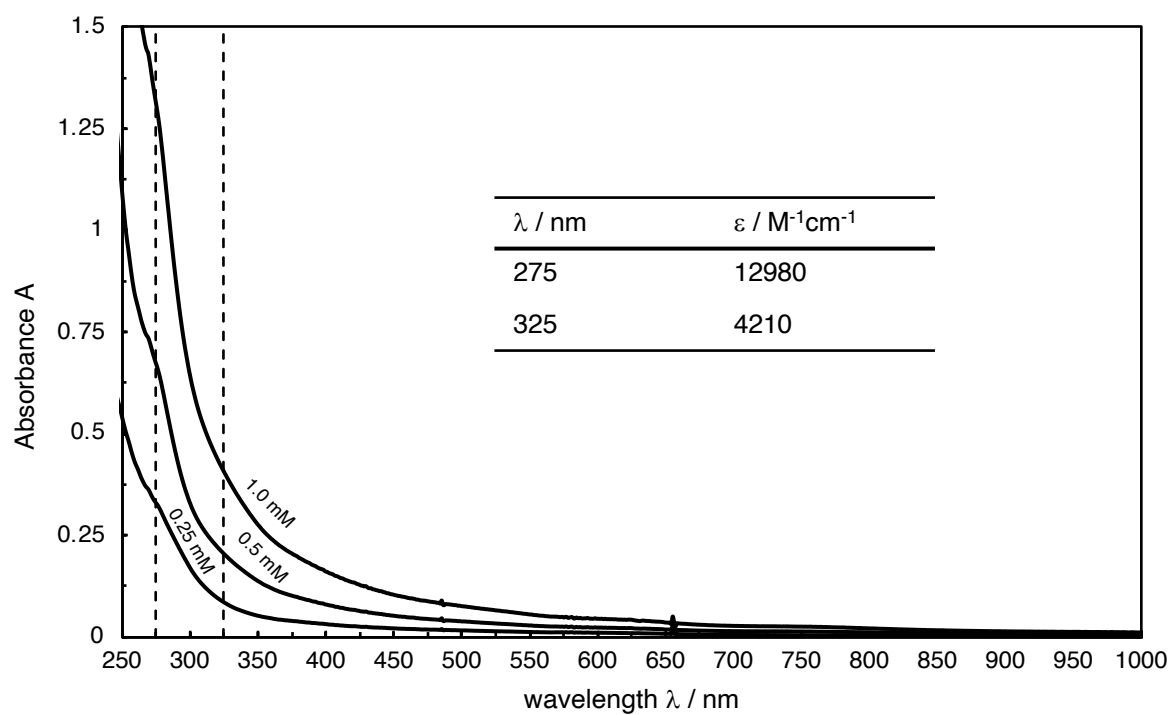


Figure 2-26 UV/visible spectrum of $[N(Mes)CHL^1Ad]Cr(HMDS)$ **2-4** at various concentrations in THF recorded at 298 K.

Computational Methods

DFT calculations were performed using ORCA version 5.0.4.⁷⁸

Gas phase geometry optimizations of characterized compounds and intermediates

Gas phase geometry optimizations were carried out using the B3LYP⁷⁹ functional and the def2-TZVPP⁸⁰ basis set on chromium, nitrogen, silicon and phosphorous atoms as well as carbon atoms coordinating to the chromium center; def2-SVP⁸⁰ was used elsewhere. Initial coordinates were obtained from the crystal structures. No truncations were performed in an effort to capture the steric interactions with the adamantyl groups on the ligand. The RIJCOSX approximation⁸¹ in conjunction with the def2/J basis set⁸² was used to speed up the calculations and Grimme's DFT-D3(BJ)⁸³ method was used to apply dispersion corrections. Tighter-than-default convergence criteria for the geometry optimization were applied using the keywords "tightOPT". Default integration grids were used during these calculations. Numerical frequency calculations performed on the optimized geometries obtained for **2-1** - **2-4** and **2-Int 1** - **2-Int 3** did not exhibit any imaginary frequencies.

Sample input file:

```
!UKS B3LYP TightOPT def2-SVP def2/J D3BJ
!Numfreq

%maxcore 4096
%PAL NPROCS 32 END

* xyz 0 5
Cr 0.00000 0.00000 0.00000 newgto "def2-TZVPP" END
P -1.22713 -2.83858 1.05996 newgto "def2-TZVPP" END
P -0.92100 3.28199 -0.38582 newgto "def2-TZVPP" END
N -0.57289 1.81883 -0.08396 newgto "def2-TZVPP" END
N -0.40633 -1.88034 0.18975 newgto "def2-TZVPP" END
N 2.91963 0.74626 0.74474 newgto "def2-TZVPP" END
N 2.87342 -0.63802 -0.87310 newgto "def2-TZVPP" END
C 2.06337 0.00000 0.00000 newgto "def2-TZVPP" END
C -3.04093 -2.89218 0.65642
C -3.90941 -3.64986 1.45297
H -3.54131 -4.20998 2.12611
...
further coordinates
...
*
```

Spin density plots

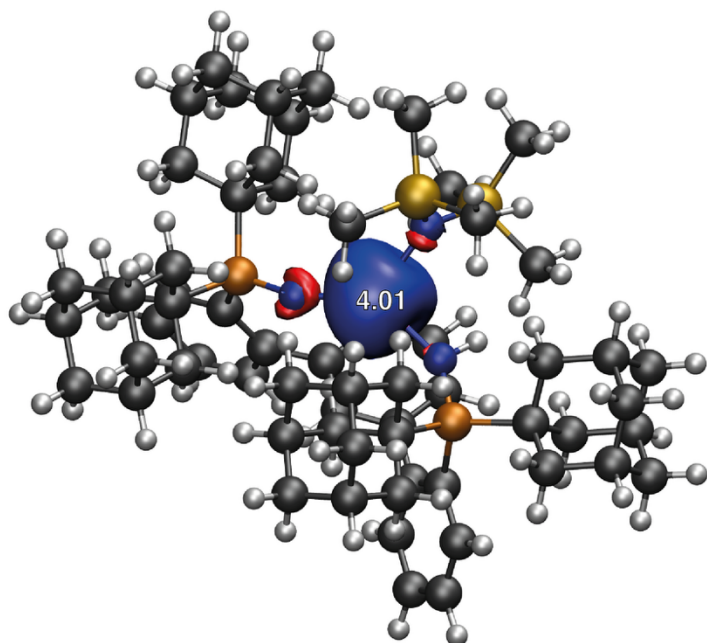


Figure 2-27 Spin density plot of HL¹AdCr(HMDS) **2-1** (isovalue 0.005). Numbers indicate Mulliken spin density for a given atom.

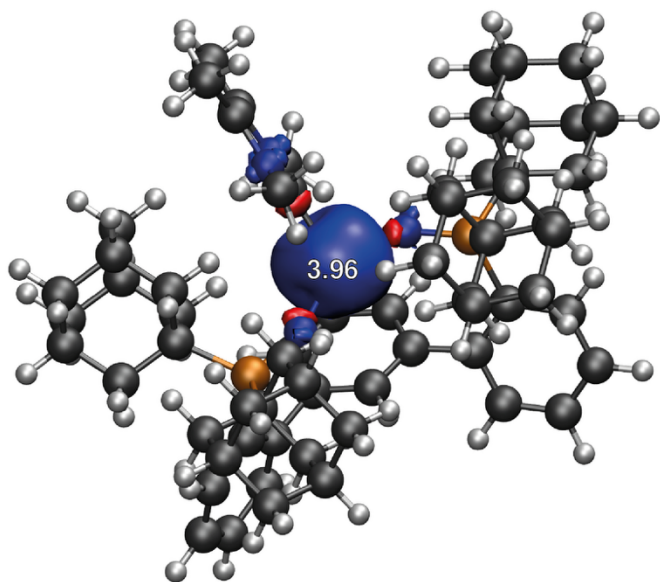


Figure 2-28 Spin density plot of L¹AdCr(IME₄) **2-2** (isovalue 0.005). Numbers indicate Mulliken spin density for a given atom.

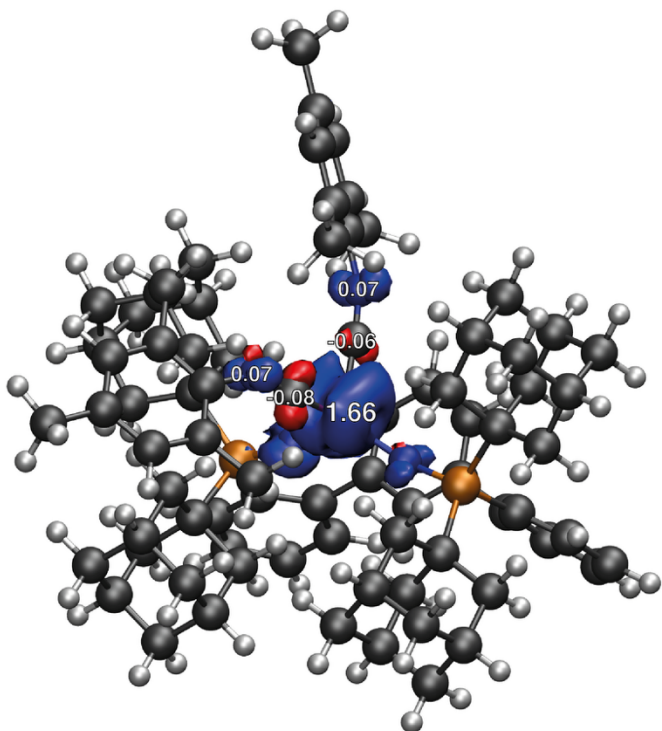


Figure 2-29 Spin density plot of $L'^{Ad}Cr(CNMes)_2$ **2-3** (isovalue 0.005). Numbers indicate Mulliken spin density for a given atom.

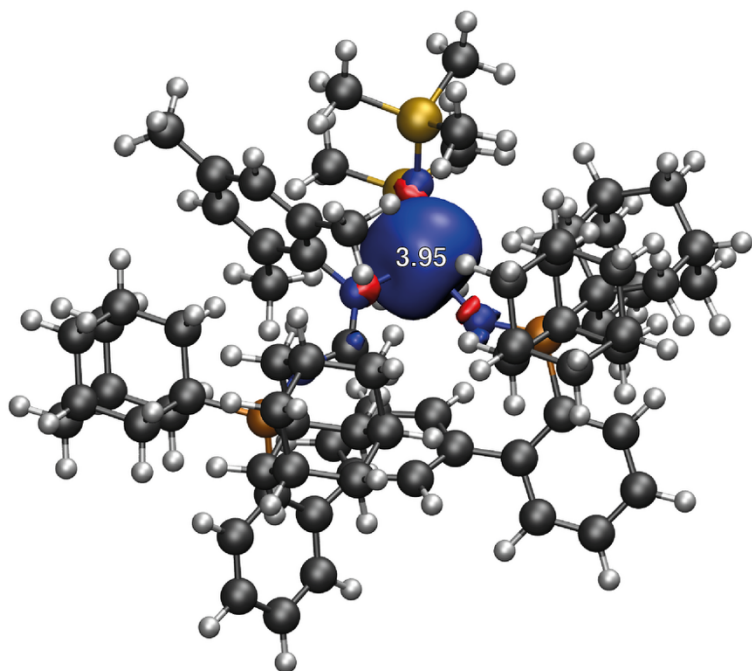


Figure 2-30 Spin density plot of $[N(Mes)CHL'^{Ad}]Cr(HMDS)$ **2-4** (isovalue 0.005). Numbers indicate Mulliken spin density for a given atom.

Relative spin state energies

Compound	S=2 / kcal mol ⁻¹	S=1 / kcal mol ⁻¹
HL ^{'Ad} Cr(HMDS) 1	± 0	+ 25.9
L ^{'Ad} Cr(IME ₄) 2	± 0	+ 22.0
L ^{'Ad} Cr(CNMe _s) ₂ 3	33.5	± 0
[N(Mes)CHL ^{'Ad}]Cr(HMDS) 4	± 0	+ 25.4
HL ^{'Ad} Cr(HMDS)(CNMe _s) Int1	± 0	+ 14.1
L ^{'Ad} Cr (CNMe _s) Int2	± 0	+ 5.47
[h ² - HL ^{'Ad} CN(Mes)]Cr(HMDS) Int3	± 0	+ 26.7

Determination of transition states

Relaxed surface scans starting from the geometry obtained for **2-Int 1** were used to provide reasonable starting geometries for subsequent transition state optimizations. In order to speed up these surface scans the BP86^{84,85} functional was initially used together with the def2-SVP⁸⁰ basis set of all atoms and Grimme's DFT-D3(BJ)⁸³ dispersion correction. The split basis set outlined above and B3LYP functional was applied after a reasonable guess for the transition states had been obtained. Default convergence criteria and integration grids were used. Figure S18 illustrates the results of the relaxed surface scans. Shown are the bond distances that were scanned along to identify a geometry close to the transition state for insertion (red) and HMDS-H loss (black).

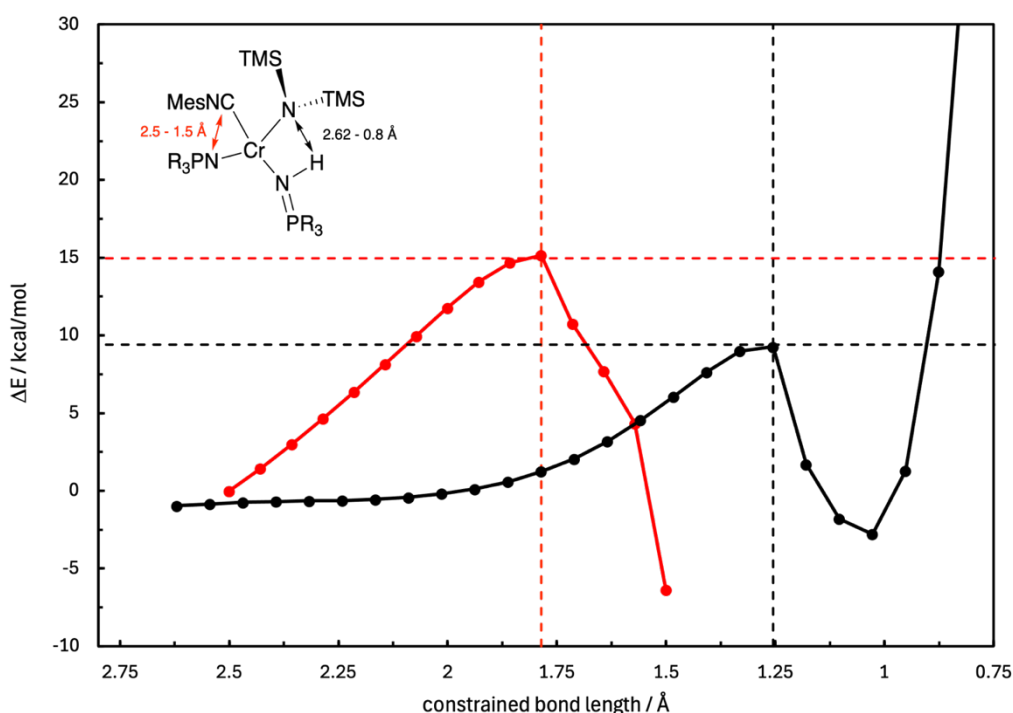


Figure 2-31 Relaxed surface scan (BP86/def2-SVP/D3BJ) varying the C–N distance in **2-Int 1** from 2.5 Å to 1.5 Å in 15 steps (red) and N–H distance in **2-Int 1** from 2.62 Å to 0.8 Å (black) in 25 steps along the quintet surface. Geometries corresponding to the steps indicated with dashed lines were used in subsequent transition state optimizations.

Sample input file:

```
!UKS BP86 OPT def2-SVP def2/J D3BJ
!NOPRINTMOS

%geom Scan B 4 5 = 2.5, 1.5, 15 end
end

%maxcore 4096
%PAL NPROCS 36 END

* xyz 0 5
Cr 0.10001150147691 0.46295332306856 0.80183296408386
P 3.41080013716779 0.25236662414478 -0.69432945685700
P -2.36829379130097 -0.21163235293610 -1.49343243614198
N 1.91849388526188 0.70925852171861 -0.37369994662818
N -1.02759657559008 0.10746276094891 -0.79943239624815
C -0.88032148229922 -0.95027253425322 1.94520916396405
N -1.33537065879833 -1.86385833588382 2.50973164771490
N 0.58460433326726 1.65530335122718 2.46272580552731
Si 0.52058803659654 1.01176146652687 4.04158588539039
Si 0.34613621699286 3.31208794830558 2.10727172833109
...
further coordinates
...
*
```

The geometries identified close to the transition states were subsequently used as starting points for “OptTS” calculations. Initially these optimizations were performed with the same method as the relaxed surface scans. A numerical Hessian was calculated once to aid the optimization.

Sample input file:

```
!UKS BP86 OPTTS def2-SVP def2/J D3BJ
!MOREAD

%geom
Calc_Hess true
NumHess true
end

%moinp "insertion_RSS_BP86_SVP.011.gbw"

%maxcore 4096
%PAL NPROCS 36 END

* xyzfile 0 5 insertion_RSS_BP86_SVP.011.xyz
```

The obtained geometries were then fed into a subsequent “OptTS” calculation still using the BP86 functional but employing the split basis set outlined above for the geometry optimizations of characterized compounds and the intermediates. During these calculations a numerical Hessian was calculated every 50 steps.

Sample input file:

```

!UKS BP86 OPTTS def2-SVP def2/J D3BJ
#!NUMFREQ

%geom
Calc_Hess true
NumHess true
Recalc_Hess 50
end

%maxcore 4096
%PAL NPROCS 36 END

* xyz 0 5
Cr 0.02669802168187 0.29762917608414 0.60945696006494      newgto "def2-TZVPP" END
P 3.37454165104357 0.33086807539873 -0.41344911529473      newgto "def2-TZVPP" END
P -2.40608124707586 -0.38243003066165 -1.59906252560957    newgto "def2-TZVPP" END
N 1.94892543752933 0.77917278293335 0.13640724098057      newgto "def2-TZVPP" END
N -0.98886495784538 -0.08576872764754 -0.94514856075977    newgto "def2-TZVPP" END
C -0.94501090589432 -0.92499591204238 1.77528330589998     newgto "def2-TZVPP" END
N -1.41511482028698 -1.80841676608574 2.43703755175346     newgto "def2-TZVPP" END
N 0.82392510053698 1.55647506396686 2.25034668357669      newgto "def2-TZVPP" END
Si 0.76573583699961 0.84692577614771 3.86407634721160     newgto "def2-TZVPP" END
Si 0.37702418293367 3.24540920431655 1.94112866117070     newgto "def2-TZVPP" END
H 1.69048345224161 1.25224984831456 1.35571466450141      newgto "def2-TZVPP" END
C -6.42553725576869 0.66839107942563 -0.43522808461396     newgto "def2-TZVPP" END
C -2.46991226124539 0.25100399363803 -3.34448827461816
...
further coordinates
...
*
```

The geometries resulting from these calculations were sufficiently close to the transition states for the “OptTS” calculation to converge when the method outlined for characterized compounds and intermediates was used (B3LYP/def2-SVP/def2-TZVPP split basis set/D3BJ dispersion correction). In order to aid the geometry optimization, the most recently calculated BP86 Hessian was fed into the B3LYP calculations. Frequency calculations performed on the obtained geometries revealed one imaginary frequency corresponding to insertion of the CNMes into the Cr-NP bond and the proton transfer between Cr-HNP and HMDS fragments, respectively.

Sample input file:

```
!UKS B3LYP OPTTS def2-SVP def2/J D3BJ
!NUMFREQ
```

```
%geom
inhess Read
InHessName "OptTS_BP86_split_basis_num_hessian_50.001.hess"
end
```

```
%maxcore 4096
%PAL NPROCS 36 END
```

```
* xyz 0 5
```

```
Cr 0.02587977960613 0.27768052695055 0.60636478118574
P 3.36288597765402 0.30763433371747 -0.41419592587075
P -2.40992633385975 -0.37271164527466 -1.59899744279940
N 1.94840396854280 0.74775017404128 0.11384295568761
N -1.02087766409431 -0.07108945676511 -0.93981879974208
C -0.94059089700094 -0.93983171684567 1.78868760085498
N -1.40716304305773 -1.80235052414228 2.46453193051651
N 0.83183675623341 1.55568480466610 2.23339863916413
Si 0.76497487528244 0.85573987764548 3.83102152196397
Si 0.38263201472050 3.22381046137742 1.92464586127491
H 1.69106432642866 1.23870696464679 1.32913186210076
C -6.41630381175428 0.68785710783446 -0.44231342943345
```

```
newgto "def2-TZVPP" END
newgto "def2-TZVPP" END
newgto "def2-TZVPP" END
newgto "def2-TZVPP" END
newgto "def2-TZVPP" END
newgto "def2-TZVPP" END
newgto "def2-TZVPP" END
newgto "def2-TZVPP" END
newgto "def2-TZVPP" END
newgto "def2-TZVPP" END
```

```
...
further coordinates
...
*
```

Chapter 3 Four-Electron Oxidative Addition of an N=N Double Bond at a Chromium Metallocyclopropene

Introduction

Oxidative addition reactions are ubiquitous across organometallic chemistry constituting critical steps in many of the stoichiometric and catalytic applications of transition metal complexes.⁸⁶ Traditionally, this process involves the cleavage of a single bond to form an organometallic complex containing two additional ligands and is accompanied by an increase of the metal oxidation state by two. Four-electron oxidative addition reactions—wherein a metal center inserts into a double bond—are significantly less common, but their exploration has the potential to substantially expand the toolkit available to synthetic chemists. This area was pioneered by the Mayer group, who utilized a tungsten(II) complex ($\text{WCl}_2(\text{PMe}_2\text{Ph})_4$) that was found to react with cumulated double bonds ($\text{E}=\text{C}=\text{E}'$) in a two-electron process to form tungsten(IV) complexes ($\text{WCl}_2(\text{E})(\text{C}=\text{E}')(\text{PR}_3)_2$).⁵ The former compound was later shown to react with cyclopentanone to form a tungsten(VI)(oxo)(alkylidene) complex $\text{W}(\text{O})(=\text{CR}_2)\text{Cl}_2(\text{PR}_3)$, which constitutes the first documented example of a 4-electron oxidative addition.⁶ With regard to nonpolar double bonds, reactions of this class are limited to the four electron reductive cleavage of oxygen^{7–11} and the oxidative addition of N=N bonds in azo compounds (Figure 3-1A).

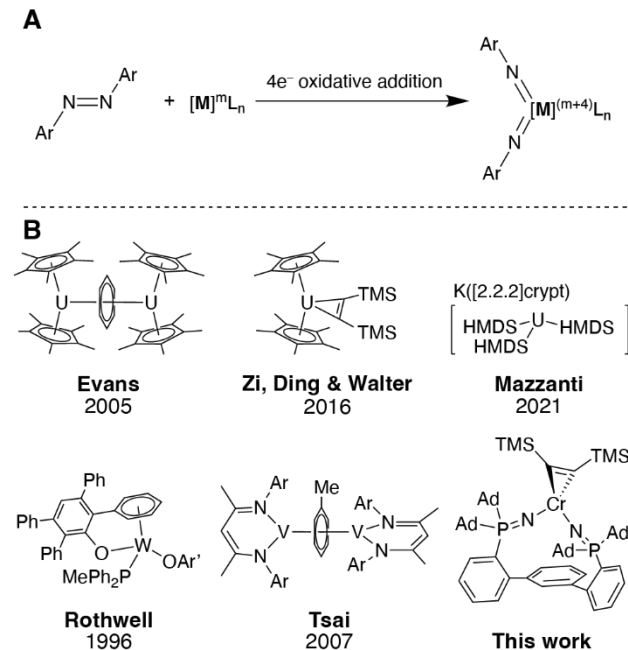


Figure 3-1. (A) Non-classical oxidative addition of azo compounds. (B) Representative complexes known to perform this reaction.

The latter was first demonstrated by the Rothwell group employing a η^6 -arene stabilized tungsten(II) aryloxide complex (Figure 3-1B).^{7,87,88} In recent years, a number of uranium complexes bearing redox active ligands have been shown to effect the splitting of

azobenzene forming uranium(VI) diimido complexes concomitant with co-ligands that are either oxidatively coupled,^{89–92} expelled,^{93,94} or remain bound to the uranium center.^{95,96} Recently, the Mazzanti group has demonstrated that a single uranium(II) center lacking redox active ligands can facilitate azobenzene cleavage in the absence of external reductants (Figure 3-1B).⁹⁷

We sought to investigate the usage of abundant, first-row transition metals in mediating this difficult bond activation. There are only two reports in this area, both of which employ vanadium centers in a formal oxidation state of vanadium(I) (Figure 3-1B).^{98,99} In this report, we report an extension of this chemistry to a formal chromium(II) center. Anionic phosphinimides (PNs) were chosen to circumvent the poorer reducing ability commonly ascribed to chromium(II) centers as compared to vanadium(I) centers. We demonstrate herein that a bis(phosphinimide)chromium(II) species engages with alkyne ligands to afford a rare chromium(IV)metallocyclopropene complex that, in turn, serves as a synthon to mediate the four-electron oxidative addition of 4,4'-difluoroazobenzene.

Results and Discussion

Previously, our group has employed tridentate phosphinimine-based pro-ligands to prepare sterically-encumbered metal-PN complexes.^{46,49} In this study a bidentate design (L'^{Ad}) was chosen to provide two open coordination sites on the metal center. The preparation of the new pro-ligand $H_2L'^{Ad}$ (**3-1**) is described in the Supporting Information file. Attempts to simultaneously deprotonate and metalate **3-1** with equimolar $Cr(Mes)_2(PMe_3)_2$ in benzene lead to the formation of intractable product mixtures suggesting the need for a hemilabile supporting ligand which stabilizes the low valent chromium center. Accordingly, Metalation utilizing the same conditions in the presence of 1.5 equivalents of $TMSC\equiv CTMS$ affords $L'^{Ad}Cr(\eta^2-TMSC\equiv CTMS)$ (**3-2**) as a red powder in 77 % yield (Figure 3-2A).¹⁰⁰ The solid-state structure of **3-2** (Figure 3-2B) features a chromium atom bound to two phosphinimide moieties and the alkyne ligand in η^2 -fashion. Unlike most four-coordinate Cr(II) complexes which adopt square planar geometries and high spin states,⁵¹ complex **3-2** features a pseudo-tetrahedral ($\tau_4' = 0.834$) Cr center and adopts an intermediate spin state at room temperature ($S = 1$, $\mu_{eff} = 2.9 \mu_B$). The bond distances between the chromium and phosphinimide nitrogen atoms ($d(Cr-N)$: 1.807(4) Å and 1.819(4) Å) are consistent with the pro-ligand being fully deprotonated, which is corroborated by the absence of peaks ascribable to $\nu(N-H)$ stretching vibrations in the FTIR spectrum of solid **3-2** (Figure 3-6). These bond distances are significantly shorter than the corresponding distances found in a three-coordinate bisphosphinimide/phosphinimine chromium(II) compound (1.936(14) Å)²⁴ and suggest considerable oxidation of the chromium center (*vide infra*).

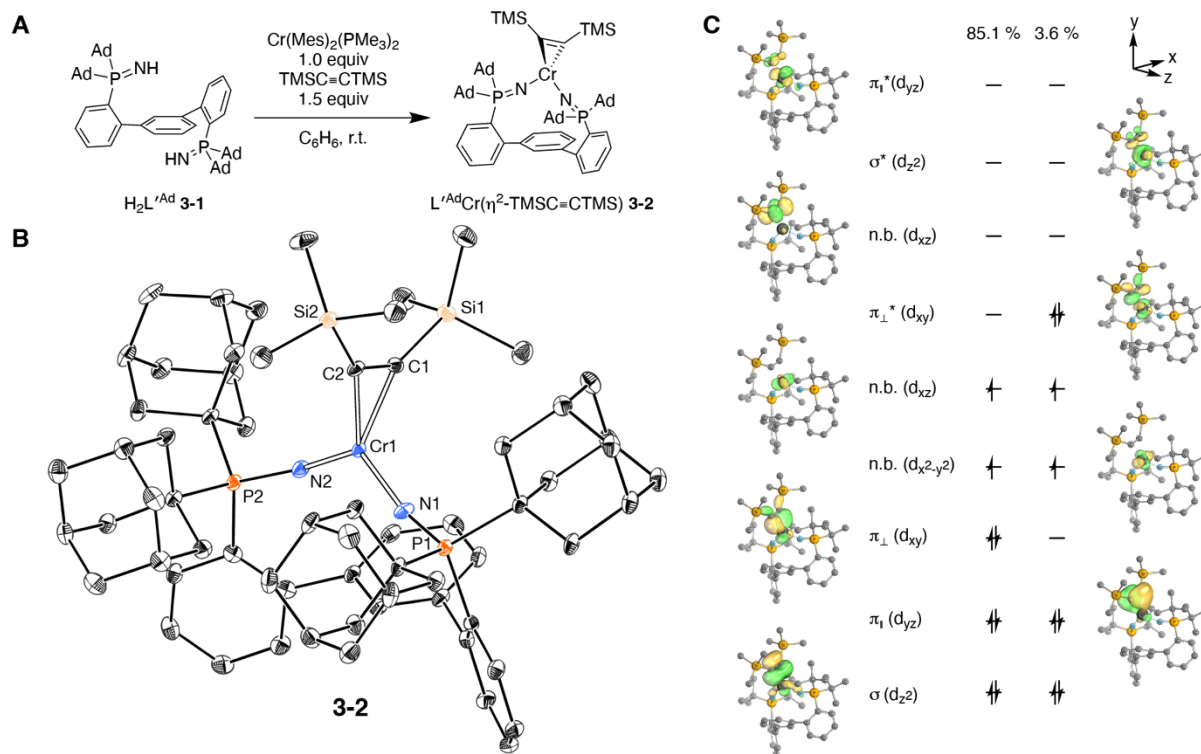


Figure 3-2 (A) Synthesis of $L'AdCr(\eta^2-TMSC\equiv CTMS)$ (**3-2**). (B) Crystal structure of **3-2** with ellipsoids shown at 50% probability.^[50] Hydrogen atoms omitted for clarity. Selected bond distances (Å), Cr1-N1 1.807(4), Cr1-N2 1.819(4), Cr1-C1 1.947(5), Cr1-C2 1.965(5), C1-C2 1.325(8). (C) Configurations obtained from a CASSCF(8,9) calculation performed on $L^{tBu}Cr(\eta^2-TMSC\equiv CTMS)$ **3-2** ($S = 1$). Additional configurations with less than 2% weight corresponding to broken symmetry solutions are described in the Supporting Information. Vertical ordering reflects qualitative energies.

Low-coordinate chromium(II) complexes bearing π -acidic ligands are exceptionally rare,^{39,101} and alkyne complexes are more commonly observed for lower oxidation states of chromium (i.e. formal oxidation states of -1,¹⁰² 0^{103–108} and 1^{100,109–112}). Notably, **3-2** exhibits a substantially elongated acetylene $C\equiv C$ bond distance of 1.324(7) Å compared to that of the free alkyne (1.208 Å),¹¹³ and other chromium η^2 - $TMSC\equiv CTMS$ complexes: $(Cr(CO)_5(\eta^2-TMSC\equiv CTMS))$: 1.239(3) Å,¹¹⁴ $Tp^{tBu,Me}Cr(\eta^2-TMSC\equiv CTMS)$: 1.288(3) Å,¹⁰⁰ and $(DippNacNac)Cr(\eta^2-TMSC\equiv CTMS)$: 1.314(4) Å¹⁰. The elongated $C\equiv C$ bond in **3-2** is accompanied by relatively short chromium carbon bond distances ($d(Cr-C)_{avg}$: 1.954(5) Å), suggesting substantial metallocyclopropene character¹¹⁵ in **3-2**. This assumption is corroborated by DFT calculations performed on a slightly truncated structure of **3-2** in which the adamantyl groups have been replaced by tert-butyl groups. Gas-phase geometry optimizations (M06L) of $L^{tBu}Cr(\eta^2-TMSC\equiv CTMS)$ reproduces the crystallographically-determined bond metrics in **3-2**. Minimal spin delocalization is found on the phosphinimide nitrogen and the alkyne carbon atoms (between -0.11 and -0.14 e⁻; $\langle S^2 \rangle = 2.07$). However, analysis of unrestricted corresponding orbitals¹¹⁶ obtained from the triplet DFT wavefunction exclusively reveals orbitals with unity overlap, suggesting that the spin polarization does not stem from a broken symmetry solution resembling radical character on the alkyne. This notion is corroborated by a CASSCF(8,9) calculation (Figure 3-2C,

Supporting Information) which reveals a dominant configuration (85.1%) corresponding to the expected Hund filling featuring two singly occupied valence *d*-orbitals and two covalent interactions between the alkyne and the metal center.

Intrinsic Bond Orbitals (IBOs)¹¹⁷ obtained from the DFT wavefunction further corroborate the metallocyclopropene description, revealing two covalent σ -type interactions within each spin manifold between the alkyne carbons and the chromium center (Figure 3-7). Collectively, these computational investigations best support a chromium(IV)metallocyclopropene description for **3-2**. This description contrasts with a report by Werncke and coworkers¹¹² who tentatively assign the electronic structure of $[\text{Cr}(\text{HMDS})_2(\eta^2\text{-PhC}\equiv\text{CPh})]^-$ predominantly as a chromium(II) center bound to an alkyne radical with a minor metallocyclopropene contribution based on similar computations. Despite their different formal Cr oxidation states, it is unclear why such divergent electronic structures are found for **3-2** and $[\text{Cr}(\text{HMDS})_2(\eta^2\text{-PhC}\equiv\text{CPh})]^-$, as both systems harbor pseudo-tetrahedral Cr centers ligated by two nitrogen-based X-type ligands. We hypothesize that the electron-releasing phosphinimide system employed here primes the formal chromium(II) center to an extent for substrate activation that exceeds traditional chromium(0) and chromium(I) synthons ligated by prototypical organometallic ligands. The potential for **3-2** to mediate challenging bond activation processes was assessed by its reaction with 4,4'-difluoroazobenzene. This compound was chosen over its parent compound azobenzene because it provides a convenient ¹⁹F NMR handle. A comparison of both molecules in the context of this study is provided in the supporting information file. Heating mixtures of compound **3-2** and one equivalent of 4,4'-difluoroazobenzene ($\text{Ar}^{\text{D-F}}\text{N}=\text{NAr}^{\text{D-F}}$) in toluene at 110°C reveals the generation of a single peak in the ³¹P{¹H} NMR spectrum (Figure 3-8) and two peaks in the ¹⁹F NMR spectrum (Figure 3-9) that reflect the generation of a new *S* = 0 chromium complex. These spectral features are reproduced upon treatment of **3-2** with 2.1 equivalents of 1-azido-4-fluorobenzene in THF at -78 °C (Figure 3-3), and the resulting complex can be isolated in 71% and 64% yield from reaction of **3-2** with $\text{Ar}^{\text{D-F}}\text{N}=\text{NAr}^{\text{D-F}}$ or the organo-azide, respectively.

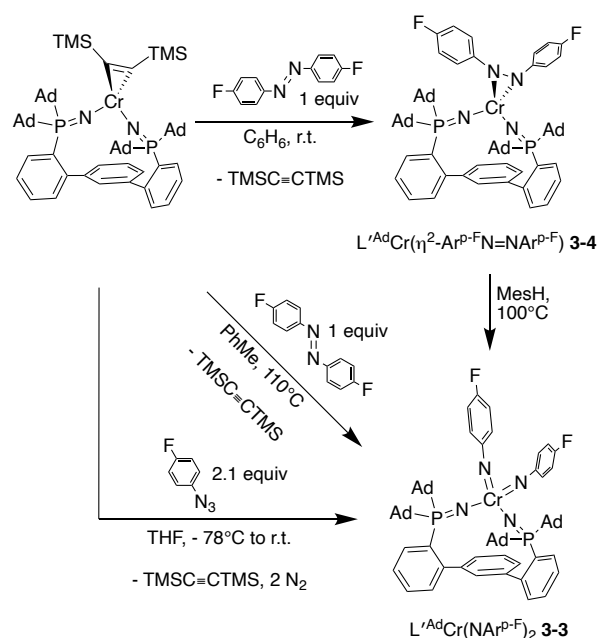


Figure 3-3 Synthesis of $\text{L}'^{\text{Ad}}\text{Cr}(\eta^2\text{-Ar}^{\text{P-F}}\text{N}=\text{NAr}^{\text{P-F}})$ **3-4** and $\text{L}'^{\text{Ad}}\text{Cr}(\text{NAr}^{\text{P-F}})_2$ **3-3**.

The crystal structure of this compound confirms its identity as $\text{L}'^{\text{Ad}}\text{Cr}(\text{NAr}^{\text{P-F}})_2$ (**3-3**) and features a tetrahedrally coordinated ($\tau_4' = 0.994$) chromium center ligated by two phosphinimide and two imido moieties (Figure 3-4A). The imido group assignment is supported by chromium nitrogen bond distances of less than $1.670 \text{ \AA}$ ¹¹⁸ and negligible N-N bonding interactions ($d(\text{N-N})$: $2.728(3) \text{ \AA}$). Compared to **3-2**, the Cr-N_{phosphinimide} distances contract slightly to $1.7797(13) \text{ \AA}$ and $1.7880(12) \text{ \AA}$, consistent with oxidation of the metal center to chromium(VI). This intimates that **3-2** is capable of oxidatively adding the N=N double bond in $\text{Ar}^{\text{P-F}}\text{N}=\text{NAr}^{\text{P-F}}$ to form **3-3** concomitant with the loss of TMS-C≡TMS.

In contrast to a number of multinuclear examples reported,^{119–121} to our knowledge, the conversion of **3-2** to **3-3** represents the first example of 4-electron oxidative addition of an N=N double bond mediated by a single chromium center. Over the course of the reaction, the azo compound is reductively cleaved by four electrons. This transformation, in which a redox active ligand is expelled during oxidative addition of an azo compound, is preceded for uranium complexes,^{93,94} a neutral bisphenoxy tungsten(II) compound reported by the Rothwell group,^{7,87,88} and a (diiminopyridine)vanadium complex in which two electrons originate from the redox-active ligand and two electrons originate on the metal center.⁹⁹

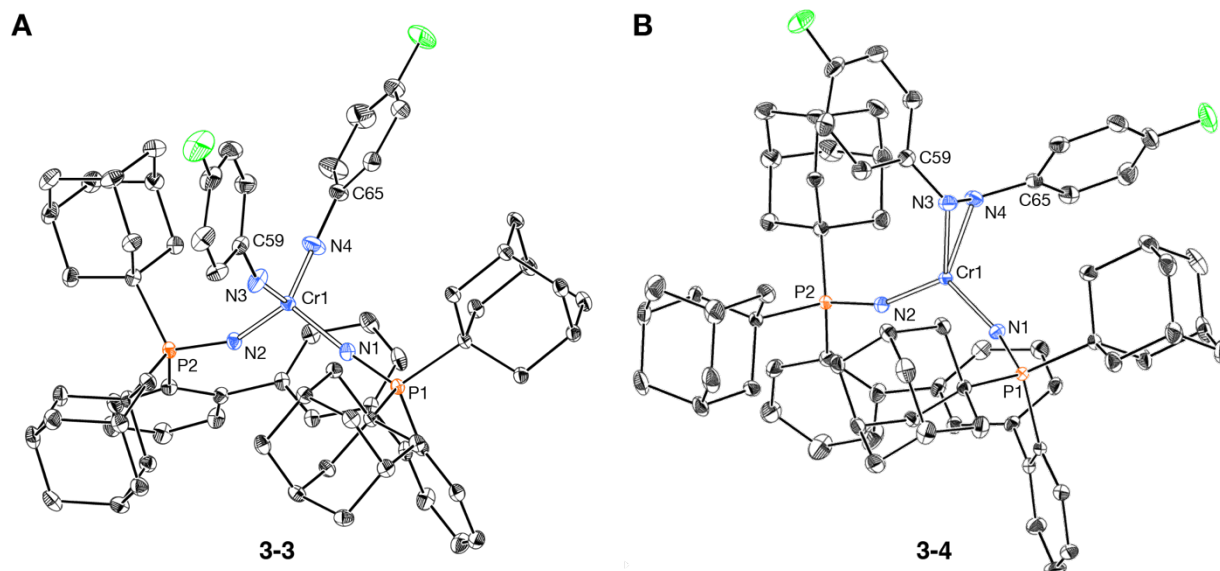


Figure 3-4 (A) Crystal structure of $L'AdCr(NAr^{P-F})_2$ (**3-3**).^[50] Selected bond distances (Å), Cr1-N3 1.6635(14), Cr1-N4 1.6685(14). (B) Crystal structure of $L'AdCr(\eta^2-Ar^{P-F}N=NAr^{P-F})$ (**3-4**).^[50] Selected bond distances (Å), Cr1-N3 1.9026(14), Cr1-N4 1.9258(13), N3-N4 1.4377(18). For both structures, ellipsoids are shown at 50% probability, hydrogen atoms and co-crystallized solvent molecules have been omitted for clarity.

In an effort to elucidate the mechanism of the 4-electron oxidative addition of the azo compound and to isolate potential intermediates, **3-2** was treated with one equivalent of at ambient temperature and *in situ* NMR spectroscopy performed on these mixtures revealed that both reagents were fully consumed within 15 min, concomitant with the formation of free $TMSC\equiv CTMS$ and a new paramagnetic species ($\mu_{eff} = 2.8 \mu_B$) identified as $L'AdCr(\eta^2-Ar^{P-F}N=NAr^{P-F})$ (**3-4**). The latter could be isolated in 68% yield (Scheme 2). Alternatively **3-4** can be synthesized directly from a equimolar mixture of **3-1** and 4,4'-difluoroazobenzene by addition of 1.0 equivalents of $Cr(Mes)_2(PMe_3)_2$ in 54% isolated yield. Its crystal structure revealed a chromium center coordinated to two phosphinimide ligands and a $Ar^{P-F}N=NAr^{P-F}$ -derived ligand bound in a side-on fashion (Figure 3-4B). This ligand exhibits a considerably elongated N-N bond ($d(N-N)$: 1.4377(18) Å) compared to that of the free azo compound (1.256(3) Å),¹²² which is suggestive of a chromium(IV)hydrazido(2-) formulation. The large dihedral angle between the $N_{hydrazido}-C_{aryl}$ bonds (107.67(14)°) is indicative of a *trans*-hydrazido conformation, which suggests that rearrangement of the azo compound into its more-reactive *cis*-conformer is not necessary for its coordination to the Cr center. An analogous hydrazido(2-) intermediate has been observed by the Mazzanti group for the oxidative addition of azobenzene to $[K(2,2,2-crypt)][U(HMDS)_3]$ and features a similar N-N bond length (1.43(2) Å).⁹⁷ The intermediacy of **3-4** in the net four-electron oxidative addition of azobenzene at **3-2** was confirmed by heating a solution of the former to 100 °C in mesitylene which leads to the formation of **3-3** in 82% spectroscopic yield (see Supporting Information file). At 373 K, this reaction proceeds with a first order rate dependence on **3-4** ($2.5 \times 10^{-4} s^{-1}$), consistent with the reaction occurring on a single chromium center (Figure 3-5A). The conversion of

the hydrazido compound **3-4** to the diimido complex **3-3** was further investigated with DFT methods. The structures of both compounds and that of the intervening transition state were optimized with the truncated L^{tBu} ligand, revealing that this reaction is exergonic by 14.7 kcal/mol with a barrier height of 30.7 kcal/mol (Figure 3-5B). This barrier height is roughly 8 kcal/mol higher than that calculated for the conversion of $[U(\eta^2\text{-PhN=NPh})(\text{HMDS})_3]^-$ to $[U(\text{NPh})_2(\text{HMDS})_3]^-$ ⁹⁷ while the overall reaction is slightly more exergonic.⁹⁷ In our case, this reaction is formally spin-forbidden, but since the lowest energy transition state lies on the triplet surface, N-N bond cleavage can proceed thermally with subsequent spin-crossover to form the singlet product **3-3**. These findings are consistent with **3-4** being a metastable intermediate at room temperature, which only converts to **3-3** upon heating to 100°C

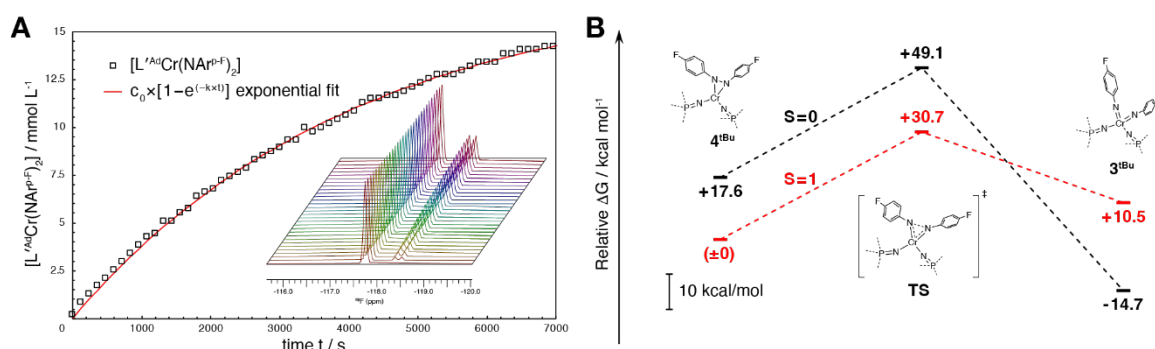


Figure 3-5 (A) Plot of the time dependence of the concentration of **3-3** generated upon heating **3-4** in mesitylene at 373 K and fit to an exponential function. (Inset) Corresponding ^{19}F NMR spectra recorded every 240 s in mesitylene at 373 K featuring 4-fluorotoluene as an internal standard. (B) M06L calculated energy surfaces corresponding to the transformation of **3-4** to **3-3**. Colors indicate the spin states of the chromium complex: triplet in red, singlet in black. Energies (kcal/mol) are relative to **3-4** ($S = 1$).

Conclusion

In summary, a bis(phosphinimide) chromium(alkyne) complex has been prepared, which features an unusual degree of $\text{C}\equiv\text{C}$ bond activation by a formal Cr(II) center that is ascribable to the electron-releasing phosphinimide co-ligands. The ability of these ligands to prime the chromium center for reductive bond activation is demonstrated by its involvement in the four-electron oxidative addition of the $\text{N}=\text{N}$ -bond in 4,4'-difluoroazobenzene. Mechanistic and computational studies intimate that this reaction proceeds via a metastable, 2-electron reduced chromium hydrazido intermediate. Taken together, these observations suggest that phosphinimide ligands engender abundant 3d metals with a prowess for multielectron substrate activation that is more commonly associated with 5d-metals and actinides.

Supporting Information

General Considerations. All reactions were performed at room temperature in a N_2 -filled glovebox or by employing standard Schlenk techniques. Glassware was oven-dried at 150 °C for at least 2 h prior to use and allowed to cool under a vacuum. All reagents were

used as received unless otherwise stated. Anhydrous pentane, diethyl ether, benzene, toluene, THF, acetonitrile and TMEDA were purified by sparging with nitrogen for 30 min and then passing under nitrogen pressure through a column of activated A2 alumina. Mesitylene was distilled from CaH_2 under a nitrogen atmosphere and stored over freshly activated 3 Å molecular sieves for 48 h prior to use. NMR solvents were purchased from Cambridge Isotope Laboratories. C_6D_6 and CD_2Cl_2 was degassed by three freeze–pump–thaw cycles and dried over freshly activated 3 Å molecular sieves for 24 h prior to use. The following compounds were synthesized according to published procedures: 1,1'-bis-(diisopropylphosphino)-ferrocene¹²³ (dippf), di(1-adamantyl)phosphine,¹²⁴ O-(2,4-dinitrophenyl)-hydroxylamine,¹²⁵ $\text{Cr}(\text{Mes})_2(\text{PMe}_3)_2$,¹²⁶ 4,4'-difluoro-azobenzene ($\text{Ar}^{\text{P-F}}\text{N}=\text{NAr}^{\text{P-F}}$).¹²⁷ All other compounds were commercially available and were used as received.

X-ray Crystallography. XRD studies were performed at the University of California, Berkeley College of Chemistry Small Molecule X-ray Crystallography Facility (ChexRay) or at beamline 12.2.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory.

For studies performed at ChexRay, crystals were mounted on a Kapton loop under Paratone oil. Data was collected on a Rigaku XtalLAB P200 (Mo K_α radiation) equipped with a MicroMax-007 HF microfocus rotating anode and a Pilatus 200 K hybrid pixel array detector at 100 K under a stream of N_2 . Data collection, integration, and scaling were carried out using the CrysAlisPro software package.⁶⁸

For XRD studies performed at beamline 12.2.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory crystals were mounted on a MiTeGen loop under Paratone oil. Data was collected on a Bruker D85 three-circle diffractometer with a PHOTON II CCD area detector using silicon monochromated synchrotron radiation ($\lambda = 0.7288$ Å) at 100 K under a stream of N_2 . Bruker APEX3 software⁶⁹ was used for data collection. Bruker SAINT⁷⁰ and SADABS⁷¹ software packages were utilized for data reduction and absorption correction, respectively.

Structures were solved using SHELXT⁷² and refined against F^2 on all data by full matrix least-squared with SHELXL⁷³ using OLEX 2 Version 1.5 crystallographic software.⁷⁴ All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms bonded to carbon atoms were placed in idealized positions and refined using a riding model.

Infrared Spectroscopy.

FTIR measurements were carried out on a Thermo Scientific Nicolet iS20 spectrometer utilizing KBr pellets.

Nuclear Magnetic Resonance Spectroscopy.

NMR spectra were recorded on Bruker 400/600 MHz or Jeol 400 MHz instruments. ^1H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane (TMS) at 0.00 ppm using residual solvent peaks as internal standards.⁷⁵ ^{19}F chemical shifts are reported in ppm relative to CFCl_3 at 0 ppm. ^{31}P chemical shifts are reported in ppm relative to 85% aqueous H_3PO_4 at 0 ppm. Solution phase magnetic measurements were performed using Evans' method.⁷⁶

UV/visible Spectroscopy.

UV/visible measurements were taken on a Hewlett-Packard 8453 spectrophotometer using 1 cm quartz cuvettes sealed with a Teflon stopcock.

Mass spectrometry.

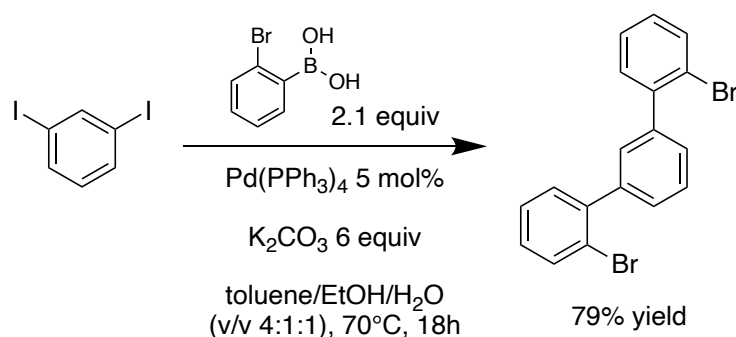
High-resolution mass spectra (HRMS) were obtained in the Catalysis Center Facility of the Lawrence Berkeley National Laboratory using a PerkinElmer AxION 2 TOF-MS.

Elemental Analysis.

Elemental analyses were performed at the University of California, Berkeley College of Chemistry Microanalytical Facility using a PerkinElmer 2400 Series II combustion analyzer.

Synthetic procedures

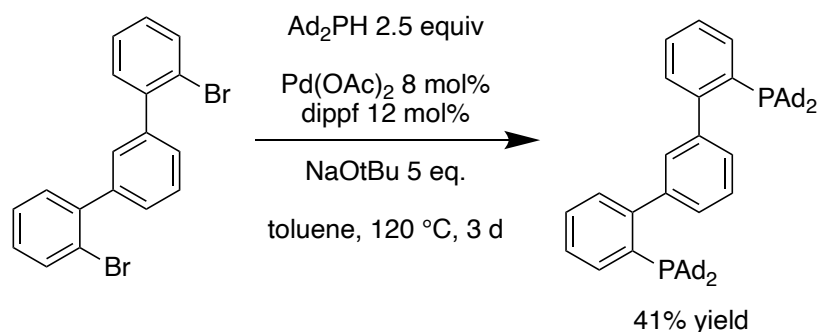
Synthesis of 2,2''-dibromo-1,1':3',1''-terphenyl "Br₂tp"



The title compound was synthesized utilizing Suzuki coupling conditions adapted from a previously published procedure¹²⁸:

In a nitrogen glovebox, 1,3-diiodobenzene (9.09 mmol, 3.00 g, 1 equiv), 2-bromophenylboronic acid (19.1 mmol, 3.84 g, 2.1 equiv) and Pd(PPh₃)₄ (0.454 mmol, 525 mg, 0.05 equiv) were dissolved in 165 mL dry toluene in a 500 mL Schlenk flask equipped with a stir bar and capped with a Teflon pin. The flask was transferred onto a Schlenk line and placed into an oil bath preheated to 70 °C. An N₂-sparged solution of K₂CO₃ (54.6 mmol, 7.54 g, 6 equiv) in a mixture of 40 mL EtOH and 40 mL deionized water was injected via syringe. The Schlenk flask was sealed with a Teflon pin and the mixture was stirred for 18 h at 70°C. Subsequently, the flask was allowed to cool to room temperature and the organic layer was separated. The remaining aqueous layer was diluted with 20 mL of deionized water and extracted twice with 40 mL DCM. The combined organic layers were dried over anhydrous MgSO₄ and the solvent was removed *in vacuo*. The remaining yellow oil was purified by column chromatography (Silica, hexanes/EtOAc 90:10 (v/v) R_f = 0.67) to afford the title compound as a faint yellow oil (yield: 7.14 mmol, 2.77 g, 79%) which crystallizes upon standing at room temperature. Care should be taken during chromatography since the separation between the title compound and triphenylphosphine is minimal (R_f ≈ 0.8). NMR spectral data matches that of previous literature reports.¹²⁸ ¹H NMR (600 MHz, C₆D₆): δ 7.48 (dd, 2H), 7.39 (t, 1H), 7.31 (dd, 2H), 7.20 (t, 1H), 7.10 (dd, 2H), 6.92 (td, 2H), 6.73 (td, 2H). ¹³C{¹H} NMR (151 MHz, C₆D₆): δ 142.85, 141.33, 133.45, 131.74, 130.90, 129.00, 128.96, 128.35, 127.53, 123.13.

Synthesis of 2,2''-di(di-1-adamantylphosphino)-1,1':3',1''-terphenyl “(PAd₂)₂tp”

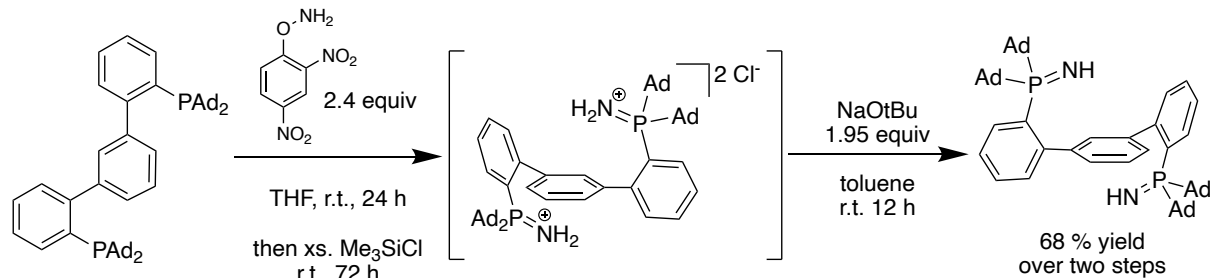


Under an N₂ atmosphere, Pd(OAc)₂ (0.557 mmol, 125 mg, 0.08 equiv) and dipfp (0.830 mmol, 347 mg, 0.12 equiv) were added to a Schlenk flask equipped with a Teflon pin, dissolved in 20 mL toluene and stirred at room temperature for 30 min. Subsequently, a mixture of 2,2''-dibromo-1,1':3',1''-terphenyl “Br₂tp” (6.96 mmol, 2.70 g, 1 equiv) and NaOtBu (34.8 mmol, 3.34g, 5 equiv) in 50 mL toluene was added and the resulting solution stirred for 1 h at room temperature, after which a solution of Ad₂PH (5.26 g, 17.4 mmol, 2.5 equiv) in 50 mL toluene was added. At this point, the Schlenk flask was capped and

placed in a preheated 120 °C oil bath. After stirring for 3 days the reaction was allowed to cool to room temperature, opened to air and the solvent was removed *in vacuo*. The resulting dark residue was dissolved in 200 mL HCCl_3 and washed with three 100 mL portions of deionized water. During the washings, a brown solid forms that settles at the phase boundary and care must be taken to avoid inclusion of this solid in the organic phases. The combined aqueous fractions were extracted with 100 mL of HCCl_3 and the organic fractions combined and dried over anhydrous Na_2SO_4 . The crude product obtained after removal of the solvent *in vacuo* was purified by column chromatography (Silica, hexanes/EtOAc 90:10 (v/v) $R_f = 0.46$) to afford the title compound as a white powder (2.80 mmol, 2.33 g, 41% yield). ^1H NMR (600 MHz, C_6D_6): δ 7.97 (d, 2H), 7.69 – 7.63 (m, 3H), 7.54 (d, 2H), 7.38 (t, 1H), 7.27 (t, 2H), 7.22 (td, 2H), 2.05 (q, 24H), 1.83 (s, 12H), 1.59 (s, 24H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ 152.84, 143.05, 136.97, 134.35, 133.71, 131.61, 129.75, 128.81, 126.07, 125.67, 42.45, 37.42, 29.32. $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, C_6D_6): δ 20.49. HRMS (ESI) m/z for $\text{C}_{58}\text{H}_{73}\text{P}_2^+$ $[\text{M-H}]^+$: calcd. 831.519, found 831.519.

Synthesis of $(\text{HN}=\text{PAd}_2)_2\text{tp}$ “ $\text{H}_2\text{L}'^{\text{Ad}}$ ” (3-1)

Caution! The electrophilic aminating agent *O*-(2,4-dinitrophenyl)-hydroxylamine and its derivatives are potentially energetic compounds in pure form. Preparations of this reagent as described typically afford material that is ~95% pure, can be handled in air, and can be stored at -35 °C for months without noticeable decomposition. Representative samples do not exhibit characteristics of a thermally induced explosive and are resistant to compression shock and sparks. Owing to the explosive nature of pure 2,4-dinitrophenol in air, all necessary safety precautions should be undertaken when handling the 2,4-dinitrophenolate intermediates derived from the amination procedures. Specifically, heating of reaction mixtures should be avoided, all manipulations should be performed under an inert atmosphere, and reaction byproducts should be diluted with water prior to disposal.

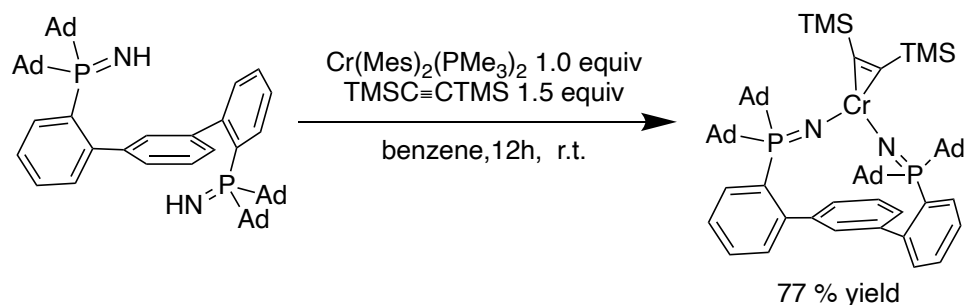


Under an N_2 atmosphere, *O*-(2,4-dinitrophenyl)hydroxylamine (2.89 mmol, 575 mg, 2.4 equiv) was added to a stirring solution of $(\text{PAd}_2)_2\text{tp}$ (1.20 mmol, 1.00 g, 1.0 equiv) in 50 mL THF. After stirring at room temperature for 18 h, TMSCl (42 mmol, 2.3 mL, 15 equiv) was added and the mixture was stirred for a further 72 h resulting in the formation of a white precipitate. The latter was collected by filtering the suspension through a coarse

frit, washed with 15 mL MeCN, 40 mL THF and dried *in vacuo* to afford the presumed intermediate $[(\text{H}_2\text{N}=\text{PAd}_2)_2\text{tp}]\text{Cl}_2$ (0.85 mmol, 790 mg, 71% yield) as an off-white powder.

NaOtBu (1.65 mmol, 159 mg, 1.95 equiv) was added to a suspension of $[(\text{H}_2\text{N}=\text{PAd}_2)_2\text{tp}]\text{Cl}_2$ (0.85 mmol, 790 mg, 1.0 equiv) in 50 mL toluene and the mixture was stirred at room temperature for 12 h which affords a faint yellow solution and a trace amount of a fine yellow precipitate. The latter was removed by filtration through a thick celite pad. The solvent was subsequently removed *in vacuo* to afford the title compound (**1**) (0.816 mmol, 703 mg, 96% yield, 68% overall yield over 2 steps) as an off-white solid. Crystals suitable for X-ray diffraction can be grown from a saturated TMEDA solution. ^1H NMR (600 MHz, CD_2Cl_2): δ 7.77 (dt, 2H), 7.50 – 7.37 (m, 5H), 7.30 (q, 1H), 7.26 – 7.11 (m, 4H), 2.24 – 1.56 (m, 60H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2): δ 149.18, 142.34, 140.81, 133.52, 132.33, 129.52, 127.98, 127.28, 125.38, 41.28, 37.68, 36.54, 28.44. $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2): δ 39.28. HRMS (ESI) m/z for $\text{C}_{58}\text{H}_{76}\text{N}_2\text{P}_2^{2+}$ $[\text{M}-\text{H}_2]^{2+}$: calcd. 431.274, found 431.270.

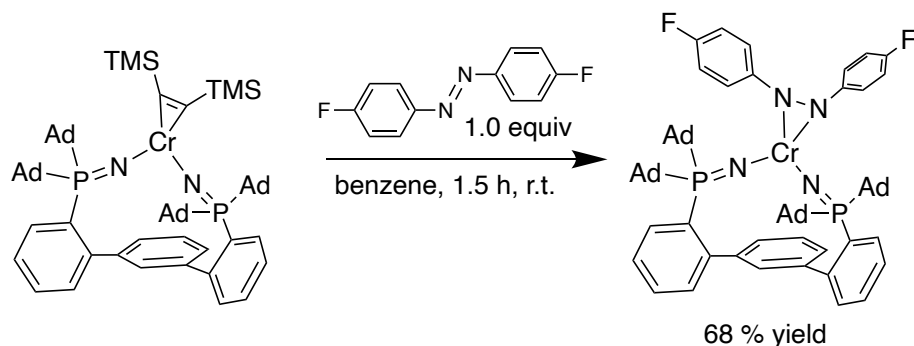
Synthesis of $\text{L}'^{\text{Ad}}\text{Cr}(\text{h}^2\text{-TMSC}\equiv\text{CTMS})$ (**3-2**)



A solution of $\text{Cr}(\text{Mes})_2(\text{PMe}_3)_2$ (0.452 mmol, 200 mg, 1.0 equiv) in 10 mL benzene was added dropwise to a mixture of $\text{H}_2\text{L}'^{\text{Ad}}$ (0.452 mmol, 390 mg, 1.0 equiv) and $\text{TMSC}\equiv\text{CTMS}$ (0.678 mmol, 116 mg, 1.5 equiv) dissolved in 50 mL benzene at room temperature. The reaction mixture was stirred for 12 h at room temperature, after which the solution was frozen and lyophilized. The resulting crimson solid was washed with 10 mL pentane, extracted into 20 mL benzene and lyophilized again, affording the title compound (**2**) as a spectroscopically clean, fluffy crimson powder (0.346 mmol, 374 mg, 77% yield). Bulk crystalline material may be obtained in lower yield by storing a saturated toluene solution at $-30\text{ }^\circ\text{C}$ over the course of a week. Crystals suitable for X-ray diffraction were obtained by storing a saturated Et_2O solution of the title compound at room temperature for multiple days. Anal. calcd. for $\text{C}_{66}\text{H}_{90}\text{CrN}_2\text{P}_2\text{Si}_2$ C, 73.29; H, 8.39; N, 2.59. Found: C, 73.48; H, 8.30; N, 2.48. μ_{eff} (C_6D_6 , 298 K, 400MHz): $2.9\ \mu_{\text{B}}$. ^1H NMR (600 MHz, C_6D_6): δ 10.51, 8.30, 4.76, 2.48, 2.16, 1.96, 1.09, 0.30, 0.16, -1.67, -3.60.

Synthesis of $L^{Ad}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ (3-4)

Method A – Direct reaction between $L^{Ad}Cr(h^2-TMSC\equiv CTMS)$ and $Ar^{p-F}N=NAr^{p-F}$



To a solution of $L^{Ad}Cr(\eta^2-TMSC\equiv CTMS)$ (0.0277 mmol, 30 mg, 1.0 equiv) in 7 mL benzene, a 0.1 M solution of $Ar^{p-F}N=NAr^{p-F}$ (0.08 mmol, 0.28 mL, 1.0 equiv) in the same solvent was added dropwise at room temperature and the resulting red brown solution was stirred for 1.5 h. Subsequently, the resulting solution was lyophilized and the solid residue triturated with 3 mL pentane, extracted into 5 mL benzene, frozen and lyophilized again to afford the title compound (**4**) as a spectroscopically clean fluffy orange brown powder (0.0074 mmol, 8.3 mg, 27% yield). Storing the pentane washings for a week at room temperature affords a second crop of the title compound as a brown crystalline solid (0.0113 mmol, 12.8 mg, 41% yield, combined yield 68%). Crystals suitable for X-ray diffraction can be obtained by storing a saturated Et_2O solution of the title compound at room temperature over the course of a week.

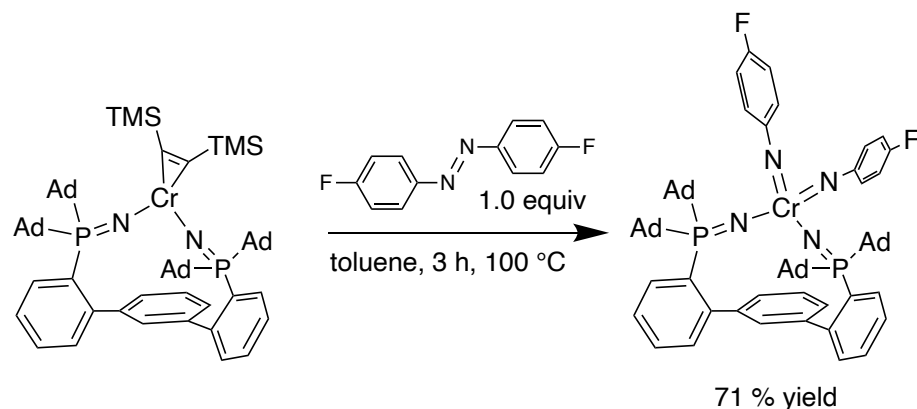
Method B – Addition of $Cr(Mes)_2(PMe_3)_2$ to a mixture of H_2L^{Ad} and $ArN^{p-F}=NAr^{p-F}$

A mixture of H_2L^{Ad} (0.035 mmol, 30 mg, 1.0 equiv) and $Ar^{p-F}N=NAr^{p-F}$ (0.035 mmol, 7.6 mg, 1.0 equiv) was dissolved in 5 mL benzene. To this mixture $Cr(Mes)_2(PMe_3)_2$ (0.035 mmol, 15 mg, 1.0 equiv) dissolved in 2 mL of the same solvent was added dropwise at room temperature, which caused a gradual color change from orange to dark brown. The resulting solution was stirred at room temperature for 12 h followed by removal of the solvent *in vacuo*, leaving behind a brown powder. The latter was extracted with 3 mL pentane. Storage on this pentane solution at room temperature for multiple days affords the title compound (**4**) as a brown crystalline solid (0.019 mmol, 21 mg, 54% yield).

^1H NMR (600 MHz, C_6D_6): δ 9.23, 8.86, 8.35, 6.82, 6.59, 6.27, 6.03, 4.29, 3.88, 3.65, 3.45, 2.21, 1.82, 1.49, 0.87, 0.73, 0.29, -0.64. Anal. calcd. for $C_{70}H_{80}CrF_2N_4P_2$ C, 74.45; H, 7.14; N, 4.96. Found: C, 74.30; H, 7.18; N, 4.78. μ_{eff} (C_6D_6 , 298 K, 400 MHz): 2.8 μ_B .

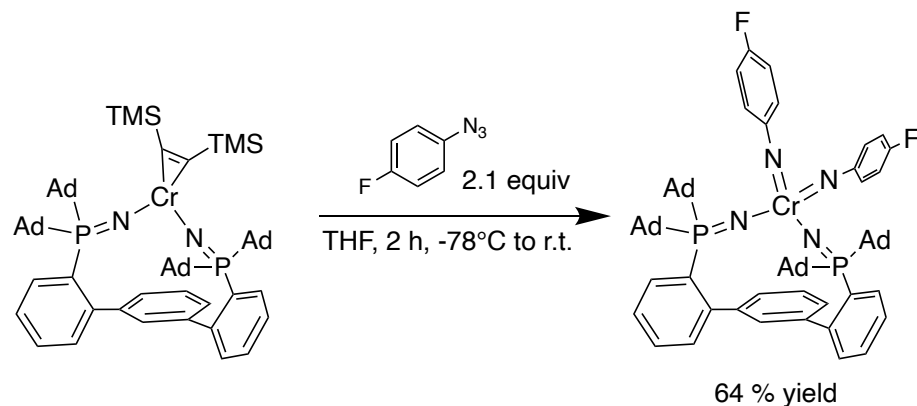
Synthesis of $L^{Ad}Cr(NAr^{p-F})_2$ (3-3)

Method A – Thermolysis of a mixture of $L^{Ad}Cr(h^2-TMSC\equiv CTMS)$ and $Ar^{p-F}N=NAr^{p-F}$



To a solution of $L^{Ad}Cr(h^2-TMSC\equiv CTMS)$ (0.0277 mmol, 30.0 mg, 1.0 eq.) in 7 mL toluene a solution of $Ar^{p-F}N=NAr^{p-F}$ (0.028 mmol, 6.0 mg, 1.0 equiv) in the same solvent was added and the resulting dark brown solution was placed in a Schlenk flask sealed with a Teflon pin. The flask was subsequently removed from the glovebox and placed in an oil bath, which had been preheated to 100 °C. The solution color gradually changed from dark brown to deep purple over the course of 3 h after which the Schlenk flask was cooled to room temperature and reintroduced into the glovebox. Removal of the solvent resulted in the formation of a purple film to which 3 mL of pentane were added. The resulting mixture was stirred for 10 min, which lead to the formation of a purple microcrystalline solid suspended in a burgundy solution. The solids were separated by filtration and the pentane filtrate was set aside. Extraction of the remaining solids with 3 mL benzene followed by lyophilization afforded the title compound (**3**) as a spectroscopically clean purple fluffy powder (0.0191 mmol, 22.1 mg, 71% yield). Crystals suitable for X-ray diffraction can be obtained by storing the pentane washings at room temperature for multiple days.

Method B – Reaction between $L^{Ad}Cr(h^2-TMSC\equiv CTMS)$ and $Ar^{p-F}N_3$



$L^{Ad}Cr(h^2-TMSC\equiv CTMS)$ (0.0185 mmol, 21.2 mg, 1.0 equiv) was dissolved in 5 mL THF and the resulting solution was cooled to -78 °C. Following dropwise addition of a 0.1 M solution of 4-azido-2-fluorobenzene (0.0388 mmol, 0.41 mL, 2.1 equiv) the solution was

warmed to reach room temperature over the course of 1 h. During this period the solution color changed from crimson to deep purple. Subsequent removal of the solvent in vacuo resulted in the formation of a purple film, which formed a suspension upon addition of 5 mL pentane. The precipitate was removed by filtration and the pentane solution was set aside. Extraction of the remaining solids into 3 mL benzene and subsequent lyophilization afforded the title compound (**3**) as a spectroscopically clean purple fluffy power (0.0118 mmol, 13.3 mg, 64% yield). Crystals suitable for X-ray diffraction can be obtained by storing the pentane washings at room temperature for multiple days.

^1H NMR (600 MHz, C_6D_6): δ 7.63 (ddd, 2H), 7.37 (dd, 2H), 7.31 – 7.25 (m, 2H), 7.21 (ddd, 4H), 7.15 – 7.12 (m, 6H), 6.82 (dt, 4H), 2.59 – 2.52 (m, 6H), 2.38 – 2.33 (m, 6H), 2.30 (dd, 6H), 2.22 (ddd, 6H), 1.99 (q, 6H), 1.82 (q, 6H), 1.77 (d, 6H), 1.68 (d, 6H), 1.49 (d, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6): δ 151.51, 143.86, 134.09, 134.02, 131.96, 131.89, 129.79, 129.34, 129.28, 126.10, 125.85, 125.38, 125.08, 125.03, 123.12, 123.06, 115.21, 115.06, 114.87, 114.72, 47.36, 47.04, 43.43, 43.13, 39.11, 38.10, 37.18, 36.81, 29.44, 29.38, 28.93, 28.87. ^{19}F NMR (376 MHz, C_6D_6): δ -118.89 (tt, 1F), -119.01 (tt, 1F). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, C_6D_6): δ 25.94. Anal. calcd. for $\text{C}_{70}\text{H}_{80}\text{CrF}_2\text{N}_4\text{P}_2$: C, 74.45; H, 7.14; N, 4.96. Found: C, 74.36; H, 7.06; N, 4.98.

Supporting Figures

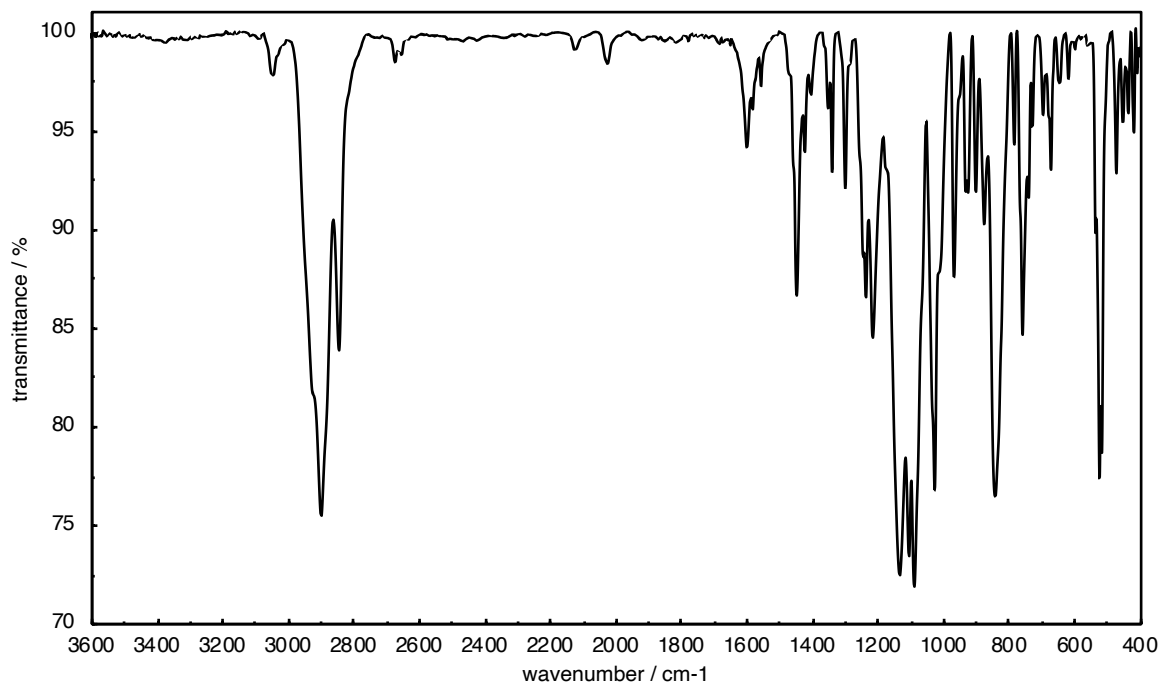


Figure 3-6 FTIR spectrum of $\text{L}'^{\text{Ad}}\text{Cr}(\text{h}^2\text{-TMSC}\equiv\text{CTMS})$ 3-2 (KBr pellet).

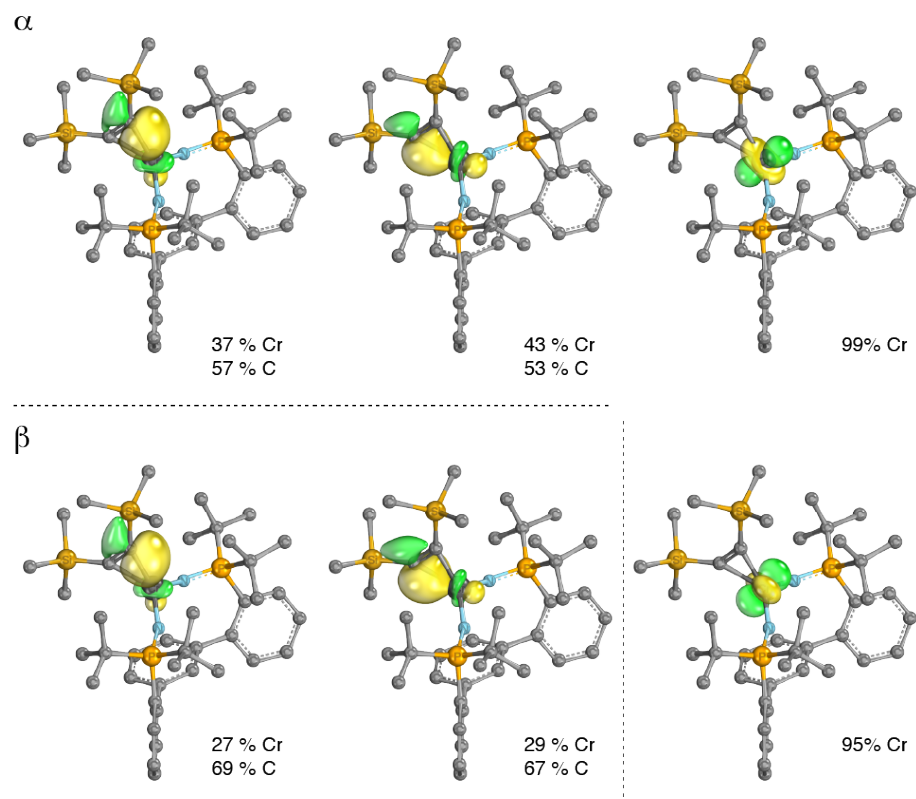


Figure 3-7 IBOs of $L^{tBu}Cr(\eta^2-TMSC\equiv CTMS)$ 3-2 with considerable metal character displaying two σ -type bonding interactions with each α and β spin with overall 4 electrons, as well as 2 non-bonding d orbitals occupied by 1 electron each in the α manifold. Hydrogen atoms removed for clarity.

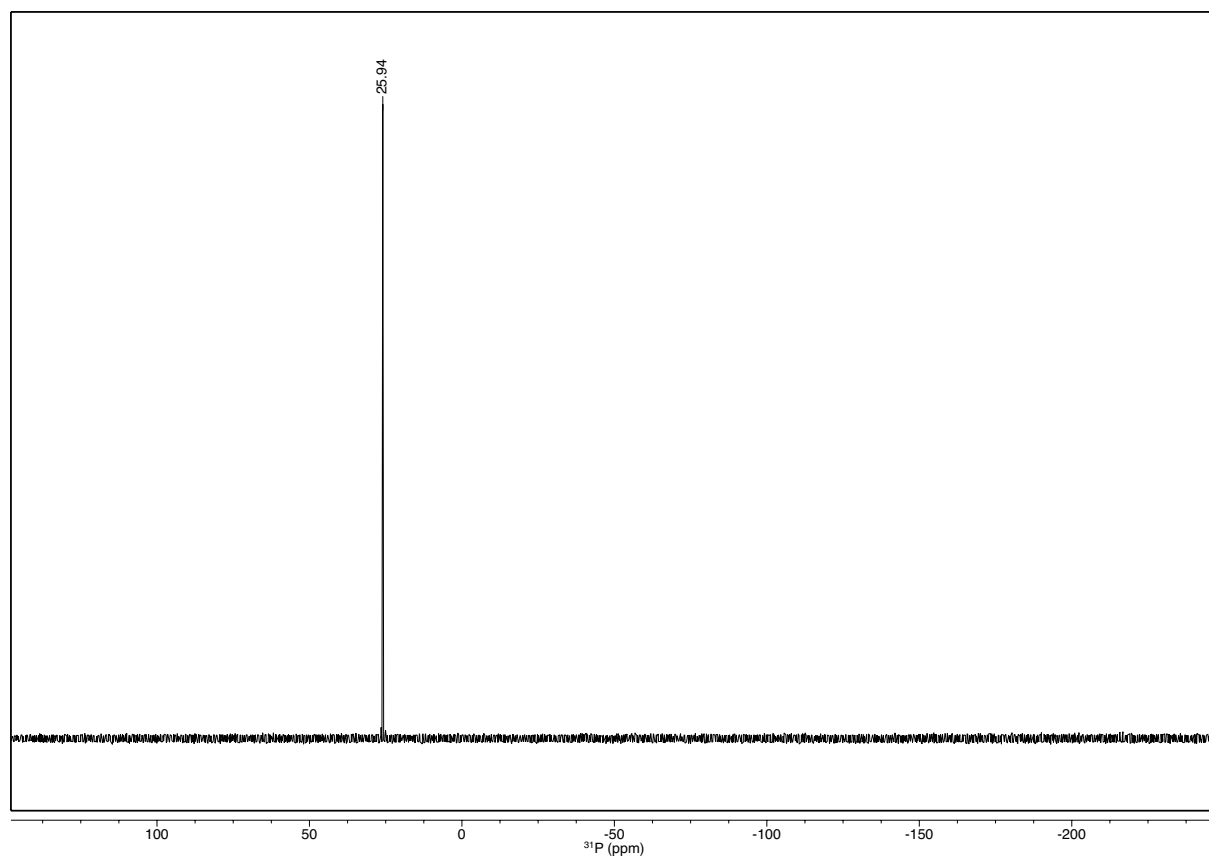


Figure 3-8 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{L}'^{\text{Ad}}\text{Cr}(\text{NAr}^{\text{p-F}})_2$ 3-3 recorded in C_6D_6 at 298 K (243 MHz).

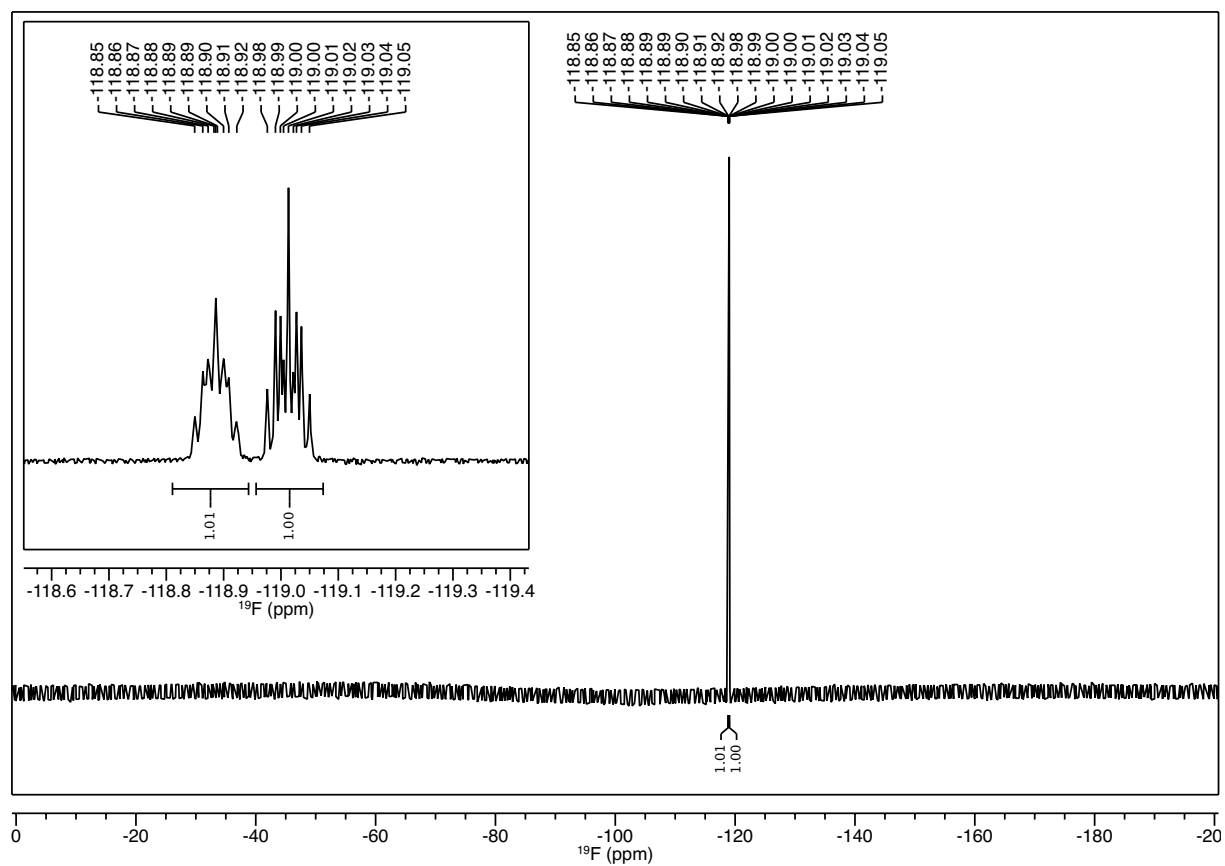


Figure 3-9 ^{19}F NMR spectrum of $\text{L}'\text{AdCr}(\text{NAr}^{\text{p-F}})_2$ 3-3 recorded in C_6D_6 at 298 K (376 MHz).

Comparison between azobenzene and 4,4'-difluoro-azobenzene in the context of this study

The presence of para fluorine atoms in 4,4'-difluoroazobenzene seems to have little effect on the oxidative addition reaction described in the paper. Reaction of the alkyne complex with 1.0 equivalents of plain azobenzene in benzene at room temperature results in the formation of a paramagnetic compound featuring an NMR spectrum very similar to that of compound **4**. This compound is stable at 65°C in benzene solution and only converts to the diamagnetic bisphenylimido compound upon heating at 100°C in toluene as evidenced by a single resonance at 25.7 ppm in its ^{31}P spectrum in C_6D_6 .

These observations are corroborated by the fact that the Hammond parameter for para-fluorine is 0.062 (i.e. very close to hydrogen at 0 and about a third in magnitude compared to the Hammond parameter for a para methyl group at -0.170).¹²⁹ Furthermore the pK_a difference between para-fluoroaniline and aniline is 0.1.¹³⁰

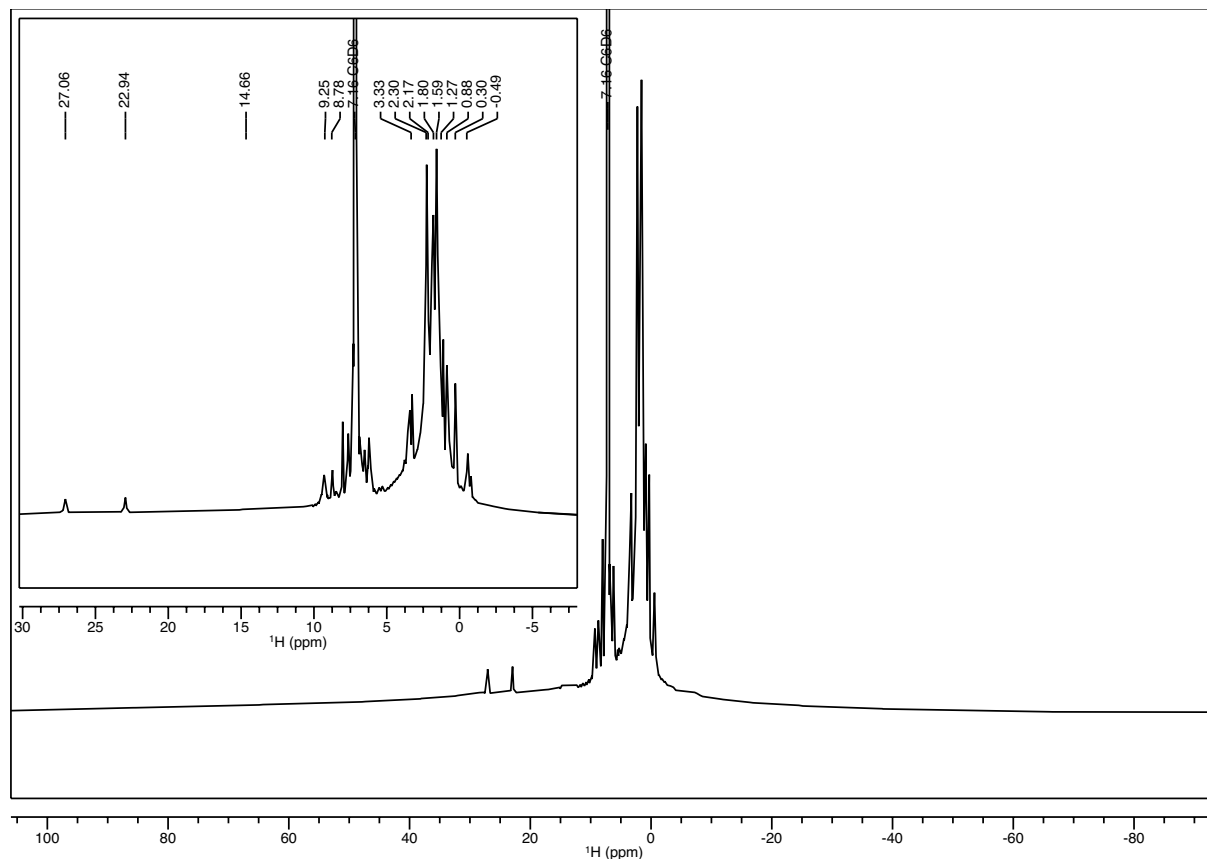


Figure 3-10 ^1H NMR spectrum of $\text{L}'\text{AdCr}(\eta^2\text{-PhNNPh})$ recorded in C_6D_6 at 298 K (400 MHz).

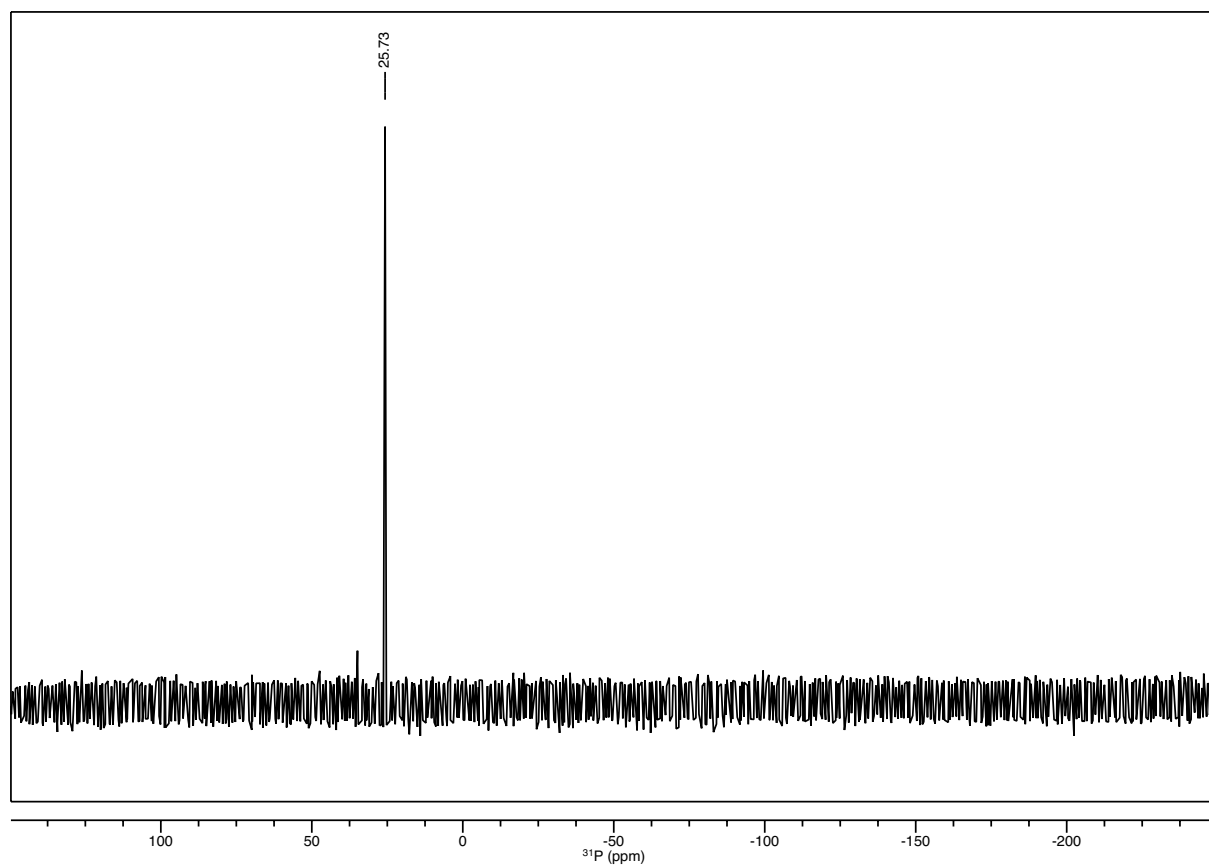


Figure 3-11 ^{31}P NMR spectrum of $\text{L}'^{\text{Ad}}\text{Cr}(\text{NPh})_2$ recorded in C_6D_6 at 298 K (162 MHz).

X-ray Crystallography

Compound	H_2L^{Al} 3-1	$L^{Al}Ct_1(\eta^2-TMSC\equiv CTMS)$ 3-2	$L^{Al}Ct_1(NAr^F)_2$ 3-3	$L^{Al}Ct_1(\eta^2-Ar^F)N=NAr^F$ 3-4
CCDC Deposition Number	2282608	2282669	2282667	2282666
Empirical formula	$C_{11}H_{14}N_4P_4$	$C_{10}H_6CrN_2P_2Si_2$	$C_{77.5}H_{66}CrF_2N_4P_2$	$C_{88}H_{104}CrF_2N_4P_2$
Formula weight	1722.26	1081.51	1237.53	1369.69
Temperature/K	100	100	100	100
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic
Space group	$Pbcn$	$P2_1/c$	$P2_1/c$	P-1
a/Å	29.795(3)	24.951(3)	19.0393(12)	15.0967(4)
b/Å	9.6606(9)	11.8242(12)	15.9023(10)	15.8333(4)
c/Å	15.8092(15)	19.307(2)	21.5564(14)	16.9906(5)
$\alpha/^\circ$	90	90	90	114.291(3)
$\beta/^\circ$	90	90.822(4)	96.751(4)	100.385(2)
$\gamma/^\circ$	90	90	90	94.796(2)
Volume/Å ³	4550.4(7)	5695.7(10)	6481.3(7)	3584.26(19)
Z	2	4	4	2
ρ_{calc}/cm^3	1.257	1.261	1.268	1.269
μ/mm^{-1}	0.146	0.363	0.297	0.260
F(000)	1864.0	2328.0	2652.0	1464.0
Crystal size/mm ³	$0.3 \times 0.3 \times 0.05$	$0.1 \times 0.01 \times 0.01$	$0.1 \times 0.05 \times 0.05$	$0.5 \times 0.1 \times 0.1$
Radiation	synchrotron ($\lambda = 0.7288$)	synchrotron ($\lambda = 0.7288$)	synchrotron ($\lambda = 0.7288$)	Mo K α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	2.804 to 71.784	1.674 to 54.534	3.432 to 66.88	5.574 to 59.802
Index ranges	-47 $\leq h \leq 47$, -15 $\leq k \leq 15$, -24 $\leq l \leq 25$	-31 $\leq h \leq 31$, -14 $\leq k \leq 14$, -24 $\leq l \leq 23$	-28 $\leq h \leq 28$, -23 $\leq k \leq 23$, -32 $\leq l \leq 32$	-20 $\leq h \leq 20$, -22 $\leq k \leq 21$, -23 $\leq l \leq 23$
Reflections collected	233534	177021	141214	85791
Independent reflections	9867 [$R_{int} = 0.1520$, $R_{sigma} = 0.0633$]	11787 [$R_{int} = 0.0865$, $R_{sigma} = 0.0363$]	23363 [$R_{int} = 0.0940$, $R_{sigma} = 0.0738$]	18661 [$R_{int} = 0.0589$, $R_{sigma} = 0.0496$]
Data/restraints/parameters	9867/0/285	11787/0/664	23363/0/806	18661/0/880
Goodness-of-fit on F^2	1.072	1.162	1.016	1.014
Final R indexes [$\geq 2\sigma$ (I)]	$R_1 = 0.0764$, $wR_2 = 0.1446$	$R_1 = 0.0817$, $wR_2 = 0.2249$	$R_1 = 0.0479$, $wR_2 = 0.1094$	$R_1 = 0.0458$, $wR_2 = 0.0988$
Final R indexes [all data]	$R_1 = 0.1104$, $wR_2 = 0.1579$	$R_1 = 0.0877$, $wR_2 = 0.2275$	$R_1 = 0.0796$, $wR_2 = 0.1238$	$R_1 = 0.0654$, $wR_2 = 0.1056$
Largest diff. peak/hole / e Å ⁻³	0.40/-0.66	1.12/-0.63	0.50/-0.58	0.41/-0.49

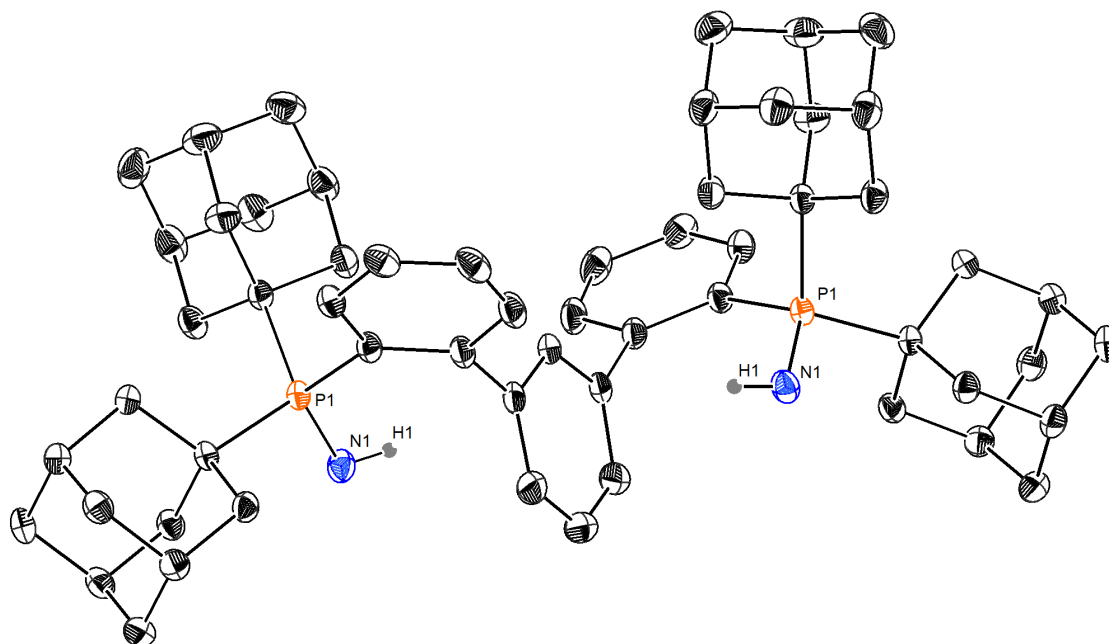


Figure 3-12 Crystal structure of $\text{H}_2\text{L}'^{\text{Ad}}$ (**3-1**). Ellipsoids shown at 50% probability. Hydrogen atoms bound to carbon removed and two asymmetric units forming a single molecule shown for clarity.

Additional IR Spectra

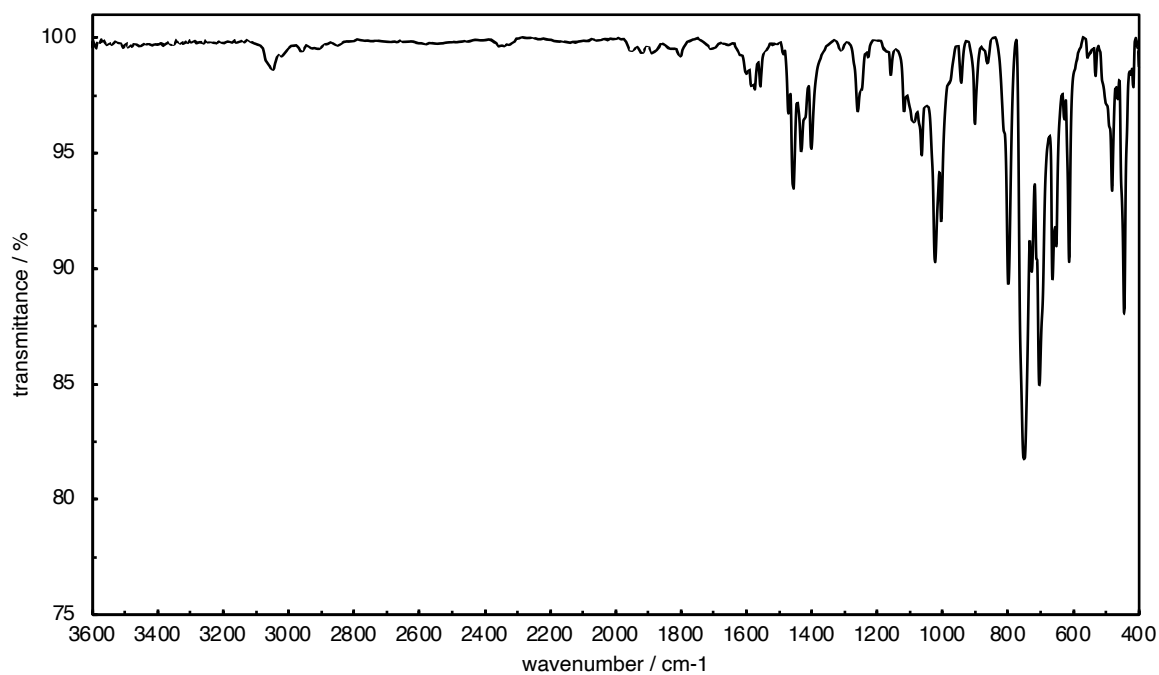


Figure 3-13 FTIR spectrum of Br_2tp (KBr pellet).

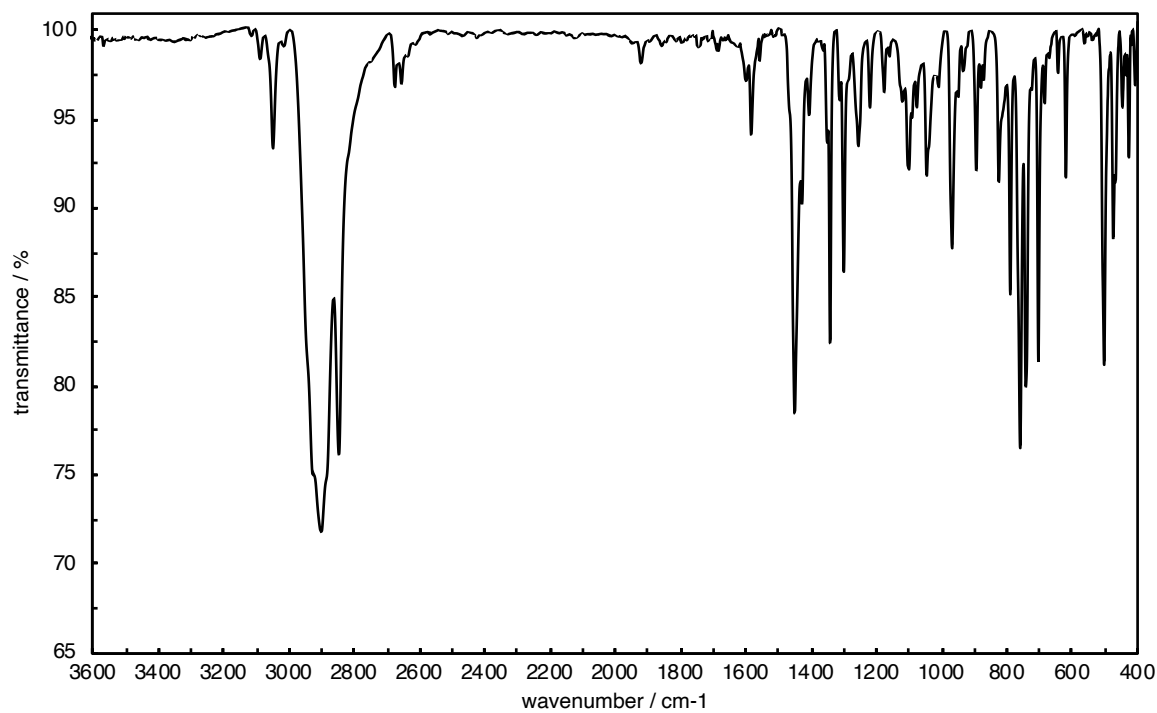


Figure 3-14 FTIR spectrum of $(\text{PAd}_2)_2\text{tp}$ (KBr pellet).

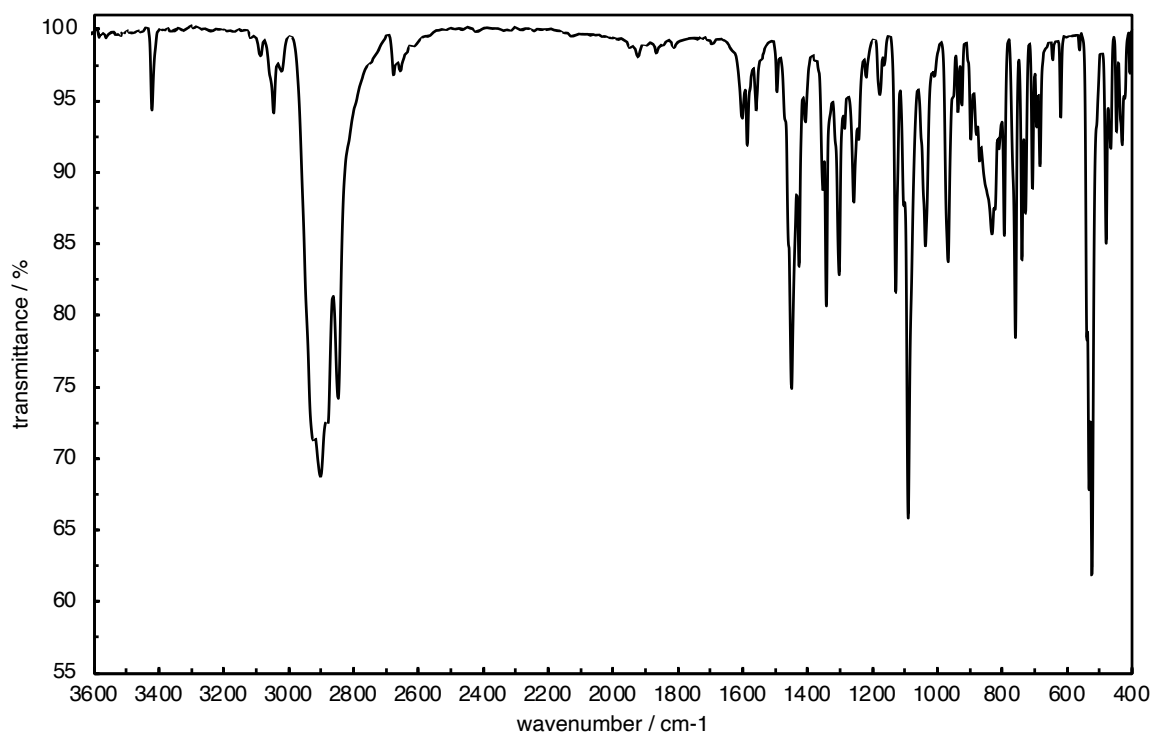


Figure 3-15 FTIR spectrum of $\text{H}_2\text{L}'^{\text{Ad}}$ (**3-1**) (KBr pellet).

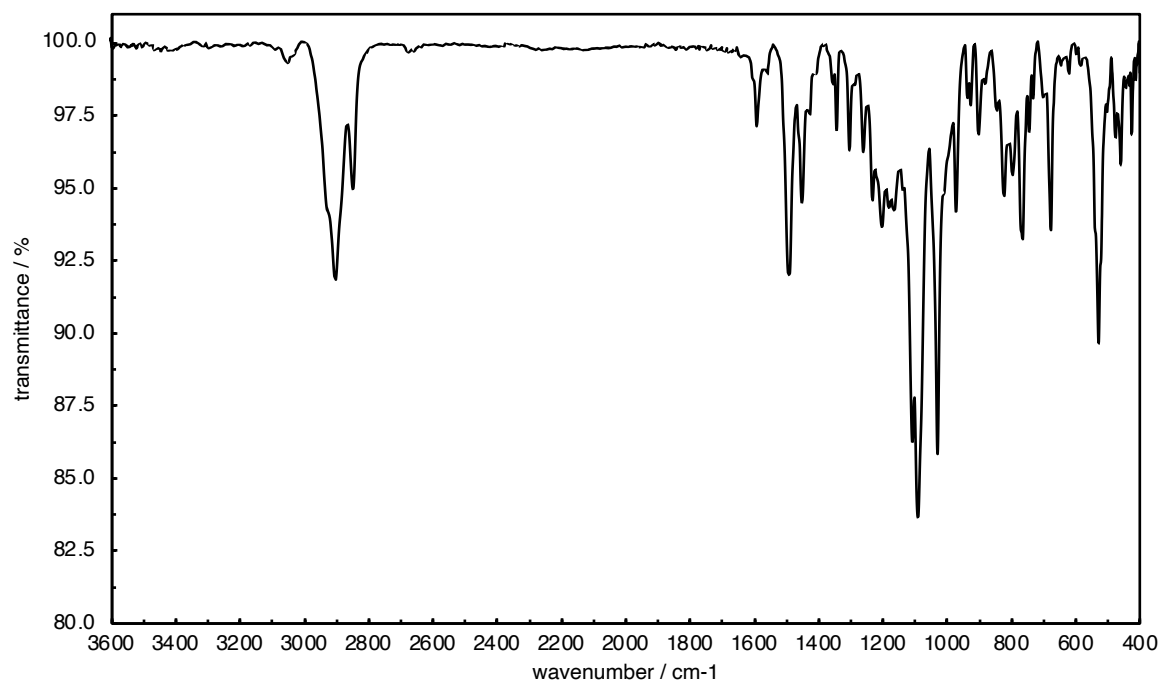


Figure 3-16 FTIR spectrum of $L^{tAd}Cr(h^2-Ar^p-FN=NAr^p-F)$ (**3-4**) (KBr pellet).

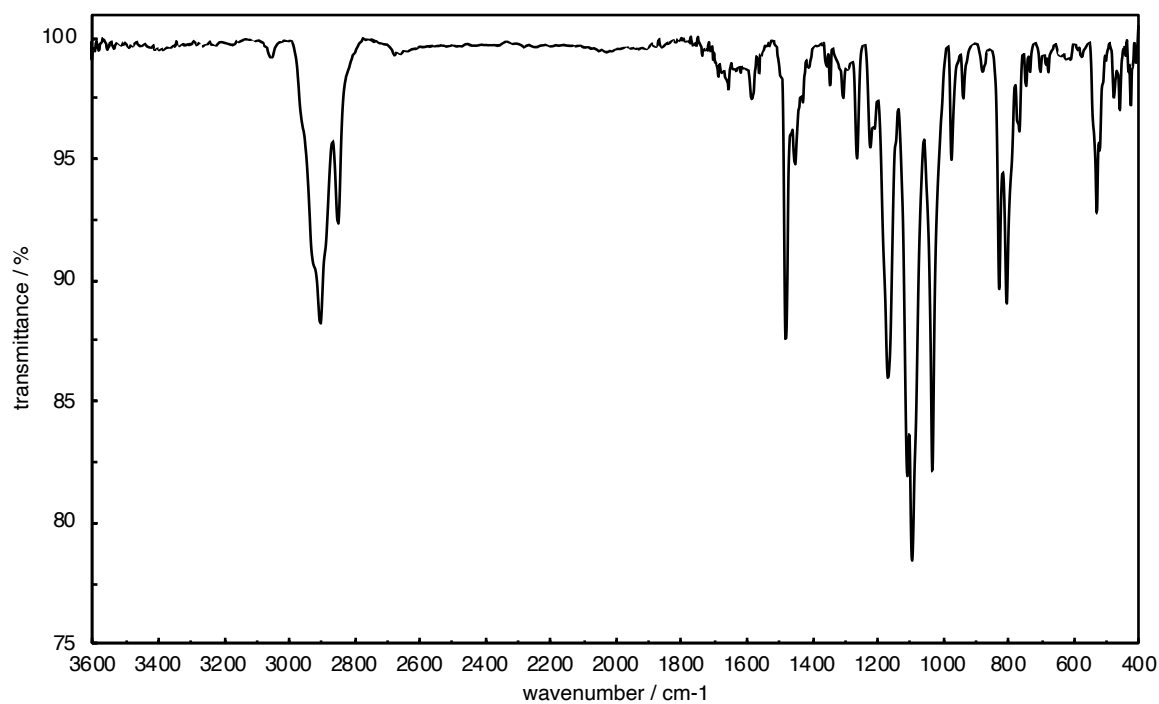


Figure 3-17 FTIR spectrum of $L^{tAd}Cr(NAr^p-F)_2$ (**3-3**) (KBr pellet).

Additional NMR Spectra

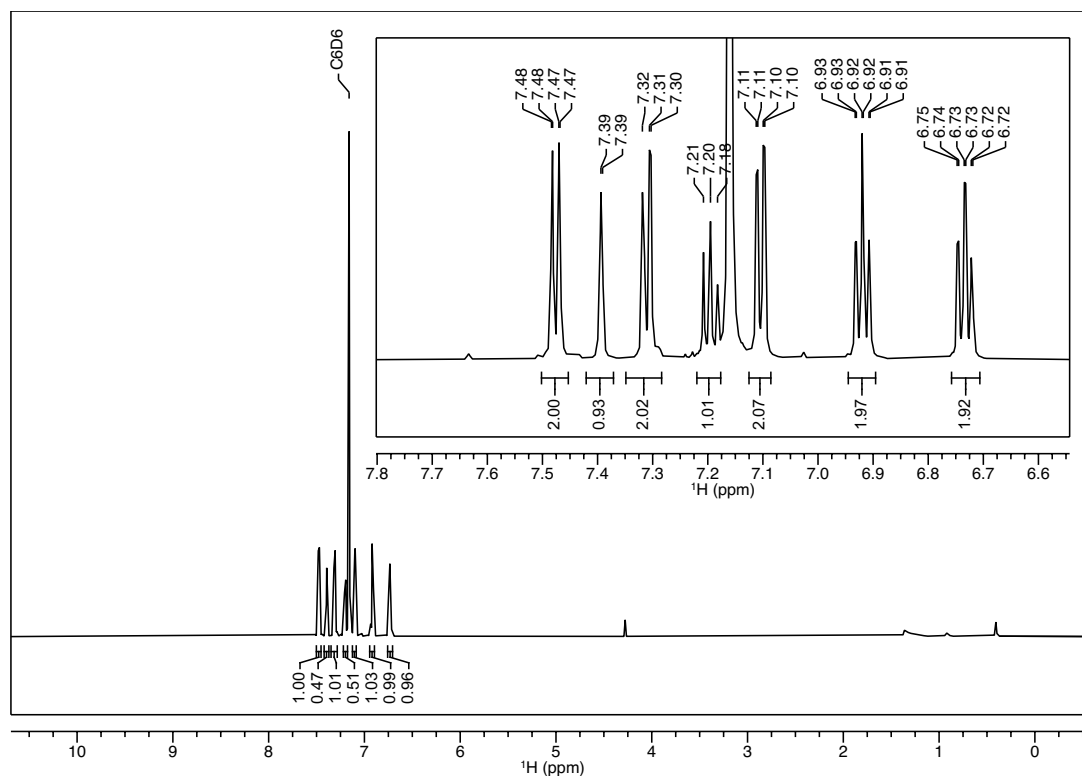


Figure 3-18 ¹H NMR spectrum of Br₂tp recorded in C₆D₆ at 298 K (600 MHz).

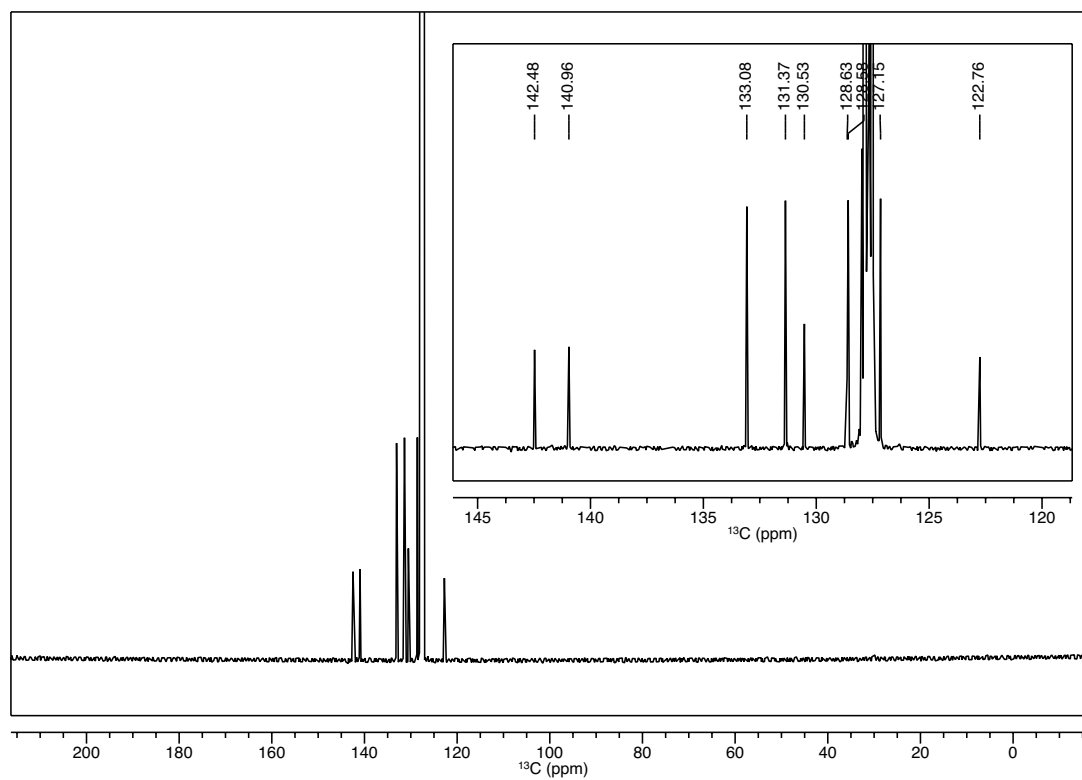


Figure 3-19 ¹³C{¹H} NMR spectrum of Br₂tp recorded in C₆D₆ at 298 K (151 MHz).

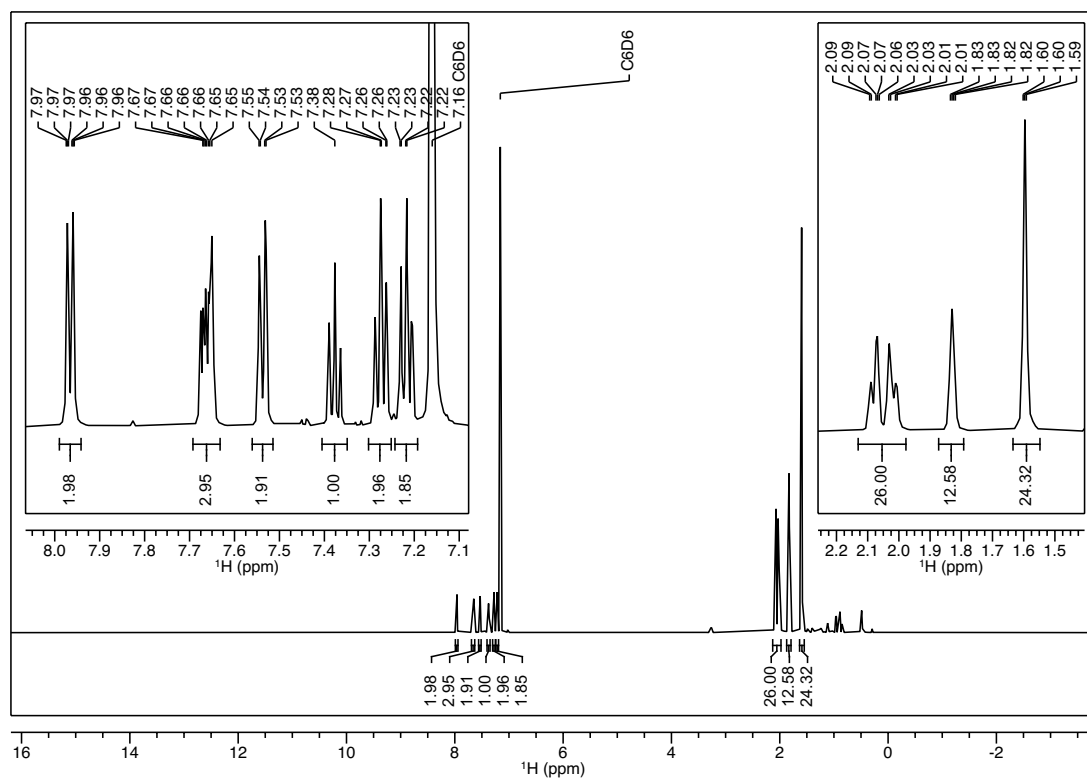


Figure 3-20 ¹H NMR spectrum of (PAd₂)₂tp recorded in C₆D₆ at 298 K (600 MHz).

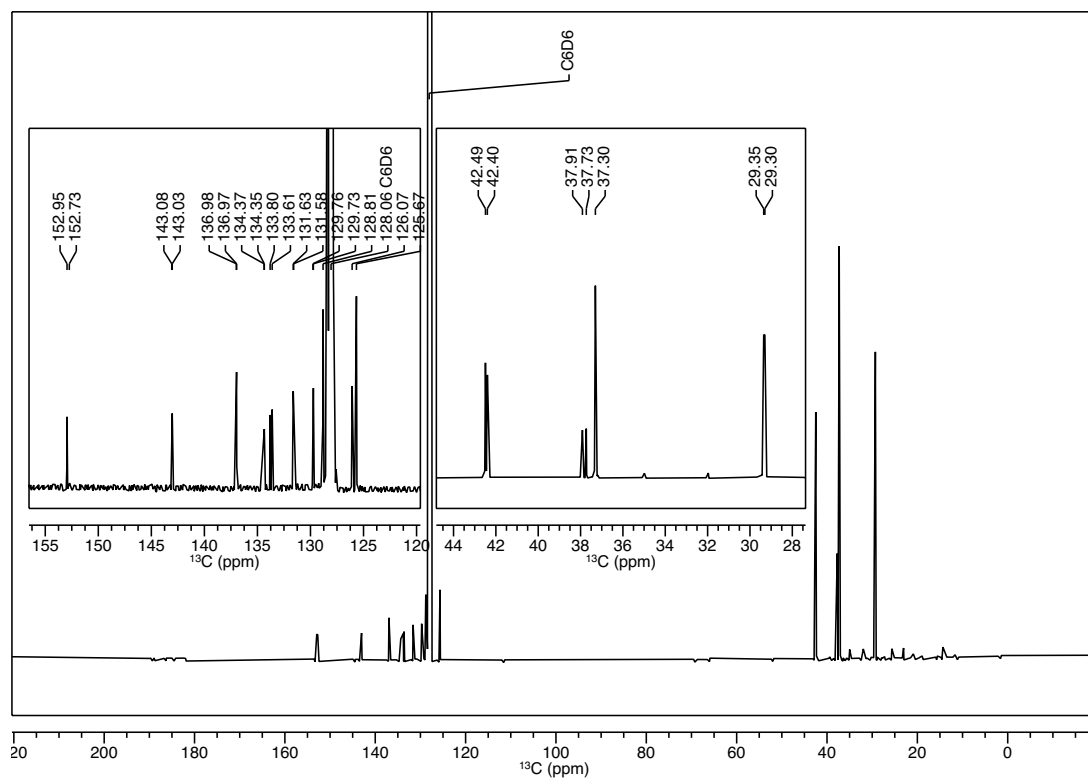


Figure 3-21 ¹³C{¹H} NMR spectrum of (PAd₂)₂tp recorded in C₆D₆ at 298 K (151 MHz).

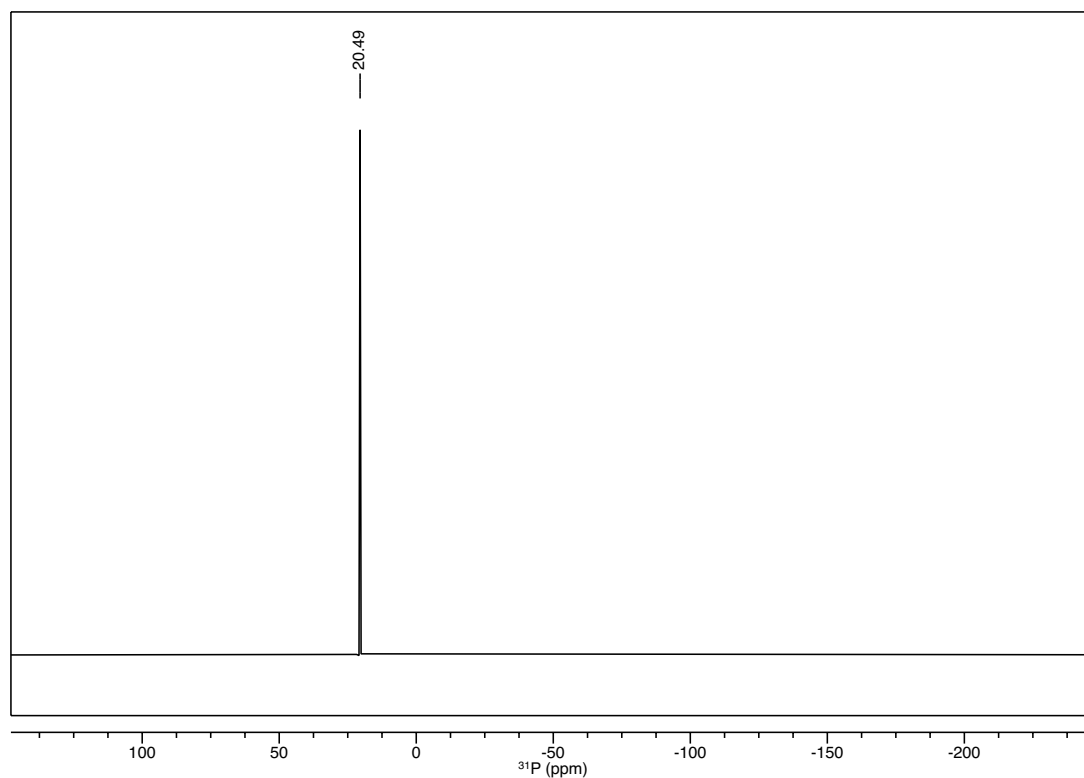


Figure 3-22 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $(\text{PAd}_2)_2\text{tp}$ recorded in C_6D_6 at 298 K (243 MHz).

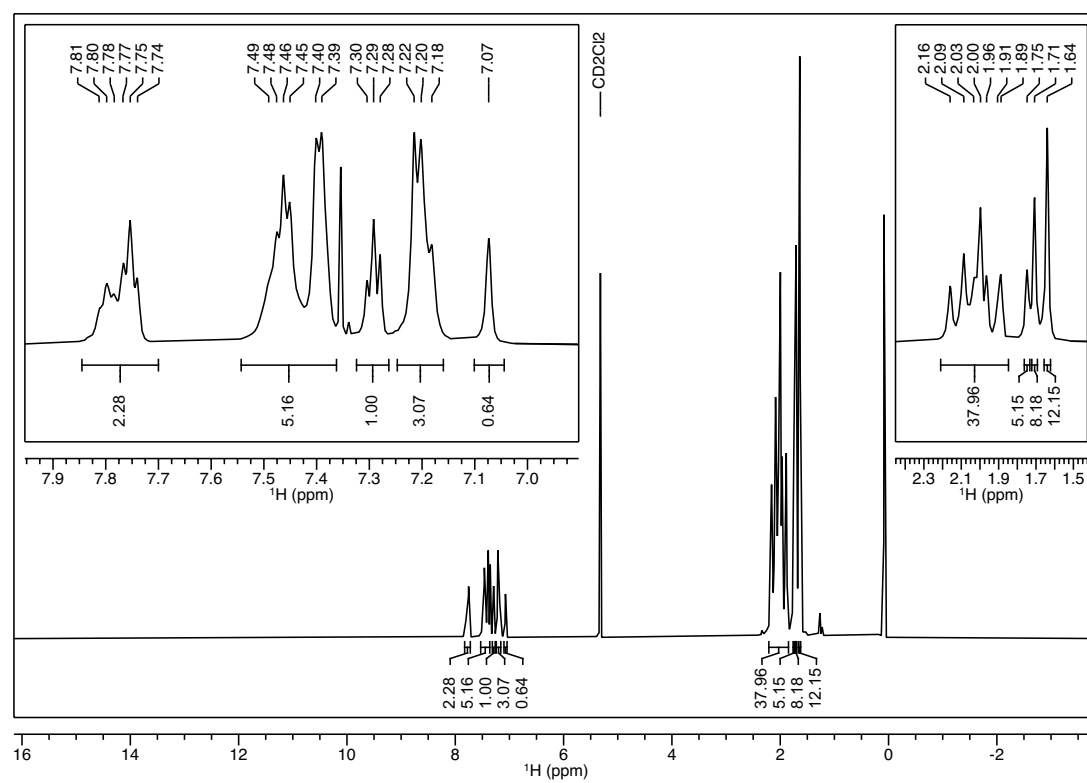


Figure 3-23 ^1H NMR spectrum of $\text{H}_2\text{L}'\text{Ad}$ (**3-1**) recorded in CD_2Cl_2 at 298 K (600 MHz).

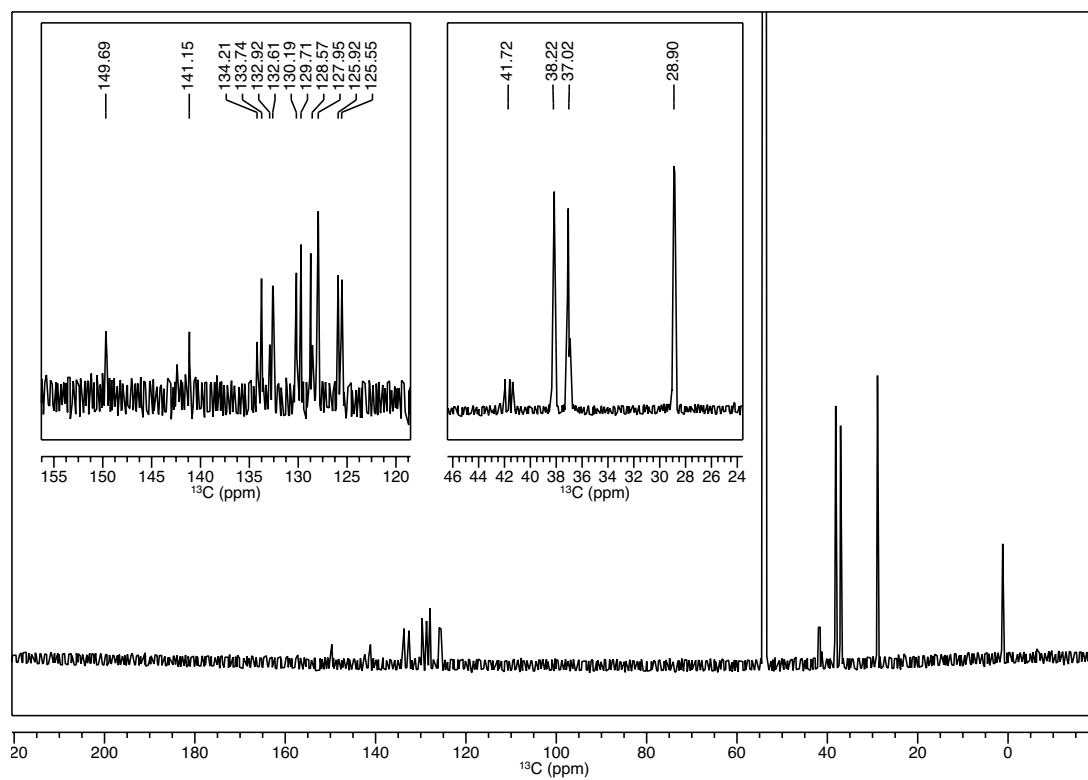


Figure 3-24 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{H}_2\text{L}^{\text{Ad}}$ (**3-1**) recorded in CD_2Cl_2 at 298 K (151 MHz).

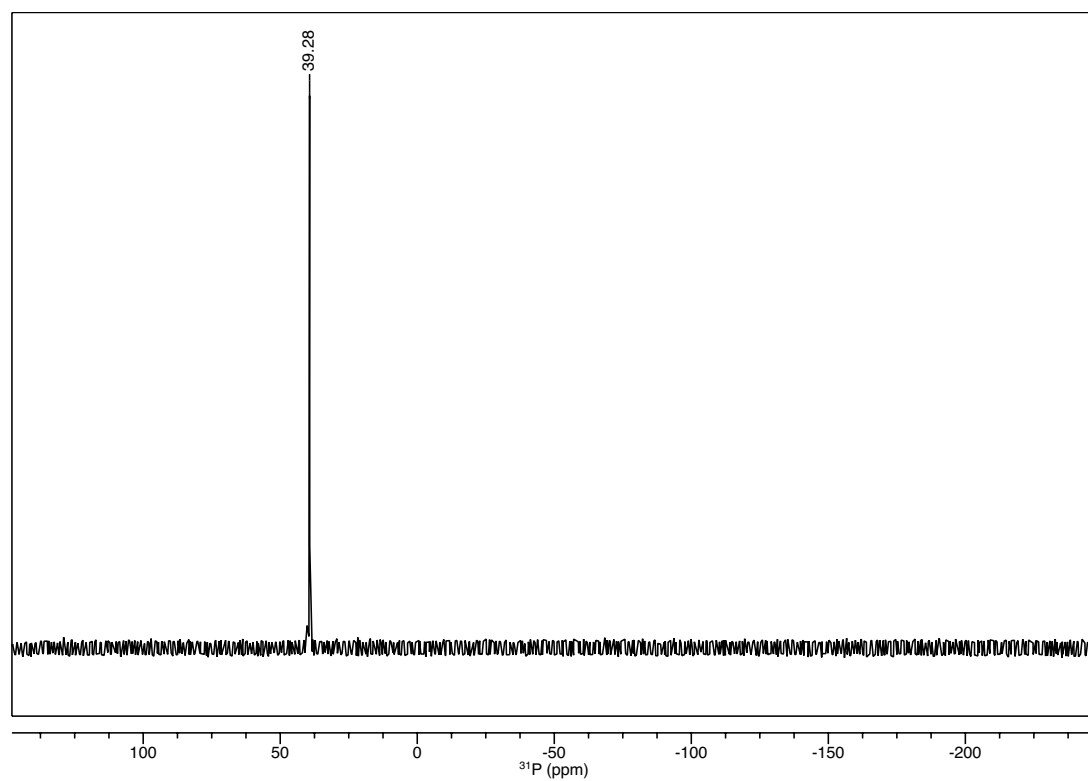


Figure 3-25 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{H}_2\text{L}^{\text{Ad}}$ (**3-1**) recorded in CD_2Cl_2 at 298 K (243 MHz).

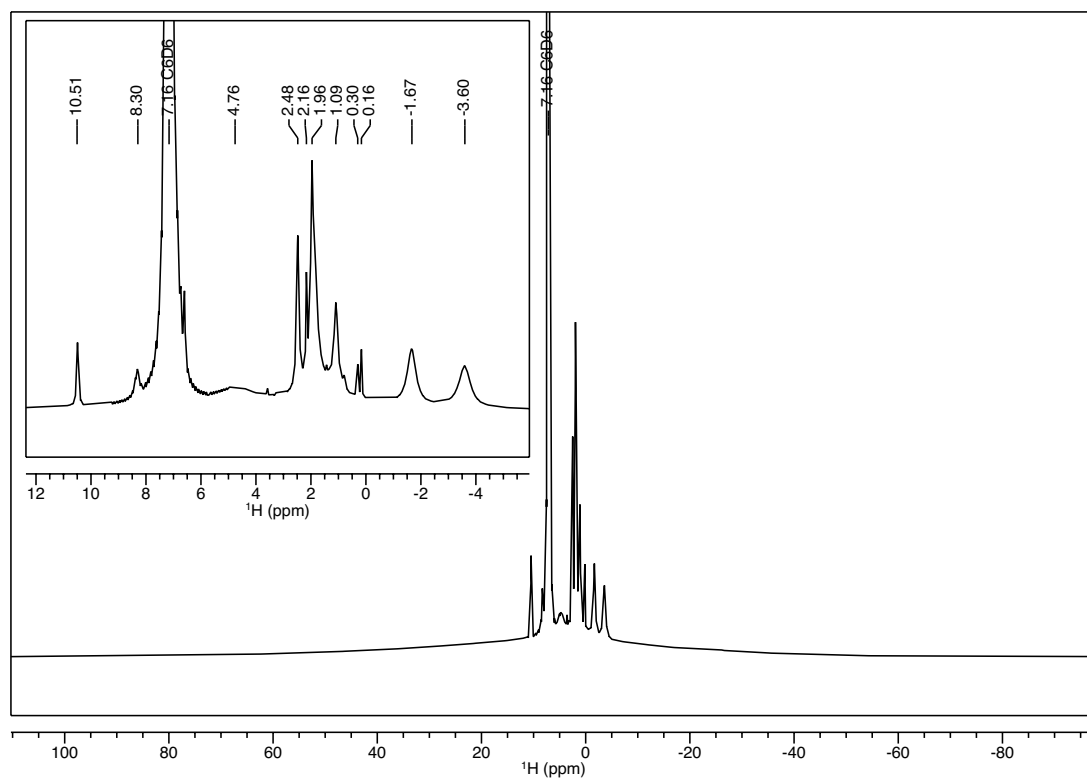


Figure 3-26 ^1H NMR spectrum of $\text{L}'\text{AdCr}(\text{h}^2\text{-TMSC}\equiv\text{CTMS})$ (**3-2**) recorded in C_6D_6 at 298 K (600 MHz).

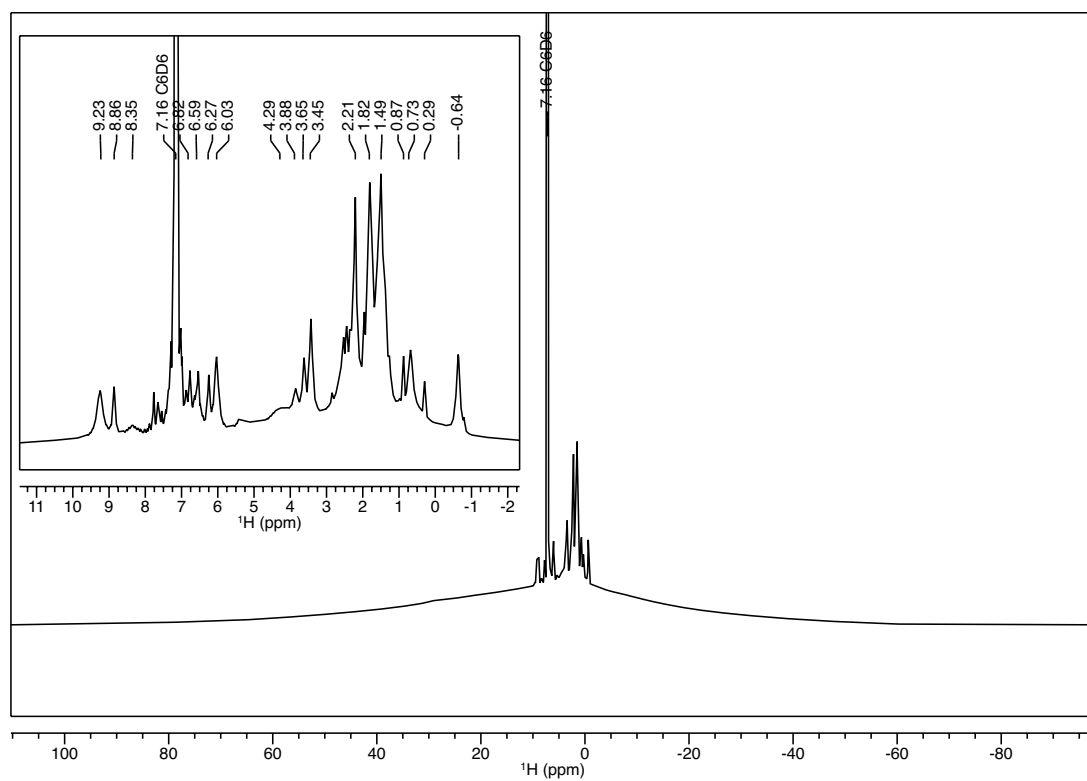


Figure 3-27 ^1H NMR spectrum of $\text{L}'\text{AdCr}(\text{h}^2\text{-Ar}^{\text{D-F}}\text{N}=\text{NAr}^{\text{D-F}})$ (**3-4**) recorded in C_6D_6 at 298 K (600 MHz).

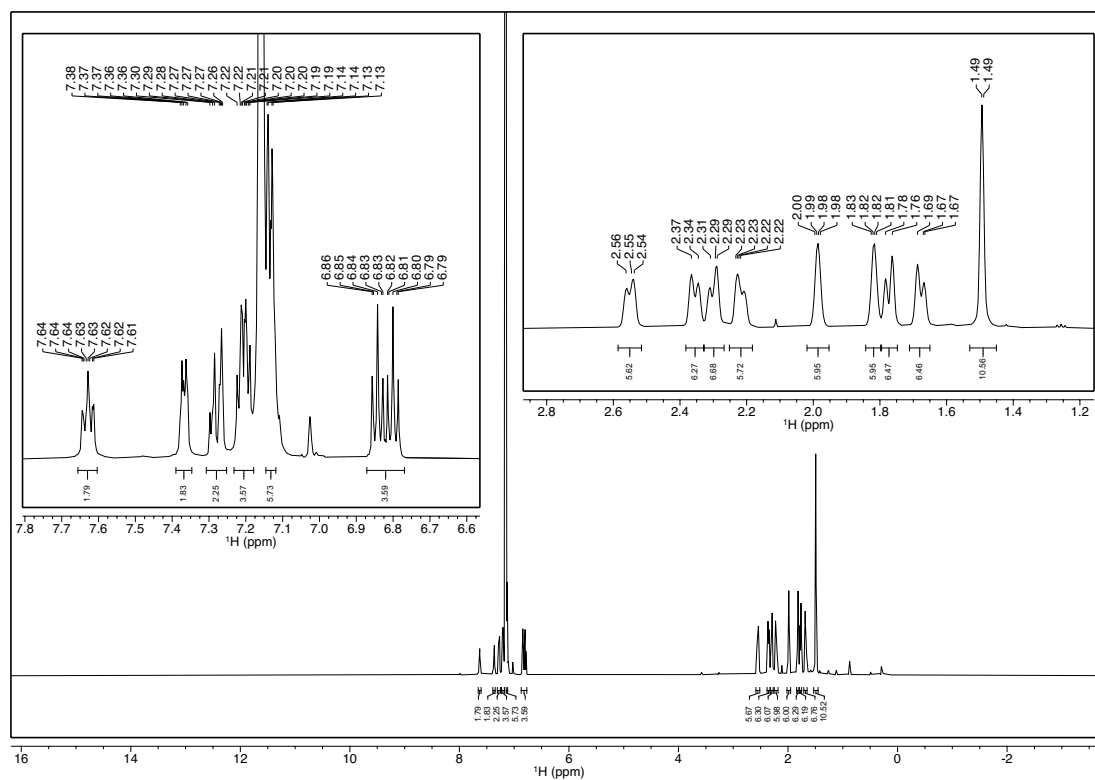


Figure 3-28 ^1H NMR spectrum of $\text{L}'\text{AdCr}(\text{NAr}^{\text{p-F}})_2$ (**3-3**) recorded in C_6D_6 at 298 K (600 MHz).

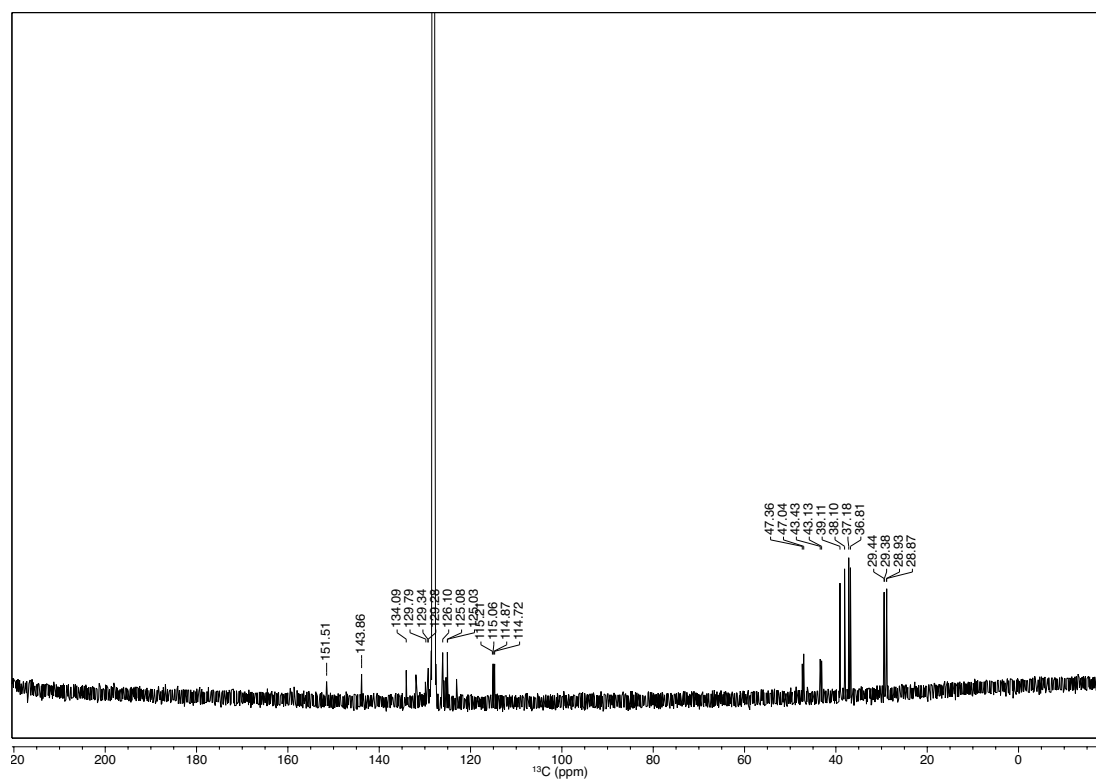


Figure 3-29 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{L}'\text{AdCr}(\text{NAr}^{\text{p-F}})_2$ (**3-3**) recorded in C_6D_6 at 298 K (151 MHz).

Kinetic experiments

Procedure for monitoring the conversion of $L'^{Ad}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ into $L'^{Ad}Cr(NAr^{p-F})_2$ using variable temperature ^{19}F NMR.

4-fluorotoluene (0.132 mmol, 14.5 mg) was dissolved in 3.1 ml of mesitylene affording a 42.5 mmol/L standard solution. 0.6 mL of this solution was used to dissolve $L'^{Ad}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ (**4**) (10.5 μ mol, 11.9 mg) and the resulting solution was transferred to a J-Young NMR tube. To a second NMR tube 0.6 mL of the standard solution were added.

The latter solution was used to shim and tune the NMR spectrometer at 373 K: Due to the absence of a deuterated solvent, gradient shimming was performed on the mesitylene methyl peak. Subsequently the sample was exchanged for the sample containing $L'^{Ad}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$. 59 individual ^{19}F NMR spectra were obtained with single scans every 120 s while the sample was held at a constant temperature of 373 K. The resulting spectra were processed in MestReNova (Version 14.1.2-25024).¹³¹ Each spectrum was individually baseline corrected using the automatic baseline correction available in MestReNova to mitigate the influence of Teflon in the NMR probe on the baseline. The spectra obtained in this way are depicted below. The concentration of $L'^{Ad}Cr(NAr^{p-F})_2$ measured at the final time point corresponds to 82% spectroscopic yield (8,61 μ mol). A minor amount ($\sim 6\%$) of $L'^{Ad}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ apparently decomposed prior to the experiment and released a constant amount of $Ar^{p-F}N=NAr^{p-F}$ (0.64 μ mol) noted in the spectra.

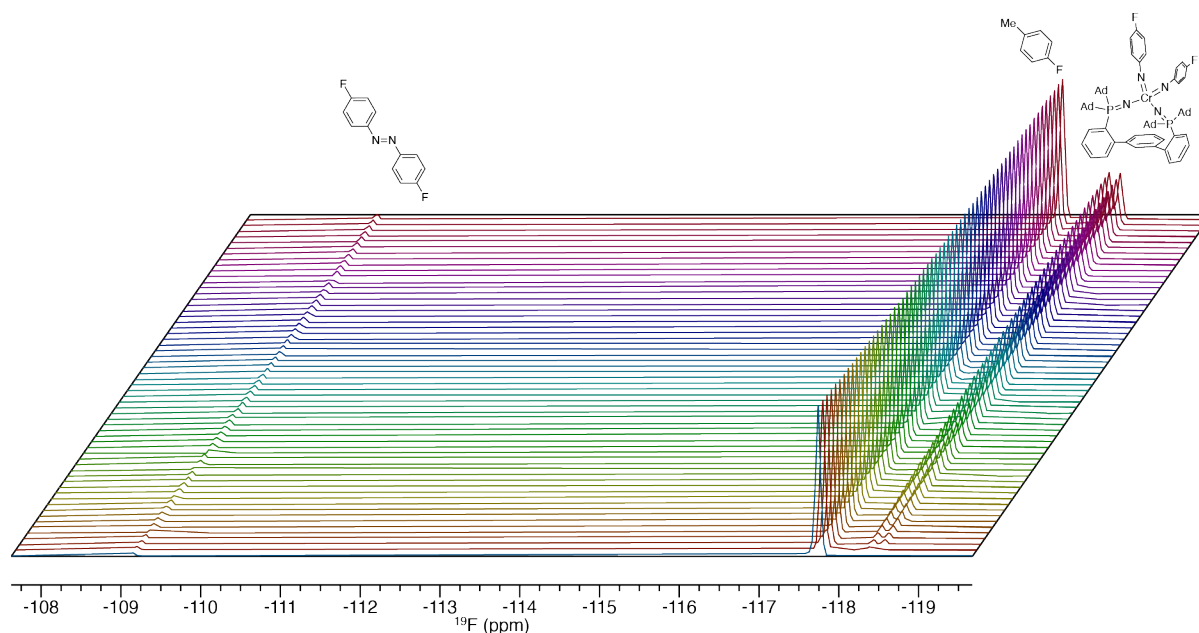


Figure 3-30 ^{19}F NMR spectra recorded every 120 s monitoring the conversion between $L'^{Ad}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ and $L'^{Ad}Cr(NAr^{p-F})_2$ in mesitylene at 373 K. 4-fluorotoluene was included as an internal standard.

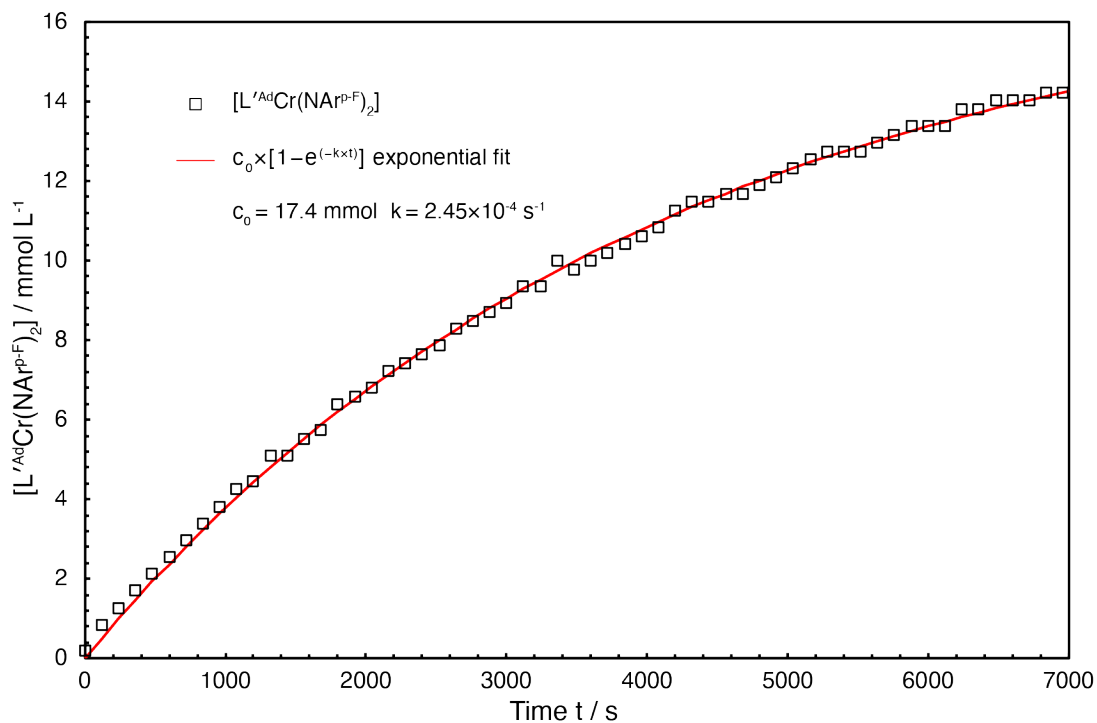


Figure 3-31 Plot of the time dependence of the concentration of $L'^{Ad}Cr(NAr^{p-F})_2$ during the conversion between $L'^{Ad}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ and $L'^{Ad}Cr(NAr^{p-F})_2$ in mesitylene at 373 K and fit to an exponential function.

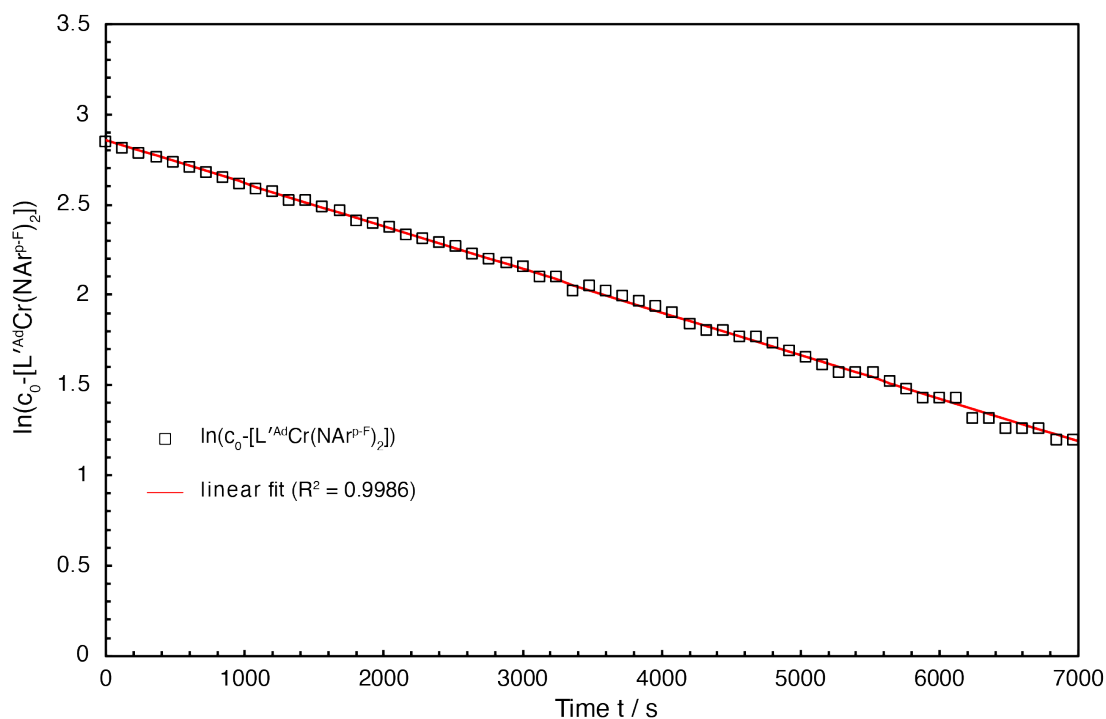


Figure 3-32 Plot of the time dependence of the natural logarithm of concentration of $L'^{Ad}Cr(NAr^{p-F})_2$ during the conversion between $L'^{Ad}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ and $L'^{Ad}Cr(NAr^{p-F})_2$ in mesitylene at 373 K and fit to a linear function. c_0 is the theoretical concentration corresponding to 100% yield.

UV/visible Spectroscopy

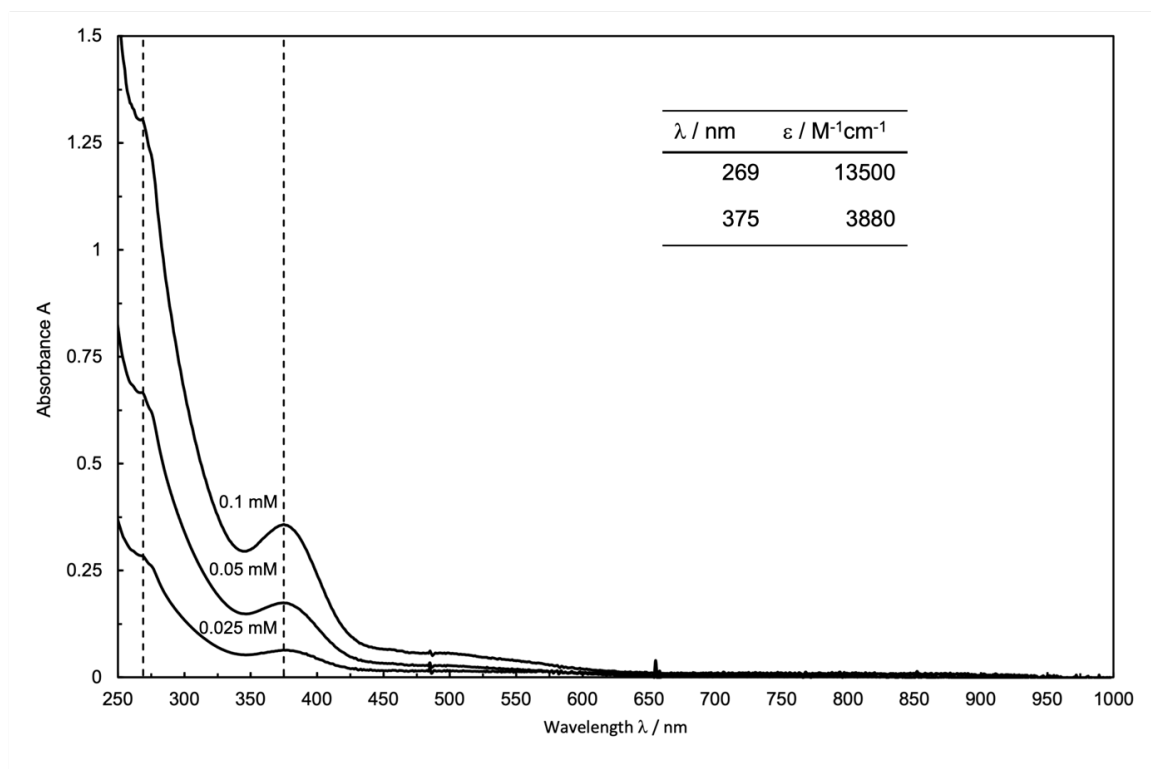


Figure 3-33 298 K UV/visible spectrum of $\text{L}^{\text{AdCr}}(\text{h}^2\text{-TMSC}\equiv\text{CTMS})$ (**3-2**) at the listed concentrations in THF.

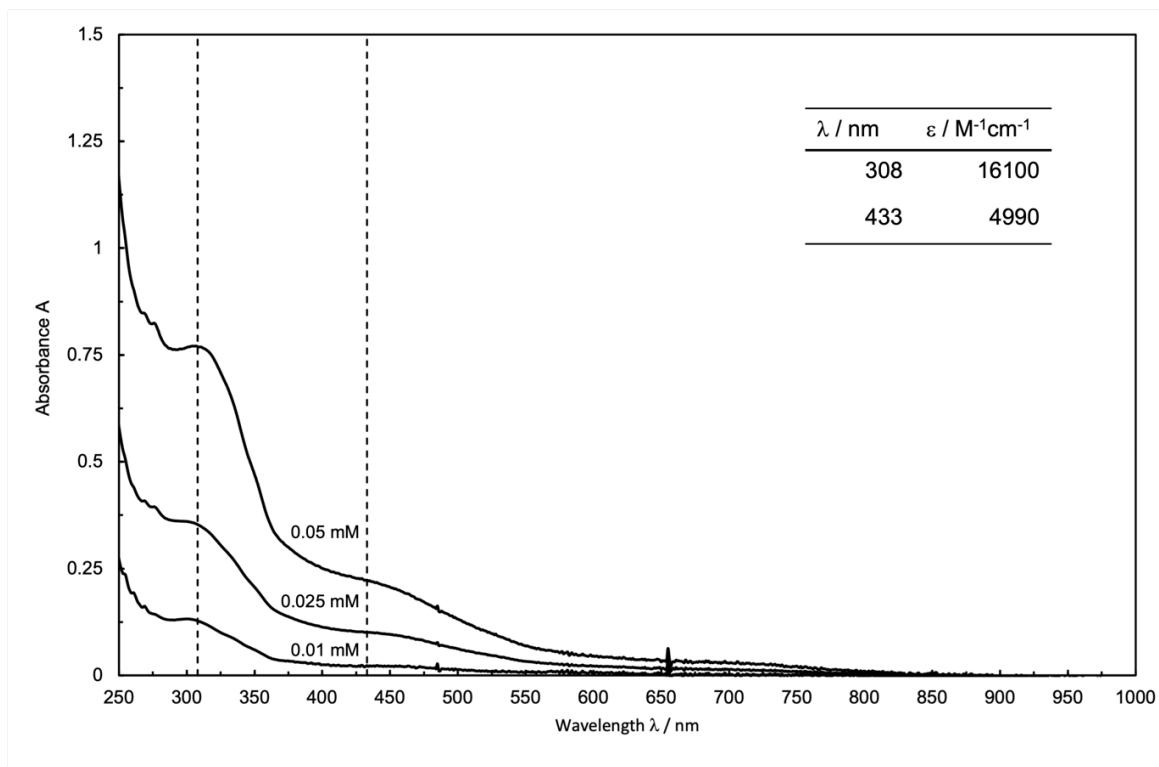


Figure 3-34 298 K UV/visible spectrum of $\text{L}^{\text{AdCr}}(\text{h}^2\text{-Ar}^{\text{p-F}}\text{N}=\text{NAr}^{\text{p-F}})$ (**3-4**) at the listed concentrations in THF.

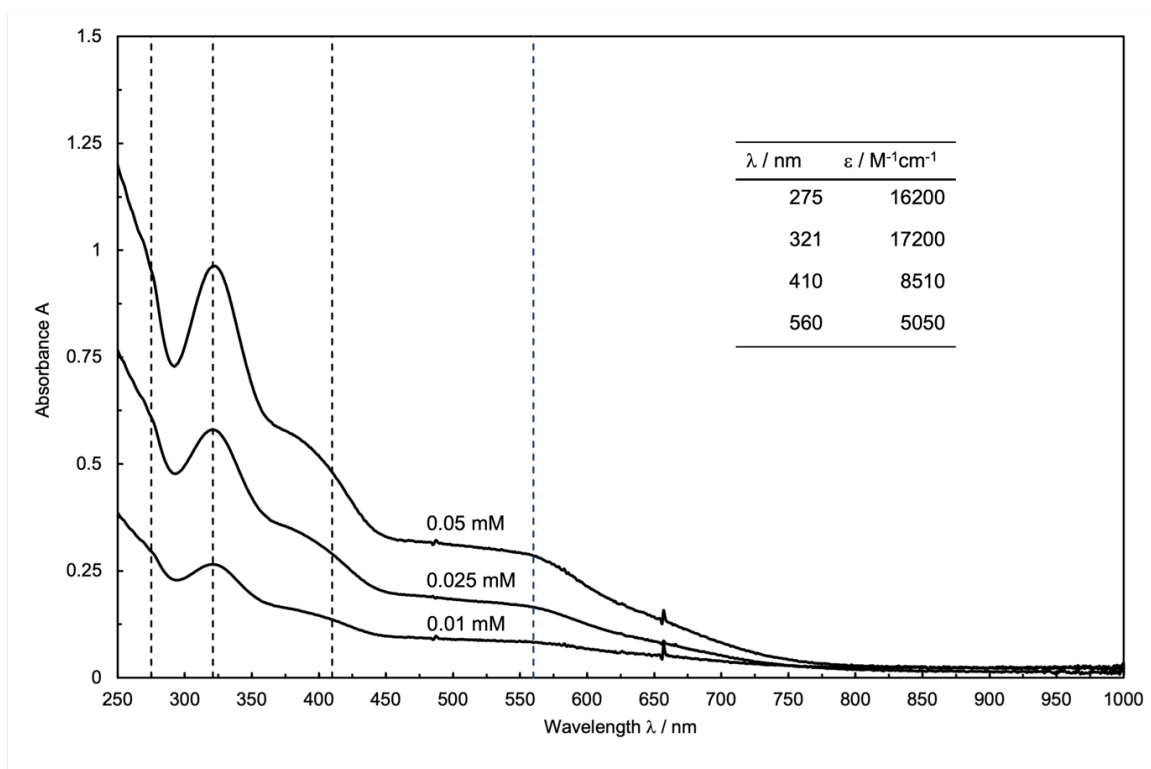


Figure 3-35 298 K UV/vis spectrum of $L^{\text{Ad}}\text{Cr}(\text{NAr}^{\text{F}})_2$ (**3-3**) at the listed concentrations in THF.

Computational methods

DFT calculations on $L^{\text{tBu}}\text{Cr}(\text{h}^2\text{-TMSC}\equiv\text{CTMS})$ ($S = 1$) were performed using ORCA version 4.2.1.¹³² Gas phase geometry optimizations were carried out using the M06L functional and the def2-TZVPP basis set on chromium, all coordinating atoms as well as silicon and phosphorous atoms and def2-SVP elsewhere. Initial coordinates were obtained from the crystal structures and by truncating the adamantyl groups to tert-butyl groups. The RI-J approximation¹³³ was applied in combination with the def2/J basis set¹³³ in order to speed up the calculation of Coulomb integrals. Tighter-than-default convergence criteria for the SCF as well as the geometry optimization were applied using the keywords “verytightOPT” and “tightSCF”. A significantly finer-than-default integration grid (“grid7”) was used during these calculations. No dispersion correction was applied. A numerical frequency calculation performed on the obtained geometry did not exhibit any imaginary frequencies.

Bond	Experimental value/Å	Optimized structure/Å	Angle	Experimental value/°	Optimized structure/°
Cr1-N1	1.807(4)	1.795	N1-Cr1-N2	121.31(19)	116.9
Cr1-N2	1.819(4)	1.804	C1-Cr1-C2	39.5(2)	40.1
Cr1-C1	1.948(5)	1.929	Cr1-N1-P1	163.0(3)	145.4
Cr1-C2	1.965(5)	1.938	P2-N2-Cr1	157.5(3)	156.5
C1-C2	1.324(7)	1.325	Si1-C1-C2- Si2	12.7(12)	5.1

Table S1. Comparison between crystallographically determined structural parameters for $L^{Ad}Cr(h^2-TMSC\equiv CTMS)$ with those obtained during the geometry optimization of $L^{tBu}Cr(h^2-TMSC\equiv CTMS)$ ($S = 1$).

IBOs for $L^{tBu}Cr(h^2-TMSC\equiv CTMS)$ ($S = 1$) were generated and visualized using IBOview version v20211019-RevA.¹¹⁷

Complete active space self-consistent field (CASSCF) calculations were performed on a single triplet root to determine whether a multiconfigurational nature of the ground state of $L^{tBu}Cr(h^2-TMSC\equiv CTMS)$ may be present. The active space consisted of 8 electrons in 9 orbitals (CASSCF(8,9)) which were chosen from the DFT generated QROs¹³⁴ to include all Chromium d -orbitals as well as both π -systems of the alkyne. The same functional, basis set, approximations and convergence criteria were used as for the DFT calculations hitherto. The following block of instructions was used to rotate the relevant QROs into the active space:

```

“%scf
rotate {197,203} end
rotate {198,204} end
rotate {210,208} end
rotate {211,209} end
rotate {215,210} end
rotate {217,211} end

```

end”

Configuration	Occupation
222110000	0.85145
220112000	0.03575
221111000	0.01764
121111010	0.01630
202110200	0.01506
211111001	0.01251
112111100	0.01066
112110011	0.00464
122110010	0.00372
212110001	0.00302

Table S2. Configurations for the ground state of $L^{tBu}Cr(h^2-TMSC\equiv CTMS)$ as obtained from CASSCF(8,9)

The natural orbitals obtained were visualized with IBOview version v20211019-RevA.¹¹⁷

DFT calculations on $L^{tBu}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$, $L^{tBu}Cr(NAr^{p-F})_2$ and the intermittent transition states were performed with Gaussian 09: ES64L-G09RevD.01.¹³⁵ Gas phase geometry optimizations were carried out using the M06L functional.¹³⁶ A finer-than-default integration grid was used for all calculations by utilizing the keyword “integral=superfine”. During these calculations the def2-TZVPP basis set⁸⁰ was used for all chromium, phosphorous and nitrogen atoms. The SVP basis set¹³⁷ was used elsewhere. Initial coordinates for the geometry optimizations were obtained from the crystal structures and by truncating the adamantyl groups to tert-butyl groups. Frequency calculations performed on the optimized geometries exhibited no imaginary frequencies.

Bond	Experimental value/Å	Optimized structure/Å	Angle	Experimental value/°	Optimized structure/°
Cr1-N1	1.7845(13)	1.774	N1-Cr1-N2	118.48(6)	115.7
Cr1-N2	1.7898(13)	1.788	N3-Cr1-N4	44.11(6)	43.4
Cr1-N3	1.9026(14)	1.928	Cr1-N1-P1	152.80(9)	149.8
Cr1-N4	1.9258(13)	1.903	P2-N2-Cr1	158.24(9)	166.6
N3-N4	1.4377(18)	1.417	C59-N3- N4-C65	107.67(14)	130.9

Table S3. Comparison between crystallographically determined structural parameters for $L'^{Ad}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ with those obtained during the geometry optimization of $L'^{tBu}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ ($S = 1$).

Bond	Experimental value/Å	Optimized structure/Å	Angle	Experimental value/°	Optimized structure/°
Cr1-N1	1.7797(13)	1.779	Cr1-N1-P1	163.53(8)	157.4
Cr1-N2	1.7880(12)	1.781	Cr1-N2-P2	151.37(8)	155.1
Cr1-N3	1.6635(14)	1.672	Cr1-N3-C59	161.86(14)	153.0
Cr1-N4	1.6685(14)	1.663	Cr1-N4-C65	161.50(13)	165.0

Table S4. Comparison between crystallographically determined structural parameters for $L'^{Ad}Cr(NAr^{p-F})_2$ with those obtained during the geometry optimization of $L'^{tBu}Cr(NAr^{p-F})_2$ $S = 0$.

The geometry used as an initial guess for the optimizations of the transition states and was obtained by modifying the input geometry of $L'^{tBu}Cr(h^2-Ar^{p-F}N=NAr^{p-F})$ to reflect the azo-compound metrics reported for the transition state associated with the conversion of $[U(HMDS)_3(PhN=NPh)]^-$ to $[U(HMDS)_3(NPh)_2]^-$ reported by Modder *et al.*⁹⁷ and is provided below. Frequency calculations performed on the obtained transition state geometries in the singlet and triplet manifolds displayed a single imaginary frequency each corresponding to N-N bond cleavage.

Chapter 4 Two-electron reactivity between Phthalazines and a Chromium Metallocyclopropene

Introduction

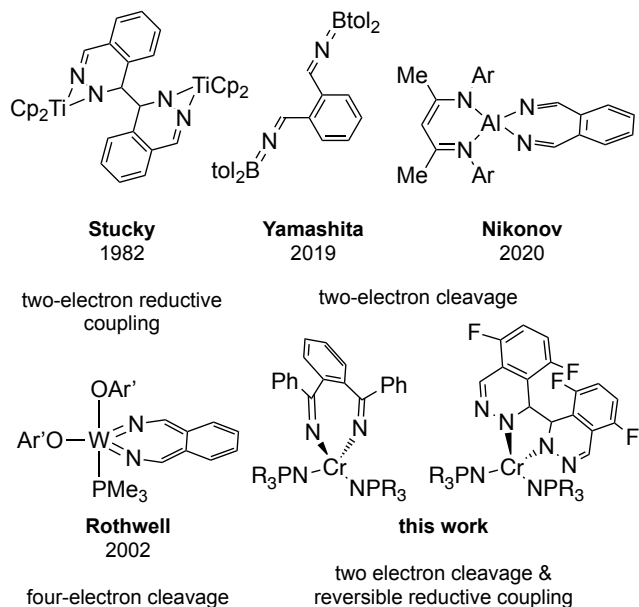


Figure 4-1 Phthalazine derived organometallic complexes reported in the literature.

Prior to our efforts on demonstrating reversible four-electron oxidative addition of benzo[c]cinnoline employing our previously reported chromium metallocyclopropene $L^{\text{Ad}}\text{Cr}(\text{btmsa})_5$ acting as the Cr(II) synthon we investigated reaction between the latter and phthalazine-derivatives. Choice of this heterocycle was guided by the assumption that 4-electron oxidative addition of phthalazines forming a metal-bisimido species would be accompanied by loss of aromaticity in the heterocycle backbone. Evidence of this notion was published by the Rothwell group, which showed that a tungsten-dialkoxide featuring bulky ligands oxidatively adds phthalazine, benzo[c]cinnoline and pyridazine in four-electron processes forming tungsten(VI) bisimido complexes (Scheme 1).²² The crystallographic data obtained for the metallocycle derived from phthalazine predominantly indicates a bisimido structure, however, when compared to the metallocycles derived from benzo[c]cinnoline and pyridazine there is a non-negligible contribution of the bisketimide form, which retains aromaticity in the backbone (Figure 4-7).¹ A canonical bisketimide example was reported by the Nikonov group and was obtained by exposing an aluminium(I) complex to phthalazine. This represents a two electron reductive cleavage of the N=N-bond¹³⁸ in line with aluminium(I) having two available valence electrons (Figure 4-1). This reaction can also be affected by diboron Lewis acids.¹³⁹ Two-electron reactivity of phthalazine is not exclusive to N=N-bond cleavage and there is an example of reductive dimerization of phthalazine upon exposure

to $\text{Cp}_2\text{Ti}(\text{CO})_2$.¹⁴⁰ We envisioned that the thermodynamic penalty associated with the anti-aromatic component would render a reductive elimination reaction more likely, but we found that, in contrast to the tungsten bisalkoxide used by the Rothwell group, our chromium bisphosphinimide complex was unable to overcome this hurdle and we observed the previously reported two-electron processes instead. Nevertheless, by investigating these reactions several crucial insights were gained which ultimately proved useful in demonstrating the 4-electron reversible cleavage of the N=N-bond in 2,9-difluorobenzo[c]cinnoline.

Results and Discussion

Addition of one equivalent of 5,8-difluorophthalazine to $\text{L}^{\text{Ad}}\text{Cr}(\text{btmsa})$ **3-2** resulted in complete consumption of the heterocycle as judged by ^{19}F NMR spectroscopy accompanied by formation of a new paramagnetic compound evident by ^1H NMR. However, $\text{L}^{\text{Ad}}\text{Cr}(\text{btmsa})$ was not fully consumed, hinting at multiple phthalazine equivalents reacting with one chromium center. Addition of two equivalents of the former to the chromium complex in benzene lead to complete conversion. Lyophilization followed by extraction into ether and subsequent storage of the solution at -35°C led to the isolation of this paramagnetic species as red crystals (Figure 4-2).

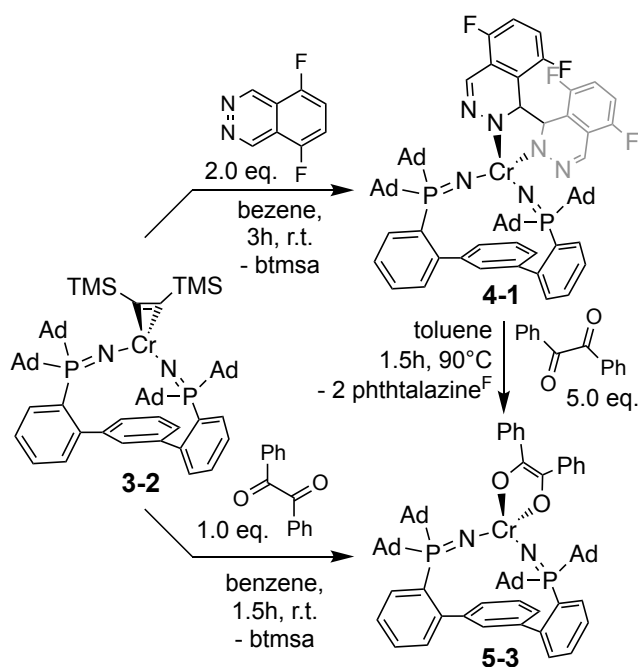


Figure 4-2 Synthesis and reactivity of $\text{L}^{\text{Ad}}\text{Cr}(\text{5,8-difluoro-bisphthalazide})$ **4-1**.

Determination of its crystal structure (Figure 4-3) identified the compound as $\text{L}^{\text{Ad}}\text{Cr}(\text{5,8-difluorobisphthalazide})$ **4-1** and revealed two phthalazine molecules, with their N-N-bonds intact, bound to a single chromium center through an individual nitrogen in an α^1 -fashion,

with both phthalazine fragments appearing reductively coupled across their 1-positions in an imino-pinacol manner. Close inspection of the bond metrics obtained from the crystal structure revealed that each bound phthalazine's C-C bond and C-N bond adjacent to the dimerization site have been considerably elongated to single bonds compared to the parent phthalazine (Figure 4-8).

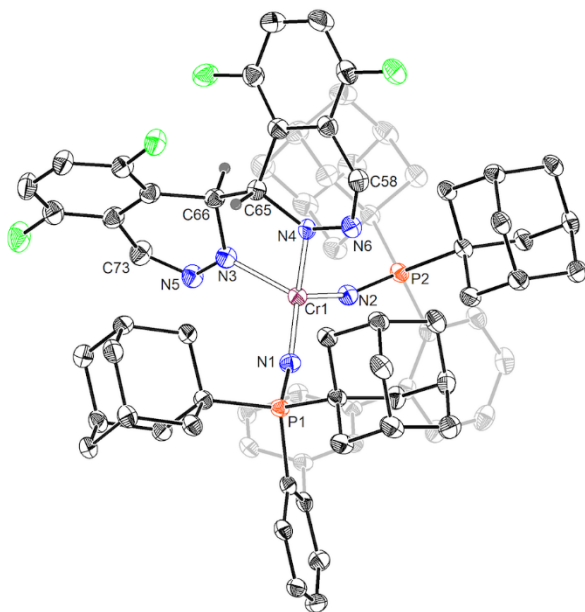


Figure 4-3 Crystal structure of $L^{\text{Ad}}\text{Cr}(5,8\text{-difluorobisphthalazide})$ 4-1 with ellipsoids shown at 50% probability. Hydrogen atoms bound to carbon atoms other than C65 and C66 have been omitted for clarity. Selected bond distances (Å), Cr1-N1 1.787(2), Cr1-N2 1.767(2), Cr1-N3 1.889(2), Cr1-N4 1.912(2), N3-C66 1.480(4), N4-C65 1.478(3), C65-C66 1.503(3), N3-N5 1.339(3), N4-N6 1.333(3).

The distance between the two phthalazine fragments of 1.503(3) Å is indicative of a $\text{sp}^3\text{-sp}^3$ C-C single bond and in conjunction with the pyramidalization at these carbons this suggests that hydrogen atoms are still present in these positions. Overall, each phthalazine fragment has been formally reduced by one electron and is acting as an X-type ligand leading to a Cr(IV) complex. This is supported by a magnetic moment of $2.7 \mu_{\text{B}}$, consistent with an $S=1$ spin state, determined by Evan's method. A similar reaction has been previously observed where two equivalents of phthalazine dimerize in the same manner upon exposure to two equivalents of $\text{Cp}_2\text{Ti}(\text{CO})_2$, albeit each phthalazine binding an individual Cp_2Ti -fragment in η^2 -fashion.¹⁴⁰ Other examples of reductive coupling of nitrogen-containing heterocycles atop metal centers include dimerization of quinoline by a Zirconium(II) pincer,¹⁴¹ isoquinoline by an aluminum(I) nacnac complex¹³⁸ as well as dimerization of pyridine by a formally uranium(III) siloxide, which ultimately leads to pyridine ring cleavage.¹⁴²

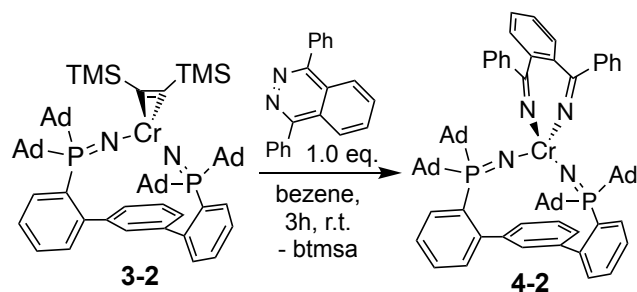


Figure 4-4 Synthesis of $L'^{Ad}Cr(o\text{-phenylenediphenylketimide})$ **4-2**.

Seeking to prevent reductive coupling 1,4-diphenylphthalazine was investigated with the intent of sterically blocking the sites prone to dimerization. Addition of one equivalent of this compound to $L'^{Ad}Cr(btmsa)$ **3-2** in benzene at room temperature resulted in complete consumption of the metallocyclopropene alongside with the formation of a new paramagnetic species as judged by ^1H NMR, hinting that dimerization had successfully been prevented. Lyophilization and extraction into pentane followed by storage of the resulting solution at room temperature afforded crimson crystals of $L'^{Ad}Cr(o\text{-phenylene-diphenylketimide})$ (**4-2**) (Figure 4-4). Notably, X-ray structure determination revealed that the N-N bond in 1,4-diphenylphthalazine had successfully been cleaved (Figure 4-6), however the magnetic moment of $2.4 \mu_B$ consistent with a spin state of $S=1$ measured by Evans' method suggested a Cr(IV) compound; phthalazine cleavage having taken place in a 2-electron manner.

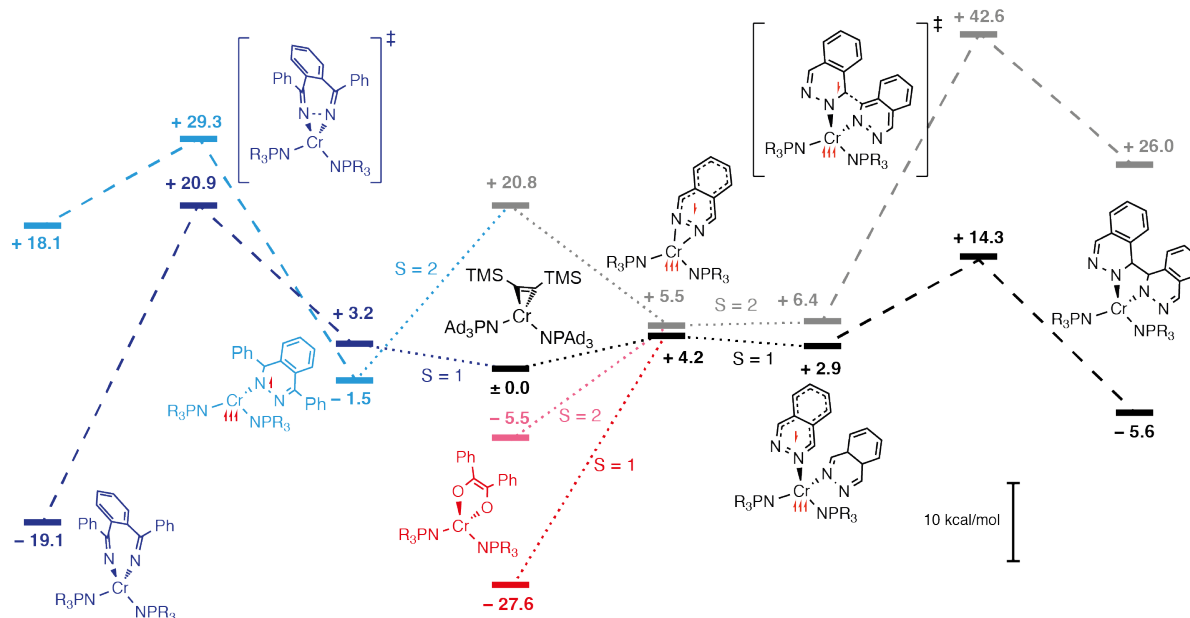


Figure 4-5 Calculated reaction coordinate for the synthesis of $L'^{Ad}Cr(5,8\text{-difluorobisphthalazide})$ and $L'^{Ad}Cr(o\text{-phenylene-diphenylketimide})$ as well as its conversion to $L'^{Ad}Cr(diphenylethenedialkoxide)$.

This was confirmed by comparison between the bond metrics of the cleaved phthalazine with those obtained for the aluminium bisketamide reported by Nikonov as a canonical 2-electron process¹³⁸ and the tungsten bisimido reported by Rothwell, representative of 4-electron cleavage,²² $L'^{Ad}Cr(o\text{-phenylene-diphenylketimide})$ **4-2** closely matching the former (Figure S1). In this case the *o*-phenylene-diphenylketimide acts as an X_2 -type ligand in a similar manner to the dimerized 5,8-difluorophthalazine *vide supra*.

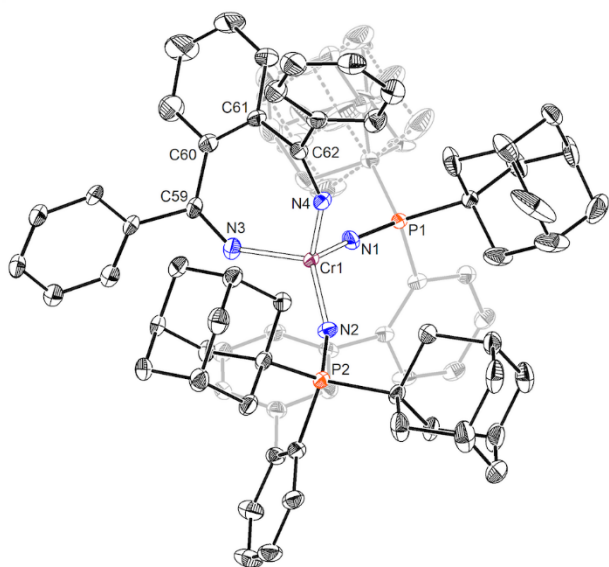


Figure 4-6 Crystal structure of $L'^{Ad}Cr(o\text{-phenylene-diphenylketimide})$ **4-2** with ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å), Cr1-N1 1.768(4), Cr1-N2 1.773(4), Cr1-N3 1.817(4), Cr1-N4 1.840(4), N3-C59 1.270(5), N4-C62 1.276(5), C59-C60 1.491(6), C61-C62 1.494(6), C60-C61 1.402(6).

We sought to gauge the feasibility of reversing these processes by investigating their reaction coordinates by DFT. Exploration of the reaction coordinate associated with 1,4-diphenylphthalazine cleavage by a relaxed surface scan along N-N bond formation starting from the bisketamide revealed a transition state as well as an intermediate corresponding to the phthalazine pre-coordinating to the chromium center. Evaluation of their energies using the M06L functional (Figure 4-5) revealed an exergonic oxidation reaction by 19.1 kcal mol⁻¹ relative to $L'^{Ad}Cr(btmsa)$ **3-2** with an associated rate-determining barrier of 20.6 kcal mol⁻¹, towards the high end of reactions possible at room temperature. Unfortunately, the return reductive elimination reaction would be associated with a barrier of around 40 kcal mol⁻¹, rendering it out of reach. Dimerization of 5,8-difluorophthalazine in contrast is significantly less exergonic at -5.6 kcal mol⁻¹ with a rate determining barrier of 14.3 kcal mol⁻¹ and a predicted barrier for the return reaction of 20.0 kcal mol⁻¹. Numbers in this realm suggested that if a scavenger that binds the chromium center with a binding energy in excess of 5.6 kcal/mol could be found, the reaction may be reversed

vide infra. It should be noted that along both reaction coordinates intermediates featuring a single phthalazine moiety bound to the chromium center are predicted to be chromium(III) compounds with a radical delocalized amongst the phthalazine ring (Figure 4-20 and Figure 4-21) and that dimerization features a lower barrier than N-N cleavage which underscores the propensity of 3d transition metals to undergo sequential 1-electron processes rather than multielectron processes.

Guided by the highly exergonic reaction with 1,4-diphenylphthalazine forming a Cr(IV) center we settled on benzil—a redox active ligand which we previously used as a suitable trap to drive return reactions. Gratifyingly, exposure of 5 eq. of benzil to L'AdCr(5,8-difluorobisphthalazide) **4-1** in an NMR tube at 90°C led to the recovery of 5,8-difluorophthalazine in 67% yield following first order kinetics. (Figure 4-9) While unprecedented this reaction is a far cry from the reversible 4-electron cleavage targeted initially, however, the concept of using benzil as a thermodynamic trap did play an important role in our investigation of the reactivity between L'AdCr (btmsa) **3-2** and 2,9-difluorobenzo[c]cinnoline.

Supporting Information

General Considerations

All reactions were performed at room temperature in a N₂-filled glovebox or by employing standard Schlenk techniques unless otherwise stated. Glassware was oven-dried at 150 °C for at least 2 h prior to use and allowed to cool under a vacuum. All reagents were used as received unless otherwise stated. Anhydrous pentane, diethyl ether, benzene, toluene, THF and acetonitrile were purified by sparging with nitrogen for 30 min and then passing under nitrogen pressure through a column of activated A2 alumina. NMR solvents were purchased from Cambridge Isotope Laboratories. C₆D₆ was degassed by three freeze–pump–thaw cycles and dried over freshly activated 3 Å molecular sieves for 24 h prior to use. L'AdCr(btmsa)⁴³ was synthesized according to a previously published procedure. Heterocycle substrates were synthesized according to various combinations of previously published synthetic procedures outlined in the synthetic procedures section.^{143–145}

X-ray Crystallography

XRD studies were performed at beamline 12.2.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory. Crystals were mounted on a MiTeGen loop under Paratone oil. Data was collected on a Bruker D85 three-circle diffractometer with a PHOTON II CCD area detector using silicon monochromated synchrotron radiation ($\lambda = 0.7288$ Å). Bruker APEX2¹⁴⁶ software was used for data collection. Bruker SAINT¹⁴⁷ and SADABS¹⁴⁸ software packages were utilized for data reduction and absorption correction, respectively.

Structures were solved using SHELXT¹⁴⁹ and refined against F^2 on all data by full matrix least-squared with SHELXL¹⁵⁰ using OLEX 2 Version 1.5¹⁵¹ crystallographic software. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms bonded to carbon atoms were placed in idealized positions and refined using a riding model.

Infrared Spectroscopy

FTIR measurements were carried out on a Thermo Scientific Nicolet iS20 spectrometer utilizing KBr pellets.

Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on Bruker or Joel 400/600 MHz instruments. ¹H chemical shifts are reported in ppm relative to tetramethylsilane (TMS) at 0.00 ppm using residual solvent peaks as internal standards.¹⁵² The widths of paramagnetic peaks at half maximum (FWHM) are reported in the experimental section. Solution phase magnetic measurements were performed using Evans' method.¹⁵³

UV/visible Spectroscopy

UV/visible measurements were taken on a Agilent Cary 60 UV-Vis Spectrophotometer using 1 cm quartz cells sealed with a Teflon stopcock.

Elemental Analysis

Elemental analyses were performed at the University of California, Berkeley College of Chemistry Microanalytical Facility using a PerkinElmer 2400 Series II combustion analyzer.

Figures supporting the main text

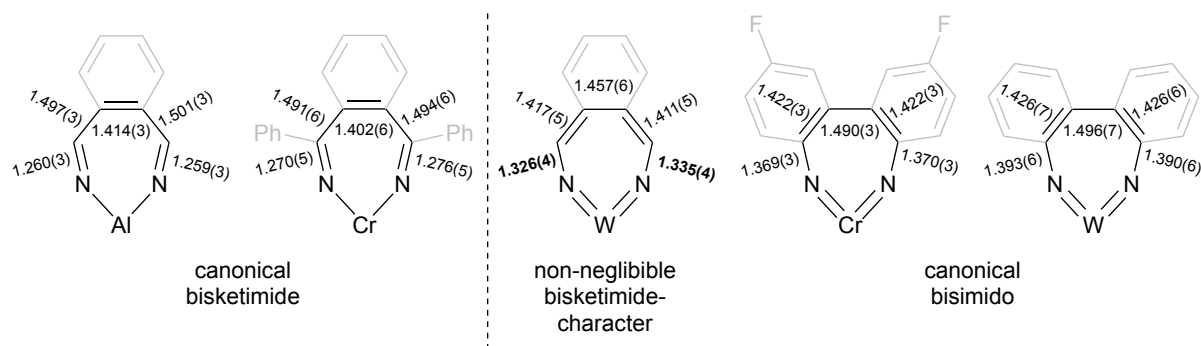


Figure 4-7 Bond metrics obtained for various metalocycles derived from N=N-bond containing heterocycles reported in the literature and comparison to compounds described in this report.

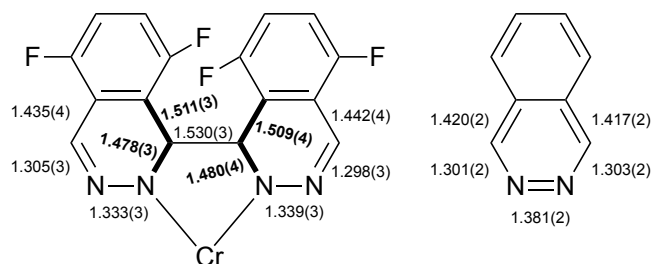


Figure 4-8 Bond metrics obtained for $L^{Ad}Cr(5,8\text{-difluorobisphthalazide})$ 4-1 described in this report compared to phthalazine reported in the literature.

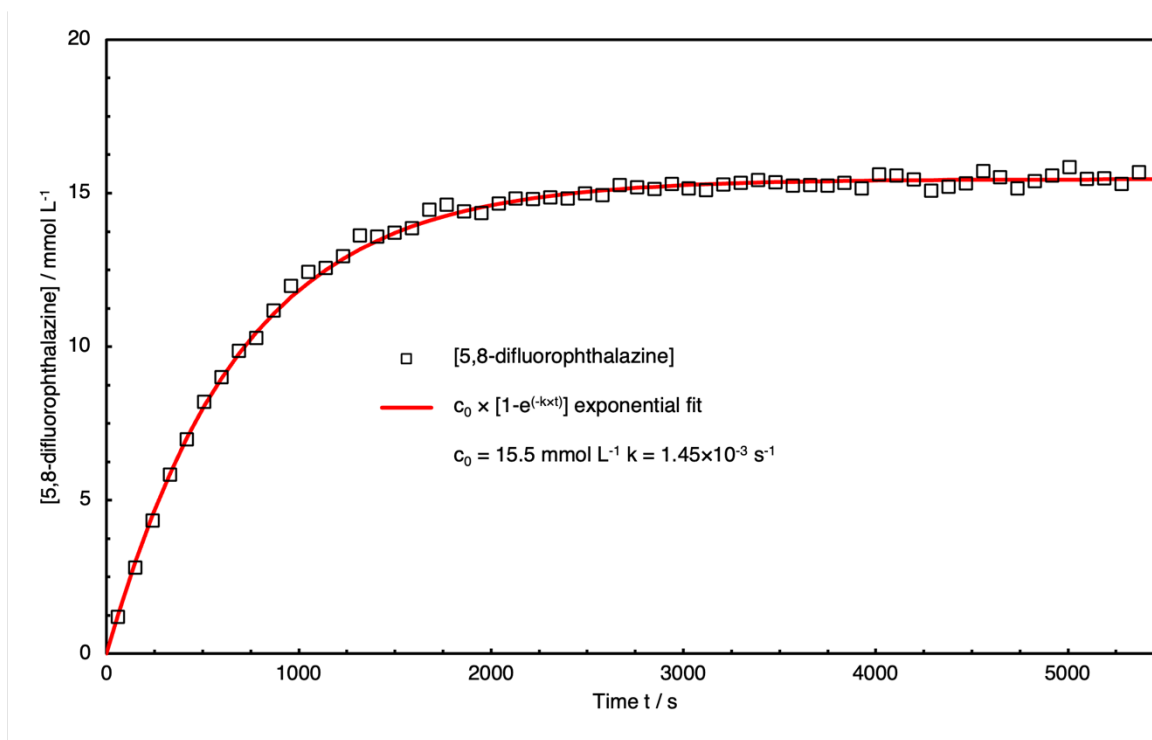
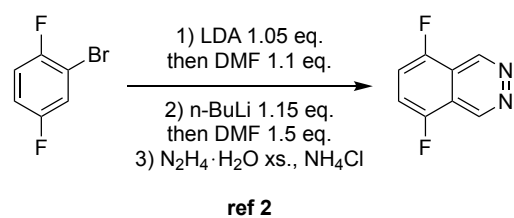


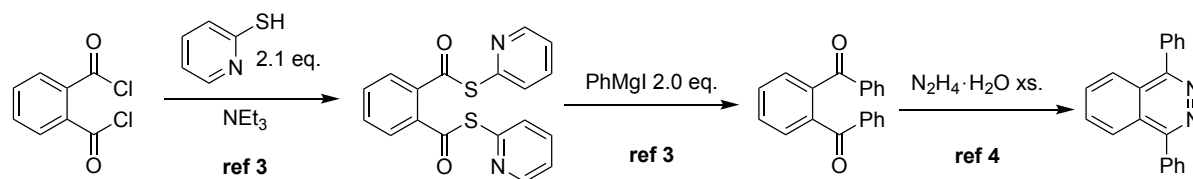
Figure 4-9 Time dependence of the concentration of 5,8-difluorophthalazine during the reaction between L'AdCr(bis-5,8-difluorophthalazide) 4-1 and 5.0 eq. of benzil in toluene at 363K (squares) Fit to an exponential function (red line).

Synthetic procedures

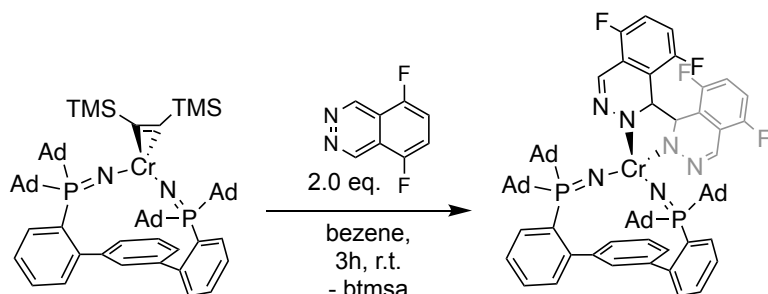
Synthesis of 5,8-difluorophthalazine



Synthesis of 1,4-diphenylphthalazine

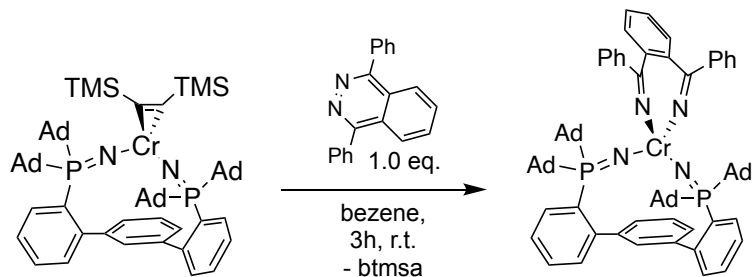


Synthesis of L'^{Ad}Cr(bis-5,8-difluorophthalazide) 4-1



A solution of 5,8-difluorophthalazine (0.146 mmol, 24.3 mg, 2.1 eq.) in benzene (3 ml) was added slowly to a stirring solution of L'Cr(btmsa) (0.069 mmol, 75 mg, 1.0 eq.) in benzene (10 ml), which resulted in an instantaneous colour change from crimson to red brown. The resulting solution was stirred overnight. Subsequently, all volatiles were removed *in vacuo* and the resulting solid washed with pentane (5 ml) and ether (3 ml). Both fractions were set aside and the residue was redissolved in benzene (15 ml), filtered and lyophilized to afford the title compound as a fluffy red brown solid (63.5 mg, 74% yield). $C_{74}H_{80}CrF_4N_6P_2$ (1243.4 g/mol). ^1H NMR (400 MHz, C_6D_6) δ 65.13 ($Dn_{1/2} = 753$ Hz), 9.64 (32), 8.43 (36), 7.90 (50), 7.64 (30), -3.18 (78), -3.61 (81), -5.39 (72), -6.97 (72). Anal. calcd. for $C_{74}H_{80}CrF_4N_6P_2$: C, 71.48; H, 6.49; N, 6.76. Found: C, 75.29; H, 7.59; N, 5.17. μ_{eff} (C_6D_6 , 298 K, 400MHz): 2.7 μ_B .

Synthesis of L'^{Ad}Cr(o-phenylene-diphenylketimide) 4-2



A solution of 1,4-diphenylphthalazine (0.020 mmol, 5.7 mg, 1.1 eq.) in benzene (3 ml) was added slowly to a stirring solution of L'Cr(btmsa) (0.0184 mmol, 20 mg, 1.0 eq.) in

benzene (3 ml). Only a minor colour change was observed after the resulting solution had been stirred overnight. Subsequently, all volatiles were removed *in vacuo* and the resulting solid washed with pentane (3 ml) and ether (1.5 ml). Both fractions were set aside and the residue was redissolved in benzene (5 ml), filtered and lyophilized to afford the title compound as a fluffy maroon solid (13.0 mg, 59% yield). $C_{78}H_{86}CrN_4P_2$ (1193.5 g/mol). ^1H NMR (400 MHz, C_6D_6) δ 21.61 ($Dn_{1/2} = 104$ Hz), 20.22 (97), 12.42 (1403), 11.76 (65), -3.36 (165), -6.72 (170), -9.23 (390), -13.58 (588), -33.00 (450), -35.31 (780), -37.37 (1073). Anal. calcd. for $C_{78}H_{86}CrN_4P_2$: C, 78.50; H, 7.26; N, 4.69. Found: C, 70.51; H, 7.09; N, 6.14. μ_{eff} (C_6D_6 , 298 K, 400MHz): $2.4 \mu_B$.

Crystals suitable for XRD were grown from the pentane fraction set aside earlier at room temperature over the course of multiple days.

X-ray crystallography

Compound	L ^{Ad} Cr(bis-5,8-difluorophthalazide) 4-1	L ^{Ad} Cr(o-phenylene-diphenylketimide) 4-2
CCDC Deposition Number		
Empirical formula	C ₇₈ H ₉₀ CrF ₄ N ₆ OP ₂	C ₈₃ H ₉₈ CrN ₄ P ₂
Formula weight	1317.49	1265.59
Temperature/K	100	100
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
a/Å	14.9138(14)	12.1816(14)
b/Å	16.6296(16)	25.765(3)
c/Å	26.474(3)	21.124(3)
$\alpha/^\circ$	90	90
$\beta/^\circ$	102.148(4)	91.308(5)
$\gamma/^\circ$	90	90
Volume/Å ³	6418.9(11)	6628.2(13)
Z	4	4
$\rho_{\text{calc}}/\text{cm}^3$	1.363	1.268
μ/mm^{-1}	0.312	0.288
F(000)	2792.0	2712.0
Crystal size/mm ³	0.1 × 0.02 × 0.02	0.05 × 0.01 × 0.01
Radiation	synchrotron ($\lambda = 0.7288$)	synchrotron ($\lambda = 0.7288$)
2 Θ range for data collection/ $^\circ$	2.986 to 51.688	3.794 to 60.05
Index ranges	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -31 ≤ l ≤ 31	-16 ≤ h ≤ 16, 0 ≤ k ≤ 35, 0 ≤ l ≤ 28
Reflections collected	187340	17783
Independent reflections	11428 [R _{int} = 0.1093, R _{sigma} = 0.0463]	17783 [R _{sigma} = 0.0557]
Data/restraints/parameters	11428/0/831	17783/450/977
Goodness-of-fit on F ²	1.033	1.061
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0441, wR ₂ = 0.1060	R ₁ = 0.0991, wR ₂ = 0.2782
Final R indexes [all data]	R ₁ = 0.0641, wR ₂ = 0.1157	R ₁ = 0.1146, wR ₂ = 0.2931
Largest diff. peak/hole / e Å ⁻³	0.33/-0.73	1.21/-1.40

FTIR spectroscopy

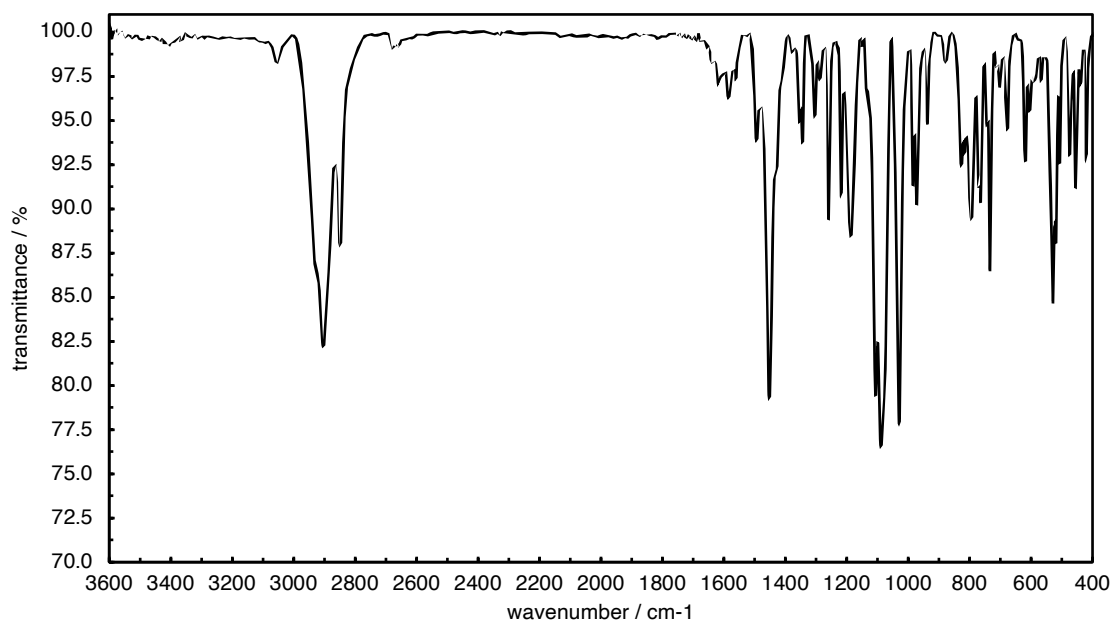


Figure 4-10 FTIR spectrum of L'^{Ad}Cr(bis-5,8-difluorophthalazide) 4-1 (KBr pellet).

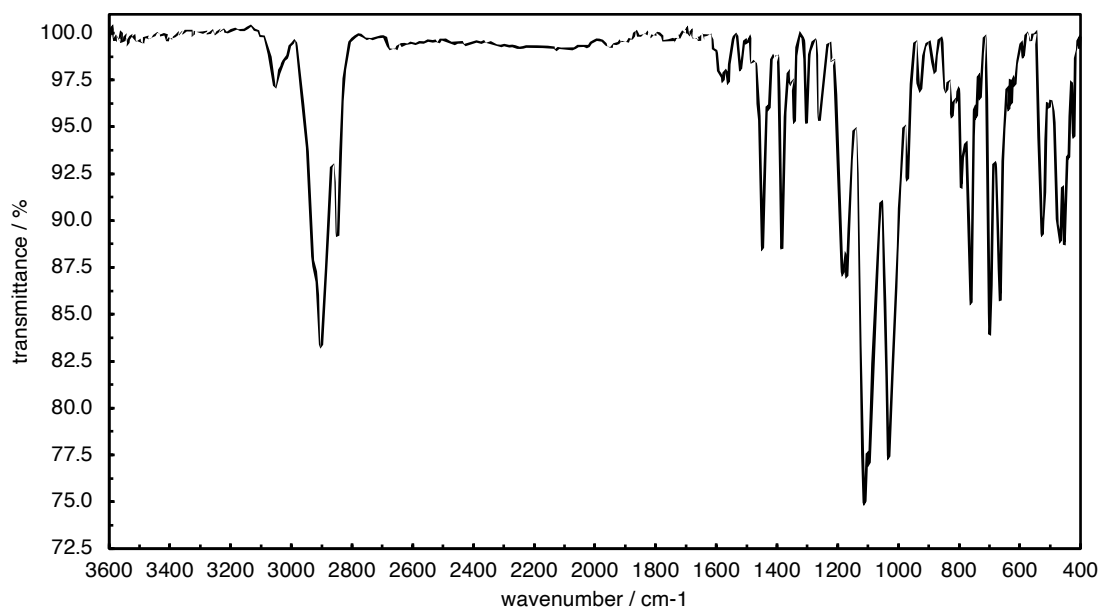


Figure 4-11 FTIR spectrum of L'^{Ad}Cr(o-phenylene-diphenylketimide) 4-2 (KBr pellet).

NMR spectroscopy

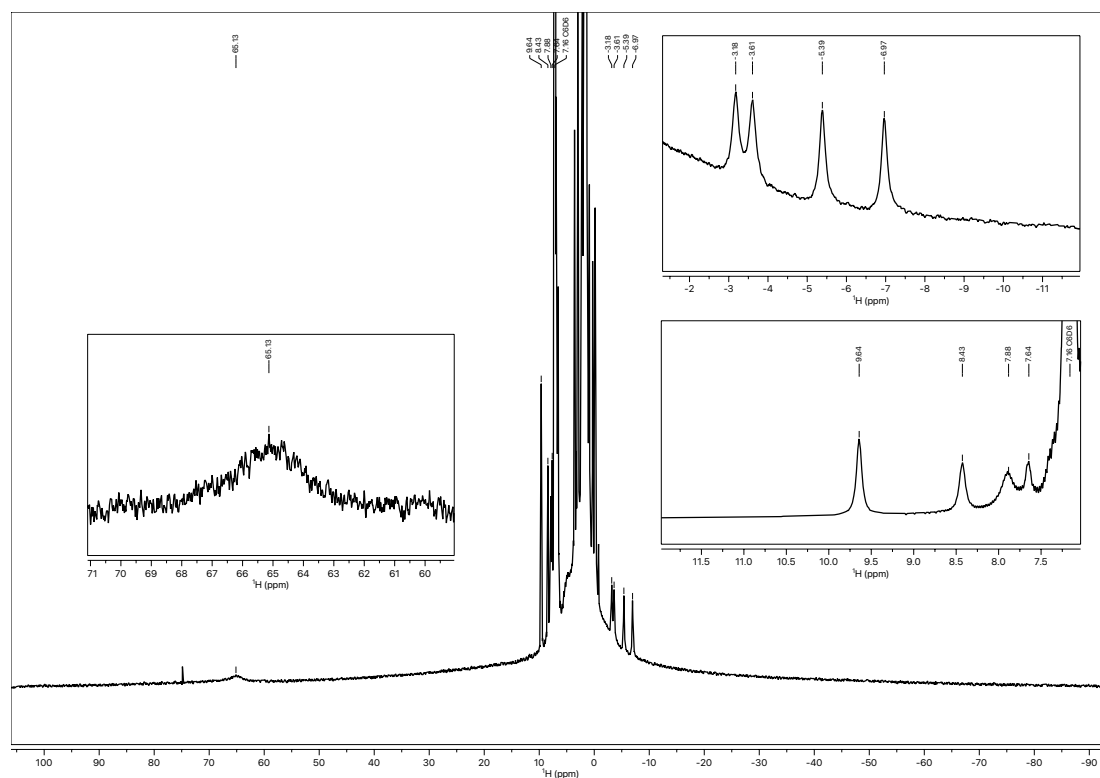


Figure 4-12 ^1H NMR spectrum (400 MHz) of $\text{L}'\text{AdCr}(\text{bis-5,8-difluorophthalazide})$ 4-1 recorded in C_6D_6 at 298 K.

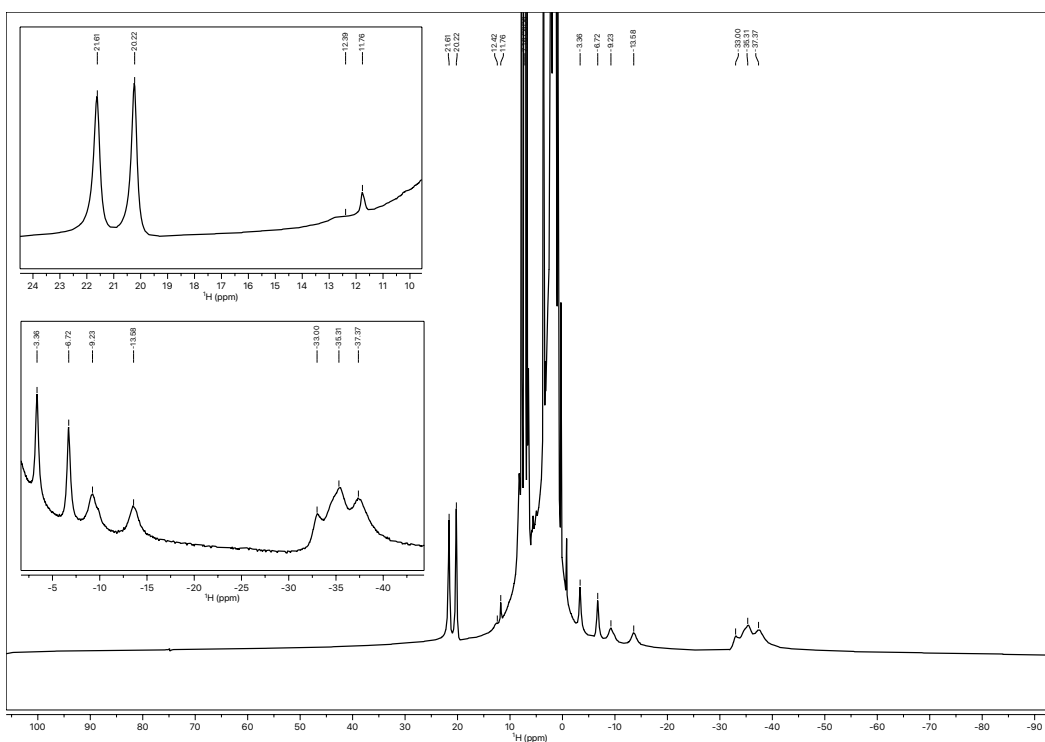


Figure 4-13 ^1H NMR spectrum (400 MHz) of $\text{L}'\text{AdCr}(\text{o-phenylene-diphenylketimide})$ 4-2 recorded in C_6D_6 at 298 K.

Quantitative NMR experiments

All spectra were processed in MestReNova (Version 15.1.0-38027).¹⁵⁴ A prescan delay of 60 s was used for quantitative ^{19}F NMR experiments to account for the T_1 -relaxation time of 4-fluorotoluene.

Reaction between $\text{L}'^{\text{Ad}}\text{Cr}(\text{bis-5,8-difluorophthalazide})$ 4-1 and 5.0 eq. of benzil

Prior to the experiment three solutions in non-deuterated toluene were prepared:

- 0.016 mol l^{-1} $\text{L}'^{\text{Ad}}\text{Cr}(\text{bis-5,8-difluorophthalazide})$
- 0.08 mol l^{-1} 4-fluorotoluene
- 0.4 mol l^{-1} benzil

From these solutions two NMR samples were prepared as follows:

1. 0.5 ml toluene, 0.1 ml 4-fluorotoluene solution and 0.1 ml benzil solution
2. 0.5 ml $\text{L}'^{\text{Ad}}\text{Cr}(\text{bis-5,8-difluorophthalazide})$, 0.1 ml 4-fluorotoluene solution and 0.1 ml benzil solution

The former solution was used to tune and shim the spectrometer at 363K. Due to the absence of deuterated solvents gradient shimming was performed on toluene's methyl peak. Subsequently the sample was exchanged for the one containing $\text{L}'^{\text{Ad}}\text{Cr}(\text{bis-5,8-difluorophthalazide})$ and 59 individual ^{19}F -scans were performed at 90 s intervals while the solution was held at a constant temperature of 363K. Each spectrum was individually phased and baseline corrected using the automatic baseline correction available in MestReNova to mitigate the influence of Teflon in the NMR probe on the baseline. The spectra obtained in this way are depicted below. The concentration of 5,8-difluorophthalazine measured at the final time point corresponds to 67.7% spectroscopic yield (0.0155 mol l^{-1}).

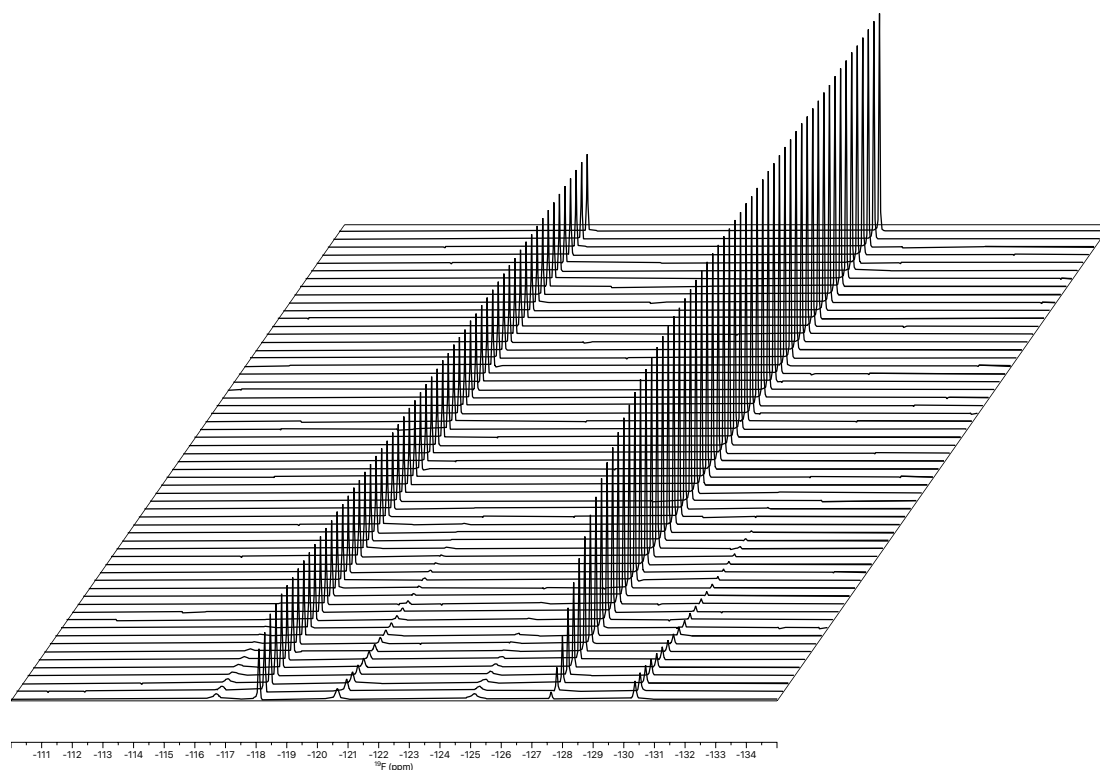


Figure 4-14 ^{19}F NMR spectra recorded every 90 seconds monitoring the reaction between $\text{L}^{\text{Ad}}\text{Cr}(\text{bis-5,8-difluorophthalazide})$ and 5.0 eq. of benzil in toluene at 363K using 4-fluorotoluene as an internal standard.

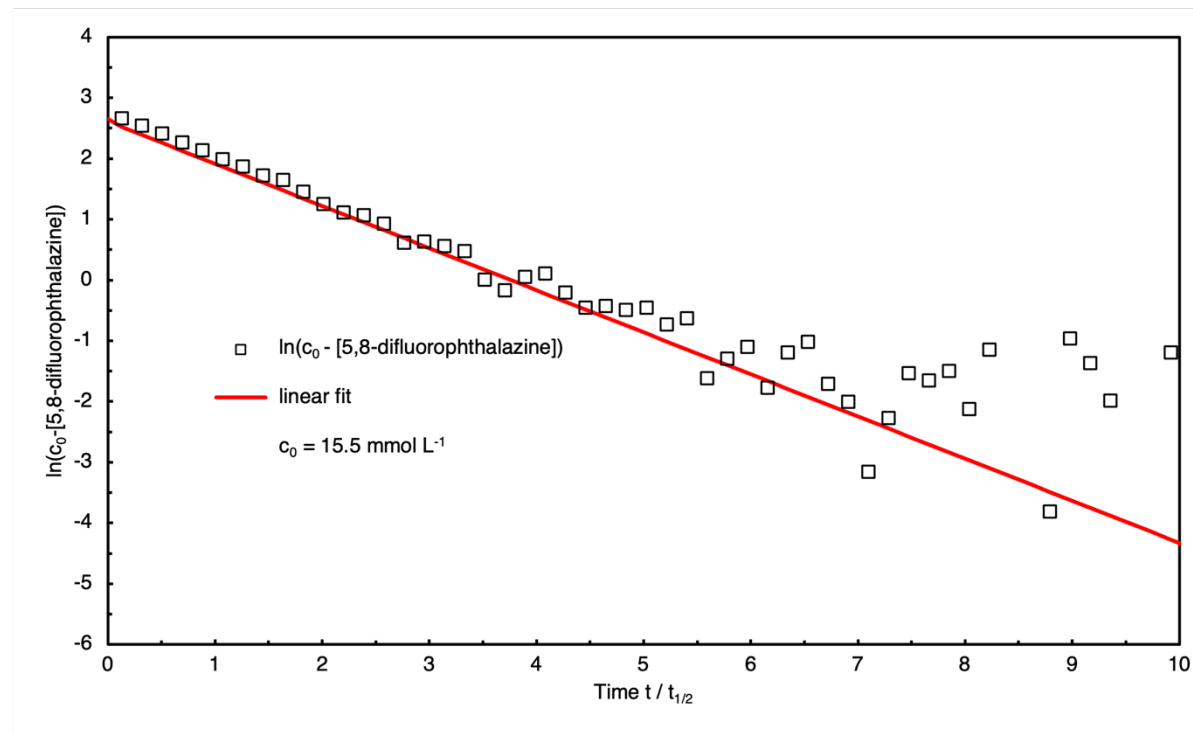


Figure 4-15 Time dependence of the natural logarithm of the concentration of 5,8-difluorophthalazine during the reaction between $\text{L}^{\text{Ad}}\text{Cr}(\text{bis-5,8-difluorophthalazide})$ and 5.0 eq. of benzil in toluene at 363K (squares) Fit to a linear function (red line).

UV/visible Spectroscopy

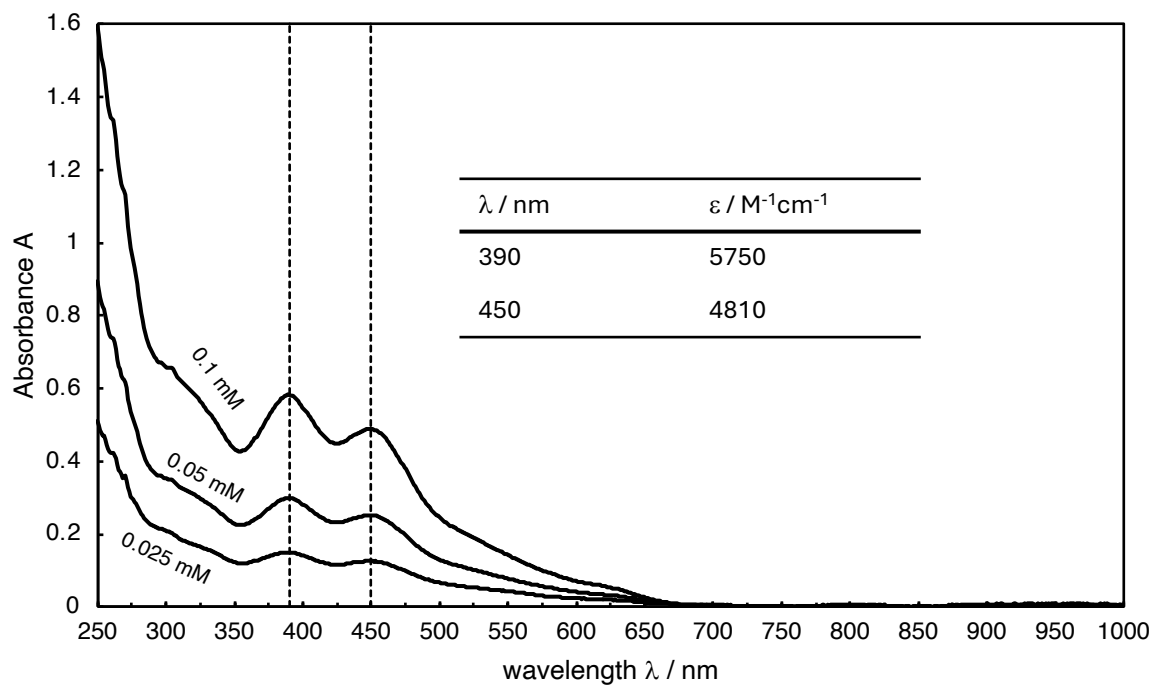


Figure 4-16 UV/visible spectrum of $\text{L}^1\text{AdCr}(\text{bis-5,8-difluorophthalazide})$ 4-1 at various concentrations in THF recorded at 298 K.

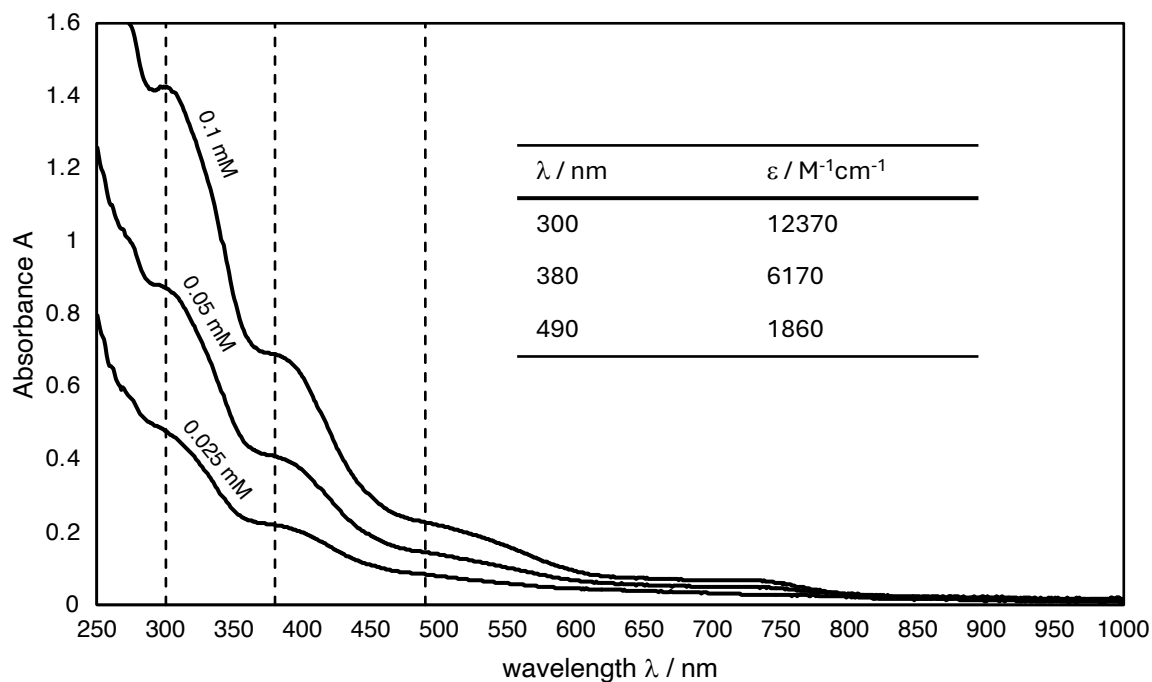


Figure 4-17 UV/visible spectrum of $\text{L}^1\text{AdCr}(\text{o-phenylene-diphenylketimide})$ 4-2 at various concentrations in THF recorded at 298 K.

Computational Methods

DFT calculations were performed using ORCA version 5.0.4.¹⁵⁵

Gas phase geometry optimizations of characterized compounds

Gas phase geometry optimizations were carried out using the M06L functional.¹⁵⁶ The basis set was constructed from the relativistically recontracted versions of the all-electron Ahlrichs basis sets¹⁵⁷ as follows: ZORA-def2-TZVPP was used on chromium; ZORA-def2-TZVP was used on the nitrogen and phosphorous atoms associated with the phosphinimide ligands as well as positions 1, 2, 3, 4, 4a & 8a of phthalazine derived ligands and the alkyne carbon and silicon atoms derived from bistrimethylsilylacetylene; ZORA-def2-SVP was used elsewhere. Initial coordinates were obtained from the crystal structures. The adamantyl groups were truncated to tert-butyl groups, fluorine atoms were removed and the RI-J approximation¹⁵⁸ was employed in conjunction with the def2/J auxiliary basis set¹⁵⁹ in an effort to speed up the calculations. Tighter-than-default convergence criteria for the geometry optimization were applied using the keywords “tightOPT”. Finer than default integration grids “defgrid3” were used during these calculations to account for the highly grid dependent nature of Minnesota functionals.¹⁶⁰ The ZORA relativistic approximation¹⁶¹ was applied. Numerical frequency calculations performed on the optimized geometries of characterized compounds and intermediates did not exhibit any imaginary frequencies. Transition states exhibited a single imaginary frequency corresponding to the reaction coordinate.

Sample input file:

```

!M06L ZORA ZORA-def2-SVP def2/J DefGrid3
!TightOPT NumFreq

%pal
nprocs 12
END

%maxcore 2048

%scf
maxiter 250
END

*xyz 0 3
Cr -0.104738 0.783604 0.148624      newGTO "ZORA-def2-TZVPP" END
P -2.992313 -0.496854 -0.331057    newGTO "ZORA-def2-TZVP" END
P 2.699450 -0.641663 -0.768663     newGTO "ZORA-def2-TZVP" END
N 1.252258 -0.284962 -0.370581     newGTO "ZORA-def2-TZVP" END
N -1.707686 0.008853 0.374690      newGTO "ZORA-def2-TZVP" END
C -0.017221 2.685966 -0.213380     newGTO "ZORA-def2-TZVP" END
C 0.196842 2.449738 1.072373       newGTO "ZORA-def2-TZVP" END
Si -0.119098 4.144558 -1.345530    newGTO "ZORA-def2-TZVP" END
Si 0.444514 3.287660 2.697797      newGTO "ZORA-def2-TZVP" END
C 5.054380 -3.904778 0.070989
C 0.083270 -2.856394 0.904947
...
further coordinates
...
*
```

Optimization of transitions states and intermediates

Relaxed surface scans along reaction coordinates outlined in the diagrams below were performed to obtain initial geometries to optimize intermediates and transition states. The same level of theory outlined above was used in conjunction with the default grid. Looser-than-default convergence criteria for the geometry optimization were applied using the keywords “looseOPT” to speed up the surface scans.

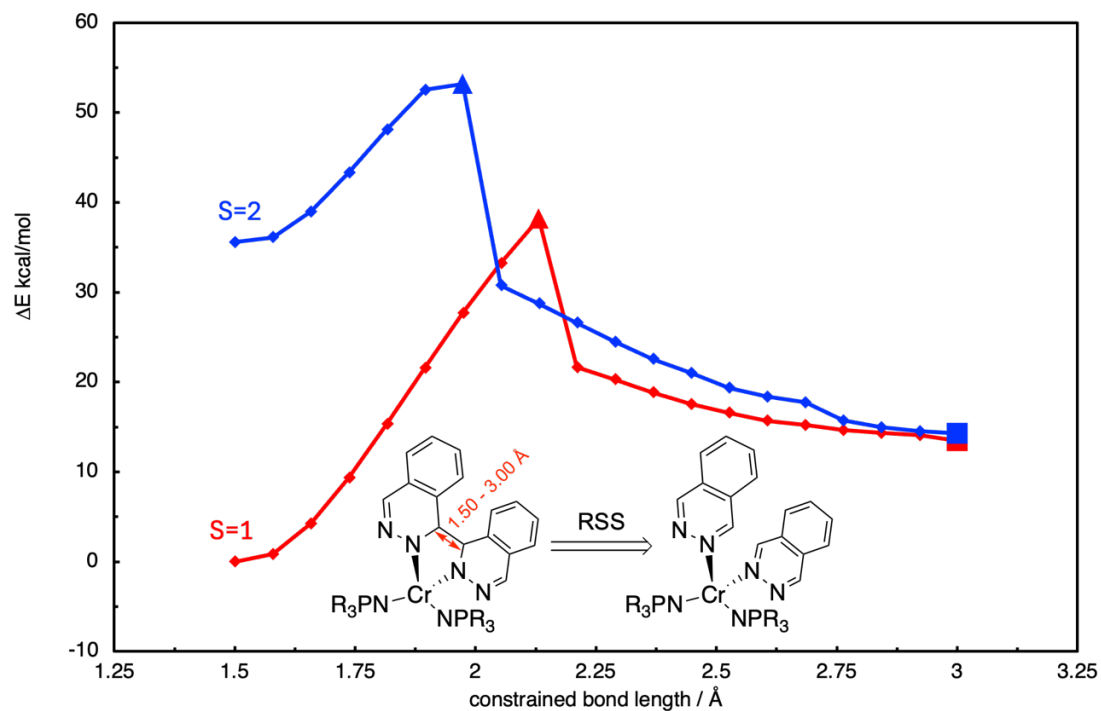


Figure 4-18 Relaxed surface scan performed to obtain initial geometries for the diphtalazine-intermediate and associated transition states related to phthalazine dimerization.

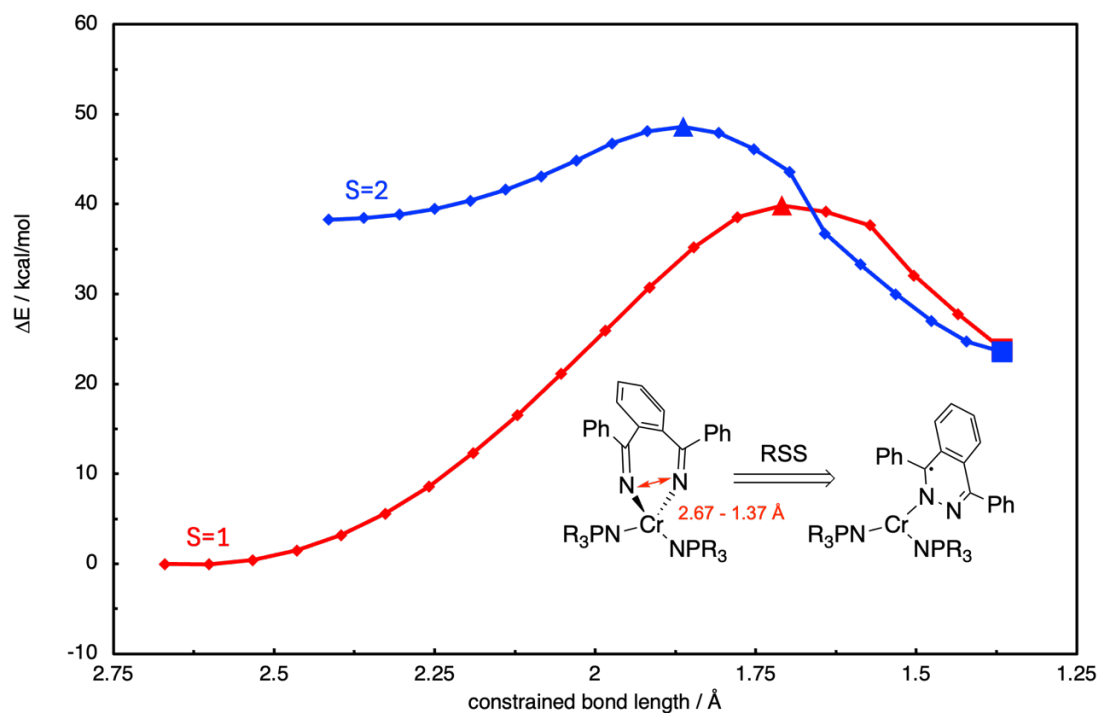


Figure 4-19 Relaxed surface scan performed to obtain initial geometries for the diphenylphthalazine-intermediate and associated transition states related to diphenylphthalazine N-N-cleavage.

Sample input file:

```
!RI M06L ZORA ZORA-def2-SVP def2/J looseOPT

%pal
nprocs 24
END

%maxcore 2048

%scf
maxiter 500
END

%geom scan
B 5 6 = 2.578, 1.360, 20 END
END

*xyz 0 1
Cr 0.00000 0.00000 0.00000 newGTO "ZORA-def2-TZVPP" END
N -1.48527 -0.00586 -0.98181 newGTO "ZORA-def2-TZVP" END
P -2.85884 -0.33098 -1.65693 newGTO "ZORA-def2-TZVP" END
N 1.50336 0.05360 -0.98198 newGTO "ZORA-def2-TZVP" END
P 3.02795 -0.17013 -1.26677 newGTO "ZORA-def2-TZVP" END
N -0.02239 1.28053 1.09018 newGTO "ZORA-def2-TZVP" END
N -0.02239 -1.29765 1.09018 newGTO "ZORA-def2-TZVP" END
C -0.69001 1.57174 2.25126 newGTO "ZORA-def2-TZVP" END
C 0.25601 -1.53461 2.40812 newGTO "ZORA-def2-TZVP" END
C 0.05379 -0.58866 3.46164 newGTO "ZORA-def2-TZVP" END
C -0.71375 0.67995 3.35531 newGTO "ZORA-def2-TZVP" END
C -1.38677 2.80158 2.32327
C 0.81640 -2.80267 2.71785
...
further coordinates
...
*
```

Intermediates were optimized in the same manner as characterized compounds starting from the geometries corresponding to minima (marked with squares) in the relaxed surface scans. The initial geometry for the monophthalazine intermediate associated with the dimerization of unsubstituted phthalazine was obtained by truncating the phenyl groups of the related diphenylphthalazine intermediate. Initial geometries were obtained from maxima in the surface scans and were optimized using the “OptTS” keyword at the same level of theory. An initial numerical hessian was calculated to aid in the optimization and orbitals obtained from the relaxed surface scan were supplied as an initial guess.

Sample input file:

```

!M06L ZORA ZORA-def2-SVP def2/J OptTS MORRead DefGrid3
!Numfreq

%pal
  nprocs 36
END

%maxcore 2048

%scf
  maxiter 500
END

%moinp "NNcoupling_M06L_split_basis_RSS.015.gbw"

%geom
  Calc_Hess true
  NumHess true
END

*xyz 0 3
Cr 0.17152536921347 -0.04854243102767 0.15671632496492
N -1.42345677829069 0.34904541415571 -0.59084995211839
N 1.56514860989858 -0.07583340481544 -0.98334379499954
P -2.68756862808562 -0.17259421932559 -1.38647094011681
P 3.07567252687207 -0.22920799694283 -1.39194463634500
N 0.33264654982972 -0.93997305416758 1.73797204467061
N 0.41595969490766 0.75365191965016 1.95224808948668
C -0.25093656968072 -1.63168109847197 2.74433648807921
C -0.54135172486060 1.18661707615623 2.77680852818551
C -1.59653287564882 0.36854853476075 3.30603911062879
C -1.40668553685336 -1.07277695743762 3.36698376498913
H -4.60993618788980 -0.52641423843966 -3.54675457234389

...
further coordinates
...
*
```

```

newGTO "ZORA-def2-TZVPP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
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newGTO "ZORA-def2-TZVP" END

```

Spin density plots

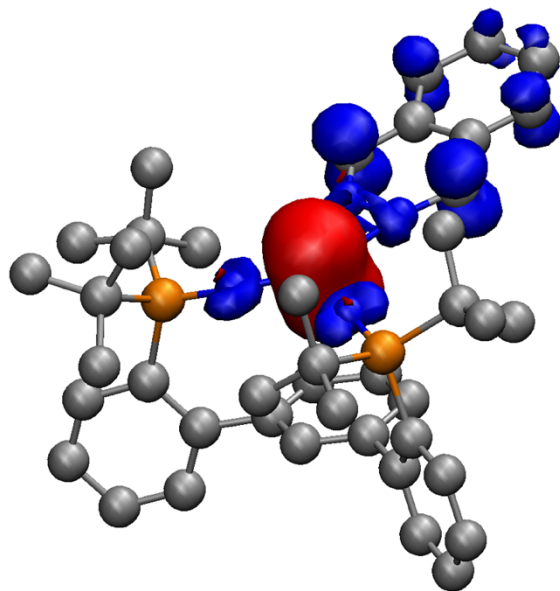


Figure 4-20 Spin density plot of L^tBuCr(η²-phthalazine) (S=1) pictured at an isovalue of 0.005.

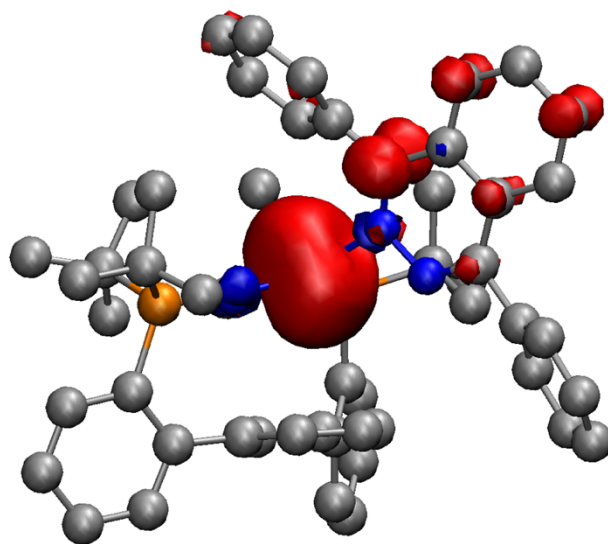


Figure 4-21 Spin density plot of L^tBuCr(χ¹-1,4-diphenylphthalazine) (S=2) pictured at an isovalue of 0.005.

Chapter 5 Demonstrating Reversible N=N-Bond Cleavage Across a Single Chromium Center

Introduction

Fundamental research into elementary organometallic reactions lies at the forefront of new synthetic method discovery. For example, the reversible addition of dihydrogen^{1,2} and dioxygen³ by Vaska's complex⁴ ($\text{IrCl}(\text{CO})[\text{PPh}_3]_2$), described following its first report in 1961, helped to establish the concepts of two-electron oxidative addition, oxidative ligation as well as reductive elimination—seminal concepts, which lie at the core of countless catalytic reactions, featuring prominently across contemporary organometallic chemistry. Seeking to expand the toolkit available for the design of new catalytic processes, we contemplated if this concept conventionally applied to two-electron reactions of single bonds could be extended into the realm of reversible four-electron reactions of non-polar double bonds. We settled on targeting reversible cleavage of N=N-double bonds in a manner outlined in Figure 5-1 because there is a healthy balance between reports of their cleavage and synthetic methods for their formation, yet no system exists which can perform this transformation reversibly.

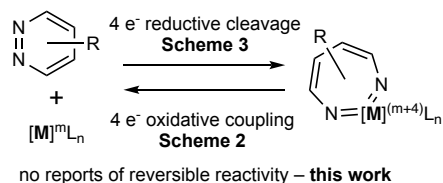


Figure 5-1 Reversible cleavage of N=N bonds targeted in this report.

Examples of the forward reaction, mainly involve highly reduced tungsten and uranium complexes.^{12–23} These metals are particularly predisposed to this type of reaction due to their large number of available valence electrons in low oxidation states as well as strong metal ligand bonds in high oxidation states mediated by the large radial extent of their frontier orbitals. However, this in turn renders the return reaction out of reach. Previous work in our group sought to circumvent this issue by translating this oxidative reactivity to chromium²⁴—a 3d metal significantly more conducive to reductive elimination and employing strongly pi-donating phosphinimide ligands did enable us to show the forward reaction with chromium, however the resulting bisimido remained too stable to demonstrate reductive elimination.⁴³

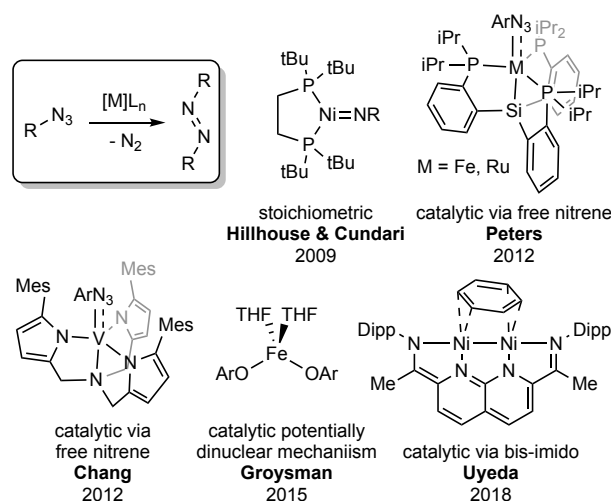


Figure 5-2 Transition metal mediated nitrene coupling.

Even though there are no concrete examples of diazine synthesis from bisimido complexes, several related transition metal mediated azide couplings have been reported in the literature (Figure 5-2). Compared to the inert imido complexes found as the result of oxidative additions of diazines, these represent the opposite extreme of the spectrum and feature highly reactive nitrenes, that rely on the formation of dinitrogen for thermodynamic driving force and are therefore inaccessible from diazo compounds. Hillhouse and Cundari showed in 2009 that diazenes can be synthesized stoichiometrically by addition of organic azides to Nickel-nitrene complexes and proposed a reaction mechanism that proceeds via 1,3-dipolar cycloaddition forming a 5-membered ring intermediate which subsequently loses dinitrogen.¹⁶² Chang and Peters showed that this reaction can be run with catalytic amounts of metal complex by employing trigonal complexes of vanadium, iron and ruthenium.^{163–165} Their mechanistic investigations suggest that these reactions proceed via transition metal mediated dinitrogen loss, resulting in free nitrenes that are subsequently captured. In 2015 Groysman reported that an iron bisalkoxide complex can dimerize bulky aryl azides, whereas less hindered substrates form an inert dimeric bisimido complex hinting at the possibility of a bimetallic mechanism.¹⁶⁶ This concept has since been exploited by Uyeda who developed highly capable catalysts based on dinickel naphthyridine diimine complexes.¹⁶⁷ This system represents the closest example to our desired reductive elimination as the reaction is proposed to go through a bisimido intermediate sharing the 4-electrons gained from reductive elimination across the two metal centers and the ligand. Close examination of the substrate scope reported by Uyeda revealed an interesting detail, which sparked the idea for this report, namely the synthesis of the N=N-bond containing heterocycle benzo[c]cinnoline. We hypothesized that the preorganization and aromaticity associated with such heterocycles could tip the thermodynamic balance towards reversibility in combination with our established chromium phosphinimide system.

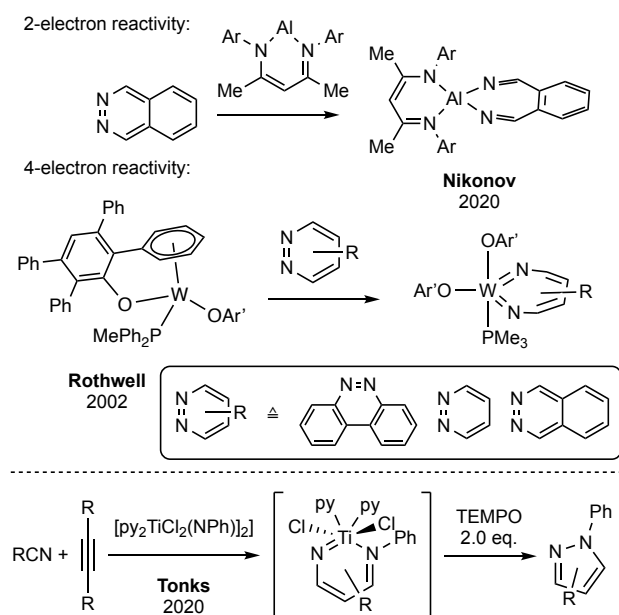


Figure 5-3 Transition metal mediated N-N cleavage and -coupling of heterocycles.

Reports regarding transitional metal mediated heterocycle cleavage (Figure 5-3) are sparse, but there are two reports of the N-N bond in phthalazine being cleaved across a single metal center. Nikonov showed that an aluminium(I) fragment cleaves the heterocycle in a 2-electron manner leading to a bisketamide¹³⁸ and Rothwell showed cleavage in a 4-electron manner forming a tungsten bisimido complex.²² The oxidative reactivity of this tungsten complex could also be extended to benzo[c]cinnoline and pyridazine. Regarding the reverse reaction N-N bond containing heterocycles are seldomly synthesized by forming the N-N bond and heavily rely on hydrazine as a starting material, however the Tonks group reported titanium mediated syntheses of pyrazoles via N-N-coupling enabled by external oxidants.¹⁶⁸

Results and Discussion

Addition of one equivalent of 2,9-difluorobenzo[c]cinnoline to $L'^{Ad}Cr(btmsa)$ lead to complete consumption of the fluorinated heterocycle and conversion to a new paramagnetic species over the course of 3h, identified by unique ^1H NMR- and UV/vis signatures. Unfortunately, prolonged storage at room temperature of this species leads to decomposition and prevented structural characterization by X-ray structural analysis but previous results combined with its reactivity and computational analysis *vide infra* provide strong evidence that this compound is best described as $L'^{Ad}Cr(\eta^2\text{-}2,9\text{-difluorobenzo[c]cinnoline})$ (**5-1**) (Figure 5-4). Heating one of these samples, prepared by addition of 1.0 equivalents of 2,9-difluorobenzo[c]cinnoline to $L'Cr(btmsa)$, at 110 °C for 1.5h, converts the compound into a diamagnetic species featuring a single ^{31}P peak at

22.92 ppm alongside two peaks in the ^{19}F spectrum at -119.22 and -119.90 ppm in 97% yield, obeying first order kinetics, as determined by quantitative ^{19}F NMR.

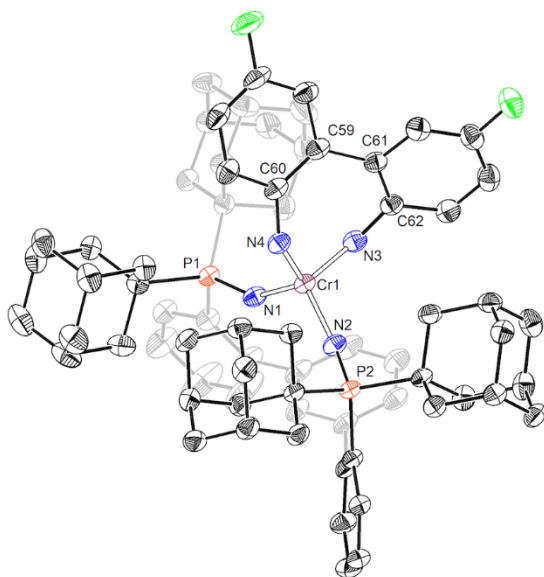


Figure 5-4. Crystal structure of $\text{L}'^{\text{Ad}}\text{Cr}(5,5'\text{-difluorobiphenyl-2,2'-bisimido})$ (5-2) with ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å), Cr1-N1 1.792(2), Cr1-N2 1.783(2), Cr1-N3 1.684(2), Cr1-N4 1.681(2), N3-C62 1.370(3), N4-C60 1.369(3), C61-C62 1.422(3), C59-C60 1.442(3), C59-C61 1.490(3). Selected bond angles ($^{\circ}$), Cr1-N3-C59 135.5(2), Cr1-N4-C60 141.0(2). Selected dihedral angle ($^{\circ}$), 39.5(4).

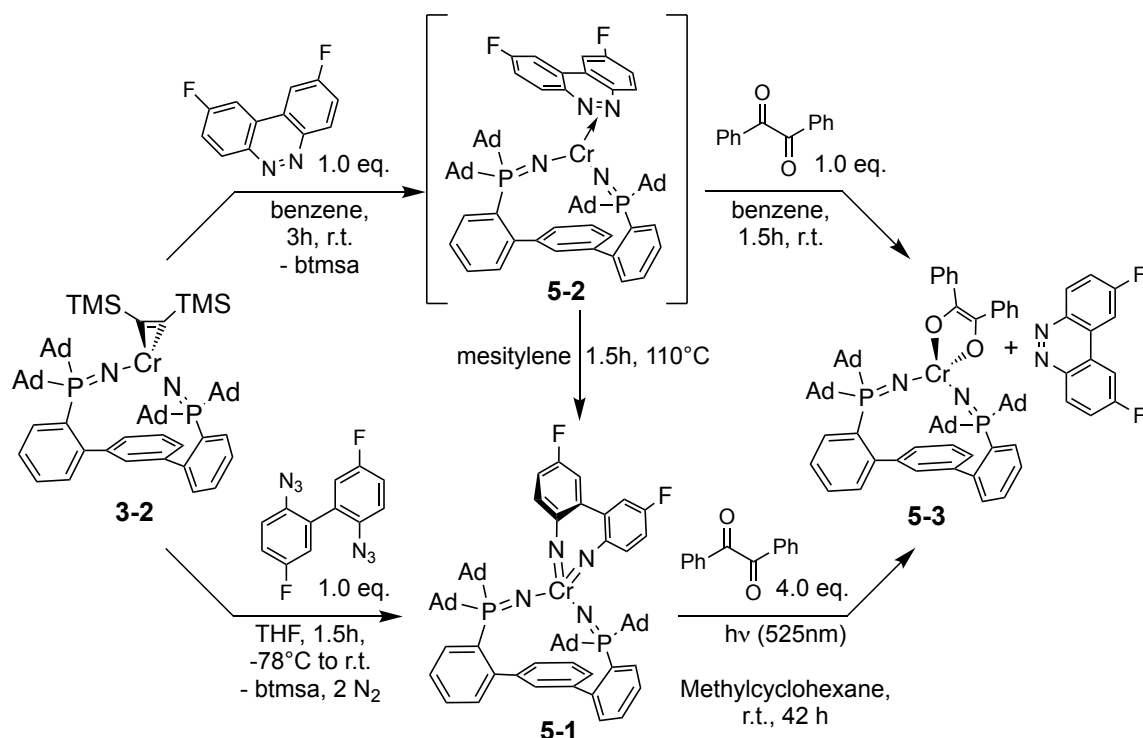


Figure 5-5 Synthesis and reactivity of $L^{Ad}Cr(5,5'$ -difluorobiphenyl-2,2'-bisimido) (5-2) and $LCr^{Ad}(1,2$ -diphenylethene-1,2-dialkoxide) (5-3).

These spectral features are also obtained by addition of one equivalent of 2,2'-diazido-5,5'-difluorobiphenyl to $L^{Ad}Cr(btmsa)$ at $-78^{\circ}C$ and warming the solution to room temperature over the course of 1.5 hours, suggesting that 2,9-difluorobenzo[c]cinnoline is coordinated at room temperature and converts to the bisimido upon heating (Figure 5-5) in a similar manner to our previous report on the 4-electron oxidative addition of 4,4'-difluoroazobenzene by the same chromium fragment.⁴³ The resultant chromium(VI) compound readily crystallizes from diethyl ether and features chromium-biphenyl-nitrogen bond distances of 1.684(2) and 1.681(2) consistent with a bisimido-formulation (Figure 1) and the internal biphenyl bond metrics match that of the non-fluorinated metallacycle reported by Rothwell.²² The constrained geometry of the heterocycle causes the imido-bond angles to deviate significantly from linear geometry at $135.3(2)^{\circ}$ and $141.0(2)^{\circ}$ and both biphenyl rings are twisted out of plane by $39.5(4)^{\circ}$, indicating minimal conjugation. This structure formed the basis for computational investigations designed to elucidate the structure of the intermediate as well as to assess the possibility of reversing the four electron oxidative addition reaction of 2,9-difluorobenzo[c]cinnoline's $N=N$ bond. Performing a relaxed surface scan progressively shortening the $N-N$ distance on the singlet and triplet surface reveals transition states on each surface as well as an $N-N$ bound intermediate corresponding to $L^{Ad}Cr(\eta^2$ -2,9-difluorobenzo[c]cinnoline) (Figure 5-6). The

latter's triplet state is lowest in energy, which matches the magnetic moment of $2.8 \mu_B$ measured by Evan's method assuming $M_w = 1127.4 \text{ g/mol}$.

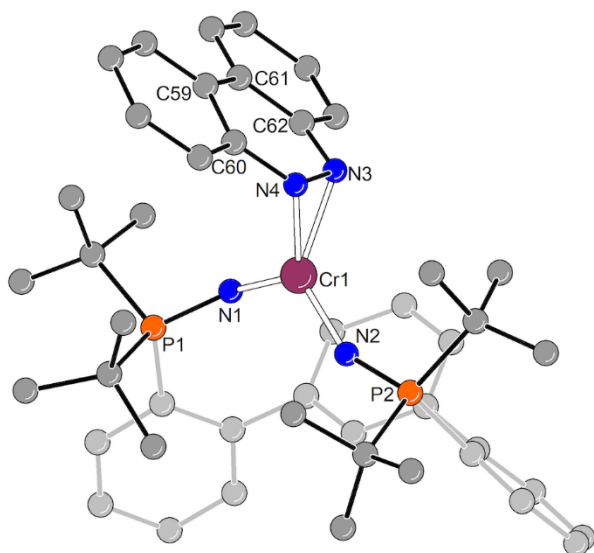


Figure 5-6 Calculated structure of $L^{tBu}Cr(benzo[c]cinnoline)$. Selected bond distances (Å), Cr1-N1 1.789, Cr1-N2 1.787, Cr1-N3 1.884, Cr1-N4 1.984, N3-N4 1.4135. Selected dihedral angle ($^\circ$), Cr1-N3-N4-C60 39.5(4).

The bound heterocycle is predicted to be significantly bent out of the plane described by its nitrogen atoms and the chromium center, which is similar to a number of benzo[c]cinnoline complexes of highly reducing 3d-metal centers^{169,170} and contrasts in plane coordination observed for less reducing lanthanide¹⁷¹ and actinide centers¹³ as well as highly oxidized 3d metal centers.¹⁷² Close inspection of the calculated triplet electronic structure reveals moderate spin polarization onto the phosphinimides and the hydrozido ligand (Figure 5-9), which lead us to further investigate its electronic structure by a $S=1$ CASSCF(6,4) calculation featuring chromium 3d orbitals and the heterocycles LUMO as the active space. Only a small contribution of antiferromagnetically coupled wavefunctions was found ($\sim 8.8\%$), with the electronic structure being predominantly described as a Z-type interaction in which the doubly occupied chromium 3d orbital donates electron density into the heterocycles LUMO in a π -manner. Sigma interactions are notably absent contrasting the description we favor for the chromium hydrazido derived from 4,4'-difluoroazobenzene we described earlier.⁴³ This difference manifest itself in the ability of the heterocycle being readily displaced from the complex *vide infra*.

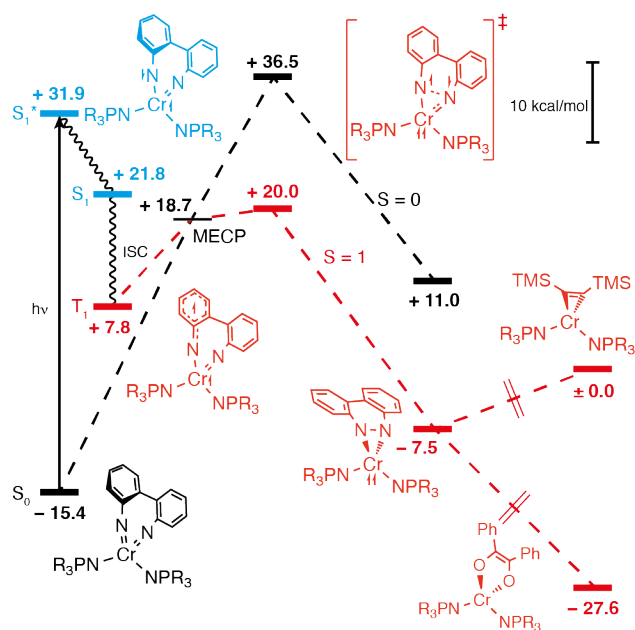


Figure 5-7 Calculated reaction coordinate for the interconversion of $L^{tBu}Cr(5,5'$ -difluorobiphenyl-2,2'-bisimido) and $L^{tBu}Cr(\text{benzo}[c]\text{cinnoline})$.

The $L^{Ad}Cr(\text{benzo}[c]\text{cinnoline})$ intermediate is stabilized by 7.5 kcal/mol in relation to $L^{Ad}Cr(\text{btmsa})$, which allows for its detection but also leads to a high rate-determining barrier for complete N=N-bond cleavage of 27.5 kcal/mol consistent with the high temperatures needed to perform the oxidative addition reaction (Figure 5-7). Numbers in this realm suggested that if a scavenger that binds the chromium center with a binding energy in excess of 15.4 kcal/mol compared to btmsa could be found, the reaction could be driven in the reverse direction, by accessing the intermediate in small amounts and thermodynamically trapping it releasing the heterocycle in the process. As a suitable trap we settled on benzil—a redox active ligand which upon exposure to a chromium(II) synthon would be reduced by two electrons and transform into an X_2 -type ligand, featuring oxygen as the coordinating atoms to exploit chromium's hard nature. Addition of 1.0 equivalents of the latter to $LCr^{Ad}(\text{btmsa})$ **3-2** in benzene resulted in an instantaneous reaction affording $LCr^{Ad}(1,2\text{-diphenylethene-1,2-dialkoxide})$ **5-3** as brown crystals upon lyophilization and crystallization from diethyl ether at -35°C . Our assumptions about the redox active nature of benzil were confirmed by the bond metrics determined by X-ray crystallography (Figure 5-8), most prominently the C-C bond between the two carbonyls appearing significantly shortened to a double bond at 1.363(3) Å compared to the parent molecule at 1.529(6) Å.¹⁷³ The magnetic moment of 2.5 measured by Evans' method is indicating a spin state of $S=1$ is consistent with this notion and the C=C bond distance

closely matches those found for benzil complexes of similarly reducing chromium fragments.¹⁷⁴

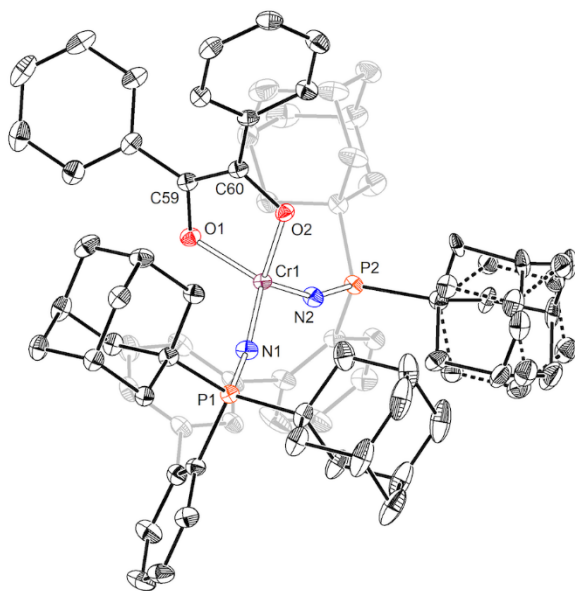


Figure 5-8 Crystal structure of $\text{LCr}^{\text{Ad}}(1,2\text{-diphenylethene-1,2-dialkoxide})$ **5-3** with ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å), Cr1-N1 1.755(2), Cr1-N2 1.766(2), Cr1-O1 1.843(2), Cr1-O2 1.854(2), O1-C59 1.359(3), O2-C60 1.361(3), C59-C60 1.363(3).

Encouragingly, evaluation of the thermodynamic stability of $\text{LCr}^{\text{Ad}}(1,2\text{-diphenylethene-1,2-dialkoxide})$ **5-3** in relation to $\text{L}^{\text{Ad}}\text{Cr}(\text{biphenyl-2,2'-bisimido})$, indicated that the reaction between benzil and the bisimido corresponding to reductively eliminating benzo[c]cinnoline and trapping the resulting chromium species with benzil, is favorable by 12.2 kcal/mol, featuring a barrier around 35.3 kcal/mol.

The ability of benzil to trap the intermediate was confirmed when, addition of one equivalent of benzil to freshly prepared samples of $\text{L}^{\text{Ad}}\text{Cr}(\eta^2\text{-2,9-difluorobenzo[c]cinnoline})$ **5-1** lead to complete recovery of 2,9-difluorobenzo[c]cinnoline along with the formation of $\text{LCr}^{\text{Ad}}(1,2\text{-diphenylethene-1,2-dialkoxide})$ **5-3**. Unfortunately, the barrier associated with the interconversion between the bisimido and the intermediate proved insurmountable by heating reaction mixtures of the bisimido and benzil, however, close inspection of the reaction coordinate revealed that if one could access the bisimido's triplet state the barrier would reduce considerably to 12.2 kcal/mol, which turned our attention towards driving the return reaction photochemically. We sought to access the triplet state by exciting an appropriate LMCT transition followed by inter-system crossing. Measuring $\text{L}^{\text{tBu}}\text{Cr}(5,5'\text{-difluorobiphenyl-2,2'-bisimido})$'s UV/vis spectrum in conjunction with simulations using TDDFT suggested that an appropriate region to excite would be between 450 and 600 nm (Figure 5-10). This region features two prominent LMCT transitions with electrons originating in bonding orbitals predominantly of imido and phosphinimide π -character into anti-bonding orbitals high in 3d character, effectively oxidizing the nitrogen coordination

sphere and reducing the metal center by one electron. Gratifyingly exposing NMR samples of mixtures of L'^{Ad}Cr(5,5'-difluorobiphenyl-2,2'-bisimido) **5-2** and excess benzil to green light provided by a 525nm Kessil lamp for 2 days lead to a recovery of 2,9-difluorobenzo[c]cinnoline in 81% yield as judged by quantitative ¹⁹F NMR.

Closer inspections of the DFT calculations (Figure 5-7) may explain the observed reactivity. According to our TDDFT calculations used to simulate the UVvis spectrum of L'^{Ad}Cr(biphenyl-2,2'-bisimido) the lowest energy transition conserving the singlet occurs at an energy of 31.8 kcal mol⁻¹. Subsequent geometric relaxation on the S₁ surface stabilizes this state by 10.1 kcal mol⁻¹. From this point onward intersystem crossing to the triplet surface is favorable by 14.0 kcal mol⁻¹. Notably, the triplet state of the bisimido features an electronic structure in which one unpaired electron resides on chromium with the second one delocalized across a single benzo[c]cinnoline phenylimido unit, in a ferromagnetically coupled manner—an electronic structure best described as a high spin metal imidyl-radical. Such electronic structures have been described for iron, cobalt and nickel imido compounds featuring weak ligand fields and are prone to activate C-H bonds, however in our case the second imido unit is pre-organized and can be attacked to reform the N-N sigma bond associated with benzo[c]cinnoline concomitantly with reduction of the chromium center by a further electron. During this reaction considerable opposite spin density is established on the second imido nitrogen. This step represents the first 2 electron step associated with the reductive elimination of the benzo[c]cinnoline. Subsequent capture of this compound by benzil completes the transformation by reductively eliminating the heterocycle reforming its N=N pi-bond. Considering the greater landscape of reactions described in the introduction the metal iminyl intermediate represents an intermediate regime between the commonly inert imidos and highly reactive nitrene compounds and proved suitable to demonstrate the first reversible 4-electron oxidative addition, reductive elimination sequence.

Conclusion

The reversible four-electron oxidative addition of 2,9-difluorobenzo[c]cinnoline suggests that phosphinimide ligands not only engender abundant 3d metals with a prowess for multielectron substrate activation that is more commonly associated with 5d-metals and actinides, but also significantly build on this reactivity by allowing such reactions to be reversible, which we believe is a significant step towards catalytic applications of these fundamental reactions.

Supporting Information

General Considerations

All reactions were performed at room temperature in a N₂-filled glovebox or by employing standard Schlenk techniques unless otherwise stated. Glassware was oven-dried at 150 °C for at least 2 h prior to use and allowed to cool under a vacuum. All reagents were used as received unless otherwise stated. Anhydrous pentane, diethyl ether, benzene, toluene and THF were purified by sparging with nitrogen for 30 min and then passing under nitrogen pressure through a column of activated A2 alumina. NMR solvents were purchased from Cambridge Isotope Laboratories. C₆D₆ and THF-d₈ were degassed by three freeze–pump–thaw cycles and dried over freshly activated 3 Å molecular sieves for 24 h prior to use. L^{Ad}Cr(btmsa)⁴³ was synthesized according to a previously published procedure. Heterocycle substrates were synthesized according to various combinations of previously published synthetic procedures outlined in the synthetic procedures section.^{175–181}

X-ray Crystallography

XRD studies were performed at the University of California, Berkeley College of Chemistry Small Molecule X-ray Crystallography Facility (CheXray) or at beamline 12.2.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory.

For studies performed at ChexRay, crystals were mounted on a Kapton loop under Paratone oil. Data was collected on a Rigaku XtalLAB P200 (Cu K_α radiation) equipped with a MicroMax-007 HF microfocus rotating anode and a Pilatus 200 K hybrid pixel array detector at 100 K under a stream of N₂. Data collection, integration, and scaling were carried out using the CrysAlisPro software package.¹⁸²

For studies performed at the Advanced Light Source, crystals were mounted on a MiTeGen loop under Paratone oil. Data was collected on a Bruker D85 three-circle diffractometer with a PHOTON II CCD area detector using silicon monochromated synchrotron radiation ($\lambda = 0.7288$ Å). Bruker APEX2¹⁴⁶ software was used for data collection. Bruker SAINT¹⁴⁷ and SADABS¹⁴⁸ software packages were utilized for data reduction and absorption correction, respectively.

Structures were solved using SHELXT¹⁴⁹ and refined against F² on all data by full matrix least-squared with SHELXL¹⁵⁰ using OLEX 2 Version 1.5¹⁵¹ crystallographic software. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen

atoms bonded to carbon atoms were placed in idealized positions and refined using a riding model.

Infrared Spectroscopy

FTIR measurements were carried out on a Thermo Scientific Nicolet iS20 spectrometer utilizing KBr pellets.

Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on Bruker or Joel 400/600 MHz instruments. ^1H chemical shifts are reported in ppm relative to tetramethylsilane (TMS) at 0.00 ppm using residual solvent peaks as internal standards.¹⁵² The widths of paramagnetic peaks at half maximum (FWHM) are reported in the experimental section. Solution phase magnetic measurements were performed using Evans' method.¹⁵³

UV/visible Spectroscopy

UV/visible measurements were taken on a Agilent Cary 60 UV-Vis Spectrophotometer using 1 cm quartz cells sealed with a Teflon stopcock.

Elemental Analysis

Elemental analyses were performed at the University of California, Berkeley College of Chemistry Microanalytical Facility using a PerkinElmer 2400 Series II combustion analyzer.

Figures supporting the main text

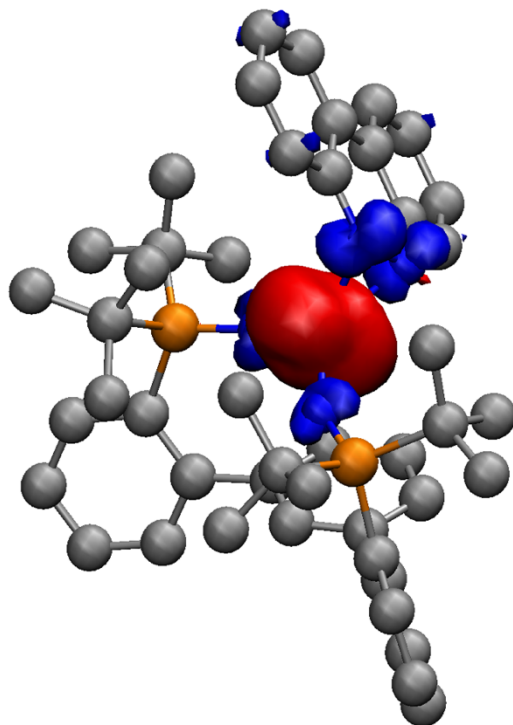


Figure 5-9 Spin density plot of $L'^{tBu}Cr(\eta^2\text{-benzo}[c]\text{cinnoline})$ ($S=1$) pictured at an isovalue of 0.005.

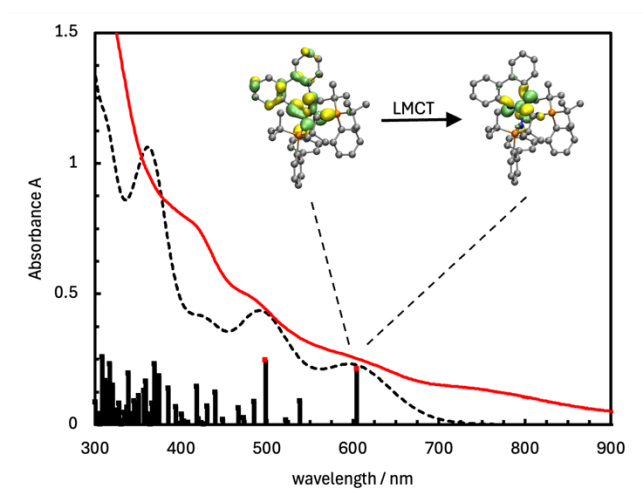
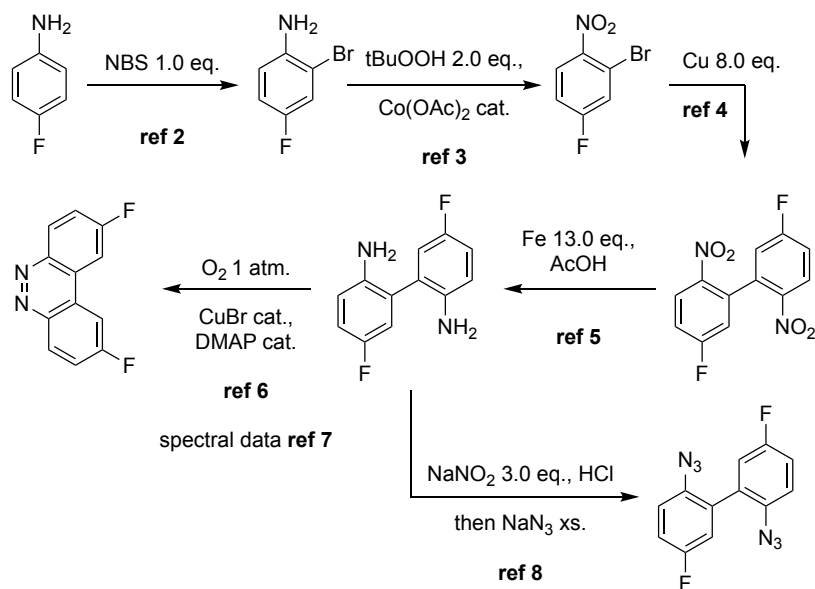


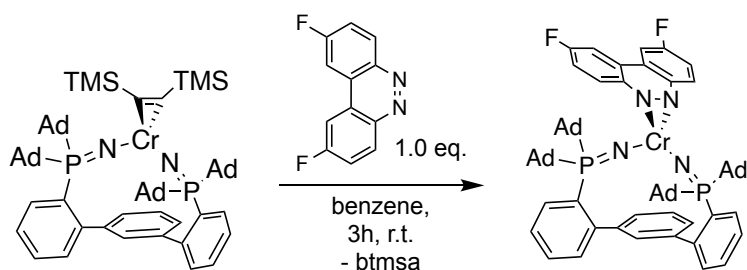
Figure 5-10 Comparison between UV/vis spectrum of $L'^{Ad}Cr(5,5'\text{-difluorobiphenyl-}2,2'\text{-bisimido})$ (red) and the one calculated for $L'^{tBu}Cr(2,2'\text{-biphenylbisimido})$ (dashed black line)

Synthetic procedures

Synthesis of 2,9-difluorobenzo[c]cinnoline and 2,2'-diazido-5,5'-difluorobiphenyl



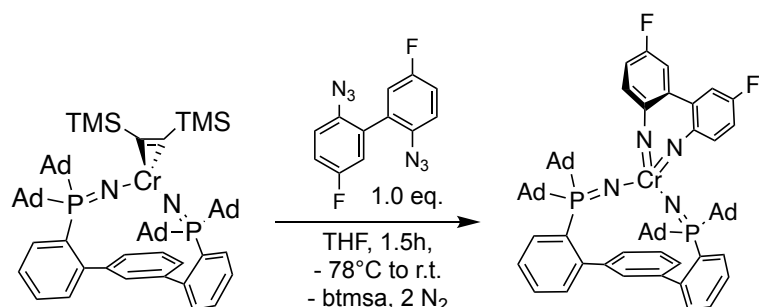
Synthesis of $\text{L}^{\text{Ad}}\text{Cr}(\text{2,9-difluorobenzo[c]cinnoline})$ 5-1



A suspension of 2,9-difluorobenzo[c]cinnoline (0.049 mmol, 10.0 mg, 1.0 eq.) in benzene (3 ml) was added slowly to a stirring solution of $\text{L}^{\text{Ad}}\text{Cr}(\text{btmsa})$ (0.049 mmol, 50 mg, 1.0 eq.) in benzene (7 ml), which resulted in an instantaneous colour change from crimson to olive green. The resulting solution was stirred overnight, after which all volatiles were

removed *in vacuo*. The resulting solid was washed with pentane (5 ml) and ether (3 ml). The residue was redissolved in benzene filtered and lyophilized to afford the title compound as a fluffy olive green solid (34.1 mg, 61.2% yield). $C_{70}H_{78}CrF_2N_4P_2$ (1127.4 g/mol). ^1H NMR (400 MHz, C_6D_6) δ 64.61 ($Dn_{1/2} = 951$ Hz), 9.64 (29), 8.43 (55), -3.18 (30), -3.61 (14), -5.38 (35), -4.02 (68), -6.96 (32). μ_{eff} (C_6D_6 , 298 K, 400MHz): 2.8 μ_B . Elemental analysis was not attempted since the compound could not be crystalized.

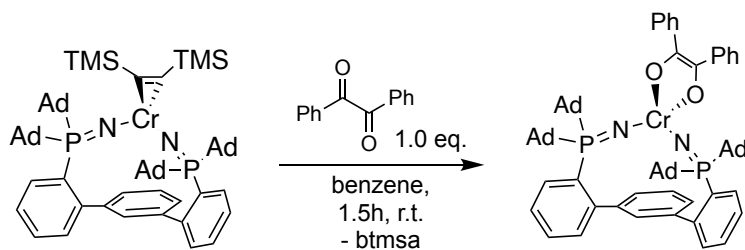
Synthesis of $L^{Ad}Cr(5,5'$ -difluorobiphenyl-2,2'-bisimido) 5-2



A solution of 2,2'-diazido-5,5'-difluorobiphenyl (0.049 mmol, 12.0 mg, 0.95 eq.) in THF (3 ml) was added dropwise to a solution of $L^{Ad}Cr(btmsa)$ (0.049 mmol, 50.0 mg, 1.0 eq.) in THF (7 ml) precooled to $-78^\circ C$ and the resulting mixture was stirred for one hour allowing it to reach room temperature. No initial color change was observed but the solution slowly turned dark brown as it warmed to room temperature. Subsequently, all volatiles were removed *in vacuo* and the resulting film was extracted with diethyl ether (5 ml). Storage of this solution at $-35^\circ C$ for multiple hours afforded the title compound as dark brown crystals which were isolated by decanting the supernatant. These crystals retain co-crystallized solvents remarkably well and were therefore redissolved in benzene and lyophilized to obtain pure samples (31.5mg, 57% yield). $C_{70}H_{78}CrF_2N_4P_2$ (1127.4 g/mol). ^1H NMR (600 MHz, THF) δ 7.67 (td, $J = 9.7, 1.4$ Hz, 2H), 7.49 – 7.39 (m, 4H), 7.39 – 7.35 (m, 2H), 7.27 (t, $J = 7.7$ Hz, 1H), 7.24 (ddd, $J = 7.7, 2.9, 1.5$ Hz, 2H), 7.10 (d, $J = 1.7$ Hz, 1H), 6.92 (dd, $J = 7.7, 1.7$ Hz, 2H), 6.90 – 6.82 (m, 2H), 6.55 (dd, $J = 8.8, 6.2$ Hz, 1H), 6.35 (dd, $J = 8.8, 6.1$ Hz, 1H), 2.44 – 2.37 (m, 6H), 2.27 – 2.20 (m, 6H), 2.01 – 1.95 (m, 12H), 1.83 – 1.67 (m, 18H) (obscured by residual solvent peak), 1.56 (q, $J = 3.3$ Hz, 6H), 1.39 (d, $J = 12.2$ Hz, 6H), 1.31 – 1.23 (m, 6H). ^{13}C NMR (151 MHz, THF) δ 159.83 (d, $J = 28.7$ Hz), 158.23 (d, $J = 28.2$ Hz), 156.43, 155.92, 152.00 (d, $J = 3.3$ Hz),

144.30 (d, $J = 2.2$ Hz), 134.23 (d, $J = 9.3$ Hz), 132.62 (d, $J = 11.8$ Hz), 130.14, 129.81 (d, $J = 2.6$ Hz), 129.60, 129.08, 126.81, 126.25, 125.82 (d, $J = 11.7$ Hz), 125.07, 117.94 (d, $J = 7.7$ Hz), 117.24 (d, $J = 23.7$ Hz), 117.02 (d, $J = 24.0$ Hz), 116.54 (d, $J = 7.9$ Hz), 114.94 (d, $J = 22.9$ Hz), 114.18 (d, $J = 22.8$ Hz), 47.00 (d, $J = 49.8$ Hz), 44.44 (d, $J = 47.9$ Hz), 39.58 (d, $J = 2.1$ Hz), 38.35, 37.81, 37.31, 30.04 (d, $J = 9.2$ Hz), 29.47 (d, $J = 9.3$ Hz). ^{31}P NMR (243 MHz, C_6D_6) δ 22.92. ^{19}F NMR (565 MHz, C_6D_6) δ -119.22 (dt, 1F), -119.90 (dt, 1F). Anal. calcd. for $\text{C}_{70}\text{H}_{78}\text{CrF}_2\text{N}_4\text{P}_2$: C, 74.58; H, 6.97; Cr, 4.61; F, 3.37; N, 4.97; P, 5.49. Found: C, 75.8; H, 7.07; N, 3.66.

Synthesis of $\text{L}'^{\text{Ad}}\text{Cr}(\text{1,2-diphenylethene-1,2-dialkoxide})$ 5-3



A solution of benzil (0.035 mmol, 7.5 mg, 1.0 eq.) was added dropwise to a solution of $\text{L}'^{\text{Ad}}\text{Cr}(\text{btmsa})$ (0.035 mmol, 38.1 mg, 1.0 eq.) in benzene (5 ml) and the resulting mixture was stirred at room temperature overnight, during which the red color of the solution deepened. Subsequent lyophilization, extraction into ether (5 ml) and storage at -35 over the course of 2 weeks afforded the title compound as dark red crystals (11.5 mg, 29% yield). $\text{C}_{72}\text{H}_{82}\text{CrN}_2\text{O}_2\text{P}_2$ (1121.4 g/mol) ^1H NMR (400 MHz, C_6D_6) δ 15.72 ($\text{Dn}_{1/2} = 207$ Hz), 9.86 (115), 9.41 (39), 8.90 (29), -12.31 (29), -32.55 (325). μ_{eff} (C_6D_6 , 298 K, 400 MHz): $2.5 \mu_{\text{B}}$. Anal. calcd. for $\text{C}_{72}\text{H}_{82}\text{CrN}_2\text{O}_2\text{P}_2$: C, 77.12; H, 7.37; N, 2.50. Found: Found: C, 73.41; H, 7.30; N, 2.30.

X-ray crystallography

Compound	L ^{Ad} Cr(5,5'-difluorobiphenyl-2,2'-bisimido) 5-2	L ^{Ad} Cr(1,2-diphenylethene-1,2-dialkoxide) 5-3
CCDC Deposition Number		
Empirical formula	C ₈₀ H ₁₀₂ CrF ₂ N ₄ P ₂	C _{78.94} H _{99.34} CrN ₂ O _{3.73} P ₂
Formula weight	1271.59	1249.89
Temperature/K	100	100
Crystal system	triclinic	monoclinic
Space group	P-1	P2 ₁ /n
a/Å	12.4636(2)	15.8944(17)
b/Å	15.0102(2)	18.8113(19)
c/Å	19.5984(2)	22.641(2)
$\alpha/^\circ$	82.5110(10)	90
$\beta/^\circ$	76.0420(10)	101.995(4)
$\gamma/^\circ$	70.3930(10)	90
Volume/Å ³	3347.02(8)	6621.8(12)
Z	2	4
$\rho_{\text{calc}}/\text{cm}^3$	1.262	1.254
μ/mm^{-1}	2.271	0.291
F(000)	1364.0	2683.0
Crystal size/mm ³	0.1 × 0.05 × 0.02	0.1 × 0.1 × 0.1
Radiation	Cu K α (λ = 1.54184)	synchrotron (λ = 0.7288)
2 Θ range for data collection/ $^\circ$	6.26 to 158.13	2.912 to 56.982
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 18, -20 ≤ l ≤ 24, 24 ≤ l ≤ 24	-20 ≤ h ≤ 20, -24 ≤ k ≤ 24, -29 ≤ l ≤ 29
Reflections collected	45050	222099
Independent reflections	13873 [R _{int} = 0.0358, R _{sigma} = 0.0359]	15333 [R _{int} = 0.1800, R _{sigma} = 0.0841]
Data/restraints/parameters	13873/53/854	15333/204/940
Goodness-of-fit on F ²	1.056	1.033
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0515, wR ₂ = 0.1387	R ₁ = 0.0585, wR ₂ = 0.1407
Final R indexes [all data]	R ₁ = 0.0578, wR ₂ = 0.1439	R ₁ = 0.0822, wR ₂ = 0.1567
Largest diff. peak/hole / e Å ⁻³	0.81/-0.84	1.13/-0.66

FTIR spectroscopy

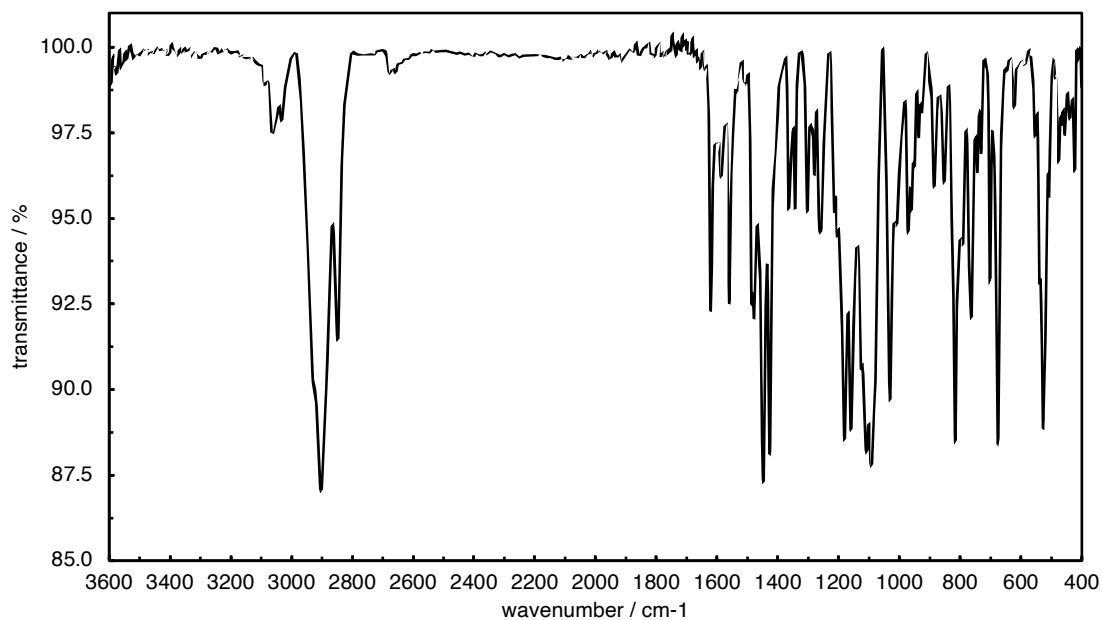


Figure 5-11 FTIR spectrum of L'AdCr(2,9-difluorobenzo[c]cinnoline) 5-1 (KBr pellet).

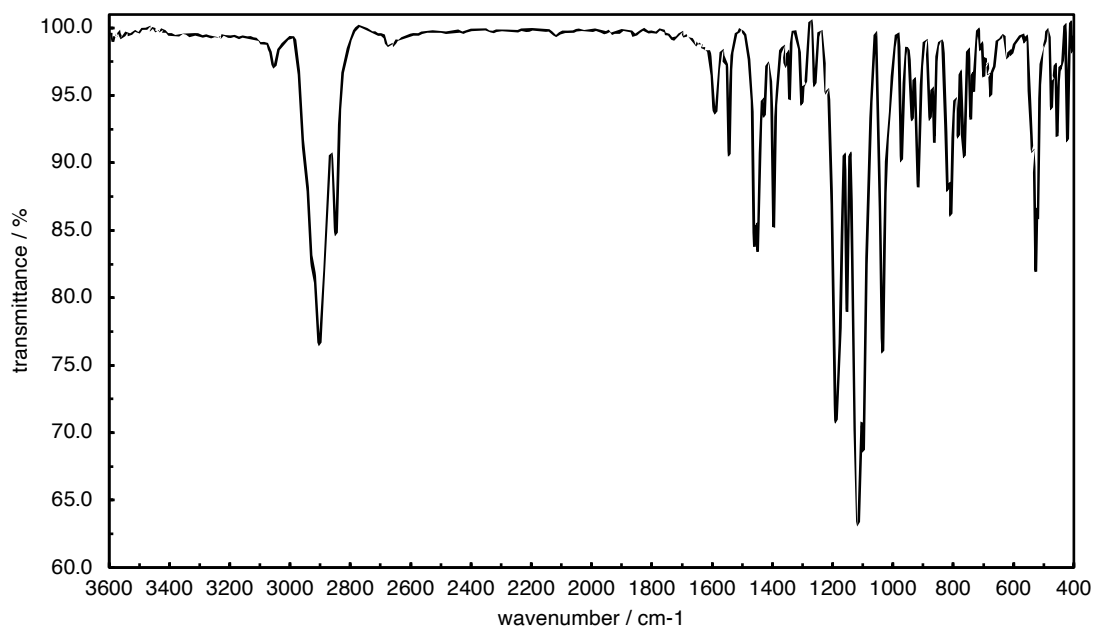


Figure 5-12 FTIR spectrum of L'AdCr(5,5'-difluorobiphenyl-2,2'-bisimido) 5-2 (KBr pellet).

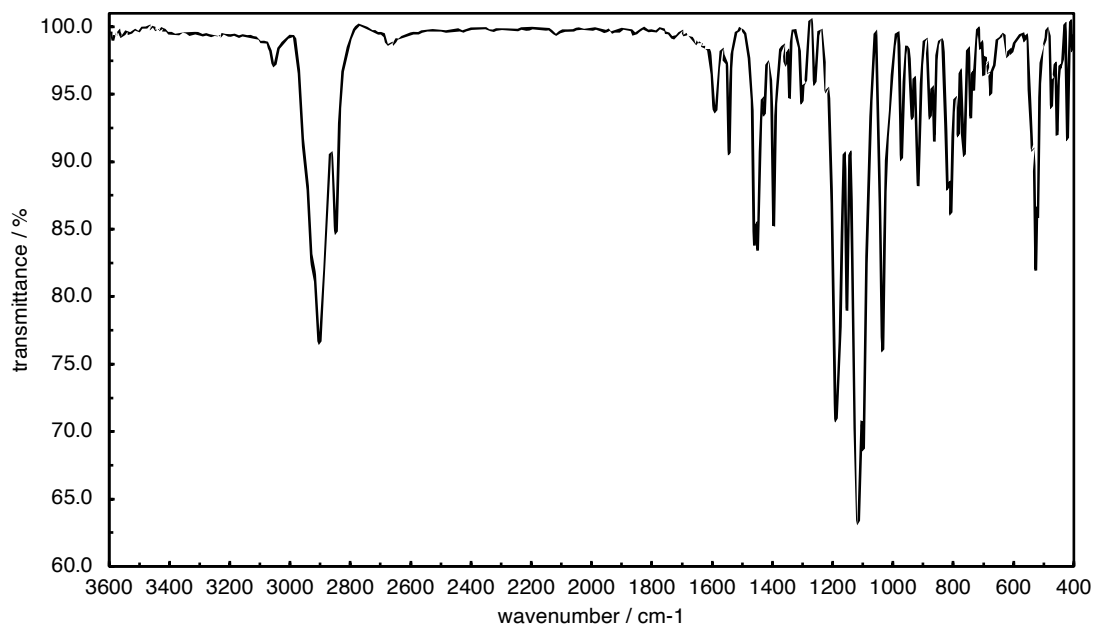


Figure 5-13 FTIR spectrum of $L'^{Ad}Cr(1,2\text{-diphenylethene-1,2-dialkoxide})$ 5-3 (KBr pellet).

NMR spectroscopy

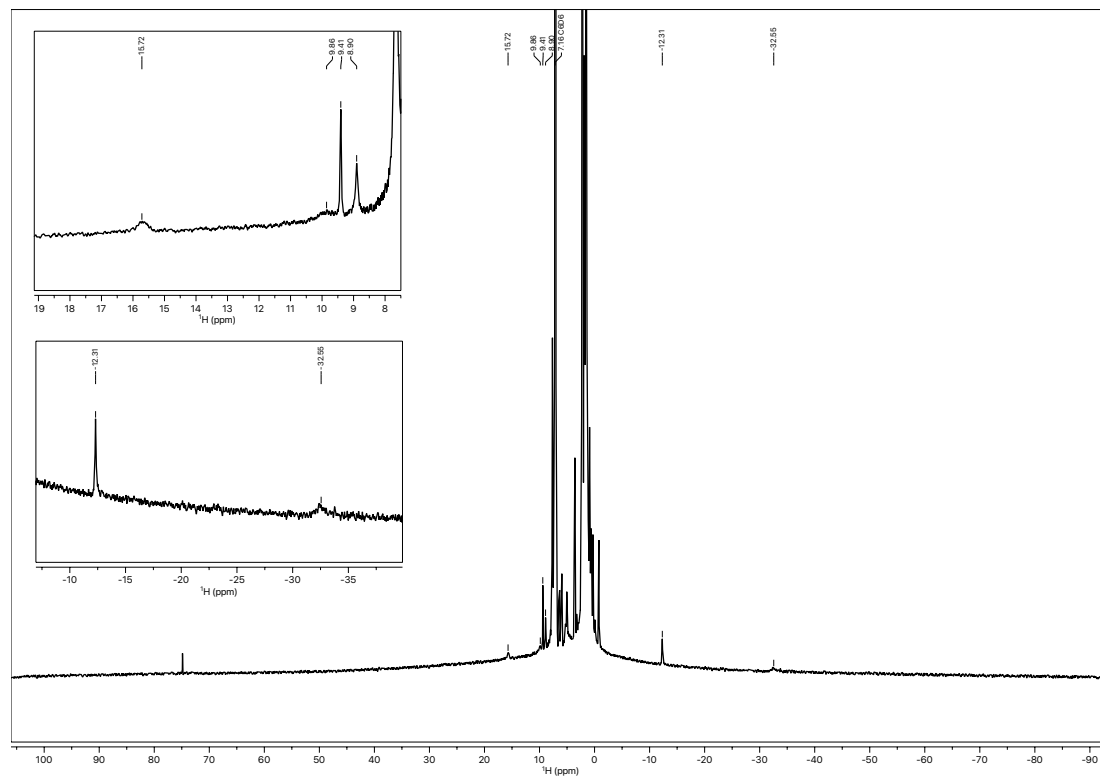


Figure 5-14 ^1H NMR spectrum (400 MHz) of $L'^{Ad}Cr(1,2\text{-diphenylethene-1,2-dialkoxide})$ 5-3 recorded in C_6D_6 at 298 K.

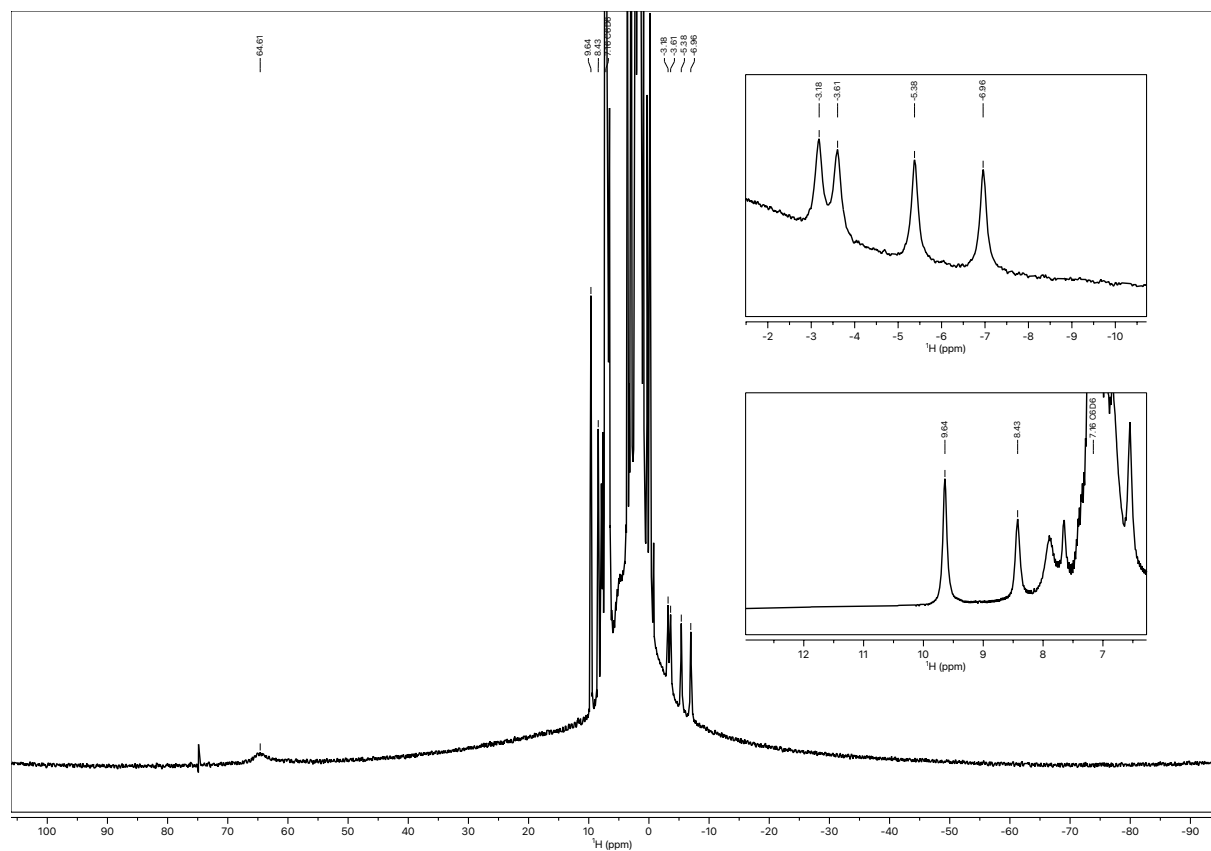


Figure 5-15 ^1H NMR spectrum (400 MHz) of $\text{L}'^{\text{Ad}}\text{Cr}(\text{2,9-difluorobenzo}[\text{c}]\text{cinnoline})$ 5-1 recorded in C_6D_6 at 298 K.

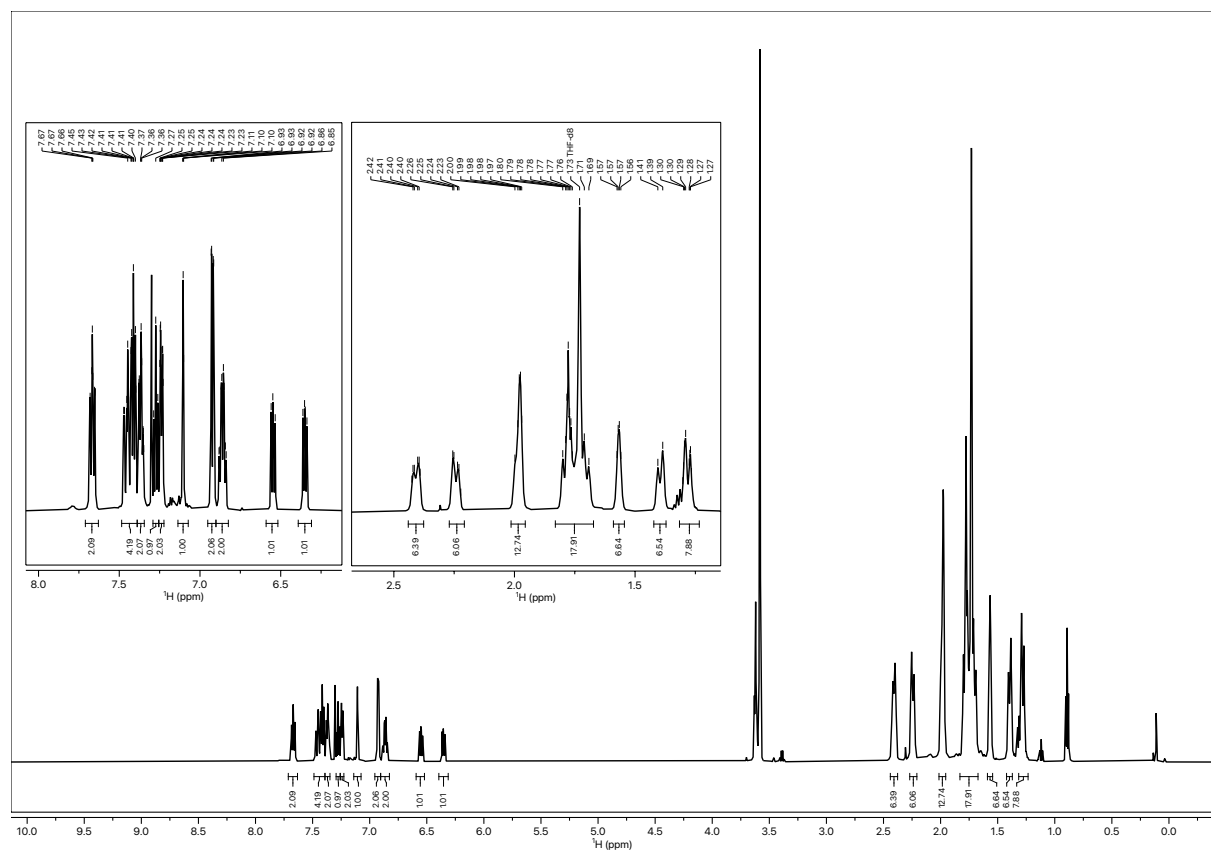


Figure 5-16 ^1H NMR spectrum (600 MHz) of $\text{L}'\text{AdCr}(\text{5,5'-difluorobiphenyl-2,2'-bisimido})$ 5-2 recorded in THF-d_8 at 298 K.

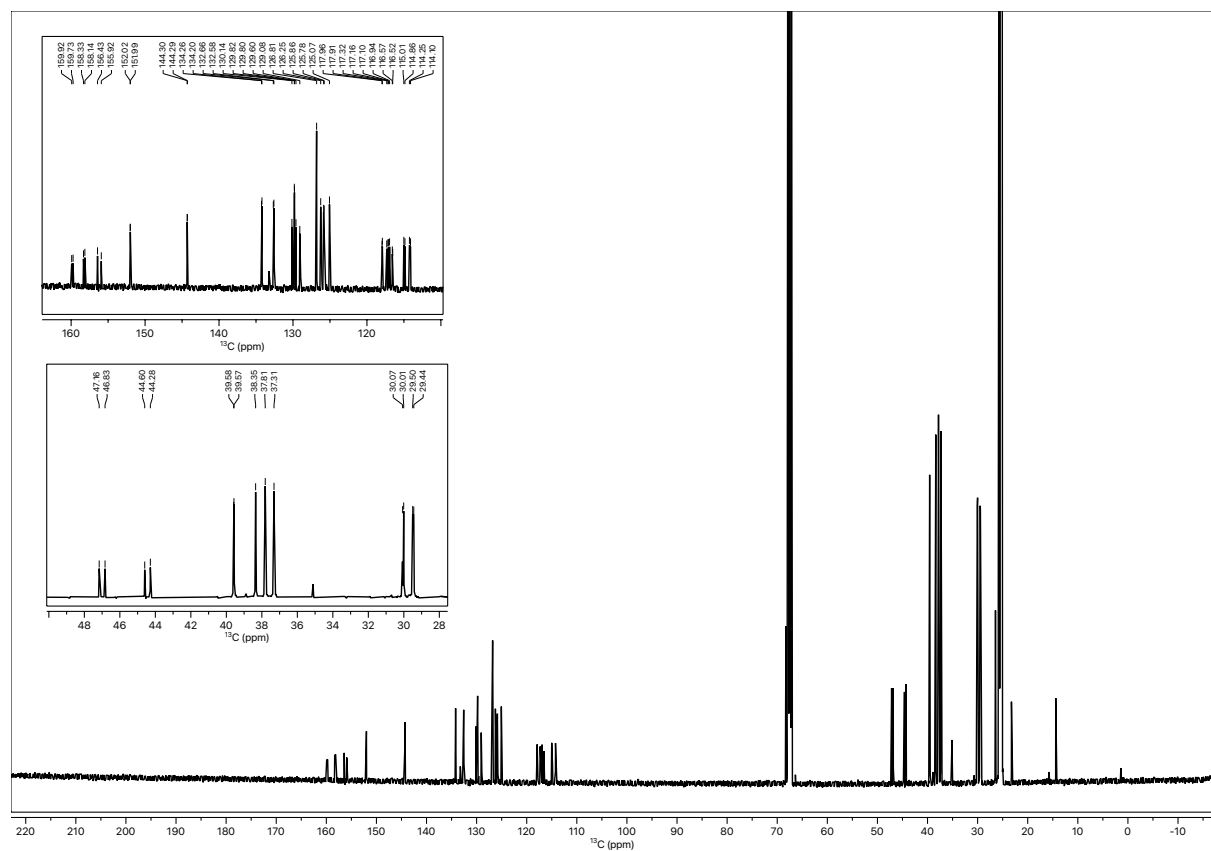


Figure 5-17 ^{13}C NMR spectrum (151 MHz) of $\text{L}'\text{AdCr}(5,5'\text{-difluorobiphenyl-}2,2'\text{-bisimido})$ 5-2 recorded in THF-d_8 at 298 K.

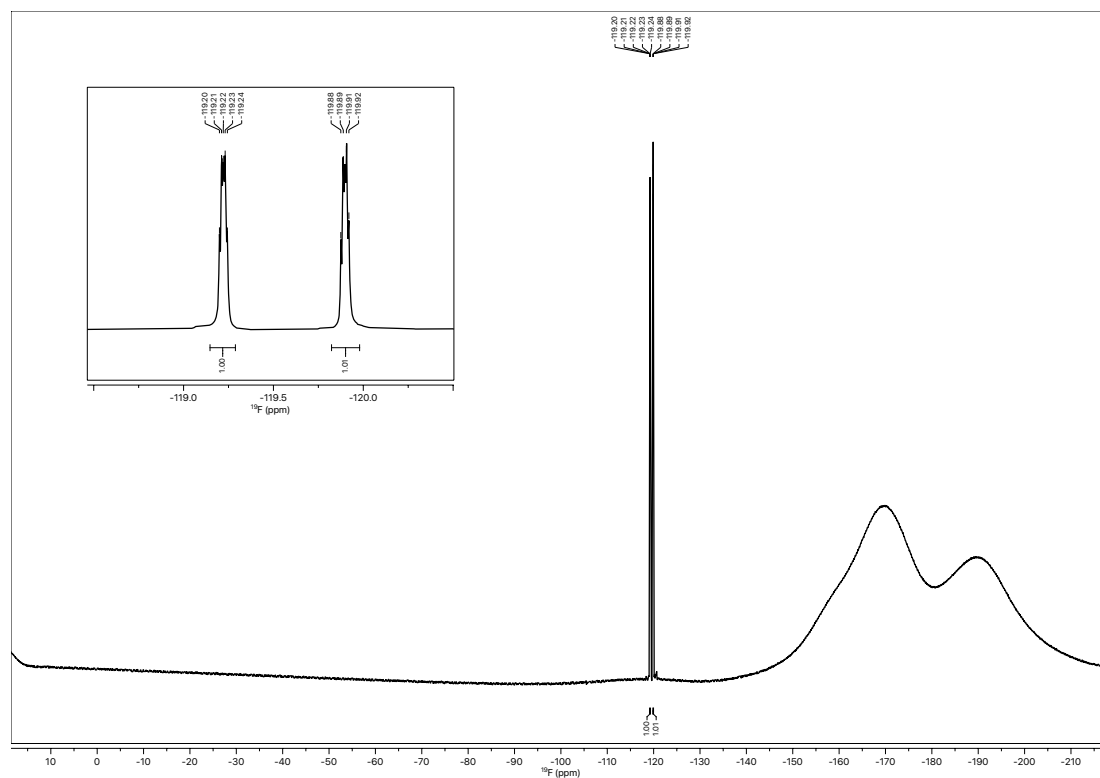


Figure 5-18 ^{19}F NMR spectrum (558 MHz) of $\text{L}'^{\text{Ad}}\text{Cr}(\text{5,5'-difluorobiphenyl-2,2'-bisimido})$ 5-2 recorded in C_6D_6 at 298 K. Broad peaks in the baseline arise due to Teflon in the NMR probe.

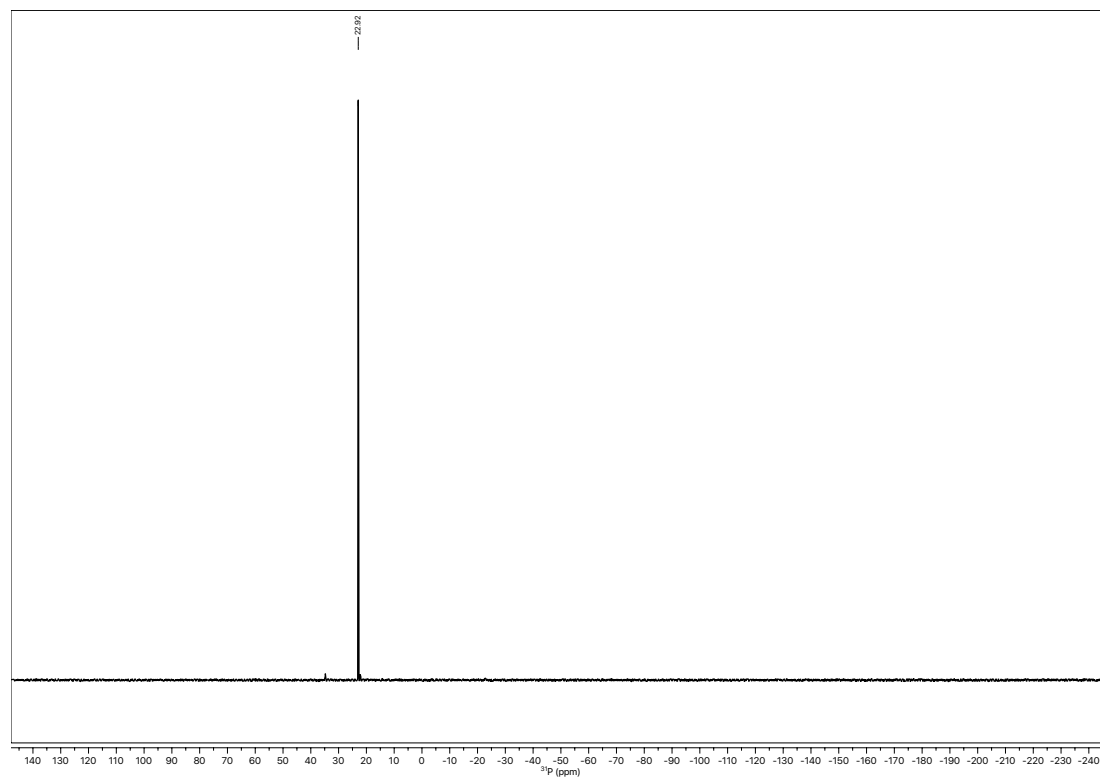
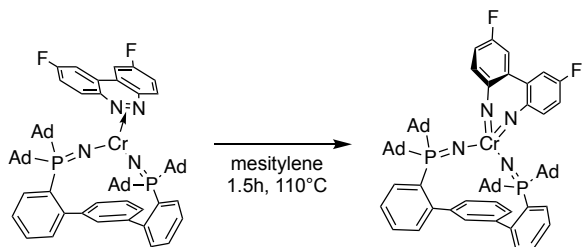


Figure 5-19 ^{31}P NMR spectrum (243 MHz) of $\text{L}'^{\text{Ad}}\text{Cr}(\text{5,5'-difluorobiphenyl-2,2'-bisimido})$ 5-2 recorded in C_6D_6 at 298 K.

All spectra were processed in MestReNova (Version 15.1.0-38027).¹⁵⁴ Each spectrum was individually phased and baseline corrected using the automatic baseline correction available in MestReNova to mitigate the influence of Teflon in the NMR probe on the baseline. A pre-scan delay of 60 s was used for quantitative ^{19}F NMR experiments to account for the T_1 -relaxation time of 4-fluorotoluene.

Interconversion between $\text{L}^{\text{Ad}}\text{Cr}(\text{2,9-difluorobenzo}[\text{c}]\text{cinnoline})$ 5-1 and $\text{L}^{\text{Ad}}\text{Cr}(\text{5,5'-difluorobiphenyl-2,2'-bisimido})$ 5-2



Prior to the experiment a saturated solution of 2,9-difluorobenzo[c]cinnoline in non-deuterated mesitylene was prepared. To 1.8 ml of this solution 0.3 ml of a 0.2 mol l^{-1} 4-fluorotoluene solution in mesitylene was added. 0.7 ml of the resulting solution were placed in a JYoung tube. Using quantitative ^{19}F NMR the concentration of 2,9-benzo[c]cinnoline in the solution was determined to be 0.0060 mol l^{-1} . 1.0 ml of the remaining solution was added to $\text{L}^{\text{Ad}}\text{Cr}(\text{btmsa})$ (0.006 mmol, 6.5 mg, 1.0 eq.) to generate $\text{L}^{\text{Ad}}\text{Cr}(\text{2,9-difluorobenzo}[\text{c}]\text{cinnoline})$ in situ and 0.7ml of the resulting solution was placed in a second JYoung tube.

The former solution was used to tune and shim the spectrometer at 383K. Due to the absence of deuterated solvents gradient shimming was performed on mesitylene's methyl peak. Subsequently the sample was exchanged for the one containing $\text{L}^{\text{Ad}}\text{Cr}(\text{2,9-difluorobenzo}[\text{c}]\text{cinnoline})$ and 59 individual ^{19}F -scans were performed at 90 s intervals while the solution was held at a constant temperature of 383K. Each spectrum was individually phased and baseline corrected using the automatic baseline correction

available in MestReNova to mitigate the influence of Teflon in the NMR probe on the baseline. The spectra obtained in this way are depicted below. The concentration of $L'^{Ad}Cr(5,5'$ -difluorobiphenyl-2,2'-bisimido) measured at the final time point corresponds to 97.1% spectroscopic yield ($0.0058 \text{ mol l}^{-1}$).

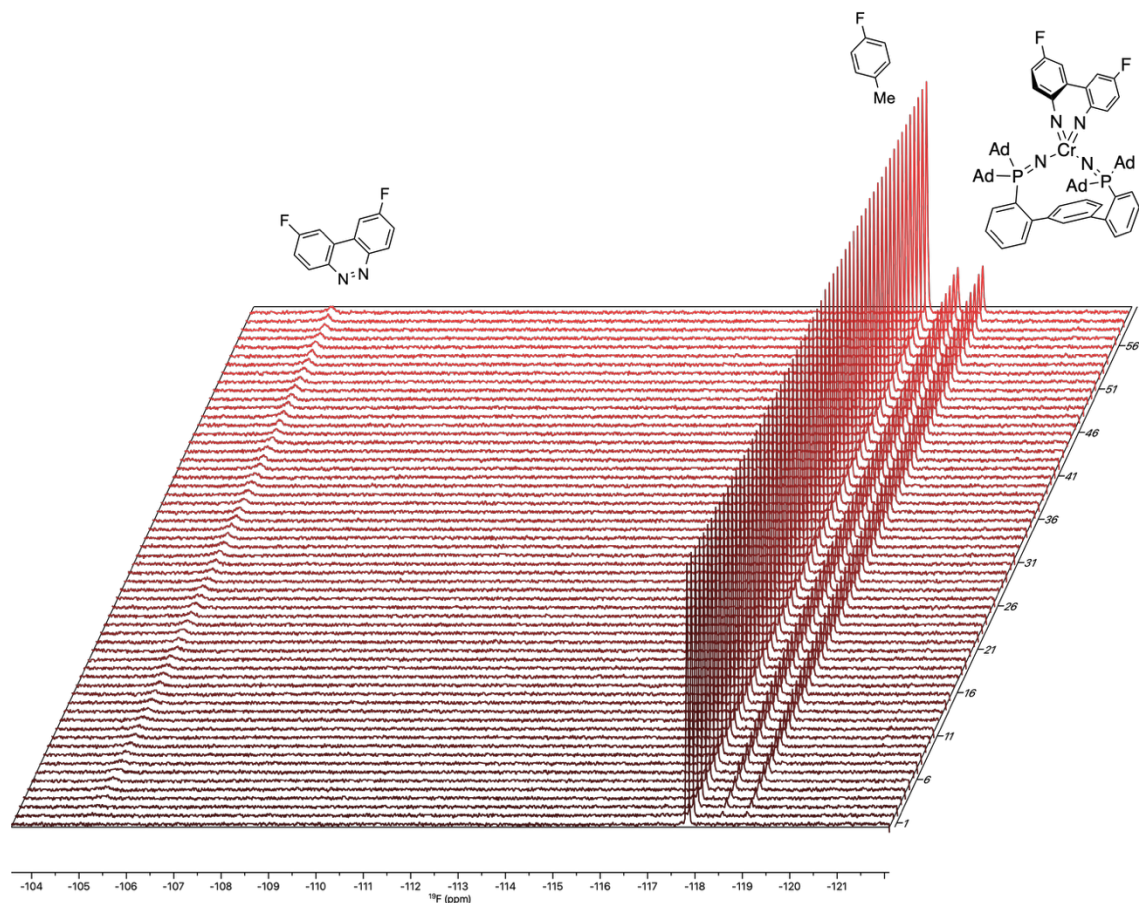


Figure 5-20 ^{19}F NMR spectra recorded every 90 seconds monitoring the interconversion between $L'^{Ad}Cr(2,9$ -difluorobenzo[c]cinnoline) 5-1 and $L'^{Ad}Cr(5,5'$ -difluorobiphenyl-2,2'-bisimido) 5-2 in mesitylene at 383K using 4-fluorotoluene as an internal standard.

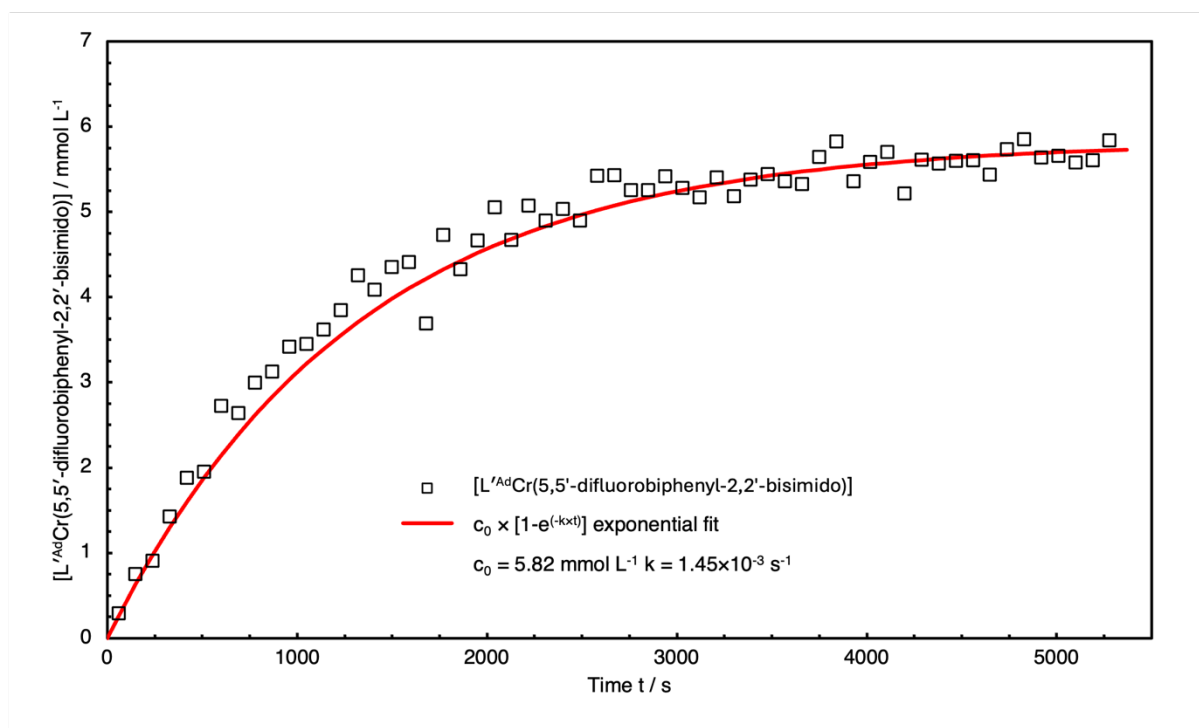


Figure 5-21 Time dependence of the concentration of $L'^{Ad}Cr(5,5'\text{-difluorobiphenyl-2,2'-bisimido})$ 5-2 during the interconversion between $L'^{Ad}Cr(2,9\text{-difluorobenzo}[c]\text{cinnoline})$ 5-1 and $L'^{Ad}Cr(5,5'\text{-difluorobiphenyl-2,2'-bisimido})$ 5-2 in mesitylene at 383K (squares). Fit to an exponential function (red line).

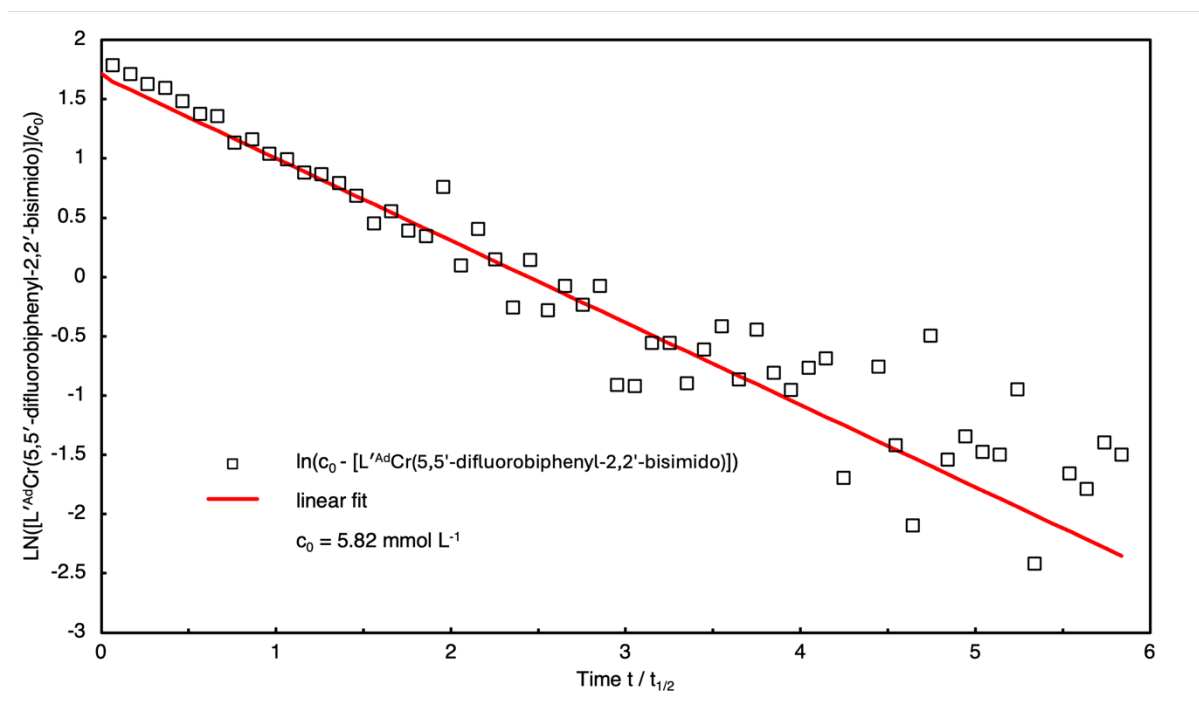
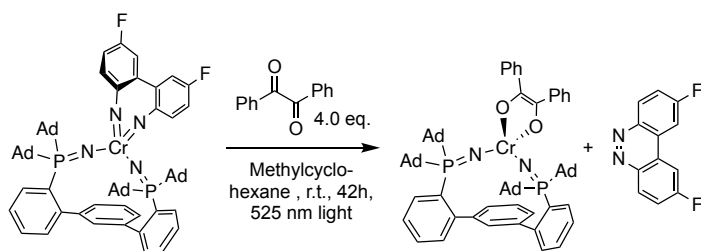
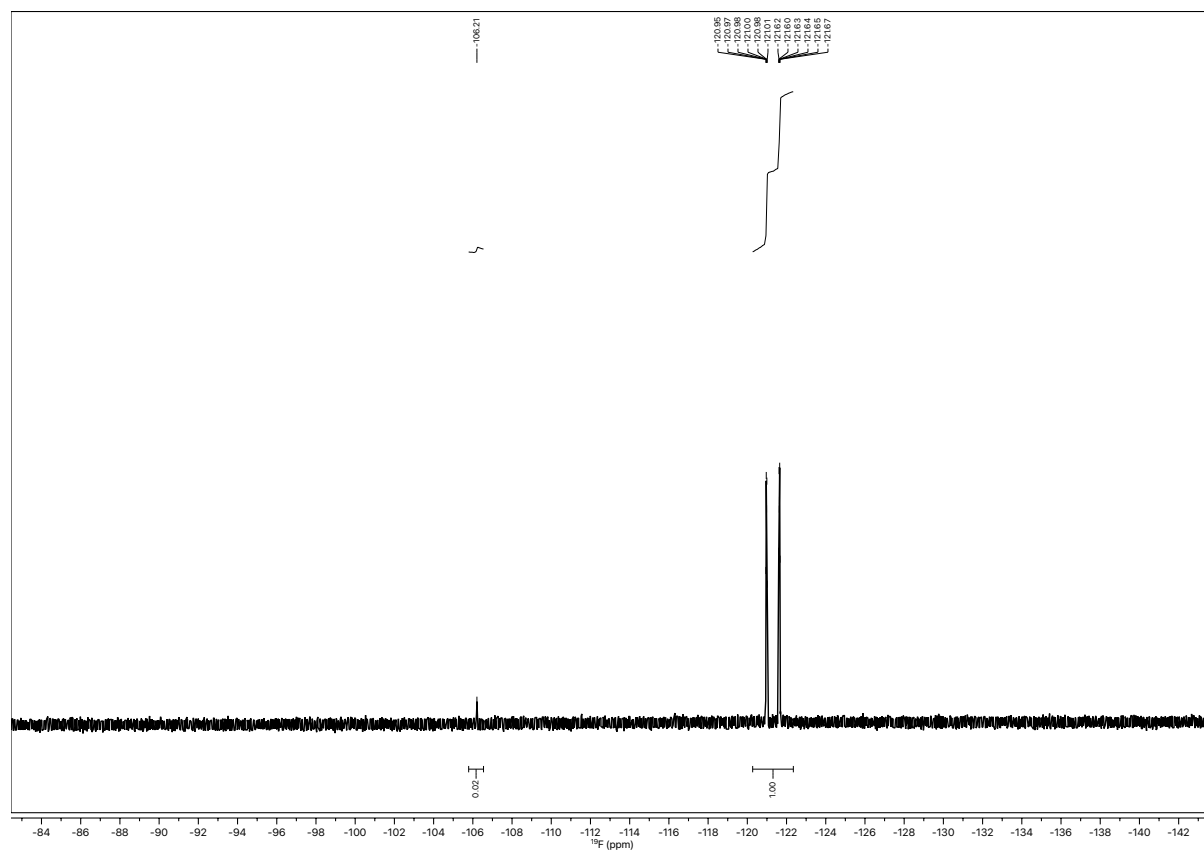


Figure 5-22 Time dependence of the natural logarithm of the concentration of $L'^{Ad}Cr(5,5'\text{-difluorobiphenyl-2,2'-bisimido})$ 5-2 during the interconversion between $L'^{Ad}Cr(2,9\text{-difluorobenzo}[c]\text{cinnoline})$ 5-1 and $L'^{Ad}Cr(5,5'\text{-difluorobiphenyl-2,2'-bisimido})$ 5-2 in mesitylene at 383K (squares). Fit to a linear function (red line).

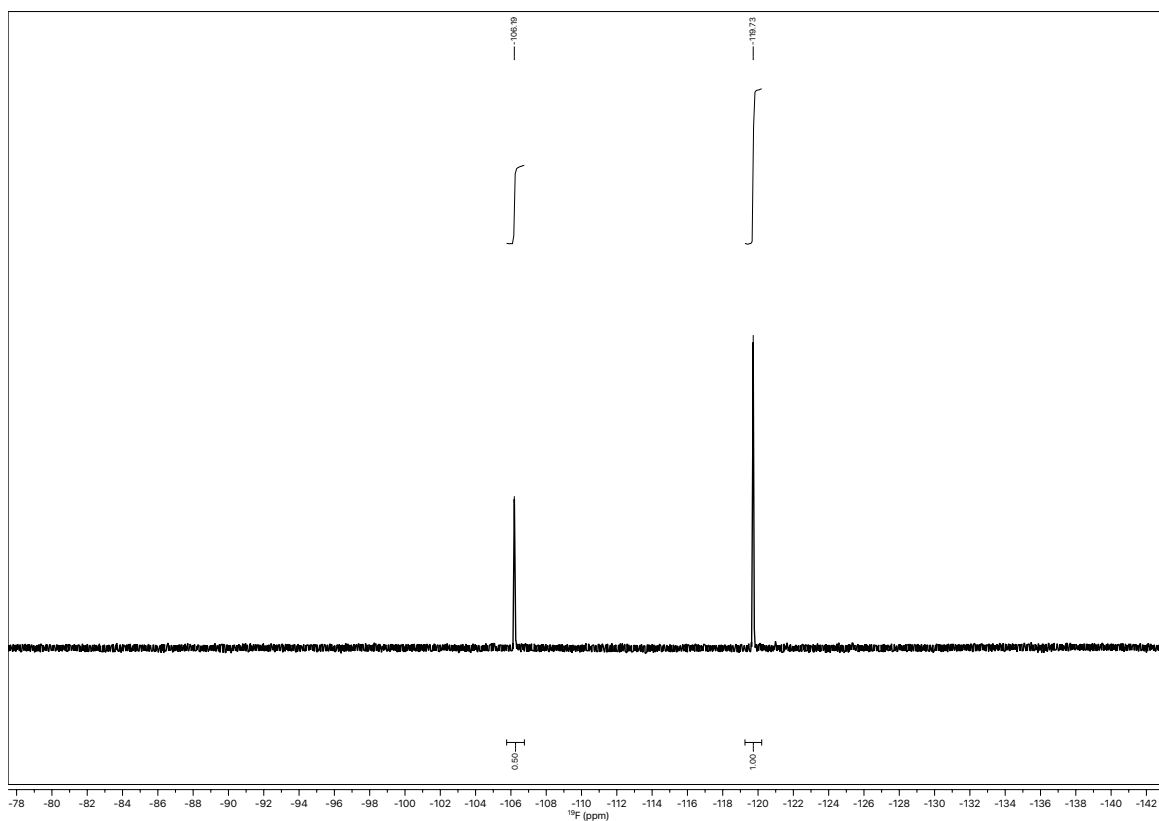
Interconversion between $L'^{Ad}Cr(5,5'$ -difluorobiphenyl-2,2'-bisimido) **5-2 and $L'^{Ad}Cr(1,2$ -diphenylethene-1,2-dialkoxide) **5-3****



Prior to the experiment $L'^{Ad}Cr(5,5'$ -difluorobiphenyl-2,2'-bisimido) (0.0132 mmol, 14.9 mg, 1.0 eq.) was dissolved in THF- d_8 and NMR spectra were measured to ensure that the initial sample was not contaminated by 2,9-difluorobenzo[c]cinnoline, only a small contamination corresponding to 2% conversion to the heterocycle was found.



The NMR-sample was transferred into a round bottom flask, featuring an inlet that can be sealed by a Teflon pin. A solution of benzil (0.052 mmol, 11mg, 4.0 eq.) dissolved in 3 ml non-deuterated THF was added to the flask. The same solvent was used to ensure that contents from both solutions had been fully transferred. Following subsequent removal of the THF solvent and exchange for 5 ml Methylcyclohexane the resulting solution was irradiated by a green 525nm Kessil lamp, while being stirred. After 42h had passed the solvent was removed in vacuo and 4-Fluorotoluene (0.044 mmol, 4.8 mg, 3.33 eq.) was transferred to the flask with the aid of three 0.4 ml portions of THF-d⁸. After all the contents of the flask had been dissolved another NMR spectrum of the resulting solution was taken. This spectrum revealed complete consumption of L'^{Ad}Cr(5,5'-difluorobiphenyl-2,2'-bisimido) alongside the formation of 2,9-difluorobenzo[c]cinnoline (0.011 mmol, 0.83 eq.), which corresponds to a yield of 81% accounting for 2% of 2,9-difluorobenzo[c]cinnoline present in the initial sample.



UV/visible Spectroscopy

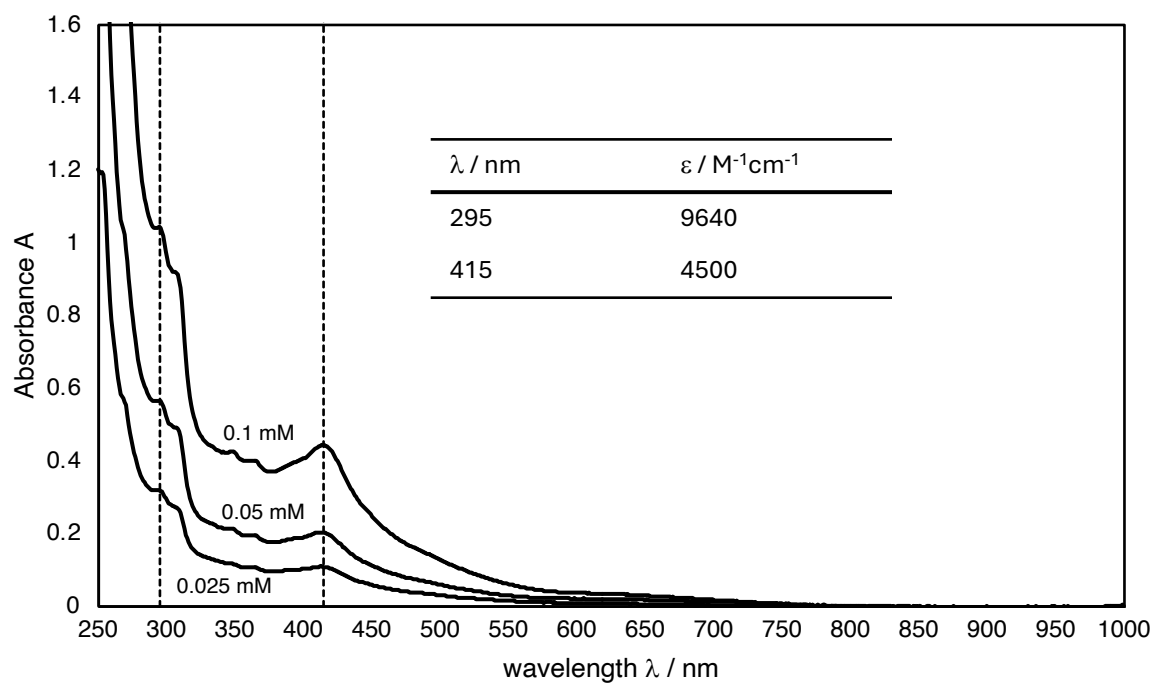


Figure 5-23 UV/visible spectrum of $\text{L}^*\text{AdCr}(2,9\text{-difluorobenzo}[\text{c}]\text{cinnoline})$ 5-1 at various concentrations in THF recorded at 298 K.

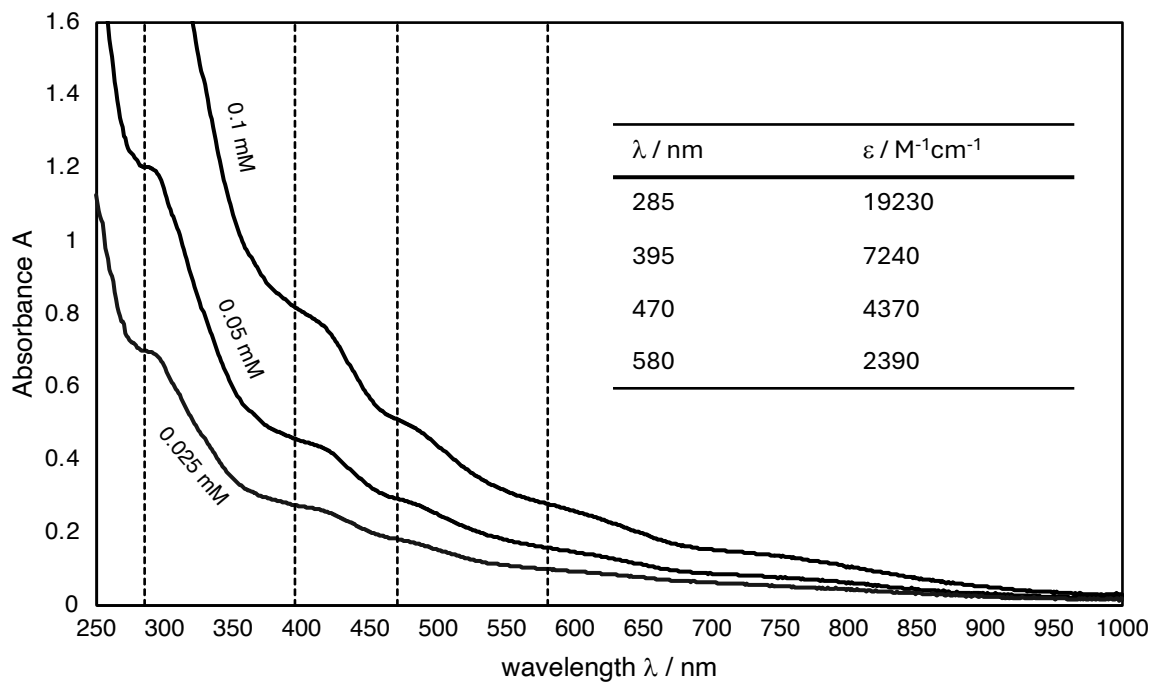


Figure 5-24 UV/visible spectrum of $\text{L}'^{\text{Ad}}\text{Cr}(\text{5,5'-difluorobiphenyl-2,2'-bisimido})$ 5-2 at various concentrations in THF recorded at 298 K.

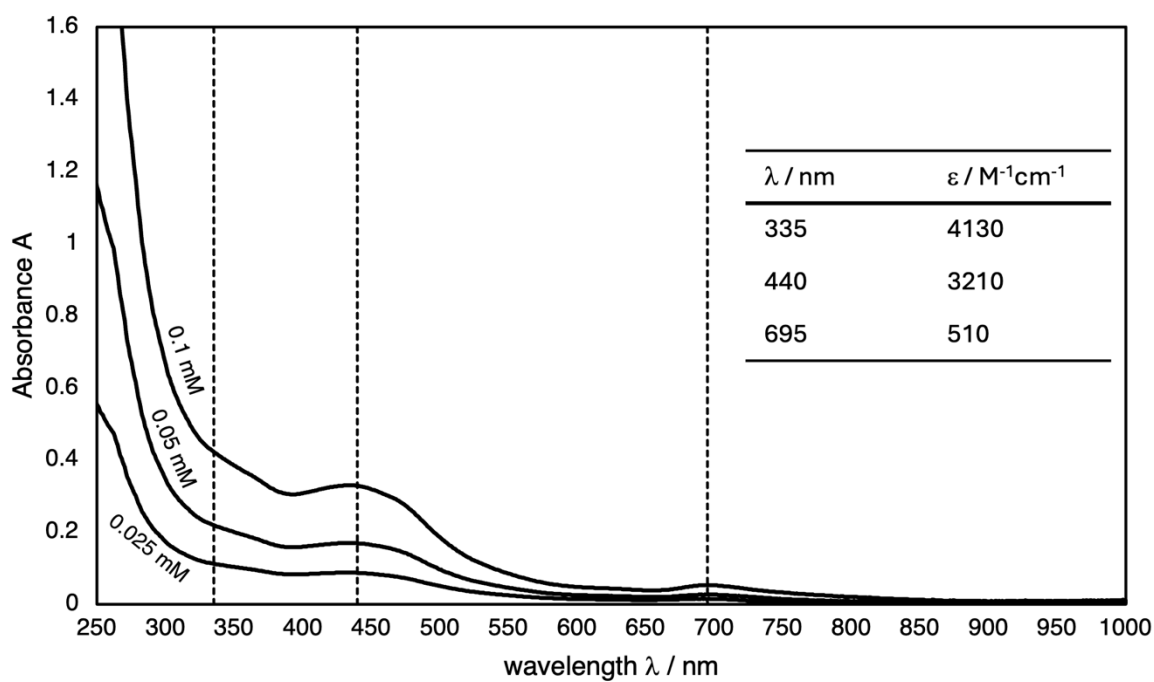


Figure 5-25 UV/visible spectrum of $\text{L}'^{\text{Ad}}\text{Cr}(\text{1,2-diphenylethene-1,2-dialkoxide})$ 5-3 at various concentrations in THF recorded at 298 K.

Computational Methods

DFT calculations were performed using ORCA version 5.0.4¹⁵⁵ unless otherwise stated.

Gas phase geometry optimizations of characterized compounds

Gas phase geometry optimizations were carried out using the M06L functional.¹⁵⁶ The basis set was constructed from the relativistically recontracted versions of the all-electron Ahlrichs basis sets¹⁵⁷ as follows: ZORA-def2-TZVPP was used on chromium; ZORA-def2-TZVP was used on the nitrogen and phosphorous atoms associated with the phosphinimide ligands as well as positions 4a, 5, 6, 6a, 10a & 10b of the benzo[c]cinnoline derived ligands as well as the alkyne carbon and silicon atoms derived from bistrimethylsilylacetylene; ZORA-def2-SVP was used elsewhere. Initial coordinates were obtained from the crystal structures. The adamantyl groups were truncated to tert-butyl groups, fluorine atoms were removed and the RI-J approximation¹⁵⁸ was employed in conjunction with the def2/J auxiliary basis set¹⁵⁹ in an effort to speed up the calculations. Tighter-than-default convergence criteria for the geometry optimization were applied using the keywords “tightOPT”. Finer than default integration grids “defgrid3” were used during these calculations to account for the highly grid dependent nature of Minnesota functionals.¹⁶⁰ The ZORA relativistic approximation¹⁶¹ was applied. Numerical frequency calculations performed on the optimized geometries of characterized compounds and intermediates did not exhibit any imaginary frequencies.

Sample input file:

```

!M06L ZORA ZORA-def2-SVP def2/J DefGrid3
!TightOPT NumFreq

%pal
nprocs 12
END

%maxcore 2048

%scf
maxiter 250
END

*xyz 0 3
Cr -0.104738 0.783604 0.148624      newGTO "ZORA-def2-TZVPP" END
P -2.992313 -0.496854 -0.331057    newGTO "ZORA-def2-TZVP" END
P 2.699450 -0.641663 -0.768663     newGTO "ZORA-def2-TZVP" END
N 1.252258 -0.284962 -0.370581     newGTO "ZORA-def2-TZVP" END
N -1.707686 0.008853 0.374690      newGTO "ZORA-def2-TZVP" END
C -0.017221 2.685966 -0.213380     newGTO "ZORA-def2-TZVP" END
C 0.196842 2.449738 1.072373       newGTO "ZORA-def2-TZVP" END
Si -0.119098 4.144558 -1.345530    newGTO "ZORA-def2-TZVP" END
Si 0.444514 3.287660 2.697797      newGTO "ZORA-def2-TZVP" END
C 5.054380 -3.904778 0.070989
C 0.083270 -2.856394 0.904947
...
further coordinates
...
*
```

Optimization of transitions states and intermediates

Relaxed surface scans along reaction coordinates outlined in the diagram below were performed to obtain initial geometries to optimize intermediates and transition states. The same level of theory outlined above was used in conjunction with the default grid. Looser-than-default convergence criteria for the geometry optimization were applied using the keywords “looseOPT” to speed up the surface scans.

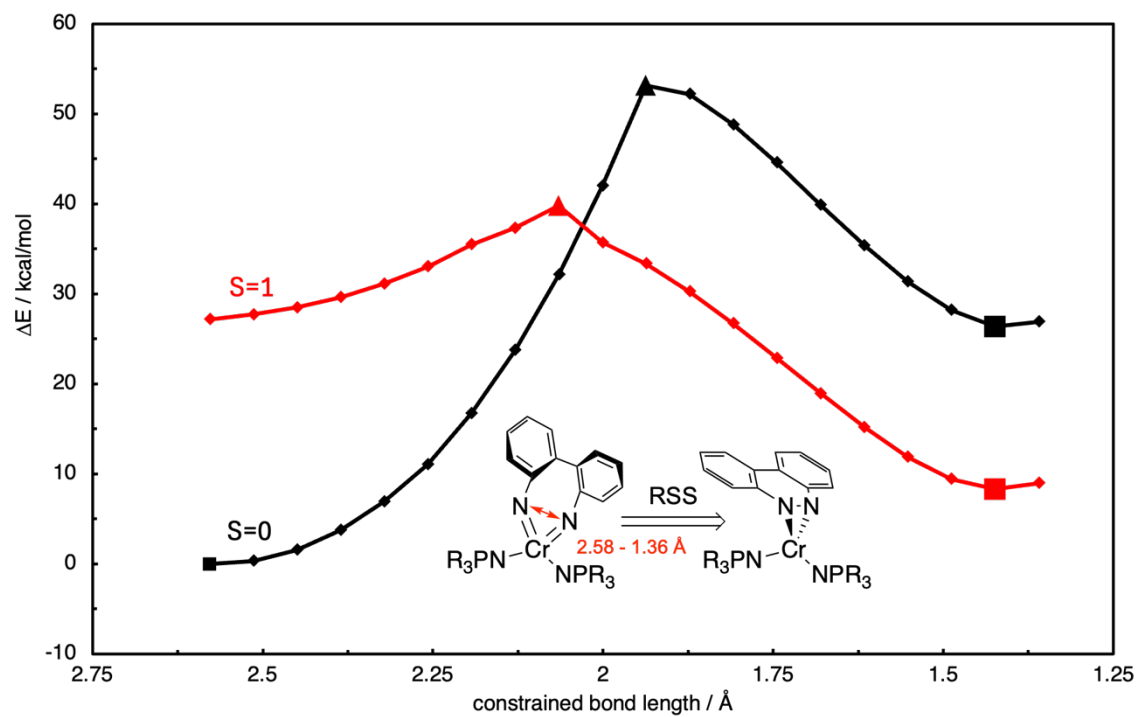


Figure 5-26 Relaxed surface scan performed to obtain initial geometries for the benzo[c]cinnoline-intermediate (squares) and associated transition states related to benzo[c]cinnoline N-N-cleavage (triangles).

Sample input file:

```
!RI M06L ZORA ZORA-def2-SVP def2/J looseOPT

%pal
  nprocs 24
END

%maxcore 2048

%scf
  maxiter 500
END

%geom scan
  B 5 6 = 2.578, 1.360, 20 END
END

*xyz 0 1
Cr 0.00000 0.00000 0.00000      newGTO "ZORA-def2-TZVPP" END
N -1.48527 -0.00586 -0.98181    newGTO "ZORA-def2-TZVP" END
P -2.85884 -0.33098 -1.65693    newGTO "ZORA-def2-TZVP" END
N 1.50336 0.05360 -0.98198      newGTO "ZORA-def2-TZVP" END
P 3.02795 -0.17013 -1.26677     newGTO "ZORA-def2-TZVP" END
N -0.02239 1.28053 1.09018      newGTO "ZORA-def2-TZVP" END
N -0.02239 -1.29765 1.09018     newGTO "ZORA-def2-TZVP" END
C -0.69001 1.57174 2.25126      newGTO "ZORA-def2-TZVP" END
C 0.25601 -1.53461 2.40812      newGTO "ZORA-def2-TZVP" END
C 0.05379 -0.58866 3.46164      newGTO "ZORA-def2-TZVP" END
C -0.71375 0.67995 3.35531      newGTO "ZORA-def2-TZVP" END
C -1.38677 2.80158 2.32327
C 0.81640 -2.80267 2.71785

...
further coordinates
...
*
```

Intermediates were optimized in the same manner as characterized compounds starting from the geometries corresponding to minima (marked with squares) in the relaxed surface scans. Quasi restricted orbitals¹⁸³ were calculated for L^tBuCr(benzo[c]cinnoline) using the “UNO” keyword to serve as a starting point for a subsequent CASSCF calculation *vide infra*. Initial for transition state geometries were obtained from maxima in the surface scans and were optimized using the “OptTS” keyword at the same level of theory. An initial numerical hessian was calculated to aid in the optimization and orbitals obtained from the relaxed surface scan were supplied as an initial guess. Using only the initial hessian was insufficient to locate the S=0 transition state and a numerical hessian was calculated every 10 steps to aid the optimization. Transition states exhibited a single imaginary frequency corresponding to N-N bond formation/cleavage.

Sample input file:

```

!M06L ZORA ZORA-def2-SVP def2/J OptTS MORRead DefGrid3
!Numfreq

%pal
nprocs 36
END

%maxcore 2048

%scf
maxiter 500
END

%moinp "NNcoupling_M06L_split_basis_RSS.015.gbw"

%geom
Calc_Hess true
NumHess true
END

*xyz 0 3
Cr 0.17152536921347 -0.04854243102767 0.15671632496492
N -1.42345677829069 0.34904541415571 -0.59084995211839
N 1.56514860989858 -0.07583340481544 -0.98334379499954
P -2.68756862808562 -0.17259421932559 -1.38647094011681
P 3.07567252687207 -0.22920799694283 -1.39194463634500
N 0.33264654982972 -0.93997305416758 1.73797204467061
N 0.41595969490766 0.75365191965016 1.95224808948668
C -0.25093656968072 -1.63168109847197 2.74433648807921
C -0.54135172486060 1.18661707615623 2.77680852818551
C -1.59653287564882 0.36854853476075 3.30603911062879
C -1.40668553685336 -1.07277695743762 3.36698376498913
H -4.60993618788980 -0.52641423843966 -3.54675457234389

...
further coordinates
...
*
```

Minimum energy crossing point calculation

The minimum energy crossing point was determined using orca's MECP module ("surfcrossopt") using the S=1 transition state geometry as a starting point and adapted frequency calculation ("surfcrossnumfreq") was performed on the geometry performed and did not exhibit any imaginary frequencies.

```

!M06L ZORA ZORA-def2-SVP def2/J DefGrid3
!SurfCrossOpt SurfCrossNumFreq

%pal
nprocs 36
END

%maxcore 2048

%scf
maxiter 500
END

%mecp
Mult 1
END

*xyz 0 3
Cr 0.302569 0.042660 0.099367 newGTO "ZORA-def2-TZVPP" END
N -1.317008 0.319566 -0.601853 newGTO "ZORA-def2-TZVP" END
P -2.580965 -0.246668 -1.312468 newGTO "ZORA-def2-TZVP" END
N 1.609336 0.133342 -1.108743 newGTO "ZORA-def2-TZVP" END
P 3.083261 -0.170192 -1.520645 newGTO "ZORA-def2-TZVP" END
N 0.520087 1.285644 1.603614 newGTO "ZORA-def2-TZVP" END
N 0.427651 -0.917271 1.477710 newGTO "ZORA-def2-TZVP" END
C -0.581585 1.627040 2.301805 newGTO "ZORA-def2-TZVP" END
C -0.024693 -1.375210 2.659878 newGTO "ZORA-def2-TZVP" END
C -0.909834 -0.613580 3.475642 newGTO "ZORA-def2-TZVP" END
C -1.343277 0.743518 3.140784 newGTO "ZORA-def2-TZVP" END
C -0.968864 2.990275 2.249409 newGTO "ZORA-def2-TZVP" END
...
further coordinates
...
*
```

Electronic Structure of $L^{\text{tBu}}\text{Cr}(\text{benzo}[c]\text{cinnoline})$

A CASSCF calculation featuring an active space of 6 orbitals occupied by 4 electrons was performed on $L^{\text{tBu}}\text{Cr}(\text{benzo}[c]\text{cinnoline})$ employing the geometry obtained from the intermediate optimization in conjunction with the QRO's obtained from that calculation as a wavefunction guess. Orbitals 210 and 212 were rotated to include all d orbitals in the active space. This calculation was performed in orca 6.1.0 and therefore the "Rescue" keyword had to be employed to convert the QRO's into a usable format. Default orbitals were used. Custom convergence settings were chosen and are outlined in the header of the input file below.

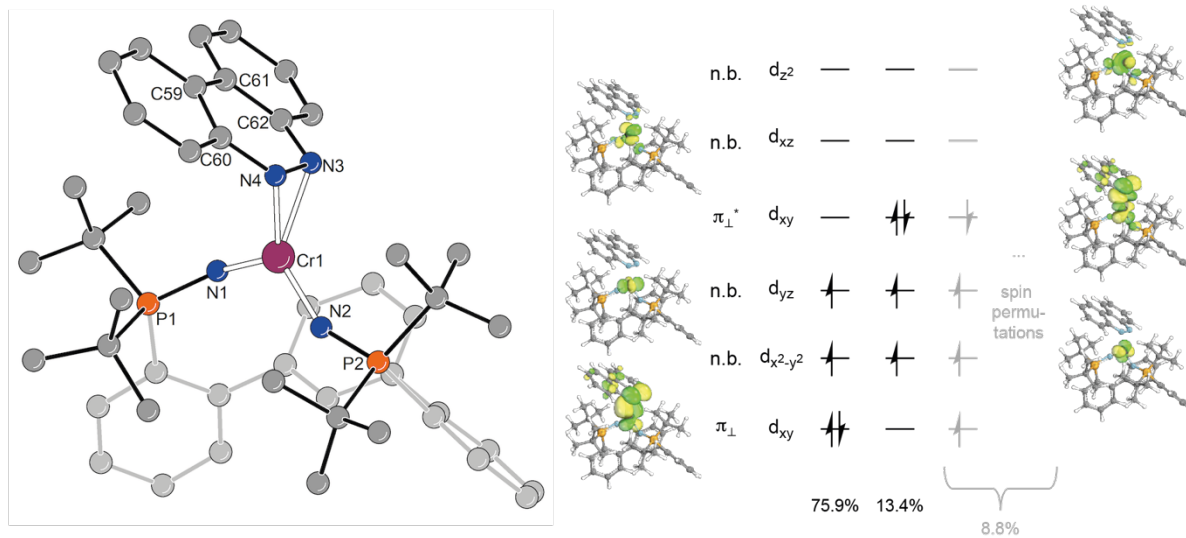


Figure 5-27 Optimized geometry of $L^{tBu}Cr(\text{benzo}[c]\text{cinnoline})$ and results of the CASSCF(6,4) calculation. Orbitals depicted are natural orbitals.

Sample input file:

```
!M06L ZORA ZORA-def2-SVP def2/J DefGrid3 MOREAD

%TDDFT
NRroots 100
maxdim 5
DoNTO true
NTOSTates 1,2,3,4,5,6,7,8,9,10
END

%pal
nprocs 24
END

%maxcore 2048

%scf
maxiter 250
END

%moinp "LCr_benzo_c_cinnoline_M06L_split_basis_S0.gbw"

*xyz 0 1
Cr -0.01938381761349 0.08428372607961 -0.01926189308545 newGTO "ZORA-def2-TZVPP" END
N -1.32627677942811 0.00478624072929 -1.21577398643467 newGTO "ZORA-def2-TZVP" END
P -2.75386122691102 -0.28512887989381 -1.75009875622478 newGTO "ZORA-def2-TZVP" END
N 1.53018681816045 0.21887878394270 -0.87471351642518 newGTO "ZORA-def2-TZVP" END
P 3.02805905461423 -0.08528680826305 -1.15399919736771 newGTO "ZORA-def2-TZVP" END
N -0.19345665378586 1.34339734356190 1.06522326477885 newGTO "ZORA-def2-TZVP" END
N -0.09814467581559 -1.22710463175659 1.00925305028875 newGTO "ZORA-def2-TZVP" END
C -0.82865412080985 1.56426559553700 2.24045862465228 newGTO "ZORA-def2-TZVP" END
C 0.15717773612798 -1.53526030180238 2.30084371705324 newGTO "ZORA-def2-TZVP" END
C -0.07632735166308 -0.63416205556114 3.38624761385221 newGTO "ZORA-def2-TZVP" END
C -0.84765217888610 0.62391874555789 3.31692416920177 newGTO "ZORA-def2-TZVP" END
C -1.51382789685697 2.78982098374354 2.38644383006982...
further coordinates
...
*
```

Optimization on the first singlet excited state surface of $L^{tBu}Cr(2,2'$ -biphenylbisimido) was performed in orca version 6.1.0 using the “IROOT 1” keyword in the TDDFT block. The switch to a newer orca version was necessary as optimization of excited states surfaces using meta-GGA functionals was not available in older versions. This also necessitates the specification of the M06L functional in the method block.

Sample input file:

```

!RI ZORA ZORA-def2-SVP def2/J DefGrid3
!TightOPT NUMFREQ

%pal
  nprocs 20
END

%maxcore 2048

%method
  Method DFT
  exchange mgga_x_m06_l
  correlation mgga_c_m06_l
END

%rel
  onecenter=1
  picturechange=1
END

%scf
  maxiter 250
END

%TDDFT
  NRoots 1
  IRoot 1
END

* xyz 0 1
Cr -0.01938381761349 0.08428372607961 -0.01926189308545
N -1.32627677942811 0.00478624072929 -1.21577398643467
P -2.75386122691102 -0.28512887989381 -1.75009875622478
N 1.53018681816045 0.21887878394270 -0.87471351642518
P 3.02805905461423 -0.08528680826305 -1.15399919736771
N -0.19345665378586 1.34339734356190 1.06522326477885
N -0.09814467581559 -1.22710463175659 1.00925305028875
C -0.82865412080985 1.56426559553700 2.24045862465228
C 0.15717773612798 -1.53526030180238 2.30084371705324
C -0.07632735166308 -0.63416205556114 3.38624761385221
C -0.84765217888610 0.62391874555789 3.31692416920177
C -1.51382789685697 2.78982098374354 2.38644383006982
...
further coordinates
...
*
newGTO "ZORA-def2-TZVPP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END
newGTO "ZORA-def2-TZVP" END

```

Spin density plots

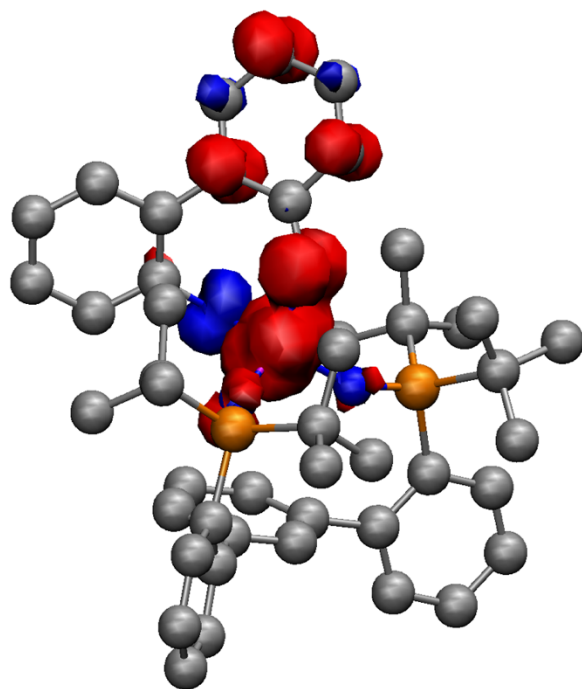


Figure 5-28 Spin density plot of $L^{tBu}Cr(\text{biphenyl-2,2'-bisimido})$ ($S=1$ excited state) pictured at an isovalue of 0.005.

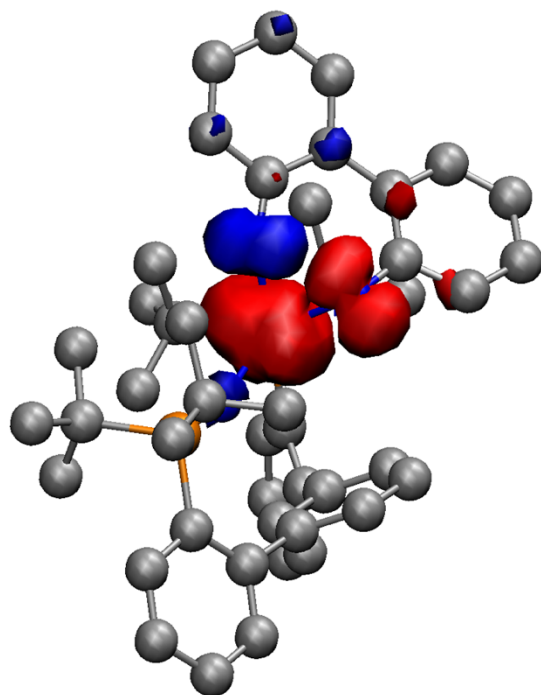


Figure 5-29 Spin density plot of the transition state interconverting $L^{tBu}Cr(\text{biphenyl-2,2'-bisimido})$ and $L^{tBu}Cr(\text{h}^2\text{-benzo}[c]\text{cinnoline})$ ($S=1$) pictured at an isovalue of 0.005.

References

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Appendix

xyz-coordinates pertaining to electronic structure calculations

Chapter 2

HLAdCr(HMDS) 1 (S = 2)	C 2.07843828452571 -5.08311793171512 -1.74402175262922
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N -1.72170666294080 -0.81231318626899 0.24147687600122	H 6.78315531768751 0.88777127715161 2.32082966584231
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H 1.34996301934551 -8.09054898591441 1.27964110383467	H 2.68576007260675 0.66571321454744 2.89386070020458
C 1.61940934178714 -5.97979942748346 0.78844165657115	C 0.10762430475584 -2.09468436668537 5.51004663027057
H 2.67666596377026 -5.96304733608209 1.10494063719148	H 0.19264769673104 -1.62428426747981 6.50511430405094
C 1.52796883352837 5.80868583482062 -2.42556811828329	H 0.80397262332524 -2.95133108154604 5.49618853278135
H 1.40913571502061 6.83339262284620 -2.81716681912885	C 3.12201598474815 3.35540943742080 -2.06589901496637
C 1.93059169308970 3.41100534745121 -3.03579477982903	H 4.05621980366886 3.61720412202188 -2.59338703941648
H 2.09454915485576 2.70307774360036 -3.86696224913835	H 3.24744431628690 2.33235242723992 -1.67548396844386
C -1.33236109407345 -2.57954705806858 5.27693399937387	C 0.06186378455809 -6.20689406563963 -1.16550869375035
H -1.60842305979857 -3.31058000077302 6.05617188209412	H -0.00311099859330 -6.35130248700018 -2.25773463143300
C -3.06368058471422 3.92685992850394 1.64147383113060	C -0.94513904281932 5.71004086947605 3.87339429155327
H -3.69962886092028 4.35032588639393 0.85084603232679	H -1.23643609652140 6.14006009180375 4.84747774501574
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C -1.78085113718033 6.33786032207650 2.74667468848457	C 4.14674594511914 0.49607725136933 0.34387018259197
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LAdCr(CNMe) ₃ (S = 1)	C -3.91846509659473 0.54439027857753 -5.48898727470718
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C -0.15112467078727 1.57992321356860 1.13446781886283	C 4.22416055901948 1.89141719145543 0.82890827374067
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C -2.70395022924931 0.39366537869413 -3.36463073112391	C 3.41193429352856 -2.93581886977937 0.04591193705193
C 1.88711889858726 1.85249000739849 -2.66814136176009	H 4.07567276956335 -2.76317419657899 0.90764302865286
C 3.31193782997052 1.47896812742196 -2.92975246021332	H 2.39619822546460 -2.65871865304472 0.35569910267405
C -3.83550146166125 0.13206329379692 -4.15936973669911	C -0.90810641482270 2.67224591466150 4.11104662364373
H -4.67835322601032 -0.40817405060275 -3.73533483475691	C -1.51545686674351 3.35776415207651 5.16555732309078
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H -0.85291089779452 5.25945403698982 0.80284124247892	H -2.10437536587347 5.77064013547277 6.74939693766343
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C 3.92061015004431 2.03354287297439 3.31727215541397	C -2.76910546597402 -2.87614855265904 -0.55348346865035
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H -3.74629671893480 2.78343874668758 1.68425397189726	H -4.86414212621465 -2.46216700050133 -2.36327862482423
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C -1.32505048486782 -2.74397351009127 2.93968850730357	H -4.67022210515765 -4.63135313489630 -3.51251700741803
C -3.04525465838523 -3.88055816992286 4.19197418502473	C -1.31603985751327 -4.14453051159091 -2.78412397071475
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C -0.77240390006063 -3.98797372398890 2.55473099510943	C -3.86054442778226 -4.91634361509952 -1.51534797687576
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H 1.32320418904819 -3.57717134926501 2.26821176056659	H -2.47264504693074 -4.22843550237530 -4.62943242019537
H 0.36223374932716 -3.43263803974396 0.80444655267205	H -2.43503507333732 -5.75911815360342 -3.73074956501241
C -3.22584417422189 -6.41094797405493 4.20900213812573	C -1.35854900939622 -4.78251626515276 -1.38693700653112
H -3.67186213755472 -6.92526496167944 3.33999145363546	H -1.26692800587675 -5.87989854804475 -1.46418552280985
H -4.03028674690146 -6.22741031276463 4.93667713569819	H -0.50501737189925 -4.43181852166854 -0.79103037915433
H -2.50952004038672 -7.11459176469508 4.66455267675900	

[N(Mes)CHLAd]Cr(HMDS) 4 (S = 2)

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P -4.17738002542196 -3.80278418382653 -1.13375207019154
Si 0.69328405391441 2.77305973687234 -1.71847995887979
Si -0.17178807491973 2.94446829579040 1.19806856587995
N 1.15298816389711 -1.44638845848592 -0.14051480583186
N -3.22388084028298 -2.59654034865683 -0.85612558488796
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C -2.01978212913022 -2.11848295645639 -0.58621199546692
N 0.22033707357892 2.08110619901033 -0.22782912055934
C -1.30821209027264 -4.17228014916369 -2.82789997642238
C -0.14326927546913 -4.54340371102663 -2.13804562825602
H -0.11109746517291 -5.50949659728185 -1.62829723916481
C 0.98197019780283 -3.70727183669722 -2.09216585021091
C 2.96326762002567 -3.61392318622107 -0.41852908645174
C -1.34075083152642 -2.94110364395305 -3.49130750955799
H -2.23311731136527 -2.65162216714057 -4.05002142965539
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C -5.75489924512100 -2.98973243192934 -1.75158132786147
C -3.69881379119143 -5.05385591248312 -2.39775010006393
C -2.14210024586707 -6.24240358633155 -3.83770806162993
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C 0.93011237715914 -2.47817127556688 -2.76871723566659
H 1.79887954611935 -1.82319474173637 -2.75972805189541
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H 4.54002920034125 -1.19995661411948 2.64963841146857
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C -1.39022122118397 -4.23478186984605 -2.22093116213157	H 2.67139447822939 4.20827490720966 1.85346026542460
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H -1.10917569976958 3.67370187462032 3.91973381715667	H 1.47521657908948 0.70627404100884 -3.8288871571500
H -0.60719850984236 5.16456104313961 3.07398287763294	C 0.28703553232152 3.79537101862593 -1.76999270653868
H 0.52843256355361 4.35498429963605 4.18869199598464	H -0.05553501764731 4.67057145913986 -1.19984990032831
H -1.92512783130131 2.82085795894640 1.20713549294689	C 4.22938195985388 1.22004575789482 -2.17095688683996
H -0.83855443983793 2.59188916166968 -0.19298282298407	C 4.53873726360043 0.61932377124916 0.72109580940068
H -1.27168240973692 4.24311662342395 0.33496795352875	C -1.25484882369561 0.93157697091285 -3.70180509213652
H 2.65338720944794 4.25449881005988 2.03163235572732	C -1.17687543986659 1.08931292788735 -5.10846318467974
H 1.58041601327820 5.18285331119086 0.93023654507283	H -0.30918574255746 1.62978487879836 -5.51657799540471
H 2.27992250966493 3.61999022653728 0.39086901967752	C 5.60764210292481 1.03266936872715 -2.43661120844896
HLAdCr(HMDS)(CNMes) CNMes insertion TS 2 (S = 2)	H 6.16969662998192 0.27173686925710 -1.88539361315312
Cr 0.27309811286615 0.46268231401455 0.76306856701175	C -4.06014579174708 0.54912941888265 -0.76356984859723
P 3.47872228877907 0.27508357690403 -0.77096643543694	C -3.34819698191740 0.09398428012817 -5.41243500883867
P -2.52252363668596 -0.38798904586593 -1.38797250017170	H -4.19718663717230 -0.19917527760650 -6.04842540287890
N 1.97853738357535 0.74159454616340 -0.42243866708817	C -2.19410571044094 0.66156536912976 -5.96793485754205
N -1.24464358574406 -0.14556280970666 -0.47769369639804	H -2.10325938893538 0.81409717821045 -7.05409085712994
C -1.08118326675429 -0.81328850945660 1.27122151975513	C 6.29493614191204 1.80802108708806 -3.37909319655894
N -1.76598210654489 -1.75017177154496 1.67735346132678	H 7.36771200187906 1.63292684990783 -3.55060925956026
N 0.75623583598358 1.44277234727810 2.47836742989787	C -0.23642168157689 1.72659567346009 -2.96285349563774
Si 0.55456838574341 0.59241800340808 3.96753497414546	C -2.91751305446038 -2.28443353397936 -1.55894388334052
Si 0.36593668265272 3.11148401081462 2.31805707351341	C 4.75794254731014 2.15710655180119 0.74834554656447
C -6.57653138015799 0.91825471588611 -0.71981228688638	H 5.34195730571879 2.47826852959183 -0.13827889136598
C -2.35983910702466 0.22579339335903 -3.14393618125652	H 3.77599229846604 2.66125875565139 0.69837552577941
C 2.08530795714938 2.48227891997843 -2.73841794831543	C 3.24670951345773 -2.42473858705172 -0.09455979138584
C 3.53898912776383 2.21736079373000 -2.91507432015435	H 4.07170269846146 -2.34610812008641 0.64151625998545
C -3.40900923352082 -0.12124602939958 -4.03034392553074	H 2.32217294262869 -2.08208212457034 0.41370703182493
H -4.31078046408370 -0.59061324437092 -3.63245602526462	C -3.88264691335685 2.05469147502341 -1.08387416667117
C 1.65197208487326 3.62400699124942 -2.04189154416324	H -3.84138171365778 2.20881620903654 -2.18273217170098
H 2.39383970169700 4.34794012458212 -1.67639392703917	H -2.92474588330372 2.40270849745061 -0.65345449734235
C -0.64417198017989 2.84521624942501 -2.20440719257641	C 5.91824914716763 -0.08608081546781 0.77119113403015
H -1.71176310062016 2.99642581986546 -2.01403430036385	H 5.79370374788392 -1.18812689266166 0.76236062786590
	H 6.54149424789872 0.18470782824261 -0.10311029071132

C 5.50614032405513 2.56503209740754 2.03258462363854	H 5.01597722975612 -1.37318546017554 -2.91922559225896
H 5.64578475731648 3.66734928855457 2.02345964076896	H 5.69916180083282 -1.87715285038782 -1.34630282619928
C -5.42429097811434 0.10725192746235 -1.35498839297405	C -6.38324715063710 2.40886789947170 -1.06036611460251
H -5.60409082844790 -0.97241741450689 -1.19655027068694	H -7.21693650252383 3.01182983129678 -0.63957751227284
H -5.44504258597594 0.28747695613661 -2.44742645073413	H -6.40264930168372 2.55106735303270 -2.16301102817431
C 4.24393296227700 2.99761329149096 -3.85639515636883	C -6.57840223950538 0.72350130936590 0.80898353349943
H 3.68714574168134 3.76433311424216 -4.41652918771778	H -6.72174261824187 -0.35095314216528 1.05728321017880
C -4.08637600982087 0.40758757255734 0.77734199189566	H -7.42874721578556 1.27755004031948 1.26230229334513
H -4.19417917837076 -0.65110185398594 1.06292914755864	C 3.10974655554452 -3.89387272247778 -0.54142135931095
H -3.11402536637970 0.74514777417884 1.18720743054484	H 2.90716332550585 -4.52014027307069 0.35231246369192
C 3.52971422138784 -3.60241807762123 -3.45032033757280	C 5.86442898272202 -0.08179971582388 3.29486577950144
H 3.43592541785989 -4.65645846919789 -3.78986104075546	H 6.41925554238279 0.18559136509319 4.22035925323894
H 3.73316321187581 -2.98728214082906 -4.35372190513238	H 5.72409789252958 -1.18479193561019 3.30794025724735
C 3.52697829887796 -1.51796799432482 -1.31856986782751	C -5.24108103189016 1.22555390582895 1.38652682101569
H -7.53732281560317 0.55752820160958 -1.14652078086765	H -5.22922043591864 1.08467014287429 2.48857297439515
C 3.73205714423442 0.21663158088764 1.98419331882149	C -5.03800537406558 2.88650650905007 -0.48181997943782
H 2.73879428301862 0.71105351674856 1.98540190756840	H -4.87426374613875 3.95495393288386 -0.73979344005554
H 3.55512250596393 -0.87433437486678 1.99795228415432	C 6.67483568389906 0.33443081888220 2.05349468420954
C 5.61153948760672 2.80481342588735 -4.09095528001271	H 7.66240351044248 -0.17531129341579 2.05674092829625
H 6.13885214357572 3.42628816354492 -4.83050361400424	C 4.49735508719783 0.62298932878409 3.25775798437187
C 1.94654548766915 -4.02065994334742 -1.53908367579270	H 3.88984533888185 0.31946515058257 4.13445500321645
H 1.00664156255285 -3.69186176068310 -1.05887193721850	H -0.90312784486563 -2.63678871148258 -2.34440010374012
H 1.80998658491722 -5.08135810064510 -1.84115203317924	C 4.69240033156822 -3.46811026099656 -2.44734477235008
C 2.35215401713513 -1.67486142800938 -2.32327792041941	H 5.64274595916197 -3.78149754565041 -2.93020566730971
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C 2.22416237358338 -3.14421943353856 -2.77342158212872	H 7.48246847447585 2.17126510027358 1.17619271611501
H 1.37643963476684 -3.22294208286451 -3.48730003762785	C -0.76709236613762 -4.65492537933410 3.76141161542793
C 4.42194775900746 -4.34678234338628 -1.21083771587319	H 0.04643102741168 -5.39796697730110 3.80887628570150
H 5.26610493384934 -4.26558371743534 -0.49163715295324	C 4.68513567344889 2.14959851732700 3.26817288868672
H 4.35214902580855 -5.41528789698300 -1.50829645892547	H 3.69039916289452 2.64214533734525 3.25305674516387
C 4.82470131596565 -1.98978051631680 -2.01869239886921	H 5.20082546532928 2.47144480032165 4.19878184807904

C -1.80797533004507 -4.71759281397250 4.70171686494379	H -4.23985193602419 -4.61372792121750 -3.81868409203092
C -5.05501608264002 2.71607350482866 1.04942460334108	C -1.66752322267244 -4.50441088104436 -1.48439396545303
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H -5.87792482988767 3.31885763589057 1.49164184933899	C -4.59766263774482 -4.77452290963313 -1.67011000326291
C -1.74984746132502 -2.70365106512630 2.68937662044081	H -4.71748206125429 -5.87985058703975 -1.68101307845467
C -2.84156097510188 -3.76651576576028 4.58793117678211	H -5.61805016720831 -4.33739696594350 -1.73893885083703
H -3.68554129761195 -3.79945776130374 5.29685602410810	C -2.34824543478325 -4.95934870155238 -2.78747731222382
C -0.71190093705373 -3.67422929398542 2.75315174755289	H -1.73590851303937 -4.65665687530082 -3.66499065252107
C -2.84740034687549 -2.77465577480890 3.59601792333646	H -2.43182304313731 -6.06756088671537 -2.81552247841405
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H 0.26280151267306 -4.54453389625293 1.02275078584675	H -2.59047826125940 -6.05979890292155 -0.25455017103981
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C -1.81747281322307 -5.74884137571054 5.80478934238711	C -1.26578443725045 0.48778127872834 4.46155940674831
H -2.82966241204265 -6.17798516480188 5.95483406390172	C 1.45690024827050 1.37931409136769 5.43907898542431
H -1.50939701201540 -5.30455482386314 6.77660819815679	C 0.12773552467308 4.06777214330249 3.92999646024651
H -1.12133093485309 -6.58382203250769 5.58974001837218	C -1.27434041108947 3.26451157870316 1.38826640686973
C -4.00818072309464 -1.82122231566913 3.48201841454439	C 1.69601480583302 4.04580668840640 1.36508907644960
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H -4.70442518508377 -1.93943872457124 4.33423315858420	H 2.31507196021694 -1.19426788725840 4.15171437220403
H -4.58235091321751 -2.00324695064986 2.54964877407772	H 1.22398570579837 -1.49631511725431 2.77161712830696
C -3.78099073452373 -2.78104412634540 -0.36614194001216	H -1.85729753681034 0.11811673564800 3.60383002544732
H -3.32068061312807 -2.45567160266639 0.58112983387309	H -1.65649833385168 1.49098282882494 4.72836703341236
H -4.79452660582156 -2.33940849811005 -0.41192893065167	H -1.44194151179441 -0.19108654013496 5.32116879473185
C -1.52479499693769 -2.96751618339965 -1.48367185034764	H 2.46326315728648 1.75035689333579 5.15994008255757
H -1.00358136606290 -2.62976205181053 -0.57067077836533	H 1.59123835947551 0.61824888400562 6.23720320881811
C -3.90994249551719 -4.31858727134036 -0.37146361169812	H 0.89895709975276 2.22631224015692 5.88187292017936
H -4.51745908700968 -4.61992177729977 0.50864978743533	H -0.65744667850018 3.62835148755009 4.57659632652803
C -3.60803211108266 -2.77831010030863 -2.85683733996428	H -0.18544611754415 5.10418824507009 3.68195336028898
H -3.03235502379330 -2.46702486872736 -3.74981995251659	H 1.06204755984514 4.13329910597754 4.52119567568731
H -4.62441455063130 -2.34276430077149 -2.94475997424674	H -2.07148808247700 2.83663483451452 2.02917858365395
C -3.74455983496272 -4.31866766589632 -2.86819778297704	H -1.26531675634521 2.66903500930460 0.45237958410446

H -1.55017869833095 4.30850591985249 1.13219729131623
H 2.60154951411004 4.17624642022487 1.99118083850198
H 1.35513787848071 5.05298892360585 1.04845872562202
H 1.97894300182053 3.46898148876295 0.46545518047950
H 1.48167739471218 0.87699813212873 -1.31133531707623

HMDS-H

N -0.00264704308189 -0.20089176722952 0.33928627354169
Si -1.56391818943841 0.44632550784924 -0.05761431813132
Si 1.59156460204799 0.33339644934240 -0.09055726051789
C -2.82900846621542 -0.91506277720881 0.18290322919704
C -1.57217835704248 1.02740163572442 -1.84023138011071
C -2.00962476416655 1.90217832661162 1.03846149392182
C 1.67546190424884 2.20415801118837 0.00299091183983
C 2.04924959227750 -0.19650227604179 -1.83029713279924
C 2.80159226427845 -0.42675012181699 1.12172117639089
H -0.02725220095576 -1.03514932874451 0.90956508635704
H -2.63121308887650 -1.76890661238364 -0.48522171895257
H -3.84718706747303 -0.54962840035843 -0.02918850861234
H -2.82314363772031 -1.28860096117084 1.22065149335475
H -1.35014042036977 0.19821876614617 -2.53075037504942
H -0.82608918427712 1.81876840582316 -2.01511034213329
H -2.55752440902659 1.44149641257144 -2.11073750454492
H -2.04105948994000 1.60532352974092 2.09963493999375
H -2.99698781523024 2.31640806576190 0.77383692774274
H -1.26866919923320 2.71168285652413 0.94181895552036
H 0.95654181579938 2.68077836353958 -0.68207151945973
H 2.67986408503438 2.56421087142866 -0.27464742136168
H 1.45497138031051 2.56089994213541 1.02178464891483
H 1.34904839546325 0.22446249758319 -2.56923392112771
H 2.01547488890467 -1.29399049645611 -1.92929423505637
H 3.06519388662873 0.13685599477565 -2.10073592215481

H 2.59351930110556 -0.10035921880418 2.15360246719595
H 3.83727079675729 -0.13797560144931 0.87852730773005
H 2.75342042019071 -1.52848807508220 1.09861664831132

IMe4

C -0.00103827940011 0.02026387528645 -0.00007714039240
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N -1.05182976364785 0.87704542423838 0.11771207624937
C 0.67836667445738 2.22173294383697 -0.09381274901134
C -0.67829844987799 2.22345006185050 0.06491312673126
C 2.41478356839011 0.41632426750486 -0.28478371465724
H 2.39878482209194 -0.67993322681271 -0.28987643637987
H 3.05068175726999 0.76394967322265 0.54578299901291
H 2.85057247356960 0.77559311158832 -1.23122445985495
C -2.41620755119094 0.42220975349244 0.28065232697215
H -2.40197478578426 -0.67403876920907 0.29151136689334
H -3.05418878957034 0.76653161858762 -0.54962988424514
H -2.84841593591390 0.78697989591831 1.22670191973749
C -1.65478680400953 3.34399173252810 0.17106728576271
H -2.40777107417632 3.31278652368517 -0.63547511558699
H -1.14011772423645 4.31338535325224 0.10566574664992
H -2.20475646533777 3.32381188406489 1.12792556266467
C 1.65605664606033 3.33989495553111 -0.21378631345765
H 2.40584157769318 3.32100068219383 0.59612856854081
H 1.14169464371748 4.31047348406936 -0.16600081927801
H 2.20992261295680 3.30384974928197 -1.16788291351560

CNMe3

C -2.03338267138861 0.24094499092186 -0.37092354034944
N -0.86510353384290 0.21694433499225 -0.35688708085302
C 0.51809892502668 0.18842474925163 -0.33984166860744
C 3.31138811149253 0.12962754744834 -0.30552132954249

C 2.6177383553649 1.33051835038399 -0.11241608692049	H -0.28724781711556 -2.50873206603849 0.08739027741304
C 1.21962327945534 1.38959586625180 -0.12494152758423	H 1.04435879667915 -3.16743251668136 -0.90287209495304
C 1.17485896745807 -1.04392975226427 -0.53818400974970	H -0.26403766340190 -2.21128774486879 -1.65201737335637
C 2.57094498361778 -1.04366808123640 -0.51625580475828	C 4.81815062365920 0.08535204301098 -0.28988730019114
C 0.47713061070022 2.68065113467778 0.08196090007722	H 5.18736841357992 -0.59392709513317 0.49653592960860
H -0.19190600041532 2.61975907034282 0.95587579602680	H 5.25126285977326 1.07981667673042 -0.10865315334316
H -0.16367643985521 2.91503229587576 -0.78383088925593	H 5.21458579590389 -0.28806112140752 -1.24892708120641
H 1.17278149039798 3.51734165872830 0.23538562872632	H 3.09781302466728 -1.99010758077904 -0.66845902996342
C 0.38213167603971 -2.30161807538251 -0.76360678112418	H 3.17982821203199 2.25359531517562 0.05361621990675

Chapter 3

Transition state optimization input geometry:

Cr 0.10058400 0.68290600 0.05906400	C 3.97303300 -0.49053600 0.59955600
P -2.72372100 -0.06319500 -1.28326900	C 3.63051200 -4.96009100 1.44285100
P 2.60877400 -1.40264300 -0.33296500	C -1.26604600 -0.97971400 3.10507600
N 1.31785200 -0.54638300 -0.47031500	C 1.61692200 -4.23282000 2.52778300
C -2.03845300 -0.18156200 -3.03739900	C 1.06682500 3.31179500 -0.92720300
C 3.11547900 -1.94048600 -2.08337300	C -3.91011300 -3.63463500 0.42547000
N 0.61534700 1.71749200 1.42629700	C 2.67585200 -5.12825100 2.44232300
C -4.07128900 1.22644700 -1.08754300	C 2.00528600 2.77736900 -1.85341200
N 0.10190100 2.56628800 -0.33858200	C 2.90990500 3.58684300 -2.52376300
C -3.55635300 -1.65676700 -0.93365700	C 2.91527500 4.95450200 -2.25970100
C -5.25403400 -3.30825500 -1.54083600	C 2.02416400 5.52834900 -1.35211100
N -1.59857700 0.22411800 -0.24421600	C 1.10714900 4.71809900 -0.70311600
C 1.48180800 -3.14959000 1.64245200	C -0.07307900 2.29853100 2.45112800
C -3.21145600 -2.44011600 0.19263300	C 0.57781900 2.45642500 3.69680500
C -2.32344400 -1.28835800 2.25700500	C -1.43069800 2.69161200 2.35308100
C -2.11176200 -2.10503000 1.13892400	C -2.11205700 3.18321500 3.45319600
C 2.47820600 -2.94285500 0.66237100	C -0.11024000 2.92640400 4.81029600
C -4.92336900 -4.06867300 -0.42192000	C -1.44685400 3.28520900 4.67580600
C 3.52702800 -3.87454000 0.58059200	F -2.11113100 3.75275700 5.74030400
C -4.57410800 -2.11944900 -1.78427600	F 3.79557500 5.74009300 -2.89546300
C -0.84743000 -2.66039800 0.93335800	C 3.41978100 -0.27765200 2.01209000
C 0.00344500 -1.51351500 2.87449200	H 2.41895000 0.17754800 1.99506900
C 0.21955100 -2.37365200 1.79158900	H 3.37427800 -1.21782800 2.58299400
	H 4.08420700 0.40666600 2.56351400

C	5.32112900	-1.19705400	0.71590600	H	-5.17271100	0.94844400	-2.98423600
H	5.82445400	-1.35267000	-0.24550300	C	-3.44345100	2.58007700	-1.42290800
H	5.99151600	-0.56734400	1.32269800	H	-4.10495100	3.39263000	-1.08345000
H	5.25419100	-2.16340600	1.23375300	H	-2.46154800	2.71473000	-0.94022300
C	4.15518200	0.86826100	-0.07050900	H	-3.30895900	2.71148200	-2.50685600
H	4.48194600	0.78610800	-1.11915700	C	-4.44783500	1.18462300	0.39594400
H	3.22855700	1.45723600	-0.04461400	H	-3.57617500	1.32108400	1.04895900
H	4.92491400	1.44720500	0.46301400	H	-5.17263900	1.98457800	0.61451500
C	2.68670900	-0.81803200	-3.03248500	H	-4.92290900	0.22920300	0.66838100
H	2.90900900	-1.11814900	-4.06884600	H	-4.84699400	-1.53715500	-2.66573700
H	1.61411000	-0.60348700	-2.95774200	H	-6.04009000	-3.63763700	-2.22418200
H	3.23101700	0.11872300	-2.84235700	H	-5.44982700	-5.00283800	-0.21208500
C	2.28882400	-3.18622300	-2.41428900	H	-3.63614600	-4.23239400	1.29901700
H	1.22866200	-3.04863900	-2.15221400	H	-3.31386800	-0.86153900	2.43579700
H	2.33680600	-3.38885500	-3.49601600	H	-1.42696700	-0.31088700	3.95494200
H	2.64447800	-4.08596400	-1.89464500	H	0.82917400	-1.27644900	3.55188500
C	4.59682800	-2.20438000	-2.34973600	H	-0.68173100	-3.32397100	0.07787500
H	5.05079200	-2.97514500	-1.71442700	H	0.84352200	-4.37532800	3.28753800
H	4.71348800	-2.55092600	-3.38940900	H	2.74546700	-5.96337200	3.14330600
H	5.20271400	-1.29204500	-2.25623800	H	4.46019700	-5.66319500	1.33978900
C	-3.03309700	-0.00135500	-4.17993200	H	4.30024400	-3.74394400	-0.17691700
H	-3.45149300	1.01492100	-4.20882000	H	-1.91374100	2.60576500	1.37745200
H	-2.51257500	-0.15350000	-5.13908400	H	-3.15894700	3.48818500	3.38943600
H	-3.86586000	-0.71689900	-4.16212300	H	0.37719400	3.03423300	5.78106900
C	-0.94926600	0.88731100	-3.17185500	H	1.63066000	2.17547400	3.77251800
H	-0.11181800	0.69947400	-2.48515200	H	1.98657900	1.69740800	-2.02701200
H	-0.53933100	0.85949700	-4.19409400	H	3.62115300	3.17932300	-3.24651700
H	-1.30172000	1.90970300	-2.98068400	H	2.06423900	6.60555100	-1.17750700
C	-1.36195100	-1.55245600	-3.11812100	H	0.39285500	5.14262900	0.00660400
H	-2.08157100	-2.38292200	-3.15252800				
H	-0.74266200	-1.61013200	-4.02808900				
H	-0.69243200	-1.70719300	-2.25499900				
C	-5.34464800	1.01798500	-1.90274100				
H	-5.90492400	0.12811300	-1.58464900				
H	-6.01228600	1.87979200	-1.74291600				

Optimized geometries:							
L ⁿ BuCr(η^2 -TMSC $\equiv$ CTMS) S = 1							
Cr	-0.104738	0.783604	0.148624				
P	-2.992313	-0.496854	-0.331057				
P	2.699450	-0.641663	-0.768663				

N	1.252258	-0.284962	-0.370581	H	-6.021226	-0.095920	-1.124663
N	-1.707686	0.008853	0.374690	C	-4.287821	0.514860	1.819659
C	-0.017221	2.685966	-0.213380	H	-4.365370	-0.502778	2.232895
C	0.196842	2.449738	1.072373	H	-3.319475	0.930287	2.129334
Si	-0.119098	4.144558	-1.345530	H	-5.090798	1.117003	2.273386
Si	0.444514	3.287660	2.697797	C	4.188416	-0.590677	-3.302213
C	5.054380	-3.904778	0.070989	H	4.095963	-0.722909	-4.392547
C	0.083270	-2.856394	0.904947	H	4.562991	0.430108	-3.142947
C	3.184329	-4.018568	1.577077	H	4.966879	-1.291882	-2.973111
C	1.267610	-2.484007	1.555029	C	1.845071	0.206216	-3.229011
C	-4.489790	-2.864478	-0.444506	H	0.820300	0.026227	-2.879386
C	-2.412312	-3.050000	0.789785	H	2.102666	1.237139	-2.951929
C	-4.733830	-4.226310	-0.300927	H	1.853584	0.145360	-4.329147
C	-1.167999	-2.563888	1.453056	C	2.310488	-2.219889	-3.000819
C	2.592607	-2.882896	0.998033	H	2.109897	-2.286834	-4.082015
C	4.398134	-4.528336	1.129571	H	3.028857	-3.012098	-2.748153
C	-2.829226	-0.497204	-2.221738	H	1.368262	-2.443710	-2.477136
C	3.274102	-2.228900	-0.054869	C	3.634750	1.973355	-0.749772
C	3.925811	0.621254	-0.095642	H	4.186614	2.768010	-0.221337
C	-1.229831	-1.917955	2.695773	H	3.950114	2.010047	-1.803088
C	-3.340039	-2.249017	0.079941	H	2.565470	2.228112	-0.699237
C	-2.667812	-4.426316	0.908761	C	3.609207	0.712678	1.399951
C	-3.807373	-5.016756	0.373349	H	4.277581	1.448623	1.874993
C	2.824910	-0.821344	-2.652992	H	2.568926	1.022476	1.578723
C	1.183948	-1.850435	2.798173	H	3.767145	-0.249915	1.910993
C	4.492199	-2.768739	-0.500214	C	5.403962	0.271544	-0.251685
C	-4.442501	0.521103	0.295419	H	6.011865	1.101941	0.142628
C	-0.061876	-1.568166	3.361165	H	5.683029	-0.622750	0.322261
C	-4.249511	1.950021	-0.215766	H	5.714168	0.120477	-1.293796
H	-3.213426	2.295658	-0.076576	C	-2.175859	0.817181	-2.654027
H	-4.510138	2.051308	-1.279880	H	-2.829028	1.689317	-2.520507
H	-4.906677	2.637279	0.340455	H	-1.240438	1.019903	-2.108600
C	-5.847963	0.033426	-0.047514	H	-1.923847	0.760488	-3.725415
H	-6.095293	-0.910038	0.457376	C	-4.114297	-0.679774	-3.022785
H	-6.580393	0.778163	0.303433	H	-4.825010	0.144525	-2.864676

H -3.875760 -0.684659 -4.098947
 H -4.628215 -1.627409 -2.815587
 C -1.841484 -1.629528 -2.524806
 H -2.270047 -2.626060 -2.344371
 H -1.535053 -1.585543 -3.582542
 H -0.929194 -1.531496 -1.911277
 H 5.026145 -2.277813 -1.315715
 H 6.003755 -4.293990 -0.303755
 H 4.826406 -5.415109 1.602733
 H 2.656258 -4.511900 2.397712
 H 0.141490 -3.364256 -0.063477
 H 2.100603 -1.574743 3.327914
 H -0.117145 -1.070334 4.332113
 H -2.204671 -1.686131 3.132882
 H -1.942427 -5.038037 1.451999
 H -3.972839 -6.090422 0.489209
 H -5.640435 -4.666095 -0.722673
 H -5.215716 -2.267561 -0.995421
 C -1.893257 4.733877 -1.430635
 H -1.971442 5.656094 -2.026089
 H -2.555600 3.988801 -1.893245
 H -2.293714 4.952192 -0.429590
 C 0.949393 5.538526 -0.695352
 H 2.002065 5.230558 -0.608815
 H 0.918790 6.414991 -1.360346
 H 0.623292 5.873173 0.300422
 C 0.478530 3.712989 -3.062905
 H 0.327121 4.552945 -3.757419
 H 1.554877 3.485178 -3.064588
 H -0.042329 2.839181 -3.479990
 C 2.098057 4.163372 2.747070
 H 2.175439 4.939020 1.972416
 H 2.259883 4.651897 3.720032
 H 2.929430 3.461023 2.592687
 C -0.938579 4.528723 2.930922

H -0.898556 5.010982 3.919106
 H -0.897244 5.325805 2.174219
 H -1.922742 4.045207 2.839046
 C 0.377919 2.011469 4.055575
 H -0.572801 1.458664 4.016699
 H 1.184091 1.271571 3.937734
 H 0.472194 2.453866 5.058052

$L^{nBu}Cr(\eta^2-Ar^P-FN=NAr^P-F) S = 1$

Cr -0.04654700 -0.72200600 0.11515600
 P 2.63047200 0.29261100 -1.33098900
 P -2.81404200 1.08332200 -0.04371500
 N -1.42247100 0.39734900 -0.11095500
 C 1.89226000 0.36227300 -3.06610600
 C -3.41799800 1.44471700 -1.80340500
 N -0.09525800 -2.27079100 1.21941200
 C 4.02967500 -0.93390500 -1.14434100
 N -0.12836300 -2.62816200 -0.15105300
 C 3.35269100 1.94664100 -1.03583400
 C 4.90452600 3.69943700 -1.74629600
 N 1.54948200 -0.03959100 -0.25087200
 C -1.78691800 3.16812600 1.65010800
 C 2.92337200 2.77088900 0.03047500
 C 2.22087500 1.76116400 2.22078700
 C 1.87702300 2.41079600 1.02903400
 C -2.84160700 2.69122500 0.83942300
 C 4.48449700 4.50692300 -0.69287900
 C -4.02251200 3.45247600 0.77390800
 C 4.34068100 2.43839100 -1.90625800
 C 0.55589500 2.82455500 0.83634300
 C -0.07302600 1.90096600 2.97178000
 C -0.43188900 2.56476200 1.79311100
 C -4.01524500 0.00502100 0.91399800
 C -4.19198700 4.63313600 1.48560900
 C 1.24840900 1.50622700 3.18043400

C -1.98320600	4.35408800	2.38100600	H -4.77984300	-2.01036500	0.73804400
C -1.29149900	-3.29680000	-0.53540000	H -4.92599900	-1.09226100	-0.76573800
C 3.50658900	4.03991800	0.17783600	C -3.27262900	-0.36609000	2.20070800
C -3.16382200	5.08244000	2.30979200	H -2.98811700	0.52586200	2.78100100
C -2.04398300	-4.07055500	0.36759700	H -3.93026000	-0.97685200	2.83852500
C -3.16737900	-4.77246100	-0.06109500	H -2.36111200	-0.94914000	2.00246400
C -3.55067700	-4.69867500	-1.39435700	C 3.49383900	-2.30564100	-1.55457200
C -2.82153800	-3.94825800	-2.31286200	H 2.50688000	-2.51308700	-1.11033100
C -1.69419600	-3.25793600	-1.88426000	H 3.41514800	-2.40833600	-2.64720400
C 1.06975500	-2.63955700	1.89908600	H 4.18466300	-3.08980000	-1.20680900
C 1.37947400	-1.96349900	3.09200500	C 4.34991000	-0.93894700	0.35385900
C 1.90865900	-3.68270800	1.47339800	H 5.16553500	-1.65219100	0.55044200
C 3.04358300	-4.01972700	2.20860500	H 4.68647700	0.05039400	0.70186600
C 2.51741500	-2.28612800	3.81984700	H 3.48419300	-1.23765800	0.96022700
C 3.34316100	-3.31175300	3.36588400	C 5.30858500	-0.61488500	-1.91371100
F 4.44322000	-3.62975600	4.06910600	H 6.01333700	-1.45277200	-1.79361600
F -4.63837600	-5.36909200	-1.81122900	H 5.15368100	-0.48270000	-2.99334400
C -4.92788300	1.53496200	-2.01995500	H 5.81478000	0.27928100	-1.52549800
H -5.12371300	1.71502500	-3.08921100	C 1.08151600	1.66080400	-3.10007300
H -5.44956000	0.60519900	-1.75854400	H 0.45129200	1.68673200	-4.00355800
H -5.41120600	2.35882300	-1.47933000	H 0.40976400	1.72284100	-2.22709600
C -2.87925500	0.30777200	-2.67836200	H 1.71625000	2.55839300	-3.10888600
H -1.78293600	0.27361400	-2.66101100	C 2.87581300	0.30704800	-4.23043000
H -3.24099800	-0.68239500	-2.36657500	H 2.31971300	0.38581800	-5.17849700
H -3.20128800	0.46870200	-3.71950300	H 3.60397400	1.12831400	-4.23012700
C -2.75496600	2.75048000	-2.24675600	H 3.42556100	-0.64431300	-4.26710100
H -2.87087200	2.87767400	-3.33481500	C 0.91220200	-0.80435400	-3.19902600
H -3.19201300	3.63422700	-1.76130300	H 0.13251200	-0.76238500	-2.42440200
H -1.67612000	2.75106900	-2.03012700	H 0.40446500	-0.74325100	-4.17494800
C -5.33890300	0.66653500	1.28824000	H 1.38933800	-1.79052000	-3.13217400
H -5.97671500	-0.07827600	1.79011800	H 4.68556700	1.82173100	-2.73647000
H -5.20659900	1.49894800	1.99291200	H 5.67019900	4.04737700	-2.44330500
H -5.90698900	1.03537600	0.42339200	H 4.91628200	5.50013300	-0.54889600
C -4.27623600	-1.26385100	0.10435900	H 3.17018300	4.66894800	1.00642800
H -3.34296200	-1.72318300	-0.24934500	H 3.25337300	1.44121300	2.38501700

H	1.52468700	1.00101100	4.10931300	C	4.35932900	-3.29581900	0.60319200
H	-0.83091400	1.71452100	3.73809800	C	-4.49484500	-2.53831100	-1.61026500
H	0.28664000	3.35887600	-0.08095200	C	-0.32611900	-3.10172800	0.71097300
H	-1.16322500	4.70932800	3.01104700	C	0.38727200	-2.12147000	2.79577100
H	-3.27568000	6.00182300	2.88919400	C	0.69606000	-2.81710200	1.62255200
H	-5.12643000	5.19249100	1.40219300	C	4.07061300	0.13778800	0.92795400
H	-4.84775100	3.10604300	0.15183200	C	4.59363900	-4.57075900	1.10389000
H	1.65413700	-4.22374200	0.55946200	C	-0.91646800	-1.69389600	3.03273500
H	3.70345500	-4.83154400	1.89433700	C	2.32782700	-4.63120800	1.90180900
H	2.77363900	-1.75912200	4.74168200	C	1.08731200	3.33129900	-0.67496900
H	0.70422500	-1.17421300	3.43095100	C	-3.13661500	-4.33865000	-0.02306600
H	-1.73001600	-4.10807200	1.41276200	C	3.56731700	-5.24469000	1.76092500
H	-3.75488800	-5.38037600	0.63011600	C	1.72564700	4.27989500	0.14750100
H	-3.14583500	-3.91658100	-3.35499800	C	2.64343300	5.18071000	-0.38718500
H	-1.11284800	-2.66576100	-2.59503000	C	2.92612800	5.14149600	-1.74660000
L ^{tiBu} Cr(η^2 -Ar ^p FN=NAr ^p F) S = 1				C	2.30284900	4.22087900	-2.58559000
Cr	0.06878500	0.59713400	0.08808200	C	1.38553100	3.32410100	-2.05183800
P	-2.76966200	-0.38873300	-1.16637400	C	-0.87575800	2.54902000	1.97559800
P	2.91354800	-0.99737400	-0.00202000	C	-1.10557500	1.90831700	3.20772700
N	1.45061000	-0.45533700	0.13002800	C	-1.71777400	3.60953800	1.59874500
C	-2.34533200	-0.35092400	-3.00705800	C	-2.77693500	3.99930300	2.41766700
C	3.33500800	-1.18530500	-1.82905200	C	-2.16461600	2.28801700	4.02179600
N	0.20626700	2.13191100	1.20195500	C	-2.99600100	3.32975100	3.61396700
C	-4.10149600	0.81307000	-0.65964500	F	-4.02111800	3.69916600	4.40335900
N	0.15467300	2.44464100	-0.16829500	F	3.81233900	6.00900900	-2.26731600
C	-3.39866000	-2.07800000	-0.85937600	C	4.82227800	-1.19947700	-2.17338000
C	-4.90634800	-3.86604100	-1.57832000	H	4.93501500	-1.31887500	-3.26256300
N	-1.46399500	-0.08067700	-0.36566900	H	5.32483300	-0.25982100	-1.90657100
C	2.07159100	-3.34465400	1.40000400	H	5.37511300	-2.02926600	-1.71340500
C	-2.72401300	-2.99601200	-0.01876200	C	2.67279900	-0.02116800	-2.57162800
C	-1.91733500	-1.93916900	2.09943900	H	1.58503300	-0.00430000	-2.41378200
C	-1.62971500	-2.64355000	0.92430300	H	3.05837600	0.96030500	-2.26354400
C	3.11382600	-2.65662000	0.73706300	H	2.86593400	-0.12888000	-3.65073500
C	-4.20727100	-4.77864000	-0.79291000	C	2.67905800	-2.49031500	-2.28765300
				H	2.69471200	-2.54589900	-3.38721300

H	3.19501900	-3.38079900	-1.90179700	H	-0.57586800	0.86196900	-2.57722300
H	1.62674300	-2.54599500	-1.97034500	H	-1.05503200	0.79840000	-4.29471500
C	5.49505300	-0.37559100	1.12249800	H	-1.95157700	1.81694100	-3.15593100
H	6.08901500	0.41105500	1.61363900	H	-5.04012200	-1.84603100	-2.25152600
H	5.53612700	-1.25670300	1.77727700	H	-5.76332900	-4.18569600	-2.17525100
H	6.01041600	-0.61922800	0.18298000	H	-4.50353600	-5.82981300	-0.76713900
C	4.08995600	1.48577300	0.20869300	H	-2.60243100	-5.04284500	0.62049100
H	3.07621900	1.84768400	-0.01491700	H	-2.93654600	-1.59209800	2.28563300
H	4.56175100	2.24104800	0.85582600	H	-1.15744700	-1.16042400	3.95507500
H	4.66564000	1.46152100	-0.72809600	H	1.17560700	-1.91649600	3.52509000
C	3.41761300	0.31370000	2.30327500	H	-0.09369600	-3.66129200	-0.20171700
H	3.31667800	-0.64621700	2.83408900	H	1.51710300	-5.15346500	2.41669700
H	4.05274900	0.96479900	2.92325700	H	3.73044100	-6.24728200	2.16314800
H	2.42240100	0.77595100	2.23038300	H	5.57485500	-5.03424700	0.97988000
C	-3.65616400	2.20525200	-1.10634900	H	5.17375100	-2.78408600	0.09027500
H	-2.59889600	2.39677800	-0.86165900	H	-1.52970400	4.12428100	0.65346900
H	-3.80128900	2.35810300	-2.18561500	H	-3.43547700	4.82556800	2.14001400
H	-4.25625400	2.96809700	-0.58649500	H	-2.35659800	1.79329300	4.97657100
C	-4.12450100	0.75325800	0.86987000	H	-0.43251500	1.09869000	3.50125400
H	-4.85280800	1.48366400	1.25429600	H	1.49438300	4.28936600	1.21495100
H	-4.43316400	-0.23995200	1.23161600	H	3.14418600	5.91984000	0.24165800
H	-3.14432900	0.99233700	1.30665900	H	2.54491800	4.22035200	-3.65032400
C	-5.50305700	0.50939000	-1.18191900	H	0.89577100	2.58734100	-2.69340600
H	-6.17968800	1.32261200	-0.87585700	L ^u BuCr(NAr ^p -F) ₂ S = 0			
H	-5.56020900	0.44485400	-2.27740000	Cr	0.33673200	-0.49058400	-0.04848100
H	-5.91413300	-0.41750000	-0.75866700	P	1.78345700	2.34922000	-0.76453200
C	-1.52567000	-1.62273100	-3.25118300	P	-2.78969000	-1.22491300	-0.55590500
H	-1.04804000	-1.57078300	-4.24212200	N	0.83841500	1.18861300	-0.35135800
H	-0.72529900	-1.72567400	-2.50130700	N	-1.43535900	-0.54657800	-0.21963500
H	-2.13775100	-2.53559000	-3.22530700	C	1.85035200	2.47017800	-2.65235000
C	-3.52602500	-0.28288200	-3.96982500	C	-4.17128000	-0.25209700	0.14123100
H	-3.14476500	-0.28219900	-5.00331300	C	1.10831100	3.95018900	-0.19268500
H	-4.20985000	-1.13830100	-3.89400700	C	-1.95725900	2.40115300	0.77856700
H	-4.10848800	0.64175500	-3.85149700	C	-3.95803000	0.88851900	0.95010500
C	-1.43667200	0.85351900	-3.26293600				

C -0.74339900	2.89571200	1.26749800	H -3.77129500	-3.28731200	-2.78100200
C 3.47374000	2.16347100	0.01731500	H -5.09282100	-2.11410600	-2.57340900
C -2.63303800	1.36852500	1.43811100	C -4.28127100	-3.58180200	0.18167900
C -5.07466600	1.63365300	1.36455400	H -4.21182400	-4.58450300	0.63295800
C -0.05592300	4.04113900	0.60684500	H -5.01566100	-3.01891900	0.77443900
C -3.06655200	-1.23821800	-2.42469200	H -4.68818700	-3.71800900	-0.82937700
C -6.37199700	1.27630200	1.01493000	C -1.87225500	-3.83032600	-0.47547200
C -2.11100100	0.87069400	2.63748200	H -2.16640700	-4.10862500	-1.49772200
C 1.69732600	5.13795800	-0.65861200	H -0.87828400	-3.35903600	-0.51981600
C -0.24001800	2.38723700	2.47081300	H -1.76635900	-4.76676200	0.09410500
C -0.92102900	1.38135700	3.14803800	C -2.48591800	-2.71675700	1.66605900
C 1.15634200	6.38903300	-0.38572500	H -3.18938600	-2.05514800	2.19539800
C -0.59811400	5.31325700	0.85551100	H -2.48072600	-3.68309200	2.19413900
C -6.58376000	0.14409800	0.23273300	H -1.48174200	-2.27476700	1.74018100
C -2.90132700	-2.92972600	0.20781000	C -3.48365300	0.18261700	-2.81131500
C -5.49050500	-0.60049700	-0.19534000	H -3.43112700	0.29935300	-3.90505400
C -0.01267700	6.47525800	0.36579000	H -4.50990200	0.42254700	-2.49992900
N 1.04834200	-1.50688400	-1.16503100	H -2.81068600	0.93211700	-2.36621400
N 0.79817800	-0.95002800	1.48305000	C -1.70309500	-1.52232600	-3.06327100
C 2.84939600	-1.67420900	2.53526500	H -0.96278000	-0.75828700	-2.79486300
C 1.44762200	-1.45881300	2.55353100	H -1.28048000	-2.49262600	-2.76930100
C 0.74831100	-1.77799500	3.74471300	H -1.81388900	-1.52674600	-4.15942600
C 2.78946900	-2.47856900	4.79482800	C 0.51310000	3.08009000	-3.08262400
C 3.51391200	-2.17935000	3.64474800	H 0.43402600	4.14881100	-2.83895200
C 1.41307100	-2.28290200	4.85459200	H 0.39422900	2.97801800	-4.17267500
C 1.81367600	-2.54010200	-1.58892100	H -0.33366900	2.55948800	-2.60757200
C 2.38397400	-3.47474400	-0.68813100	C 3.00890200	3.25120700	-3.26689100
C 2.05613500	-2.72113900	-2.97297200	H 3.98469900	2.79281600	-3.05212300
F 3.43203200	-2.96337200	5.86749300	H 2.89856500	3.24746400	-4.36343300
C 3.38788800	-4.66266700	-2.51581500	H 3.05060200	4.30621600	-2.96627100
C 3.16525900	-4.52588100	-1.14790100	C 1.90555900	1.03480600	-3.18207400
C 2.83924600	-3.77197100	-3.43299800	H 2.82530200	0.50637000	-2.89754800
F 4.14185500	-5.67871200	-2.96023900	H 1.06404900	0.43156700	-2.81994800
C -4.07574700	-2.24740600	-2.96513000	H 1.86860400	1.05820500	-4.28292600
H -4.14815800	-2.13206000	-4.05864900	C 4.12537700	0.90395300	-0.55347300

H	4.48873500	1.04688800	-1.58140200	P	-2.92561700	-1.17975300	-0.62838800
H	4.99915400	0.62926700	0.05822600	N	1.14639700	0.65660300	-0.13306800
H	3.43600600	0.04455000	-0.55120800	N	-1.52204100	-0.57736700	-0.31060400
C	4.40379500	3.36388000	-0.13443500	C	1.35222100	1.55841400	-2.86414600
H	4.01056000	4.25575000	0.37316400	C	-4.23976800	-0.01374400	-0.12072800
H	5.37080100	3.13175000	0.33980900	C	1.34495800	3.42579100	-0.63808800
H	4.61771400	3.62889200	-1.17825300	C	-1.83901600	2.34759600	0.46908600
C	3.18814400	1.95690900	1.50673000	C	-3.99263200	1.09497400	0.72293700
H	2.74887100	2.85974000	1.95742000	C	-0.58917300	2.75926700	0.93486400
H	2.49841700	1.11958400	1.68564900	C	3.70652800	1.59969300	-0.79201500
H	4.12891800	1.74795500	2.04002500	C	-2.65102700	1.49910000	1.23212800
H	-5.67299400	-1.47712700	-0.81853500	C	-5.07865400	1.89487600	1.11417800
H	-7.59516400	-0.15762200	-0.04868300	C	0.22971600	3.74075700	0.17041300
H	-7.21604700	1.88013700	1.35654500	C	-3.11528400	-1.44335900	-2.49133600
H	-4.90241100	2.51558300	1.98738600	C	-6.37680700	1.63425100	0.68986700
H	-2.36317400	2.79828600	-0.15774000	C	-2.22066000	1.11070300	2.50365700
H	0.69013000	2.78867000	2.87978500	C	2.06196800	4.47995200	-1.22947400
H	-0.51903900	0.99411600	4.08769500	C	-0.16352200	2.33985900	2.20286100
H	-2.64450300	0.07875200	3.17049900	C	-0.97912800	1.52843600	2.98149600
H	2.60121700	5.08604700	-1.26652400	C	1.69916700	5.81075200	-1.05919000
H	1.64208000	7.29012100	-0.76699700	C	-0.13421100	5.09009200	0.31659400
H	-0.46339200	7.44706500	0.58081700	C	-6.61962800	0.55033300	-0.14987900
H	-1.50157300	5.37519300	1.46820600	C	-3.27532100	-2.73522700	0.35713100
H	2.19007800	-3.35279900	0.38066200	C	-5.55774100	-0.25772400	-0.53977600
H	1.61133700	-2.01247600	-3.67574300	C	0.58071600	6.11745700	-0.28813000
H	3.03164400	-3.91628700	-4.49791700	N	0.94972800	-2.16378900	-0.76182400
H	3.60694300	-5.24944700	-0.45984700	N	0.30188400	-1.46357300	1.76306400
H	-0.33149900	-1.61580200	3.77437100	C	2.00418800	-0.21286700	2.97506200
H	0.87809400	-2.52970700	5.77379200	C	0.93687800	-1.16057500	2.89965800
H	4.59271200	-2.34707900	3.63446300	C	0.53409900	-1.78680900	4.12044600
H	3.40127700	-1.43286500	1.62305400	C	2.18176300	-0.54562600	5.34059400
L ⁿ BuCr(NAr ^p -F) ₂ S = 1				C	2.61616200	0.09291000	4.17672900
Cr	0.19757800	-0.85388600	0.08181500	C	1.14845200	-1.48429500	5.32310200
P	1.83764400	1.71350700	-1.05264200	C	2.13699900	-2.78548300	-0.94186100
				C	3.05803500	-2.99709700	0.11874700

C	2.48984600	-3.28148900	-2.22504000	H	2.96843500	2.68542800	-3.86966500
F	2.76805300	-0.24747900	6.50458700	H	1.53100700	2.37588900	-4.84450900
C	4.58135900	-4.09212900	-1.37632100	H	1.47994500	3.62218900	-3.59930700
C	4.25876300	-3.65772300	-0.09296500	C	1.78221000	0.16879400	-3.33183100
C	3.70960200	-3.90657700	-2.44579000	H	2.87376200	0.07754200	-3.43686800
F	5.75334800	-4.70996000	-1.58491400	H	1.44149900	-0.61738100	-2.64069800
C	-4.13394600	-2.48678500	-2.94410700	H	1.34352800	-0.04568600	-4.31968500
H	-4.14196700	-2.52162200	-4.04548800	C	4.02430500	0.11888600	-0.57148200
H	-3.87989600	-3.49873000	-2.60007700	H	3.76144800	-0.50939300	-1.43501000
H	-5.16534100	-2.27054200	-2.63478200	H	5.10499000	-0.00058400	-0.39612000
C	-4.69950400	-3.27919700	0.26387200	H	3.49363400	-0.28941200	0.29697400
H	-4.76822700	-4.18784700	0.88315000	C	4.59543900	2.10077700	-1.92879300
H	-5.44107500	-2.57328700	0.66264100	H	4.46405200	3.16357900	-2.17122400
H	-5.00617700	-3.56629400	-0.74982000	H	5.64991200	1.97854700	-1.63374300
C	-2.26904900	-3.80439200	-0.06825000	H	4.46030300	1.52061400	-2.85225800
H	-2.47704300	-4.20157300	-1.07298400	C	4.02610600	2.36627700	0.49385200
H	-1.23188800	-3.43534100	-0.05417500	H	3.96746300	3.45581000	0.36357700
H	-2.32252900	-4.65494700	0.62912300	H	3.34078600	2.09536800	1.31187000
C	-3.01133100	-2.33739000	1.81214500	H	5.04818400	2.12568000	0.82575400
H	-3.72953700	-1.57844900	2.15947800	H	-5.76186700	-1.10802600	-1.19310600
H	-3.13627400	-3.22126500	2.45789600	H	-7.63133900	0.33133500	-0.49864300
H	-1.99057400	-1.95321200	1.95479600	H	-7.19706400	2.28003400	1.01217300
C	-3.46481300	-0.08361000	-3.10261600	H	-4.88075300	2.74791800	1.76895300
H	-3.30936900	-0.11379100	-4.19281000	H	-2.17962500	2.66581900	-0.52202200
H	-4.51111700	0.20126600	-2.92573200	H	0.81427500	2.65860900	2.57620000
H	-2.83077500	0.72113400	-2.70136900	H	-0.64137800	1.20951200	3.97134200
C	-1.73571000	-1.87419500	-3.00147600	H	-2.85577100	0.46723300	3.11814100
H	-0.97101000	-1.11124900	-2.81224800	H	2.93078600	4.25390400	-1.84918200
H	-1.37560800	-2.79974900	-2.53101800	H	2.28498000	6.60206600	-1.53220800
H	-1.79101000	-2.04414000	-4.08855200	H	0.27119900	7.15590100	-0.14829100
C	-0.17607800	1.63739400	-2.84537700	H	-1.00128400	5.32450900	0.93997800
H	-0.52848000	2.64991400	-2.59181800	H	2.79156900	-2.63493400	1.11510000
H	-0.57348100	1.39180300	-3.84368900	H	1.78262700	-3.14024900	-3.04648400
H	-0.61760200	0.93795100	-2.11834400	H	3.99425900	-4.26989700	-3.43533000
C	1.87405900	2.62230900	-3.82636200	H	4.96414300	-3.83313600	0.72180700

H -0.28061300	-2.51341300	4.07696000	C -3.91011300	-3.63463500	0.42547000
H 0.84623100	-1.95742500	6.25941800	C 2.67585200	-5.12825100	2.44232300
H 3.42474600	0.82480900	4.24255000	C 2.00528600	2.77736900	-1.85341200
H 2.28505600	0.28784200	2.04493300	C 2.90990500	3.58684300	-2.52376300
L ^t BuCr(η^2 -Ar ^p -FN=NAr ^p -F) $\rightarrow$ L ^t BuCr(NAr ^p -F) ₂ Transition			C 2.91527500	4.95450200	-2.25970100
state S = 1			C 2.02416400	5.52834900	-1.35211100
Cr 0.10058400	0.68290600	0.05906400	C 1.10714900	4.71809900	-0.70311600
P -2.72372100	-0.06319500	-1.28326900	C -0.07307900	2.29853100	2.45112800
P 2.60877400	-1.40264300	-0.33296500	C 0.57781900	2.45642500	3.69680500
N 1.31785200	-0.54638300	-0.47031500	C -1.43069800	2.69161200	2.35308100
C -2.03845300	-0.18156200	-3.03739900	C -2.11205700	3.18321500	3.45319600
C 3.11547900	-1.94048600	-2.08337300	C -0.11024000	2.92640400	4.81029600
N 0.61534700	1.71749200	1.42629700	C -1.44685400	3.28520900	4.67580600
C -4.07128900	1.22644700	-1.08754300	F -2.11113100	3.75275700	5.74030400
N 0.10190100	2.56628800	-0.33858200	F 3.79557500	5.74009300	-2.89546300
C -3.55635300	-1.65676700	-0.93365700	C 3.41978100	-0.27765200	2.01209000
C -5.25403400	-3.30825500	-1.54083600	H 2.41895000	0.17754800	1.99506900
N -1.59857700	0.22411800	-0.24421600	H 3.37427800	-1.21782800	2.58299400
C 1.48180800	-3.14959000	1.64245200	H 4.08420700	0.40666600	2.56351400
C -3.21145600	-2.44011600	0.19263300	C 5.32112900	-1.19705400	0.71590600
C -2.32344400	-1.28835800	2.25700500	H 5.82445400	-1.35267000	-0.24550300
C -2.11176200	-2.10503000	1.13892400	H 5.99151600	-0.56734400	1.32269800
C 2.47820600	-2.94285500	0.66237100	H 5.25419100	-2.16340600	1.23375300
C -4.92336900	-4.06867300	-0.42192000	C 4.15518200	0.86826100	-0.07050900
C 3.52702800	-3.87454000	0.58059200	H 4.48194600	0.78610800	-1.11915700
C -4.57410800	-2.11944900	-1.78427600	H 3.22855700	1.45723600	-0.04461400
C -0.84743000	-2.66039800	0.93335800	H 4.92491400	1.44720500	0.46301400
C 0.00344500	-1.51351500	2.87449200	C 2.68670900	-0.81803200	-3.03248500
C 0.21955100	-2.37365200	1.79158900	H 2.90900900	-1.11814900	-4.06884600
C 3.97303300	-0.49053600	0.59955600	H 1.61411000	-0.60348700	-2.95774200
C 3.63051200	-4.96009100	1.44285100	H 3.23101700	0.11872300	-2.84235700
C -1.26604600	-0.97971400	3.10507600	C 2.28882400	-3.18622300	-2.41428900
C 1.61692200	-4.23282000	2.52778300	H 1.22866200	-3.04863900	-2.15221400
C 1.06682500	3.31179500	-0.92720300	H 2.33680600	-3.38885500	-3.49601600
			H 2.64447800	-4.08596400	-1.89464500

C	4.59682800	-2.20438000	-2.34973600
H	5.05079200	-2.97514500	-1.71442700
H	4.71348800	-2.55092600	-3.38940900
H	5.20271400	-1.29204500	-2.25623800
C	-3.03309700	-0.00135500	-4.17993200
H	-3.45149300	1.01492100	-4.20882000
H	-2.51257500	-0.15350000	-5.13908400
H	-3.86586000	-0.71689900	-4.16212300
C	-0.94926600	0.88731100	-3.17185500
H	-0.11181800	0.69947400	-2.48515200
H	-0.53933100	0.85949700	-4.19409400
H	-1.30172000	1.90970300	-2.98068400
C	-1.36195100	-1.55245600	-3.11812100
H	-2.08157100	-2.38292200	-3.15252800
H	-0.74266200	-1.61013200	-4.02808900
H	-0.69243200	-1.70719300	-2.25499900
C	-5.34464800	1.01798500	-1.90274100
H	-5.90492400	0.12811300	-1.58464900
H	-6.01228600	1.87979200	-1.74291600
H	-5.17271100	0.94844400	-2.98423600
C	-3.44345100	2.58007700	-1.42290800
H	-4.10495100	3.39263000	-1.08345000
H	-2.46154800	2.71473000	-0.94022300
H	-3.30895900	2.71148200	-2.50685600
C	-4.44783500	1.18462300	0.39594400
H	-3.57617500	1.32108400	1.04895900
H	-5.17263900	1.98457800	0.61451500
H	-4.92290900	0.22920300	0.66838100
H	-4.84699400	-1.53715500	-2.66573700
H	-6.04009000	-3.63763700	-2.22418200
H	-5.44982700	-5.00283800	-0.21208500
H	-3.63614600	-4.23239400	1.29901700
H	-3.31386800	-0.86153900	2.43579700
H	-1.42696700	-0.31088700	3.95494200
H	0.82917400	-1.27644900	3.55188500

H	-0.68173100	-3.32397100	0.07787500
H	0.84352200	-4.37532800	3.28753800
H	2.74546700	-5.96337200	3.14330600
H	4.46019700	-5.66319500	1.33978900
H	4.30024400	-3.74394400	-0.17691700
H	-1.91374100	2.60576500	1.37745200
H	-3.15894700	3.48818500	3.38943600
H	0.37719400	3.03423300	5.78106900
H	1.63066000	2.17547400	3.77251800
H	1.98657900	1.69740800	-2.02701200
H	3.62115300	3.17932300	-3.24651700
H	2.06423900	6.60555100	-1.17750700
H	0.39285500	5.14262900	0.00660400

$\text{L}^{\text{tBu}}\text{Cr}(\eta^2\text{-Ar}^{\text{p-F}}\text{N}=\text{NAr}^{\text{p-F}}) \rightarrow \text{L}^{\text{tBu}}\text{Cr}(\text{NAr}^{\text{p-F}})_2$ Transition
state S = 0

Cr	0.07175200	0.68886300	0.13544900
P	-2.62984400	-0.14600900	-1.44927300
P	2.82958800	-1.02650200	-0.34231900
N	1.42845900	-0.33602900	-0.36120400
C	-1.90273700	-0.45477400	-3.14928000
C	3.44283100	-1.18333500	-2.13420300
N	0.41351200	1.45868300	1.66516300
C	-3.88065900	1.25672600	-1.41635800
N	-0.08711100	2.61919200	0.29828400
C	-3.51507900	-1.67977500	-1.00906400
C	-5.41115700	-3.16540400	-1.42272300
N	-1.50563800	0.19119800	-0.42098100
C	1.75008100	-3.27523600	1.10305900
C	-3.09599600	-2.51404900	0.05334300
C	-2.06442800	-1.62284000	2.15366900
C	-1.90848600	-2.27210900	0.92259300
C	2.80161600	-2.72858000	0.33223400
C	-4.99769800	-3.98798900	-0.37782700

C	3.95367100	-3.50770200	0.12788100	H	3.06212100	1.79332100	0.38718000
C	-4.67218200	-2.02763300	-1.72622900	H	4.70848500	1.90972700	1.03069900
C	-0.65068600	-2.77614300	0.57647100	C	2.87528100	0.01862500	-2.89406400
C	0.27401300	-1.96478200	2.65046200	H	3.13918000	-0.07123400	-3.95953700
C	0.45126300	-2.61573100	1.42387300	H	1.78239700	0.08110200	-2.81154500
C	4.02667000	-0.12818500	0.79029800	H	3.29373300	0.96923800	-2.53444500
C	4.09418100	-4.78447800	0.65757300	C	2.82577000	-2.45688000	-2.71967500
C	-0.97751800	-1.46842300	3.00762500	H	1.75731800	-2.54656000	-2.47465900
C	1.91309800	-4.56573900	1.63732100	H	2.90948600	-2.43497600	-3.81771000
C	0.72303700	3.49376400	-0.35966900	H	3.32225800	-3.37208600	-2.37144300
C	-3.85629100	-3.65834100	0.34482100	C	4.95395000	-1.18608100	-2.35614700
C	3.06268000	-5.31701500	1.42568900	H	5.48848900	-2.00273700	-1.85362600
C	1.62565500	3.12028500	-1.39309300	H	5.15288800	-1.30106900	-3.43376700
C	2.31674700	4.06683100	-2.13789900	H	5.41913000	-0.23853600	-2.05069200
C	2.14797700	5.41574700	-1.84097000	C	-2.88261300	-0.95529800	-4.20794900
C	1.29598300	5.83448700	-0.81848400	H	-3.72085700	-0.27239800	-4.39527200
C	0.59713600	4.88625800	-0.08832900	H	-2.34626800	-1.06908200	-5.16340600
C	-0.35255800	1.78128800	2.76268800	H	-3.29181900	-1.94378400	-3.95831600
C	0.27149800	1.93590600	4.01500400	C	-1.22589600	0.83275300	-3.61792500
C	-1.75986000	1.87777100	2.69698000	H	-0.56603300	1.25770400	-2.84298100
C	-2.51373300	2.10886400	3.83647000	H	-0.60461700	0.62311700	-4.50279000
C	-0.48043500	2.15082400	5.16774600	H	-1.95151600	1.60586600	-3.90977100
C	-1.86321800	2.23739000	5.06380400	C	-0.84019100	-1.53208600	-2.92465300
F	-2.59312800	2.44352000	6.16878700	H	-1.29028000	-2.48886000	-2.61604800
F	2.82978900	6.33473600	-2.54470800	H	-0.29803300	-1.71378500	-3.86667500
C	3.38869600	-0.21839700	2.18019000	H	-0.11005000	-1.23206700	-2.15690800
H	2.34381000	0.12458700	2.17350700	C	-4.76863400	1.40109600	-2.64899900
H	3.42628200	-1.24353700	2.57975800	H	-5.38521300	0.51775100	-2.86353200
H	3.94905000	0.42389400	2.87794200	H	-5.46863700	2.23608300	-2.48719000
C	5.44326700	-0.68971100	0.87770300	H	-4.19264000	1.64729700	-3.55197100
H	6.00676000	-0.62793100	-0.06070900	C	-3.08423300	2.55378300	-1.23462600
H	6.00524200	-0.10182500	1.62085400	H	-3.79163400	3.39374000	-1.15331900
H	5.46316400	-1.73075000	1.22867100	H	-2.45193600	2.54561400	-0.33689200
C	4.06051600	1.33501300	0.35125000	H	-2.41960300	2.77062300	-2.08215700
H	4.46170700	1.46986100	-0.66545300	C	-4.74423000	1.03488800	-0.17192600

H -4.12841900 0.84079800 0.71980500
H -5.33920500 1.93887700 0.02988500
H -5.44442600 0.19505700 -0.28514600
H -5.01244500 -1.38745500 -2.54185200
H -6.30738000 -3.40538200 -1.99910300
H -5.56610000 -4.88524100 -0.12189400
H -3.53010500 -4.29817400 1.16913200
H -3.04432800 -1.22626700 2.43556100
H -1.10533500 -0.94683700 3.95984700
H 1.12233600 -1.84812000 3.32999600
H -0.52055700 -3.29852800 -0.37656300
H 1.09688500 -4.97936900 2.23580000

H 3.14991200 -6.31694900 1.85712300
H 5.00522300 -5.35725100 0.47056600
H 4.77081800 -3.10461500 -0.47182000
H -2.23376300 1.74886700 1.72100100
H -3.60311600 2.17987100 3.80027800
H -0.00977700 2.26171800 6.14631200
H 1.36040600 1.87047100 4.06888000
H 1.75340100 2.05326900 -1.59021300
H 2.99694600 3.77934200 -2.94400500
H 1.19530700 6.90293100 -0.61582800
H -0.08394600 5.19053400 0.71006100

Chapter 4

LCrphthal_S1

Cr -0.04999703099125 -0.27516552580689 0.20012450792815
N -1.34989014964886 -0.61244716833090 -1.02528440278416
N 1.59383713428465 -0.60582715676881 -0.47102951715439
P -2.60893750770591 -0.66127907085706 -1.91362010197055
P 3.05121914826277 -0.73372478032192 -0.95375346275070
N 0.30124159819036 0.33442316746291 2.06179326626790
N -1.01262314296027 0.21093317679440 1.90117095377648
C 0.83049113054964 0.77634188926952 3.19566873333048
C -1.85941335558858 0.51657190990452 2.87575487994319
C -1.39788041180447 0.98116704805475 4.14807086671560
C 0.00909174548245 1.12200359231679 4.31370334575827
H 1.90965713933920 0.84093715836801 3.23109536152056
H -2.91081972079409 0.37720836489149 2.66368018383354
C -3.80276657604381 0.62972131106983 -4.10202371499724
H -4.45954883818382 -0.23798002906305 -4.11775373613396
C 1.55695163688792 2.09814582419204 -1.68893491655659
C -2.79893993260169 0.71651912573032 -3.12287504957525
C 0.48848343674330 1.82144542435801 -2.54835793261208
H 0.68466744897511 1.35506638729625 -3.51592542052101

C 3.73703856921353 0.72518756106513 -1.84846399967504
C -3.13448831708267 2.71568409432768 -5.08751149059063
H -3.25268226128963 3.49354611513034 -5.84068344597679
C 1.29278542421303 2.69717848397746 -0.45050435639586
H 2.11863694028480 2.92121584132776 0.22585345954436
C 3.11309931204281 -2.12598110188048 -2.21808659786464
C 4.41344306202469 -2.32074537379559 -2.99263416527233
C -1.94526907357832 1.84245255865205 -3.13835533822598
C -3.86241146876977 -2.85912775359177 -3.38663025079648
C 5.07293630489369 0.70126640173029 -2.28501954144158
H 5.68905125354016 -0.17008129190625 -2.07732714401115
C -2.53165322520321 -2.23417188857970 -2.97135559836394
C -3.98059205001390 1.60920356891136 -5.07341391088501
H -4.77035563130171 1.50443213813814 -5.81605019794122
C 4.19651977471169 -0.99951022233449 0.52154954669804
C -2.13170226463540 2.82014939236036 -4.12975929082944
H -1.46543496770299 3.68322964917164 -4.13353876481004
C -1.07634371763718 2.69703913902564 -0.93611351295085
H -2.09857895153617 2.93164591930509 -0.64117934760015
C 5.64633464596757 1.75855512454650 -2.98374087727285

H	6.68639030245415	1.70114680472244	-3.30191464419297	H	5.28214010276102	-2.50708285470338	-2.35156349303410
C	2.96592693711166	1.87676003399080	-2.12566966597439	H	4.64218089148527	-1.46890202044800	-3.64154664346156
C	3.42260878003735	-1.84600896396041	1.53691092509654	H	1.87022741899469	-2.57932285185891	-3.93653659623452
C	-4.16450000544418	-0.55412548488359	-0.85958656897766	H	2.23051872977356	-0.85291741162127	-3.76692086655116
C	4.87645817571488	2.88277217256832	-3.27212183825567	H	1.04531478354870	-1.61075030441321	-2.68595606333809
H	5.30298492583610	3.72043463531169	-3.82231703505964	H	-1.66063802002599	-4.19297515488257	-2.71968806670289
C	3.55495233206994	2.93179249862955	-2.84220310390857	H	-2.27601224016774	-3.51526221064240	-1.20256494226883
H	2.94860530712200	3.81347833928671	-3.05137416917769	H	-0.76474560868659	-2.90860628984429	-1.87162902528240
C	-0.83322960944956	2.09232954378733	-2.17607287865326	H	-3.66265197350019	-3.74807508034821	-4.00115968331933
C	5.53267439507954	-1.68269419096319	0.23975143770629	H	-4.49415781742437	-2.20138620279856	-3.99222730021533
C	-0.01749330494290	2.99428375223126	-0.07980727539126	H	-4.45068896214398	-3.19947703429942	-2.52704531643056
H	-0.21607550910033	3.45002386417449	0.89056792732075	H	-1.38935050226128	-2.83757734912263	-4.70922113398337
C	-1.76346410266438	-3.26613787206193	-2.13875988648129	H	-0.79939224139168	-1.34194141461472	-3.97234818154848
C	4.43166510312801	0.38601934614408	1.12996611076474	H	-2.26945960560129	-1.32234374209893	-4.95595872274010
C	1.99792786253726	-1.76821759015156	-3.20581315593836	H	-3.07187854151527	0.85812138303446	0.40848669930712
C	0.51248345072168	1.57767238477332	5.52923361855527	H	-4.83622709569605	0.86705561854789	0.63059019634725
H	1.59030760034753	1.68337107871766	5.65195747938039	H	-4.12258027517623	1.62992249583369	-0.79605453110629
C	-0.35556236743403	1.89689413919772	6.58679627407461	H	-4.28618583186441	-2.68009765401429	-0.32621728468091
H	0.05235695480971	2.25253890457000	7.53205564566319	H	-4.89111547839484	-1.57329043155016	0.90726493753749
C	2.73899983324280	-3.42145436939201	-1.49684572259240	H	-3.14188662144413	-1.74502263107099	0.65764314228249
C	-1.70683734075320	-1.90665412556839	-4.21987675021028	H	-5.69469558223765	-1.45228811791947	-2.17658645059993
C	-2.24696306088336	1.29767651343650	5.20447432283486	H	-5.61636654865957	0.31945473913599	-2.24622610304204
H	-3.32314781818940	1.18619205082573	5.07267814369673	H	-6.31299158149856	-0.48320230791472	-0.84550280743430
C	-1.72664131479262	1.75731004064800	6.42612208855015	H	4.90511607926912	0.28552450182214	2.11603777885281
H	-2.40273720553473	2.00314306130942	7.24387888649971	H	3.48419536769115	0.92297480130580	1.27115031627261
C	-4.11070471662639	-1.70536656678332	0.14533209789188	H	5.08438046367279	1.01316115749001	0.51199880790323
C	-5.50609464652733	-0.54959546036563	-1.58859320195607	H	5.40822468762691	-2.69780673381461	-0.15412354299682
C	-4.03202935815154	0.77570219736497	-0.11253228450149	H	6.09336037654358	-1.77813851875079	1.18001474157709
H	2.52634076842061	-4.20760316611374	-2.23406353946271	H	6.17710962041630	-1.12474072870107	-0.44685320527298
H	1.84308158890108	-3.29161234255465	-0.87820046147389	H	3.21158348800945	-2.85596044644873	1.17031269574261
H	3.54906857492903	-3.79318420134499	-0.85773364006864	H	2.46525109363630	-1.38670838903189	1.80118957463436
H	4.31080393977260	-3.19677885946893	-3.64804993155940	H	4.02145784198529	-1.94728598847576	2.45215084623095

LCrphthal_S2

Cr -0.05963852424352 -0.52781416263667 0.32567155759380
 N -1.30538517707875 -0.79497964575731 -1.00748937551660
 N 1.65231876134295 -0.76119171161751 -0.28314436124062
 P -2.54573005200918 -0.80703499002548 -1.91498227413499
 P 3.05216135327596 -0.83494093365708 -0.90501133831485
 N 0.21268365487071 -0.00533671691031 2.27757420108303
 N -1.11557278943850 -0.06985960044906 2.10624470010294
 C 0.74797216596938 0.71498534039773 3.25392345713926
 C -1.92858733255247 0.58249480506654 2.92050035934706
 C -1.45472940289968 1.38920426865213 3.98986008168829
 C -0.04329638988119 1.46045737694651 4.16280428117331
 H 1.82951063238420 0.71220748907570 3.30555320821423
 H -2.98775904169565 0.47771657965959 2.72115057781272
 C -3.76493441569094 0.64658752964966 -3.99039507774589
 H -4.36574179431657 -0.25150142454217 -4.12410577739000
 C 1.49249062906973 2.02109473185280 -1.36214076429682
 C -2.77926384429427 0.67200395155184 -2.98989005831892
 C 0.42992872935246 1.79849890101282 -2.24375409297835
 H 0.63492007751943 1.41665190189689 -3.24582829383279
 C 3.70201775595871 0.71739709396407 -1.66022205278400
 C -3.22699838420730 2.88037148136231 -4.69076334606577
 H -3.38955571914831 3.73933328213115 -5.34054160025274
 C 1.21428499245328 2.51625465498967 -0.08075597216911
 H 2.03506051985533 2.69803927338013 0.61444213728257
 C 3.04247234157423 -2.05840550097573 -2.33715178165126
 C 4.30933743176510 -2.17600206027808 -3.17968231017111
 C -1.99703089041349 1.84053900935090 -2.85205617536000
 C -3.75459518998429 -2.91817866995288 -3.54884576688589
 C 5.03150081412174 0.76221646013218 -2.11293911665163
 H 5.66670581127938 -0.11251896398092 -1.99024947136609

C -2.43822241558498 -2.28356885965859 -3.10379529934887
 C -3.99602829484389 1.72786060263718 -4.83453249131647
 H -4.76849259266100 1.66815647542145 -5.60015140149976
 C 4.31295391623034 -1.29703663013972 0.43330934981537
 C -2.24045274111363 2.92498632418026 -3.71099033846370
 H -1.63018661622295 3.82132353388180 -3.59599439115142
 C -1.15336728696762 2.53201755611856 -0.58023194254440
 H -2.17962302794783 2.73758961087396 -0.27621689659813
 C 5.57570787957146 1.89127095613003 -2.71595962652958
 H 6.61197854761800 1.88513166060294 -3.05147744184813
 C 2.90538538434750 1.87284718614204 -1.81929790402472
 C 3.56691845869588 -2.18913005591856 1.43083463188100
 C -4.12966314111706 -0.82689152266986 -0.88420493258059
 C 4.78121975677824 3.02284990768557 -2.88511222664325
 H 5.18413940628105 3.91758982459062 -3.35792953064727
 C 3.46494724445001 3.00420747558126 -2.43665171781680
 H 2.83890999088488 3.88914878030316 -2.55497117860459
 C -0.89722919717276 2.02459348626849 -1.86025895450280
 C 5.57183541138771 -2.03613436248975 -0.01654569601533
 C -0.10086182076584 2.77264298299975 0.30319699207737
 H -0.30868199053492 3.16133048522513 1.30097657616490
 C -1.62371315261388 -3.35150894843746 -2.36603964169662
 C 4.69903967685805 -0.00006741175486 1.14912508385099
 C 1.90588812626530 -1.55706739020761 -3.23259019153623
 C 0.48506649258138 2.24719030475536 5.19245409918860
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 C -0.36682122221231 2.94245248619103 6.05215793613077
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LCr_phthal_2_not_coupled_S1

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H	4.02975564559303	-3.59653600190010	-3.23842960171241	C	0.502612	1.975987	3.806914
H	5.00005495287978	-2.48878660442308	-2.27538506318299	C	-0.015052	-2.382491	3.964193
H	4.27187543713093	-1.94637345979302	-3.79970796532536	C	-0.223747	3.131554	3.443858
H	1.56964906725830	-3.22591969722458	-3.60750041549454	C	0.681488	-2.804353	2.789891
H	1.88297204162556	-1.54243425632751	-4.05415474792680	C	-0.417874	3.340768	2.037451
H	0.72476042854245	-1.90907335177415	-2.75947951056090	H	-1.336526	0.321382	2.413359
H	2.27544139578877	-4.15728723688298	-1.50926348748790	H	1.660954	0.360662	2.951673
H	1.67592199299660	-2.87338318829649	-0.43914578650981	C	-1.134550	1.292492	-3.274012
H	3.39119681470343	-3.33556659234931	-0.41792585350689	H	1.873063	3.578441	-2.326444
H	-3.74571046769960	-4.51835018507704	-1.55083978044044	C	-1.338258	2.478071	-2.553937
H	-3.77913668491615	-3.37778958650896	-2.88959486537169	H	-2.349343	2.752978	-2.258737
H	-4.97350883289056	-3.25848563766046	-1.58162236034099	C	3.409774	0.370045	-3.190880
H	-1.34462046919745	-3.99349299378039	-1.48675062324713	C	-2.297952	0.479372	-3.719538
H	-0.74894330335021	-2.41570072859850	-0.94467190896412	C	4.694406	0.146150	-3.715561
H	-1.41144188426774	-2.60233868262264	-2.58185874157248	H	5.309493	-0.650130	-3.304879
H	-2.65109686605318	-4.00719024514243	0.60426244145197	C	-3.206674	-0.203819	-2.871523
H	-4.05904932192265	-2.96913988387577	0.83465059238321	C	1.027759	2.948455	-2.605498
H	-2.42716393845241	-2.32484897898233	1.09403272618969	C	-4.607714	-0.711145	-4.819495
				H	-5.518738	-1.149848	-5.224070
TS_LCr_phthalazine_dimerization_S1				H	1.244699	-3.730981	2.790388
Cr	0.168146	0.189229	-0.005631	C	2.440632	-3.282380	-1.170608
N	-1.554078	0.141942	-0.603558	C	4.467478	1.967277	-5.265856
P	-2.890978	-0.495117	-1.079586	H	4.866118	2.594447	-6.062190

C	-4.361801	-0.756476	-3.451016
H	-5.093104	-1.251796	-2.818526
C	3.949709	-2.927355	-3.138045
C	-4.584354	1.669328	-0.785214
C	1.254175	1.767460	-3.317242
C	2.634611	1.416011	-3.743558
C	-0.267159	3.298878	-2.225433
H	-0.437046	4.210309	-1.654396
C	-3.900452	0.521900	1.290063
C	0.162643	0.966893	-3.675219
H	0.332191	0.054510	-4.248001
C	-3.989921	-3.190439	-1.563127
C	1.548340	-2.364162	-3.314816
C	2.749424	-2.381433	-2.366722
C	-2.540407	0.475287	-5.104413
H	-1.827053	0.990509	-5.748237
C	-4.339255	0.295245	-0.159496
C	-2.890878	-2.380602	-0.876123
C	-1.547896	-2.825457	-1.462160
C	-1.485988	-0.715975	4.956618
C	4.242421	-0.400679	-0.446320
C	5.224241	0.922629	-4.740816
H	6.224800	0.716318	-5.118117
C	3.191376	2.201902	-4.766154
H	2.586977	3.011459	-5.176037
C	-3.670249	-0.114875	-5.658771
H	-3.828681	-0.085726	-6.736024
C	3.631681	-0.774733	0.907257
C	0.753276	1.723909	5.161325
C	-2.903980	-2.689394	0.622748
C	4.576324	1.093962	-0.422417
C	-5.640401	-0.504894	-0.170121
C	0.278078	2.597715	6.134796
H	0.466970	2.387099	7.186751
C	-1.509983	-1.447889	6.140192
H	-2.085790	-1.086120	6.990979
C	-0.052874	-3.111437	5.156800
H	-0.958869	4.215728	1.689390
C	-0.688331	4.003873	4.426792
C	5.517060	-1.222428	-0.628226
C	-0.446712	3.738124	5.773499
H	-0.815813	4.417034	6.540641
C	-0.790650	-2.644397	6.240505
H	-0.812553	-3.214305	7.168575
H	-1.240425	4.895979	4.129627
H	1.309660	0.829491	5.443945
H	-2.033700	0.223716	4.872601
H	0.494998	-4.051396	5.225900
H	5.114668	1.422223	-1.318885
H	5.212778	1.314283	0.444900
H	3.668530	1.703856	-0.326294
H	5.331147	-2.300256	-0.563054
H	6.214314	-0.976616	0.184796
H	6.051189	-1.020059	-1.561440
H	3.306364	-1.818503	0.959711
H	2.764855	-0.149311	1.136939
H	4.380974	-0.616826	1.694924
H	-3.674389	-0.406550	1.825778
H	-4.707150	1.028707	1.836955
H	-3.012815	1.162070	1.329597
H	-5.540232	-1.486008	0.305160
H	-6.052305	-0.649274	-1.174316
H	-6.402604	0.044380	0.399552
H	-4.902600	1.610960	-1.832772

H	-3.682690	2.290431	-0.731471	N	0.607397	2.408313	1.025782
H	-5.374070	2.191126	-0.228164	C	0.275412	-1.486335	4.156649
H	3.750413	-3.974757	-3.404224	C	-0.710930	2.108709	3.461803
H	4.883166	-2.920656	-2.566678	C	0.879687	-2.710456	3.798758
H	4.117950	-2.391793	-4.078439	C	-0.956814	3.232903	2.640371
H	1.311171	-3.388614	-3.632718	C	0.776262	-3.116850	2.441284
H	1.760163	-1.779941	-4.219791	C	-0.153664	3.372849	1.480608
H	0.661473	-1.938731	-2.834544	H	-1.386160	-0.337187	3.349312
H	2.088673	-4.260544	-1.526652	H	1.071481	0.886291	3.741517
H	1.663920	-2.866094	-0.515723	C	-1.075529	1.440396	-3.139218
H	3.329423	-3.468507	-0.554847	H	2.147702	3.382103	-2.147419
H	-3.878265	-4.244710	-1.273538	C	-1.160811	2.649438	-2.435072
H	-3.914984	-3.155611	-2.654726	H	-2.141685	3.047352	-2.177009
H	-5.004617	-2.893245	-1.277973	C	3.512104	0.238133	-2.948025
H	-1.450394	-3.917022	-1.380349	C	-2.334586	0.797430	-3.611331
H	-0.696920	-2.376992	-0.935598	C	4.798942	-0.002726	-3.458006
H	-1.466835	-2.566470	-2.526284	H	5.433793	-0.742446	-2.975205
H	-2.629058	-3.740910	0.782450	C	-3.287485	0.141367	-2.790828
H	-3.892218	-2.544995	1.074189	C	1.243263	2.846440	-2.436639
H	-2.178841	-2.079705	1.170790	C	-4.816150	0.015891	-4.702762
				H	-5.789908	-0.264298	-5.102248
TS_LCr_phthalazine_dimerization_S2				H	1.166613	-4.074209	2.113401
Cr	0.155026	-0.024844	0.158556	C	2.344559	-3.399946	-1.068177
N	-1.458717	0.038378	-0.678468	C	4.503982	1.626173	-5.197314
P	-2.901675	-0.368310	-1.065563	H	4.873686	2.168939	-6.066523
N	1.657750	-0.118391	-0.870537	C	-4.525709	-0.203295	-3.359679
P	2.934949	-0.722923	-1.496312	H	-5.288678	-0.669376	-2.742045
N	-0.276453	-1.179569	1.799066	C	3.874081	-3.035553	-3.015128
N	0.760819	1.270777	1.697986	C	-4.165880	1.977640	-0.389855
C	-0.386513	-0.703746	3.106630	C	1.352720	1.646233	-3.144381
C	0.291609	1.135831	3.019273	C	2.709068	1.210823	-3.586092
N	0.263956	-2.360717	1.508942	C	-0.009216	3.346373	-2.093548

H	-0.084033	4.291460	-1.557529	C	5.497069	-1.617375	-0.390621
C	-3.591392	0.474569	1.485936	C	-2.708727	3.984918	4.133410
C	0.185060	0.968665	-3.519832	H	-3.481747	4.705234	4.397501
H	0.255999	0.048661	-4.100826	C	1.619096	-3.053079	6.078053
C	-4.380395	-2.834318	-1.727768	H	2.135685	-3.654628	6.824588
C	1.506171	-2.320501	-3.147028	H	-2.129589	5.011571	2.332114
C	2.709981	-2.457897	-2.213027	H	-1.342723	1.085729	5.254211
C	-2.628799	0.969724	-4.974502	H	-0.051762	-0.111315	5.786161
H	-1.882653	1.460937	-5.599722	H	2.003073	-4.421525	4.457143
C	-4.138364	0.514315	0.055259	H	5.375071	1.065882	-1.026039
C	-3.154157	-2.247638	-1.030745	H	5.435911	0.922899	0.737216
C	-1.901662	-2.807315	-1.712501	H	3.946388	1.472308	-0.052713
C	0.374507	-1.065007	5.484962	H	5.197353	-2.671152	-0.355397
C	4.311800	-0.672647	-0.199823	H	6.211800	-1.466130	0.430584
C	5.300842	0.675963	-4.563525	H	6.055036	-1.454141	-1.317820
H	6.306156	0.462527	-4.924389	H	3.219661	-2.017206	1.159283
C	3.229195	1.884046	-4.704798	H	2.856001	-0.301849	1.392291
H	2.603113	2.634736	-5.187965	H	4.411412	-0.966307	1.937295
C	-3.844285	0.578858	-5.525793	H	-3.611940	-0.528539	1.924254
H	-4.039446	0.738347	-6.585586	H	-4.197396	1.128365	2.128812
C	3.652490	-1.011029	1.143674	H	-2.557084	0.838535	1.522345
C	-1.485940	1.953263	4.614829	H	-5.597832	-1.095367	0.370516
C	-3.149248	-2.693233	0.432638	H	-6.026118	0.008816	-0.952932
C	4.793304	0.779224	-0.142185	H	-6.189922	0.525975	0.718532
C	-5.554828	-0.053773	0.034200	H	-4.552092	2.101982	-1.408990
C	-2.471561	2.873471	4.952723	H	-3.163152	2.419225	-0.346760
H	-3.064242	2.723278	5.853922	H	-4.812534	2.556704	0.283493
C	1.031652	-1.834625	6.438537	H	3.604722	-4.045328	-3.357000
H	1.093216	-1.482377	7.467229	H	4.799517	-3.135729	-2.439176
C	1.543661	-3.481442	4.762800	H	4.092610	-2.449255	-3.913955
H	-0.191144	4.273647	0.879431	H	1.182389	-3.311832	-3.494074
C	-1.954948	4.157104	2.985678	H	1.754751	-1.726159	-4.035895

H	0.659821	-1.838500	-2.643553	H	-1.33438719751450	-0.97503931789589	2.90729636391557
H	2.002125	-4.362319	-1.474315	H	1.13481138021545	0.74180678542135	3.14091425027797
H	1.534489	-2.993553	-0.449624	C	-1.11543552832601	1.41262185384320	-3.49334841497371
H	3.200620	-3.613742	-0.415655	H	2.35238957084604	2.96167869509891	-2.67599538237377
H	-4.408106	-3.916551	-1.537275	C	-1.02795593094862	2.66891750059036	-2.88180956797192
H	-4.344955	-2.707400	-2.814672	H	-1.94181295378102	3.21522684316087	-2.65059786520531
H	-5.331023	-2.427910	-1.364586	C	3.44680910252727	-0.09868863386639	-3.03736278781221
H	-1.972608	-3.902150	-1.771989	C	-2.45544921493048	0.90682396124536	-3.90108524347998
H	-0.993479	-2.559759	-1.150481	C	4.69912664254875	-0.50163557327834	-3.53323659411036
H	-1.783347	-2.426852	-2.736512	H	5.40172973017222	-1.00698026786519	-2.87760678752203
H	-2.996720	-3.780052	0.483945	C	-3.40162506968168	0.30514684075939	-3.03771951737253
H	-4.097776	-2.478335	0.938953	C	1.37769070907650	2.52700802925326	-2.89570772506860
H	-2.335487	-2.224367	0.996830	C	-5.04016978141001	0.32498801904197	-4.85925283494128
LCrphthal_dimer_S1				H	-6.05050453276390	0.11479383497058	-5.20704424534148
Cr	0.01918060723997	0.05001689645379	-0.06303235701363	H	-0.13230196266158	-4.48035122579007	1.68691757086565
N	-1.49408830195741	0.09438220838274	-0.99824846238715	C	3.07501282350726	-2.80707850108844	0.26983765651366
P	-2.98951264093596	-0.20077672779455	-1.32219438783098	C	4.19525721529906	0.34437756710292	-5.72498735981977
N	1.52761849459084	-0.04232396586408	-1.00303026948271	H	4.46668750458518	0.51051083839584	-6.76665800600504
P	2.97178733621358	-0.53945232794792	-1.32012600405377	C	-4.68972749813599	0.05136775988288	-3.54104538855758
N	-0.01884553082570	-1.27213633725435	1.32853171810775	H	-5.44681352534374	-0.37871654677479	-2.89280122614136
N	0.01241745275326	1.18549813964907	1.44768740466058	C	4.33375811702443	-3.07874516768410	-1.85761589705986
C	-0.24886382299555	-0.84455383179248	2.71921799416521	C	-3.89378881818663	2.27853969155007	-0.62842529766393
C	0.08367467903696	0.63441274831433	2.81308822362890	C	1.30966709034487	1.26734842404024	-3.50299101744469
N	-0.13509330993849	-2.55719568717526	1.03950172227393	C	2.57833489896602	0.60129080263170	-3.90855727953261
N	0.04780952399307	2.49966407779484	1.25944294799052	C	0.21352006251712	3.22028131950879	-2.58139453736051
C	0.49936130289634	-1.75107382136658	3.65031301784493	H	0.27381288127280	4.19635555386648	-2.10209743176847
C	-0.78550651651480	1.43754512269654	3.73617528944352	C	-3.58715092077478	0.70073634204845	1.25069579450031
C	0.45876473605884	-3.11253184618596	3.30101209058405	C	0.05932162587488	0.72936827946948	-3.82114398332636
C	-0.82094367064106	2.81828910172100	3.48297731288551	H	-0.00165640769540	-0.25165065939749	-4.29745446249087
C	-0.04129426238794	-3.44512329472823	1.99521345125068	C	-4.64972789739269	-2.55736966908908	-1.87679682294115
C	-0.23882867036698	3.29055142118812	2.25308685695680	C	1.85763971255705	-2.93803948007651	-1.90618712361808
				C	3.11913856016992	-2.41687161218393	-1.20881145705069

C	-2.81661137785812	1.14711242372599	-5.23688891118227	H	1.16395361917577	-0.29346986157759	5.08515598109094
H	-2.07465171026560	1.60217377224022	-5.89335283076154	H	1.01156215128905	-5.11085707373141	3.88102468396467
C	-4.09403030690627	0.82554909885107	-0.18978102365467	H	4.68562019714110	1.87470261642980	-1.68191761738577
C	-3.36644428993945	-2.04747891076740	-1.22302768044093	H	4.89704506116799	2.37201851594165	0.00371978303188
C	-2.17435405224318	-2.71343303178717	-1.91914247082768	H	3.26641693439825	2.24734130325599	-0.67378236938266
C	1.13799393777621	-1.34966358253349	4.81363262936149	H	5.60367549278953	-1.30157715274178	0.20127310209929
C	4.19302026877487	0.33737081621342	-0.18623912008195	H	6.22081967224377	0.31166051105907	0.53651551627332
C	5.08104310956415	-0.28253503351250	-4.85291488304896	H	6.09888011569779	-0.23180129580136	-1.12860728624848
H	6.06199302569831	-0.60842850793505	-5.19560975148041	H	3.54084894686524	-0.63447992404507	1.69150166696478
C	2.96631502486583	0.78438687866136	-5.24565494735393	H	2.61375546343677	0.80538731208653	1.24186273911346
H	2.28327929682425	1.31600958754266	-5.90851564513119	H	4.26058142917193	0.96749052299387	1.87319574454555
C	-4.08660188499108	0.85656699353923	-5.72300371369067	H	-3.81308021609317	-0.26864613002964	1.70466550731807
H	-4.33414824587853	1.06335101235391	-6.76333530629993	H	-4.07095449595211	1.46746814218058	1.87183393513690
C	3.61223537678401	0.35584540486997	1.23156363455622	H	-2.50629704638840	0.86665288973147	1.31501281088799
C	-1.48914446157115	0.91195264244312	4.80925459079515	H	-5.77212797773893	-0.56951053677501	0.05445429358339
C	-3.37354516232505	-2.44868563782185	0.25288718436369	H	-6.03290909162033	0.64882097565764	-1.21523304726079
C	4.26199949249266	1.78656678321765	-0.67407507122086	H	-6.12077650172018	1.10200505799490	0.47933990901236
C	-5.57753891379223	0.46923872719336	-0.23573014236304	H	-4.24286244210080	2.46132582356710	-1.65230771604666
C	-2.20270553607406	1.75425703537363	5.66596408154412	H	-2.83709786194281	2.56594389631244	-0.56498463439579
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H	-3.47912556845368	2.03611198188021	-6.64786744409574	C	-1.00464510187317	2.21720257523302	-2.77129571711586
C	1.14619151015076	3.53322963509423	-1.54610211964842	C	1.03027212803879	-5.09309900142160	2.29483832377345
H	1.98252801269381	4.04471900951574	-1.06615538118482	H	1.42942652307427	-5.71347394242652	1.49241956079752
				C	0.46580661871901	-4.77796467514892	4.61705962903896

H	0.43667135818021	-5.14426809810270	5.64276078392168	C	-4.23796440592552	1.42683155057314	0.05436920358488
C	0.04332945114017	-2.98875120135826	3.02151024220201	H	2.48904564965647	-3.73328511753839	-1.64790883068959
C	0.59017152057080	4.29032952252034	5.08545246350084	H	1.33895394967866	-2.41156216484826	-1.34712700403058
H	0.58588450291022	4.58068651146569	6.13561530438439	H	2.61745075162569	-2.75603683452920	-0.17653897628285
C	0.62905341264172	3.52390936450565	2.41058959360036	H	4.76433563206455	-3.33173387826598	-2.35882603491055
H	0.64324238916856	3.21192642305322	1.36623654043421	H	5.06738904251785	-2.44307976236629	-0.87080368849750
C	5.60341050258379	0.41223932045131	-0.10766671640501	H	5.49188959042131	-1.73638772255282	-2.43995572041713
C	-0.16763079509235	3.83845328395772	-1.18089603716731	H	2.81017705831670	-2.76764286311213	-3.86986216299617
H	-0.35750137607885	4.59682420248321	-0.42126509398912	H	3.57362562823834	-1.19029704868652	-4.12025372005975
C	-1.78315770092315	-2.78386880189416	-0.77478125690184	H	1.88614383491437	-1.28376792908215	-3.58797213012118
C	3.63620903687041	1.71776506584125	0.64702058142330	H	-1.48669128481338	-3.79428765305061	-1.08942724463566
C	0.14451929585372	3.02189543257331	4.72281279884130	H	-2.46045650667802	-2.89465176238183	0.07856885135884
H	-0.19092703275481	2.32712579210809	5.49248278060183	H	-0.88089532728923	-2.27861833696884	-0.41229887354954
C	2.87717658613878	-1.74294200419179	-3.47966028837995	H	-3.26703193897168	-3.87046936321259	-2.72401737097229
C	0.00153941526902	-3.49620962310656	4.33297473901380	H	-4.06261838740167	-2.44192382962874	-3.36187330854417
H	-0.36965485364412	-2.86793101549890	5.14181960176698	H	-4.37513850138900	-2.97302176987773	-1.69352575340340
C	-2.42666918702686	-1.57500366031730	4.12101158209098	H	-0.93632830755588	-2.95088070890621	-3.28029150307649
H	-2.47833356057750	-2.65886098894116	4.02811484592936	H	-0.49176765954083	-1.32453670969364	-2.73225335654506
C	-3.43490492993204	-0.89025821818176	4.79348414205752	H	-1.72610856629632	-1.53609518995815	-3.99653454503722
H	-4.26093700567673	-1.44042908559703	5.24216902713917	H	-3.32736719302833	1.64615670052547	0.62267672163350
C	1.06564331648610	4.79189944044640	2.77491045198430	H	-5.10677467086238	1.63426565206115	0.69359036784990
H	1.41972675876367	5.48092384285418	2.00729058494849	H	-4.28197123724482	2.11975463708719	-0.79608077541705
C	2.38675975027709	-2.71501123370857	-1.24720442406188	H	-4.34207151560559	-1.99361873846543	0.58637113792819
C	-1.33561031883015	-1.95096570963751	-3.05941135191021	H	-4.90605495465257	-0.64431933471878	1.57430424178311
C	-2.32994902739728	1.18833891034777	4.28109296273517	H	-3.17293790826384	-0.85356626197733	1.29634702551247
H	-2.30644742396667	2.27545746427317	4.32255681481158	H	-5.70398433419464	-1.28458788658585	-1.53604886858492
C	1.04864630222696	5.18454942196377	4.11603543129874	H	-5.82265881854525	0.45407695737873	-1.87845494615543
H	1.39234431287686	6.17707605955827	4.40373320430825	H	-6.42341223889922	-0.19348880666888	-0.35613636887307
C	-3.38901550261618	0.50140026068880	4.86529286347982	H	4.20530579476967	2.00343881360856	1.54202519560786
H	-4.18091006133602	1.05427766613256	5.36892736102206	H	2.57396500622133	1.72144875349259	0.91403181478017
C	-4.15955827594789	-0.93860326290825	0.82423409496526	H	3.80600526132976	2.49429986941627	-0.11091406659012
C	-5.61701248776678	-0.28460746878953	-1.09667742375275	H	6.02381636315213	-0.51084427049211	-0.51897116329297

H	6.12524650692074	0.60195861581831	0.84067054934858	C	-3.85719737934037	-2.93402342742861	-2.32585143831582
H	5.86486169750394	1.23643852353247	-0.78038395368009	C	4.81484816793805	0.98902343628498	-3.21284041264536
H	4.23305888017176	-1.68254712757085	1.00495577547240	H	5.39564026239315	0.10600525490378	-2.95499522610388
H	2.73203383838111	-0.82470377727447	1.42035835553860	C	-2.58800504878715	-2.17243384571466	-1.94909452912888
H	4.25734928571702	-0.37965700668663	2.19376965143040	C	-4.14165184676346	0.58500693778445	-5.22535198278620
LCrphthal_Ph_bisketimide_S1				H	-4.94665577031678	0.21154792168712	-5.85664612606744
Cr	0.09043568303753	0.12562225682430	0.09440569596473	C	4.05344367380594	0.24993595636534	0.08872188357889
N	-1.54596694316264	0.13232143058315	-0.63920323093860	C	-2.24231126653007	2.00694059260445	-4.86228110194997
N	1.44711145329756	0.19317453581699	-1.05560804163269	H	-1.55104841050102	2.77114418496057	-5.21827543579395
P	-2.76483957303010	-0.34359216162376	-1.46922063410903	C	-1.21587064926970	3.01344841363563	-1.68921109331581
P	2.94555070319381	-0.03674669841529	-1.39894431465063	H	-2.23654519126260	3.15975741579348	-1.33887391418181
N	0.18229047922825	1.38989147230224	1.38694909340404	C	1.53052864919273	-4.90283229662735	4.44551534301395
N	0.23213960338190	-1.26396722620856	1.25579989145620	H	1.98618594989169	-5.75418423562727	4.94962581714878
C	-0.31097320464355	1.52289266233089	2.55904515121626	C	5.37123955739780	1.91213877179476	-4.09215034755868
C	-0.20598167053984	-1.52753235023801	2.42917707476535	H	6.36023822382313	1.73634876797325	-4.51279125487275
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C	-1.38690643815342	0.64192523513085	3.08965892897919	C	0.18263898585085	2.62788369609121	3.42236973193549
C	-3.98528158009635	0.09397134606770	-3.93398588725618	C	3.74073675222458	-0.82172164245811	1.13529773428505
H	-4.67479971135504	-0.67306584123202	-3.59416292253319	C	-4.33389944353881	0.01050602962683	-0.49901400525774
C	1.41403521319021	2.59331407078990	-2.54630594847167	C	4.65476914488249	3.06142425604501	-4.41803008648171
C	-2.96598549308814	0.53777747543923	-3.07285867424741	H	5.07653387496413	3.80176973794841	-5.09660487433326
C	0.34183844042903	1.98335263660364	-3.20749266602935	C	0.93969865173138	-3.74572829331907	2.40767033037615
H	0.54409645243456	1.31116334788790	-4.04412712237145	H	0.92240254364528	-3.67672101455698	1.31971842624573
C	3.54196546999146	1.16893939848675	-2.64727760541244	C	3.38681693328396	3.25311410509741	-3.87860683068823
C	-3.25109640582459	1.54496807456781	-5.69897861363469	H	2.81131179486465	4.14073034913894	-4.14235515788418
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C	3.16400921963301	-1.75624156739341	-2.15076545339902	C	0.95259277588125	-3.87398188102609	5.18945218563390
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H 1.06126483129293 3.66347893968558 1.76121216173563	H 4.90877737637285 -2.51934779291020 -1.06389600585252
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H -0.36489425225321 4.33481836264177 -0.22388545669553	H 3.39485937306908 -1.11420815054604 -4.24139821417158
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C 1.43059304032193 4.70662687548900 3.62104966300725	H -5.06254626770523 1.73991244446144 0.57457853582635
H 1.98595730486466 5.51719668428862 3.14982163812333	H -4.23103149022414 2.15234023336379 -0.93200246892995
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H -2.57325337631224 2.33698033493518 3.64827461504442	H -5.80160965996037 -1.17166800650869 -1.64854813490446
C 1.24058409312500 4.70388870000029 5.00564613033713	H -5.77099207839511 0.55516563688715 -2.06116929944995
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C -4.21217400234387 1.47479578561808 -0.06834091314661	H 6.08809474317894 0.40967745442132 0.75762399199887
H 2.25927290209692 -3.68823266591836 -1.81570737048061	H 5.84023183387803 1.12526537508025 -0.83097895224049
H 1.16911830715226 -2.33081279468944 -1.45753762088799	H 4.13609991792083 -1.80655738862734 0.85776775277043

H	2.66343789195869	-0.92847993222927	1.31659287985292	C	-2.54321886100454	-2.01631934442757	-2.29242069628926
H	4.20850612789501	-0.54682151147695	2.08989995632768	C	-4.27092183247170	1.28797874684386	-5.08564670657525
LCrphthal_Ph_bisketimide_S2				H	-5.14740980033501	1.02930324770891	-5.67813408474256
Cr	0.19405990774665	0.27752497174723	0.17775042759029	C	4.56721338372230	-0.05595952963653	0.25664677588813
N	-1.05480563369935	0.07907041323774	-1.14296011077206	C	-2.35104907546724	2.67501669835841	-4.66783722813214
N	1.89597748793496	0.35859454465141	-0.46305743825458	H	-1.71761870026845	3.51924356488603	-4.94150560968287
P	-2.46582472524255	-0.21340614987614	-1.70496506758765	C	-0.84089539476908	3.29785042463614	-1.77018847476296
P	3.23751523050379	-0.14575586753454	-1.06984981926973	H	-1.81107142510716	3.68457331221018	-1.45677672307181
N	-0.65861522152585	1.26310099870928	1.56772828617784	C	2.12034000613919	-4.90097918529107	3.90934858170685
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C	-1.28503017050787	-0.96679784444387	3.54505094197709	C	2.98315214311238	1.86189945139392	-3.08182498065243
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C	-3.93953790650518	0.53486970749897	-3.96403223702817	C	4.15080648584267	-1.01428536628571	1.37732437437810
H	-4.57048090708683	-0.31307542326513	-3.70148940565128	C	-3.85350394203589	0.18619540815467	-0.49535177107468
C	1.65484633166905	2.30910312913718	-2.57321881495560	C	4.65394336686208	2.18768059572459	-4.83909322312419
C	-2.81832085578874	0.82791323386793	-3.17075540819515	H	4.96737252722302	2.69932276855102	-5.74818475486421
C	0.48416425655675	1.90287485995033	-3.22042363813985	C	0.83894334282740	-3.73663039538111	2.22304454235891
H	0.54586766915307	1.18180425139919	-4.03857669559895	H	0.44919693441011	-3.66415710818320	1.20805168402882
C	3.80660305522683	0.87595022032417	-2.48658623451060	C	3.42816459637233	2.49106893860851	-4.25604451465093
C	-3.46829879817937	2.37028303228978	-5.43901570955786	H	2.78386328652462	3.24482261902377	-4.70922644079797
H	-3.70847032553882	2.97445782205089	-6.31297786837926	C	-0.77285522709570	2.35970518627811	-2.80526037910201
C	1.56461775877436	3.23370567303624	-1.52491351626139	C	1.62034256491691	-4.82247728053954	2.60799052045084
H	2.47157032156515	3.55489125329703	-1.01273989491028	H	1.84013884865654	-5.61185860360601	1.88932268823615
C	2.99367705618568	-1.85403421748441	-1.83868622565384	C	1.81935985163567	-3.89251539805869	4.82608183893387
C	4.23528147919933	-2.55078781880775	-2.38467312422414	H	2.20626629802901	-3.94639998023126	5.84308682703756
C	-2.00214660677654	1.92521271127492	-3.53258024507144	C	0.53554201985604	-2.71699986256516	3.13522299493752
C	-3.91540288639895	-2.68382312641763	-2.34496885973889	C	-0.74373279709741	4.45067239420693	5.07230307782940
C	5.04082186317171	0.58363220212392	-3.09266465475183	H	-0.55231011201372	4.65243929627902	6.12572898762231
H	5.68196836363582	-0.18198706681561	-2.66489225250512	C	-1.20678702198633	3.92259423263852	2.37781730909628
				H	-1.38317205026990	3.69817830790829	1.32566750871008

C	6.01418979774771	-0.33899558570714	-0.14144575499482	H	4.70985035332829	-2.00227757634542	-3.20480405943233
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C	4.02126855237496	-1.04571046228331	-3.64655197348519	C	-1.77650032375754	-1.38302253828206	-2.36116841009474
H	3.79527916455198	-1.25904890706007	-4.70120467203319	H	-2.23378267353470	-2.37302598449586	-2.24523687549532
H	4.48679448433054	-0.05385532550676	-3.62351077849332	H	-1.47157987088118	-1.28118683499448	-3.41286713883149
H	4.77293925868068	-1.78011807899983	-3.34111534207491	H	-0.86114991065860	-1.35519079592970	-1.74896857086005
C	1.76865385006723	-0.06140654211116	-3.43115069666630	H	5.00204917846558	-2.50383917805256	-1.59963655785089
H	0.81192169793506	-0.04264913317142	-2.89921405956884	H	6.06040668849563	-4.41326551010154	-0.48746974286581
H	2.18272418067933	0.95152476315460	-3.39360103758058	H	5.09551997634301	-5.28760566487418	1.65183077529827
H	1.57710664465737	-0.29933463640839	-4.48692762190570	H	3.01199574882064	-4.28255784452595	2.54405464915507
C	2.08066480819116	-2.47984461892833	-2.97651595887229	H	0.34381417178397	-3.12897739071511	-0.07047081467202
H	1.79831603526451	-2.65747791712458	-4.02338181132133	H	2.39870722353682	-1.65978056773591	3.40812783626565
H	2.74958566109027	-3.29251696273597	-2.67192833135291	H	0.20718416446374	-1.17936012270864	4.48525891311371
H	1.16539494865044	-2.55742909093476	-2.37532438907714	H	-1.90918107783751	-1.66602878050240	3.28444836497756
C	3.89278288875890	1.80569936542431	-1.27722351731328	H	-1.61388641695588	-4.90179051863319	1.37222203126021
H	4.55373171599730	2.60113702407256	-0.90537913538065	H	-3.62995204125899	-5.96077898630214	0.39138775415986
H	4.05386950374314	1.73373168817527	-2.36041860046614	H	-5.37563129667316	-4.51634233354076	-0.67507232342879
H	2.85625489014120	2.12215898753579	-1.10167989245650	H	-5.04387123932827	-2.09966200620086	-0.78593265045568
C	4.06920079028875	0.73195339310372	0.95863956243358	C	-1.26868639914350	5.12453527576320	-1.62470788793503
H	4.83578279948725	1.44826087548318	1.28432022443855	H	-1.22264108813537	5.91720134785705	-2.38128995916509
H	3.08586766905929	1.13623147018926	1.22699075587259	H	-2.04800536932407	4.41788166271710	-1.93254456522431
H	4.21713317730871	-0.19279568928962	1.53178651658308	H	-1.59365497486984	5.57799460262714	-0.68111241498982
C	5.62579522630109	0.05476723370911	-0.84559798436737	C	1.69500827032476	5.47691626033984	-0.88013290975031
H	6.30921153034470	0.88375236583149	-0.61404953213581	H	2.65134427993049	4.96972713933226	-0.70856419245468
H	5.93610496275637	-0.79007612117097	-0.22190424531074	H	1.86337601492785	6.25325395694490	-1.63638105094244
H	5.79849761619962	-0.21267722144921	-1.89273562205170	H	1.41531098633749	5.97545858866610	0.05478145074682
C	-2.05779540901440	1.07323274281062	-2.37573918840935	C	0.88113668748409	3.46783164472475	-3.02463138151191

H	0.80307406671014	4.19504140373044	-3.84232696368054	H	-2.97125892525410	2.51284409506002	-0.92638260981505
H	1.91943725129272	3.12078112298913	-2.99979085117691	H	-3.51664406179652	-1.60192051565892	-1.99430371141175
H	0.25021120719564	2.61118582659248	-3.28538522336435	H	-3.50249184941222	0.01083277348119	-2.71458502554698
C	0.36937474977274	4.58431520567117	3.55959591856570	H	-4.83614630715767	-0.47334699241201	-1.65911254566706
H	0.25155778469060	5.52652470004597	3.01214622679597	H	1.82568482176962	0.03157075169431	-3.60881698303483
H	0.17265590699157	4.79228440889513	4.61850993761916	H	3.43919374076574	0.42838229689687	-3.00372704808415
H	1.41827261603688	4.27980936653405	3.47102308994506	H	2.10337799523824	1.56470667270918	-2.77679552126095
C	-2.53958084876876	3.89402482176755	2.97059783032883	H	1.87068542140532	-2.64301678715961	-2.00556599526500
H	-2.80204748826688	4.18766208007882	3.99467362672261	H	2.16977113650173	-2.62530123485333	-0.26476063957828
H	-2.67326893962133	4.77398345737891	2.33065501545335	H	3.48333429114071	-2.25834890162193	-1.39037145140060
H	-3.26139258712273	3.13729510674150	2.64871286641102	H	2.63165346737992	1.59894681963133	0.29573335436029
C	-0.58629295794408	1.68156752714943	3.85628322024599	H	3.97160821605858	0.46401350244472	0.08718582894648
H	-1.18567523431827	0.88930165471801	3.39173675340396	H	2.65524407179434	0.08524522449412	1.20566952672290
H	0.45783288810195	1.34423747784442	3.83041767378000				
H	-0.88383606767698	1.78214743984669	4.90702015125422				
btmsa_S0				LCr_enedialcoxide_S1			
C	-1.02948732640874	-0.05092785135697	-0.63363582922182	Cr	-0.30719142286394	0.43869814954524	0.26486049961282
C	0.16733182012237	-0.15509133979352	-0.84116953611188	N	-1.94443246536043	0.67998197595911	-0.38662828299342
Si	-2.83173337845295	0.10562695041041	-0.32256094117180	P	-3.26679263676054	0.16589949708943	-1.02682716738969
Si	1.96986310304830	-0.31109788786348	-1.15082815320137	N	0.93444837189003	0.37500423283748	-1.00753756918625
C	-3.26376407446514	-0.88802061636575	1.19529113833417	P	2.38210553685249	0.08335612422653	-1.50207791083434
C	-3.75211551933566	-0.54875305678017	-1.80664213880345	O	-0.17626112380265	-0.98721069530234	1.45769083070354
C	-3.23553179693248	1.90621552855176	-0.05345716196506	O	0.11803997765763	1.41782997626744	1.76433094838472
C	2.36787553073211	0.50176428276120	-2.78130964342274	C	0.16235284066761	-0.64493356634714	2.71390160713308
C	2.41069194282805	-2.12218394110794	-1.20744393581772	C	0.39427069359057	0.69758580892805	2.87098828404791
C	2.88729837906015	0.53559265828324	0.23449884086055	H	5.36224082164332	1.50490919535500	-5.18048292589107
H	-3.01969970504382	-1.94795567630877	1.06575769249689	C	-3.76749138571640	1.19616701419348	-2.45835146264767
H	-4.33594117838659	-0.81993728933431	1.41524486438702	C	-2.93003666572435	2.19584098296112	-3.01016794536450
H	-2.72210159038493	-0.53131366039486	2.07800258597357	C	4.44534103863560	1.74358460868826	-4.64369945072423
H	-2.69562389225413	2.31576657032326	0.80712616484834	C	2.07137890217315	2.33056126984170	-3.23502435582695
H	-4.30746433256021	2.04354762426991	0.13266887385030	C	2.46589469609165	-1.67392054338840	-2.19601870104095
				C	2.84806563321641	1.20571392608615	-2.87083408016275
				C	0.97473571633213	1.45359572323615	3.97375674120169

C	4.02396280856562	0.93833914455476	-3.59129092913291	C	-0.07889864795741	-1.56633497730208	5.04231526208021
H	4.62844690267970	0.07286619850196	-3.32590367177456	H	-0.33311534816474	-0.57460897823243	5.41438211707423
C	-1.63120804211161	2.65414181559153	-2.43995177152085	C	-0.43090408650733	2.28079500010994	-3.05075720810850
C	0.80102279756382	2.74106242015695	-2.56953040221839	H	-0.45132526463104	1.58222190695371	-3.89051995347670
C	0.20016955910766	-1.74063123612827	3.67417625754143	C	3.64339984872670	0.39083264668878	-0.14874598426526
C	0.81639025354872	3.64136818074710	-1.50102379372419	C	-3.03643421823492	-1.55865447688222	-1.76032911800545
H	1.76740202837591	4.02166128546494	-1.12880319825962	C	0.46544272651240	-3.04339030090203	3.21312816686210
C	-6.06053208771302	0.07634265557422	-0.19397360089410	H	0.65127047226067	-3.19010041191771	2.14958712549241
C	-4.97350616470723	0.89699668517306	-3.11601017811977	C	2.13904013109628	3.01828483089488	6.01286846608499
H	-5.62749811562867	0.12715186512687	-2.71652705400657	H	2.58670521623969	3.62006727151605	6.80266905930124
C	-5.36120190766634	1.54432728347062	-4.28505698966782	C	1.90701386747841	0.89719473968458	4.86952700388650
H	-6.30452991584821	1.28480402353747	-4.76329974889770	H	2.20071989771528	-0.14616682697885	4.75850283839395
C	1.23951645083392	3.59034368491199	5.11257465230362	C	2.47296158258211	1.66818929801929	5.87947381614239
H	0.98020519673753	4.64542995070414	5.19800107794815	H	3.19482960291306	1.21569615152420	6.55898916170329
C	0.23530650403565	-3.93159836806630	5.45031416644905	C	-2.02559424707635	-1.34405140617061	-2.89406030039681
H	0.25088562105256	-4.77590961259702	6.13820600765838	C	-4.50302235086063	1.74231686625942	0.78475944245309
C	-0.05356310747653	-2.64661314624941	5.91745937817348	C	-4.28123824681771	-2.25303273317164	-2.30441467252882
H	-0.27722775937974	-2.48790839857670	6.97207098651864	C	-2.39503532258345	-2.45737802870219	-0.69982012608568
C	0.66922457267509	2.82112233849437	4.10241086435095	C	3.68151797456001	2.85298467627241	-4.99946753927132
H	-0.02579090314089	3.26624525110182	3.39195890370823	H	3.99294338869487	3.49788571656278	-5.82012015518714
C	-4.28271344390390	-0.66785857055009	1.39553441916677	C	3.34851274546666	1.80322877872800	0.36611110493883
C	-0.37828075186155	4.03493638779175	-0.89704748922079	C	2.51257827853362	3.13343688396460	-4.29940787674110
H	-0.35583958502672	4.72339363939291	-0.05319392828556	H	1.91006107175734	3.99952271389312	-4.57389598039115
C	-4.52764982845579	2.51367669673490	-4.83597162360508	C	3.39787893654537	-0.61594591356631	0.97602047455791
H	-4.80696553875024	3.02740884432802	-5.75486325342527	C	5.10409007249939	0.34004758235478	-0.59395537432276
C	-3.33160424703149	2.82683195012650	-4.19890921487862	C	1.52437169056109	-2.51339677625259	-1.32423187086440
H	-2.67721280363605	3.59089520044836	-4.61897574828740	C	3.83568433818872	-2.34965182534367	-2.21463281607649
C	-1.59447838954435	3.54432150805389	-1.35857882183939	C	1.89130741232325	-1.62324844310153	-3.61425419754818
H	-2.52535793814405	3.83733114453832	-0.87334900952594	H	0.49777520008184	-2.13700531626761	-1.36374236500174
C	0.48754845511364	-4.12307331632339	4.09152125591502	H	1.81845247708193	-2.53017059887643	-0.26909368591427
H	0.70310847854702	-5.12207717397055	3.71299337938729	H	1.52350170889919	-3.54972587232307	-1.68829408247684
C	-4.62163587172589	0.30536674800075	0.26365232454106	H	1.66770855377718	-2.64196257976923	-3.95863488477935

H 2.58344601758431 -1.17457510174023 -4.33520262768981
H 0.95475252800891 -1.05217502062949 -3.65104559424314
H 4.25099574591198 -2.48236872917820 -1.20978370417710
H 4.58010850376959 -1.82774224034783 -2.82453018434979
H 3.73161080036832 -3.35457421296287 -2.64657583642134
H -5.04474783650720 -2.41597112430838 -1.53488199964599
H -4.00058644112318 -3.24679274565289 -2.68002834220230
H -4.73796296143744 -1.72216685411610 -3.14559699001761
H -2.45521195539326 -0.78712384633205 -3.73633136217737
H -1.68963233620935 -2.31705843256933 -3.27861672998436
H -1.13836608435301 -0.79788394913434 -2.54170496680124
H -3.10600296806448 -2.78128679527828 0.06603527602045
H -1.55438870607141 -1.98163364378828 -0.18273637392679
H -2.01173202739171 -3.36527033263212 -1.18489537716660
H 2.34693202560275 -0.63909723672665 1.28938008042671
H 3.99022932944399 -0.33284970251789 1.85629345480353
H 3.69511200608148 -1.63513992893294 0.70177066415193
H 5.74518818297158 0.50988579849019 0.28151502310204
H 5.34360700451732 1.12774872332184 -1.31664592239865
H 5.40319732213020 -0.62157901933642 -1.02191148624056
H -6.71725962091353 0.09181898808755 0.68641936103784
H -6.21767262410457 -0.88972253144128 -0.68623755868166
H -6.41557884404147 0.86733010934622 -0.86242635981124
H -5.25657534972060 1.90970545440110 1.56549790548985
H -4.68293781354027 2.47983669018852 -0.00855484672935
H -3.51383874775057 1.93850698899344 1.21103796256351
H -4.86134927309317 -0.40305884794694 2.28992118934854
H -3.22026130667137 -0.63679366910188 1.66901902372063
H -4.54303261246810 -1.70133496335531 1.14174957452963
H 2.31962307884503 1.91447689011400 0.72629218982308

H 3.52513366812703 2.55855127242523 -0.41049462535805
H 4.02109007822393 2.03137965475250 1.20371103007663

Benzil_freq_calc_M06L

C 0.017929 0.049434 0.975517
O 0.032733 1.137991 1.516622
C 1.316505 -0.753332 0.977442
O 1.303860 -1.835997 1.530281
C -3.558832 -1.587991 -0.684396
C -3.583179 -0.365670 -0.006558
C -2.412275 0.147226 0.536844
C -1.205940 -0.558925 0.414649
C -1.188495 -1.784586 -0.267295
C -2.362715 -2.293936 -0.815883
H -2.346658 -3.246184 -1.343510
H -4.476455 -1.990586 -1.111562
H -0.259362 -2.343953 -0.359975
H -4.518205 0.183409 0.093812
H -2.400324 1.098968 1.066866
C 2.538267 -0.150952 0.405617
C 2.518149 1.066877 -0.290139
C 3.690376 1.570328 -0.848372
C 4.887183 0.866321 -0.712802
C 4.914195 -0.348208 -0.021193
C 3.745254 -0.855282 0.531832
H 3.735379 -1.800969 1.072622
H 5.803248 1.264327 -1.147543
H 5.849747 -0.895793 0.082383
H 1.588507 1.624835 -0.386182
H 3.672245 2.516517 -1.386717

Chapter 5

$\text{L}^{\text{tBu}}\text{Cr}(\text{biphenyl-2,2'-bisimido}) \text{S}=0$

Cr -0.03747666248307 0.05434971989982 -0.05784986870329
N -1.28545210496233 -0.02855226692797 -1.32211140858595
P -2.73391857762264 -0.28480332620582 -1.82272414238570
N 1.55121158039363 0.20820961985383 -0.83028605228028
P 3.05522437935597 -0.07998801807218 -1.09036458496676
N -0.26500627210957 1.30128524998045 1.03443981909255
N -0.14275761462765 -1.26550828360850 0.95485338944191
C -0.87102203806595 1.50035378227758 2.22833510895833
C 0.13510258985958 -1.59494292414719 2.23664683029267
C -0.08650333646112 -0.71030927501104 3.33621687494640
C -0.86481425142335 0.54488600461587 3.29191714829233
C -1.55601020072620 2.72190892776702 2.40985814522167
C 0.70402811003980 -2.86434197502199 2.47557307646541
C -2.29891688876357 2.98576686565216 3.54697522076005
C 1.17042527356347 -3.23024048109113 3.72713637089221
C -2.36676948083255 2.02343333750125 4.55702126546169
C 1.06140980747754 -2.32710596514355 4.78675076569880
C -1.64988170469389 0.84170846550825 4.41656329553501
C 0.42987878689359 -1.10622341087177 4.57858536461845
H -2.07510399950922 3.53304941469941 -1.84248927886674
C -0.98449847284853 2.16644749834703 -3.10362387292945
C -2.04707435415631 -2.89312486603669 -1.31097065268809
C -1.09247990135185 3.14999252444509 -2.11481268721624
C -3.08449268597514 0.68870068012023 -3.33331756102486
C -4.01997414751982 0.23735775306574 -0.56339080704842
C -2.88352822601651 -2.10190781516082 -2.32309591066765
C 3.65178294451309 0.91013537924355 -2.51121173722976
C 0.28742588090197 1.71680961616902 -3.47849287328519
H 0.38103466146910 0.95393342919088 -4.25457500871412
C 1.43428675498030 2.18383755437162 -2.82862492735661
C -2.20696586698256 1.68938685137560 -3.81245129815418
C 2.79397027185649 1.75396098203220 -3.25614640377445
C 3.30289445730234 -1.87511596327458 -1.62812162777009

C 4.08294248854579 0.39965724601549 0.40126479356854
C -3.81985304894261 -0.60258415036936 0.69926632814404
C -2.22290643585974 -2.24038197859829 -3.69749916032680
C 3.73681552188016 -0.54919511224149 1.54995251421702
C 4.72373575443832 -2.42821426675516 -1.55348516136154
C 2.77337380057194 -1.96060257069097 -3.06354225853102
C 1.30310957955156 3.15568099452649 -1.82898698555766
H 2.19394319957699 3.53380026601099 -1.32866393500337
C 4.95600419749902 0.69215596187722 -2.98693529803253
H 5.63413004968068 0.05644998867710 -2.42360117899872
C 0.04719578484016 3.63726795307766 -1.47927132297346
H -0.04476987920413 4.39685983957682 -0.70389307311692
C -4.28786968602962 -2.70171178864376 -2.35384275036151
C 2.40045174034749 -2.73677439902215 -0.74146753182239
C -3.68300427020665 1.69841239465706 -0.25574037760670
C 5.59444564025550 0.43904337936517 0.18693613378025
C -4.23553676445158 0.38884119044586 -4.08051471107881
H -4.91931792474265 -0.37941111267102 -3.72484865952374
H 0.34905667816155 -0.40996963813902 5.41188217997071
C -5.47294953204907 0.16931470893352 -1.02791908393030
H -1.50569189061647 3.44091866208903 1.59295202748328
C -4.52857256695709 1.03344225332817 -5.27740476971013
H -5.43057613618581 0.77472770693653 -5.82996358156429
H -1.71992736419707 0.09100677645081 5.20221882112318
C 3.60551168421450 1.81053787280369 0.75946503226764
C 3.26335602587818 2.28661515106868 -4.46795522396779
H 2.59222798298473 2.92790266000732 -5.03972518343477
C 5.41266704611242 1.25112136844265 -4.17609166723956
H 6.43093795105978 1.06026653314050 -4.51160272813676
C -2.51159627233295 2.31985778534523 -5.03004781424458
H -1.82906379875529 3.08736806511748 -5.39561628064144
H 0.79384784738554 -3.53635821546053 1.62320801774142
C 4.55044985553171 2.03999891517657 -4.93373302306537
H 4.88176934285137 2.47382051030006 -5.87626694196523
C -3.65226282446540 2.00272888234564 -5.76029596081508

H -3.85782358622177 2.51497927624352 -6.69932245965985
 H -2.83679806683283 3.92895578651149 3.64054348891064
 H -2.97226944245864 2.19045095476601 5.44645554477477
 H 1.63226486056563 -4.20627747970995 3.87394194225727
 H 1.45723040891454 -2.57364038527505 5.77072687610256
 H 2.65326897486948 -0.65292392186082 1.68557152787336
 H 4.14361047683946 -0.15259428157615 2.48959141615000
 H 4.16348280448491 -1.55007101370050 1.41382365028537
 H 2.52598579238798 1.84589313804425 0.94789583324574
 H 3.83606881125385 2.52739890459436 -0.03889240990064
 H 4.12503784816034 2.15173812853514 1.66449819906364
 H 5.88901994709784 1.21353593158654 -0.52941498727603
 H 6.01787950110314 -0.51529694631341 -0.14362931402384
 H 6.08167798517518 0.68839960920044 1.13936879633486
 H -4.97575855581398 -2.19972727839033 -3.04148755436614
 H -4.75236618361620 -2.72420169908345 -1.36177569329271
 H -4.21978723873295 -3.74544738126443 -2.69052318881173
 H -2.39606696710427 -2.77849919579385 -0.27911987286813
 H -0.99746060328846 -2.58656072675782 -1.32489496175312
 H -2.09777568505792 -3.96089123368731 -1.56329455030820
 H -2.82883346330543 -1.81601447531484 -4.50556508490316
 H -2.06577923674013 -3.30333751243709 -3.92378708854722
 H -1.24055884075168 -1.75058625458353 -3.71993852477144
 H -4.38998956345657 -0.16260113344333 1.52889063059426
 H -2.76789524518265 -0.63569278270418 1.01218020999355
 H -4.17055170303469 -1.63425177517386 0.57541904763209
 H -4.29716579925411 2.04972995609831 0.58408032188149
 H -3.89622487844574 2.34653913814262 -1.11528322487567
 H -2.63035264702115 1.82667817665850 0.01997442773307
 H -6.12190619817849 0.51327234527675 -0.21102582897355
 H -5.80638623274456 -0.83849290011850 -1.29261358400993
 H -5.66391861091457 0.83094467710918 -1.88024808356970
 H 1.34849090001036 -2.44907990715405 -0.82626095305879
 H 2.66291631247119 -2.68369868735554 0.32024863201402
 H 2.49195990594959 -3.78675792853013 -1.05135665998396

H 4.71965621224348 -3.46892913503962 -1.90614207718157
 H 5.11029775471366 -2.44856199143716 -0.52815242540520
 H 5.44081635285572 -1.89301122397097 -2.18349674733726
 H 1.78030911096456 -1.49803980279880 -3.14788672941241
 H 2.67225148501019 -3.01430285755806 -3.35543080544116
 H 3.43586081523950 -1.47780903040170 -3.79109089243029

L^uBuCr(biphenyl-2,2'-bisimido) S=1

Cr 0.145167 0.241785 0.075569
 N -1.415039 0.435398 -0.778144
 P -2.664708 -0.144267 -1.509914
 N 1.525063 0.029702 -1.018297
 P 3.024839 -0.231643 -1.334599
 N 0.314770 1.416424 1.291507
 N -0.083550 -1.252378 1.083970
 C -0.653731 1.660110 2.213033
 C -0.029659 -1.506717 2.369586
 C -0.335210 -0.564705 3.446094
 C -0.980444 0.734971 3.251696
 C -1.344297 2.890480 2.156277
 C 0.352219 -2.841302 2.751429
 C -2.344992 3.207033 3.057174
 C 0.553766 -3.208204 4.059837
 C -2.679111 2.301150 4.070696
 C 0.350945 -2.261906 5.081248
 C -1.992194 1.098907 4.155659
 C -0.099564 -0.985693 4.757915
 H -1.897682 3.628186 -1.492139
 C -0.934764 2.286172 -2.879096
 C -2.159096 -2.846199 -1.115712
 C -0.943627 3.259246 -1.870406
 C -3.101497 0.890677 -2.958182
 C -4.124660 -0.106551 -0.320529
 C -2.371985 -1.847430 -2.254298
 C 3.587070 0.752057 -2.772197

C	0.290385	1.815538	-3.359021	C	-2.592494	2.518908	-4.679276
H	0.307902	1.057575	-4.144997	H	-1.905813	3.259494	-5.089844
C	1.499016	2.262962	-2.810316	H	0.518682	-3.542426	1.934104
C	-2.222428	1.858411	-3.496285	C	4.513614	2.106173	-5.063560
C	2.804944	1.781442	-3.344989	H	4.859079	2.634894	-5.950939
C	3.216644	-2.046917	-1.831934	C	-3.803764	2.269027	-5.315595
C	4.141121	0.252817	0.089472	H	-4.060835	2.804797	-6.228398
C	-3.573014	-0.494427	1.055525	H	-2.872703	4.157051	2.971365
C	-1.068226	-1.698363	-3.043526	H	-3.474782	2.527287	4.778698
C	3.778687	-0.613129	1.296858	H	0.883125	-4.218218	4.303097
C	4.599419	-2.674319	-1.664559	H	0.538512	-2.523824	6.121694
C	2.769012	-2.156555	-3.292442	H	2.701427	-0.595555	1.506010
C	1.469889	3.243979	-1.814931	H	4.287257	-0.227236	2.189901
H	2.404067	3.621614	-1.401816	H	4.088902	-1.657792	1.175825
C	4.823449	0.439701	-3.361967	H	2.721929	1.849757	0.607417
H	5.435255	-0.352586	-2.934848	H	4.065906	2.368978	-0.441598
C	0.252581	3.735028	-1.346828	H	4.355139	2.045687	1.271344
H	0.243099	4.493204	-0.564565	H	5.943327	0.859047	-0.994609
C	-3.455064	-2.361401	-3.201633	H	5.991783	-0.829935	-0.450950
C	2.229176	-2.832165	-0.960205	H	6.187633	0.480885	0.706250
C	-4.594644	1.348758	-0.251522	H	-3.542944	-1.750762	-4.106473
C	5.640102	0.173849	-0.195120	H	-4.444750	-2.433370	-2.738999
C	-4.325438	0.662505	-3.608322	H	-3.185314	-3.374966	-3.529259
H	-5.016929	-0.073239	-3.203686	H	-3.090688	-3.079177	-0.586157
H	-0.261663	-0.268737	5.562087	H	-1.424774	-2.489174	-0.380860
C	-5.298331	-1.028061	-0.647785	H	-1.781767	-3.791981	-1.528811
H	-1.070376	3.574814	1.354792	H	-1.184455	-1.015620	-3.896219
C	-4.686146	1.341137	-4.767327	H	-0.766016	-2.676161	-3.444206
H	-5.646197	1.139977	-5.240332	H	-0.249952	-1.316480	-2.419658
H	-2.279183	0.378146	4.920632	H	-4.384704	-0.448677	1.794137
C	3.788366	1.711762	0.392226	H	-2.788337	0.194336	1.379159
C	3.289152	2.433338	-4.490905	H	-3.153920	-1.506607	1.082385
H	2.679190	3.223914	-4.928369	H	-5.303939	1.466663	0.578542
C	5.292382	1.103167	-4.490610	H	-5.097657	1.676005	-1.168734
H	6.255967	0.833659	-4.920378	H	-3.753903	2.027498	-0.059349

H	-6.068051	-0.907612	0.126676	C	-2.18123284984139	-2.82846677617689	-1.39715986412792
H	-5.012796	-2.085673	-0.643449	C	-1.11662557831458	3.01512452351277	-2.18080950040353
H	-5.786209	-0.809492	-1.602938	C	-3.19722191978168	0.78037348191088	-3.36201400217953
H	1.196218	-2.501938	-1.103012	C	-4.13440429116610	0.30412505604033	-0.56437678468138
H	2.441640	-2.739864	0.110564	C	-3.00138491840925	-1.99823689804000	-2.38923898414670
H	2.291736	-3.897400	-1.221566	C	3.66301010261791	0.90996801076203	-2.46503929505677
H	4.560752	-3.714478	-2.016566	C	0.27593918266546	1.65692163842827	-3.61213583690096
H	4.916801	-2.711501	-0.616643	H	0.37759647568396	0.93457724222112	-4.42484521552323
H	5.388191	-2.182410	-2.242634	C	1.41206309206907	2.06419016140248	-2.90238682819654
H	1.835901	-1.607672	-3.473248	C	-2.22479738585232	1.63715681120751	-3.93280631033620
H	2.583594	-3.209609	-3.543286	C	2.77668798840256	1.63623537321026	-3.29891788983949
H	3.519754	-1.776419	-3.993866	C	3.42378195117289	-1.85739285779413	-1.48873491435193
L ^u BuCr(biphenyl-2,2'-bisimido) S=0 Iroot 1				C	4.01060691325046	0.51489095677850	0.49378271625889
Cr	-0.09802540624984	0.06599513488760	-0.15193311602623	C	-3.92825209498139	-0.58547265737242	0.66346680452104
N	-1.40941935413894	0.06359352207717	-1.34573127540277	C	-2.32565366305222	-2.10074512162352	-3.75995129756352
P	-2.86297340455058	-0.19224461728938	-1.84469734756508	C	3.67602023313292	-0.44097299630621	1.63968809138547
N	1.53044199625492	0.05969434288160	-0.84634529729736	C	4.87255579350813	-2.32071449210256	-1.36239046188385
P	3.07479442054099	-0.05633447222941	-1.02313036399466	C	2.93965497934154	-2.01771892187432	-2.93359077566744
N	-0.34047040449324	1.34688283116155	0.98191058162131	C	1.26630581552832	2.97494577025138	-1.84747879484964
N	-0.18908513934709	-1.39739373700659	0.82821522378993	H	2.15022664503189	3.31238158003817	-1.30940509041808
C	-0.82419029821265	1.46285845602919	2.22627907190936	C	4.98817598638735	0.72747844993117	-2.89573490451308
C	0.11849537975683	-1.64907123299915	2.09741522953659	H	5.68982241463468	0.18788564162653	-2.26528100479484
C	0.06194332896722	-0.74639273501140	3.23569946954509	C	0.01026495258888	3.45630125365049	-1.49713274776052
C	-0.68532107860491	0.50375707988289	3.29444865223302	H	-0.09122902767285	4.16113178572827	-0.67378768810265
C	-1.51862772349274	2.67492290363885	2.51073767906885	C	-4.41407746238605	-2.57299798615392	-2.45531536248793
C	0.60721072334772	-2.97512629940670	2.34177390978012	C	2.55032390408640	-2.74279954811408	-0.59529432546861
C	-2.11441398387535	2.92770340915141	3.72595866078514	C	-3.77151202234140	1.74797995886160	-0.20498429796166
C	1.20003335334722	-3.34737509353699	3.52503282858553	C	5.52365512436073	0.64325695377405	0.33220156426583
C	-2.02488393831528	1.96943557374788	4.74806535592413	C	-4.37603989231369	0.53027742909604	-4.08382615043436
C	1.28892837109090	-2.41138516847380	4.57032046516436	H	-5.13542264346507	-0.12490356323473	-3.66258920102680
C	-1.31449412351632	0.80415177333506	4.51998614890818	H	0.76998424092468	-0.45565537704295	5.23895116915904
C	0.70551982308753	-1.16465371944156	4.41520096553363	C	-5.59414255719709	0.27195966818027	-1.01126536760288
H	-2.10412854013901	3.37775342592915	-1.89988609661404	H	-1.57883252655249	3.39482595805298	1.69505420483678
C	-0.99733008754319	2.08966324306206	-3.22588147423015	C	-4.59709892256794	1.07116046710680	-5.34648817216560
				H	-5.52299161012386	0.85508832665209	-5.87720795679979

H -1.27833972146650 0.05524244341448 5.30910611140125
 C 3.43585040809839 1.89695669773095 0.81682333695566
 C 3.23493990493158 2.06041767634355 -4.55656720245577
 H 2.54202279509078 2.60723384062721 -5.19630103637168
 C 5.43511053976036 1.19127377846976 -4.12886700397216
 H 6.46969231171919 1.03103944100469 -4.42794533431372
 C -2.45058974991430 2.14839634034089 -5.22024972606859
 H -1.69151974633240 2.79869394475729 -5.65552050361688
 H 0.55428462070759 -3.66021163470629 1.49672605216926
 C 4.54120661338210 1.83808463794127 -4.97897246175845
 H 4.86431711001378 2.18781527206142 -5.95837766568589
 C -3.61574757331039 1.87081346979488 -5.92781973249396
 H -3.76141185835223 2.28856922098558 -6.92299075770585
 H -2.65873836618324 3.85835643645923 3.88644829552547
 H -2.51558721525336 2.13049456661867 5.70658078779486
 H 1.61350891316120 -4.34905735142906 3.64188643339642
 H 1.79852060114285 -2.66244207895054 5.49927758609442
 H 2.59697069189730 -0.62299455793885 1.72095037520195
 H 4.00162865053548 -0.00210102587106 2.59181003978798
 H 4.18091839831857 -1.40900032493041 1.54229611405390
 H 2.34408792547741 1.87912487303471 0.92712141735591
 H 3.69384368308866 2.62918818451773 0.04190366590360
 H 3.86752455437792 2.25751015956070 1.75944607932775
 H 5.79622294761060 1.41742320289637 -0.39323594298394
 H 6.01602149513779 -0.29063731163429 0.04121586409662
 H 5.96009342662299 0.94448111442897 1.29404213716890
 H -5.07810623378981 -2.04255893349274 -3.14523622414605
 H -4.89528872808162 -2.60746809256982 -1.47160783738100
 H -4.35898243601270 -3.61012433972552 -2.81360811568074
 H -2.52753128853132 -2.73869706561930 -0.36258559366728
 H -1.12594416704205 -2.54186692258735 -1.39638283721880
 H -2.24993371118585 -3.88723473032631 -1.68094457369146
 H -2.91824775801202 -1.65085898823168 -4.56413393059221
 H -2.17392739376357 -3.15852653373163 -4.01192778747079
 H -1.33864317222563 -1.61958679883253 -3.75478077631804

H -4.48734810346234 -0.17366371542524 1.51423559538006
 H -2.87248306748002 -0.63754020170960 0.96127889279404
 H -4.28808522123944 -1.60884519403450 0.50334572460893
 H -4.38899606322076 2.08128352389715 0.63963658883977
 H -3.96672181079751 2.42856966177020 -1.04359273296367
 H -2.71881385467041 1.84836977465296 0.08649008510753
 H -6.23007573426755 0.57195958286306 -0.16735240238340
 H -5.93833824347164 -0.71690126482016 -1.32943310327553
 H -5.79240902337172 0.98369716400911 -1.82018478576021
 H 1.49147449362719 -2.47006869057014 -0.64551759099541
 H 2.84229209523555 -2.70941593057170 0.45906645363145
 H 2.65342671725454 -3.78532095534493 -0.92583851298904
 H 4.93128856372850 -3.37545022026874 -1.66389350240872
 H 5.23828159042793 -2.27158705722223 -0.33068431403817
 H 5.57064135889583 -1.77738784579709 -2.00639900546215
 H 1.91525418484604 -1.64057597111052 -3.05277944382643
 H 2.93265368529182 -3.08336576012312 -3.19690052957764
 H 3.58049161777384 -1.50293943358314 -3.65843146575835

L^uBuCr(biphenyl-2,2'-bisimido) S=0 Transition state

Cr 0.309887 0.140808 0.003644
 N -1.292424 0.153551 -0.651183
 P -2.633498 -0.325652 -1.313729
 N 1.651880 0.056921 -1.120424
 P 3.139523 -0.178720 -1.536869
 N 0.500403 1.381094 1.563511
 N 0.542047 -0.557221 1.532768
 C -0.485717 1.734327 2.384274
 C 0.008727 -1.124975 2.634461
 C -1.063224 -0.507866 3.336889
 C -1.414102 0.870551 3.082797
 C -0.624908 3.138706 2.610957
 C 0.483270 -2.394952 3.011399
 C -1.742016 3.670086 3.219014
 C -0.157731 -3.122793 3.999968

C	-2.748022	2.823043	3.718940	H	-4.819498	-0.559071	-3.187619
C	-1.247273	-2.551335	4.670016	H	-2.472956	-0.825737	4.936785
C	-2.546543	1.454286	3.674393	C	-5.457959	-0.204549	-0.716921
C	-1.664313	-1.266210	4.356835	H	0.151571	3.781487	2.198204
H	-2.018570	3.186805	-1.246028	C	-4.406164	0.676414	-4.871542
C	-0.932563	2.109560	-2.771500	H	-5.290985	0.341624	-5.410636
C	-1.721172	-2.872237	-0.654665	H	-3.300570	0.802476	4.116525
C	-1.038895	2.973444	-1.673047	C	3.918813	1.566311	0.379973
C	-3.007714	0.575464	-2.863280	C	3.290955	2.875832	-4.330835
C	-4.055005	-0.025113	-0.141280	H	2.664635	3.711760	-4.642854
C	-2.372863	-2.121145	-1.821521	C	5.303797	1.579158	-4.555297
C	3.629850	0.963567	-2.881492	H	6.261420	1.384069	-5.035540
C	0.331874	1.844968	-3.304597	C	-2.418007	2.016197	-4.721727
H	0.424564	1.159092	-4.150002	H	-1.738479	2.752029	-5.151983
C	1.487732	2.378752	-2.723360	H	1.326719	-2.808045	2.459092
C	-2.137815	1.539259	-3.429989	C	4.512904	2.653319	-4.957036
C	2.823982	2.049621	-3.296120	H	4.843813	3.314382	-5.756887
C	3.295781	-1.929093	-2.223640	C	-3.530543	1.596817	-5.441894
C	4.314574	0.175705	-0.127410	H	-3.717001	1.994622	-6.438468
C	-3.869237	-0.946899	1.064103	H	-1.848122	4.752731	3.296327
C	-1.366927	-2.054807	-2.977537	H	-3.651341	3.234539	4.166271
C	4.062253	-0.853447	0.975575	H	0.186851	-4.124148	4.254629
C	4.694063	-2.543950	-2.214679	H	-1.754441	-3.104319	5.459872
C	2.750929	-1.889608	-3.654310	H	2.998968	-0.915931	1.238779
C	1.360293	3.255146	-1.641702	H	4.604103	-0.552749	1.881696
H	2.251474	3.689459	-1.189210	H	4.420509	-1.854062	0.705265
C	4.858741	0.753106	-3.529095	H	2.879116	1.613336	0.728060
H	5.488336	-0.081420	-3.227295	H	4.063015	2.331687	-0.393796
C	0.100512	3.549289	-1.121483	H	4.564658	1.835484	1.225928
H	0.007727	4.215192	-0.265303	H	6.034611	1.015685	-1.194183
C	-3.625934	-2.877962	-2.252843	H	6.155205	-0.737682	-0.941599
C	2.372426	-2.815543	-1.379434	H	6.385498	0.371526	0.405468
C	-3.888387	1.434718	0.294710	H	-4.099742	-2.461676	-3.147054
C	5.794985	0.199247	-0.504339	H	-4.374234	-2.940226	-1.454184
C	-4.134954	0.174744	-3.603071	H	-3.347870	-3.910844	-2.502035

H -2.403106 -3.037736 0.184786
 H -0.836053 -2.349922 -0.269187
 H -1.399907 -3.860188 -1.010514
 H -1.801197 -1.623520 -3.887813
 H -1.019867 -3.067827 -3.222490
 H -0.485664 -1.457835 -2.702312
 H -4.506384 -0.602311 1.889229
 H -2.837356 -0.945222 1.434204
 H -4.159700 -1.980419 0.840774
 H -4.653001 1.680923 1.042609
 H -4.018756 2.124617 -0.549422
 H -2.909549 1.621102 0.750099
 H -6.187322 -0.063513 0.091795
 H -5.637428 -1.202319 -1.133441
 H -5.691679 0.539576 -1.485345
 H 1.336769 -2.462624 -1.404870
 H 2.671391 -2.860682 -0.326599
 H 2.399118 -3.839366 -1.776209
 H 4.640895 -3.553961 -2.643566
 H 5.096191 -2.653986 -1.201807
 H 5.424978 -1.992852 -2.814765
 H 1.784206 -1.372574 -3.703144
 H 2.595912 -2.914077 -4.018136
 H 3.432755 -1.390131 -4.351455
 H 1.784206 -1.372574 -3.703144
 H 2.595912 -2.914077 -4.018136
 H 3.432755 -1.390131 -4.351455
 H 4.063015 2.331687 -0.393796
 H 4.564658 1.835484 1.225928
 H 6.034611 1.015685 -1.194183
 H 6.155205 -0.737682 -0.941599
 H 6.385498 0.371526 0.405468
 H -4.099742 -2.461676 -3.147054
 H -4.374234 -2.940226 -1.454184
 H -3.347870 -3.910844 -2.502035

H -2.403106 -3.037736 0.184786
 H -0.836053 -2.349922 -0.269187
 H -1.399907 -3.860188 -1.010514
 H -1.801197 -1.623520 -3.887813
 H -1.019867 -3.067827 -3.222490
 H -0.485664 -1.457835 -2.702312
 H -4.506384 -0.602311 1.889229
 H -2.837356 -0.945222 1.434204
 H -4.159700 -1.980419 0.840774
 H -4.653001 1.680923 1.042609
 H -4.018756 2.124617 -0.549422
 H -2.909549 1.621102 0.750099
 H -6.187322 -0.063513 0.091795
 H -5.637428 -1.202319 -1.133441
 H -5.691679 0.539576 -1.485345
 H 1.336769 -2.462624 -1.404870
 H 2.671391 -2.860682 -0.326599
 H 2.399118 -3.839366 -1.776209
 H 4.640895 -3.553961 -2.643566
 H 5.096191 -2.653986 -1.201807
 H 5.424978 -1.992852 -2.814765
 H 1.784206 -1.372574 -3.703144
 H 2.595912 -2.914077 -4.018136
 H 3.432755 -1.390131 -4.351455

LⁿBuCr(biphenyl-2,2'-bisimido) S=1 Transition state

Cr 0.315592 0.084501 0.092593
 N -1.323764 0.349732 -0.568272
 P -2.574759 -0.246393 -1.280603
 N 1.608138 0.066837 -1.137489
 P 3.084119 -0.190460 -1.563270
 N 0.524123 1.276245 1.626759
 N 0.509495 -0.819864 1.554511
 C -0.559775 1.627919 2.343526
 C -0.014643 -1.312042 2.688803

C	-0.992813	-0.610001	3.450033	H	0.082630	4.497175	-0.421554
C	-1.384107	0.758235	3.135879	C	-3.547786	-2.838796	-2.216022
C	-0.870302	3.013758	2.337602	C	2.311102	-2.819786	-1.366093
C	0.415858	-2.596469	3.087022	C	-3.954515	1.438689	0.318401
C	-2.015221	3.509508	2.929942	C	5.761598	0.187361	-0.574101
C	-0.158434	-3.234886	4.170934	C	-4.065365	0.222746	-3.600940
C	-2.883652	2.642817	3.605789	H	-4.730078	-0.540900	-3.208923
C	-1.127676	-2.561409	4.923220	H	-2.216181	-0.751975	5.215086
C	-2.542236	1.304523	3.711962	C	-5.435335	-0.227743	-0.769748
C	-1.506454	-1.271934	4.575492	H	-0.187614	3.668524	1.799770
H	-1.961263	3.400099	-1.291457	C	-4.347876	0.750000	-4.856677
C	-0.893668	2.198608	-2.735510	H	-5.219866	0.402278	-5.408681
C	-1.623630	-2.789369	-0.657259	H	-3.217917	0.638911	4.246913
C	-0.985820	3.144958	-1.705813	C	3.907983	1.577282	0.317866
C	-2.954802	0.635836	-2.843406	C	3.381836	2.929519	-4.272579
C	-4.054714	-0.015513	-0.152062	H	2.806507	3.815173	-4.543052
C	-2.308136	-2.046870	-1.808973	C	5.310258	1.523975	-4.566070
C	3.599021	0.928601	-2.921188	H	6.255021	1.294501	-5.056654
C	0.366215	1.875353	-3.244257	C	-2.400566	2.140559	-4.662599
H	0.447709	1.134340	-4.042883	H	-1.736588	2.901427	-5.073269
C	1.531669	2.445306	-2.718623	H	1.186564	-3.077408	2.485590
C	-2.107054	1.630285	-3.386377	C	4.590592	2.666511	-4.908445
C	2.858477	2.076543	-3.287275	H	4.964895	3.347754	-5.671444
C	3.244813	-1.956072	-2.222310	C	-3.501628	1.714578	-5.396694
C	4.286951	0.176816	-0.173727	H	-3.697988	2.136775	-6.381329
C	-3.883174	-0.950643	1.045666	H	-2.240921	4.573687	2.859142
C	-1.317876	-1.969988	-2.976680	H	-3.805502	3.011885	4.052017
C	4.055080	-0.832057	0.952259	H	0.158822	-4.239593	4.447041
C	4.635741	-2.588037	-2.196237	H	-1.568515	-3.034501	5.799591
C	2.704525	-1.942780	-3.655014	H	2.998351	-0.892177	1.241068
C	1.419371	3.408113	-1.713560	H	4.617230	-0.518067	1.841591
H	2.316650	3.879040	-1.311807	H	4.404694	-1.838318	0.691866
C	4.813872	0.677964	-3.580440	H	2.876519	1.630152	0.685758
H	5.397023	-0.200404	-3.311822	H	4.032289	2.328766	-0.472804
C	0.163153	3.749574	-1.209354	H	4.572221	1.861386	1.144656

H	5.995079	0.991423	-1.280221	N	1.60746038319136	0.12710760018903	-1.10576194282819
H	6.109639	-0.757817	-1.003049	P	3.08431848577854	-0.17674157015491	-1.50551268299500
H	6.367842	0.369334	0.323605	N	0.52128374193744	1.26886085942253	1.60343249157973
H	-4.063021	-2.425463	-3.088299	N	0.40248638220520	-0.93144214306065	1.46744790505365
H	-4.269998	-2.934877	-1.396892	C	-0.58319257043282	1.61692887855159	2.29616517299189
H	-3.248521	-3.860197	-2.489965	C	-0.03536786222095	-1.38750584780240	2.65607571565963
H	-2.265810	-2.921485	0.218834	C	-0.90261301396059	-0.61765192712227	3.48296445134933
H	-0.712075	-2.283164	-0.318800	C	-1.33788459832857	0.73887160111833	3.14567468648030
H	-1.330046	-3.790613	-1.000913	C	-0.97614541888541	2.97730052883630	2.22984131933774
H	-1.769620	-1.554502	-3.885614	C	0.37869809097166	-2.67546472074981	3.05079926991540
H	-0.947068	-2.975614	-3.219885	C	-2.11398795893279	3.44537308001701	2.86077643800648
H	-0.446602	-1.350247	-2.716407	C	-0.08236422180111	-3.24317862522628	4.22586940220973
H	-4.555527	-0.638201	1.856150	C	-2.90630012632538	2.57012083630032	3.61112584092880
H	-2.862800	-0.925217	1.446596	C	-0.91760966791671	-2.49377402314533	5.05951177478353
H	-4.135944	-1.989093	0.799168	C	-2.49767900140268	1.25170131362272	3.74660875408028
H	-4.776921	1.656535	1.012873	C	-1.29112638154511	-1.20606765175331	4.69482181513010
H	-4.036206	2.141275	-0.521781	H	-1.91007737048365	3.46084787973013	-1.28672764218431
H	-3.010415	1.636865	0.836448	C	-0.90440049001692	2.22452340648262	-2.74521529562277
H	-6.191414	-0.128454	0.020873	C	-1.68960006661260	-2.84835473967659	-0.84876574978344
H	-5.572624	-1.220051	-1.213875	C	-0.94994911390506	3.17860575814445	-1.71964073785664
H	-5.671827	0.526155	-1.527790	C	-3.00452854856085	0.71135727397742	-2.83659693632249
H	1.273018	-2.483144	-1.442478	C	-4.02900835654551	-0.08549675928639	-0.14772879006058
H	2.576957	-2.814975	-0.302647	C	-2.29279284330116	-2.00283271042910	-1.97347276723452
H	2.358459	-3.859480	-1.717204	C	3.59899132711107	0.88003136072699	-2.90941334418214
H	4.571957	-3.605582	-2.605977	C	0.33594699124573	1.85939116060705	-3.27479304236477
H	5.034287	-2.683847	-1.180547	H	0.38019054332281	1.10817466973202	-4.06693722342813
H	5.376960	-2.058993	-2.803114	C	1.52656565964952	2.40120173525075	-2.77594321018606
H	1.745044	-1.413405	-3.717908	C	-2.15403601632949	1.70739522121496	-3.37207755754937
H	2.535121	-2.972564	-3.997445	C	2.83871965313447	1.98835074571711	-3.35091420643749
H	3.394096	-1.468114	-4.361718	C	3.24008084012081	-1.96801833057868	-2.09179977041045
L ^{ti} BuCr(biphenyl-2,2'-bisimido) MECP Transition state				C	4.27533112467326	0.23734044428527	-0.11970463887483
Cr	0.29317825705651	0.03264642704396	0.09380207957344	C	-3.77969639783753	-1.03989174951076	1.02170805809765
N	-1.31394524459315	0.32435905508948	-0.62561680132008	C	-1.23213429696965	-1.83283375604628	-3.06769441976074
P	-2.58064817068693	-0.24252803915701	-1.33116512855960	C	4.01761978938980	-0.71658415060576	1.04790720646245
				C	4.62437186603625	-2.60884708593354	-2.00604269270433

C	2.73702467835523	-2.00983654720502	-3.53764060779120	H	2.95810471372519	-0.74330306364439	1.33094435814743
C	1.45974655941662	3.38043646498626	-1.78237722295032	H	4.57853721976387	-0.37333089440547	1.92699427698008
H	2.37659782162627	3.83439257460773	-1.40684461637324	H	4.34784301965744	-1.74076857071257	0.83711447164255
C	4.81268673121197	0.59780974033402	-3.55805585174471	H	2.86693655140962	1.73787675722221	0.65166025577150
H	5.40859357915026	-0.25257677376698	-3.23212335473111	H	4.05514943386946	2.37832573181280	-0.51004708422805
C	0.22481771321957	3.75929356693223	-1.25530320142855	H	4.55678710290110	1.96969959587041	1.13519432201553
H	0.18228322382261	4.51900748534593	-0.47593097204972	H	5.99737827989925	0.97712982055207	-1.25418951827506
C	-3.50407129441742	-2.74160253751819	-2.53528755482782	H	6.10167192055194	-0.75344864407189	-0.87275855754273
C	2.27566058455041	-2.78628992128757	-1.22476205662788	H	6.35226758133368	0.44942977621659	0.38697085799914
C	-3.94585179114357	1.36018831694376	0.35274614929956	H	-3.92860404802910	-2.26094535452034	-3.42196286625480
C	5.75383730183427	0.21675821940010	-0.50419529954648	H	-4.29933419803727	-2.87402824529726	-1.79256863306162
C	-4.15704567518988	0.35810376471007	-3.56049034940788	H	-3.19690359792735	-3.74981794715706	-2.84674024444699
H	-4.82294404974251	-0.40703277209927	-3.17310662168159	H	-2.41687395652602	-3.11749199593540	-0.07698934519535
H	-1.89610209486208	-0.62584058031513	5.38842550021859	H	-0.85076396850315	-2.34828458976126	-0.34986524681217
C	-5.43103453746842	-0.32145178761450	-0.70534690010200	H	-1.30466066824133	-3.78647990050757	-1.27124371122861
H	-0.35540531807054	3.64120520177012	1.63150708128121	H	-1.62392019475419	-1.31821972139748	-3.95401806059761
C	-4.47856469089480	0.94786950626170	-4.77885471852380	H	-0.86812275256601	-2.81824327280581	-3.39071747866034
H	-5.38221353593638	0.64703070569944	-5.30693973588229	H	-0.36741223147186	-1.26106085352341	-2.69931150019344
H	-3.12091364686653	0.57234744168874	4.32692192397055	H	-4.39919589839665	-0.74146568566465	1.87816067220030
C	3.90498261402143	1.66114951847793	0.30730674806506	H	-2.73559908902306	-1.01941205826771	1.35796221959384
C	3.33633297215477	2.76499724158188	-4.40956921856430	H	-4.04678183338408	-2.07410987746374	0.77433627521953
H	2.74599242805006	3.61961567265899	-4.74064410601563	H	-4.75229286839199	1.54478051229060	1.07488219903324
C	5.28689984041558	1.37305370463182	-4.61050206381719	H	-4.06343898513979	2.08174402622771	-0.46705316559485
H	6.23172428020054	1.12211048243949	-5.09027470414778	H	-2.99251205866744	1.56417569899618	0.85041314987438
C	-2.48793067781686	2.28063390306478	-4.61064174916712	H	-6.14871389580697	-0.28115383678794	0.12529506006887
H	-1.82287244292054	3.04290002971150	-5.01696367486604	H	-5.55893826481387	-1.29871418836392	-1.18422478147957
H	1.05313878291133	-3.21419813610400	2.38613043949566	H	-5.73198534196514	0.45489654732292	-1.41621003166374
C	4.54221792688282	2.47038058107082	-5.03708902334694	H	1.23926810920411	-2.46189370777393	-1.36269057609243
H	4.89662567522749	3.09383790029770	-5.85687655196277	H	2.49505151302739	-2.71749809891436	-0.15282565690790
C	-3.63067857296157	1.91404588913372	-5.31312124973491	H	2.33919681489992	-3.84410102668144	-1.51357708509443
H	-3.85773787177610	2.38391388818702	-6.26918308617421	H	4.56380523792893	-3.63885836115788	-2.38390308030787
H	-2.39493912074128	4.49360106864573	2.75612247743582	H	4.99515601366860	-2.67336863056637	-0.97745444800606
H	-3.82467515666925	2.91255457317975	4.08479086604352	H	5.38515466516396	-2.10410446111721	-2.60975504353343
H	0.22719369694910	-4.24857955984835	4.50784517300527	H	1.79538343379964	-1.45820655759934	-3.65413877316770
H	-1.25982041682659	-2.90547785678881	6.00796025818818	H	2.54698916137469	-3.05024575193833	-3.83404566656477

H 3.45817716554070 -1.58997514550914 -4.24725949014890

L^{tt}BuCr(benzo[c]cinnoline) S=0

Cr -0.46922328240538 0.06066491929188 -0.05628723156475

N -1.52257440082924 -0.10210904893424 -1.43104812854965

P -2.82445095626634 -0.51708101088183 -2.18402921220181

N 1.22713393034080 0.34144708143589 -0.27828812153260

P 2.72535921867727 0.07085584996071 -0.65726181690837

N -1.20278248608814 0.64719867086926 1.60005900128882

N -0.98439111078982 -0.73930360564626 1.56633837037521

C -0.46787684978176 1.42235885509175 2.47875066419530

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C 0.65024725468089 -3.41428181640721 3.46647282086875

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C 1.21394231078022 -2.69766004576894 4.52584089051173

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 H 4.02319346667486 -1.45939310238199 1.74620917899032
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 H 3.46771551260975 2.64848280075127 0.46723043797950
 H 3.84829654422730 2.21537476232808 2.14056743802838
 H 5.57032021561310 1.40905261218504 -0.11274785787024
 H 5.73446877079874 -0.33662215754880 0.18410583107494
 H 5.79857348156777 0.80281421515390 1.52400912134956
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 H -4.50632318007206 -3.20437812087568 -2.18370565256184
 H -3.64953358409737 -4.06122266598173 -3.45923007567763
 H -2.31714954067276 -3.09201925621352 -0.79851697879914
 H -0.83520866040869 -2.56975435158840 -1.59314654623592
 H -1.64378124545663 -4.06692262531607 -2.11566899529074
 H -2.34987280521987 -1.77982972080618 -4.94942732316924
 H -1.44830596528794 -3.19740086412672 -4.39131824724791
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 H -4.94616583107971 -1.03714870780114 0.84994798794140
 H -3.21234596249874 -1.23654449755786 0.57879016084396
 H -4.38152686642589 -2.31823320519748 -0.22148439127021
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 H -5.83719675711366 0.32996121887824 -2.51818594480617
 H 1.05592779666642 -2.22429139474519 -0.10571760752072

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 H 2.05004436363126 -2.80579498195152 -2.91446715164379
 H 2.73849387247060 -1.23915286444145 -3.37324736808260

LⁿBuCr(benzo[c]cinnoline) S=1

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 P -2.53320552859402 -0.25543840046971 -1.17718551645810
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 P 3.09611406200057 -0.26632730928673 -1.62657261929492
 N 0.52726070505703 1.10889076834729 1.83415185992400
 N 0.65992952151820 -0.29743352192961 1.88584646843121
 C -0.58050426523944 1.66439263270096 2.45406029441369
 C -0.13768269216852 -1.06408281244373 2.71226880472424
 C -1.15205884479019 -0.48788906701525 3.50377399273620
 C -1.42269614910202 0.93331124608642 3.32069524240466
 C -0.81166852885230 3.03117427185161 2.25191351362296
 C 0.09830848708816 -2.44308403706879 2.75530775361719
 C -1.87708246575876 3.67030733271522 2.86773337190127
 C -0.65765206667646 -3.25858435542763 3.58646829222212
 C -2.72877984621667 2.95109965624529 3.71315150190310
 C -1.64599888604458 -2.69635939665565 4.39988859040627
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 C -1.87875726781766 -1.32396806158000 4.35300539301995
 H -2.04207360319486 3.45536035673952 -1.40472334187202
 C -0.91430661204648 2.16127184927337 -2.71551814496557
 C -1.45048522176981 -2.69479646021994 -0.43363129415469
 C -1.04991785971378 3.17854577615924 -1.76127113427989
 C -2.92332062902043 0.53457674110450 -2.78564414122232
 C -4.02630580872057 -0.00645097456827 -0.07033976273610

C	-2.21521024686334	-2.07120759575736	-1.60586248870629	C	5.31235986769503	1.67181106496807	-4.49832833733058
C	3.58187314420789	0.93553871980220	-2.92908790591085	H	6.26008994355039	1.48173372544247	-4.99994555938384
C	0.36398782167179	1.81603370233510	-3.15913505508882	C	-2.40184757284783	1.99042176252182	-4.65370810023775
H	0.47778577735834	1.02907618611406	-3.90792799110286	H	-1.75954477777988	2.75731502820332	-5.08707613264877
C	1.50685929087683	2.44078450401805	-2.64417218721690	H	0.88558563603503	-2.85057606193861	2.11958746751891
C	-2.10404564710230	1.53529527432609	-3.35818564344206	C	4.60562791663817	2.84885068281416	-4.73466643761809
C	2.84904325290812	2.11418262376647	-3.19965720918867	H	4.99227941938949	3.59779165054263	-5.42451359862024
C	3.32193851254285	-1.99230903785529	-2.36825825211106	C	-3.48086823038521	1.50004484562268	-5.38041040898956
C	4.29475952294441	0.08983378870944	-0.22845998329101	H	-3.68287483643798	1.87944145590682	-6.38116603335106
C	-3.84637998304028	-0.88112095921655	1.17037551382993	H	-2.04563322968836	4.73326767620605	2.69527515747045
C	-1.28234279815541	-2.05179819688682	-2.82145411228349	H	-3.56912948420449	3.44310205643315	4.20026098134980
C	4.10508750477904	-0.97316725087112	0.85452798414439	H	-0.46902060839590	-4.33139101766315	3.61338422368736
C	4.73546337880852	-2.57418233678888	-2.36815750472569	H	-2.23168131209682	-3.32519675506450	5.06852710610980
C	2.77750351501776	-1.93862777961510	-3.79814902179873	H	3.05344222286478	-1.07092043826002	1.15198447775171
C	1.35184517325906	3.45937801235526	-1.69975174881278	H	4.66672801920966	-0.68170860499897	1.75180316274952
H	2.23219028232290	3.96895095737347	-1.30664176737935	H	4.48021811572992	-1.95689847178447	0.54830810723036
C	4.80150702031078	0.74211944710448	-3.59938429517431	H	2.85036834312972	1.45222789287867	0.72689943572703
H	5.38276310084804	-0.15567967387632	-3.40150715066672	H	3.94378156180473	2.24325834897872	-0.43126768758396
C	0.07622760239954	3.82279395703795	-1.26290741516293	H	4.54276684054380	1.73092725237533	1.15157797488152
H	-0.03780111972972	4.62223438155949	-0.53206907177190	H	5.96529465874701	1.01590374630320	-1.30369522944779
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C	2.42637508220463	-2.93128522984823	-1.55074662716218	H	6.37193635203621	0.32982887836183	0.26546892505611
C	-3.96336047351776	1.46786481287664	0.34260581762453	H	-4.01998438845714	-2.58259148926921	-2.76066864598731
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C	-4.00957429503556	0.05285735157948	-3.53737099433959	H	-3.12216600758545	-3.95340771454054	-2.13150104023539
H	-4.64958806983540	-0.72053059807679	-3.12263477725726	H	-2.00964291470522	-2.69744041735410	0.50738226478176
H	-2.66108109195618	-0.90001905532860	4.98095613639222	H	-0.49725045411970	-2.18268735643142	-0.24618151861735
C	-5.39244424827032	-0.27555234113455	-0.69761580596720	H	-1.20640684348129	-3.73864734943804	-0.67487293581456
H	-0.12697721650428	3.56775093266033	1.59718541621871	H	-1.78961809236303	-1.73017203847177	-3.73870029753988
C	-4.29697233638610	0.52434857540476	-4.81398909088646	H	-0.88343301779478	-3.06033156205836	-2.99978027875435
H	-5.14935036839732	0.12527734235422	-5.36184585796714	H	-0.42431845242321	-1.38413292295341	-2.65128261225687
H	-3.16135686590924	1.04263128080900	4.58404601685992	H	-4.54805295655886	-0.56069777016909	1.95275303160992
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C	3.39169773544750	3.05663501028717	-4.08964019722770	H	-4.04672861514695	-1.94113335406859	0.97240116213392
H	2.82214611106341	3.96590116460736	-4.28336844149929	H	-4.80231350845349	1.69424917515350	1.01425757411499

H	-4.04492837741884	2.13580605827158	-0.52523253673821	C	-2.76040521711455	-0.55114354241152	-2.23650555556841
H	-3.03176564093655	1.70578993551304	0.86729923754748	C	3.26532073461677	-2.22195991566935	-0.07705387321764
H	-6.16246784885013	-0.15366522783850	0.07605460667582	C	3.96796633431352	0.62644757202534	-0.10496463613390
H	-5.50314695330645	-1.29063085958484	-1.09501055797942	C	-1.20820526246136	-1.90391101027848	2.72539441727985
H	-5.63125245822355	0.43617313031751	-1.49478686892506	C	-3.33953132103618	-2.23266974204818	0.09458905854230
H	1.37672534783757	-2.63133882957770	-1.60628517995824	C	-2.73079320876691	-4.38633036640183	1.02664004325324
H	2.69948669606945	-2.96487096414545	-0.48976244146464	C	-3.88321854949710	-4.97050837571924	0.51157487960250
H	2.51623886107583	-3.95057051985883	-1.95015500775785	C	2.78682935241827	-0.79526276666903	-2.64331775038179
H	4.70627615974150	-3.57753953034680	-2.81490951745829	C	1.20786187768470	-1.85228611499596	2.77388064820096
H	5.13785294573536	-2.69376793682481	-1.35648505112997	C	4.46630553459968	-2.77859172658960	-0.54818813698827
H	5.45866116989376	-1.99925914634962	-2.95421427023609	C	-4.41199395514502	0.54238510295202	0.24972174203747
H	1.78606870300058	-1.46886006435365	-3.83345117582258	C	-0.02268019716832	-1.56345786056769	3.36568764712289
H	2.67101097346078	-2.95794549132730	-4.19310660429450	C	-4.17293564936148	1.97363288088354	-0.23389148406402
H	3.43281604657005	-1.38665034448827	-4.48083051746102	H	-3.12839488051335	2.27951736401873	-0.09036963790585
Li ¹⁰⁰ Cr(btmsa) (S=1)				H	-4.43132908758753	2.10225332020095	-1.29173326702674
Cr	-0.09243030535861	0.83290586549549	0.17716697638623	H	-4.80448384864453	2.66905438116678	0.33541492605563
P	-2.96369383292526	-0.49442793994348	-0.35219777501609	C	-5.82099164055108	0.09597158389591	-0.13341796011010
P	2.70792378704486	-0.61147726508864	-0.75608199393741	H	-6.10668629450201	-0.84157690787448	0.35447554197267
N	1.27958908465491	-0.22890420618875	-0.31103046032122	H	-6.53824714966279	0.85609133951155	0.20559380666605
N	-1.68330477880778	0.02320866559143	0.35726587006104	H	-5.96962006212226	-0.01751378050011	-1.21278428497510
C	-0.01953716140764	2.72774455093413	-0.18005049978376	C	-4.29513726423756	0.50930032087421	1.77783966635770
C	0.18465430252419	2.48967463570509	1.10886284062069	H	-4.40978164356994	-0.50848376122265	2.17335004544025
Si	-0.13430940396701	4.17044820615716	-1.32763535072491	H	-3.32707486729008	0.89475334009931	2.11548644499486
Si	0.41801992467687	3.30419472904873	2.74558632538862	H	-5.09056709013061	1.12484467371660	2.21896686583526
C	4.98900095306344	-3.96070548648906	-0.03563754737112	C	4.14276992547249	-0.59372274278534	-3.31789434441591
C	0.05839484749589	-2.84259008792118	0.90135666903829	H	4.02495879445713	-0.71392372610093	-4.40406589099534
C	3.11367549650726	-4.08835435203583	1.46185755771056	H	4.54351382076220	0.41332301515487	-3.15738454854810
C	1.25822728931915	-2.48372175559821	1.52798460735955	H	4.90602427875121	-1.31574014830135	-3.01088172844892
C	-4.50195518452438	-2.84024083139957	-0.41112862678687	C	1.82035034931622	0.25144671056857	-3.20547294890718
C	-2.43754871517839	-3.02497946820954	0.84313930410254	H	0.80926161600888	0.12548889695916	-2.80486907027943
C	-4.78255336129162	-4.18793520069832	-0.20759979568313	H	2.13333196210585	1.27541298875067	-2.97630941564708
C	-1.17774253785619	-2.54255712574703	1.47847721388644	H	1.77433246400986	0.15727022636456	-4.29939719093090
C	2.56501210783748	-2.90258108708118	0.94425443445939	C	2.23862555145636	-2.18523896984032	-2.97556976069408
C	4.30856870322661	-4.61784517153329	0.98702457013918	H	2.01534902272455	-2.25106859095816	-4.04921092080440
				H	2.94533322447748	-2.98712349253199	-2.73495249994861

H 1.30582863687124 -2.38956325929110 -2.43384488473647
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 H 4.26809922469277 2.76472276246864 -0.24116412860449
 H 3.97236644768611 2.01333382400395 -1.81044379665632
 H 2.62674314634408 2.25866494623759 -0.67176405758517
 C 3.68149816974534 0.72175108210113 1.39697871684255
 H 4.37001379301723 1.44375720744442 1.85698327503894
 H 2.65339348002454 1.04856517308181 1.59510534198854
 H 3.83179488897977 -0.24181104926741 1.90163269121947
 C 5.43721277753013 0.25164834879966 -0.28901293103960
 H 6.06435112573600 1.06848464198009 0.09408904207867
 H 5.70933883340835 -0.64605294921806 0.27656281423498
 H 5.72460479743125 0.09718267211479 -1.33374031409066
 C -2.20024434998075 0.79236871974989 -2.70862763292923
 H -2.94917848502566 1.59114685345854 -2.69923962394205
 H -1.34692903091391 1.12664835627754 -2.10187570922145
 H -1.84790995557166 0.69367333179308 -3.74491613699986
 C -3.99688759215216 -0.88034345434739 -3.06735600466932
 H -4.79739130852314 -0.14148757230359 -2.94540128483687
 H -3.72659194132686 -0.87415505732949 -4.13271404974990
 H -4.40302659870255 -1.87488972182920 -2.85867850259503
 C -1.68449251534936 -1.62152521011731 -2.45962338394462
 H -2.04466703389836 -2.63153903456358 -2.22702142271544
 H -1.36857079293884 -1.61734191278151 -3.51232679251400
 H -0.79414270353052 -1.42636999398748 -1.84333264427935
 H 5.01542450697841 -2.27147431006373 -1.33866649600692
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 H 2.56858763434267 -4.60262506169192 2.25378817384259
 H 0.09096983803339 -3.34818564486340 -0.06649955114565
 H 2.13612312972376 -1.58861158257677 3.28263905818670
 H -0.05261295413998 -1.07252231570989 4.33758404680670
 H -2.16875232249138 -1.67157056171749 3.18558932997980
 H -2.02637022645335 -4.98969153014486 1.59965533029250
 H -4.07837573467438 -6.02942612763724 0.67609331534031

H -5.69484126901510 -4.62156624121964 -0.61485902268118
 H -5.20808415036730 -2.25169938406741 -0.99007644860994
 C -1.93044788088143 4.67167546041818 -1.49666036273150
 H -2.02998662092469 5.56820114080490 -2.12115995821760
 H -2.52446677770738 3.87808979913557 -1.96456530003591
 H -2.38613443583062 4.89243701105748 -0.52402169022220
 C 0.86027400470789 5.60639862653840 -0.65013128670707
 H 1.91673616579714 5.33252597910141 -0.53687987179031
 H 0.81703366736657 6.48038013630903 -1.31194757112868
 H 0.49758066024628 5.92206839263094 0.33545435434956
 C 0.53474466536640 3.73842806510484 -3.02032246764704
 H 0.37582165868993 4.56159620479728 -3.72794950268775
 H 1.61378763808338 3.54444417842564 -2.98786431687118
 H 0.05199816245422 2.84598075193199 -3.43633025990572
 C 2.05570039751398 4.21202791983990 2.80061288373395
 H 2.10682628941010 5.00776393226469 2.04891489150062
 H 2.22105382522222 4.67356625049825 3.78226416945812
 H 2.89391213436017 3.53018210488903 2.61525302099191
 C -0.99896398003004 4.50418384883759 3.00014163831823
 H -0.96676557088758 4.97778225885795 3.98910780619855
 H -0.98849224464855 5.30450190136878 2.25057887375897
 H -1.96408467181634 3.98982905691279 2.91172993275193
 C 0.38416986079337 2.00726168548115 4.08854543456872
 H -0.55444191193083 1.44019694762893 4.05208817232206
 H 1.20034477291977 1.28504610587537 3.96015425955968
 H 0.47677066752587 2.44192851796223 5.09118748234255

L^{tt}BuCr(1,2-diphenylethene-1,2-dialkoxide) (S=1)

Cr -0.30719142286394 0.43869814954524 0.26486049961282
 N -1.94443246536043 0.67998197595911 -0.38662828299342
 P -3.26679263676054 0.16589949708943 -1.02682716738969
 N 0.93444837189003 0.37500423283748 -1.00753756918625
 P 2.38210553685249 0.08335612422653 -1.50207791083434
 O -0.17626112380265 -0.98721069530234 1.45769083070354
 O 0.11803997765763 1.41782997626744 1.76433094838472

C	0.16235284066761	-0.64493356634714	2.71390160713308	C	-3.33160424703149	2.82683195012650	-4.19890921487862
C	0.39427069359057	0.69758580892805	2.87098828404791	H	-2.67721280363605	3.59089520044836	-4.61897574828740
H	5.36224082164332	1.50490919535500	-5.18048292589107	C	-1.59447838954435	3.54432150805389	-1.35857882183939
C	-3.76749138571640	1.19616701419348	-2.45835146264767	H	-2.52535793814405	3.83733114453832	-0.87334900952594
C	-2.93003666572435	2.19584098296112	-3.01016794536450	C	0.48754845511364	-4.12307331632339	4.09152125591502
C	4.44534103863560	1.74358460868826	-4.64369945072423	H	0.70310847854702	-5.12207717397055	3.71299337938729
C	2.07137890217315	2.33056126984170	-3.23502435582695	C	-4.62163587172589	0.30536674800075	0.26365232454106
C	2.46589469609165	-1.67392054338840	-2.19601870104095	C	-0.07889864795741	-1.56633497730208	5.04231526208021
C	2.84806563321641	1.20571392608615	-2.87083408016275	H	-0.33311534816474	-0.57460897823243	5.41438211707423
C	0.97473571633213	1.45359572323615	3.97375674120169	C	-0.43090408650733	2.28079500010994	-3.05075720810850
C	4.02396280856562	0.93833914455476	-3.59129092913291	H	-0.45132526463104	1.58222190695371	-3.89051995347670
H	4.62844690267970	0.07286619850196	-3.32590367177456	C	3.64339984872670	0.39083264668878	-0.14874598426526
C	-1.63120804211161	2.65414181559153	-2.43995177152085	C	-3.03643421823492	-1.55865447688222	-1.76032911800545
C	0.80102279756382	2.74106242015695	-2.56953040221839	C	0.46544272651240	-3.04339030090203	3.21312816686210
C	0.20016955910766	-1.74063123612827	3.67417625754143	H	0.65127047226067	-3.19010041191771	2.14958712549241
C	0.81639025354872	3.64136818074710	-1.50102379372419	C	2.13904013109628	3.01828483089488	6.01286846608499
H	1.76740202837591	4.02166128546494	-1.12880319825962	H	2.58670521623969	3.62006727151605	6.80266905930124
C	-6.06053208771302	0.07634265557422	-0.19397360089410	C	1.90701386747841	0.89719473968458	4.86952700388650
C	-4.97350616470723	0.89699668517306	-3.11601017811977	H	2.20071989771528	-0.14616682697885	4.75850283839395
H	-5.62749811562867	0.12715186512687	-2.71652705400657	C	2.47296158258211	1.66818929801929	5.87947381614239
C	-5.36120190766634	1.54432728347062	-4.28505698966782	H	3.19482960291306	1.21569615152420	6.55898916170329
H	-6.30452991584821	1.28480402353747	-4.76329974889770	C	-2.02559424707635	-1.34405140617061	-2.89406030039681
C	1.23951645083392	3.59034368491199	5.11257465230362	C	-4.50302235086063	1.74231686625942	0.78475944245309
H	0.98020519673753	4.64542995070414	5.19800107794815	C	-4.28123824681771	-2.25303273317164	-2.30441467252882
C	0.23530650403565	-3.93159836806630	5.45031416644905	C	-2.39503532258345	-2.45737802870219	-0.69982012608568
H	0.25088562105256	-4.77590961259702	6.13820600765838	C	3.68151797456001	2.85298467627241	-4.99946753927132
C	-0.05356310747653	-2.64661314624941	5.91745937817348	H	3.99294338869487	3.49788571656278	-5.82012015518714
H	-0.27722775937974	-2.48790839857670	6.97207098651864	C	3.34851274546666	1.80322877872800	0.36611110493883
C	0.66922457267509	2.82112233849437	4.10241086435095	C	2.51257827853362	3.13343688396460	-4.29940787674110
H	-0.02579090314089	3.26624525110182	3.39195890370823	H	1.91006107175734	3.99952271389312	-4.57389598039115
C	-4.28271344390390	-0.66785857055009	1.39553441916677	C	3.39787893654537	-0.61594591356631	0.97602047455791
C	-0.37828075186155	4.03493638779175	-0.89704748922079	C	5.10409007249939	0.34004758235478	-0.59395537432276
H	-0.35583958502672	4.72339363939291	-0.05319392828556	C	1.52437169056109	-2.51339677625259	-1.32423187086440
C	-4.52764982845579	2.51367669673490	-4.83597162360508	C	3.83568433818872	-2.34965182534367	-2.21463281607649
H	-4.80696553875024	3.02740884432802	-5.75486325342527	C	1.89130741232325	-1.62324844310153	-3.61425419754818

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H 0.95475252800891 -1.05217502062949 -3.65104559424314
H 4.25099574591198 -2.48236872917820 -1.20978370417710
H 4.58010850376959 -1.82774224034783 -2.82453018434979
H 3.73161080036832 -3.35457421296287 -2.64657583642134
H -5.04474783650720 -2.41597112430838 -1.53488199964599
H -4.00058644112318 -3.24679274565289 -2.68002834220230
H -4.73796296143744 -1.72216685411610 -3.14559699001761
H -2.45521195539326 -0.78712384633205 -3.73633136217737
H -1.68963233620935 -2.31705843256933 -3.27861672998436
H -1.13836608435301 -0.79788394913434 -2.54170496680124
H -3.10600296806448 -2.78128679527828 0.06603527602045
H -1.55438870607141 -1.98163364378828 -0.18273637392679
H -2.01173202739171 -3.36527033263212 -1.18489537716660
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H 3.99022932944399 -0.33284970251789 1.85629345480353
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H 5.74518818297158 0.50988579849019 0.28151502310204
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H 5.40319732213020 -0.62157901933642 -1.02191148624056
H -6.71725962091353 0.09181898808755 0.68641936103784
H -6.21767262410457 -0.88972253144128 -0.68623755868166
H -6.41557884404147 0.86733010934622 -0.86242635981124
H -5.25657534972060 1.90970545440110 1.56549790548985
H -4.68293781354027 2.47983669018852 -0.00855484672935
H -3.51383874775057 1.93850698899344 1.21103796256351
H -4.86134927309317 -0.40305884794694 2.28992118934854
H -3.22026130667137 -0.63679366910188 1.66901902372063
H -4.54303261246810 -1.70133496335531 1.14174957452963
H 2.31962307884503 1.91447689011400 0.72629218982308
H 3.52513366812703 2.55855127242523 -0.41049462535805

H 4.02109007822393 2.03137965475250 1.20371103007663

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Benzo[c]cinnoline (S=0)

N 0.63803133544004 0.00221997310680 0.000000011323763
N -0.63829181705212 0.00221983899274 0.00000008765027
C -1.33957203006875 1.19447404768837 0.00000008808796
C -0.71511464238321 2.45974432737173 0.000000014234670
C 0.71485372705399 2.45974446263993 0.000000011398922
C 1.33931135198951 1.19447431096544 0.00000008974364
C -2.73956939515061 1.09162805529625 -0.00000005473729
C -3.51679978289589 2.23191428085778 -0.00000009793486
C -2.90002834674423 3.49700692069424 0.00000001233115
C -1.52189505473845 3.60905011389837 0.000000011081937
H -3.17448006038645 0.09350167681311 -0.000000014882678
H -4.60306085615141 2.15724312677950 -0.000000021260665
H -3.51391933771967 4.39668933483461 -0.00000000791102
H -1.06216585140739 4.59580564220297 0.000000013319623
C 1.52163385009284 3.60905042490910 0.00000003801220
C 2.89976720214432 3.49700750714404 -0.00000007441380
C 3.51653891021894 2.23191500411016 -0.00000007169186
C 2.73930872895392 1.09162862448588 0.00000001759087
H 4.60279999185840 2.15724404748520 -0.000000016014263
H 3.17421958497828 0.09350234187293 -0.00000000392660
H 1.06190451558854 4.59580588800598 0.00000004018165
H 3.51365797637942 4.39669004984486 -0.000000015499540

Btmsa (S0)

C -1.02948732640874 -0.05092785135697 -0.63363582922182
C 0.16733182012237 -0.15509133979352 -0.84116953611188
Si -2.83173337845295 0.10562695041041 -0.32256094117180
Si 1.96986310304830 -0.31109788786348 -1.15082815320137
C -3.26376407446514 -0.88802061636575 1.19529113833417
C -3.75211551933566 -0.54875305678017 -1.80664213880345
C -3.23553179693248 1.90621552855176 -0.05345716196506
C 2.36787553073211 0.50176428276120 -2.78130964342274

C	2.41069194282805	-2.12218394110794	-1.20744393581772	C	1.316505	-0.753332	0.977442
C	2.88729837906015	0.53559265828324	0.23449884086055	O	1.303860	-1.835997	1.530281
H	-3.01969970504382	-1.94795567630877	1.06575769249689	C	-3.558832	-1.587991	-0.684396
H	-4.33594117838659	-0.81993728933431	1.41524486438702	C	-3.583179	-0.365670	-0.006558
H	-2.72210159038493	-0.53131366039486	2.07800258597357	C	-2.412275	0.147226	0.536844
H	-2.69562389225413	2.31576657032326	0.80712616484834	C	-1.205940	-0.558925	0.414649
H	-4.30746433256021	2.04354762426991	0.13266887385030	C	-1.188495	-1.784586	-0.267295
H	-2.97125892525410	2.51284409506002	-0.92638260981505	C	-2.362715	-2.293936	-0.815883
H	-3.51664406179652	-1.60192051565892	-1.99430371141175	H	-2.346658	-3.246184	-1.343510
H	-3.50249184941222	0.01083277348119	-2.71458502554698	H	-4.476455	-1.990586	-1.111562
H	-4.83614630715767	-0.47334699241201	-1.65911254566706	H	-0.259362	-2.343953	-0.359975
H	1.82568482176962	0.03157075169431	-3.60881698303483	H	-4.518205	0.183409	0.093812
H	3.43919374076574	0.42838229689687	-3.00372704808415	H	-2.400324	1.098968	1.066866
H	2.10337799523824	1.56470667270918	-2.77679552126095	C	2.538267	-0.150952	0.405617
H	1.87068542140532	-2.64301678715961	-2.00556599526500	C	2.518149	1.066877	-0.290139
H	2.16977113650173	-2.62530123485333	-0.26476063957828	C	3.690376	1.570328	-0.848372
H	3.48333429114071	-2.25834890162193	-1.39037145140060	C	4.887183	0.866321	-0.712802
H	2.63165346737992	1.59894681963133	0.29573335436029	C	4.914195	-0.348208	-0.021193
H	3.97160821605858	0.46401350244472	0.08718582894648	C	3.745254	-0.855282	0.531832
H	2.65524407179434	0.08524522449412	1.20566952672290	H	3.735379	-1.800969	1.072622
Benzil (S=0)				H	5.803248	1.264327	-1.147543
C	0.017929	0.049434	0.975517	H	5.849747	-0.895793	0.082383
O	0.032733	1.137991	1.516622	H	1.588507	1.624835	-0.386182
				H	3.672245	2.516517	-1.386717