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Reactivity of Bis(amino)cyclopropenylidenes (BACs) and Cyclic (alkyl)(amino)carbenes (CAACs): Coordination Chemistry, Catalysis, and Small Molecule Activation

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

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by

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Chapter 3: E. Bauer, G. T. S. Andavan, T. K. Hollis, R. J. Rubio, J. Cho, G. Kuchenbeiser, T. R. Helgert, C. S. Letko, and F. Tham, Organic Letters, **2008**, 10(6), 1175-1178.

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ABSTRACT OF THE DISSERTATION

Reactivity of Bis(amino)cyclopropenylidenes (BACs) and
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Coordination Chemistry, Catalysis, and Small Molecule Activation

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Glenn Richard Kuchenbeiser

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University of California, Riverside, August 2009
Dr. Guy Bertrand, Chairperson

Carbenes have played an important role as reactive intermediates in synthetic organic chemistry for many years. The isolation of stable versions of these important carbon species has resulted in an explosion of research and applications not only as ancillary ligands for transition metal (TM) based catalysts, but also as small molecule activators, and organocatalysts in their own right. One aspect of my work is exploration of the reactivity of bis(diisopropylamino)cyclopropenylidene (BAC) and cyclic(alkyl)(amino) carbenes (CAACs), first isolated by our group. Due to their unique steric and electronic properties, these species are perhaps the most distinct representatives of the carbene ligand set and as such allow the isolation of a variety of catalytically active TM complexes unobtainable by other routes and

frequently different from those derived from their cyclic diamino carbene (NHCs) counterparts.

Inspired by the novel reactivity of these new carbenes in TM chemistry, I have also explored the activation of heteroallenes using these species. Similarly to NHCs, CAACs and BACs react with carbon dioxide and carbon disulfide to give the corresponding zwitterionic betaines. However, unlike NHCs, a second equivalent of CS_2 reacts with the BAC-CS_2 adduct leading to a bicyclic thieno[2,3-diamino]-1,3-dithiole-2-thione, which results from a novel ring expansion process. Surprisingly, and also in contrast to NHCs, CAAC does not react with carbodiimide, whereas BAC exclusively gives a ring expanded product, analogous to that obtained with CS_2. The intermediate amidinate can be trapped, using a lithium tetrafluoroborate adduct of BAC as a carbene surrogate.

In related work, it is demonstrated that depending on their electronic and steric properties, stable singlet carbenes can react with white phosphorus at room temperature to yield P_4, P_3, P_2, and even P_1 fragments that are stabilized by the carbene moiety. Therefore, stable singlet carbenes can achieve the tasks that transition metals do with P_4, namely activation, aggregation, and importantly, fragmentation. The next challenge is to use the resulting adducts for the preparation of useful organophosphorus derivatives. This would avoid the use of Cl_2 gas, which is important to meet the growing demand in phosphorus derivatives using environmentally friendly processes.

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Introduction

Stable Cyclic Carbenes

Carbenes have long played an important role as reactive intermediates in synthetic organic chemistry.[1,2] However, not until the isolation of a stable derivative; the acyclic phosphinosilylcarbene in 1988,[3] and later the cyclic imidazolylidenes in 1991,[4] did the field of carbene chemistry see a renaissance (Figure 0.1). Since that time, a number of stable carbenes have been synthesized leading to the rapid development of a diverse set of applications;[5,6] as ligands for homogeneous transition metal catalysis,[5-12] in small molecule activation,[13-19] in the stabilization of reactive species,[20-26] and even as organocatalysts in their own right.[27,28]

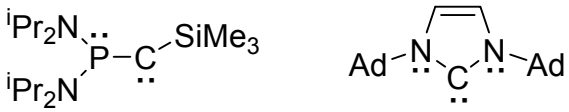

Figure 0.1. The first stable acyclic and cyclic carbenes.

Carbenes are divalent, neutral, congeners of carbon containing two bonding and two non-bonding valence electrons. Orbitals available to the non-bonding electrons include a p-type orbital perpendicular to the bonding plane and a σ-type orbital coplanar with the valence bonds. This description allows two possible primary forms (Figure 0.2). Triplet form **A** contains two singly occupied orbitals bearing electrons of the same spin and react as

diradicals. Singlet form **B** features a lone pair of electrons in an σ-type orbital and a vacant p-type orbital. The preferred configuration (either **A** or **B**) is dependent upon the difference between the pairing energy and the singlet-triplet gap and is intimately related to the HOMO-LUMO gap. In typical stable carbenes the singlet form **B** is the lowest energy form due to influence of adjacent substituents.

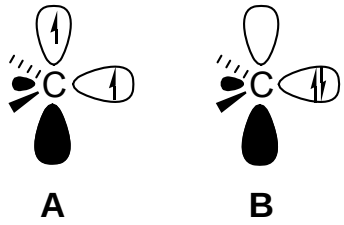

Figure 0.2. Some possible electronic configurations for carbenes.

Electronic stabilization of singlet carbene **B** is typically afforded via two sources, namely σ-electron withdrawal via inductive effects of the carbene substituents and/or π-donation into the vacant p-type orbital from an available lone pair adjacent to the carbene center. In the most prevalent stable carbenes, the so called imidazol(in)ylidenes (NHCs), the carbene center is flanked by two nitrogen substituents providing two lone pairs for donation while concurrently displaying strong σ withdrawing effects due to the greater electronegativity of nitrogen. Combined, these effects allow a singlet-triplet gap of roughly 85 kcal/mol.[29] The cyclic nature of this form also results in a constrained geometry, thereby enforcing planarization of the amino groups and ensuring donation of the nitrogen lone pairs into the vacant carbene p-

type orbital. Additional kinetic stabilization can be provided by the use of bulky substituents adjacent to the carbene center, although this is not a prerequisite for their isolation.[30-33]

More recently, we have shown that stable cyclic carbenes can be isolated wherein the carbene center contains only one [cyclic (alkyl)(amino) carbenes (CAACs)][34] or even no [bis(amino)cyclopropenylidenes (BACs)][35,36] flanking heteroatom substituents (Figure 0.3). In each case, sufficient donation is observed into the vacant p-type orbital either via a sole amino substituent (CAACs), or even via remote β-amino substitution (BACs)[37] respectively. The addition of CAACs and BACs to the carbene ligand set greatly expands the available electronic and steric diversity for this important class of compounds. This is can be exemplified by examination of the bond angle at the carbene center which is 102°, 106°, 57° for NHCs CAACs and BACs respectively. These new carbenes also display stronger σ donation relative to their NHC counterparts as shown by IR spectroscopy of the corresponding $LM(CO)_2Cl$ complexes (L = carbene, M = Rh, Ir).[34,38] It is clear that relative to classical NHCs, and due to a quaternary carbon adjacent to the carbene center, CAACs can provide a more demanding steric environment, whereas BACs show the least steric hindrance. These extremes hold promise for unique and unexpected reactivity both in transition metal complexes, catalysis, and in the development of small molecule activation as will be discussed in this dissertation.

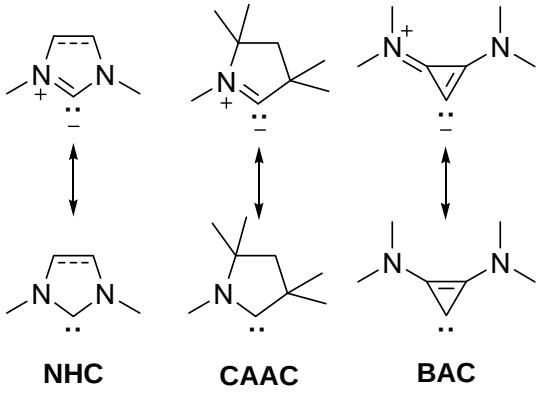

Figure 0.3. Schematic representations of amino stabilized cyclic carbenes and contributing resonance forms.

As ligands, carbenes are able to stabilize catalytically active transition metal fragments allowing for efficient catalysis while remaining strongly bound to a metal center even at elevated temperatures owing to relatively strong carbon metal bonds. One classic example is the Grubb's 2nd generation olefin metathesis catalyst (Figure 0.4). In this case, a phosphine has been replaced with an NHC leading to a more robust and active catalyst.[39] More recently, it has even been reported that CAACs can improve catalytic efficiency beyond that of NHCs in certain cases.[40,41]

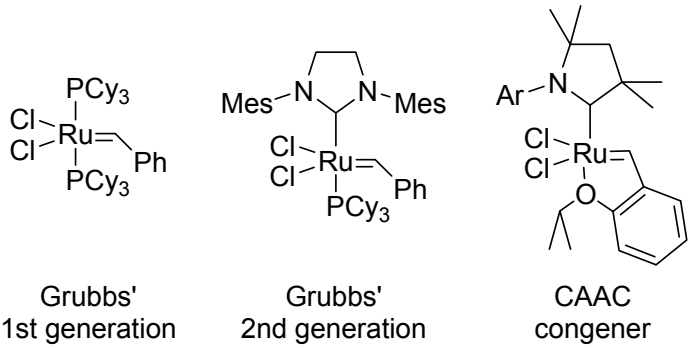

Figure 0.4. Evolution of the Grubbs Olefin Metathesis Catalyst.

Transition metal carbene complexes may be formed via a number of routes. When isolable, free carbenes may be used directly in L ligand exchange reactions, splitting of dimeric metal fragments (such as the classical $[Rh(COD)Cl]_2$), or simple association with coordinatively unsaturated species to name a few. Alternatively, these complexes can be obtained from the carbene conjugate acids either via in situ deprotonation using an external strong base (i.e. sodium hydride, lithium dimethylamide, potassium bis(trimethylsilyl)amide, etc.) or by the judicious choice of basic ligands at the metal center (i.e. Ag_2O, $Pd(OAc)_2$, $Zr(NMe_2)_4$, etc.). Additionally, the use of low oxidation state metal fragments (i.e. $Pd(PPh_3)_4$, $Ni(COD)_2$, etc.) sometimes allows for the formation of carbene-metal complexes by oxidative addition of the appropriate carbene precursors (i.e. the C-Cl bond in chloroimidazolium salts). More recently, Crabtree and others have demonstrated that carbene complexes of Rh, Ru, and Pd can also be formed via decarboxylation of NHC-CO_2 betaines.[42-45]

In small molecule activation, stable carbenes display a diverse set of reactivities which is dominated by their nucleophilic nature. CAACs have been shown to activate CO,[14] H_2, and NH_3,[13] whereas the classical NHCs are inert towards these substrates.[46-48] With heteroallenes such as carbon dioxide, carbon disulfide, and carbodiimides, NHC's react to form zwitterionic betaines.[19] However, when NHCs are reacted with isocyanates, isothiocyanates, keteneimines, etc., a variety of spirocyclic products are

obtained.[19,49] Meanwhile, the reaction of stable carbenes with white phosphorus (P_4) leads to different products depending on which carbene is used. For saturated NHCs, aggregation to a P_{12} cluster has been reported.[16] In contrast, the reaction of P_4 with a bulky CAAC leads to isolation of a ring opened, linear P_4 unit.[15]

In this work, the coordination chemistry of bis-NHCs, CAACs, and BACs is explored. The resulting transition metal fragments prove to be active precatalysts for C-C and C-N bond forming reactions. The differences in reactivity of stable carbenes are subsequently examined from a small molecule activation perspective. Indeed, our new carbenes also react with a variety of substrates such as white phosphorus, carbon dioxide, carbon disulfide, and carbodiimide. The broad palette of products obtained from these reactions are shown to strongly depend upon the nature of the carbene employed. Thus, although certain trends carry over from NHCs, the reactivity of CAACs and BACs can often display unexpected results setting a foundation for their anticipated use in a variety of transformations.

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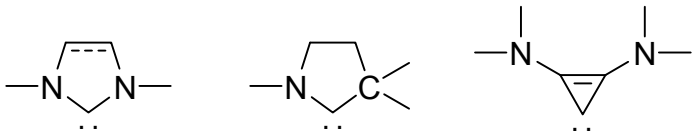
Chapter 1

Bis(diisopropylamino)cyclopropenylidene (BAC) as a Ligand for Transition Metal Complexes

Introduction

Over the years the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of the various systems. In many cases the use of σ-donors as ancillary ligands are required to achieve high efficiency. Spectacular results in this area have been reported using cyclic diaminocarbenes (NHCs)[1-11] (Fig. 1.1). It is noteworthy that although NHC-transition metal complexes have been known since the sixties,[12,13] the recent developments in their application as scaffolds in catalysis have only been made possible because of the availability of bottle-able NHCs.[14-18] Although it is possible to cursorily tune the structure of NHCs, any diversity is still far from matching their phosphorus-based counterparts. Recently, our group has reported the synthesis of two new families of stable carbenes, namely cyclic (alkyl)(amino)carbenes (CAACs),[19-26] and bis(amino)cyclopropenylidenes (BACs)[27-29] (figure 1.1).



NHCs CAACs BACs

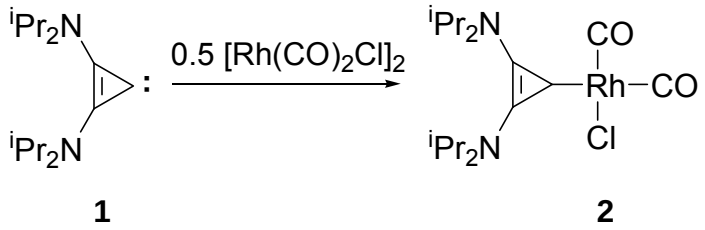
Figure 1.1. Schematic representation of NHCs, CAACs, and BACs.

It has already been shown that CAACs are excellent ligands for transition metal centers, and the catalytic activity of the corresponding complexes can even be superior to that of NHC analogues. Isolated cyclopropenylidenes have never been used to prepare transition metal complexes. However, it should be noted that a few cyclopropenylidene complexes have been prepared via oxidative addition using a carbene precursor.[30-43] With few exceptions the three-membered ring was substituted by aryl groups. Interestingly, recent works have shown that aryl-substituted cyclopropenylidene transition metal complexes are active catalysts for Heck and Suzuki C-C coupling reactions, as well as for Buchwald-Hartwig aryl aminations, and hydroformylation.[39-42]

Due to their availability as free species, bis(amino)cyclopropenylidenes (BACs) should give increased flexibility in the synthesis of complexes otherwise inaccessible by existing methodologies. Moreover, due to the presence of the strong π-donor amino groups, BACs should act as strong σ-donor ligands. Here we report the first syntheses of transition metal complexes using stable BACs as ligands.

Results and Discussion

First, it was of interest to compare the donor properties of bis(diisopropylamino)cyclopropenylidene (BAC) **1** with other L ligands. The carbonyl stretching frequencies of cis-[$RhCl(CO)_2(L)$] complexes are recognized as an excellent measure of the ratio of σ-donor to π-acceptor properties of ligands L.[44-48] When a benzene solution of free carbene **1** was reacted with half an equivalent of $[Rh(CO)_2Cl]_2$ a bright red solution was readily obtained (Scheme 1.1).

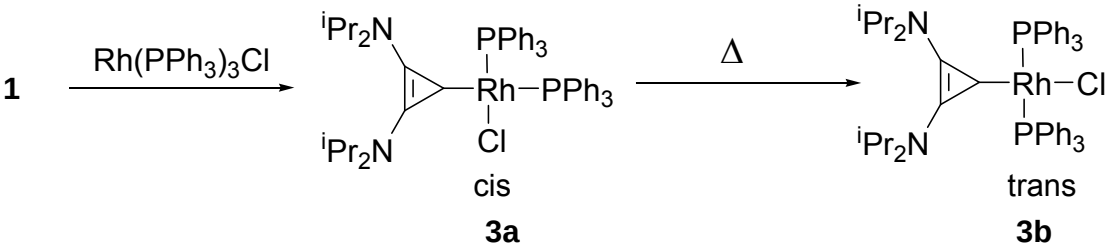


1 **2**

Scheme 1.1. Preparation of $Rh(CO)_2(L)Cl$ complex **2**.

The ^{13}C NMR spectrum of the resulting complex **2** revealed a doublet at 141 ppm (J_{Rh-C} = 44 Hz). The coupling constant is similar to those observed for other Rh-carbene complexes, and the chemical shift agrees well with the literature, the carbene signal being at half way between that for free **1** (185 ppm) and the cyclopropenium salt precursor (99 ppm). The infrared carbonyl stretching frequencies of **2** were observed at ν = 2070 and 1992 cm^{-1} in methylene chloride (ν_{avg} = 2031 cm^{-1}). These values indicate that the strong donor power of BAC **1** is superior to that of unsaturated NHCs (ν_{avg} ≈ 2041 cm^{-1}) and even the most basic saturated NHCs (ν_{avg} ≈ 2038 cm^{-1}).[45-47]

Since BAC **1** appeared to be a strong σ-donor, standard L ligand exchange reactions should allow for the synthesis of a variety of complexes hardly available without the free ligand. To test this hypothesis we first studied the reaction of **1** with the classical Wilkinson's catalyst (Scheme 1.2). Monitoring the reaction at room temperature by ^{31}P NMR spectroscopy, we observed the primary formation of complex **3a**, which gave a pair of doublets at 53 ppm ($^{1}J_{P\text{-}Rh}$ = 206.6 Hz, $J_{P\text{-}P}$ = 37.6 Hz) and 37 ppm ($J_{P\text{-}Rh}$ = 123.6 Hz, $J_{P\text{-}P}$ = 37.6 Hz) indicative of a *cis*-arrangement of the phosphines. Upon heating for 2 hours at 80 °C, a new doublet in the ^{31}P NMR spectrum appears at 33 ppm ($J_{P\text{-}Rh}$ = 156.7 Hz) suggesting the formation of the *trans*-isomer **3b**.



***Scheme 1.2*.** Reaction of BAC **1** with Wilkinson's catalyst.

After work up, the thermodynamic complex **3b** was isolated as orange crystals from a benzene solution in 91% yield, and unambiguously characterized by single crystal X-ray analysis (Figure 1.2). The complex displays a distorted square planar geometry while the rhodium-carbene bond length of 1.943 Å is shorter than that for known analogous NHC complexes, which range from 2.053 to 1.987 Å.[49-51] Both the C1-Rh-Cl and P-Rh-P angles

are contracted from linear by ca. 5° (angles equal 175.2° and 174.6° respectively) most likely due to steric interactions.

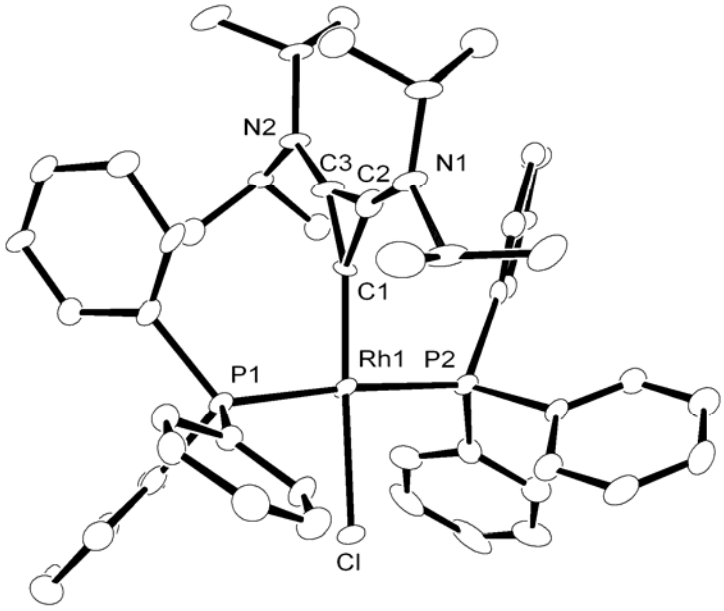
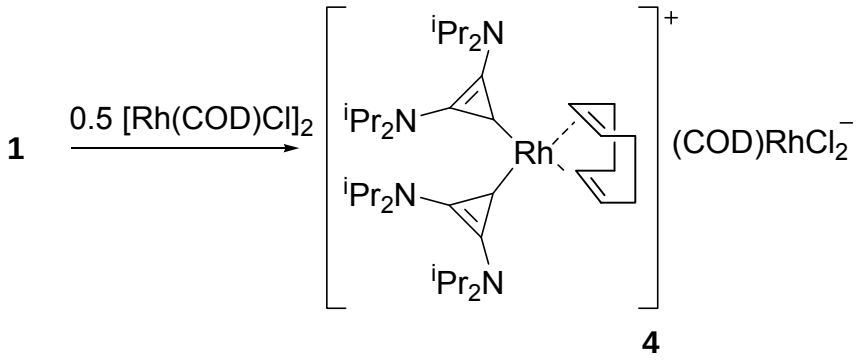


***Figure 1.2*.** Molecular view of the solid state structure of **3b**. Selected bond lengths [Å] and angles [°]: Rh(1)-C(1) 1.943(10), Rh(1)-P(1) 2.294(2), Rh(1)-Cl(1) 2.411(3), C(1)-Rh(1)-P(2) 92.21(6), C(1)-Rh(1)-P(1) 92.21(6), P(2)-Rh(1)-P(1) 174.58(11), C(1)-Rh(1)-Cl 175.2(3).

Another classical rhodium complex precursor is $[Rh(COD)Cl]_2$, which typically reacts with an L ligand to afford monomeric Rh(COD)Cl(L) species. By combining a benzene solution of free carbene **1** with half an equivalent of $[Rh(COD)Cl]_2$, a new product crystallized readily out of benzene (Scheme 1.3). ^{13}C NMR analysis revealed the disappearance of signals for the free carbene and a new doublet at 149.1 ppm with a coupling of 54 Hz in the range typical for Rh bound carbenes.



***Scheme 1.3*.** Unexpected formation of Rh complex **4**.

Indeed, X-ray analysis of these crystals demonstrated the unexpected structure **4** shown in figure 1.3. It is a cationic rhodium complex, featuring two cyclopropenylidene ligands, and $[Rh(COD)Cl_2]^-$ as a counter anion. Although a few examples of cationic $[Rh(L)_2(NHC)_2]^+$ are known,[52-57] a search in the Cambridge data base revealed that the only analog containing both a Rh(COD)(L)(carbene) cation and $Rh(COD)Cl_2$ anion is restricted to chelating pyridine functionalized NHC's.[58] We believe that the formation of **4** is a good indication that metals are able to accommodate several BACs, thanks to their restricted steric bulk.

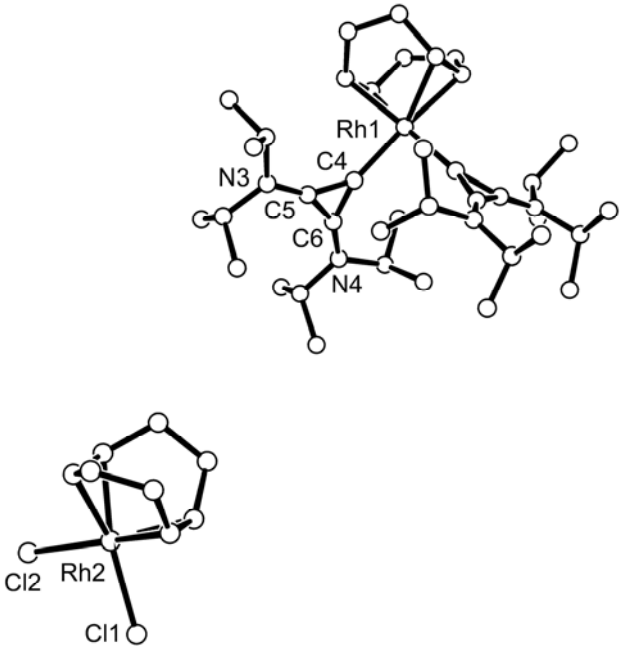
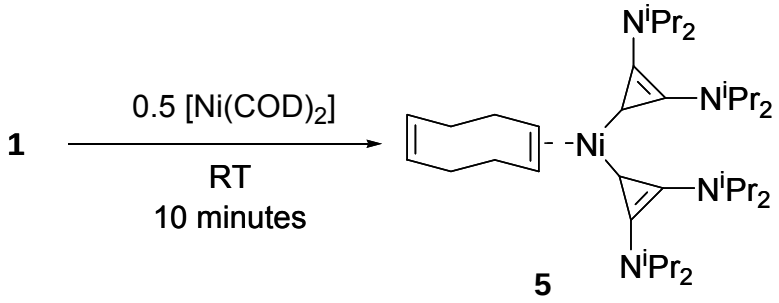


Figure 1.3**.** Molecular view of the solid state structure of **4**. Selected bond lengths [Å] and angles [°]: Rh(1)-C(4) 2.028(6), C(4)-C(5) 1.380(9), C(4)-C(6) 1.389(9) C(5)-C(6) 1.368(9), N(4)-C(6) 1.324(8), N(3)-C(5) 1.342(8); C(4)-Rh(1)-C(1) 91.8(2).

Metal(0) cyclopropenylidene complexes have not been reported to date, and thus it was of interest to react BAC **1** with bis(1,5-cyclooctadiene)nickel(0) (Scheme 1.4). The exchange reaction occurred readily in benzene within 10 minutes at room temperature, and complex **5** was isolated as an orange solid in 86% yield. Room temperature solution ^{13}C and ^{1}H NMR revealed a single set of signals and integration consistent with coordination of two BAC ligands with a single chelating COD. Broadening of the COD signals could indicate fast exchange of this ligand on the NMR timescale.



***Scheme 1.4*.** Synthesis of Nickel(0) complex **5**.

In contrast, the solid state crystal structure of **5** reveals a distorted trigonal planar structure whereby the COD is coordinated in a pendant η^2 fashion (Figure 1.4). The Ni-C_{BAC} and Ni-C_{COD} bond lengths are in the range 1.861(19)-1.902(19) Å and 1.947(19)-1.959(19) Å respectively while the C_{BAC}-Ni-C_{BAC} angle is 122.0(8)°, consistent with known $(NHC)_2$Ni(0)-COD complexes. Both BAC ligands lie nearly perpendicular to the coordination plane. This type of structure was originally suggested by Pörschke[59] for the analogous chelating diphosphine nickel(0) COD complexes based upon VT NMR data and displays a similarity to the corresponding isolated Ni(0) cyclooctatetraene complexes.[60]

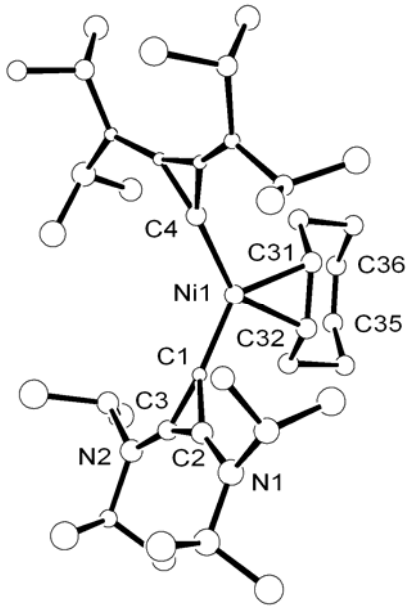
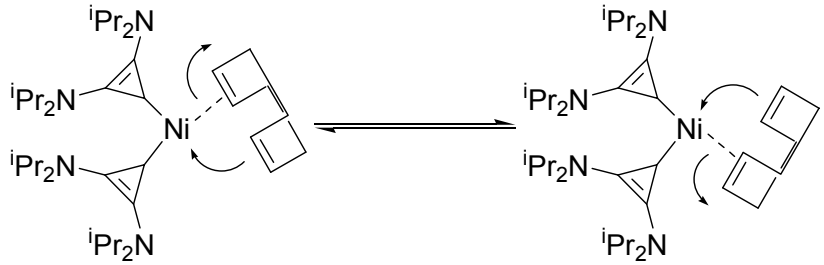


Figure 1.4. Molecular view of the solid state structure of **5.** Selected bond lengths [Å] and angles [°]: Ni(1)-C(1) 1.861(19), Ni(1)-C(4) 1.902(19), Ni(1)-C(31) 1.947(19), Ni(1)-C(32) 1.959(19), C(35)-C(36) 1.38(2), C(31)-C(32) 1.27(2), C(1)-Ni(1)-C(4) 122.0(8).

The disparity between the NMR and crystal data could be explained by dynamic coordination of the COD ligand at room temperature in solution which is frozen out by crystal packing forces in the solid state (Scheme 1.5). This structure is unknown for the corresponding NHC complexes wherein a bridging COD connects two Ni(^{i}Pr$_2$Im)$_2$ fragments,[61] and stands in contrast to the homoleptic Ni(IMes)$_2$ product formed via the analogous synthetic routes.[62-66]

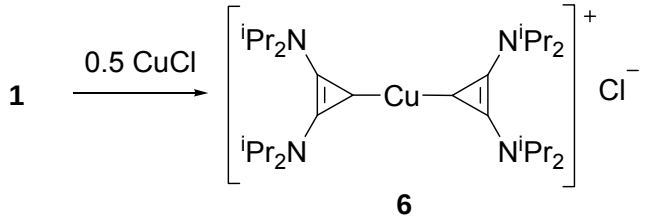


***Scheme 1.5*.** Rapid exchange of π-coordinated COD.

Copper cyclopropenylidene complexes are unknown and hardly accessible via traditional oxidative addition routes. Therefore it was of interest to examine the reaction of BAC **1** with the classical metal fragment copper(I) chloride. First, a 0 °C solution of one equivalent **1** in THF was added slowly to a suspension of CuCl. After stirring for 30 min. and allowing the pale red suspension to warm to room temperature, removing solvent in vacuo, washing with hexanes, and extracting with CH_2Cl_2 an off-white solid was obtained. ^{13}C NMR spectral analysis in $CDCl_3$ revealed a new set of signals at 146.9 (C2-3) and 139.4 (C1) ppm suggesting a new compound consistent with the clean formation of a BAC-Cu complex.

Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a chloroform solution of this complex. To our surprise, the structure revealed the homoleptic bis-BAC copper cation with chloride counteranion shown below (Figure 1.5). These results are in contrast to the analogous synthesis of NHC_2Cu cations reported by Nolan in which the addition of bulky NHCs afforded the monoadduct at room temperature and only after heating for 24 hours was the L_2Cu cation isolated.[67,68] The

structural features of **6** are analogous to known homoleptic bis-NHC Cu cations with the Cu(I) metal center linear (C_{BAC}-Cu-C_{BAC} angle 180.0°). The propylidene rings are coplanar and Cu-C_{BAC} bond lengths averaging at 1.881 Å. Once again, these results show the facility with which metals can accommodate multiple BAC ligands due to their small steric size.



***Scheme 1.6*.** Synthesis of homoleptic copper(I) cationic complex **6.**

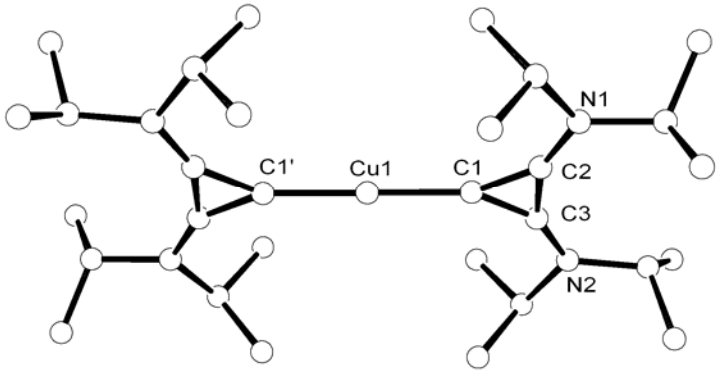
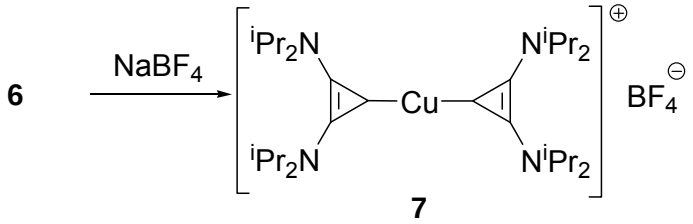


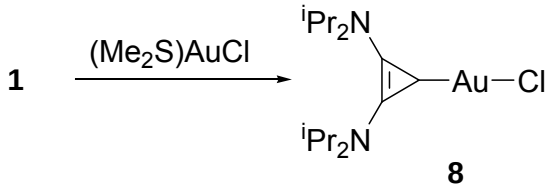
***Figure 1.5*.** Molecular view of the solid state structure of **6** (counteranion and hydrogens omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu(1)-C(1) 1.881(4), N(1)-C(2) 1.328(6), N(2)-C(3) 1.320(6), C(1)-C(2) 1.383(7), C(1)-C(3) 1.387(7), C(2)-C(3) 1.377(7), C(1)-Cu(1)-C(1') 180.000(1).

Complex **6** readily undergoes salt metathesis with $NaBF_4$ to yield complex **7** (Scheme 1.7). The ^{13}C and ^{1}H chemical shifts for this complex exhibit almost no change from the precursor **6**, however the ^{19}F NMR spectra reveals a characteristic signal at -156 ppm and the melting point is decreased by 12 °C from the parent complex. These results demonstrate the minimal effect of the counteranion on these cationic copper species.



Scheme 1.7. Salt metathesis to afford complex **7**.

Given the recent interest in gold carbene complexes, we next sought to obtain a BAC-Au adduct. Addition of a THF solution of BAC **1** to a THF suspension of $(Me_2S)AuCl$ at -78 °C resulted in a faint purple suspension which slowly turned orange upon warming to room temperature. ^{13}C NMR revealed a symmetric species with the carbene signal shifted from 185.0 ppm to 134.0 ppm, similar to that observed for BAC-Cu complex **6**, and the complete disappearance of dimethylsulfide, indicating formation of a BAC-Au species.



Scheme 1.8. Synthesis of gold(I) complex **8.**

Single crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a chloroform solution to reveal the linear complex **8** shown (figure 1.6). The Au-C_{BAC} bond length is 2.00(2) Å and is within the observed range for analogous NHC-AuCl complexes while the C_{BAC} -Au-Cl bond angle of 174.3° in **8** is smaller than that for known bulky carbene ligated L-AuCl (range 176-180°). It is of interest to note the tilting of the propylidene ring plane with respect to the C_{BAC}-Au-Cl coordination plane. By comparison, the NHC-Au complexes reported by Nolan[69] and CAAC-Au complexes reported by our group[26,70] all feature the heterocyclic ligands coplanar with $C_{carbene}$-Au-Cl coordination plane. No discernable aurophilic interactions are observed in the solid state with the closest Au-Au distance in the unit cell being 7.755 Å.

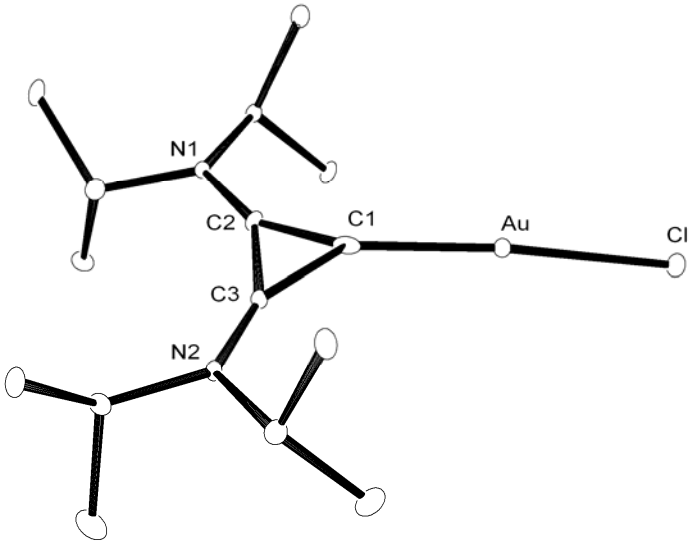
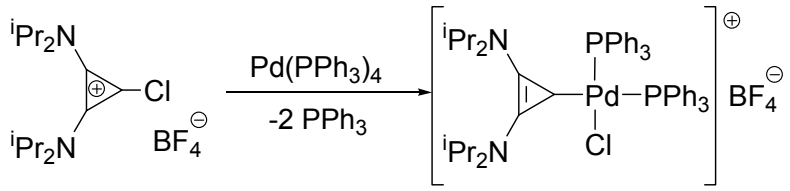


Figure 1.6. Molecular views of the crystal structure of **8.** Selected bond lengths [Å] and angles [°]: Au(1)-C(1) 2.00(2), Au(1)-Cl(1) 2.296(4), 1.40(2), C(1)-Au(1)-Cl(1) 174.3(5).

We next sought to generate a cationic Pd(II) cyclopropenylidene complex via oxidative addition of our chlorocyclopropenium salts to Pd(0) precursors in a method analogous to that reported by Wass and coworkers.[39] Stirring a suspension of the BAC precursor salt bis(diisopropylamino) (chloro)cyclopropenium tetrafluoroborate (BAC-ClBF$_4$)[28] and Pd(PPh$_3$)$_4$ in toluene at 40 °C overnight and subsequent workup led to isolation of the cationic Pd(II) complex **9** in 92% yield. The ^{13}C NMR spectrum revealed the presence of a coordinated BAC ligand with $^2J_{C\text{-}P}$ = 45 Hz, while ^{31}P NMR shows the presence of two distinct phosphine ligands in a cis arrangement as evidenced by shifts at 31.6 and 21.9 ppm respectively ($^2J_{P\text{-}P}$ = 23.6 Hz) typical for this type of complex.[71] Additionally, integration of the ^{1}H NMR signals was

consistent with formation of a complex bearing one BAC ligand with two triphenylphosphine ligands (Scheme 1.9).



BAC-ClBF$_4$ **9**

Scheme 1.9. Synthesis of cationic Pd(II) complex **9**.

Single crystals suitable for an X-Ray diffraction experiment were obtained by slow evaporation of a chloroform solution, confirming the spectroscopic analysis. The structure shows **9** to have a distorted square planar palladium center coordinated by two triphenylphosphine ligands arranged in a cis fashion, a single BAC ligand, and a chloride. The Pd-C_{BAC} bond length is 2.010(8) Å and Pd-P bonds ranging 2.279(2) to 2.353(2) Å with C(1)-Pd-P angles of 89.6(2) and 171.14(8)° (Figure 1.7). The complex is a Pd(II) cation as evidenced by the presence of the non-coordinating tetrafluoroborate anion.

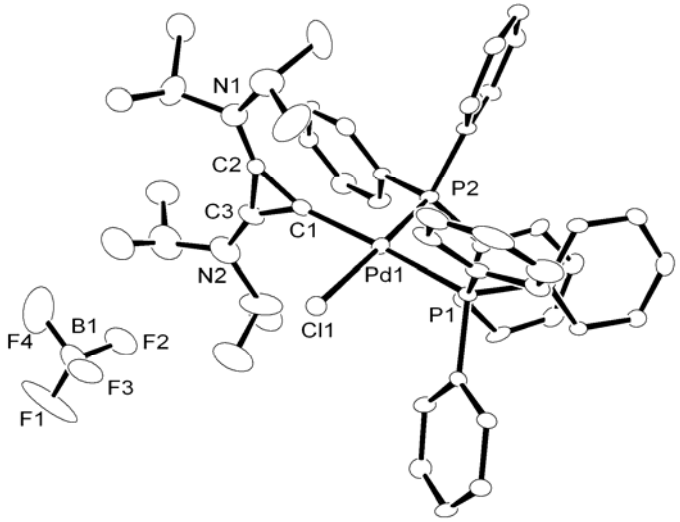


***Figure 1.7*.** Molecular view of the crystal structure of **9.** Selected bond lengths [Å] and angles [°]: Pd(1)-C(1) 2.010(8), Pd(1)-P(2) 2.279(2), Pd(1)-Cl(1) 2.347(2), Pd(1)-P(1) 2.353(2), C(1)-Pd(1)-P(2) 89.6(2), C(1)-Pd(1)-Cl(1) 85.0(2), P(2)-Pd(1)-Cl(1) 171.14(8), C(1)-Pd(1)-P(1) 169.4(2), P(2)-Pd(1)-P(1) 99.83(7), Cl(1)-Pd(1)-P(1) 86.19(7).

Conclusion

From the infra-red carbonyl stretching frequencies of the cis $[RhCl(CO)_2(BAC)]$ complex **2**, it appears that the stable bis(diisopropylamino) cyclopropenylidene is a strong σ-donor ligand. It promotes the cleavage of $[Rh(COD)Cl]_2$ but in contrast to NHCs it leads to a $Rh(COD)(BAC)_2$ cationic complex. Additionally, the BAC ligand readily adds twice at room temperature to CuCl suggesting that metals can easily accommodate several BAC ligands because of their unique steric properties. BAC is able to substitute L ligands such as triphenylphosphine and dimethyl sulfide, as well as bidentate ligands such as TMEDA and COD. Thus, a wide range of BAC transition metal complexes are obtained, providing new opportunities for catalyst development.

Experimental Section

General. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or using an MBraun glovebox. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC200, WM250, Avance 300, Varian Inova 300 or Inova 500 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to TMS as external standard or referenced relative to residual solvent peaks, and ^{31}P chemical shifts are reported in ppm relative to H_3PO_4 as external standard.

Bis(diisopropylamino)cyclopropenylidene (BAC) 1. Prepared with modification to the literature procedure[27] as follows. A 1:1 mixture of the cyclopropenium salt (BAC-HBF_4, 10.00 g, 30.86 mmol) and potassium bis(trimethylsilyl)amide (6.16 g, 30.86 mmol) was cooled to -78 °C, and Et_2O (80 ml) was slowly added. The suspension was stirred vigorously for 30 min. and then warmed to room temperature and stirred for an additional hour. After evaporation of the volatiles in vacuo, the product was extracted with 3 X 60 ml dry hexanes. After filtration, the amber solution was concentrated to approximately 60 ml and kept at -20 °C overnight to give air and water sensitive yellow needles (6.56 g, 90 %). ^{1}H NMR (300 MHz, C_6D_6) δ = 3.66 (sept, *J* = 6.8 Hz, 4 H), 1.24 (broad s, 24 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ = 185.3, 158.6, 50.9 (broad s), 21.6.

[Bis(diisopropylamino)cyclopropenylidene][cis-dicarbonyl](chloro) rhodium(I) complex 2. To a room temperature solution of BAC **1** (224 mg, 0.90 mmol) in C_6D_6 (0.5 mL) was added (chloro)(dicarbonyl)rhodium(I) dimer (176 mg, 0.45 mmol). A bright red solution was formed immediately and stirred for 30 minutes. The solvent was removed in vacuo and complex **2** was isolated as a red, microcrystalline solid. Yield: 295 mg (0.69 mmol, 74 %); m.p. 95 °C, dec.; ^{1}H NMR (300 MHz, C_6D_6) δ = 3.82-3.60 (broad m, 4 H), 1.27 (broad d, 24 H); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ = 187.2 (d, $^1J_{Rh\text{-}C}$ = 54.3 Hz, *C*O), 184.3 (d, $^1J_{Rh\text{-}C}$ = 72.8 Hz, *C*O), 149.2 (C_{ring}), 141.2 (d, $^1J_{Rh\text{-}C}$ = 43.9 Hz, C_{carb}), 53.34 (broad, *C*H), 48.64 (broad, *C*H), 21.83 (broad, *C*H_3); IR (CH_2Cl_2): ν [cm^{-1}] 2070 (s) 1992 (s).

[Bis(diisopropylamino)cyclopropenylidene)]bis(triphenylphosphine) (chloro)rhodium(I) complexes 3a-b. BAC **1** (251 mg, 1.00 mmol) was combined with Wilkinson's catalyst (924 mg, 1.00 mmol), and the mixture dissolved in freshly distilled toluene (20 mL) with stirring at room temperature for one hour. Monitoring this reaction by multinuclear NMR spectroscopy allowed for the characterization of the *cis*-isomer **3a**. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6) δ = 53.4 (dd, $^1J_{P\text{-}Rh}$ = 206.6 Hz, $^2J_{P\text{-}P}$ = 37.6 Hz), 37.7 (dd, $^1J_{P\text{-}Rh}$ = 123.6 Hz, $^2J_{P\text{-}P}$ = 37.6 Hz). ^{1}H NMR (300 MHz, C_6D_6) δ = 8.09 (m, 5 H), 7.88 (m, 5 H), 7.09 (m, 10 H), 7.00 (m, 10H), 4.04 (m, 4 H), 1.43-0.96 (m, 24 H); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ = 147.5 (C_{ring}), 138.2 (d, $^1J_{Rh\text{-}C}$ = 33.4 Hz, C_{carb}), 136.0 (d, *J* = 11.3 Hz), 134.6 (d, *J* = 12.3 Hz), 128.0, 126.9-126.6 (m), 49.4, 21.8.

Then the toluene solution was heated at 80 °C for 2 h. The solvent was removed in vacuo to afford a brown oil. This material was washed with hexanes leading to the *trans*-isomer **3b** as an off-white microcrystalline solid. Yield: 816 mg (0.91 mmol, 91 % yield). Single crystals were obtained from a saturated benzene solution at room temperature; mp 218 °C, dec; $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6) δ = 33.0 (d, J = 156.7 Hz);); ^{1}H NMR (300 MHz, C_6D_6) δ = 7.74-6.98 (m, 30 H), 4.34 (m, 4 H), 1.34-0.84 (m, 24 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ = 148.9 (C_{ring}), 139.8 (d, $^{1}J_{Rh\text{-}C}$ = 39.3 Hz, C_{carb}), 135.4 (m), 132.1 (d, J = 9.6 Hz), 131.4, 127.8, 48.8, 22.3.

Di[bis(diisopropylamino)cyclopropenylidene](COD)rhodium(I) [dichloro-(COD) rhodium(III)] complex 4. To a solution of BAC **1** (52 mg, 0.21 mmol) in C_6D_6 (0.5 mL), (chloro)(1,5-cyclooctadiene)rhodium(I) dimer (74 mg, 0.10 mmol) was added forming a dark orange solution. Blocky orange crystals of complex **4** were formed upon standing at room temperature overnight. Yield: 103 mg, (0.21 mmol, 81%). ^{1}H NMR (300 MHz, C_6D_6) δ = 4.20 (broad, 8 H), 4.02 (broad, 8 H), 2.35 (broad, 4 H), 2.15 (broad, 4 H), 2.00 (d, 4 H, J = 8.0 Hz), 1.60 (d, 4 H, J = 7.8 Hz), 1.21 (broad, 48 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ = 149.8 (C_{ring}), 149.1 (d, $^{1}J_{Rh\text{-}C}$ = 54.0 Hz, C_{carb}), 85.9 (broad, *C*H), 49.3 (broad, *C*HCH$_3$), 31.0 (broad, *C*H$_2$), 21.6 (broad, CH*C*H$_3$).

Di[bis(diisopropylamino)cyclopropenylidene)](COD)nickel(0) complex 5. BAC **1** (115 mg, 0.458 mmol) was dissolved in C_6D_6 (0.5 mL) and the solution added to bis(1,5-cyclooctadienyl)nickel(0) (63 mg, 0.229 mmol) at room

temperature. The solution immediately changed color from yellow to red. After stirring for 1 h, the volatiles were removed in vacuo to give complex **5** as an orange solid. Yield 126 mg (0.197 mmol, 86 %); m.p. 121 °C, dec; ^{1}H NMR (300 MHz, C_6D_6) δ = 4.41 (broad s, 4 H), 3.95 (sept, *J* = 6.7 Hz, 8 H), 2.42 (broad s, 8 H), 1.27 (d, *J* = 6.7 Hz, 48 H); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ = 176.8 (C_{carb}), 149.2 (C_{ring}), 92.1, 49.5, 33.7, 22.8.

Di[bis(diisopropylamino)cyclopropenylidene]copper(I) chloride complex 6. A solution of BAC **1** (235 mg, 0.994 mmol) in 10 mL THF was slowly added to stirred -78 °C suspension of CuCl (50 mg, 0.505 mmol) in 10 mL THF. After one hour, the pink suspension was allowed to warm to room temperature and stirred for an additional hour to afford a reddish orange solution. Solvent was removed in vacuo and the brown powder washed with 2 X 10 mL hexanes and extracted as a deep orange solution in CH_2Cl_2. Upon removal of solvent in vacuo, complex **6** was isolated as an off white solid. Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of a $CDCl_3$ solution. Yield: 274 mg (0.479 mmol, 96 %); m.p. 153 °C, dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.57 (broad s, 8 H); 1.25 (broad s, 24 H); 1.04 (broad s, 24 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 146.9 (C_{ring}), 139.4 (C_{carb}), 55.3, 47.8, 21.0, 20.8; ESI-MS m/z 535.3785 (535.3795 calcd for $C_{30}H_{56}N_4Cu$, M^+ - Cl).

Di[bis(diisopropylamino)cyclopropenylidene]copper(I) tetrafluoroborate salt 7. Sodium tetrafluoroborate (98.5 mg, 0.8971 mmol) was added to a solution of complex **6** (502 mg, 0.8779 mmol) in CH_2Cl_2 and stirred at room

temperature overnight. The resulting suspension was washed with 3 X 20 mL deionized water, dried over $MgSO_4$ and solvent removed in vacuo. The Yield: 493 mg (0.7912 mmol, 90.1 %); m.p. 141 °C, dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.74 (broad s, 8 H); 1.41 (d, *J* = 5.6 Hz, 12 H); 1.20 (d, *J* = 6.0 Hz, 12 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 147.2 (C_{ring}), 139.4 (C_{carb}), 55.7, 48.0, 21.2, 20.9.

[Bis(diisopropylamino)cyclopropenylidene]gold(I) chloride complex 8. To a -78 °C suspension of $Au(Me_2S)Cl$ (293 mg, 0.995 mmol) in 10 mL THF, slowly added a solution of BAC **1** (241 mg, 1.02 mmol) in 10 mL THF and stirred at 0 °C for 3 hours to afford a white suspension. Upon warming to room temperature a faint purple solution is formed. Volatiles were removed in vacuo and the light purple solid washed with 2 X 20 mL hexanes. The resulting orange solid was dissolved in CH_2Cl_2 and filtered. Removal of solvent in vacuo afforded complex **8** as an off white powder. Single crystals suitable for X-ray diffraction study were formed by slow evaporation of a chloroform solution. Yield: 445 mg (0.949 mmol, 95 %); m.p. 182 °C, dec; ^{1}H NMR (300 MHz, C_6D_6) δ = 3.79 (broad s, 4 H); 1.48 (broad s, 12 H); 1.27 (broad s, 4 H); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ = 144.4 (C_{ring}), 134.0 (C_{carb}), 54.8, 48.9, 21.9, 21.4; ESI-MS m/z 474.2200 (474.2183 calcd for $C_{17}H_{31}AuN_3$, M^+ -Cl + MeCN).

Bis(diisopropylamino)chlorocyclopropenium tetrafluoroborate salt BAC-ClBF$_4$. Procedure adapted from Lavallo and coworkers.[28] Diisopropylamine

(1.73 g, 17.122 mmol) was added slowly to a stirred 0 °C solution of tetrachlorocyclopropene (1.45 g, 8.1534 mmol) in 300 mL of CH_2Cl_2. After 6 hours the yellow suspension was allowed to warm to room temperature and sodium tetrafluoroborate (895 mg, 8.1534 mmol) was added and allowed to stir overnight. The resulting suspension was washed with 5 X 200 mL deionized water, dried over $MgSO_4$, filtered, and solvent removed in vacuo to afford a sticky yellow solid. After washing with 2 X 200 mL hexanes, the BAC salt was isolated as a white powder. Compound was purified by preparative crystallization from a refluxing solution in CH_2Cl_2/Et_2O. Yield: 2.90 g (8.092 mmol, 99 %); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.00 (sept, *J* = 6.7 Hz, 2 H), 3.80 (sept, *J* = 6.8 Hz, 2 H), 1.31 (d, *J* = 6.8 Hz, 24 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 131.9, 93.1, 57.9, 48.2, 22.3, 20.4.

[Bis(diisopropylamino)cyclopropenylidene][bis(triphenylphosphino)] (chloro)palladium(II) tetrafluoroborate complex 9. In the glovebox, chlorocyclopropenium salt **BAC-ClBF$_4$** (240 mg, 0.670 mmol) and $Pd(PPh_3)_4$ (900 mg, 0.779 mmol) were combined in a Schlenk flask and dry toluene (20 mL) added. The resulting orange suspension was stirred overnight while heating at 40 °C. After cooling to room temperature, the yellow suspension was filtered and washed with 2 X 20 mL hexanes and volatiles removed in vacuo. Yield: 608 mg (0.616 mmol, 92 %); mp 162-163 °C, dec; Crystals of **9** suitable for X-ray analysis were formed by slow evaporation of a chloroform solution. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ = 31.6 (d, $^2J_{P\text{-}P}$ = 23.6 Hz), 21.9 (d,

$^{2}J_{P\text{-}P}$ = 23.6 Hz); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45-7.19 (m, 30 H), 4.13 (broad s, 2 H), 3.74 (broad s, 2 H), 1.46 (broad s, 12 H), 1.13 (broad s, 12H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ = 145.3 (C_{ring}), 134.9, 134.8, 134.0, 133.8, 132.2, 130.8, 129.8 (d, $^{2}J_{C\text{-}P}$ = 45.0 Hz, C_{carb}), 129.0, 128.8, 128.4, 128.3, 51.0, 50.7, 23.0, 21.7.

Crystal structure determination of complexes 3b, 4, 5, 6, 8, and 9. The Bruker X8-APEX X-ray diffraction instrument with Mo-radiation was used for data collection**.** All data frames were collected at low temperatures (T = 100 K) using an ω, φ-scan mode (0.5° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package.[72] The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program.[73] The SIR97 was used for direct methods of phase determination, and Bruker SHELXTL software package for structure refinement and difference Fourier maps.[74] Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of compounds were refined by means of a full matrix least-squares procedure on F^2. All H-atoms were included in the refinement in calculated positions riding on the C atoms. Drawings of molecules were performed using Ortep 3.

Crystal and structure parameters of 3b: size 0.36 x 0.13 x 0.09 mm^3, monoclinic, space group P 2(1)/m, a = 11.379(3) Å, b = 23.388(7) Å, c =

11.507(4) Å, $\alpha = \gamma = 90.0°$ $\beta = 104.245(4)°$, V = 2968.0(16) Å^3, ρ_{calcd} = 1.006 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 16677, independent reflections = 4385 (R_{int} = 0.0970), absorption coefficient μ = 0.414 mm^{-1}; max/min transmission = 0.9637 and 0.8651, 278 parameters were refined and converged at R1 = 0.0891, wR2 = 0.1886, with intensity I>2σ(I).

Crystal and structure parameters of 4: size 0.22 x 0.13 x 0.10 mm^3, monoclinic, space group P 2(1)/n, a = 11.8164(15) Å, b = 22.759(3) Å, c = 20.536(3) Å, $\alpha = \gamma = 90.0°$, $\beta = 90.907(2)°$, V = 5522.0(12) Å^3, ρ_{calcd} = 1.303 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 24998, independent reflections = 5930 (R_{int} = 0.0860), absorption coefficient μ = 0.732 mm^{-1}; max/min transmission = 0.9304 and 0.8556, 641 parameters were refined and converged at R1 = 0.0449, wR2 = 0.0900, with intensity I>2σ(I).

Crystal and structure parameters of 5: size 0.20 x 0.11 x 0.14 mm^3, monoclinic, space group P 2(1)/c, a = 10.745(4) Å, b = 31.754(12) Å, c = 11.684(4) Å, $\alpha = \gamma = 90.0°$, $\beta = 103.187(5)°$, V = 3882(3) Å^3, ρ_{calcd} = 1.095 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 10880, independent reflections = 2336 (R_{int} = 0.0850), absorption coefficient μ = 0.528 mm^{-1}; max/min transmission = 0.9304 and 0.8556, 404 parameters

were refined and converged at R1 = 0.1538, wR2 = 0.3579, with intensity $I>2\sigma(I)$.

Crystal and structure parameters of 6: size 0.38 x 0.16 x 0.12 mm^3, monoclinic, space group P 2(1)/c, a = 15.277(3) Å, b = 9.755(2) Å, c = 11.486(2) Å, $\alpha = \gamma = 90.0°$, $\beta = 107.711(3)°$, V = 1630.5(6) $Å^3$, ρ_{calcd} = 1.165 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 8366, independent reflections = 2132 (R_{int} = 0.0759), absorption coefficient μ = 0.775 mm^{-1}; max/min transmission = 0.9128 and 0.7573, 184 parameters were refined and converged at R1 = 0.0531, wR2 = 0.1186, with intensity $I>2\sigma(I)$.

Crystal and structure parameters of 8: size 0.25 x 0.11 x 0.08 mm^3, orthorhombic, space group P2(1)2(1)2(1), a = 8.4314(16) Å, b = 15.911(3) Å, c = 16.684(3) Å, $\alpha = \beta = \gamma = 90.0°$, V = 2238.2(7) $Å^3$, ρ_{calcd} = 1.748 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 12771, independent reflections = 3216 (R_{int} = 0.0631), absorption coefficient μ = 7.051 mm^{-1}; max/min transmission = 0.6199 and 0.2706, 253 parameters were refined and converged at R1 = 0.0616, wR2 = 0.1499, with intensity $I>2\sigma(I)$.

Crystal and structure parameters of 9: size 0.32 x 0.13 x 0.10 mm^3, monoclinic, space group P 2(1)/c, a = 17.907(4) Å, b = 17.594(4) Å, c = 18.296(5) Å, $\alpha = \gamma = 90.0°$, $\beta = 110.986(3)°$, V = 5382(2) $Å^3$, ρ_{calcd} = 1.326

g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 22868, independent reflections = 5807 (R_{int} = 0.0860), absorption coefficient μ = 0.602 mm^{-1}; max/min transmission = 0.9422 and 0.8307, 594 parameters were refined and converged at R1 = 0.0621, wR2 = 0.1465, with intensity I>2σ(I).

Structural data for compounds **3b,** and **4** have been deposited in the Cambridge Crystallographic Data Center under CCDC 662010 and 662011, and can be obtained free of charge at: www.ccdc.cam.ac.uk.

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Chapter 2

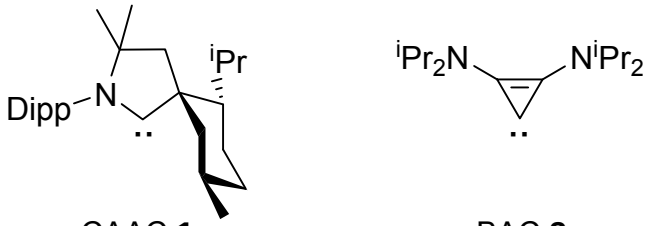
Reactivity of Cyclic (Alkyl)(amino) Carbenes (CAACs) and Bis(amino)cyclopropenylidenes (BACs) with $PdMe_2$(TMEDA): Formation of Effective C-C Coupling Catalysts

Introduction

Palladium catalyzed C-C coupling reactions have become a cornerstone of synthetic organic chemistry. Among these methods the Heck, Suzuki, Stille, and other coupling reactions afford direct access to complex molecules hardly available via traditional routes.[1-4] As ancillary supporting ligands, the classical phosphines have increasingly been replaced by cyclic diamino carbenes (NHCs) due to the increased donor ability and decreased lability of these species.[5-7] In order to expand the variety of available carbene ligand frameworks our group has recently isolated stable cyclic(alkyl)(amino) carbenes (CAACs)[8-10] and bis(amino)cyclopropenylidenes (BACs)[11-13] which have proven to be both sterically distinct, and more strongly donating than their NHC counterparts.[14,15] Preliminary communications have already demonstrated the effectiveness of these new carbenes in transitional metal catalysis[8,16-20] and small molecule activation.[21-24]

As part of our program to develop highly reactive, low oxidation state metal centers we sought to test for the thermal generation of reactive 'naked' $L_nPd(0)$ species via $L_nPd(II)$ dialkyl precursors since these should be readily

synthesized from the Pd fragment dimethyl (N,N,N',N'-tetramethyl ethanediamine) palladium(II) [$PdMe_2$(TMEDA)].[25] The strong trans-effect of CH_3 ligands gives rise to facile ligand exchange from the chelating tetramethylethylenediamine (TMEDA) to strong donor ligands such as phosphines and N-heterocyclic carbenes NHCs.[25] Herein we report the synthesis and catalytic properties of $PdMe_2(BAC)_2$ and $Pd(CAAC)_2$ species obtained by ligand exchange from $PdMe_2$(TMEDA) using stable CAAC and BAC (Figure 2.1).



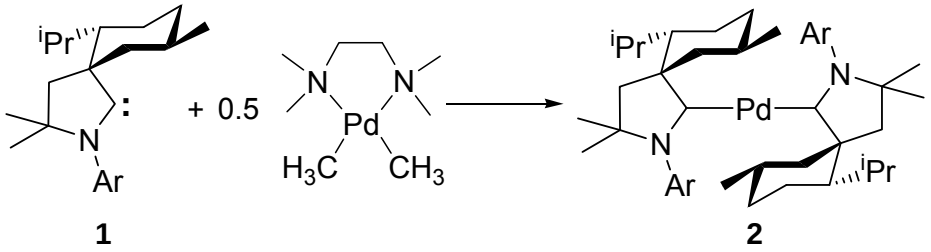
CAAC **1** BAC **3**

Figure 2.1. Representative carbenes used in this study. Dipp = 2,6-$^{i}Pr_2C_6H_3$.

Synthesis

Upon addition of a room temperature benzene solution of two equivalents of the bulky, menthyl substituted CAAC **1** to a benzene solution of the palladium fragment $PdMe_2$(TMEDA)[25] we observed the immediate formation of a deep green solution. Following the reaction by ^{13}C NMR we found that despite the intense color change the reaction proceeded slowly at ambient temperature. Heating the reaction at 65 °C in a sealed tube for 6 hours readily afforded a clean product with complete disappearance of the free carbene

signal at 319.0 ppm which was replaced by a new signal at 269 ppm, characteristic of CAAC-Pd complexes.[8,14] Additionally, the complete disappearance of the Pd-Me signal and presence of only uncoordinated TMEDA led us to speculate the formation of the coordinatively and electronically unsaturated 14 electron homoleptic Pd(0) complex **2** (Scheme 2.1).



1 **2**

Ar = 2,6-diisopropylphenyl

Scheme 2.1. Synthesis of homoleptic Pd(0) complex **2**.

Single crystals of **2** suitable for an X-ray diffraction study were grown from a toluene solution layered with diethyl ether at -20 °C, allowing for the unambiguous structural confirmation of our NMR analysis (Figure 2.2). Complex **2** features a nearly linear geometry with the C-Pd-C bond angle of 173.99(16)°. The two C-Pd bond lengths are identical within error limits averaging 2.053(4) Å, longer than those for reported NHC analogs (range 1.995-2.041 Å),[26-29] possibly due to a combination of the extreme steric bulk of the CAAC ligand and strong sigma donation to the Pd center. The CAAC ring planes exhibit a torsion angle of ca 49° with respect to each other. All of these features are consistent with the published results for both the

analogous homoleptic $(CAAC)_2Au(I)$ cations[30] and $(NHC)_2Pd(0)$ complexes.[26-29,31-33] Concurrent work by Danopoulos using NHC's in this transformation yielded similar results.[29] All attempts to isolate a monoaddition product of **1** with $PdMe_2(TMEDA)$ resulted only in a 1:1 mixture of the Pd(0) product **2** and starting material regardless of temperature, solvent, or relative concentration of the reagents.

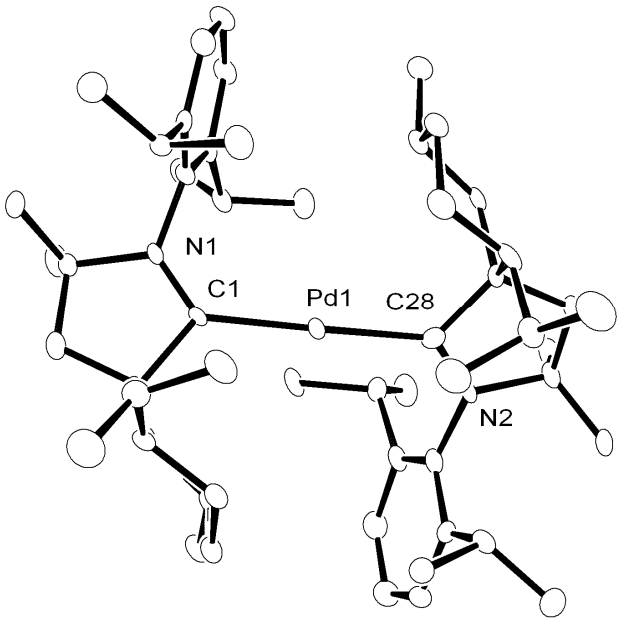
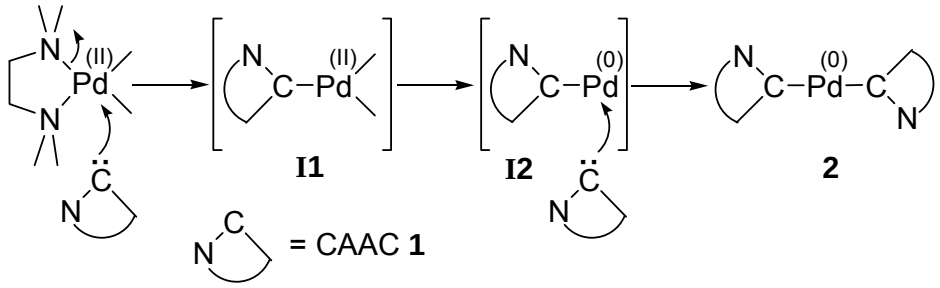


***Figure* 2.2.** Molecular view of the crystal structure of **2.** Selected bond lengths [Å] and angles [°]: Pd(1)-C(1) 2.046(4), Pd(1)-C(28) 2.053(4), C(1)-Pd(1)-C(28) 173.99(16), N(1)-C(1)-Pd(1) 129.1(3), C(2)-C(1)-Pd(1) 125.1(3).

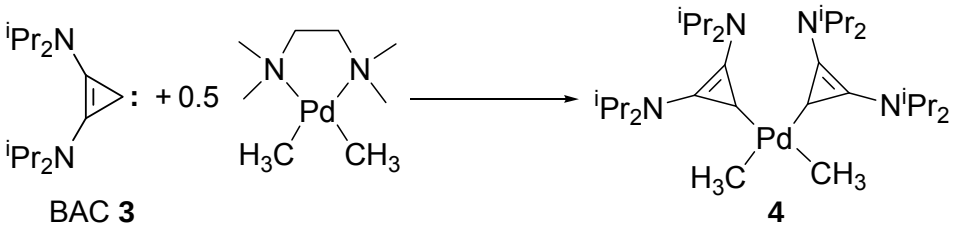
This result could be explained due to the increased reactivity of a transient species such as $LPdMe_2$ (**I1**) formed upon displacement of the chelating diamine by **1** (Scheme 2.2). Reductive elimination of ethane would be greatly encouraged due to the extreme steric bulk provided by the CAAC ligand could

result in a second transient species LPd(0) (**I2**) which can consequently be trapped by an additional equivalent of CAAC to form the observed product **2**.



***Scheme 2.2*.** Possible mechanism for formation of **2**.

We reasoned that the reduced steric bulk of the BAC ligand would enable the isolation of the desired L_2PdMe_2 precursor without the spontaneous elimination of ethane as observed for the bulky CAAC ligand. Indeed, monitoring by ^{13}C NMR the addition of two equivalents of BAC **3** to a toluene solution of $PdMe_2$(TMEDA) revealed the loss of free carbene signal at 185 pm and concurrent appearance of a new signal at 165 ppm characteristic of a BAC transition metal complex.[34] The presence of uncoordinated TMEDA indicated complete L ligand exchange had occurred while a signal for Pd-Me at -3.8 ppm was also observed indicating preservation of the dialkyl moiety. Integration of the ^1H NMR signals was consistent with the formation of the Pd(II) species **4** (Scheme 2.3).



BAC **3** **4**

***Scheme 2.3*.** Synthesis of Palladium(II) complex **4**.

Colorless crystals of **4** suitable for a single crystal X-ray diffraction study were obtained by slow diffusion of hexanes into a saturated toluene solution cooled to -20 °C (89% yield). The metal center is in a distorted square planar environment, and the three-membered BAC rings are tilted by 63° with respect to the square plane (Figure 2.3). The two palladium-carbene bond lengths are equivalent within experimental error (average 2.027 Å), and are shorter than those observed separately by Douthwaite and Danopoulos for analogous complexes bearing bis-NHC[29,35] and NHC-phosphine[36] bidentate ligands (2.07-2.08 Å).

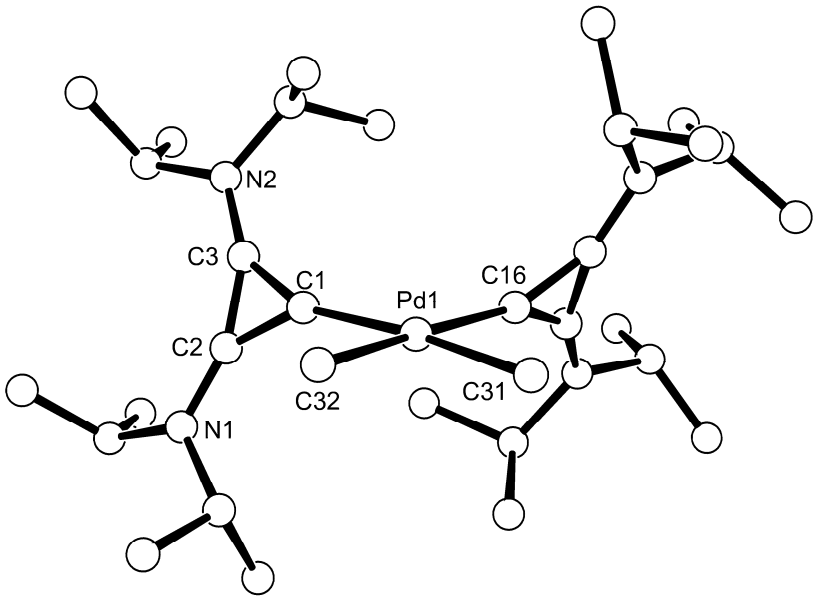


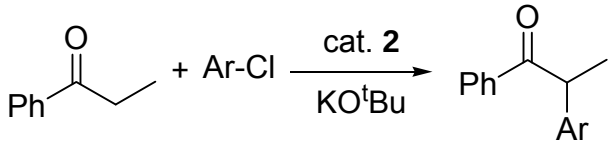
***Figure 2.3*.** Molecular view of the crystal structure of **4.** Selected bond lengths [Å] and angles [°]: Pd(1)-C(1) 2.0242(13), Pd(1)-C(16) 2.0306(12), Pd(1)-C(31) 2.0904(14), Pd(1)-C(32) 2.0913(13); C(1)-Pd(1)-C(16) 97.42(5), C(1)-Pd(1)-C(31) 173.64(5), C(1)-Pd(1)-C(32) 88.61(6), C(16)-Pd(1)-C(32) 173.88(6), C(31)-Pd(1)-C(32) 86.00(6).

Catalysis

Palladium catalyzed α-arylation of ketones was first reported in 1997 by the groups of Buchwald,[37] Hartwig,[38] and Miura.[39] Previous investigations by our group had shown that Pd(II) CAAC complexes are highly active catalysts in this important transformation[8] and so it made sense to test complex **2** for analogous activity. A preliminary test using the standard conditions at room temperature from our earlier work resulted in only trace formation of the arylated product, even at long reaction times (Table 2.1 entry 1). Dramatic enhancement of the conversion was achieved upon increasing the reaction

temperature to 60 °C, with good yields even at reduced catalyst loading (Turnover number = 870) (entries 2-3). As expected, use of ortho-substituted aryl halides gave substantially lower yields (entries 4-5) likely due to steric congestion at the metal center from the bulky CAAC ligand **1**. Indeed this effect was also observed in our previous studies. It is quite possible that the catalytically active species is formed from **2** via ligand dissociation, and that this step is slow at room temperature. In any case, although the results compare well with some systems, the PdCl(allyl)CAAC system seems to be considerably more efficient.

Table 2.1. Results for the α-arylation of propiophenone using Pd(0) precatalyst **2**.[a]

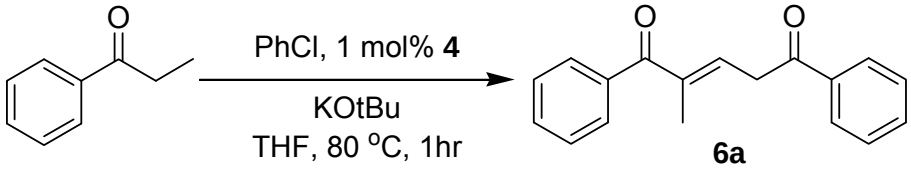


Entry	Ar	Catalyst Loading [mol %]	T [°C]	T [h]	Yield [%][b]
1	Ph	1.0	23	48	<5
2	Ph	1.0	60	1	>98
3	Ph	0.1	60	3	87
4	2-MePh	1.0	60	48	92
5	2,6-Me2Ph	1.0	60	48	14

a) Conditions: THF (1 mL), KOtBu (1.1 mmol), propiophenone (1.0 mmol), aryl chloride (1.1 mmol). b) Yields determined by NMR spectroscopy.

We next tested complex **4** under identical conditions for the α-arylation of propiophenone. At room temperature, no conversion was observed even after

72 hours. However, upon increasing the reaction temperature to 80 °C, the solution turned bright red and a white precipitate rapidly formed. Upon workup, we were surprised to find a clean reaction that did not result in the expected arylated propiophenone product. Instead, the ^{1}H and ^{13}C NMR data gave evidence of a trisubstituted olefin bearing two inequivalent carbonyl groups, while high resolution mass spectrometry (HRMS) gave an MH^{+} that seemed to indicate a homocoupled *ketone*. Slow evaporation of a room temperature chloroform solution yielded single crystals suitable for an X-ray diffraction study, revealing unambiguous determination of the product as the unsaturated diketone **6a** (Figure 2.4) which is formally a dehydrogenatively coupled dimer of propiophenone (Scheme 2.4).



Scheme 2.4. Catalytic dehydrogenative coupling of propiophenone using Pd(II) precatalyst **4**.

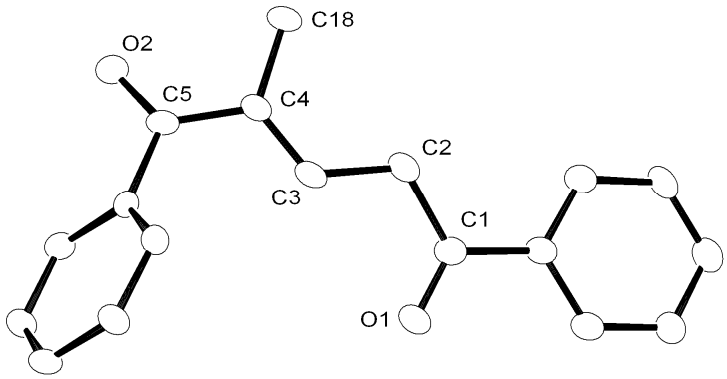
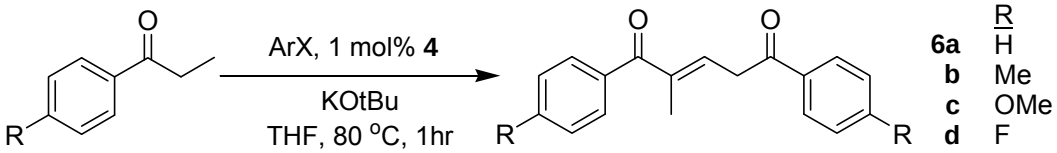


Figure 2.4. Molecular view of compound **6a** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)-C(2) 1.510(6), C(2)-C(3) 1.493(5), C(3)-C(4) 1.344(5), C(4)-C(5) 1.479(5), C(4)-C(18) 1.500(5), C(3)-C(2)-C(1) 114.5(3), C(4)-C(3)-C(2) 124.1(3), C(3)-C(4)-C(5) 119.8(3), C(3)-C(4)-C(18) 122.6(4), C(5)-C(4)-C(18) 117.4(3).

A series of control reactions were performed indicating that both complex **4**, and a strong base were required for the transformation. Since aryl halide is not incorporated into the product, it made sense to remove this reagent from the reaction mixture. To our surprise no reaction was observed in this case leading us to suspect that the aryl halide served as a kind of transfer hydrogenation acceptor. The results for variation of aryl halide are shown for entries 1-6 in Table 2.2. The coupling occurs cleanly regardless of steric bulk of the aryl group or halide present for those tested demonstrating the limited steric interactions of the BAC ligands. Even in the case of 2,4,6-triisopropylphenyl bromide (TIPP-Br, Table 2.2, entry 4), dehalogenated arene was isolated in good yield and unambiguously identified by both ^{13}C and ^{1}H NMR suggesting that a transfer hydrogenation type step had occured.

Table 2.2. Effect of variation of Ar-X and substrate on coupling conversion.



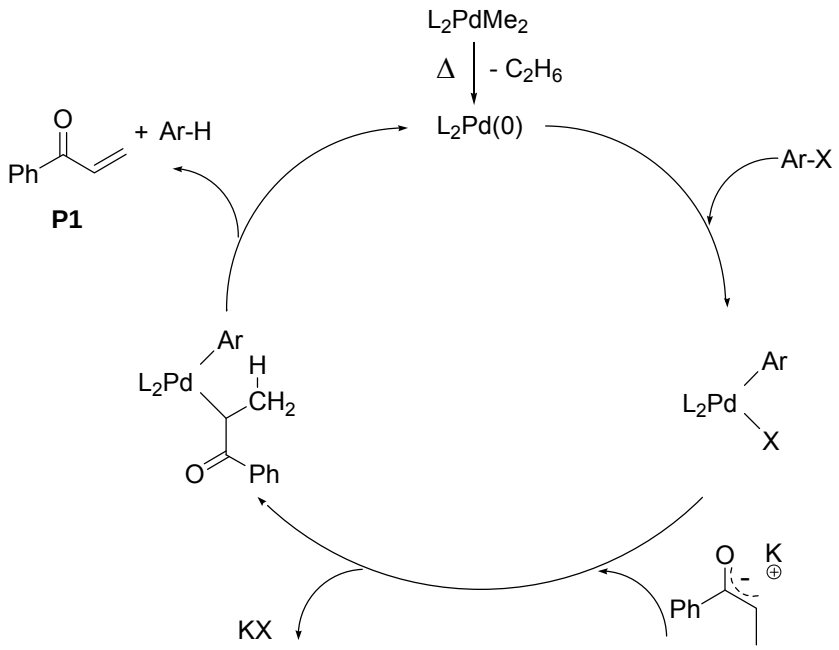
Entry	R	Ar-X	Yield(%)[a]
1	H	none	no rxn
2	H	Ph-Cl	97
3	H	2-MePhCl	95
4	H	Tipp-Br	96
5	Me	2-MePhCl	76
6	OMe	2-MePhCl	81
7	F	2-MePhCl	93

[a] Isolated yields, average of two runs.

Para substitution of the substrate appeared to have only a small effect on conversion with both electron donating and withdrawing groups both showing good yields (Table 2.2, entries 5-7). Unfortunately, the scope of this reaction seems limited to substitution on the aryl ring of propiophenone. When dialkyl ketones, butyrophenone, or indanones were employed as substrates, only complicated mixtures of unidentified products were observed.

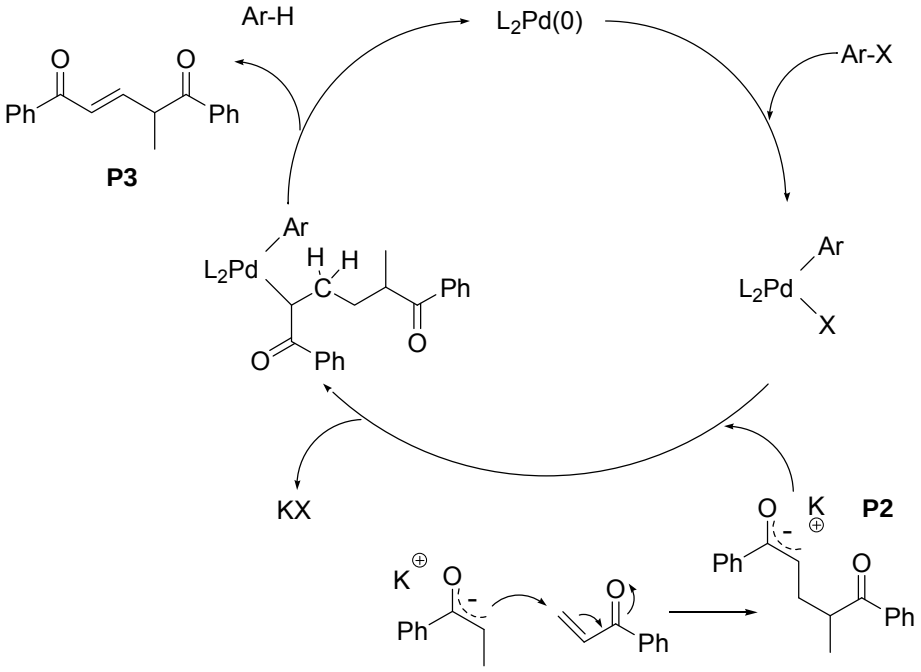
A tandom set of catalytic cycles **A** and **B** are proposed in this transformation (Schemes 2.5 and 2.6). In **A**, the precatalyst **4** likely undergoes thermally induced reductive elimintion to generate a catalytically active Pd(0) source which would readily insert into the Ar-X bond. Potassium

enolate could then coordinate to palladium with loss of KX, followed by β-hydride elimination of Ar-H to produce an α, β-unsaturated ketone **P1** and regenerate the catalyst.

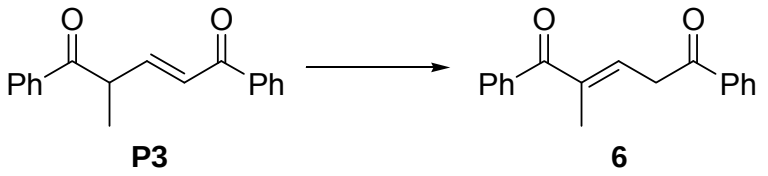


***Scheme 2.5*.** Proposed catalytic cycle **A** leading to formation of an α, ß unsaturated ketone intermediate **P1**.

In the next step, a Michael type addition can occur via enolate attack at **P1** (either free or at Pd) to form a C-C coupled enolate product **P2** (Scheme 2.6). This can enter the catalytic cycle **B** resulting in a second β-hydride elimination sequence to afford the kinetic unsaturated diketone product **P3**. Subsequent isomerization could then occur to yield the observed thermodynamic unsaturated diketone product **6** (Scheme 2.7).



Scheme 2.6. Proposed catalytic cycle **B** for catalytic dehydrogenative coupling of propiophenones.



Scheme 2.7. Isomerization of the kinetic coupling product to the observed thermodynamic product **6**.

Conclusion

The recently reported stable carbenes CAAC **1** and BAC **3** readily form Pd complexes upon reaction with the Pd fragment $Pd(Me)_2$(TMEDA). The outcome of this reaction is strongly dependent upon the steric bulk of the ligand. In the case of CAAC **1**, the product is the coordinatively and electronically unsaturated homoleptic Pd(0) complex **2** which catalyses the α-arylation of propiophenone using aryl chlorides. However, when BAC **3** is employed, L ligand exchange results in the formation of Pd(II) dialkyl complex **4** which displays catalytic activity in the dehydrogenative coupling of propiophenones.

Experimental:

Bis(menthylCAAC)palladium(0) complex 2. A solution of menthyl-CAAC **1**[8] (1.108 g, 2.903 mmol) in 10 mL THF was added to a room temperature, stirred suspension of $PdMe_2$(TMEDA) (365.2 mg, 1.445 mmol) in 10 mL THF immediately forming a deep green solution and stirred for three hours at 65 °C. Volatiles were removed in vacuo while heating at 50 °C for 8 hours and washed with cold hexanes to afford a deep green powder. Yield: 1.238 g (1.421 mmol, 98 %); The product crystallized from a toluene solution layered with diethyl ether at -20 °C overnight. m.p. 137-140 °C, dec; ^{1}H NMR (300 MHz, 25 °C, C_6D_6) δ = 7.30-7.23 (m, 6 H), 3.76-3.63 (m, 2 H), 3.30-3.09 (m, 4 H), 2.21-2.05 (m, 4 H), 1.79 (d, *J* = 6.2 Hz, 8 H), 1.74-1.72 (overlapping m, 6H), 1.57 (d, *J* = 6.3 Hz, 8 H), 1.44 (d, *J* = 6.8 Hz, 8 H), 1.36 (d, *J* = 6.7 Hz, 8 H), 1.23 (s, 12 H), 1.13 (d, *J* = 6.5 Hz, 8 H), 1.07 (d, *J* = 6.3 Hz, 4 H), 0.97 (s, 12 H), 0.81 (d, *J* = 5.6 Hz, 8 H),; ^{13}C{^{1}H} NMR (75 MHz, 25 °C, C_6D_6) δ = 268.7, 145.4, 145.2, 139.0, 127.5, 125.6, 123.7, 74.2, 66.9, 59.2, 53.8, 52.9, 50.5, 45.3, 36.4, 30.9, 29.3, 28.6, 28.5, 27.8, 27.6, 24.7, 24.6, 24.3, 24.1, 23.6, 22.2; ESI-MS m/z 868.5818 (868.5826 calcd for $C_{54}H_{86}N_2Pd$, M^+).

Cis-Di[bis(diisopropylamino)cyclopropenylidene]-di(methyl)palladium(II) complex 4. In the glovebox, cyclopropenylidene **3** (767 mg, 3.23 mmol) was added to a solution of $PdMe_2$(TMEDA) (386 mg, 1.53 mmol) in toluene (10mL) and stirred at room temperature for 2 hours. After removal of the volatiles with gentle heating under vacuum, the resulting yellow, sticky foam

was washed with hexanes giving a fine grey powder. Crystallization from a minimum of warm toluene, layered with hexanes, and cooled to -20 °C overnight led to complex **4**, which was isolated as colorless, blocky crystals. Yield: 834 mg (1.37 mmol, 89 %); m.p. 107 °C, dec; ^{1}H NMR (300 MHz, 25 °C, C_6D_6) δ = 4.11 (broad s, 8 H), 1.29 (d, *J* = 6.5 Hz, 48 H), 0.57 (s, 6 H); ^{13}C{^{1}H} NMR (75 MHz, 25 °C, C_6D_6) δ = 165.5, 148.8, 48.9, 21.7, -3.8; ESI-MS m/z 593.3768 (593.3774 calcd for $C_{31}H_{59}N_4Pd$, M^+ - CH_3).

General Catalytic Procedure

In the glovebox, 1 equiv. propiophenone, 1.1 equiv. potassium tert-butoxide, 1.1 equiv. chlorobenzene, and 1 mol% **2** were added to a Teflon coated screw-cap vial and dissolved in THF. The resulting mixture was heated in an oil bath at 80 °C. Within 15 min. the solution turned bright red with formation of a white precipitate. After 1 hour, the mixture was cooled to room temperature and treated with dilute aqueous HCl. Organics were extracted with hexanes and solvent removed in vacuo to afford a reddish orange microcrystalline solid. Product **6a** was recrystallized by slow evaporation of a saturated chloroform solution to afford red crystals suitable for single crystal X-ray diffraction.

Propiophenone 'dimerization' product 6a (R = H)

^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) δ = 8.14-7.42 (m, 10H), 6.68 (td, *J* = 7.4, 1.4 Hz, 1 H), 4.01 (d, *J* = 6.8 Hz, 2 H), 2.07 (s, 3 H); ^{13}C{^{1}H} NMR (75 MHz,

25 °C, $CDCl_3$) δ = 197.2, 195.1, 136.9, 136.3, 133.7, 133.6, 131.9, 130.2, 129.6, 128.8, 128.5, 128.2, 38.6, 13.3; ESI-MS m/z 265.1226 (265.1223 calcd for $C_{18}H_{17}O_2$, MH^+).

Propiophenone 'dimerization' product 6b (R = Me).

^1H NMR (300 MHz, 25 °C, $CDCl_3$) δ = 7.89 (d, *J* = 8.2 Hz, 2 H), 7.67 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 6.63 (td, *J* = 6.8, 1.3 Hz, 1 H), 3.96 (d, *J* = 6.7 Hz, 2 H), 2.43 (s, 3H), 2.41 (s, 3H), 2.05 (d, *J* = 0.6 Hz, 3 H); $^{13}C\{^1H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) δ = 198.2, 196.0, 144.4, 142.5, 138.6, 136.2, 135.2, 133.9, 130.2, 129.8, 129.5, 129.2, 128.9, 128.3, 38.5, 21.7, 21.5, 13.4; ESI-MS m/z 293.1532 (293.1536 calcd for $C_{20}H_{21}O_2$, MH^+).

Propiophenone 'dimerization' product 6c (R = OMe)

^1H NMR (300 MHz, 25 °C, $CDCl_3$) δ = 7.97 (d, *J* = 8.8 Hz, 2 H), 7.79 (d, *J* = 8.8 Hz, 2 H), 6.96 (d, *J* = 8.9 Hz, 2 H), 6.92 (d, *J* = 8.9 Hz, 2 H), 6.56 (td, *J* = 6.8, 1.3 Hz, 1 H), 3.92 (d, *J* = 6.8 Hz, 2 H), 3.87 (s, 3H), 3.85 (s, 3H), 2.03 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) δ = 197.4, 195.0, 163.8, 162.8, 138.8, 135.1, 130.5, 130.2, 113.9, 113.7, 113.5, 55.5, 55.4, 38.2, 13.6; ESI-MS m/z 325.1437 (325.1434 calcd for $C_{20}H_{21}O_4$, MH^+).

Propiophenone 'dimerization' product 6d (R = F).

^1H NMR (300 MHz, 25 °C, $CDCl_3$) δ = 8.05-8.01 (m, 2 H), 7.83-7.78 (m, 2 H), 7.21-7.10 (m, 4 H), 6.60 (td, *J* = 6.6, 1.4 Hz, 1 H), 3.98 (d, *J* = 6.3, 2 H), 2.04 (d, *J* = 0.8 Hz, 3 H); $^{13}C\{^1H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) δ = 196.9, 194.6,

166.0 (d, $J_{C\text{-}F}$ = 252.9 Hz), 165.1 (d, $J_{C\text{-}F}$ = 252.0 Hz), 138.7, 135.9, 132.9, 132.8, 132.2 (d, $J_{C\text{-}F}$ = 8.9 Hz), 130.8 (d, $J_{C\text{-}F}$ = 9.3 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.6 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.7 Hz), 38.3, 13.4; $^{19}F\{^{1}H\}$ NMR (282 MHz, 25 °C, $CDCl_3$) δ = -100.5, -104.3; ESI-MS m/z 301.1041 (301.1035 calcd for $C_{18}H_{15}F_2O_2$, MH^+).

Crystal structure determination of complexes 2, 4, and 6a. The Bruker X8-APEX[40] X-ray diffraction instrument with Mo-radiation was used for data collection**.** All data frames were collected at low temperatures (T = 100 K) using an ω, φ-scan mode (0.5° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS[41] software package. The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program. The SIR97 was used for direct methods of phase determination, and Bruker SHELXTL[42] software package for structure refinement and difference Fourier maps. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of compounds were refined by means of a full matrix least-squares procedure on F^2. All H-atoms were included in the refinement in calculated positions riding on the C atoms. Drawings of molecules were performed using Ortep 3.[43]

Crystal and structure parameters of 2: size 0.36 x 0.26 x 0.13 mm^3, Orthorhombic, space group P2(1)2(1)2(1), a = 11.3028(13) Å, b =

11.5737(13) Å, c = 45.065(5) Å, $\alpha = \beta = \gamma = 90.0°$, V = 5895.1(12) $Å^3$, ρ_{calcd} = 0.980 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 33398, independent reflections = 8484 (R_{int} = 0.0784), absorption coefficient μ = 0.344 mm^{-1}; max/min transmission = 0.9566 and 0.8861, 533 parameters were refined and converged at R1 = 0.0423, wR2 = 0.0809, with intensity $I>2\sigma(I)$.

Crystal and structure parameters of 4: size 0.34 x 0.21 x 0.10 mm^3, monoclinic, space group P 2(1)/c, a = 14.7185(5) Å, b = 14.8792(5) Å, c = 19.3392(7) Å, $\alpha = \gamma = 90.0^o$, $\beta = 110.208(2)^o$, V = 3974.6(2) $Å^3$, ρ_{calcd} = 1.018 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 76871, independent reflections = 13230 (R_{int} = 0.0246), absorption coefficient μ = 0.488 mm^{-1}; max/min transmission = 0.8557 and 0.7961 352 parameters were refined and converged at R1 = 0.0286, wR2 = 0.0761, with intensity $I>2\sigma(I)$.

Crystal and structure parameters of 6a: size 0.10 x 0.10 x 0.03 mm^3, orthorhombic, space group Pna2(1), a = 11.766(4) Å, b = 5.772(2) Å, c = 20.174(8) Å, $\alpha = \beta = \gamma = 90.0^o$**,** V = 1370.1(9) $Å^3$, ρ_{calcd} = 1.281 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 6971, independent reflections = 1974 (R_{int} = 0.0784), absorption coefficient μ = 0.082 mm^{-1}; max/min transmission = 0.9975 and 0.9918, 183 parameters

were refined and converged at R1 = 0.0483, wR2 = 0.0944, with intensity $I>2\sigma(I)$.

Structural data for compound **4** has been deposited in the Cambridge Crystallographic Data Center under CCDC 662012, and can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

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Chapter 3

Air and Water Stable Catalysts for Hydroamination/ Cyclization: Synthesis and Application of CCC-NHC Pincer Complexes of Rh and Ir

Introduction

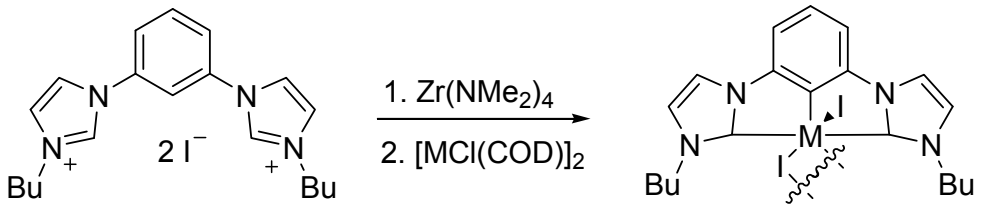
The ability to functionalize alkenes with nitrogen is still in its infancy, despite examples of efficient and asymmetric C-N bond formation.[1-5] Recently, the Overman group has developed highly efficient catalysts for the allylic imidate rearrangement to afford C-N bonds[6,7] and has found ever broadening applicability of their chiral variants.[8,9] C-N bond formation through asymmetric aminohydroxylation has also seen advances.[1] Aryl amination is another area of C-N bond formation that has seen breakthroughs in recent years.[10] A most atom economical method of C-N bond formation is the direct addition of N-H to unactivated C-C double bonds, hydroamination/ cyclization. Marks' seminal report of lanthanide catalysts for hydroamination has sparked a flurry of activity in the field.[11-17] Recent reports include a breakthrough in hydroamination/cyclization employing a Pt catalyst that was not sensitive to the addition of water,[18] Rh,[19-24] and numerous other examples.[12,25-29] Several groups have recently reported modestly successful asymmetric variants.[28-33]

Herein we report the extension of the metallation/transmetallation methodology for the synthesis of CCC-NHC pincer complexes to Ir[34] and the

first examples of Rh and Ir NHC pincer complexes for the catalysis of intramolecular hydroamination/ cyclization of unactivated alkenes. These systems are highly active catalysts giving near quantitative yields with low catalyst loadings for secondary amine substrates. They function in the presence of air and with water as solvent. The new CCC-NHC pincer catalysts have been prepared in high yield by a general synthetic methodology and have been structurally characterized.

Synthesis of NHC pincer complexes has been an area of intense research activity of late.[35] Numerous groups have contributed to the development of pyridyl bridged,[36] xylyl bridged,[37-40] and 2,6-lutidinyl bridged systems.[37,41] We have been focused on developing phenylene bridged systems,[42] and have developed a methodology for the synthesis of the ligand precursor and an efficient metallation strategy.[34,43] Pincer complexes, in general, have shown a great variety of chemistries.[44] A notable recent example is in the area of N-H bond activation.[45]

We recently reported a general methodology for the synthesis of CCC-NHC pincer complexes that exploited the basicity and electrophilicity of $Zr(NMe_2)_4$ to activate three C-H bonds simultaneously, coupled with transmetallation from Zr to prepare late transition metal CCC-NHC complexes of Rh (Scheme 3.1, **2b**).[34,43] We have extended that methodology to include Ir(III) complex **2a.**



1 **2a M = Ir 68%**
2b M = Rh 66%

Scheme 3.1. Synthesis of Pincer Complexes **2a** and **2b**.

While evaluating several routes to late transition metal CCC-NHC pincer complexes, it was found that metallation with Zr followed by transmetallation to Rh or Ir was a high yielding process providing Ir **2a** in 68% and Rh **2b** in 66% (see supporting information). The bis imidazolium salt **1** was treated in situ with 2.5 equiv of $Zr(NMe_2)_4$. It was then stirred with $[IrCl(COD)]_2$ for 8 h. The resulting iodo-bridged dimer was isolated in 68% yield. An X-ray quality crystal was grown by slow evaporation of a CH_2Cl_2 solution.

A single-crystal X-ray analysis of **2a** revealed a structure that is isomorphous with the Rh analogue (Figure 3.1). The iodo-bridges between the Ir centers complete the octahedral environment. The molecular structure contains a center of symmetry that relates the two halves of the molecular structure. Unlike the Rh analogue, no Ir ammine adduct was noted spectroscopically, but it is anticipated that in solution this dimer is readily split by coordination to the amine functional group of the substrate. Select metric data are included in Figure 3.1. Other than the geometric constraints of the

tridentate ligand, the geometry of the complex is within the normal range. Due to the chelating rings the C6-Ir-C2 angle is only 78°, a significant deviation from the idealized 90°. Likewise the C2-Ir1-C2' angle is 156°, compared to the idealized angle of 180°.

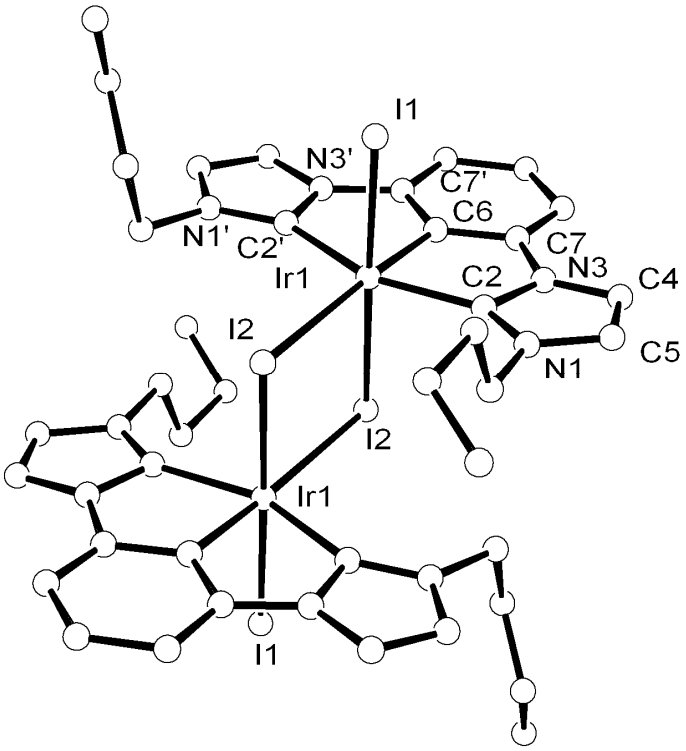
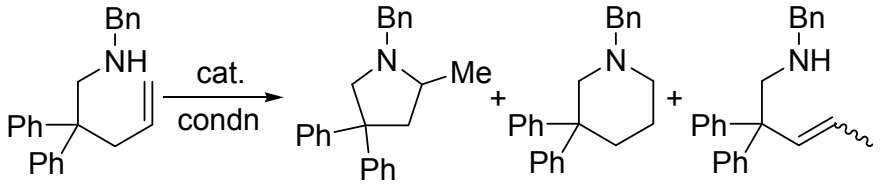


Figure 3.1. Molecular representation of the crystal structure of **2a**. Selected bond lengths [Å] and angles [°]: Ir1-C6 1.965(3), Ir1-I1 2.6720(3), Ir1-I2 2.6803(3), Ir1-I2' 2.8175(3), C6-Ir1-C2 78.36(14), C2-Ir1-C2' 156.47(13), C6-Ir1-I1 92.38(10), C2-Ir1-I1 89.07(10), I1-Ir1-I2 177.705(9), C6-Ir1-I2' 174.89(10).

Our initial evaluation of these complexes as catalysts for the intramolecular hydroamination/cyclization focused on alkenylamine **3** (Scheme 3.2). The crude product from the preparation of **3** was employed in

the evaluations without further purification. No purification of solvents or attempt to exclude air was performed in the assay of the catalysts. Initial results indicated the formation of pyrrolidine **4** with no evidence for the formation of piperidine **5**. In some experiments new resonances appeared in the olefin region of the ^{1}H NMR spectrum consistent with trace formation of internal alkene isomers **6**.



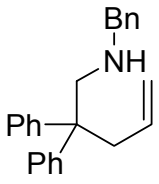
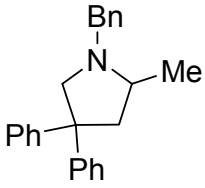
cat. = 2.5 mol % **2b**. condn = C_6D_6, 110 ^{o}C, overnight

Scheme 3.2. Initial Hydroamination Results with **2a** and **2b**.

The use of "environmentally-friendly" solvents such as water for the synthesis of organic compounds serves as a cornerstone of green chemistry.[46,47] Since no special purification or exclusion of water was required in the initial experiments, the catalysts were evaluated with water as the solvent. The results are presented in Table 3.1. Evaluation of pincer complexes **2a** and **2b** in water showed no appreciable loss of catalytic activity. In all cases there was no detectable formation of isomerization products. The only cyclized product observed by ^{1}H NMR was pyrrolidine **4**.

Similar results were obtained when THF, benzene, or toluene were employed as solvent.

Table 3.1. Comparison of Benzene and Water as Solvent for Hydroamination/ Cyclization of Unactivated Alkenes with 2.5 mol % **2b**.

amine	heterocycle	solvent	cycl / isom[a]	
			catalyst	
			2a	**2b**
		benzene	>98 / <2	>95 / <5
		water	>98 / <2	>95 / <5
3	**4**	[a] % alkene isomerization		

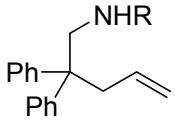
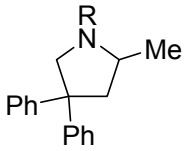
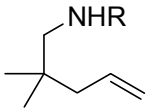
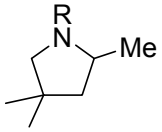
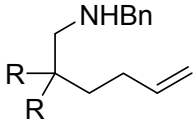
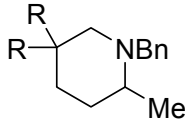
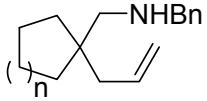
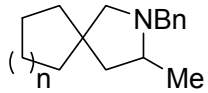
Control experiments were performed without adding catalyst by heating the substrate neat, in benzene, or in water. In each of these cases no reaction occurred, and only starting material was recovered. A control experiment that excluded air and used purifed solvent showed no loss of activity. Additional control experiments were run adding catalytic quantities of I_2 in place of **2a** and **2b** to check for iodine or acid catalyzed hydroamination as reported by Bergman.[48] Under these conditions the product formed was a cyclized iodine addition product based on ^{1}H NMR and MS data.

An examination of the scope of these catalysts is presented in Table 3.2. Secondary aminoalkene substrates gave good yields of the desired hydroamination/cyclization products. Excellent isolated yields were obtained for selected examples (entries 1, 3, 9, see footnotes). Exo-trig cyclization products were obtained exclusively (entries 1, 10). Lack of substitution on the

β- position (R = H) lead to a dramatic decrease in the rate of cyclization and an increase in the isomerization product as the only product (entry 11). Primary amines did not yield cyclization products (entry 4). Aryl amines were cyclized successfully also (entries 3, 9). The presence of an aryl bromide was tolerated by the catalysts (entry 5). The Ir catalyst **2a** was found to give superior results for the diphenyl derivatives and was employed in the evaluation of the dimethyl derivatives (entries 6–9). Pincer complexes **2a** or **2b** typically had produced near 90% conversion at 6 hours.

Attempts at intermolecular coupling did not yield any desired hydroamination products. 6-exo-trig cyclization was found exclusively in the formation of the piperidinyl derivative (entry 10). Finally, spirocyclic compounds could be formed in excellent yields efficiently (entries 12 and 13). Analysis of this data suggests that the chelate effect along with the Thorpe-Ingold effect are required of the substrate to achieve efficient cyclization. The lack of hydroamination with primary amines is not consistent with the formation of imido complexes as part of the catalytic mechanism.[49] It is consistent with M-N bond formation, olefin coordination, and migratory insertion followed by reductive elimination.[50,51]

Table 3.2. Intramolecular Hydroamination/Cyclization of Unactivated Alkenes Yielding Pyrrolodines and Piperidines Catalyzed by 2.5 mol. % **2a** or **2b**[a].

entry	amine	heterocycle
		
		catalyst (cycl / isom[b])
	R	**2a(Ir)** **2b(Rh)**
1	Bn	>98[d]/c >90/c
2	*n*-Pr	95/<5 75 /<5
3	Ph	>98[e]/<2 -
4	H	0/50 0/75
5	CH_2p-C_6H_4Br	>98/b -
		
	R	**2a(Ir)**
6	Bn	90/<5
7	*n*-Pr	80/10
8	*i*-Pr	90/5
9	Ph	>80[f]/15
		
	R	**2a(Ir)**
10	Ph	90/c
11	H	0/100
		
	n	**2b(Rh)**
12	1	>98/c
13	2	79[g]/c

[a] Reaction conditions: C_6D_6, 110 °C, 16 h. Conversion determined by ^{1}H NMR. [b] (% conversion to heterocycle/% alkene isomerization). [c] Isomerization not detected. [d] Isolated yield: 77%. [e] Isolated yield: 80%. [f] Isolated yield: 80%. [g] 22 h.

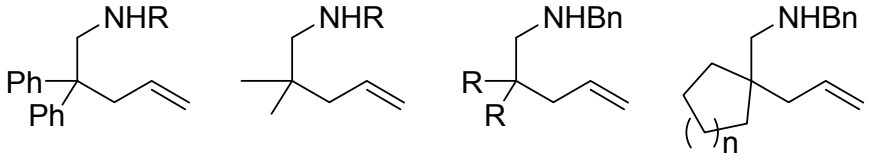
Conclusion

In summary we have reported the efficient synthesis of a CCC-(bis)NHC Ir pincer complex with applications of the Rh and Ir pincer complexes as air and water-stable hydroamination/cyclization catalysts for the formation of 5 and 6 membered nitrogen containing rings.

Experimental Section

1,3-bis(imidazolene-3-yl)benzene-tetra(iodo)-di[iridium(III)] complex 2a. A mixture of 1,3-bis (1-butylimidazolium-3-yl) benzene iodide (0.150 g, 0.26 mmol) and $Zr(NMe_2)_4$ (0.173 g, 0.65 mmol) were weighed in glove box and dry THF (16 ml) was added to this vial. The mixture was stirred for 45 minutes at room temperature to afford colorless homogenous solution. $[Ir(COD)Cl]_2$ (0.174 g, 0.26 mmol) was added to the vial and stirring continued vigorously at room temperature for another 6h. The reaction mixture was concentrated under vacuum to afford red solid, washed with hexane and discarded by filtration. The red solid was extracted with toluene (2 × 5 ml) and evaporated in high vacuum to obtain the red colored crystalline solid (0.270 g, 68 %). The X-ray quality single crystal was grown by the slow evaporation of saturated methylene chloride solution at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, *J* = 2.1 Hz, 2 H), 7.54 (d, *J* = 1.8 Hz, 2 H), 7.51 (d, *J* = 2.1, 2 H), 7.25 (t, *J* = 2.1 Hz, 2 H), 7.11 (dd, *J* = 2.1 and 8.1 Hz, 4 H), 7.07 (d, *J* = 2.1 Hz, 2 H), 5.04-4.95 (m, 4 H), 4.85-4.72 (m, 4 H), 2.11-1.99 (m, 8 H), 1.61-1.49 (m, 8 H), 1.03(t, *J* = 7.5 Hz, 12 H) . $^{13}C\{^1H\}$ (75 MHz, THF): δ 171 (s, NHC-Ir), 164.1(C-aromatic-Ir), 145.8, 128.2, 120.6, 119.5, 114.8, 105.9, 51, 43.3, 34.5, 20.1, 13.9. LSIMS: 1475(M^+ - 2Bu), 1381(M^+ - Bu, I), 1114(M^+ - 2Bu, 3I), 1022(M^+ - ligand, Ir), 896(M^+ - ligand, Ir, I), 511(M^+ - ligand, Ir, 4I).

Table 3.3. Substrates Used in Evaluation of Catalytic Hydroamination/ Cyclization.



	R		R		R		n
4	Bn	**S6**	Bn	**S10**	Ph	**S12**	1
S1	n-Pr	**S7**	n-Pr	**S11**	H	**S13**	2
S2	i-Pr	**S8**	i-Pr				
S3	Ph	**S9**	Ph				
S4	H						
S5	CH_2-*p*-C_6H_4Br						

Compounds **4**, **S4**, **S5**, and **S6**,[18] **S7**,[52] **S11**[53] were prepared by literature procedures. Analytical data matched those reported in the literature. Other substrates were prepared based on analogy with the established procedures.

(*n*-Propyl)-(2,2-diphenyl-4-pentenyl)-amine (S1): obtained as a yellow oil (0.99 g, 81% yield) from reaction of **S4** (1.03 g, 4.30 mmol), propionaldehyde (0.32 ml, 4.518 mmol) and sodium borohydride (0.239 g, 6.45 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34-7.20 (m, 10 H), 5.50-5.36 (m, 1 H), 5.10-4.97 (m, 2 H), 3.24 (s, 2 H), 3.05 (d, *J* = 6.9, 2 H), 2.54 (t, *J* = 7.2, 2 H), 1.43 (m, 2 H), 0.84 (t, *J* = 7.2, 3 H); ^{13}C{^{1}H} NMR: δ = 147.2, 135.3, 128.3, 128.2, 126.2, 117.8, 56.1, 52.1, 50.4, 42.0, 23.1, 11.9. MS-CI m/z 280.2058 (280.2065 calcd for $C_{20}H_{26}N$, MH^+).

(*i*-Propyl)-(2,2-diphenyl-4-pentenyl)-amine (S2): obtained as a white solid (3.17 g, 81% yield) from reaction of **S4** (3.31g, 13.94 mmol), acetone (1.13 ml, 15.34 mmol) and sodium borohydride (0.791g, 20.92 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.20 (m, 10 H), 5.51-5.38 (m, 1 H), 5.09 (d, *J* = 17.1 Hz, 1 H), 5.00 (d, *J* = 9.9 Hz, 1 H), 3.26 (s, 2 H), 3.07 (d, *J* = 6.9 Hz, 2 H), 2.70 (sept, *J* = 6.0 Hz, 1 H), 1.01 (d, *J* = 6.0 Hz, 6 H), 0.32 (br s, 1 H). ^{13}C{^{1}H} NMR: δ = 147.2, 135.2, 128.3, 128.1, 126.1, 117.7, 53.8, 50.1, 49.4, 41.8, 23.3. MS-CI m/z 280.2064 (280.2065 calcd for $C_{20}H_{26}N$, MH^+).

Phenyl-(2,2-diphenyl-4-pentenyl)-amine (S3): obtained as a white solid (3.64 g, 45% yield) from reaction of 2,2-diphenyl-4-pentenal (6.13 g, 25.94 mmol), aniline (14.6 ml, 160.4 mmol) and sodium borohydride (1.47 g, 38.91 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42-7.26 (m, 10 H), 7.21 (t, *J* = 7.8 Hz, 2 H), 6.75 (t, *J* = 7.5 Hz, 1 H), 6.62 (d, *J* = 7.5 Hz, 2 H), 5.54-5.40 (m, 1 H), 5.11-5.03 (m, 2 H), 3.81 (s, 2 H), 3.30 (br s, 1 H), 3.09 (d, *J* = 7.2 Hz, 2 H). ^{13}C{^{1}H}NMR: δ = 148.6, 145.9, 134.4, 129.3, 128.5, 128.2, 126.6, 118.6, 117.6, 113.3, 50.4, 50.2, 42.3. MS-CI m/z 314.1919 (314.1909 calcd for $C_{23}H_{24}N$, MH^+).

(*i*-Propyl)-(2,2-dimethyl-4-pentenyl)-amine (S8): obtained as a colorless liquid (1.16 g, 37% yield) from reaction of 2,2-dimethyl-4-pentenyl-amine (2.29 g, 20.24 mmol), acetone (1.63 ml, 22.20 mmol) and sodium borohydride (1.15 g, 30.37 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.89-5.75 (m, 1 H), 5.06-4.98 (m, 2 H), 2.70 (sept, *J* = 6.3 Hz, 1 H), 2.34 (s, 2 H), 2.03 (d, *J* = 7.5

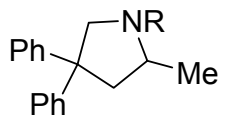
Hz, 2 H), 1.03 (d, *J* = 6.3 Hz, 6 H), 0.88 (s, 6 H). $^{13}C\{^{1}H\}$NMR: δ = 135.9, 116.9, 58.2, 49.7, 44.9, 34.3, 25.7, 23.4. MS-CI m/z 156.1755 (156.1752 calcd for $C_{10}H_{22}N$, MH^+).

Benzyl-(2,2-diphenyl-4-hexenyl)-amine (S10): obtained as a white solid (0.95 g, 97% yield) from reaction of **S11** (0.68 g, 2.87 mmol), benzaldehyde (0.31 ml, 3.01 mmol) and sodium borohydride (0.163 g, 4.30 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.20 (m, 15 H), 5.90-5.77 (m, 1 H), 5.04-4.95 (m, 2 H), 3.80 (s, 2 H), 3.28 (s, 2 H), 2.43-2.38 (m, 2 H), 1.77-1.70 (m, 2 H), 1.04 (br s, 1 H). $^{13}C\{^{1}H\}$NMR: δ = 147.2, 140.8, 139.3, 128.4, 128.2, 128.1, 128.0, 126.9, 126.1, 114.3, 55.4, 54.2, 50.4, 36.5, 28.8. MS-CI m/z 342.2225 (342.2222 calcd for $C_{25}H_{28}N$, MH^+).

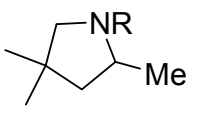
(1-allyl-cyclopentylmethyl)-benzyl-amine (S12): Obtained as clear oil (2.4 g, 86% yield) from reaction of (1-allyl-cyclopentyl)-methylamine (1.7 g, 12.90 mmol), benzaldehyde (1.30 mL, 12.81 mmol) and sodium borohydride (0.677 g, 18.3 mmol). TLC (Hexanes/EtOAc = 6:1): R*f* = 0.43. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34-7.24 (m, 5 H), 5.85-5.74 (m, 1 H), 5.07-5.00 (m, 2 H) 3.80 (s, 2 H), 2.45 (s, 2 H), 2.16 (d, *J* = 3.6 Hz, 2 H), 1.57-1.53 (m, 4 H), 1.46-1.38 (m, 4 H). $^{13}C\{^{1}H\}$ NMR: δ = 141.0, 136.3, 128.3, 127.9, 126.7, 116.5, 57.2, 54.7, 46.0, 42.4, 35.8, 25.0. MS-ESI m/z 230.1918 (230.1909 calcd for $C_{16}H_{24}N$, MH^+).

(1-allyl-cyclohexylmethyl)-benzyl-amine (S13): Obtained as brown oil (3.77 g, 72% yield) from reaction of (1-Allyl-cyclohexyl)-methylamine (3.3 g, 21.53mmol), benzaldehyde (2.3 mL, 22.60 mmol) and sodium borohydride (1.12 g, 32.30 mmol). TLC (Hexanes/EtOAc = 6:1): R_f = 0.49. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35-7.25 (m, 5 H), 5.84-5.72 (m, 1 H), 5.05-4.99 (m, 2 H), 3.79 (s, 2 H), 2.43 (s, 2 H), 2.13 (d, *J* = 7.5 Hz, 2 H), 1.40-1.33 (m, 8 H). $^{13}C\{^1H\}$ NMR: δ = 140.9, 135.4, 128.3, 128.0, 126.8, 116.6, 55.8, 54.7, 40.5, 36.7, 34.0, 26.4, 21.6. MS-ESI m/z 244.2075 (244.2065 calcd for $C_{17}H_{26}N$, MH^+).

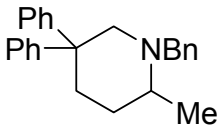
Table 3.4. Products Obtained via Catalytic Hydroamination/Cyclization Using Catalysts **2a** and **2b**.



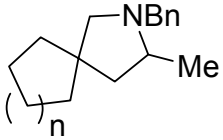
	R
S14	Bn
S15	n-Pr
S16	i-Pr
S17	Ph
S18	CH_2-*p*-C_6H_4Br



	R
S19	Bn
S20	n-Pr
S21	i-Pr
S22	Ph



	R
S23	Ph



	n
S24	1
S25	2

Typical catalytic procedure: In air, 2 mmol alkenylamine, 5.0 mol % catalyst, and 0.5 mL C_6D_6 were added to a 2 mL vial and sealed with an airtight Teflon coated cap. The vial was then placed in 110°C oil bath and heated for 16 hours. The reaction mixture was subsequently cooled to room temperature, transferred to an NMR tube and ^{1}H NMR obtained.

Compounds **S14, S18, and S19**,[18] and **S21**[54] were confirmed by comparison of analytic data with that reported in the literature. All other heterocyclic products were analyzed as follows.

2-methyl-4,4-diphenyl-1-(n-propyl)pyrrolidine (S15): Obtained as a pale, yellow oil. TLC (hexanes-EtOAc = 4:1): R_f = 0.34. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.42 (d, *J* = 7.2 Hz, 2 H), 7.00-7.15 (m, 8 H), 3.81 (d, *J* = 9.6 Hz, 1 H), 2.58-2.72 (m, 2 H), 2.63 (d, *J* = 9.5 Hz, 1 H), 2.46-2.48 (m, 1 H), 1.96-2.07 (m, 2 H), 1.44-1.51 (m, 2 H), 1.00 (d , *J* = 6.0 Hz, 3 H), 0.92 (t, *J* = 7.3 Hz, 3 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 128.1, 127.9, 127.4, 127.2, 125.8, 66.8, 60.3, 56.1, 47.9, 22.1, 19.4, 12.2, 1.0. MS-CI m/z 280.2074 (280.2065 calcd for $C_{20}H_{26}N$, MH^+).

2-methyl-4,4-diphenyl-1-(phenyl)pyrrolidine (S17): TLC (hexanes-EtOAc = 10:1): R_f = 0.40. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.28 (t, *J* = 7.9 Hz, 2 H), 6.90-7.15 (m, 12 H), 6.81 (t, *J* = 7.3 Hz, 1 H), 6.60 (d, *J* = 8.0 Hz, 2 H), 3.94 (d, *J* = 10.0 Hz, 1 H), 3.79 (d, *J* = 10.1 Hz, 1 H), 3.45-3.56 (m, 1 H), 2.34-2.40 (m, 1 H), 2.13-2.20 (m, 1 H), 1.00 (d, *J* = 6.0 Hz, 3 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 147.3, 147.2, 146.9, 129.4, 128.8, 128.6, 128.5, 127.4, 127.0, 126.6, 126.3, 116.3, 113.2, 60.4, 53.1, 52.7, 47.1, 19.9. MS-CI m/z 314.1910 (314.1909 calcd for $C_{23}H_{23}N$, MH^+).

2,4,4-trimethyl-1-(n-propyl)pyrrolidine (S20): Only a crude spectrum of this compound was obtained due to product volatility. The assignment of the crude product was made based on analogy to other compounds reported herein. ^{1}H NMR (300 MHz, C_6D_6): δ = 3.11-3.17 (m, 1 H), 2.79-2.88 (m, 1 H), 2.17-2.20 (m, 2 H), 1.64-1.73 (m, 3 H), 1.43-1.58 (m, 5 H), 1.22 (d, *J* = 6.1 Hz, 3 H), 1.12 (s, 3 H), 1.00 (s, 3 H), 0.77-0.87 (m, 7 H).

2,4,4-trimethyl-1-(isopropyl)pyrrolidine (S21): Only a crude spectrum of this compound, originally referenced by DeKimpe, et al.[54] was obtained due to product volatility. The assignment of the crude product was made based on analogy to other compounds reported herein. ^{1}H NMR (300 MHz, C_6D_6): δ = 3.85 (d, *J* = 9.5 Hz, 1 H), 3.05-3.20 (m, 1 H), 2.62-2.78 (m, 2 H), 2.64 (d, *J* = 9.4 Hz, 1 H), 2.39-2.49 (m, 1 H), 2.00-2.16 (m, 3 H), 1.42-1.62 (m, 3 H), 1.16-1.26 (m, 5 H), 0.91-0.98 (m, 3 H), 0.81-0.88 (m, 3 H).

2,4,4-trimethyl-1-(phenyl)pyrrolidine (S22): Obtained as a clear liquid. TLC (hexanes): R_f = 0.22. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.28 (t, *J* = 7.9 Hz, 1 H), 7.15-7.21 (m, 2 H), 6.74-6.85 (m, 1 H), 6.57 (d, *J* = 8.1 Hz, 1 H), 6.46-6.51 (m, 1 H), 3.54-3.67 (m, 1 H), 2.71 (d, *J* = 5.8 Hz, 1 H), 1.56-1.62 (m, 1 H), 1.53 (d, *J* = 5.3 Hz, 1 H), 1.15-1.21 (m, 1 H), 1.08 (d, *J* = 6.1 Hz, 2 H), 0.91-0.92 (m, 4 H), 0.74 (d, *J* = 3.3 Hz, 3 H). MS-CI m/z 190.1594 (190.1596 calcd for $C_{13}H_{20}N$, MH^+).

2-methyl-4,4-diphenyl-1-(benzyl)piperidine (S23): Obtained as a clear oil**.** TLC (hexanes-EtOAc = 10:1): R_f = 0.47. ^{1}H NMR (300 MHz, C_6D_6): δ = 6.98-7.32 (m, 15 H), 3.86 (d, *J* = 13.3 Hz, 1 H), 3.40 (d, *J* = 12.3 Hz, 1 H), 2.92 (d, *J* = 13.3 Hz, 1 H), 2.36 (d, *J* = 12.3 Hz, 1 H), 2.21-2.32 (m, 2 H), 1.95-2.05 (m, 1 H), 1.28-1.48 (m, 2 H), 0.94 (d, *J* = 6.1 Hz, 3 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 148.6, 146.7, 139.4, 129.5, 128.4, 128.0, 127.9, 127.6, 127.0, 126.8, 125.6, 125.3, 61.0, 58.9, 56.1, 46.5, 34.2, 31.0, 18.6. MS-CI m/z 342.2229 (342.2222 calcd for $C_{25}H_{28}N$, MH^+).

2-Benzyl-3-methyl-2-aza-spiro[4.4]nonane (S24): Obtained as brown oil (79% yield from NMR experiment) from reaction of **S12** and Rh catalyst. TLC (Hexanes/*i*-PrOH = 9:1): R_f = 0.43. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.36-7.22 (m, 5 H), 4.04 (d, *J* = 13.2 Hz, 1 H), 3.16 (d, *J* = 13.2 Hz, 1 H), 2.80 (d, *J* = 9.3 Hz, 1 H), 2.61-2.53 (m, 1 H), 2.09 (d, *J* = 9.3 Hz, 1 H), 1.88 (dd, *J* = 12.6 Hz, 1 H), 1.62-1.42 (m, 10 H), 1.17 (d, *J* = 6 Hz, 3 H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 140.1, 128.9, 128.2, 126.8, 66.9, 59.8, 58.3, 47.7, 47.2, 41.0, 39.8, 24.4, 24.3, 19.6. MS-ESI m/z 230.1900 (230.1909 calcd for $C_{16}H_{24}N$, MH^+).

2-Benzyl-3-methyl-2-aza-spiro[4.5]decane (S25): Obtained as brown oil (Quantitative yield from NMR experiment) from reaction of **S13** and Rh catalyst. TLC (Hexanes/*i*-PrOH = 9:1): R_f = 0.55. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.37-7.26 (m, 5 H), 4.05 (d, *J* = 13.0 Hz, 1 H), 3.12 (d, *J* = 13 Hz, 1 H), 2.81 (d, *J* = 9.3 Hz, 1 H), 2.55-2.48 (m, 1 H), 1.90 (d, *J* = 9.3 Hz, 1 H), 1.78 (dd, *J* = 12.5 Hz, 1 H), 1.44-1.29 (m, 10 H) 1.17 (d, *J* = 6.0 Hz, 3 H). ^{13}C{^{1}H} NMR (75

MHz, C_6D_6): δ = 140.1, 128.8, 128.2, 126.7, 66.8, 59.2, 58.1, 47.1, 39.5, 38.7, 26.2, 23.8, 23.7, 19.4. MS-ESI m/z 244.2061 (244.2065 calcd for $C_{17}H_{26}N$, MH^+).

X-Ray Structure Determination

An orange fragment of a prism (0.21 x 0.19 x 0.12 mm^3) was used for the single crystal x-ray diffraction study of $C_{40}H_{50}I_4Ir_2N_8$ (sample kh35r_0m). The crystal was coated with perfluoropolyethers (PFPE) oil and mounted on to a glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2 (version 1.0-22)[55] platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 5.0380 cm from the crystal.

A total of 1800 frames were collected for a hemisphere of reflections (with scan width of 0.3° in ω, starting 2θ and ω angles of –30°, and ϕ angles of 0°, 90°, and 180° for every 600 frames, 10 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package (version V7.06A)[56] and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 25150 reflections at a maximum 2θ angle of 61.02° (0.70 Å resolution), of which 6588 were independent reflections (R_{int} = 0.0341, R_{sig} = 0.0332, redundancy = 3.8, completeness = 99.5 %) and 5605 (85.1 %) reflections were greater than 2σ(I). The unit cell parameters were, **a** = 12.5312(6) Å, **b** = 14.8952(7) Å, **c** =

13.1069(6) Å, β = 117.558(1)°, V = 2168.90(18) Å^3, Z = 2, calculated density D_c = 2.350 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 9.015 mm^{-1}; max/min transmission = 0.4109/0.2497) to the raw intensity data using the SADABS program (version 2004/1).[57]

The Bruker SHELXTL software package (Version 6.14)[58] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.955) and systematic absent reflections indicated one possible space group, P2(1)/c. The space group P2(1)/c was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was half a molecule of $C_{40}H_{50}I_4Ir_2N_8$ present in the asymmetry unit of the unit cell. The molecule was located at the inversion center.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0242, wR2 = 0.0582, with intensity, I>2σ(I). The largest peak/hole in the final difference map was 1.358/-1.555 e/Å^3. (The

high electron density peak of 1.36 e/Å^3 near both the I and Ir atoms was probably due to Fourier truncation and absorption correction error).

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Chapter 4

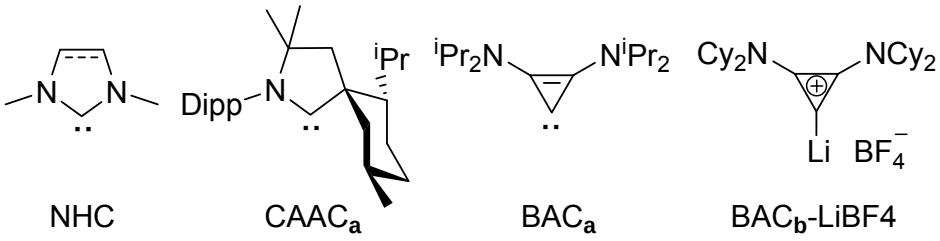
Reactivity of Cyclic (Alkyl)(amino)carbenes (CAACs) and Bis(amino)cyclopropenylidenes (BACs) with Heteroallenes: Comparisons with their N-heterocyclic Carbene (NHCs) Counterparts

Introduction

The reactivity of stable cyclic diamino carbenes, the so-called NHCs,[1-3] towards a variety of organic and organometallic substrates has been widely investigated.[4-10] In contrast, little is known about the reactivity of the more recently discovered stable cyclic (alkyl)(amino)carbenes (CAACs),[11-13] and bis(amino)cyclopropenylidenes (BACs)[14,15] (Figure 4.1). However, it is already clear that the chemical behavior of CAACs and BACs can be strikingly different from that of NHCs. For examples, CAACs react with CO,[16] H_2,[17] and NH_3,[17] to give the corresponding adducts, whereas NHCs are inert under the same experimental conditions.[18-20] CAACs induce the ring opening of white phosphorus giving P_4-species,[21] and BACs promote the degradation of P_4 into P_1 and P_3 fragments,[22] whereas NHCs induce the aggregation of elemental phosphorus affording novel phosphorus P_{12} clusters.[23]

NHCs are known to react with heteroallenes, such as carbon dioxide,[24-31] carbon disulfide,[24,31-42] carbodiimide,[43] etc.,[32,38,44-53] to afford betaines or

spirocyclic bis-adducts. An exhaustive review by DeLaude[54] was recently published highlighting this field. We show that the unique steric and electronic parameters of CAACs and BACs induce chemical reactions that can be distinct from those observed with NHCs.



NHC CAAC**a** BAC**a** BAC**b**-LiBF4

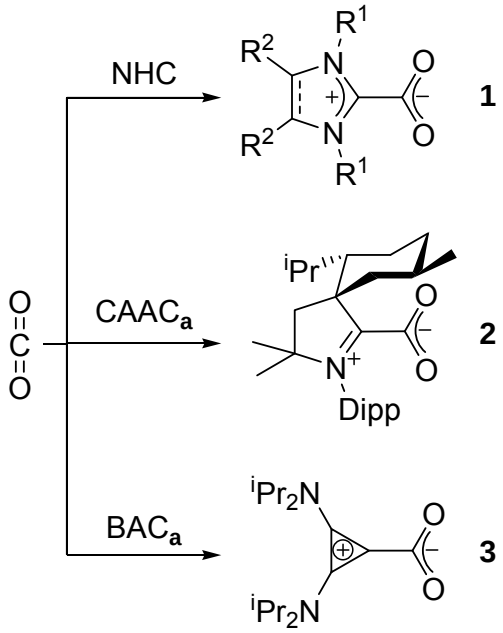
Figure 4.1. Representative stable carbenes (and lithium adduct) used in this study. Dipp = 2,6-*i*$Pr_2C_6H_3$.

Results and Discussion

The most studied heteroallene, with respect to reactivity towards NHCs, is carbon dioxide.[24-31] It has been shown that NHC betaines **1** are readily formed and are thermally stable (Scheme 4.1). Crabtree and others have shown that these betaines can serve as air- and moisture stable free carbene surrogates.[26,55-57] Of particular interest, NHC-CO_2 adducts have been used to transfer NHCs to a variety of transition metal fragments. More recently, these species have also been involved in catalytic systems, such as in the coupling reaction of carbon dioxide with epoxides[58] the carboxylative cyclization of propargyl alcohols,[59] and the conversion of carbon dioxide into methanol.[60]

We began our investigation by bubbling CO_2 gas through a room temperature THF solution of either free CAAC**a** or BAC**a**. In both cases, a

white precipitate immediately formed. The ^{13}C NMR spectrum of CAAC product **2** displayed resonances at 195 ppm and 160 ppm in the region expected for an iminium salt and a carboxylate carbon, respectively. Similarly, the BAC product **3** give signals at 157 ppm (carboxylate), and at 128 and 112 ppm, typical for a diamino cyclopropenium salt.[61] High resolution mass spectrometry (HRMS) was consistent with the monocarboxylated betaine structure of **3**; however, the CAAC adduct **2** gave a strong signal at m/z 382.3471 corresponding to decarboxylation/protonation under the MS conditions. Both **2** and **3** are not air-sensitive, and are thermally stable in the solid sate [m.p.: 123 °C, dec. (**2**); 143 °C, dec. (**3**)].

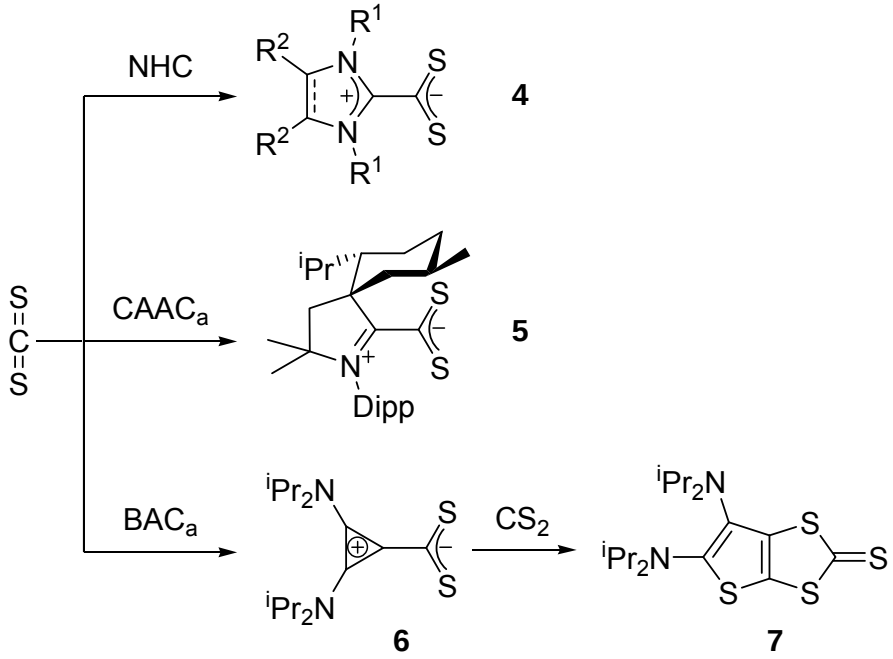


Scheme 4.1. Reaction of NHC, CAAC$_a$, and BAC$_a$ with carbon dioxide.

Recent literature has suggested the use of IR spectra of carbene-CO_2 betaines as a means to assess the relative σ-donor strength of carbenes.[31] Indeed, the values of the carboxylate asymmetric stretching frequency typically range from 1540 to 1640 cm^{-1}, a region not usually complicated by other signals. Moreover, the limited possible π back-donation from the CO_2 fragment to the carbene moiety should reveal purely the σ-donation effects of the carbene (which is not the case in the method using transition metal carbonyl fragments).[62-64] The FT-IR spectrum (KBr pellets) of the BAC adduct **3** showed a strong infrared absorption band at 1660 cm^{-1}, shifted to lower frequency relative to that of NHC analogs (1663-1684 cm^{-1}),[26] confirming the stronger σ-donating capability of BAC, predicted using the corresponding $LRh(CO)_2Cl$ complex.[65] Since CAAC ligands have also been predicted, using $LRh(CO)_2Cl$ complexes, to be stronger donors than NHC's,[66] it was surprising to observe the $\nu_{asym}(CO_2)$ for CAAC adduct **2** at 1676 cm^{-1}, a value nearly identical to that reported for the analogous IMes-CO_2 adduct (1675 cm^{-1}).[26] Clearly, this discrepancy indicates a limitation towards the use of IR spectroscopy in the ranking of ligand σ-donating ability.

We next turned our attention to carbon disulfide. Addition at room temperature of excess CS_2 to a toluene solution of $CAAC_{\mathbf{a}}$ resulted in the slow formation of an orange solution. Upon workup, the product was identified by ^1H and ^{13}C NMR, as well as HRMS, as the betaine **5**, which is analogous to the adduct **4** observed with NHCs[24,31-42] (Scheme 4.2).

However, in the reaction of excess CS_2 with BAC_a, a different type of product was formed. Indeed, the ^{13}C NMR spectrum showed five low-field signals for quaternary carbons, instead of three as expected for the symmetrical betaine **6**. The HRMS data indicated that the observed species **7** was composed of two equivalents of CS_2 for one equivalent of BAC_a. The exact structure of **7** was unambiguously established by a single crystal X-ray diffraction study.[67] It is a ring expanded, bicyclic thieno[2,3-diamino]-1,3-dithiole-2-thione (Figure 4.2). In the solid state, the two rings are coplanar, while the exocyclic amino groups are twisted out of plane, precluding any significant interaction of the N lone pairs with the ring π-system.



Scheme 4.2. Reaction of NHC, $CAAC_a$, and BAC_a with carbon disulfide.

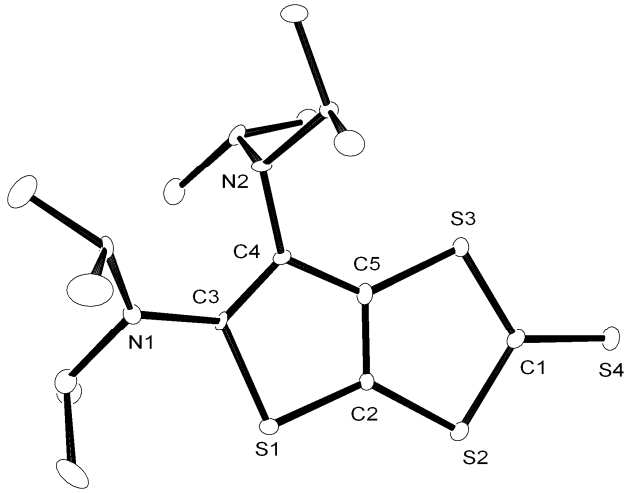
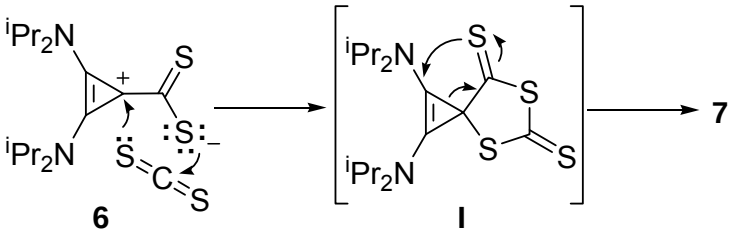


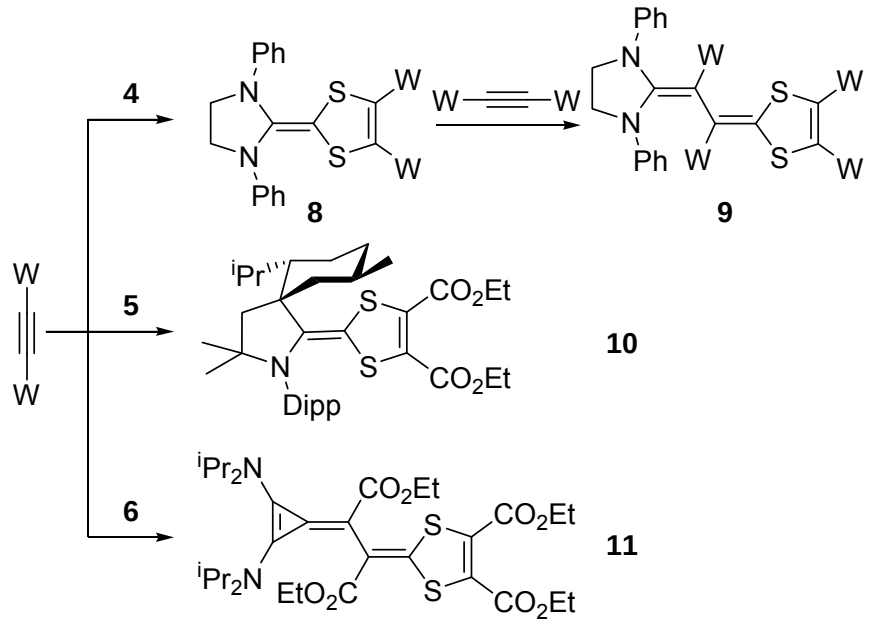
Figure 4.2. Molecular view of the solid state structure of **7** (hydrogen atoms omitted for clarity).

In order to obtain further insight into the mechanism of the reaction leading to **7**, one equivalent of CS_2 was added dropwise to a vigorously stirred, room temperature solution of BAC in THF. Under these experimental conditions, the betaine **6** was obtained and isolated in high yield. This species proved to be robust, with a decomposition point of 209-210 °C, and minimal decomposition even in refluxing toluene for 24 hours. Not surprisingly addition of one equivalent of CS_2 afforded heterocycle **7** in quantitative yield. Mechanistically, one can envision that betaine **6** can undergo either stepwise addition/cyclization or concerted [3+2]-cycloaddition with CS_2 to form the spirocyclic intermediate **I** (Scheme 4.3). It should be noted that related spirocyclic species have been isolated in the reaction of NHCs with iso(thio)cyanates.[32,33,37,38,41,44,45] Due to ring strain, ring expansion of the cyclopropene occurs yielding the final product **7**.



***Scheme 4.3*.** Possible mechanism for the formation of **7**.

Depending on the nature of NHCs, electron deficient alkynes react with NHC-betaines of type **4** to afford either electron-rich alkenes **8**, or butadienic species **9** (Scheme 4.4).[33] The reaction of CAAC betaine **5** with excess acetylene dicarboxylate yielded only the mixed-carbene dimer **10**. All attempts to liberate the corresponding carbenes from **10**, under thermolytic and photolytic conditions, failed. In the case of BAC-betaine **6**, reaction with acetylene dicarboxylate leads directly to the butadienic product **11** by incorporation of two acetylenes. X-Ray analysis of single crystals obtained from a benzene solution of **11** ascertained the structural assignment (Figure 4.3). It is interesting to note that, at least in the solid state, the double bond between the three-membered ring and the adjacent carbon is twisted by 31°, which indicate a strong polarization of the bond.



Scheme 4.4. Reactions of carbene-CS_2 betaines with electron deficient alkynes.

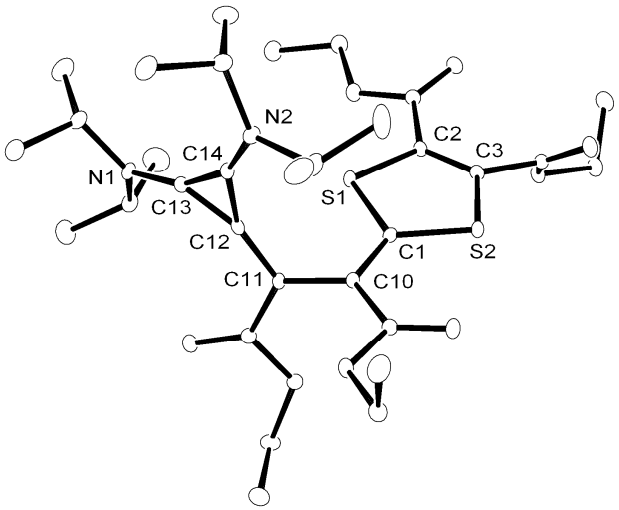
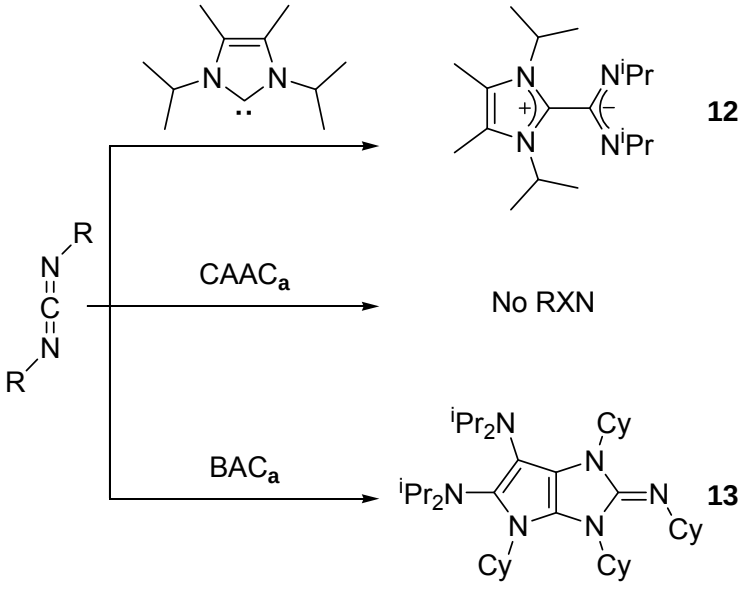


Figure 4.3. Molecular view of the solid state structure of **12** (hydrogen atoms omitted for clarity).

Although NHC reacts with N,N'-di*iso*propylcarbodiimide to form a stable amidinate **12**,[43] $CAAC_a$ does not react under similar experimental conditions (Scheme 4.5). In contrast, the addition of one equivalent N,N'-

dicyclohexylcarbodiimide to a THF solution of BAC_a resulted in the complete consumption of the carbodiimide, and the formation of a new compound **13**, along with 50% of BAC_a remaining. Addition to this solution of a second equivalent of carbodiimide, and stirring at RT overnight, resulted in the complete consumption of BAC_a and quantitative formation of **13**. HRMS confirmed the presence of two carbodiimide units with one BAC_a, and an X-ray diffraction study revealed the bicyclic structure of **13** (Figure 4.4), which is analogous to that observed with carbon disulfide. Interestingly, in contrast to **7,** the fused-ring system has a butterfly structure (folding angle: 17.6°). All attempts to characterize the mono-carbodiimide adduct of BAC_a, by monitoring the reaction by NMR spectroscopy at low temperatures failed. Thus, BAC_a is uniquely able to activate carbodimide and subsequently be incorporated into a heterocyclic framework.



Scheme 4.5. Reaction of NHC, $CAAC_a$, and BAC_a with carbodiimides.

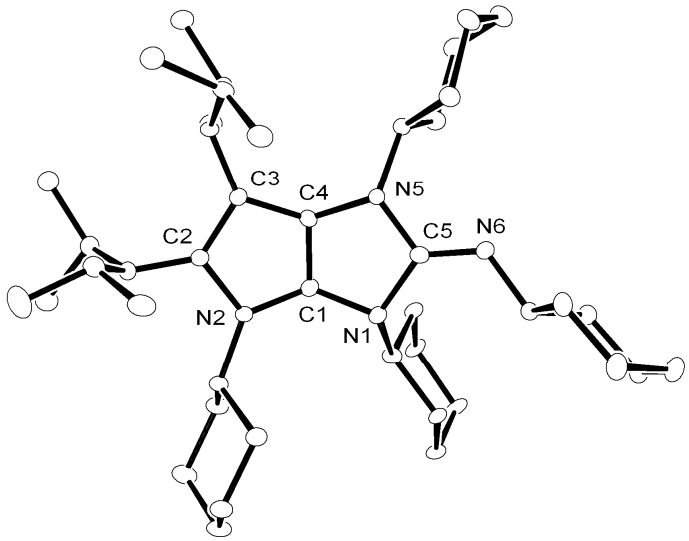
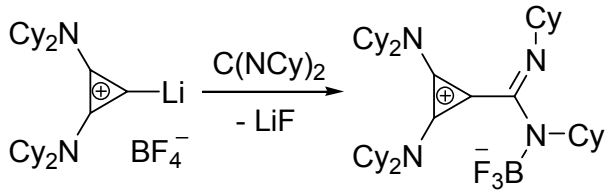


Figure 4.4. Molecular view of the solid state structure of **13** (hydrogen atoms omitted for clarity).

In order to tame the nucleophilicity of the postulated amidinate inner salt intermediate, we next tested the reaction of a carbodiimide with the BAC_b-Li salt, reasoning that the presence of the Li cation should limit this reaction to mono-addition. Addition of N,N'-dicyclohexylcarbodiimide to a room temperature suspension of bis(dicyclohexylamino)(lithio)cyclopropenium tetrafluoroborate in THF, resulted in the clean formation of a new product **14** as revealed by ^{13}C NMR, with chemical shifts for the ring carbons at 134 and 103 ppm, indicative of a betaine product (Scheme 4.6). Single crystals were obtained by slow evaporation of a THF solution, and analyzed by X-ray diffraction (Figure 4.4). Product **14** appeared to be the BF_3 adduct of the expected betaine, the process being accompanied by extrusion of LiF. The overall structural features are consistent with other known cyclopropenium

salts with the exception of a possible fluorophilic interaction between C2 of the propenium ring and a fluorine from BF_3 measured at 2.612Å.



BAC_b-$LiBF_4$ **14**

Scheme 4.6. Reactions of BAC_b-$LiBF_4$ adduct with N,N'-dicyclohexyl carbodiimide.

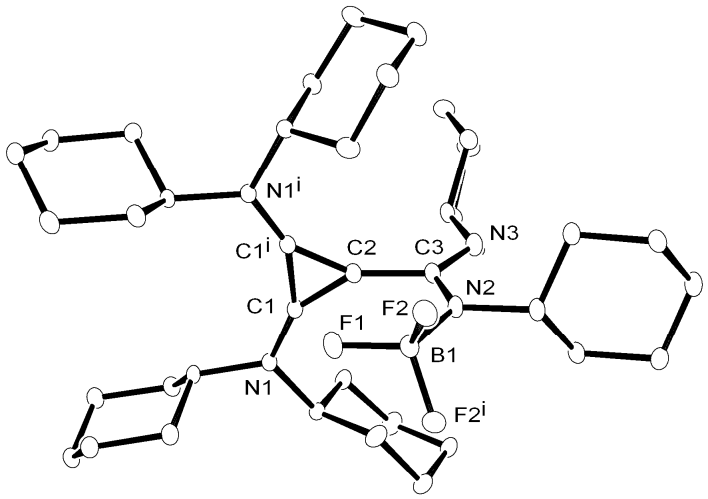


Figure 4.5. Molecular view of the solid state structure of **14** (hydrogen atoms omitted for clarity).

Conclusion

Based on these results, it is apparent that stable CAACs, BACs, and BAC-Li salts react as strong nucleophiles in the activation of heteroallenes. Based on the asymmetric C-O stretching frequency of the BAC-CO_2 adduct **3**, BAC_a appears to provide greater donation to activated substrates relative to their N-heterocyclic carbene counterparts. However, the result observed for CAAC-CO_2 adduct **2** calls into question the generality of this type of analysis. Like NHCs, both CAACs and BACs form stable mono-adduct betaines with both carbon dioxide and carbon disulfide. However, due to increased ring strain, and lack of heteroatoms bearing lone pairs adjacent to the carbene center, BAC adducts display an increased electrophilicity. Reaction of these species with an excess of either CS_2 or carbodiimide leads to the formation of electron rich, fused ring heterocycles, likely via a spirocyclic intermediate. The use of a BAC-$LiBF_4$ adduct hinders formation of this spirocyclic species by trapping of the intermediate amidinate by BF_3. The spiro to ring expansion sequence using various partners should lead to a more generalized synthetic methodology towards a wide range of electron rich, fused ring systems.

Experimental Section

All manipulations were performed in an inert atmosphere of dry argon using standard Schlenk techniques or in an mBraun glovebox. Dry, oxygen-free solvents were employed. NMR spectra were recorded on a Bruker Avance 300, or Varian Inova 400 and 500 spectrometers. ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ or referenced to residual solvent peaks. ^{19}F NMR chemical shifts are reported relative to $CFCl_3$. FTIR spectra were recorded on a Bruker Equinox 55 spectrometer from KBr pellets.

2: Carbon dioxide was bubbled through a room temperature, stirred solution of $CAAC_{\mathbf{a}}$ (300 mg, 0.788 mmol) in THF (10 mL) for 30 min. affording an off-white precipitate. Volatiles were removed under vacuum and the residue washed with hexanes to afford a white powder. Yield: 322 mg (96 %). m.p. 143 °C, dec; ^{1}H NMR (300 MHz, CD_3CN/THF, 25 °C) δ = 7.48-7.33 (m, 3 H), 2.87-2.77 (m, 2 H), 2.61-2.51 (broad, overlapping m, 3 H), 2.14-2.05 (broad, overlapping m, 2 H), 1.51-0.88 (overlapping m, 33 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3CN/THF, 25 °C) δ = 194.8, 160.5, 147.6, 147.4, 131.5, 130.9, 127.0, 126.5, 78.0, 58.8, 53.8, 53.7, 50.6, 35.7, 31.1, 30.8, 30.7, 29.6, 29.4, 28.7, 27.3, 27.0, 26.9, 25.4, 24.9, 24.3, 23.0, 19.2; IR (KBr, v cm^{-1}): 3453, 2956, 2953, 2947, 1676 (CO_2), 1567, 1473, 1343, 1147, 1053, 810, 747; ESI-MS m/z 382.3471 (382.3468 calcd for $C_{27}H_{44}N$, MH^+ - CO_2).

3: At room temperature, carbon dioxide was bubbled through a vigorously stirred solution of $BAC_{\mathbf{a}}$ (501 mg, 2.12 mmol) in THF (20 mL) for 1 hour.

Solvent was removed under vacuum, and the resulting white precipitate washed with 10 mL hexanes to afford **6** as a white powder. Yield: 576 mg (97%). mp 123 °C, dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.81 (overlapping m, 4 H), 1.40 (d, *J* = 6.8 Hz, 12 H), 1.26 (d, *J* = 6.8 Hz, 12 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ = 157.2, 128.3, 112.2, 55.3, 49.6, 21.3, 21.2; IR (KBr, v cm^{-1}): 2982, 2935, 2880, 1898, 1660 (CO_2), 1540, 1468, 1387, 1371, 1333, 1292, 1217, 1161, 1053, 1019, 893, 802; ESI MS m/z 281.2230 (281.2224 calcd for $C_{16}H_{29}N_2O_2$, MH^+).

5: Carbon disulfide (48 µL, 0.798 mmol) was added to a room temperature solution of $CAAC_{\mathbf{a}}$ (300 mg, 0.788 mmol) in THF (10 mL) and stirred overnight affording an orange solution. Volatiles were removed under vacuum, and the residue washed with hexanes to give an orange powder. Yield: 331 mg (92 %). m.p. 219 °C, dec; ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ = 7.02-6.94 (m, 3 H), 3.21 (m, 1 H), 2.99 (broad, overlapping m, 2 H), 2.76 (broad s, 1 H), 2.53 (broad d, 2 H), 2.01 (broad m, 2 H), 1.68-0.86 (broad, overlapping m, 32 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6, 25 °C) δ = 229.7, 187.2, 147.6, 147.5, 131.0, 130.7, 126.9, 126.5, 74.9, 59.6, 55.3, 54.8, 51.8, 35.2, 31.1, 30.7, 30.4, 29.6, 29.3, 29.2, 28.8, 28.7, 28.6, 26.6, 26.1, 25.5, 22.9, 22.3; ESI-MS m/z 458.2913 (458.2921 calcd for $C_{28}H_{44}NS_2$, M^+).

6. Carbon disulfide (55 µL, 0.910 mmol) was added dropwise to a stirred room temperature solution of $BAC_{\mathbf{a}}$ (214 mg, 0.905 mmol) in hexanes (10 mL) forming an immediate deep red precipitate. After one hour, volatiles were removed under vacuum, and the product washed with hexanes yielding a pink

powder. Yield: 230 mg (81 %). Deep red, blocky crystals of **3** formed readily from a hexanes/THF solution at -20 °C overnight. m.p. 209-210 °C, dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.87-3.78 (overlapping m, 2 H), 1.44 (d, *J* = 6 Hz, 6 H), 1.33 (d, *J* = 6 Hz, 6 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ = 231.6, 122.9, 120.8, 55.6, 49.1, 22.5, 21.3; ESI MS m/z 313.1781 found (313.1772 calcd for $C_{16}H_{29}N_2S_2$, MH^+).

7. An excess of carbon disulfide (95 µL, 1.572 mmol) was added to a room temperature solution of $BAC_{\mathbf{a}}$ (119 mg, 0.503 mmol) in THF (5 mL), rapidly yielding a bright yellow solution. Volatiles were removed under vacuum to afford an orange powder. Yield: 188 mg (96 %); m.p. 97-99 °C; Single crystals of **7** were obtained from a diethyl ether solution at -20 °C. ^{1}H NMR (500 MHz, C_6D_6) δ = 3.55 (sept, *J* = 7 Hz, 2 H), 3.16 (sept, *J* = 6 Hz, 2 H), 1.04 (d, *J* = 7 Hz, 12 H), 0.92 (d, *J* = 6 Hz, 12 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) δ = 214.0, 153.0, 138.2, 133.1, 121.8, 51.2, 51.1, 22.7, 22.1; ESI-MS m/z 389.1219 (389.1208 calcd for $C_{17}H_{29}N_2S_4$, MH^+).

10: Diethylacetylene dicarboxylate (75 µL, 0.469 mmol) was added dropwise to a stirred solution of **5** (210 mg, 0.459 mmol) in toluene resulting in an immediate darkening of the red solution. Volatiles were removed under vacuum to obtain **10** as a purple powder. ^{1}H NMR (300 MHz, C_6D_6) δ = 7.15-7.01 (overlapping m, 3 H), 3.90 (q, *J* = 7 Hz, 2 H), 3.73 (dq, *J* = 1, 7 Hz, 2 H), 3.63 (m, 1 H), 3.07-2.84 (overlapping m, 3 H), 2.79 (d, *J* = 13 Hz, 1 H), 2.22 (m, 1 H), 2.00 (m, 1 H), 1.89 (d, *J* = 13 Hz, 1 H), 1.80-1.68 (overlapping m, 3 H), 1.63 (d, *J* = 7 Hz, 3 H), 1.56 (d, *J* = 7 Hz, 3 H), 1.46-1.40 (m, 1 H), 1.36 (s,

3 H), 1.31 (d, *J* = 7 Hz, 3 H), 1.25 (d, *J* = 7 Hz, 3 H), 1.18 (d, *J* = 7 Hz, 6 H), 0.97-0.83 (overlapping m, 12 H), 0.76 (t, *J* = 7 Hz, 3 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ = 161.2, 161.1, 151.1, 149.5, 149.4, 137.9, 135.5, 130.8, 129.1, 125.3, 125.2, 88.7, 64.3, 62.0, 61.8, 60.0, 53.1, 50.2, 46.2, 31.7, 30.2, 29.6, 29.5, 29.0, 28.5, 26.4, 26.3, 25.9, 25.5, 24.2, 23.0, 22.6, 22.3, 14.2, 14.1; ESI-MS m/z 628.3466 (628.3489 calcd for $C_{36}H_{54}NO_4S_2$, MH^+).

11: Diethylacetylene dicarboxylate (173 µL, 1.08 mmol) was added dropwise to a stirred solution of **6** (331 mg, 1.06 mmol) in THF (10 mL) resulting in an immediate darkening of the red solution. The solution was stirred at room temperature overnight and volatiles removed under vacuum to afford a deep red powder. After washing with hexanes (20 mL) a purple powder was obtained. Yield: 313 mg (48 %); Single crystals of **11** were obtained from a hexanes solution at -20 °C. m.p. 112-114 °C; ^{1}H NMR (300 MHz, C_6D_6) δ = 4.36-3.54 (overlapping m, 12 H), 1.44-0.81 (overlapping m, 36 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ = 168.4, 168.2, 160.8, 160.5, 155.2, 136.7, 131.1, 122.0, 121.7, 116.5, 68.2, 62.5, 60.6, 58.6, 51.2, 26.2, 23.1, 22.5, 15.9, 15.1, 14.1, 14.0; ESI-MS m/z 653.2826 (653.2925 calcd for $C_{32}H_{49}N_2O_8S_2$, MH^+).

13: A room temperature solution of N,N'-dicyclohexylcarbodiimide (200 mg, 0.969 mmol) in THF (1 ml) was slowly added to a stirred solution of BAC_a (115 mg, 0.486 mmol) in THF (1 ml) after which the solution became bright yellow. After stirring at room temperature overnight, solvent was removed under vacuum to afford a sticky orange powder. Slow evaporation of a benzene solution of the product affords yellow crystals of **13**. Yield: 293 mg

(93 %). m.p. 143-147 °C; ^{1}H NMR (300 MHz, C_6D_6) δ = 3.74-3.13 (broad overlapping m, 8 H), 2.19-1.11 (broad overlapping m, 64 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ = 155.5, 136.4, 122.6, 119.8, 115.6, 58.4, 57.3, 55.5, 54.4, 51.7, 36.5, 32.6, 31.2, 29.4, 27.1, 27.0, 26.7, 26.6, 26.0, 25.7, 25.2, 24.4, 23.3; ESI-MS m/z 649.5895 (649.5891 calcd for $C_{41}H_{73}N_6$, MH^+).

Synthesis of **BAC_b-$LiBF_4$**. Procedure adapted from Lavallo, et al.[68] **BAC_bClBF_4**: Dicyclohexylamine (22 mL, 0.133 mol) was added dropwise at 0 °C to a stirred solution of tetrachlorocyclopropene (2.7 mL, 0.0215 mol) in CH_2Cl_2 (300 mL). After warm up to room temperature and stirring for six hours. a pale yellow suspension was formed. $NaBF_4$ (2.36 g, 0.0215 mmol) was added and the suspension stirred vigorously for 16 hours. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) δ = 3.55 (pseudo t, *J* = 11.8 Hz, 2 H) 3.33 (pseudo t, *J* = 11.7 Hz, 2 H), 2.00-1.11 (broad overlapping m, 40 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C, $CDCl_3$) δ = 132.4, 93.6, 65.8, 56.9, 32.7, 30.8, 25.7, 25.5, 24.9, 24.7. **BAC_b-HBF_4**: Triphenylphosphine (5.64 g, 0.021 mol) was added, followed immediately by deionized water (250 mL), and the suspension was stirred at room temperature for 10 hours with a vent to open air. The aqueous layer was decanted and the resulting suspension washed with deionized water (4 x 250 mL) to afford a yellow solution which was dried over $MgSO_4$. Volatiles were removed under vacuum at 50 °C for 6 hours to afford a yellow, sticky solid. **BAC_b-HBF_4** was purified by two recrystallizations from refluxing THF. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$) δ = 7.49 (s, 1 H), 3.53-3.45 (m, 2 H), 3.35-3.31 (m, 2 H), 1.92-1.21 (overlapping m, 40 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, 25 °C,

$CDCl_3$) δ = 134.3, 100.3, 64.9, 58.1, 31.2, 30.8, 25.6, 25.5, 24.7, 24.6. **BAC_b-$LiBF_4$**: To suspension of CyBAC-HBF_4 (2.0 g, 4.128 mmol) in Et_2O (30 mL) at -78 °C, a 2.5M solution of *n*BuLi in hexanes (1.65 mL, 4.128 mmol) was added. The suspension was stirred for one hour, and allowed to warm to room temperature for an additional one hour. Volatiles were removed under vacuum and the resulting sticky, yellow solid washed with hexanes to afford an off-white powder. Yield 1.34 g (66%), ^{1}H NMR (300 MHz, 25 °C, C_6D_6) δ = 3.43 (broad s, 2 H), 2.54 (broad s, 4 H), 2.15-0.88 (broad, overlapping m, 40 H); $^{13}C\{^1H\}$ NMR (75 MHz, 25 °C, THF) δ = 167.3, 155.5, 61.1, 58.1, 32.3, 26.6, 25.7.

14: A room temperature solution of N,N'-dicyclohexylcarbodiimide (52 mg, 0.252 mmol) in THF (1 mL) was slowly added to a stirred suspension of BAC_b-$LiBF_4$ (124 mg, 0.253 mmol) in THF (1 mL). After stirring for 10 hrs, a pale yellow solution with a white precipitate was formed. After filtration, volatiles were removed under vacuum to afford an off-white powder. Yield 137 mg (81 %). m.p. 185-187 °C, dec; Single crystals of **14** formed readily by slow evaporation of a THF solution. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ = 3.67 (broad s, 4 H), 3.55 (broad m, 1 H), 3.22 (broad m, 1 H), 1.86-1.19 (broad, overlapping m, 60 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ = 141.5, 134.3, 103.4, 64.8, 61.3, 57.9, 49.1, 35.8, 34.9, 32.0, 31.7, 31.5, 31.3, 30.2, 25.7, 25.6, 24.9, 24.7; $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, 25 °C) δ = 152.9; ESI-MS m/z 603.5363 (603.5371 calcd for $C_{40}H_{67}N_4$, $[M\text{-}BF_3]^+$).

Crystal structure determination of complexes 7, **11**, **13**, **and 14**. The Bruker X8-APEX X-ray diffraction instrument with Mo-radiation was used for data collection.[69] All data frames were collected at low temperatures (T = 100 K) using an ω, φ-scan mode (0.5° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package.[70] The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program.[71] The SIR97 was used for direct methods of phase determination, and Bruker SHELXTL software package for structure refinement and difference Fourier maps.[72] Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of compounds were refined by means of a full matrix least-squares procedure on F^2. All H-atoms were included in the refinement in calculated positions riding on the C atoms.

Crystal and structure parameters of 7: size 0.32 x 0.17 x 0.10 mm^3, Monoclinic, space group C2/c, a = 16.716(2) Å, b = 20.872(3) Å, c = 8.6398(10) Å, $\alpha = \gamma = 90.0°$, $\beta = 108.930(2)°$, V = 2851.4(6) $Å^3$, ρ_{calcd} = 1.283 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 10275, independent reflections = 2907 (R_{int} = 0.0285), absorption coefficient μ = 0.224 mm^{-1}; max/min transmission = 0.9779 and 0.9317, 177 parameters were refined and converged at R1 = 0.0478, wR2 = 0.1335, with intensity $I>2\sigma(I)$.

Crystal and structure parameters of 11: size 0.36 x 0.26 x 0.13 mm^3, Orthorhombic, space group P2(1)2(1)2(1), a = 10.6247(13) Å, b =

12.8788(15) Å, c = 14.6789(17) Å, $\alpha = \beta = \gamma = 90.0°$, V = 2008.6(4) $Å^3$, ρ_{calcd} = 1.285 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 14242, independent reflections = 1405 (R_{int} = 0.0171), absorption coefficient μ = 0.474 mm^{-1}; max/min transmission = 0.9566 and 0.8861, 216 parameters were refined and converged at R1 = 0.0221, wR2 = 0.0571, with intensity $I>2\sigma(I)$.

Crystal and structure parameters of 13: size 0.32 x 0.19 x 0.10 mm^3, Orthorhombic, space group P2(1)2(1)2(1), a = 13.1055(9) Å, b = 16.3119(11) Å, c = 18.1862(12) Å, $\alpha = \beta = \gamma = 90.0°$, V = 3887.8(5) $Å^3$, ρ_{calcd} = 1.109 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 48633, independent reflections = 9976 (R_{int} = 0.0539), absorption coefficient μ = 0.065 mm^{-1}; max/min transmission = 0.9935 and 0.9794, 487 parameters were refined and converged at R1 = 0.0436, wR2 = 0.0829, with intensity $I>2\sigma(I)$.

Crystal and structure parameters of 14: size 0.28 x 0.16 x 0.12 mm^3, Monoclinic, space group P2(1)/m, a = 11.7142(18) Å, b = 13.427(2) Å, c = 13.275(2) Å, $\alpha = \gamma = 90.0°$, β = 100.169(2)°, V = 2055.1(5) $Å^3$, ρ_{calcd} = 1.084 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 16422, independent reflections = 5258 (R_{int} = 0.0367), absorption coefficient μ = 0.072 mm^{-1}; max/min transmission = 0.9914 and 0.9801, 233 parameters were refined and converged at R1 = 0.0491, wR2 = 0.1255, with intensity $I>2\sigma(I)$.

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Chapter 5

Nonmetal Mediated Fragmentation of P_4. Isolation of P_1 and P_2 (Bis)carbene Adducts

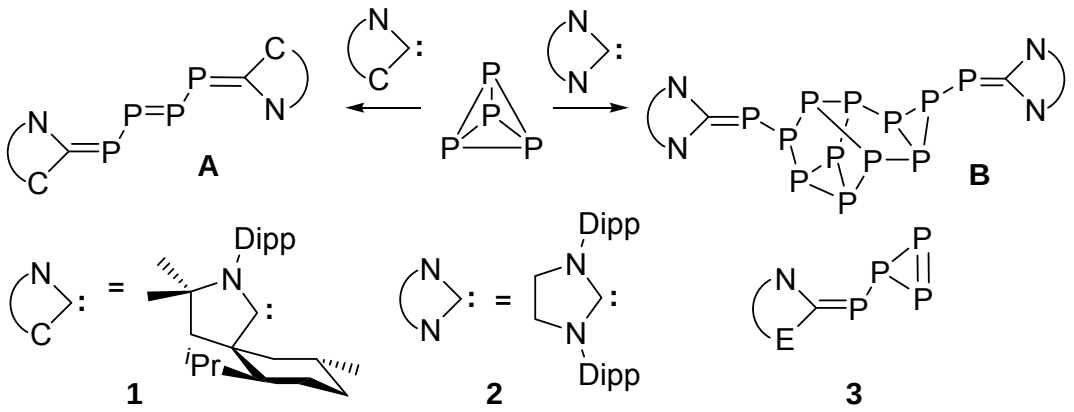
Introduction

Transition metals are well known for activating small molecules and for stabilizing highly reactive species. A recent trend is to use non-metals,[1-14] and especially stable singlet carbenes, to accomplish one or the other of these tasks. For example, Robinson *et al.* have reported that N-heterocyclic carbenes (NHCs) give rise to stable adducts with HBBH[15,16] and Si_2,[17,18] two fragments that are otherwise not isolable.[19-21] We have shown that cyclic (alkyl)(amino)carbenes (CAACs) can activate CO,[22] H_2,[23] and even NH_3,[23] the last of these being a difficult task even for transition metal centers.[24-28]

White phosphorus (P_4) is a small molecule that is of industrial interest, because this is the classical starting material for the large scale preparation of organophosphorus derivatives.[29,30] The reactivity of P_4 with either main group compounds[31-35] or transition metals has been widely studied,[36-44] and therefore it is an excellent model to test further if carbenes can achieve tasks that transition metals do. Our group has already shown that the bulky rigid CAAC **1** opens P_4, and at the same time stabilizes the resulting otherwise highly reactive acyclic P_4 species (**A**, Scheme 5.1).[45] Moreover, when a bulky

NHC **2** was used, the NHC stabilized P_{12} cluster **B** was isolated in high yield.[46] Therefore, similar to transition metals, singlet carbenes can activate, induce the aggregation of white phosphorus, and stabilize the resulting species.[47] However, the most synthetically useful organophosphorus derivatives contain only one or two phosphorus atoms, and therefore it is of primary importance to induce the fragmentation of P_4. Transition metals are able to do so,[36-40] and the Cummins group has even shown that the resulting P_1- and P_2-nobium complexes, can be used as phosphorus transfer agents.[48-52] Here we report, that just like transition metals, carbenes can induce the fragmentation of white phosphorus. Depending on the nature of the activator, carbene stabilized P_2 and P_1 species can be isolated.

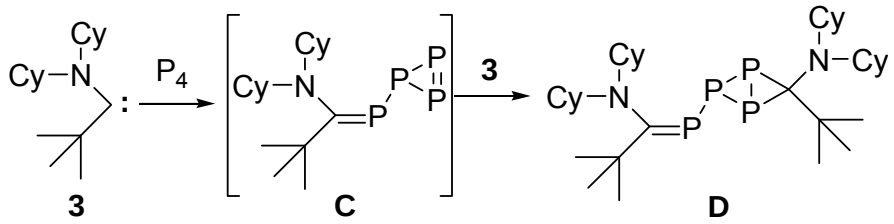
Our preliminary mechanistic studies of the reaction leading to **A** and **B**, and in particular trapping experiments, showed that, with both carbenes **1** and **2**, an unstable mono-carbene adduct of type **3** is first formed; then a second molecule of carbene induces a ring opening and the formation of bis-carbene adducts of type **A**.[45,46] The different outcome of reactions shown in Scheme 1 can be rationalized by the different electronic properties of CAACs versus NHCs. CAACs are more electrophilic (π-acceptor) and strengthen the PC bonds of **A**,[22,23] and concurrently NHCs are less basic and therefore better leaving groups, favoring the formation of clusters such as **B**. This analysis indicates that strongly basic, but electrophilic carbenes should be the best candidates to induce the fragmentation of white phosphorus, as long as they are small enough to attack further the P_4 fragments of adducts of type **A** or **C**.



Scheme 5.1. Activation and aggregation of white phosphorus with singlet carbenes. Dipp = 2,6-$^{i}Pr_2C_6H_3$.

Results and Discussion

According to our previous investigations, the acyclic (alkyl)(amino)carbene **3**[53] (Scheme 5.2) is one the most electrophilic stable carbenes known. Excess of carbene **3** (3.5 equivs.) was added to an ether suspension of white phosphorus. After two hours at room temperature, and subsequent workup, bis-carbene P_4 adduct **D** was isolated as light yellow crystals in 66% yield (based on P_4). The presence of two signals at very high field (-168.2 ppm, dd, J_{PP} = 167 and 87 Hz; -105.8 ppm, dt, J_{PP} = 220 and 167 Hz) and a signal at low field (+238.7 ppm, dt, J_{PP} = 220 and 87 Hz) suggested the presence of a triphosphosphorus three-membered ring substituted by a low coordinate phosphorus center.



Scheme 5.2. Reaction of white phosphorus with acyclic (alkyl)(amino) carbene **3**.

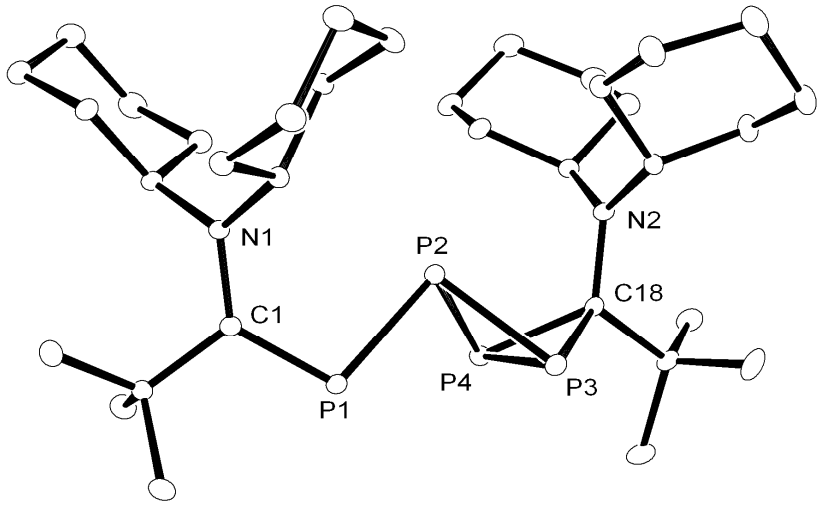
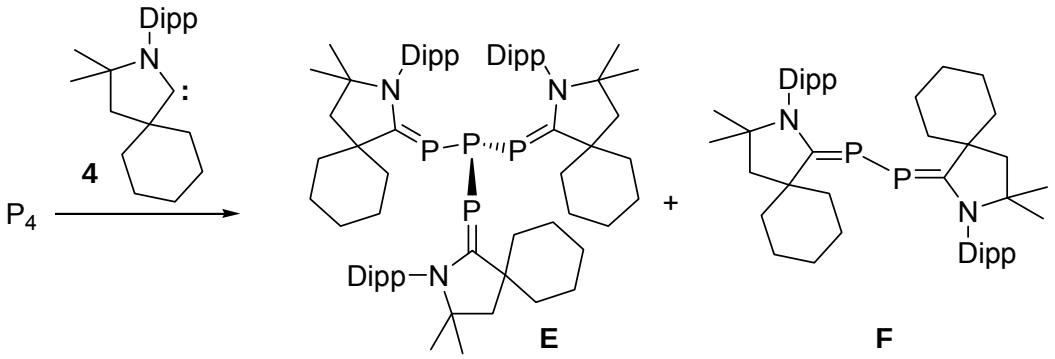


Figure 5.1. Molecular view of **D** in the solid state (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): P(1)-P(2) 2.2320(19), P(2)-P(3) 2.220(2), P(2)-P(4) 2.2342(17), P(3)-P(4) 2.1700(19), C(1)-P(1) 1.747(2), C(18)-P(3) 1.912(2), C(18)-P(4) 1.925(2), N(1)-C(1) 1.3893(19), N(2)-C(18) 1.4472(18); P(1)-P(2)-P(3) 93.29(3), P(1)-P(2)-P(4) 91.99(6), P(3)-P(2)-P(4) 58.31(7), P(2)-P(4)-P(3) 60.51(5), P(3)-P(4)-P(2) 60.51(5).

The structure of bis-carbene P_4 adduct **D** was unambiguously assigned by a single crystal X-ray diffraction study[54] (Fig. 5.1). This bicyclic compound clearly results from the cycloaddition of carbene **3** on the primary formed adduct of type **C**.

This result indicates that the acyclic (alkyl)(amino)carbene **3** is nucleophilic enough to open the P_4 tetrahedron, but so electrophilic that it undergoes a "cyclopropanation" reaction, rather than inducing a ring-opening of the primary formed adduct **C**. Therefore, we decided to choose the cyclohexyl CAAC **4**,[55,56] in the hope that such a small CAAC would be able to induce the formation of an adduct of type **A**, but then to react again and induce the fragmentation of the P_4 chain. Indeed, upon addition of three equivalents of CAAC **4** to an ether suspension of P_4, and subsequent work up, two new products were isolated in moderate yields (**E**, 67% and **F**, 12%, based on P_4) (Scheme 5.3).



Scheme 5.3. Reaction of white phosphorus with the non-hindered CAAC **4**.

The ^{31}P NMR spectrum of the major product **E** shows a doublet at +68.1 ppm and a quartet at -66.2 ppm, with a large PP coupling constant (227 Hz). These data indicated the presence of three magnetically equivalent P nuclei, directly connected to another phosphorus center. This hypothesis was confirmed by a single crystal X-ray diffraction study (Fig. 5.2). Very

surprisingly, the formation of tris-carbene P_4-adduct **E** implies that two CAACs **4** react on the primary formed adduct of type **C**.

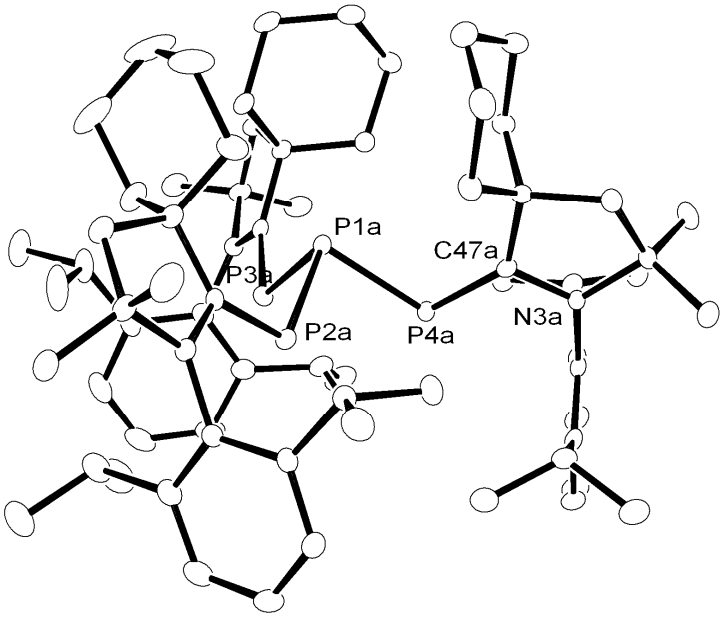


Figure 5.2. Molecular view of **E** in the solid state (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): P(1a)-P(2a) 2.2168(6), P(1a)-P(3a) 2.2270(6), P(1a)-P(4a) 2.2192(7), C(1a)-P(2a) 1.7328(19), C(24a)-P(3a) 1.7343(18), C(47a)-P(4a) 1.7324(18), N(1a)-C(1a) 1.374(2), N(2a)-C(24a) 1.370(2), N(3a)-C(47a) 1.368(2); P(2a)-P(1a)-P(4a) 90.15(2), P(3a)-P(1a)-P(4a) 90.15(2), P(2a)-P(1a)-P(4a) 90.15(2).

The minor product **F** was determined to be a bis-carbene P_2 adduct, and therefore the reaction leading to **F** represents the first example of fragmentation of P_4 with a neutral organic nucleophile. Interestingly, compound **F** is reminiscent of compounds **F'** and **F"**, prepared as shown in Scheme 5.4,[57,58] and described as 2,3-diphosphabutadiene and NHC stabilized bis-phosphinidene, respectively. The ^{31}P NMR chemical shift for **F**

(+59.4 ppm) is comparable to that of **F'** (54.2 ppm), and shifted at lower field compared to **F"** (-52.4 ppm); similarly the PC bond length (Figure 5.3) in **F** [1.719(7) Å] is shorter than in **F"** (1.750(2) Å). Both of these data are in favor of a 2,3-diphosphabutadiene structure for **F**, as expected due to the higher electrophilicity of CAACs versus NHCs.

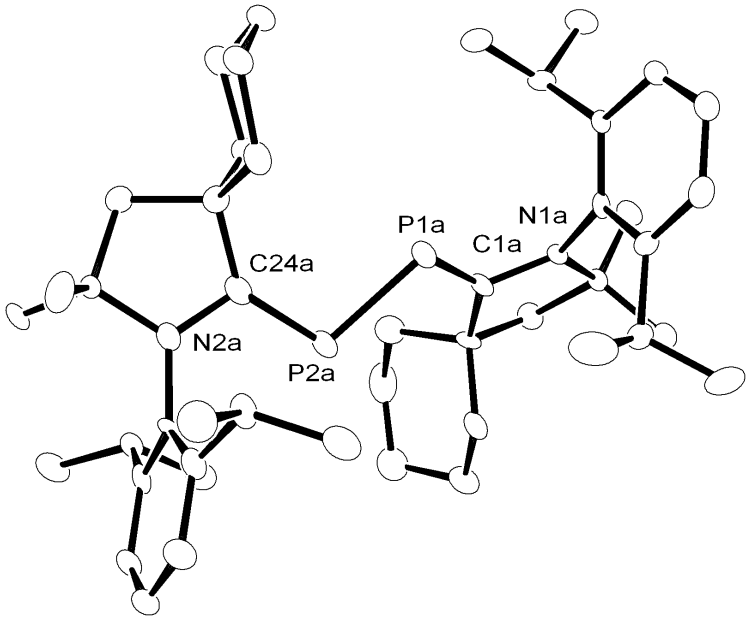
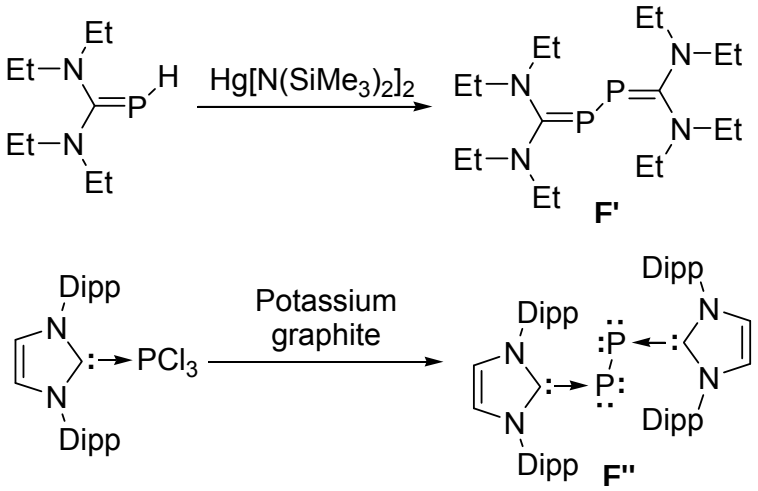
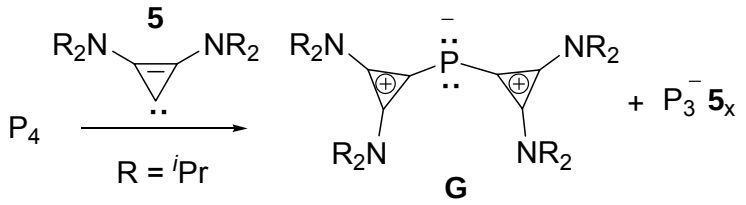


Figure 5.3. Molecular view of **F** in the solid state (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Selected bond distances (Å) and angles (deg): P(1a)-P(2a) 2.184(3), C(1a)-P(1a) 1.719(7), N(1a)-C(1a) 1.387(9); C(1a)-P(1a)-P(2a) 105.1(2); C(1a)-P(1a)-P(2a)-C(24a) 149.22.



Scheme 5.4. Reported syntheses[57,58] and electronic structure of compounds related to **F**.

Compound **F** most probably results from the attack of the carbene to the β-phosphorus centers of a bis-carbene adduct of type **A**. In order to obtain a P_1 adduct, by attack of a phosphorus center in a position α to the carbene(s) of adducts **A** or **C**, we chose the least sterically demanding stable carbene known so far, namely the bis(diisopropylamino)cyclopropenylidene **5**.[59] After 12 hours at room temperature, using three equivalents of carbene **5**, the ^{31}P NMR spectrum revealed an ABX system (δ_A = 242.8, δ_B = 237.0, δ_X = 157.1 ppm, J_{AX} = -484.7 Hz, J_{AB} = 38.8 Hz, J_{BX} = -481.7 Hz)(Figure 6.8) along with an AB system (pair of doublets δ_A = 149.5, δ_B = 122.6, J_{AB} = -432.0 Hz), and a singlet at -93.2 ppm. All attempts to purify the mixture led to the disappearance of the higher order systems, but in the presence of chloroform or any salts ($NaBF_4$, KPF_6, etc.), the singlet at high field remained unchanged.



Scheme 5.5. Reaction of P_4 with the cyclopropenylidene **5**.

When chloroform was used, single crystals suitable for an X-Ray diffraction study readily formed upon standing at room temperature. The isolated product is the bis-carbene P_1-cation **G** with Cl^- as counterion (74% yield based on P_4) (Scheme 5.5, Figure 5.4).

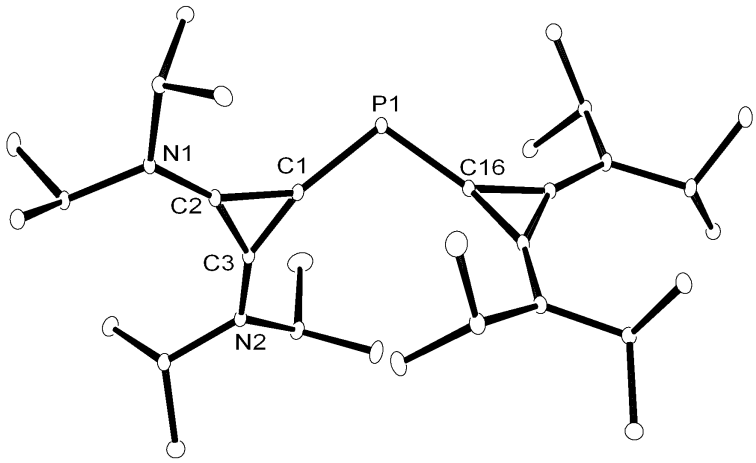


Figure 5.4. Molecular view of **G**, Cl^- in the solid state. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-C(1) 1.787(2), P(1)-C(16) 1.788(2), N(1)-C(2) 1.323(3), N(2)-C(3) 1.328(3), C(1) C(3) 1.397(3), C(1)-C(2) 1.404(3), C(2)-C(3) 1.388(3); C(1)-P(1)-C(16) 104.68(9).

The two C-P bond lengths are equivalent within the error limits at 1.781Å which indicates delocalization of the positive charge and a bond order intermediate between a single and a double bond while the CPC bond angle lies at 104.8°. Note that analogous $(NHC)_2P^+$ systems have previously been

reported by Schmidpeter,[60] and Macdonald,[61] but using $(R_3P)_2P^+$, $(RNPCl)_2$, or PCl_3 as P_I source. Figure 5.5 (top) shows some possible Lewis structures for cation **G**. The form **Ga** is isovalent with allenes and contains a formal P^V phosphorus cation flanked by mutually perpendicular cyclopropenyl units. In **Gb** the phosphorus center is formally P^{III} with the positive charge delocalized into the three membered ring systems, giving an expected coplanar arrangement for this species. Lastly, the BAC_2P^+ system could be viewed in the extreme case **Gc** as a donor-acceptor complex with a P^I center bearing two lone pairs and two coordinated BAC ligands. In this case, the system approaches an electronic situation similar to that of our recently reported 'carbodicarbenes'[62,63] (**H**, Figure 5.5, bottom). With the availability of two lone pairs for donation, **2** holds potential as an excellent ligand for transition metal species.[64-66]

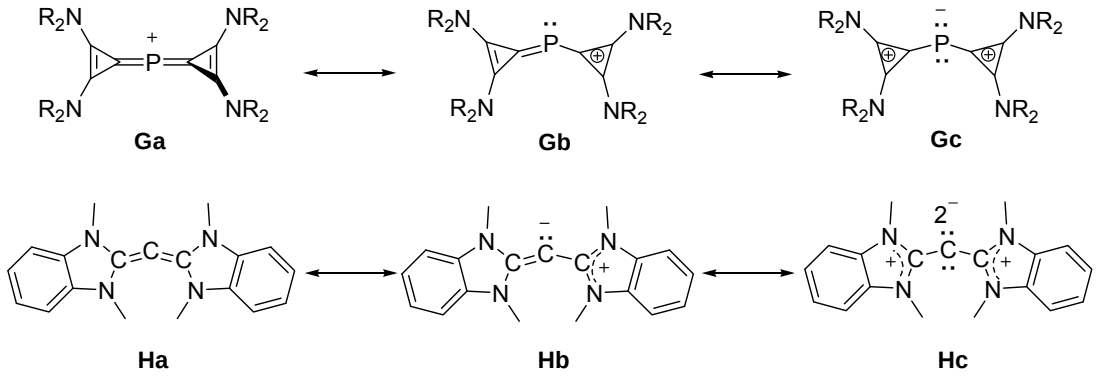
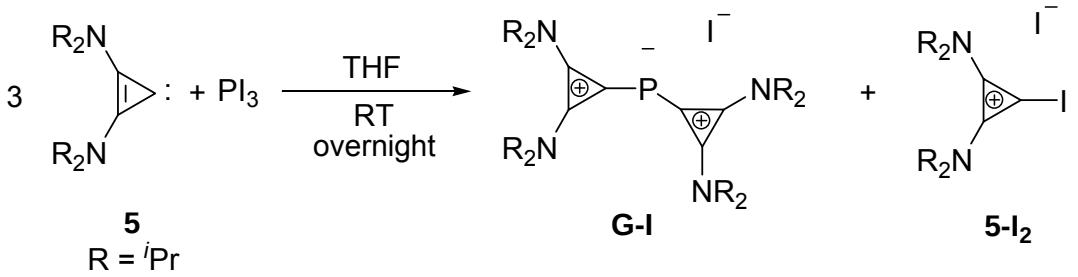


Figure 5.5. Resonance forms for the $(BAC)_2P^+$ cation **2** and comparison to carbodicarbenes.

Cation **G** was independently synthesized by a procedure adapted from Macdonald and coworkers[61] wherein three equivalents of BAC **5** was added

to a THF solution of PI_3. ^{31}P NMR of the reaction mixture revealed a new peak at -93 ppm consistent with the literature for similar $(NHC)_2P^+$ compounds and identical to that of **G** obtained by reaction of **5** with P_4. Analysis of the ^{13}C and ^1H NMR spectra additionally revealed the formation of the side product bis(diamino)(iodo)cyclopropenium iodide **5-I$_2$** as indicated by the characteristic quaternary C1 signal at 97 ppm and C2-3 backbone signal at 134 ppm consistent with that of known halo(diamino)cyclopropenium salts (Scheme 5.6).[59,67,68] The formation of this second product can be understood as a result of trapping of free BAC in the presence of extruded I_2 as observed by Macdonald for the reaction of NHCs with PCl_3.



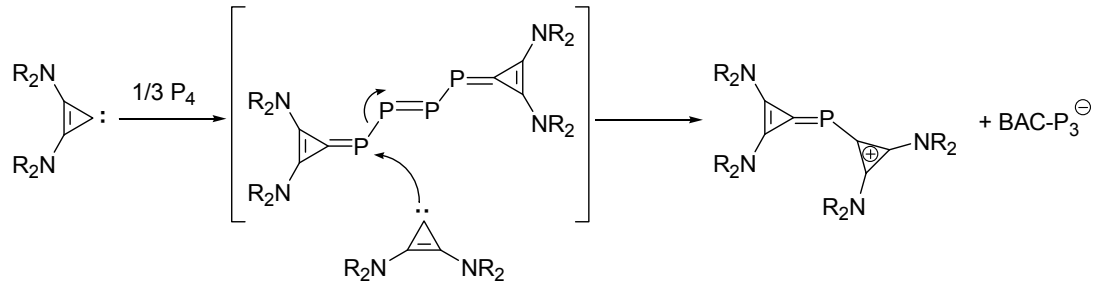
5
R = ^{i}Pr

G-I

5-I$_2$

Scheme 5.6. Independent Synthesis of $(BAC)_2P^+$ cation **G**.

The formation of **G** via BAC activation of P_4 could be rationalized as shown in scheme 5.7. Initial encounter of white phosphorus with an excess of **5** can quickly lead to an intermediate BAC-P_4-BAC ring opened product analogous to that observed for CAACs and saturated NHCs. Subsequent nucleophilic attack at P1 by free **5** may occur due to the reduced steric bulk of this carbene allowing formation of **G** by loss of BAC-P_3^-.



Scheme 5.7. Possible mechanism for the activation of P_4 using **5**.

All attempts to obtain definitive structural information for the P_3 anionic fragment failed, however some speculative structures can be proposed based on the literature as well as our observations from other studies. Spectral parameters for this spin system were determined iteratively using full lineshape analysis (Figure 5.6).[69]

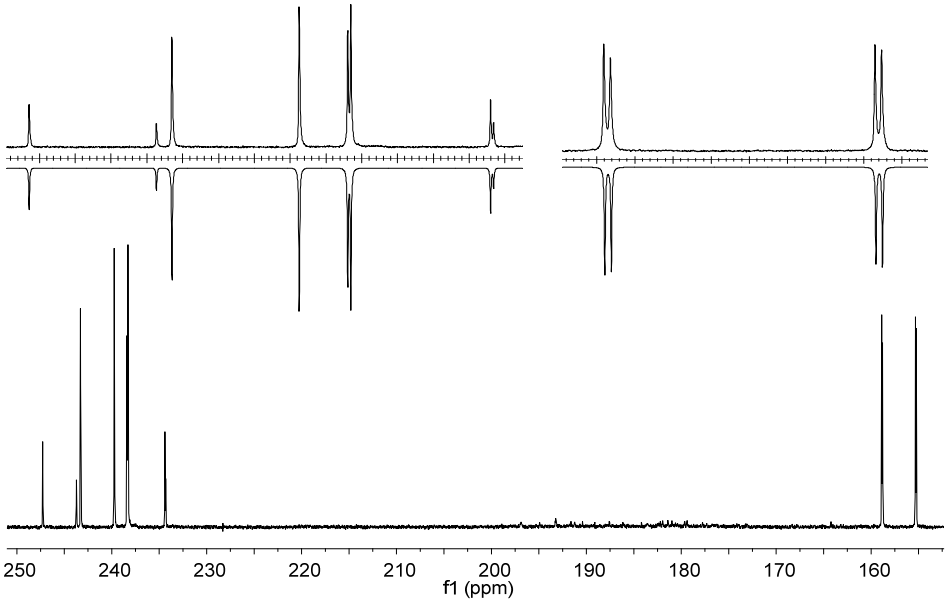
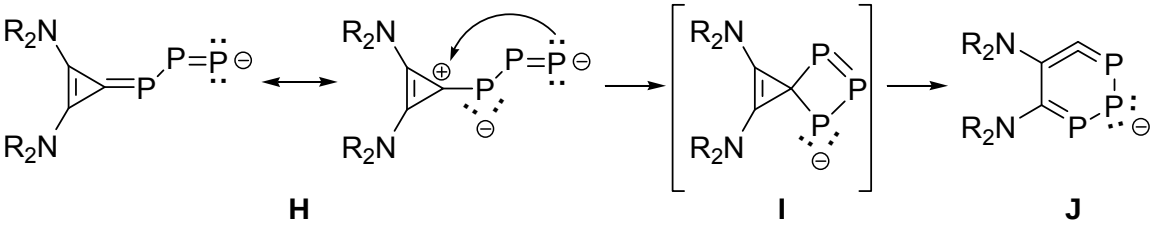


Figure 5.6. $^{31}P\{^{1}H\}$ NMR Spectrum (121.5 MHz) for P_3 fragment. Full spectrum (bottom) and expansions (inset) showing the experimental (upright) and simulated ABX (inverted) spectra. (δ = 242.8, 237.0, and 157.1 ppm, J_{AX} = -484.7, J_{BX} = -481.1, J_{AB} = 38.8 Hz).

On the other hand, although we have not yet been able to identify the P_3 fragment, its anionic nature seems clear, and therefore it is likely an allylic triphosphorus anion, unsymmetrically substituted by cyclopropenylidenes. One possibility is for the extruded BAC-P_3 anion to undergo a ring expansion thereby releasing ring strain while further delocalizing the negative charge. In this case, the strongly nucleophilic, the terminal phosphorus in **H** could attack at the electrophilic C1 ring carbon in a fashion analogous to what we have shown in chapter 4 for the reaction of BAC with carbon disulfide and carbodiimide (scheme 5.8). From this, a transient [3.4] spirocycle **I** could be formed. Since the final P_3 anion displays an unsymmetrical spin system, it is unlikely to be this symmetrical spirocycle. Subsequent rearrangement could then afford a six membered heterocycle such as **J**.



Scheme 5.8. Possible ring expansion pathway for BAC-P_3 anion.

The resonance stabilized structures shown above are not without literature precedent (figure 5.7). For example, as early as 1987, Baudler had reported the triphosphacyclobutenide anion (entry 1) formed during thermolysis of P_4 in the presence of Na/diglyme.[70] This was followed in 1994 by Mathey with the synthesis of 1,2,3-triphospholide anion (entry 2).[71,72] Later, in 2008, the

groups of Russell and Green, and Wright and Rawson independently isolated the bicyclic 1,2,3-triphosphaindenyl anion (entry 3).[73,74] Most recently, Scheer and coworkers reported the isolation of a tungsten carbonyl stabilized triphosphaallyl anion (entry 4).[75]

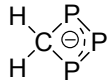
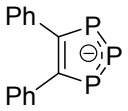
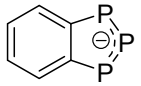
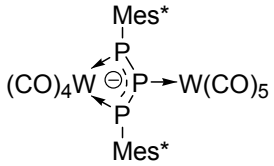
Entry		δ (ppm)	$^1J_{P\text{-}P}$ (Hz)
1		272, 263	- 485
2		297, 271	476
3		335, 261	~ 500
4		469, 108	378

Figure 5.7. Isolated triphosphaallyl anions.

Conclusion

The results reported here demonstrate that stable singlet carbenes can achieve the tasks that transition metals do with P_4, namely activation, aggregation, and importantly, fragmentation. The next challenge is to use the resulting adducts, especially **F** and **G**, to prepare useful organophosphorus derivatives. This would avoid the use of Cl_2 gas, which is important to meet the growing demand in phosphorus derivatives using environmentally friendly processes.

Experimental Section

General

All manipulations were performed under an inert atmosphere of dry argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker Avance 300 and 600 or Varian Inova 400 and 500 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$. ^{31}P NMR chemical shifts are reported relative to 85% H_3PO_4.

NOTE: White phosphorus (P_4, also known in an impure form as yellow phosphorus) is highly toxic and reacts vigorously with atmospheric oxygen. Care should be taken when dealing with this material.

Synthesis of **D**: Ether (40 ml) was added at room temperature to a mixture of carbene **3** (4.07 mmol) and P_4 (1.16 mmol), and the resulting suspension stirred for 2 h. The solvent was removed under vacuum, and the solid residue washed with 6 ml of hexane at -35 °C, to afford 480 mg of **D** (66.4% based on P_4). Single crystals of **D** were grown by layering acetonitrile on top of a THF solution. m.p. 150 °C; $^{31}P\{^{1}H\}$ NMR ([D_8]THF, 25 °C, 202.5 MHz): δ = 238.8 (dt, $^{1}J_{P\text{-}P}$ = 220 Hz and $^{2}J_{P\text{-}P}$ = 87 Hz), -105.8 (dt, $^{1}J_{P\text{-}P}$ = 220 Hz and $^{2}J_{P\text{-}P}$ = 167 Hz), -168.2 (dd, $^{1}J_{P\text{-}P}$ = 167 Hz and $^{2}J_{P\text{-}P}$ = 87 Hz); ^{1}H NMR ([D_8]THF, 25 °C, 500 MHz): δ = 3.64 (t, 2 H, $^{3}J_{H\text{-}H}$ = 12 Hz, C*H*), 2.70 (t, 2 H, $^{3}J_{H\text{-}H}$ = 12 Hz, C*H*), 2.46 (t, 2 H, $^{3}J_{H\text{-}H}$ = 12 Hz), 2.23 (t, 4 H, $^{3}J_{H\text{-}H}$ = 12 Hz), 2.12 (t, 2 H, $^{3}J_{H\text{-}H}$ = 12 Hz), 1.70-1.82 (m, 10 H), 1.48-1.66 (m, 10 H), 1.06-1.36 (m, 12 H), 1.33

(s, 9 H), 1.16 (s, 9 H); ^{13}C NMR ([D_8] THF, 25 °C, 125.75 MHz): δ = 227.6 (d, $^1J_{P\text{-}C}$ = 89 Hz), 101.5 (br s), 69.8 (s), 67.0 (d, $J_{P\text{-}C}$ = 5 Hz), 62.7 (s), 54.9 (s), 46.3 (d, $J_{P\text{-}C}$ = 29 Hz), 45,3 (t, $J_{P\text{-}C}$ = 15 Hz), 39.7 (s), 38.9 (d, $J_{P\text{-}C}$ = 6 Hz), 37.5 (s), 37.2 (s), 36.8 (d, $J_{P\text{-}C}$ = 10 Hz), 35.7 (s), 34.3 (d, $J_{P\text{-}C}$ = 17 Hz), 32.4 (s), 28.9 (s), 28.7 (s), 28.5 (s), 27.5 (s), 27.1 (s).

Synthesis of **E** and **F**. A solution of carbene **4** (3.25 g, 10.01 mmol) in ether (20 mL) was added at room temperature to a suspension of P_4 (0.41 g, 3.34 mmol) in ether (20 mL). Immediately upon addition the color of the solution turns dark red. The mixture was stirred at room temperature for 2 hours and then half of the solvent was removed under vacuum. A precipitate was formed when the remaining solution was cooled down to -30 °C. Filtration gave **F** as a bright yellow powder (580 mg, 12.1% yield based on P_4). Single crystals of **F** were grown from a saturated diethyl ether solution at room temperature Evaporation of the filtrate gave a dark red powder, which was washed three times with acetonitrile (3 x 30 mL), and dried under vacuum to give **E** as a bright yellow powder (2.5 g, 67.4% yield based on P_4). Single crystals of **E** were obtained by slow evaporation of a hexane solution at room temperature.

E: m.p. 142 °C; ^{31}P{^{1}H} NMR ([D_6]benzene, 25 °C, 162 MHz): δ = 68.13 (d, $^1J_{P\text{-}P}$ = 228 Hz), 66.2 (q, $^1J_{P\text{-}P}$ = 228 Hz); ^{1}H NMR ([D_6]benzene, 25 °C, 500 MHz): δ = 7.19 (t, 3 H, $^3J_{H\text{-}H}$ = 8 Hz), 7.07 (d, 6 H, $^3J_{H\text{-}H}$ = 8 Hz), 3.39 (m, 6 H), 2.92 (sept, 6 H, $^3J_{H\text{-}H}$ = 6 Hz), 1.97 (s, 6 H), 1.00-1.90 (m, 24 H), 1.34 (d, 18 H, $^3J_{H\text{-}H}$ = 6 Hz), 1.24 (d, 18 H, $^3J_{H\text{-}H}$ = 6 Hz), 1.08 (s, 18 H); ^{13}C NMR ([D_6]benzene, 25 °C, 125.75 MHz): δ = 207.4. (m), 149.1 (s), 134.8 (s), 128.9

(sr), 125.5 (s), 68.1 (s), 55.4 (s), 50.9 (s), 38.1 (d, J_{P-C} = 13 Hz), 30.2 (s), 29.4 (s), 28.2 (s), 25.7 (s), 25.1 (s), 24.3 (s).

F: m.p. 216 °C; $^{31}P\{^{1}H\}$ NMR ([D_6]benzene, 25 °C, 162 MHz): δ = 59.38 (s); ^{1}H NMR ([D_6]benzene, 25 °C, 500 MHz): δ = 7.20 (t, 2 H, $^{3}J_{H-H}$ = 6 Hz), 7.17 (d, 4 H, $^{3}J_{H-H}$ = 6 Hz), 3.36 (m, 4 H), 3.11 (sept, 4 H, $^{3}J_{H-H}$ = 7 Hz), 1.92 (s, 4 H), 1.00-1.60 (m, 16 H), 1.59 (d, 12 H, $^{3}J_{H-H}$ = 7 Hz), 1.27 (d, 12 H, $^{3}J_{H-H}$ = 7 Hz), 1.04 ppm (s, 12 H); $^{13}C\{^{1}H\}$ NMR ([D_6]benzene, 25 °C, 125.75 MHz): δ = 202.2 (dd, $^{1}J_{P-C}$ = 32 Hz, $^{2}J_{P-C}$ = 26 Hz), 149.3 (s), 136.1 (s), 128.9 (s), 125.4 (s), 67.8 (s), 55.4 (s), 51.3 (s), 36.9 (t, J_{P-C} = 12 Hz), 30.2 (s), 29.5 (s), 27.4 (s), 25.4 (s), 24.8 (s), 24.2 (s).

Synthesis of **G**. To a solution of carbene **5** (1.00 g, 4.24 mmol) in THF (5 mL) was added white phosphorus (P_4) (0.17 g, 1.40 mmol). Immediately the solution turns from colorless to deep red. After stirring for 12 hours at room temperature, chloroform (5 mL) was added to the crude reaction mixture. After stirring at room temperature for 30 min, volatiles were removed under vacuum, and the resulting red solid washed with Et_2O (3 x 20 mL) to afford a dark orange powder. Yield: 564 mg (74 % based on P_4). Single crystals of **G**(Cl^-) were readily obtained by slow evaporation of a chloroform solution at room temperature. mp 174 °C (dec.); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$, 25 °C) δ = -93.2; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) d = 3.79 (sept, J = 6.5 Hz, 4 H), 1.25 (d, J = 6.5 Hz, 24 H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ = 136.5 (s), 123.7 (d, $^{1}J_{C-P}$ = 104.6 Hz), 51.3 (s), 21.5 (s); ESI MS m/z 535.4151 (535.4141 calcd for $C_{30}H_{56}N_4PO_2$, MO_2^+).

X-ray crystal structure determinations for compounds D-G

The Bruker X8-APEX[76] X-ray diffraction instrument with Mo-radiation was used for data collection**.** All data frames were collected at low temperatures (T = 100 K) using an ω, φ-scan mode (0.5° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package.[77] The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program.[78] The SIR97 was used for direct methods of phase determination, and Bruker SHELXTL software package[79] for structure refinement and difference Fourier maps. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of two compounds were refined by means of a full matrix least-squares procedure on F^2. All H-atoms were included in the refinement in calculated positions riding on the C atoms. Drawings of molecules were performed using Ortep 3.[80] Counter anion: Cl^- of compound G was found to be statistically disordered on two positions. Racemic twins were spotted for compounds F and G, both were refined in non-centrosymmetric space groups with the aid of the following matrix: -1 0 0, 0 -1 0, 0 0 -1 and a BASF parameter.

Crystal and structure parameters of D: size 0.38 x 0.16 x 0.10 mm^3, monoclinic, space group P 2(1)/c, a = 21.14(2) Å, b = 9.515(10) Å, c = 18.39(2) Å, $\alpha = \gamma = 90.0°$, β =107.049(11)°, V = 3535(7) $Å^3$, ρ_{calcd} = 1.170 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 34707, independent reflections = 8751 (R_{int} = 0.0282), absorption coefficient μ = 0.239 mm^{-1}; max/min transmission = 0.9765 and 0.9148, 367 parameters were refined and converged at R1 = 0.0313, wR2 = 0.0742, with intensity I>2σ(I), the final difference map was 0.431 and -0.206 e.$Å^{-3}$.

Crystal and structure parameters of E: size 0.27 x 0.20 x 0.10 mm^3, triclinic,

space group P -1, a = 13.8738(5) Å, b = 20.0598(8) Å, c = 23.8799(10)° Å, α = 80.6490(10)°, β = 88.1130(10)° γ = 88.4260(10)° , V = 6552.4(4) Å^3, ρ_{calcd} = 1.116 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 65352, independent reflections = 26438 (R_{int} = 0.0435), absorption coefficient μ = 0.156 mm^{-1}; max/min transmission = 0.9765 and 0.9148, 367 parameters were refined and converged at R1 = 0.0313, wR2 = 0.0742, with intensity I>2σ(I), the final difference map was 0.431 and -0.206 e.Å^{-3}.

Crystal and structure parameters of F: size 0.28 x 0.15 x 0.10 mm^3, monoclinic, space group P n, a = 10.913(5) Å, b = 17.074(8) Å, c = 22.713(11)° Å, α = 90.0°, β = 101.773(7)° γ = 90.0°, V = 4143(4) Å^3, ρ_{calcd} = 1.143 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 24614, independent reflections = 11087 (R_{int} = 0.0833), absorption coefficient μ = 0.138 mm^{-1}; max/min transmission = 0.9863 and 0.9623, 925 parameters were refined and converged at R1 = 0.1717, wR2 = 0.0742, with intensity I>2σ(I), the final difference map was 0.781 and -0.375 e.Å^{-3}.

Crystal and structure parameters of G: size 0.28 x 0.14 x 0.10 mm^3, orthorhombic, space group P na2(1), a = 27.315(5) Å, b = 12.121(2) Å, c = 9.9198(18)° Å, α = β = γ = 90.0°, V = 3284.4(10) Å^3, ρ_{calcd} = 1.090 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 19452, independent reflections = 7786 (R_{int} = 0.0286), absorption coefficient μ = 0.188 mm^{-1}; max/min transmission = 0.9814 and 0.9492, 352 parameters were refined and converged at R1 = 0.0548, wR2 = 0.1405, with intensity I>2σ(I), the final difference map was 0.532 and -0.295 e.Å^{-3}.

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Appendix

Tables of Crystallographic Data for Unpublished Compounds

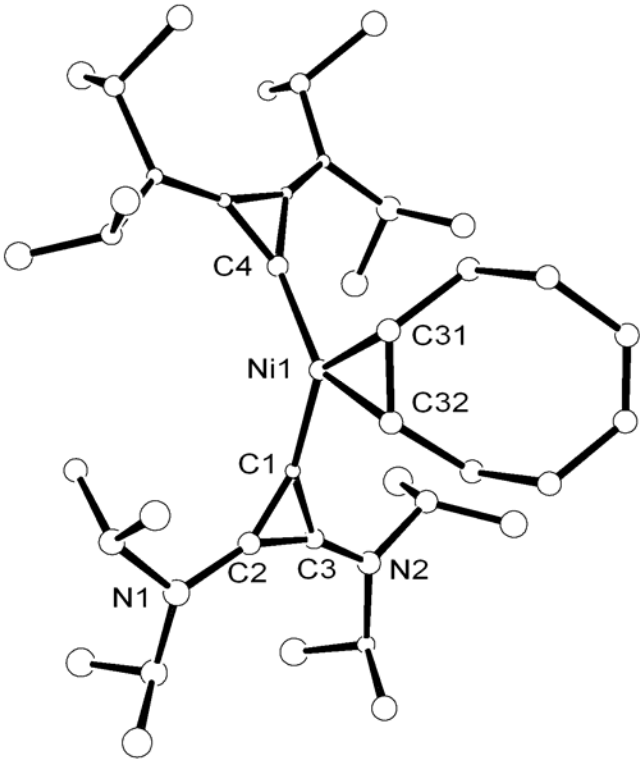

Table 1. Crystal data and structure refinement for compound **5** chapter 1.

Empirical formula	$C_{38}H_{68}N_4Ni$	
Formula weight	639.67	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.745(4) Å	α = 90°.
	b = 31.754(12) Å	β = 103.187(5)°.
	c = 11.684(4) Å	γ = 90°.
Volume	3882(3) $Å^3$	
Z	4	
Density (calculated)	1.095 g/cm^3	
Absorption coefficient	0.528 mm^{-1}	
F(000)	1408	
Index ranges	-8<=h<=8, -26<=k<=26, -9<=l<=9	

Reflections collected	10880
Independent reflections	2336 [R(int) = 0.0850]
Completeness to theta = 17.30°	98.5 %
Absorption correction	Sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2336 / 352 / 404
Goodness-of-fit on F^2	1.106
Final R indices [I>2sigma(I)]	R1 = 0.1538, wR2 = 0.3579
R indices (all data)	R1 = 0.1654, wR2 = 0.3662
Largest diff. peak and hole	4.151 and -0.510 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	8587(2)	1089(1)	6516(2)	19(1)
N(1)	11391(15)	1049(5)	9647(13)	28(2)
N(2)	7970(15)	772(5)	9721(13)	27(2)
N(3)	9246(14)	2101(4)	4749(13)	20(2)
N(4)	5848(14)	2004(4)	5034(13)	20(2)
C(1)	9087(18)	1052(6)	8147(16)	22(3)
C(2)	10025(19)	1016(6)	9138(16)	24(2)
C(3)	8885(19)	912(6)	9214(16)	24(2)
C(4)	8011(17)	1603(6)	5737(15)	17(3)
C(5)	8279(18)	1930(6)	5076(16)	18(2)
C(6)	7069(18)	1880(6)	5172(16)	17(2)
C(7)	8950(20)	502(6)	6243(16)	27(3)
C(8)	8160(20)	175(5)	6712(17)	28(3)
C(9)	8150(20)	-265(6)	6046(17)	30(3)

	x	y	z	U(eq)
C(10)	6930(20)	-343(6)	5207(17)	33(3)
C(11)	6490(20)	-166(6)	4225(18)	33(3)
C(12)	7160(20)	181(6)	3684(17)	32(3)
C(13)	7177(19)	630(6)	4325(17)	31(3)
C(14)	8500(20)	706(6)	5187(16)	28(3)
C(15)	11884(19)	998(6)	10898(17)	30(3)
C(16)	12210(20)	1417(6)	11489(17)	35(4)
C(17)	13038(19)	710(6)	11169(18)	37(4)
C(18)	12157(19)	1255(6)	8892(17)	30(3)
C(19)	12174(19)	978(6)	7837(16)	32(4)
C(20)	11716(18)	1694(6)	8545(16)	29(4)
C(21)	8235(19)	649(6)	11006(16)	27(3)
C(22)	8683(19)	1007(6)	11771(17)	32(4)
C(23)	9041(19)	263(6)	11181(17)	28(4)
C(24)	6620(18)	804(6)	9040(17)	29(3)
C(25)	5863(19)	415(6)	8903(17)	32(4)
C(26)	5977(19)	1180(6)	9591(17)	33(4)
C(27)	5011(18)	1767(6)	5655(16)	23(3)
C(28)	5506(18)	1798(6)	6975(15)	26(4)
C(29)	4850(18)	1311(6)	5256(17)	27(4)
C(30)	5358(17)	2375(6)	4321(16)	22(3)
C(31)	4240(17)	2246(6)	3298(16)	27(4)
C(32)	4981(18)	2709(6)	5051(16)	25(4)
C(33)	10547(17)	1920(6)	5136(16)	22(3)
C(34)	11527(17)	2234(6)	5778(17)	26(4)
C(35)	10985(18)	1702(6)	4156(16)	26(4)
C(36)	9113(18)	2462(6)	3867(16)	22(3)
C(37)	8693(18)	2861(6)	4364(16)	23(4)
C(38)	8234(17)	2325(6)	2703(16)	25(4)

Table 3. Bond lengths [Å] and angles [°].

Ni(1)-C(1)	1.861(19)	Ni(1)-C(4)	1.902(19)
Ni(1)-C(7)	1.947(19)	Ni(1)-C(14)	1.959(19)
N(1)-C(15)	1.45(2)	N(1)-C(2)	1.46(2)
N(1)-C(18)	1.49(2)	N(2)-C(3)	1.33(2)
N(2)-C(24)	1.49(2)	N(2)-C(21)	1.51(2)
N(3)-C(5)	1.30(2)	N(3)-C(33)	1.48(2)
N(3)-C(36)	1.53(2)	N(4)-C(6)	1.34(2)
N(4)-C(30)	1.47(2)	N(4)-C(27)	1.48(2)
C(1)-C(2)	1.36(2)	C(1)-C(3)	1.39(3)
C(2)-C(3)	1.29(2)	C(4)-C(5)	1.36(2)
C(4)-C(6)	1.39(2)	C(5)-C(6)	1.34(2)
C(7)-C(14)	1.38(2)	C(7)-C(8)	1.52(3)
C(8)-C(9)	1.60(3)	C(9)-C(10)	1.47(3)
C(10)-C(11)	1.27(2)	C(11)-C(12)	1.53(3)
C(12)-C(13)	1.61(3)	C(13)-C(14)	1.56(3)
C(15)-C(16)	1.51(3)	C(15)-C(17)	1.51(3)
C(18)-C(20)	1.50(3)	C(18)-C(19)	1.52(3)
C(21)-C(22)	1.46(3)	C(21)-C(23)	1.49(3)
C(24)-C(25)	1.47(3)	C(24)-C(26)	1.59(3)
C(27)-C(28)	1.52(3)	C(27)-C(29)	1.52(3)
C(30)-C(32)	1.47(3)	C(30)-C(31)	1.54(2)
C(33)-C(35)	1.50(3)	C(33)-C(34)	1.52(2)
C(36)-C(37)	1.51(2)	C(36)-C(38)	1.53(2)

C(1)-Ni(1)-C(4)	122.0(8)	C(1)-Ni(1)-C(7)	94.9(8)
C(4)-Ni(1)-C(7)	143.0(8)	C(1)-Ni(1)-C(14)	136.3(8)
C(4)-Ni(1)-C(14)	101.7(8)	C(7)-Ni(1)-C(14)	41.4(7)
C(15)-N(1)-C(2)	120.4(16)	C(15)-N(1)-C(18)	121.7(15)
C(2)-N(1)-C(18)	115.6(14)	C(3)-N(2)-C(24)	117.8(15)
C(3)-N(2)-C(21)	122.4(15)	C(24)-N(2)-C(21)	119.1(15)
C(5)-N(3)-C(33)	120.6(15)	C(5)-N(3)-C(36)	123.5(15)
C(33)-N(3)-C(36)	115.6(14)	C(6)-N(4)-C(30)	121.1(15)

C(6)-N(4)-C(27)	118.5(14)	C(30)-N(4)-C(27)	120.3(14)
C(2)-C(1)-C(3)	56.2(13)	C(2)-C(1)-Ni(1)	149.8(16)
C(3)-C(1)-Ni(1)	150.8(15)	C(3)-C(2)-C(1)	63.1(14)
C(3)-C(2)-N(1)	151.0(19)	C(1)-C(2)-N(1)	145.7(18)
C(2)-C(3)-N(2)	157.3(19)	C(2)-C(3)-C(1)	60.7(14)
N(2)-C(3)-C(1)	142.0(18)	C(5)-C(4)-C(6)	58.2(13)
C(5)-C(4)-Ni(1)	146.8(15)	C(6)-C(4)-Ni(1)	153.3(14)
N(3)-C(5)-C(6)	158.0(18)	N(3)-C(5)-C(4)	140.1(17)
C(6)-C(5)-C(4)	61.8(13)	C(5)-C(6)-N(4)	153.5(17)
C(5)-C(6)-C(4)	60.0(13)	N(4)-C(6)-C(4)	145.9(17)
C(14)-C(7)-C(8)	122.2(18)	C(14)-C(7)-Ni(1)	69.8(11)
C(8)-C(7)-Ni(1)	116.4(14)	C(7)-C(8)-C(9)	111.4(16)
C(10)-C(9)-C(8)	112.4(16)	C(11)-C(10)-C(9)	128(2)
C(10)-C(11)-C(12)	125(2)	C(11)-C(12)-C(13)	113.7(16)
C(14)-C(13)-C(12)	110.5(15)	C(7)-C(14)-C(13)	125.8(17)
C(7)-C(14)-Ni(1)	68.8(11)	C(13)-C(14)-Ni(1)	118.5(13)
N(1)-C(15)-C(16)	110.9(16)	N(1)-C(15)-C(17)	111.9(16)
C(16)-C(15)-C(17)	110.0(16)	N(1)-C(18)-C(20)	112.6(16)
N(1)-C(18)-C(19)	109.7(16)	C(20)-C(18)-C(19)	112.4(16)
C(22)-C(21)-C(23)	117.2(17)	C(22)-C(21)-N(2)	111.6(16)
C(23)-C(21)-N(2)	108.7(15)	C(25)-C(24)-N(2)	116.6(16)
C(25)-C(24)-C(26)	113.3(17)	N(2)-C(24)-C(26)	107.2(15)
N(4)-C(27)-C(28)	110.7(14)	N(4)-C(27)-C(29)	111.9(15)
C(28)-C(27)-C(29)	111.3(15)	N(4)-C(30)-C(32)	111.0(15)
N(4)-C(30)-C(31)	109.9(14)	C(32)-C(30)-C(31)	111.8(15)
N(3)-C(33)-C(35)	112.6(15)	N(3)-C(33)-C(34)	113.3(15)
C(35)-C(33)-C(34)	112.1(15)	C(37)-C(36)-N(3)	111.2(15)
C(37)-C(36)-C(38)	113.8(15)	N(3)-C(36)-C(38)	109.3(14)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for gb492_final. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	14(2)	18(2)	26(2)	2(1)	3(1)	2(1)
N(1)	22(5)	37(5)	24(5)	3(4)	1(4)	4(4)
N(2)	26(5)	34(5)	21(5)	4(4)	6(4)	1(4)
N(3)	15(4)	20(5)	25(5)	4(4)	7(4)	1(4)
N(4)	15(4)	17(5)	27(5)	7(4)	6(4)	-2(4)
C(1)	21(5)	27(6)	18(5)	-1(5)	5(4)	2(5)
C(2)	22(5)	30(5)	21(5)	0(4)	4(4)	4(5)
C(3)	23(5)	29(5)	19(5)	1(4)	5(4)	2(5)
C(4)	16(5)	16(5)	22(6)	1(4)	8(5)	1(4)
C(5)	16(4)	16(5)	23(5)	3(4)	9(4)	1(4)
C(6)	16(4)	15(5)	23(5)	4(4)	7(4)	-1(4)
C(7)	44(7)	15(6)	23(6)	3(5)	7(5)	-2(5)
C(8)	45(7)	15(6)	25(6)	2(5)	9(5)	-2(5)
C(9)	48(7)	16(6)	27(6)	1(5)	9(5)	-4(5)
C(10)	51(7)	18(6)	30(7)	1(5)	7(5)	-8(5)
C(11)	50(7)	19(6)	30(6)	0(5)	5(5)	-8(5)
C(12)	49(7)	17(6)	28(6)	2(5)	4(5)	-4(5)
C(13)	47(7)	16(6)	27(6)	3(5)	2(5)	-2(5)
C(14)	44(7)	14(6)	24(6)	3(5)	5(5)	-2(5)
C(15)	25(5)	39(6)	24(5)	4(5)	1(5)	5(5)
C(16)	35(9)	42(8)	23(7)	3(6)	-1(8)	4(7)
C(17)	31(8)	44(9)	30(8)	5(7)	-6(7)	9(6)
C(18)	23(5)	39(6)	24(5)	1(5)	1(5)	1(5)
C(19)	24(9)	41(8)	29(8)	-3(7)	4(7)	-3(8)
C(20)	24(9)	40(7)	21(8)	2(6)	2(7)	0(7)
C(21)	26(6)	36(6)	20(5)	3(5)	7(5)	1(5)
C(22)	30(9)	41(8)	23(7)	1(6)	5(8)	1(7)
C(23)	30(9)	39(8)	19(8)	7(6)	11(7)	3(6)

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(24)25(5)	38(6)	24(6)	8(5)	7(5)	-1(5)
C(25)26(8)	41(7)	28(9)	8(7)	4(7)	-1(6)
C(26)27(8)	43(8)	32(9)	9(7)	9(7)	4(6)
C(27)16(5)	21(5)	33(5)	6(5)	8(5)	-5(5)
C(28)21(8)	28(8)	32(6)	7(6)	11(7)	-5(8)
C(29)18(8)	23(6)	41(8)	4(6)	8(8)	-9(7)
C(30)16(5)	19(6)	30(6)	7(4)	4(5)	0(4)
C(31)21(8)	23(8)	34(8)	7(6)	-2(6)	2(7)
C(32)20(8)	22(7)	32(8)	6(6)	4(7)	4(7)
C(33)15(5)	23(6)	28(6)	4(4)	6(5)	1(4)
C(34)19(7)	27(8)	32(9)	1(6)	3(7)	-2(6)
C(35)21(8)	24(8)	33(8)	1(6)	6(7)	7(7)
C(36)16(5)	22(6)	27(6)	7(4)	6(4)	-2(5)
C(37)18(8)	20(6)	30(8)	10(6)	4(7)	0(7)
C(38)15(8)	31(9)	28(7)	7(6)	3(6)	3(7)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(7)	9885	435	6408	33
H(8A)	7274	278	6611	34
H(8B)	8521	133	7563	34
H(9A)	8846	-268	5621	36
H(9B)	8310	-495	6633	36
H(10)	6400	-554	5428	40
H(11)	5671	-256	3791	40
H(12A)	6724	213	2845	39
H(12B)	8050	92	3719	39
H(13A)	7009	856	3728	37

	x	y	z	U(eq)
H(13B)	6494	638	4767	37
H(14)	9195	761	4762	33
H(15)	11197	866	11231	37
H(16A)	12529	1375	12337	41
H(16B)	11449	1596	11348	41
H(16C)	12876	1555	11168	41
H(17A)	12790	428	10858	44
H(17B)	13369	694	12022	44
H(17C)	13702	822	10801	44
H(18)	13057	1275	9365	35
H(19A)	12409	690	8104	38
H(19B)	12800	1088	7420	38
H(19C)	11324	977	7307	38
H(20A)	10909	1683	7951	34
H(20B)	12363	1839	8220	34
H(20C)	11587	1847	9237	34
H(21)	7393	566	11165	32
H(22A)	8901	912	12591	38
H(22B)	8008	1220	11671	38
H(22C)	9442	1128	11566	38
H(23A)	9789	307	10847	34
H(23B)	8542	25	10787	34
H(23C)	9323	204	12023	34
H(24)	6656	896	8229	35
H(25A)	6326	192	8593	38
H(25B)	5038	464	8356	38
H(25C)	5721	329	9668	38
H(26A)	5932	1107	10395	40
H(26B)	5113	1229	9115	40
H(26C)	6490	1436	9602	40
H(27)	4148	1902	5455	28

	x	y	z	U(eq)
H(28A)	6332	1654	7204	31
H(28B)	4895	1665	7369	31
H(28C)	5611	2095	7206	31
H(29A)	4556	1300	4399	32
H(29B)	4219	1174	5618	32
H(29C)	5671	1164	5494	32
H(30)	6061	2488	3977	26
H(31A)	4515	2017	2853	32
H(31B)	3978	2488	2779	32
H(31C)	3517	2152	3614	32
H(32A)	4248	2613	5350	30
H(32B)	4745	2963	4576	30
H(32C)	5698	2772	5713	30
H(33)	10483	1696	5722	26
H(34A)	11678	2449	5224	31
H(34B)	12329	2087	6115	31
H(34C)	11205	2368	6409	31
H(35A)	10382	1477	3833	31
H(35B)	11835	1581	4459	31
H(35C)	11025	1906	3536	31
H(36)	9978	2515	3714	26
H(37A)	7852	2818	4539	27
H(37B)	8638	3089	3790	27
H(37C)	9314	2937	5088	27
H(38A)	8517	2052	2466	30
H(38B)	8266	2535	2096	30
H(38C)	7355	2301	2802	30

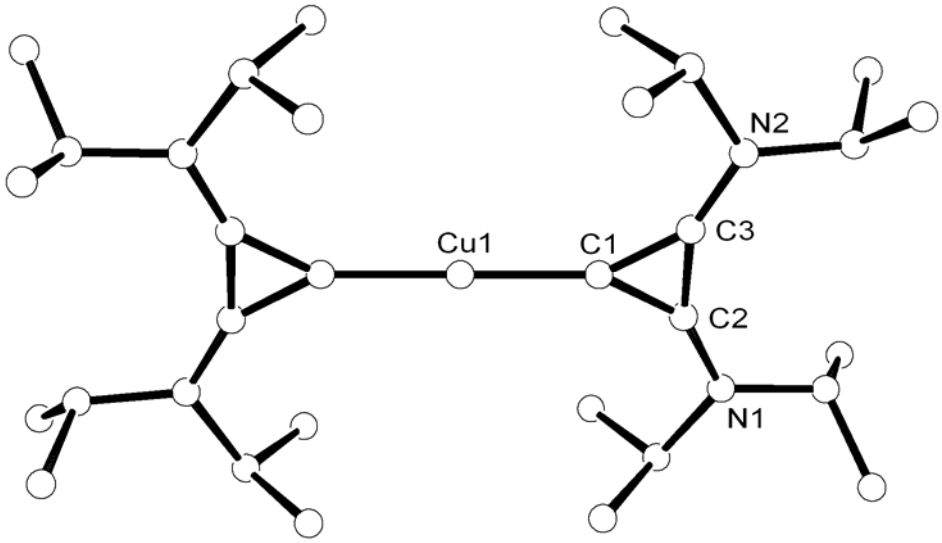

Table 1. Crystal data and structure refinement for compound **6** chapter 1.

Empirical formula	$C_{30}H_{56}ClCuN_4$	
Formula weight	285.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.277(3) Å	α = 90°
	b = 9.755(2) Å	β = 107.711(3)°
	c = 11.486(2) Å	γ = 90°
Volume	1630.5(6) $Å^3$	
Z	4	
Density (calculated)	1.165 g/cm^3	
Absorption coefficient	0.775 mm^{-1}	
F(000)	620	
Crystal size	0.38 x 0.16 x 0.12 mm^3	
Theta range for data collection	2.51 to 22.46°	
Index ranges	-16<=h<=16, -10<=k<=10, -12<=l<=12	
Reflections collected	8366	

Independent reflections	2132 [R(int) = 0.0759]
Completeness to theta = 22.46°	99.9 %
Absorption correction	Sadabs
Max. and min. transmission	0.9128 and 0.7573
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2132 / 0 / 184
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2 = 0.1186
R indices (all data)	R1 = 0.0916, wR2 = 0.1354
Extinction coefficient	0.0018(12)
Largest diff. peak and hole	0.960 and -0.270 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	0	5000	5000	32(1)
N(1)	2018(3)	3529(4)	8026(4)	36(1)
N(2)	2694(3)	6364(5)	6317(4)	40(1)
C(1)	1192(3)	4988(6)	6113(4)	32(1)
C(2)	1838(3)	4440(5)	7126(5)	31(1)
C(3)	2084(3)	5493(5)	6490(4)	30(1)
C(4)	1305(3)	2517(6)	8057(5)	38(1)
C(5)	1033(4)	1637(6)	6923(5)	54(2)
C(6)	486(4)	3226(6)	8261(5)	47(2)
C(7)	2963(3)	3403(6)	8894(5)	43(2)
C(8)	2968(4)	3333(7)	10206(5)	55(2)
C(9)	3470(4)	2201(8)	8591(6)	75(2)
C(10)	2410(4)	7273(6)	5241(5)	41(2)
C(11)	2111(4)	6479(7)	4059(5)	56(2)

	x	y	z	U(eq)
C(12)	1673(4)	8267(7)	5350(6)	63(2)
C(13)	3673(4)	6324(7)	7098(5)	51(2)
C(14)	4267(4)	5628(7)	6420(6)	68(2)
C(15)	4043(4)	7724(7)	7552(6)	70(2)
Cl(1A)	5000	5000	0	154(14)
Cl(1B)	4817(17)	5520(30)	190(20)	86(4)

Table 3. Bond lengths [Å] and angles [°].

Cu(1)-C(1)#1	1.881(4)	Cu(1)-C(1)	1.881(4)
N(1)-C(2)	1.328(6)	N(1)-C(4)	1.479(6)
N(1)-C(7)	1.489(6)	N(2)-C(3)	1.320(6)
N(2)-C(10)	1.475(6)	N(2)-C(13)	1.493(6)
C(1)-C(2)	1.383(7)	C(1)-C(3)	1.387(7)
C(2)-C(3)	1.377(7)	C(4)-C(5)	1.509(7)
C(4)-C(6)	1.510(7)	C(7)-C(9)	1.502(8)
C(7)-C(8)	1.506(7)	C(10)-C(11)	1.508(7)
C(10)-C(12)	1.520(8)	C(13)-C(15)	1.508(8)
C(13)-C(14)	1.524(8)		

C(1)#1-Cu(1)-C(1)	180.000(1)	C(2)-N(1)-C(4)	119.1(4)
C(2)-N(1)-C(7)	120.4(4)	C(4)-N(1)-C(7)	120.0(4)
C(3)-N(2)-C(10)	118.2(4)	C(3)-N(2)-C(13)	121.1(4)
C(10)-N(2)-C(13)	120.3(4)	C(2)-C(1)-C(3)	59.6(3)
C(2)-C(1)-Cu(1)	150.4(4)	C(3)-C(1)-Cu(1)	149.9(4)
N(1)-C(2)-C(3)	152.5(5)	N(1)-C(2)-C(1)	147.1(5)
C(3)-C(2)-C(1)	60.4(4)	N(2)-C(3)-C(2)	151.5(5)
N(2)-C(3)-C(1)	148.5(5)	C(2)-C(3)-C(1)	60.0(4)
N(1)-C(4)-C(5)	111.7(4)	N(1)-C(4)-C(6)	110.4(4)
C(5)-C(4)-C(6)	111.8(5)	N(1)-C(7)-C(9)	111.9(5)
N(1)-C(7)-C(8)	112.4(4)	C(9)-C(7)-C(8)	110.5(5)

N(2)-C(10)-C(11)	112.1(5)	N(2)-C(10)-C(12)	110.5(4)
C(11)-C(10)-C(12)	111.9(5)	N(2)-C(13)-C(15)	112.7(5)
N(2)-C(13)-C(14)	110.4(5)	C(15)-C(13)-C(14)	111.2(5)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1 #2 -x+1,-y+1,-z.

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)22(1)	33(1)	36(1)	7(1)	2(1)	-2(1)
N(1) 24(2)	36(3)	41(3)	8(2)	1(2)	-3(2)
N(2) 29(3)	48(3)	38(3)	12(2)	4(2)	-9(2)
C(1) 29(3)	29(3)	37(3)	4(3)	7(2)	-4(3)
C(2) 24(3)	33(3)	34(3)	-1(3)	6(3)	0(2)
C(3) 30(3)	30(3)	31(3)	4(2)	11(3)	-5(2)
C(4) 34(3)	36(4)	43(3)	14(3)	10(3)	-2(3)
C(5) 61(4)	39(4)	62(4)	-2(3)	18(3)	-7(3)
C(6) 39(4)	50(4)	51(4)	6(3)	13(3)	0(3)
C(7) 29(3)	51(4)	42(3)	11(3)	0(3)	1(3)
C(8) 44(4)	76(5)	40(3)	-2(3)	5(3)	12(3)
C(9) 47(4)	109(6)	60(4)	-20(4)	2(4)	25(4)
C(10)36(3)	44(4)	43(3)	9(3)	12(3)	-9(3)
C(11)65(4)	60(5)	40(3)	9(3)	13(3)	-3(4)
C(12)74(5)	50(4)	70(4)	12(4)	30(4)	8(4)
C(13)29(3)	63(5)	55(4)	13(3)	1(3)	-13(3)
C(14)38(4)	56(4)	97(5)	-2(4)	1(4)	1(3)
C(15)42(4)	78(5)	83(5)	-31(4)	5(4)	-16(4)
Cl(1A)87(13)	260(30)	61(9)	80(15)	-61(10)	-124(17)
Cl(1B)80(10)	86(7)	91(10)	-9(9)	24(8)	-17(8)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$).

	x	y	z	U(eq)
H(4)	1573	1898	8771	46
H(5A)	772	2217	6204	81
H(5B)	575	961	6986	81
H(5C)	1577	1162	6841	81
H(6A)	686	3772	9012	70
H(6B)	39	2538	8338	70
H(6C)	200	3828	7566	70
H(7)	3307	4249	8805	51
H(8A)	2598	4086	10372	83
H(8B)	3601	3412	10746	83
H(8C)	2708	2455	10353	83
H(9A)	3163	1349	8698	113
H(9B)	4103	2197	9137	113
H(9C)	3473	2274	7742	113
H(10)	2959	7829	5235	49
H(11A)	2607	5863	4016	83
H(11B)	1969	7118	3369	83
H(11C)	1563	5939	4025	83
H(12A)	1108	7760	5294	95
H(12B)	1551	8941	4687	95
H(12C)	1884	8741	6139	95
H(13)	3702	5751	7830	62
H(14A)	4005	4730	6122	102
H(14B)	4891	5506	6976	102
H(14C)	4288	6198	5726	102
H(15A)	4198	8219	6898	106
H(15B)	4594	7625	8257	106
H(15C)	3575	8238	7795	106

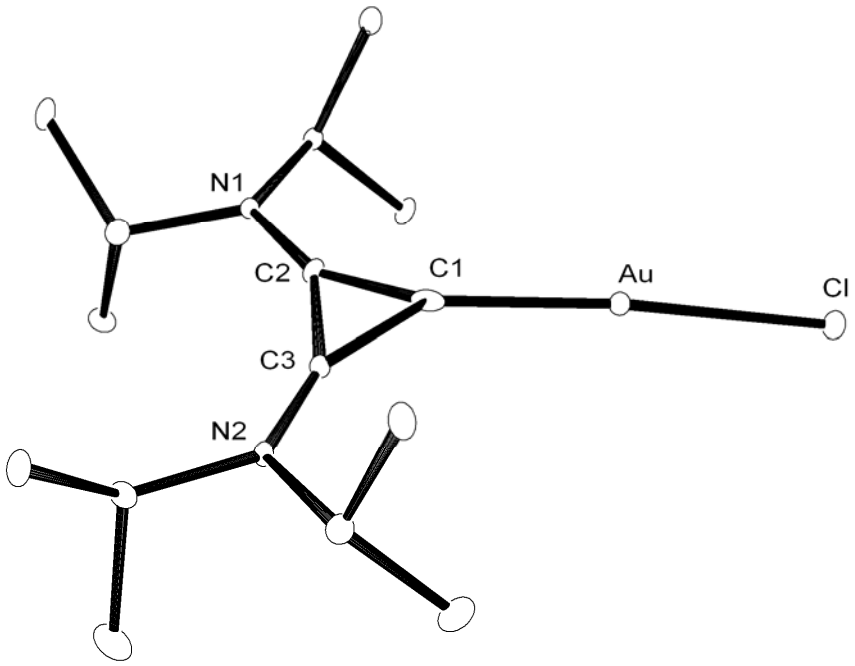

Table 1. Crystal data and structure refinement for compound **8** chapter 1.

Empirical formula	$C_{16}H_{30}AuCl_4N_2$	
Formula weight	589.19	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.4314(16) Å	α = 90°
	b = 15.911(3) Å	β = 90°
	c = 16.684(3) Å	γ = 90°
Volume	2238.2(7) $Å^3$	
Z	4	
Density (calculated)	1.748 g/cm^3	
Absorption coefficient	7.051 mm^{-1}	
F(000)	1148	
Crystal size	0.25 x 0.11 x 0.08 mm^3	

Theta range for data collection	1.77 to 23.24°
Index ranges	-9<=h<=9, -17<=k<=17, -18<=l<=18
Reflections collected	12771
Independent reflections	3216 [R(int) = 0.0631]
Completeness to theta = 23.24°	100.0 %
Absorption correction	Sadabs
Max. and min. transmission	0.6199 and 0.2706
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3216 / 96 / 253
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	R1 = 0.0616, wR2 = 0.1499
R indices (all data)	R1 = 0.0645, wR2 = 0.1525
Absolute structure parameter	0.01(2)
Extinction coefficient	0.0013(4)
Largest diff. peak and hole	6.864 and -0.746 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	2779(1)	7894(1)	1914(1)	24(1)
Cl(1)	4031(6)	9144(3)	1644(3)	33(1)
N(1)	890(16)	6051(8)	3490(8)	18(3)
N(2)	-813(16)	6164(8)	1449(7)	20(3)
C(1)	1500(20)	6873(11)	2176(10)	30(4)
C(2)	880(20)	6358(11)	2750(10)	24(4)
C(3)	203(18)	6407(10)	1984(10)	22(4)

	x	y	z	U(eq)
C(4)	1920(20)	6419(10)	4091(9)	22(4)
C(5)	3680(20)	6196(11)	3915(12)	34(5)
C(6)	1710(20)	7377(10)	4167(12)	33(4)
C(7)	-360(20)	5445(11)	3730(10)	29(4)
C(8)	-1710(20)	5892(12)	4150(11)	35(5)
C(9)	310(30)	4720(12)	4246(12)	39(5)
C(10)	-700(20)	6430(12)	606(11)	35(5)
C(11)	-880(30)	7371(13)	507(14)	52(6)
C(12)	900(20)	6147(13)	259(12)	43(5)
C(13)	-2210(20)	5653(10)	1695(10)	30(4)
C(14)	-2240(30)	4795(11)	1288(11)	40(5)
C(15)	-3820(30)	6109(16)	1558(17)	67(8)
C(16A)	7029(17)	8689(8)	3014(10)	39(3)
Cl(2A)	6007(9)	8042(4)	3661(4)	51(2)
Cl(3A)	8740(7)	8259(5)	2628(4)	50(2)
Cl(4A)	7423(9)	9666(4)	3487(5)	64(2)
C(16B)	7750(70)	8750(30)	3270(40)	44(3)
Cl(2B)	6220(90)	8290(40)	3810(40)	45(4)
Cl(3B)	8300(70)	8110(40)	2470(40)	45(4)
Cl(4B)	7350(80)	9770(30)	2980(40)	60(5)

Table 3. Bond lengths [Å] and angles [°].

Au(1)-C(1)	2.00(2)	Au(1)-Cl(1)	2.296(4)
N(1)-C(2)	1.33(2)	N(1)-C(4)	1.45(2)
N(1)-C(7)	1.48(2)	N(2)-C(3)	1.30(2)
N(2)-C(10)	1.47(2)	N(2)-C(13)	1.49(2)
C(1)-C(3)	1.36(2)	C(1)-C(2)	1.36(2)
C(2)-C(3)	1.40(2)	C(4)-C(6)	1.54(2)
C(4)-C(5)	1.56(2)	C(7)-C(8)	1.52(3)
C(7)-C(9)	1.55(2)	C(10)-C(11)	1.51(3)

C(10)-C(12)	1.53(3)	C(13)-C(14)	1.52(2)
C(13)-C(15)	1.55(3)		

C(16A)-Cl(3A)	1.720(12)	C(16A)-Cl(2A)	1.722(13)
C(16A)-Cl(4A)	1.776(12)	C(16B)-Cl(4B)	1.736(18)
C(16B)-Cl(3B)	1.736(18)	C(16B)-Cl(2B)	1.736(18)

C(1)-Au(1)-Cl(1)	174.3(5)	C(2)-N(1)-C(4)	119.9(14)
C(2)-N(1)-C(7)	119.0(14)	C(4)-N(1)-C(7)	120.1(13)
C(3)-N(2)-C(10)	122.1(14)	C(3)-N(2)-C(13)	119.8(13)
C(10)-N(2)-C(13)	118.0(13)	C(3)-C(1)-C(2)	62.0(13)
C(3)-C(1)-Au(1)	145.7(14)	C(2)-C(1)-Au(1)	148.0(13)
N(1)-C(2)-C(1)	150.6(17)	N(1)-C(2)-C(3)	150.6(16)
C(1)-C(2)-C(3)	58.8(12)	N(2)-C(3)-C(1)	149.0(17)
N(2)-C(3)-C(2)	151.7(16)	C(1)-C(3)-C(2)	59.2(12)
N(1)-C(4)-C(6)	112.7(14)	N(1)-C(4)-C(5)	110.5(13)
C(6)-C(4)-C(5)	110.6(15)	N(1)-C(7)-C(8)	110.7(14)
N(1)-C(7)-C(9)	112.0(15)	C(8)-C(7)-C(9)	111.7(15)
N(2)-C(10)-C(11)	112.5(17)	N(2)-C(10)-C(12)	109.4(15)
C(11)-C(10)-C(12)	109.7(17)	N(2)-C(13)-C(14)	112.2(15)
N(2)-C(13)-C(15)	113.2(15)	C(14)-C(13)-C(15)	110.0(17)

Cl(3A)-C(16A)-Cl(2A)	114.6(10)	Cl(3A)-C(16A)-Cl(4A)	110.9(8)
Cl(2A)-C(16A)-Cl(4A)	109.7(8)	Cl(4B)-C(16B)-Cl(3B)	113(2)
Cl(4B)-C(16B)-Cl(2B)	113(2)	Cl(3B)-C(16B)-Cl(2B)	111(2)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	24(1)	24(1)	23(1)	2(1)	-2(1)	-3(1)
Cl(1)	37(2)	28(2)	33(2)	4(2)	-2(2)	-8(2)
N(1)	21(5)	21(5)	13(5)	1(4)	1(4)	-2(4)
N(2)	30(8)	19(7)	11(7)	-2(6)	-6(6)	-9(6)
C(1)	27(9)	29(10)	33(10)	-22(8)	-4(7)	17(8)
C(2)	33(9)	20(9)	21(9)	4(7)	-2(7)	-2(8)
C(3)	20(8)	26(9)	20(9)	5(8)	4(8)	-2(7)
C(4)	28(10)	20(8)	19(8)	0(7)	-3(7)	-3(8)
C(5)	40(12)	18(9)	43(11)	-9(8)	-11(9)	-9(8)
C(6)	45(11)	13(9)	41(11)	2(7)	3(9)	-1(7)
C(7)	40(11)	29(10)	18(9)	-5(8)	-5(8)	-3(8)
C(8)	22(9)	52(12)	31(10)	7(9)	13(8)	4(8)
C(9)	54(13)	28(10)	34(11)	12(9)	-7(10)	-15(9)
C(10)	45(11)	36(11)	25(10)	3(8)	-15(9)	-11(10)
C(11)	60(14)	43(13)	53(14)	14(10)	8(11)	15(11)
C(12)	40(11)	45(13)	43(12)	7(10)	5(10)	-13(10)
C(13)	29(9)	31(9)	31(9)	-8(7)	-5(8)	-2(8)
C(14)	43(11)	29(10)	47(11)	3(8)	10(10)	-9(10)
C(15)	31(12)	61(17)	110(20)	-18(15)	-4(12)	4(11)
C(16A)	22(5)	64(5)	31(6)	-19(4)	8(5)	-16(5)
Cl(2A)	52(4)	44(4)	58(4)	16(3)	-2(3)	-11(3)
Cl(3A)	43(4)	67(4)	40(4)	-19(3)	8(3)	16(3)
Cl(4A)	48(4)	35(3)	110(5)	-25(3)	13(4)	-6(3)
C(16B)	30(6)	57(5)	45(6)	-20(5)	10(5)	-8(5)
Cl(2B)	38(7)	57(8)	39(8)	-8(7)	5(6)	-10(7)
Cl(3B)	33(8)	61(7)	40(7)	-19(6)	3(7)	5(8)
Cl(4B)	43(10)	39(6)	98(12)	-24(7)	18(11)	-24(8)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(4)	1636	6163	4620	27
H(5A)	3872	5604	4045	50
H(5B)	4376	6551	4243	50
H(5C)	3909	6293	3346	50
H(6A)	2112	7652	3683	50
H(6B)	2295	7580	4636	50
H(6C)	579	7509	4232	50
H(7)	-797	5190	3228	35
H(8A)	-1356	6092	4675	52
H(8B)	-2602	5502	4221	52
H(8C)	-2060	6372	3825	52
H(9A)	1283	4502	3996	59
H(9B)	-473	4269	4284	59
H(9C)	561	4930	4784	59
H(10)	-1568	6147	298	43
H(11A)	-1933	7497	285	78
H(11B)	-63	7581	142	78
H(11C)	-770	7646	1030	78
H(12A)	1760	6396	572	64
H(12B)	978	6331	-300	64
H(12C)	970	5533	284	64
H(13)	-2113	5551	2284	36
H(14A)	-2078	4865	710	60
H(14B)	-3264	4524	1385	60
H(14C)	-1388	4444	1509	60
H(15A)	-3761	6676	1786	100
H(15B)	-4667	5793	1820	100
H(15C)	-4030	6147	982	100
H(16A)	6311	8806	2550	59
H(16B)	8684	8771	3634	66

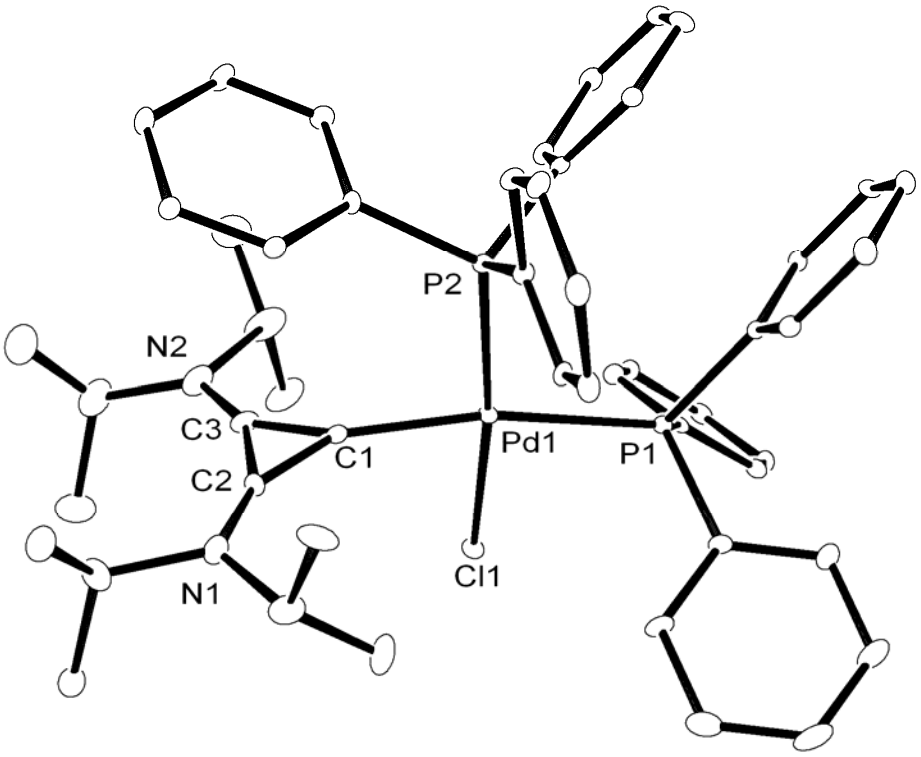

Table 1. Crystal data and structure refinement for compound **9** chapter 1.

Empirical formula	$C_{84}H_{136}Cl_4N_8Pd_2$	
Formula weight	1612.61	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 14.1563(4) Å	α = 90°
	b = 15.6293(4) Å	β = 89.995(10)°
	c = 19.7508(5) Å	γ = 90°
Volume	4369.9(2) $Å^3$	
Z	2	
Density (calculated)	1.226 g/cm^3	
Absorption coefficient	0.578 mm^{-1}	
F(000)	1712	

Crystal size	0.32 x 0.18 x 0.12 mm^3
Theta range for data collection	1.30 to 39.69°
Index ranges	-25<=h<=25, -27<=k<=26, -13<=l<=33
Reflections collected	82083
Independent reflections	41067 [R(int) = 0.0258]
Completeness to theta = 39.69°	90.6 %
Absorption correction	Sadabs
Max. and min. transmission	0.9338 and 0.8365
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	41067 / 1 / 876
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.1234
R indices (all data)	R1 = 0.0620, wR2 = 0.1342
Absolute structure parameter	0.00
Largest diff. peak and hole	1.710 and -2.756 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1A)	7514(1)	5469(1)	9999(1)	13(1)
Cl(1A)	6407(1)	4325(1)	10004(1)	39(1)
Cl(2A)	8585(2)	6552(1)	9999(2)	98(1)
N(1A)	9390(4)	3730(3)	9055(2)	15(1)
N(2A)	9378(4)	3702(3)	10961(2)	20(1)
N(3A)	5416(5)	7017(4)	9043(3)	18(1)
N(4A)	5403(4)	6991(4)	10947(3)	19(1)
C(1A)	8582(2)	4575(1)	9994(4)	9(1)
C(2A)	9096(5)	4034(4)	9657(3)	17(1)
C(3A)	9116(4)	3995(3)	10349(3)	13(1)

	x	y	z	U(eq)
C(4A)	6457(2)	6299(2)	9951(4)	16(1)
C(5A)	5728(4)	6766(4)	9641(3)	16(1)
C(6A)	5782(5)	6765(3)	10332(3)	16(1)
C(7A)	9923(6)	2895(4)	11019(4)	23(1)
C(8A)	9295(8)	2173(6)	11213(5)	43(2)
C(9A)	10724(5)	2975(5)	11511(3)	32(2)
C(10A)	8997(5)	4174(4)	11564(3)	21(1)
C(11A)	7940(5)	4072(5)	11615(3)	23(1)
C(12A)	9342(6)	5066(4)	11562(3)	26(2)
C(13A)	9027(4)	4147(4)	8437(3)	15(1)
C(14A)	9348(6)	5112(4)	8440(3)	23(1)
C(15A)	7948(6)	4121(5)	8394(3)	26(2)
C(16A)	9886(5)	2912(4)	8986(4)	21(1)
C(17A)	9195(7)	2188(5)	8782(6)	49(3)
C(18A)	10765(7)	2993(7)	8513(4)	50(2)
C(19A)	5886(5)	6649(4)	8432(3)	16(1)
C(20A)	5737(5)	5695(4)	8387(3)	25(2)
C(21A)	6885(6)	6916(6)	8396(4)	33(2)
C(22A)	4579(5)	7536(4)	8988(3)	19(1)
C(23A)	3755(7)	7037(6)	8683(5)	38(2)
C(24A)	4738(5)	8349(4)	8559(3)	20(1)
C(25A)	5808(5)	6651(5)	11558(4)	23(1)
C(26A)	5734(7)	5664(4)	11615(4)	34(2)
C(27A)	6894(5)	6915(5)	11613(3)	25(2)
C(28A)	4516(5)	7524(5)	11019(4)	21(1)
C(29A)	3722(5)	6979(5)	11315(5)	33(2)
C(30A)	4713(5)	8321(4)	11421(3)	25(1)
Pd(1B)	7555(1)	4413(1)	5002(1)	12(1)
Cl(1B)	6288(2)	5331(1)	4991(2)	95(1)
Cl(2B)	8878(1)	3486(1)	4994(1)	39(1)
N(1B)	5716(4)	2578(4)	4056(2)	18(1)

	x	y	z	U(eq)
N(2B)	5745(4)	2593(3)	5942(3)	16(1)
N(3B)	9043(5)	6439(3)	4042(3)	20(1)
N(4B)	9056(4)	6427(3)	5954(2)	15(1)
C(1B)	6617(2)	3422(2)	5010(4)	18(1)
C(2B)	6040(4)	2866(3)	4666(3)	18(1)
C(3B)	6035(4)	2881(3)	5360(3)	12(1)
C(4B)	8380(2)	5448(2)	5026(4)	11(1)
C(5B)	8802(5)	6124(4)	4650(3)	17(1)
C(6B)	8845(4)	6119(3)	5345(3)	13(1)
C(7B)	6050(4)	3030(4)	3441(3)	16(1)
C(8B)	5837(6)	3948(4)	3396(3)	25(1)
C(9B)	7181(5)	2822(5)	3344(4)	24(1)
C(10B)	4923(6)	2001(4)	4025(3)	22(1)
C(11B)	5069(6)	1296(4)	3524(4)	29(2)
C(12B)	3983(7)	2483(6)	3897(6)	61(3)
C(13B)	6121(5)	2970(4)	6576(3)	21(1)
C(14B)	7099(6)	2885(5)	6633(4)	29(1)
C(15B)	5827(7)	3954(4)	6578(3)	31(2)
C(16B)	4908(4)	1987(4)	5963(3)	17(1)
C(17B)	5051(7)	1256(4)	6472(3)	29(2)
C(18B)	4005(5)	2471(6)	6083(5)	44(2)
C(19B)	8860(6)	5867(4)	3444(3)	20(1)
C(20B)	9384(7)	5052(5)	3487(4)	29(2)
C(21B)	7811(6)	5763(5)	3343(4)	28(2)
C(22B)	9462(6)	7278(4)	3956(4)	17(1)
C(23B)	8808(6)	7896(5)	3656(4)	33(2)
C(24B)	10437(5)	7224(4)	3555(3)	22(1)
C(25B)	9502(5)	7293(4)	6040(3)	17(1)
C(26B)	10383(6)	7277(5)	6426(3)	24(1)
C(27B)	8784(4)	7914(4)	6387(3)	21(1)
C(28B)	8867(4)	5905(4)	6547(3)	15(1)

	x	y	z	U(eq)
C(29B)	9454(6)	5062(4)	6507(3)	23(1)
C(30B)	7810(5)	5704(5)	6649(3)	21(1)
C(1S)	6711(6)	9346(6)	2461(4)	40(2)
C(2S)	7137(7)	9640(6)	1889(4)	41(2)
C(3S)	7834(6)	10276(6)	1924(4)	39(2)
C(4S)	8074(7)	10596(6)	2552(4)	38(2)
C(5S)	7757(6)	10214(6)	3128(4)	32(2)
C(6S)	7023(6)	9592(5)	3094(4)	26(1)
C(7S)	7713(6)	237(5)	6867(4)	32(2)
C(8S)	8160(8)	548(6)	7465(4)	38(2)
C(9S)	7139(6)	-331(5)	8135(4)	31(2)
C(10S)	6864(8)	-724(6)	7535(4)	49(2)
C(11S)	7132(7)	-386(6)	6909(4)	38(2)
C(12S)	7795(5)	288(4)	8085(3)	26(1)
C(13S)	8124(3)	9985(3)	-12(6)	39(1)
C(14S)	7323(4)	10468(4)	-2(5)	43(1)
C(15S)	6437(3)	10062(3)	-23(6)	41(1)
C(16S)	6399(3)	9183(3)	16(6)	39(1)
C(17S)	7201(4)	8694(3)	12(6)	38(1)
C(18S)	8086(3)	9113(3)	0(6)	40(1)
C(19S)	6894(3)	9854(3)	5016(6)	35(1)
C(20S)	7726(4)	9374(4)	5004(6)	42(1)
C(21S)	8574(3)	9777(4)	4986(5)	47(1)
C(22S)	8637(3)	10653(3)	5005(5)	41(1)
C(23S)	7802(3)	11133(3)	4978(5)	32(1)
C(24S)	6957(3)	10745(3)	5016(6)	31(1)

Table 3. Bond lengths [Å] and angles [°].

Pd(1A)-C(4A)	1.982(3)	Pd(1A)-C(1A)	2.059(2)
Pd(1A)-Cl(2A)	2.272(3)	Pd(1A)-Cl(1A)	2.3777(10)
N(1A)-C(2A)	1.346(7)	N(1A)-C(16A)	1.465(8)
N(1A)-C(13A)	1.476(7)	N(2A)-C(3A)	1.345(7)
N(2A)-C(7A)	1.483(8)	N(2A)-C(10A)	1.501(8)
N(3A)-C(5A)	1.320(7)	N(3A)-C(22A)	1.439(9)
N(3A)-C(19A)	1.494(8)	N(4A)-C(6A)	1.375(8)
N(4A)-C(25A)	1.439(9)	N(4A)-C(28A)	1.513(9)
C(1A)-C(2A)	1.300(8)	C(1A)-C(3A)	1.373(7)
C(2A)-C(3A)	1.368(4)	C(4A)-C(5A)	1.405(7)
C(4A)-C(6A)	1.417(8)	C(5A)-C(6A)	1.366(4)
C(7A)-C(8A)	1.488(12)	C(7A)-C(9A)	1.499(9)
C(10A)-C(12A)	1.477(10)	C(10A)-C(11A)	1.508(11)
C(13A)-C(15A)	1.530(10)	C(13A)-C(14A)	1.576(8)
C(16A)-C(17A)	1.549(10)	C(16A)-C(18A)	1.561(12)
C(19A)-C(21A)	1.477(11)	C(19A)-C(20A)	1.510(9)
C(22A)-C(23A)	1.527(12)	C(22A)-C(24A)	1.545(9)
C(25A)-C(26A)	1.551(10)	C(25A)-C(27A)	1.595(11)
C(28A)-C(30A)	1.503(10)	C(28A)-C(29A)	1.527(11)
Pd(1B)-C(4B)	1.996(3)	Pd(1B)-C(1B)	2.040(3)
Pd(1B)-Cl(1B)	2.297(2)	Pd(1B)-Cl(2B)	2.3672(10)
N(1B)-C(2B)	1.366(7)	N(1B)-C(10B)	1.440(9)
N(1B)-C(7B)	1.483(8)	N(2B)-C(3B)	1.300(7)
N(2B)-C(13B)	1.482(8)	N(2B)-C(16B)	1.517(8)
N(3B)-C(5B)	1.342(8)	N(3B)-C(22B)	1.449(8)
N(3B)-C(19B)	1.504(8)	N(4B)-C(6B)	1.331(7)
N(4B)-C(28B)	1.451(8)	N(4B)-C(25B)	1.503(8)
C(1B)-C(3B)	1.369(7)	C(1B)-C(2B)	1.373(7)
C(2B)-C(3B)	1.371(4)	C(4B)-C(6B)	1.389(7)
C(4B)-C(5B)	1.422(8)	C(5B)-C(6B)	1.373(4)

C(7B)-C(8B)	1.468(8)	C(7B)-C(9B)	1.645(10)
C(10B)-C(11B)	1.495(10)	C(10B)-C(12B)	1.550(13)
C(13B)-C(14B)	1.395(11)	C(13B)-C(15B)	1.595(9)
C(16B)-C(18B)	1.505(9)	C(16B)-C(17B)	1.535(9)
C(19B)-C(20B)	1.476(10)	C(19B)-C(21B)	1.507(11)
C(22B)-C(23B)	1.463(11)	C(22B)-C(24B)	1.594(10)
C(25B)-C(26B)	1.461(10)	C(25B)-C(27B)	1.563(9)
C(28B)-C(30B)	1.541(9)	C(28B)-C(29B)	1.561(8)

C(1S)-C(2S)	1.360(12)	C(1S)-C(6S)	1.382(10)
C(2S)-C(3S)	1.403(11)	C(3S)-C(4S)	1.380(10)
C(4S)-C(5S)	1.362(11)	C(5S)-C(6S)	1.424(10)
C(7S)-C(11S)	1.278(11)	C(7S)-C(8S)	1.427(11)
C(8S)-C(12S)	1.389(11)	C(9S)-C(12S)	1.345(10)
C(9S)-C(10S)	1.390(11)	C(10S)-C(11S)	1.398(11)
C(13S)-C(18S)	1.364(7)	C(13S)-C(14S)	1.363(7)
C(14S)-C(15S)	1.406(7)	C(15S)-C(16S)	1.377(7)
C(16S)-C(17S)	1.368(7)	C(17S)-C(18S)	1.415(7)
C(19S)-C(24S)	1.395(6)	C(19S)-C(20S)	1.396(7)
C(20S)-C(21S)	1.357(8)	C(21S)-C(22S)	1.372(7)
C(22S)-C(23S)	1.401(6)	C(23S)-C(24S)	1.343(6)

C(4A)-Pd(1A)-C(1A)	176.5(3)	C(4A)-Pd(1A)-Cl(2A)	90.96(11)
C(1A)-Pd(1A)-Cl(2A)	90.85(7)	C(4A)-Pd(1A)-Cl(1A)	89.74(9)
C(1A)-Pd(1A)-Cl(1A)	88.46(7)	Cl(2A)-Pd(1A)-Cl(1A)	179.27(6)
C(2A)-N(1A)-C(16A)	122.6(5)	C(2A)-N(1A)-C(13A)	117.9(5)
C(16A)-N(1A)-C(13A)	118.3(5)	C(3A)-N(2A)-C(7A)	120.1(5)
C(3A)-N(2A)-C(10A)	116.5(5)	C(7A)-N(2A)-C(10A)	123.0(5)
C(5A)-N(3A)-C(22A)	120.7(5)	C(5A)-N(3A)-C(19A)	117.4(6)
C(22A)-N(3A)-C(19A)	121.4(5)	C(6A)-N(4A)-C(25A)	119.4(5)
C(6A)-N(4A)-C(28A)	123.3(5)	C(25A)-N(4A)-C(28A)	117.1(5)
C(2A)-C(1A)-C(3A)	61.48(18)	C(2A)-C(1A)-Pd(1A)	148.8(6)
C(3A)-C(1A)-Pd(1A)	148.3(6)	C(1A)-C(2A)-N(1A)	148.8(6)
C(1A)-C(2A)-C(3A)	61.9(5)	N(1A)-C(2A)-C(3A)	149.3(7)

N(2A)-C(3A)-C(2A)	156.8(7)	N(2A)-C(3A)-C(1A)	146.6(6)
C(2A)-C(3A)-C(1A)	56.6(5)	C(5A)-C(4A)-C(6A)	57.91(19)
C(5A)-C(4A)-Pd(1A)	156.3(5)	C(6A)-C(4A)-Pd(1A)	145.0(5)
N(3A)-C(5A)-C(6A)	155.9(7)	N(3A)-C(5A)-C(4A)	142.1(6)
C(6A)-C(5A)-C(4A)	61.5(5)	C(5A)-C(6A)-N(4A)	149.3(7)
C(5A)-C(6A)-C(4A)	60.6(5)	N(4A)-C(6A)-C(4A)	149.9(5)
N(2A)-C(7A)-C(8A)	110.7(7)	N(2A)-C(7A)-C(9A)	111.9(6)
C(8A)-C(7A)-C(9A)	110.4(7)	C(12A)-C(10A)-N(2A)	110.0(6)
C(12A)-C(10A)-C(11A)	115.4(7)	N(2A)-C(10A)-C(11A)	111.0(6)
N(1A)-C(13A)-C(15A)	112.4(5)	N(1A)-C(13A)-C(14A)	108.6(4)
C(15A)-C(13A)-C(14A)	108.3(6)	N(1A)-C(16A)-C(17A)	111.0(6)
N(1A)-C(16A)-C(18A)	111.5(6)	C(17A)-C(16A)-C(18A)	114.0(7)
C(21A)-C(19A)-N(3A)	110.9(5)	C(21A)-C(19A)-C(20A)	114.2(6)
N(3A)-C(19A)-C(20A)	111.4(5)	N(3A)-C(22A)-C(23A)	111.8(6)
N(3A)-C(22A)-C(24A)	112.7(6)	C(23A)-C(22A)-C(24A)	108.3(6)
N(4A)-C(25A)-C(26A)	113.7(6)	N(4A)-C(25A)-C(27A)	110.2(6)
C(26A)-C(25A)-C(27A)	108.5(6)	C(30A)-C(28A)-N(4A)	110.6(6)
C(30A)-C(28A)-C(29A)	113.4(6)	N(4A)-C(28A)-C(29A)	109.8(6)

C(4B)-Pd(1B)-C(1B)	174.89(16)	C(4B)-Pd(1B)-Cl(1B)	87.19(9)
C(1B)-Pd(1B)-Cl(1B)	88.03(9)	C(4B)-Pd(1B)-Cl(2B)	91.93(7)
C(1B)-Pd(1B)-Cl(2B)	92.88(8)	Cl(1B)-Pd(1B)-Cl(2B)	178.67(11)
C(2B)-N(1B)-C(10B)	120.4(6)	C(2B)-N(1B)-C(7B)	117.3(5)
C(10B)-N(1B)-C(7B)	120.8(4)	C(3B)-N(2B)-C(13B)	119.7(5)
C(3B)-N(2B)-C(16B)	119.1(5)	C(13B)-N(2B)-C(16B)	120.4(5)
C(5B)-N(3B)-C(22B)	122.7(6)	C(5B)-N(3B)-C(19B)	116.2(5)
C(22B)-N(3B)-C(19B)	121.1(5)	C(6B)-N(4B)-C(28B)	119.0(5)
C(6B)-N(4B)-C(25B)	121.5(5)	C(28B)-N(4B)-C(25B)	119.5(5)
C(3B)-C(1B)-C(2B)	60.0(2)	C(3B)-C(1B)-Pd(1B)	149.9(6)
C(2B)-C(1B)-Pd(1B)	149.8(6)	N(1B)-C(2B)-C(3B)	152.4(7)
N(1B)-C(2B)-C(1B)	147.7(6)	C(3B)-C(2B)-C(1B)	59.9(5)
N(2B)-C(3B)-C(1B)	148.2(6)	N(2B)-C(3B)-C(2B)	151.6(7)
C(1B)-C(3B)-C(2B)	60.1(5)	C(6B)-C(4B)-C(5B)	58.47(18)
C(6B)-C(4B)-Pd(1B)	154.1(6)	C(5B)-C(4B)-Pd(1B)	146.7(6)

N(3B)-C(5B)-C(6B)	152.2(8)	N(3B)-C(5B)-C(4B)	147.7(6)
C(6B)-C(5B)-C(4B)	59.6(5)	N(4B)-C(6B)-C(5B)	155.7(7)
N(4B)-C(6B)-C(4B)	142.2(6)	C(5B)-C(6B)-C(4B)	62.0(5)
C(8B)-C(7B)-N(1B)	116.8(6)	C(8B)-C(7B)-C(9B)	112.7(6)
N(1B)-C(7B)-C(9B)	108.1(5)	N(1B)-C(10B)-C(11B)	112.5(7)
N(1B)-C(10B)-C(12B)	111.9(5)	C(11B)-C(10B)-C(12B)	111.7(7)
C(14B)-C(13B)-N(2B)	112.8(7)	C(14B)-C(13B)-C(15B)	110.5(7)
N(2B)-C(13B)-C(15B)	106.9(5)	C(18B)-C(16B)-N(2B)	110.7(5)
C(18B)-C(16B)-C(17B)	112.5(7)	N(2B)-C(16B)-C(17B)	112.3(5)
C(20B)-C(19B)-N(3B)	112.4(6)	C(20B)-C(19B)-C(21B)	114.2(7)
N(3B)-C(19B)-C(21B)	109.8(6)	N(3B)-C(22B)-C(23B)	112.7(7)
N(3B)-C(22B)-C(24B)	111.4(5)	C(23B)-C(22B)-C(24B)	112.4(6)
C(26B)-C(25B)-N(4B)	113.8(6)	C(26B)-C(25B)-C(27B)	109.7(5)
N(4B)-C(25B)-C(27B)	109.6(6)	N(4B)-C(28B)-C(30B)	113.6(5)
N(4B)-C(28B)-C(29B)	109.7(5)	C(30B)-C(28B)-C(29B)	110.5(6)

C(2S)-C(1S)-C(6S)	121.0(7)	C(1S)-C(2S)-C(3S)	120.7(7)
C(4S)-C(3S)-C(2S)	118.3(7)	C(5S)-C(4S)-C(3S)	120.8(8)
C(4S)-C(5S)-C(6S)	120.0(7)	C(1S)-C(6S)-C(5S)	117.8(7)
C(11S)-C(7S)-C(8S)	119.4(7)	C(12S)-C(8S)-C(7S)	117.7(8)
C(12S)-C(9S)-C(10S)	116.7(7)	C(9S)-C(10S)-C(11S)	120.7(8)
C(7S)-C(11S)-C(10S)	121.4(8)	C(9S)-C(12S)-C(8S)	122.1(7)
C(18S)-C(13S)-C(14S)	121.4(5)	C(13S)-C(14S)-C(15S)	119.4(5)
C(16S)-C(15S)-C(14S)	119.0(4)	C(17S)-C(16S)-C(15S)	121.6(4)
C(16S)-C(17S)-C(18S)	118.5(4)	C(13S)-C(18S)-C(17S)	119.8(4)
C(24S)-C(19S)-C(20S)	118.9(4)	C(21S)-C(20S)-C(19S)	119.9(5)
C(20S)-C(21S)-C(22S)	121.3(4)	C(21S)-C(22S)-C(23S)	118.6(4)
C(24S)-C(23S)-C(22S)	120.5(4)	C(23S)-C(24S)-C(19S)	120.5(4)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1A)	16(1)	12(1)	10(1)	0(1)	-1(1)	2(1)
Cl(1A)	37(1)	42(1)	38(1)	6(1)	-23(1)	-11(1)
Cl(2A)	96(1)	82(1)	116(2)	-69(1)	-64(2)	32(1)
N(1A)	18(2)	10(2)	16(2)	2(1)	-6(2)	6(2)
N(2A)	31(3)	21(2)	8(2)	3(2)	-10(2)	1(2)
N(3A)	25(3)	21(2)	8(2)	2(2)	-3(2)	4(2)
N(4A)	17(2)	20(2)	18(2)	-1(2)	-2(2)	7(2)
C(2A)	27(3)	20(2)	5(2)	3(2)	-8(2)	-3(2)
C(3A)	11(2)	9(2)	20(2)	-2(2)	-4(2)	5(2)
C(4A)	24(1)	14(1)	10(2)	-5(2)	-9(2)	6(1)
C(5A)	6(2)	23(3)	19(2)	-2(2)	-3(1)	3(2)
C(6A)	33(3)	8(2)	8(2)	1(1)	-5(2)	1(2)
C(7A)	26(3)	23(3)	21(3)	3(2)	1(2)	19(2)
C(8A)	34(3)	31(4)	63(5)	12(3)	15(3)	14(3)
C(9A)	22(2)	54(5)	21(3)	-2(3)	-10(2)	22(3)
C(10A)	39(3)	17(2)	9(2)	1(2)	-6(2)	5(2)
C(11A)	24(3)	23(3)	20(3)	1(2)	-1(2)	4(2)
C(12A)	36(4)	24(3)	17(3)	-3(2)	-4(2)	1(3)
C(13A)	14(2)	17(2)	13(2)	4(2)	-4(2)	-4(2)
C(14A)	37(4)	13(2)	19(3)	1(2)	-1(2)	-13(2)
C(15A)	32(3)	33(3)	12(3)	3(2)	-8(2)	-8(3)
C(16A)	20(3)	24(3)	19(3)	-7(2)	-1(2)	1(2)
C(17A)	38(4)	10(2)	98(7)	-10(3)	-21(4)	2(2)
C(18A)	52(5)	67(6)	30(4)	-10(4)	-5(3)	19(5)
C(19A)	23(2)	15(2)	9(2)	-4(2)	4(2)	7(2)
C(20A)	28(3)	20(3)	27(3)	-12(2)	-9(2)	7(2)
C(21A)	34(4)	43(4)	20(4)	-6(3)	2(3)	-10(3)
C(22A)	24(3)	19(2)	14(3)	5(2)	-1(2)	5(2)

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(23A)37(4)	31(3)	46(5)	16(3)	-6(3)	-6(3)
C(24A)34(3)	10(2)	16(2)	0(2)	-4(2)	-6(2)
C(25A)23(2)	28(3)	18(3)	-5(2)	6(2)	4(2)
C(26A)63(5)	20(3)	20(4)	1(2)	5(3)	2(3)
C(27A)24(3)	30(3)	21(3)	-7(2)	-9(2)	9(3)
C(28A)15(2)	28(3)	21(3)	-8(2)	-4(2)	11(2)
C(29A)8(2)	32(4)	59(5)	-15(3)	6(2)	-3(2)
C(30A)18(2)	29(3)	28(3)	-7(2)	0(2)	13(2)
Pd(1B)15(1)	10(1)	10(1)	0(1)	0(1)	-2(1)
Cl(1B)110(2)	63(1)	113(2)	2(2)	-83(2)	-4(1)
Cl(2B)44(1)	31(1)	41(1)	-2(1)	-19(1)	5(1)
N(1B)24(2)	21(2)	9(2)	-1(2)	-9(2)	-3(2)
N(2B)16(2)	11(2)	22(2)	-2(2)	-3(2)	-7(2)
N(3B)36(3)	16(2)	7(2)	1(2)	0(2)	-5(2)
N(4B)19(2)	15(2)	11(2)	0(2)	-2(2)	-9(2)
C(2B)18(2)	7(2)	30(3)	1(2)	-9(2)	-8(2)
C(3B)15(2)	17(2)	5(2)	1(1)	-3(1)	2(2)
C(4B)9(1)	16(1)	8(1)	1(2)	5(2)	3(1)
C(5B)21(3)	19(3)	11(2)	-1(2)	-5(2)	-3(2)
C(6B)17(2)	10(2)	11(2)	0(2)	-4(2)	-5(2)
C(7B)18(2)	19(2)	12(2)	-1(2)	-6(2)	-6(2)
C(8B)31(3)	20(3)	23(3)	8(2)	-2(3)	4(3)
C(9B)25(2)	29(3)	18(3)	2(2)	6(2)	4(2)
C(10B)29(3)	16(3)	20(3)	6(2)	-9(2)	-5(3)
C(11B)42(4)	19(3)	25(4)	3(2)	-3(3)	-16(3)
C(12B)40(5)	28(4)	116(9)	-11(5)	-17(5)	-16(4)
C(13B)34(3)	11(2)	17(3)	-1(2)	-5(2)	2(2)
C(14B)28(3)	33(3)	25(3)	-3(2)	-10(2)	2(2)
C(15B)52(5)	17(3)	25(3)	-6(2)	17(3)	-11(3)
C(16B)12(2)	15(3)	23(3)	5(2)	0(2)	-3(2)

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(17B)48(5)	21(3)	18(3)	7(2)	2(3)	-8(3)
C(18B)10(2)	33(4)	89(7)	5(4)	14(3)	8(2)
C(19B)38(3)	17(2)	6(2)	-2(2)	1(2)	-12(2)
C(20B)34(3)	32(3)	19(3)	7(2)	4(2)	3(3)
C(21B)36(4)	36(3)	13(3)	1(2)	-8(2)	-7(3)
C(22B)23(3)	11(2)	17(3)	-2(2)	3(2)	-5(2)
C(23B)46(4)	27(3)	27(4)	-3(2)	9(3)	-13(3)
C(24B)18(2)	18(2)	29(3)	6(2)	8(2)	-7(2)
C(25B)18(3)	21(3)	12(3)	-4(2)	2(2)	-5(2)
C(26B)23(3)	36(3)	13(3)	1(2)	-2(2)	0(2)
C(27B)20(2)	12(2)	32(3)	-7(2)	-2(2)	9(2)
C(28B)18(2)	15(2)	13(3)	-1(2)	-1(2)	4(2)
C(29B)35(3)	17(2)	17(3)	7(2)	1(2)	9(2)
C(30B)18(2)	26(3)	18(3)	7(2)	2(2)	-2(2)
C(1S)33(2)	68(5)	19(3)	-4(3)	0(2)	-32(3)
C(2S)61(5)	46(5)	16(3)	-8(3)	-18(3)	-9(4)
C(3S)40(4)	55(5)	22(4)	8(3)	-3(3)	-29(3)
C(4S)44(4)	48(4)	20(3)	-3(3)	2(3)	-28(3)
C(5S)26(3)	50(4)	20(3)	-8(3)	-4(2)	-4(3)
C(6S)24(2)	28(3)	25(3)	-2(2)	1(2)	-16(2)
C(7S)49(5)	28(3)	17(3)	2(2)	1(3)	-15(3)
C(8S)41(4)	42(4)	30(4)	-1(3)	4(3)	-18(3)
C(9S)30(3)	38(4)	24(3)	3(3)	-4(2)	-15(3)
C(10S)66(6)	45(4)	37(4)	6(3)	9(3)	-28(4)
C(11S)41(4)	55(4)	16(3)	3(3)	-1(2)	-2(3)
C(12S)30(3)	29(3)	17(3)	-1(2)	0(2)	9(2)
C(13S)42(2)	49(2)	25(2)	9(5)	5(5)	-13(2)
C(14S)73(3)	25(2)	30(2)	3(4)	18(6)	5(2)
C(15S)44(2)	54(2)	26(2)	5(4)	-8(4)	19(2)
C(16S)49(2)	48(2)	19(2)	5(4)	14(4)	-14(2)
C(17S)59(2)	28(2)	28(2)	3(4)	-1(5)	5(2)

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(18S)48(2)	48(2)	24(2)	-1(6)	-2(6)	12(2)
C(19S)42(2)	46(2)	18(2)	2(4)	-2(4)	-10(2)
C(20S)74(3)	33(2)	20(2)	-2(4)	2(6)	11(3)
C(21S)50(2)	69(3)	24(2)	-24(4)	-5(4)	34(2)
C(22S)30(2)	68(3)	23(2)	-1(5)	-11(4)	0(2)
C(23S)46(2)	31(2)	20(2)	8(3)	2(4)	-5(2)
C(24S)30(2)	40(2)	24(2)	9(4)	7(4)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(7A)	10197	2764	10564	28
H(8A1)	9082	2250	11681	64
H(8A2)	9643	1633	11175	64
H(8A3)	8747	2159	10910	64
H(9A1)	11249	3282	11297	48
H(9A2)	10936	2403	11648	48
H(9A3)	10512	3292	11912	48
H(10A)	9273	3894	11974	26
H(11A)	7634	4414	11263	34
H(11B)	7727	4266	12062	34
H(11C)	7773	3468	11555	34
H(12A)	10034	5068	11550	39
H(12B)	9125	5358	11972	39
H(12C)	9097	5364	11162	39
H(13A)	9299	3855	8031	18
H(14A)	9177	5376	8873	35
H(14B)	9033	5418	8070	35
H(14C)	10034	5144	8378	35

	x	y	z	U(eq)
H(15A)	7738	3527	8344	38
H(15B)	7738	4456	8003	38
H(15C)	7678	4364	8809	38
H(16A)	10132	2763	9446	25
H(17A)	8797	2039	9171	73
H(17B)	9555	1684	8639	73
H(17C)	8795	2384	8408	73
H(18A)	10560	2979	8040	75
H(18B)	11198	2516	8599	75
H(18C)	11089	3535	8604	75
H(19A)	5563	6905	8029	19
H(20A)	6010	5418	8787	38
H(20B)	6046	5474	7979	38
H(20C)	5059	5571	8366	38
H(21A)	6923	7542	8400	49
H(21B)	7168	6698	7977	49
H(21C)	7229	6686	8786	49
H(22A)	4393	7719	9455	23
H(23A)	3936	6821	8235	57
H(23B)	3207	7415	8638	57
H(23C)	3595	6555	8978	57
H(24A)	5272	8673	8743	30
H(24B)	4167	8704	8571	30
H(24C)	4874	8186	8090	30
H(25A)	5466	6909	11952	28
H(26A)	5107	5479	11465	52
H(26B)	5830	5492	12087	52
H(26C)	6218	5398	11330	52
H(27A)	7265	6577	11291	37
H(27B)	7121	6805	12074	37
H(27C)	6963	7525	11508	37

	x	y	z	U(eq)
H(28A)	4318	7705	10555	25
H(29A)	3679	6439	11065	50
H(29B)	3122	7289	11279	50
H(29C)	3856	6859	11793	50
H(30A)	4733	8180	11904	38
H(30B)	4211	8741	11339	38
H(30C)	5321	8562	11282	38
H(7B)	5720	2755	3050	20
H(8B1)	5170	4044	3506	37
H(8B2)	5963	4150	2935	37
H(8B3)	6235	4263	3717	37
H(9B1)	7532	3039	3735	36
H(9B2)	7411	3100	2931	36
H(9B3)	7272	2202	3308	36
H(10B)	4869	1727	4480	26
H(11D)	4873	1489	3074	43
H(11E)	4691	798	3657	43
H(11F)	5739	1137	3514	43
H(12D)	3937	2971	4206	92
H(12E)	3451	2094	3975	92
H(12F)	3966	2688	3428	92
H(13B)	5816	2679	6971	25
H(14D)	7281	2294	6529	43
H(14E)	7294	3025	7097	43
H(14F)	7410	3275	6315	43
H(15D)	6072	4232	6169	47
H(15E)	6092	4234	6979	47
H(15F)	5137	4002	6586	47
H(16B)	4858	1720	5504	20
H(17D)	5555	878	6312	43
H(17E)	4463	930	6516	43

	x	y	z	U(eq)
H(17F)	5225	1495	6914	43
H(18D)	3988	2675	6552	66
H(18E)	3465	2092	6001	66
H(18F)	3973	2961	5775	66
H(19B)	9104	6175	3036	24
H(20D)	10057	5171	3552	43
H(20E)	9296	4728	3066	43
H(20F)	9146	4717	3870	43
H(21D)	7549	5417	3713	42
H(21E)	7692	5476	2910	42
H(21F)	7508	6327	3342	42
H(22B)	9614	7493	4420	21
H(23D)	8554	7663	3232	50
H(23E)	9144	8431	3562	50
H(23F)	8289	8006	3972	50
H(24D)	10870	6840	3795	32
H(24E)	10719	7796	3527	32
H(24F)	10324	7004	3098	32
H(25B)	9645	7524	5579	20
H(26D)	10242	7181	6906	36
H(26E)	10710	7826	6373	36
H(26F)	10786	6815	6257	36
H(27D)	8160	7842	6181	32
H(27E)	8996	8506	6326	32
H(27F)	8748	7783	6872	32
H(28B)	9088	6231	6952	18
H(29D)	9258	4732	6110	35
H(29E)	9346	4722	6917	35
H(29F)	10127	5201	6471	35
H(30D)	7458	6240	6703	31
H(30E)	7731	5352	7056	31

	x	y	z	U(eq)
H(30F)	7570	5393	6254	31
H(1S)	6190	8965	2424	48
H(2S)	6960	9412	1461	49
H(3S)	8134	10482	1525	47
H(4S)	8465	11088	2582	45
H(5S)	8024	10363	3553	38
H(6S)	6757	9354	3493	31
H(7S)	7847	491	6440	38
H(8S)	8690	921	7441	45
H(9S)	6877	-492	8559	37
H(10S)	6489	-1228	7551	59
H(11S)	6877	-624	6506	45
H(12S)	8016	556	8487	31
H(13S)	8721	10261	-27	47
H(14S)	7362	11075	20	51
H(15S)	5874	10388	-65	49
H(16S)	5801	8909	47	47
H(17S)	7163	8087	17	46
H(18S)	8654	8788	1	48
H(19S)	6296	9579	5024	42
H(20S)	7697	8767	5008	51
H(21S)	9136	9446	4961	57
H(22S)	9234	10928	5035	49
H(23S)	7833	11737	4933	39
H(24S)	6398	11079	5043	37

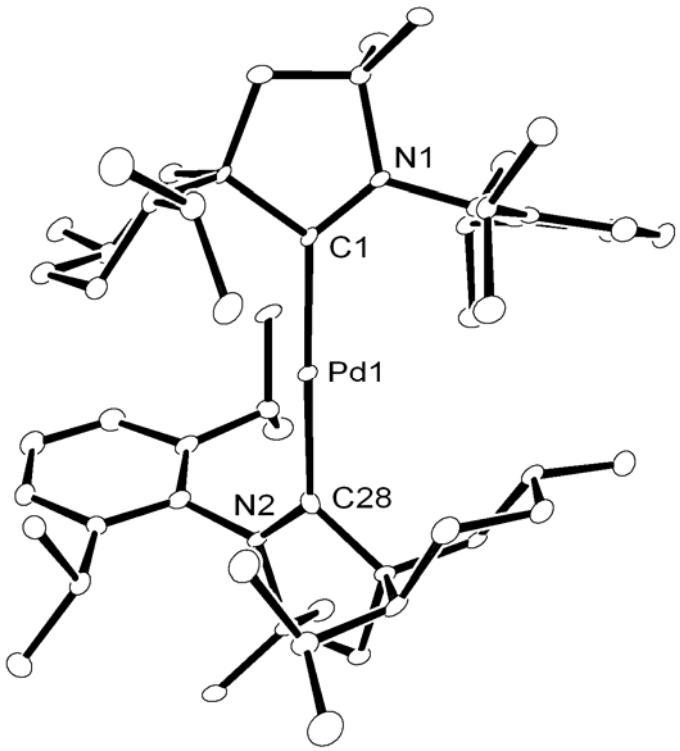

Table 1. Crystal data and structure refinement for compound **2** chapter 2.

Empirical formula	$C_{54}H_{86}N_2Pd$	
Formula weight	869.65	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.3028(13) Å	α = 90°
	b = 11.5737(13) Å	β = 90°
	c = 45.065(5) Å	γ = 90°
Volume	5895.1(12) $Å^3$	
Z	4	
Density (calculated)	0.980 g/cm^3	
Absorption coefficient	0.344 mm^{-1}	
F(000)	1880	

Crystal size	0.36 x 0.26 x 0.13 mm^3
Theta range for data collection	1.81 to 23.30°
Index ranges	-12<=h<=12, -12<=k<=11, -50<=l<=50
Reflections collected	33398
Independent reflections	8484 [R(int) = 0.0784]
Completeness to theta = 23.30°	99.8 %
Absorption correction	Sadabs
Max. and min. transmission	0.9566 and 0.8861
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8484 / 0 / 533
Goodness-of-fit on F^2	0.993
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.0809
R indices (all data)	R1 = 0.0525, wR2 = 0.0840
Absolute structure parameter	0.01(2)
Extinction coefficient	0.00006(5)
Largest diff. peak and hole	0.696 and -0.520 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	9237(1)	5853(1)	1188(1)	17(1)
N(1)	8890(3)	4269(3)	651(1)	15(1)
N(2)	10472(3)	7435(3)	1635(1)	17(1)
C(1)	8947(3)	4391(3)	943(1)	13(1)
C(2)	8903(4)	3147(4)	1070(1)	19(1)
C(3)	10111(4)	2787(4)	1208(1)	23(1)
C(4)	10383(4)	3198(4)	1529(1)	27(1)
C(5)	9353(4)	2963(4)	1734(1)	30(1)
C(6)	8225(4)	3465(4)	1604(1)	27(1)
C(7)	7914(4)	2937(4)	1309(1)	22(1)
C(8)	8660(4)	2355(4)	797(1)	25(1)

	x	y	z	U(eq)
C(9)	8939(4)	3036(4)	524(1)	20(1)
C(10)	8834(4)	5213(4)	437(1)	20(1)
C(11)	9868(4)	5692(4)	326(1)	18(1)
C(12)	9774(4)	6469(4)	85(1)	24(1)
C(13)	8681(4)	6790(4)	-21(1)	28(1)
C(14)	7671(4)	6359(4)	105(1)	26(1)
C(15)	7721(4)	5576(4)	334(1)	17(1)
C(16)	10189(4)	2810(4)	404(1)	34(1)
C(17)	8051(4)	2827(4)	281(1)	30(1)
C(18)	11540(4)	2601(4)	1633(1)	35(1)
C(19)	6634(4)	3241(4)	1207(1)	28(1)
C(20)	6253(4)	4468(4)	1284(1)	33(1)
C(21)	5758(5)	2378(4)	1334(1)	45(1)
C(22)	11115(4)	5490(4)	448(1)	21(1)
C(23)	11526(4)	6600(4)	600(1)	29(1)
C(24)	12026(4)	5129(4)	211(1)	30(1)
C(25)	6540(4)	5150(4)	456(1)	20(1)
C(26)	5903(4)	6123(4)	627(1)	29(1)
C(27)	5689(4)	4705(4)	214(1)	32(1)
C(28)	9701(4)	7324(4)	1414(1)	21(1)
C(29)	9294(4)	8568(3)	1332(1)	19(1)
C(30)	9717(4)	8908(4)	1017(1)	21(1)
C(31)	8993(4)	8492(4)	751(1)	23(1)
C(32)	7691(4)	8743(4)	804(1)	31(1)
C(33)	7274(4)	8237(4)	1094(1)	30(1)
C(34)	7933(4)	8772(4)	1353(1)	26(1)
C(35)	9926(4)	9376(4)	1555(1)	22(1)
C(36)	10875(4)	8678(3)	1717(1)	22(1)
C(37)	11041(4)	6484(4)	1791(1)	23(1)
C(38)	12103(4)	6010(4)	1680(1)	23(1)
C(39)	12686(4)	5196(4)	1859(1)	31(1)

	x	y	z	U(eq)
C(40)	12274(5)	4859(4)	2132(1)	35(1)
C(41)	11212(4)	5320(4)	2227(1)	31(1)
C(42)	10585(4)	6138(4)	2067(1)	23(1)
C(43)	12113(4)	8914(4)	1601(1)	33(1)
C(44)	10841(5)	8892(3)	2048(1)	28(1)
C(45)	9459(4)	9078(4)	470(1)	34(1)
C(46)	7392(4)	8476(4)	1656(1)	29(1)
C(47)	6922(4)	7217(4)	1678(1)	37(1)
C(48)	6398(5)	9315(5)	1733(1)	54(2)
C(49)	12611(4)	6241(4)	1374(1)	24(1)
C(50)	13892(4)	6659(4)	1387(1)	37(1)
C(51)	12531(4)	5120(3)	1187(1)	30(1)
C(52)	9399(4)	6549(4)	2191(1)	23(1)
C(53)	8491(4)	5563(4)	2193(1)	31(1)
C(54)	9507(4)	7014(4)	2509(1)	34(1)

Table 3. Bond lengths [Å] and angles [°].

Pd(1)-C(1)	2.046(4)	Pd(1)-C(28)	2.053(4)
N(1)-C(1)	1.323(4)	N(1)-C(10)	1.460(5)
N(1)-C(9)	1.540(5)	N(2)-C(28)	1.331(5)
N(2)-C(37)	1.456(5)	N(2)-C(36)	1.553(5)
C(1)-C(2)	1.549(5)	C(2)-C(8)	1.557(6)
C(2)-C(3)	1.558(6)	C(2)-C(7)	1.572(6)
C(3)-C(4)	1.551(6)	C(4)-C(5)	1.511(6)
C(4)-C(18)	1.553(6)	C(5)-C(6)	1.517(6)
C(6)-C(7)	1.508(6)	C(7)-C(19)	1.558(6)
C(8)-C(9)	1.497(6)	C(9)-C(17)	1.505(6)
C(9)-C(16)	1.534(6)	C(10)-C(11)	1.386(6)

C(10)-C(15)	1.406(6)	C(11)-C(12)	1.418(6)
C(11)-C(22)	1.529(6)	C(12)-C(13)	1.375(6)
C(13)-C(14)	1.371(6)	C(14)-C(15)	1.373(6)
C(15)-C(25)	1.525(6)	C(19)-C(21)	1.518(6)
C(19)-C(20)	1.524(6)	C(22)-C(23)	1.528(6)
C(22)-C(24)	1.540(6)	C(25)-C(26)	1.543(6)
C(25)-C(27)	1.545(6)	C(28)-C(29)	1.556(6)
C(29)-C(30)	1.549(5)	C(29)-C(35)	1.550(5)
C(29)-C(34)	1.559(6)	C(30)-C(31)	1.528(5)
C(31)-C(32)	1.519(6)	C(31)-C(45)	1.530(6)
C(32)-C(33)	1.506(6)	C(33)-C(34)	1.516(6)
C(34)-C(46)	1.535(6)	C(35)-C(36)	1.527(6)
C(36)-C(44)	1.513(5)	C(36)-C(43)	1.519(6)
C(37)-C(42)	1.404(6)	C(37)-C(38)	1.411(6)
C(38)-C(39)	1.407(6)	C(38)-C(49)	1.515(6)
C(39)-C(40)	1.370(6)	C(40)-C(41)	1.380(6)
C(41)-C(42)	1.386(6)	C(42)-C(52)	1.528(6)
C(46)-C(48)	1.525(6)	C(46)-C(47)	1.554(6)
C(49)-C(50)	1.528(6)	C(49)-C(51)	1.550(5)
C(52)-C(53)	1.535(6)	C(52)-C(54)	1.535(6)

C(1)-Pd(1)-C(28)	173.99(16)	C(1)-N(1)-C(10)	125.4(3)
C(1)-N(1)-C(9)	117.9(3)	C(10)-N(1)-C(9)	116.6(3)
C(28)-N(2)-C(37)	125.3(4)	C(28)-N(2)-C(36)	117.3(3)
C(37)-N(2)-C(36)	117.2(3)	N(1)-C(1)-C(2)	105.4(3)
N(1)-C(1)-Pd(1)	129.1(3)	C(2)-C(1)-Pd(1)	125.1(3)
C(1)-C(2)-C(8)	105.2(3)	C(1)-C(2)-C(3)	111.6(3)
C(8)-C(2)-C(3)	108.3(3)	C(1)-C(2)-C(7)	114.8(3)
C(8)-C(2)-C(7)	108.8(3)	C(3)-C(2)-C(7)	107.9(3)
C(4)-C(3)-C(2)	117.7(4)	C(5)-C(4)-C(3)	111.2(4)
C(5)-C(4)-C(18)	112.5(4)	C(3)-C(4)-C(18)	108.2(4)
C(4)-C(5)-C(6)	110.1(3)	C(7)-C(6)-C(5)	112.3(4)
C(6)-C(7)-C(19)	112.7(4)	C(6)-C(7)-C(2)	112.1(4)
C(19)-C(7)-C(2)	115.1(3)	C(9)-C(8)-C(2)	107.6(4)

C(8)-C(9)-C(17)	112.0(4)	C(8)-C(9)-C(16)	113.2(4)
C(17)-C(9)-C(16)	109.4(4)	C(8)-C(9)-N(1)	99.9(3)
C(17)-C(9)-N(1)	113.4(3)	C(16)-C(9)-N(1)	108.8(3)
C(11)-C(10)-C(15)	121.1(4)	C(11)-C(10)-N(1)	120.0(4)
C(15)-C(10)-N(1)	118.8(4)	C(10)-C(11)-C(12)	117.8(4)
C(10)-C(11)-C(22)	126.0(4)	C(12)-C(11)-C(22)	116.2(4)
C(13)-C(12)-C(11)	120.3(4)	C(14)-C(13)-C(12)	120.4(4)
C(13)-C(14)-C(15)	121.2(4)	C(14)-C(15)-C(10)	118.8(4)
C(14)-C(15)-C(25)	116.7(4)	C(10)-C(15)-C(25)	124.6(4)
C(21)-C(19)-C(20)	110.0(4)	C(21)-C(19)-C(7)	110.2(4)
C(20)-C(19)-C(7)	113.9(4)	C(23)-C(22)-C(11)	108.2(4)
C(23)-C(22)-C(24)	109.5(4)	C(11)-C(22)-C(24)	114.2(4)
C(15)-C(25)-C(26)	110.6(4)	C(15)-C(25)-C(27)	113.4(4)
C(26)-C(25)-C(27)	107.8(4)	N(2)-C(28)-C(29)	106.4(4)
N(2)-C(28)-Pd(1)	128.3(3)	C(29)-C(28)-Pd(1)	125.0(3)
C(30)-C(29)-C(35)	107.5(4)	C(30)-C(29)-C(28)	111.2(3)
C(35)-C(29)-C(28)	105.5(3)	C(30)-C(29)-C(34)	108.8(3)
C(35)-C(29)-C(34)	108.9(3)	C(28)-C(29)-C(34)	114.7(4)
C(31)-C(30)-C(29)	118.2(3)	C(32)-C(31)-C(30)	109.6(4)
C(32)-C(31)-C(45)	112.2(4)	C(30)-C(31)-C(45)	108.9(4)
C(33)-C(32)-C(31)	111.4(4)	C(32)-C(33)-C(34)	110.8(4)
C(33)-C(34)-C(46)	113.5(4)	C(33)-C(34)-C(29)	112.1(4)
C(46)-C(34)-C(29)	114.4(4)	C(36)-C(35)-C(29)	108.3(3)
C(44)-C(36)-C(43)	109.5(4)	C(44)-C(36)-C(35)	111.4(4)
C(43)-C(36)-C(35)	112.8(4)	C(44)-C(36)-N(2)	112.2(3)
C(43)-C(36)-N(2)	110.8(3)	C(35)-C(36)-N(2)	99.9(3)
C(42)-C(37)-C(38)	121.1(4)	C(42)-C(37)-N(2)	118.7(4)
C(38)-C(37)-N(2)	119.9(4)	C(39)-C(38)-C(37)	117.0(4)
C(39)-C(38)-C(49)	117.7(4)	C(37)-C(38)-C(49)	125.2(4)
C(40)-C(39)-C(38)	123.2(5)	C(39)-C(40)-C(41)	117.6(5)
C(40)-C(41)-C(42)	123.2(5)	C(41)-C(42)-C(37)	117.9(4)
C(41)-C(42)-C(52)	118.1(4)	C(37)-C(42)-C(52)	123.9(4)
C(48)-C(46)-C(34)	110.8(4)	C(48)-C(46)-C(47)	109.3(4)
C(34)-C(46)-C(47)	113.7(4)	C(38)-C(49)-C(50)	112.4(4)

C(38)-C(49)-C(51)	108.9(4)	C(50)-C(49)-C(51)	109.8(4)
C(42)-C(52)-C(53)	110.9(4)	C(42)-C(52)-C(54)	112.4(4)
C(53)-C(52)-C(54)	108.0(3)		

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	23(1)	10(1)	19(1)	-1(1)	-2(1)	0(1)
N(1)	16(2)	8(2)	20(2)	-1(2)	-2(1)	1(2)
N(2)	21(2)	9(2)	21(2)	-1(2)	-1(2)	1(2)
C(1)	11(2)	9(3)	18(2)	4(2)	1(2)	-2(2)
C(2)	32(3)	7(2)	19(2)	4(2)	-3(2)	2(2)
C(3)	27(3)	15(2)	28(3)	-2(2)	-4(2)	-2(2)
C(4)	34(3)	15(3)	31(3)	0(2)	-4(2)	0(2)
C(5)	43(3)	16(3)	30(3)	0(2)	-10(3)	-2(3)
C(6)	41(3)	16(3)	24(3)	2(2)	7(2)	-4(2)
C(7)	33(3)	14(3)	20(3)	5(2)	2(2)	-1(2)
C(8)	31(3)	16(3)	28(3)	-6(2)	-1(2)	2(2)
C(9)	24(3)	14(3)	21(3)	-1(2)	-2(2)	-1(2)
C(10)	29(3)	12(3)	19(3)	1(2)	1(2)	1(2)
C(11)	16(2)	13(3)	24(3)	-7(2)	2(2)	1(2)
C(12)	28(3)	17(3)	26(3)	3(2)	10(2)	-5(2)
C(13)	36(3)	17(3)	30(3)	5(2)	-1(2)	4(2)
C(14)	25(3)	22(3)	31(3)	-1(2)	-4(2)	1(2)
C(15)	20(3)	13(3)	17(2)	-5(2)	-1(2)	-1(2)
C(16)	35(3)	21(3)	44(3)	-8(3)	2(3)	3(2)
C(17)	49(3)	18(3)	23(3)	-7(2)	-5(2)	-1(2)
C(18)	47(4)	17(3)	42(3)	4(2)	-13(3)	2(3)
C(19)	31(3)	26(3)	28(3)	3(3)	-3(3)	-4(2)
C(20)	28(3)	26(3)	44(3)	7(2)	7(2)	-6(2)
C(21)	39(3)	45(3)	52(3)	6(3)	0(3)	-13(3)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(22)	18(3)	14(3)	32(3)	0(2)	2(2)	-1(2)
C(23)	25(3)	24(3)	37(3)	-6(2)	3(2)	-5(2)
C(24)	24(3)	24(3)	42(3)	2(2)	5(2)	3(2)
C(25)	25(3)	16(3)	21(3)	2(2)	-8(2)	-1(2)
C(26)	21(3)	27(3)	39(3)	-2(2)	4(2)	1(2)
C(27)	33(3)	30(3)	33(3)	-1(2)	-5(3)	3(3)
C(28)	22(3)	24(3)	15(2)	1(2)	2(2)	-4(2)
C(29)	25(3)	12(2)	20(2)	-5(2)	-4(2)	4(2)
C(30)	31(3)	7(3)	26(3)	0(2)	-2(2)	0(2)
C(31)	31(3)	11(2)	28(3)	1(2)	-2(2)	0(2)
C(32)	44(3)	17(3)	31(3)	1(2)	-14(2)	6(2)
C(33)	25(3)	24(3)	40(3)	1(2)	-7(2)	4(2)
C(34)	29(3)	12(3)	36(3)	4(2)	-2(2)	9(2)
C(35)	30(3)	12(3)	25(3)	-3(2)	-3(2)	-2(2)
C(36)	22(3)	12(2)	31(3)	-3(2)	-2(2)	2(2)
C(37)	28(3)	13(3)	27(3)	-3(2)	-6(2)	-5(2)
C(38)	25(3)	13(3)	32(3)	-2(2)	-5(2)	-4(2)
C(39)	30(3)	26(3)	36(3)	-3(2)	-5(2)	6(2)
C(40)	45(4)	26(3)	34(3)	2(2)	-16(3)	8(3)
C(41)	52(4)	19(3)	22(3)	3(2)	-7(2)	-1(3)
C(42)	35(3)	17(3)	17(2)	-3(2)	-6(2)	-3(2)
C(43)	36(3)	19(3)	43(3)	-3(2)	1(2)	-4(2)
C(44)	43(3)	14(3)	28(2)	-7(2)	-5(2)	2(3)
C(45)	50(3)	22(3)	30(2)	3(3)	-11(2)	1(3)
C(46)	31(3)	22(3)	33(3)	-1(2)	7(2)	4(2)
C(47)	30(3)	35(3)	44(3)	5(3)	7(2)	0(3)
C(48)	56(4)	44(4)	60(4)	7(3)	20(3)	19(3)
C(49)	28(3)	20(3)	24(3)	-4(2)	-1(2)	-3(2)
C(50)	32(3)	29(3)	48(3)	-8(3)	3(2)	2(2)
C(51)	36(3)	12(2)	42(3)	-4(3)	-2(3)	13(2)
C(52)	28(3)	15(2)	26(2)	4(2)	1(2)	-1(2)
C(53)	48(3)	23(3)	22(3)	0(2)	4(2)	-2(2)
C(54)	46(4)	29(3)	25(3)	-4(2)	6(2)	-10(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(3A)	10155	1932	1206	28
H(3B)	10748	3077	1077	28
H(4)	10522	4051	1524	32
H(5A)	9509	3313	1930	35
H(5B)	9260	2119	1761	35
H(6A)	7566	3334	1745	33
H(6B)	8322	4310	1580	33
H(7)	7909	2083	1343	26
H(8A)	9163	1656	807	30
H(8B)	7821	2110	795	30
H(12)	10470	6771	-5	28
H(13)	8626	7313	-183	33
H(14)	6922	6607	34	31
H(16A)	10274	1989	356	50
H(16B)	10773	3024	555	50
H(16C)	10319	3274	225	50
H(17A)	7252	2972	356	45
H(17B)	8109	2024	213	45
H(17C)	8213	3348	114	45
H(18A)	12180	2780	1494	53
H(18B)	11419	1763	1641	53
H(18C)	11750	2883	1832	53
H(19)	6609	3167	986	34
H(20A)	6182	4543	1500	49
H(20B)	5487	4633	1192	49
H(20C)	6845	5016	1211	49
H(21A)	5765	2426	1551	68
H(21B)	5980	1596	1272	68
H(21C)	4962	2556	1260	68

	x	y	z	U(eq)
H(22)	11073	4866	601	26
H(23A)	11011	6766	769	43
H(23B)	11489	7242	458	43
H(23C)	12342	6504	669	43
H(24A)	12769	4911	308	45
H(24B)	12169	5777	76	45
H(24C)	11720	4469	99	45
H(25)	6701	4503	598	24
H(26A)	5148	5834	704	44
H(26B)	5756	6774	493	44
H(26C)	6400	6379	793	44
H(27A)	6100	4139	89	48
H(27B)	5424	5354	91	48
H(27C)	5002	4338	307	48
H(30A)	9755	9762	1007	26
H(30B)	10535	8617	992	26
H(31)	9099	7638	730	28
H(32A)	7565	9589	806	37
H(32B)	7219	8414	639	37
H(33A)	7404	7391	1093	35
H(33B)	6415	8379	1117	35
H(34)	7825	9625	1330	31
H(35A)	10293	10034	1449	27
H(35B)	9348	9687	1700	27
H(39)	13401	4864	1789	37
H(40)	12703	4328	2251	42
H(41)	10897	5063	2411	37
H(43A)	12303	9733	1628	49
H(43B)	12151	8720	1389	49
H(43C)	12684	8441	1710	49
H(44A)	10024	8828	2119	42

	x	y	z	U(eq)
H(44B)	11142	9668	2090	42
H(44C)	11334	8317	2149	42
H(45A)	10303	8905	447	51
H(45B)	9349	9916	486	51
H(45C)	9024	8789	297	51
H(46)	8027	8570	1808	34
H(47A)	6211	7136	1555	55
H(47B)	6729	7040	1885	55
H(47C)	7531	6681	1607	55
H(48A)	5963	9024	1906	80
H(48B)	5857	9384	1564	80
H(48C)	6734	10074	1779	80
H(49)	12121	6851	1276	29
H(50A)	14390	6056	1474	55
H(50B)	13939	7360	1508	55
H(50C)	14170	6829	1185	55
H(51A)	11699	4930	1151	45
H(51B)	12910	4484	1295	45
H(51C)	12935	5236	997	45
H(52)	9093	7182	2061	27
H(53A)	7754	5834	2284	46
H(53B)	8805	4912	2308	46
H(53C)	8335	5314	1989	46
H(54A)	9691	6376	2644	50
H(54B)	8758	7373	2568	50
H(54C)	10142	7590	2517	50

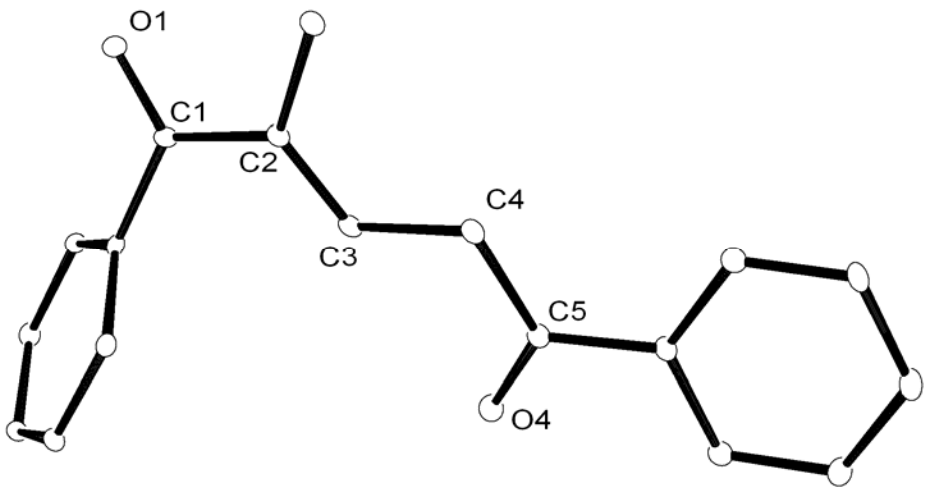

Table S1. Crystal data and structure refinement for compound **6a** chapter 2.

Empirical formula	$C_{18}H_{16}O_2$	
Formula weight	264.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 11.766(4) Å	α = 90°
	b = 5.772(2) Å	β = 90°
	c = 20.174(8) Å	γ = 90°
Volume	1370.1(9) $Å^3$	
Z	4	
Density (calculated)	1.281 g/cm^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	560	
Crystal size	0.10 x 0.10 x 0.03 mm^3	
Theta range for data collection	2.02 to 23.26°	
Index ranges	-13<=h<=12, -6<=k<=6, -22<=l<=22	
Reflections collected	6971	
Independent reflections	1974 [R(int) = 0.0784]	

Completeness to theta = 23.26°	99.9 %
Absorption correction	Sadabs
Max. and min. transmission	0.9975 and 0.9918
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1974 / 1 / 183
Goodness-of-fit on F^2	0.985
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.0944
R indices (all data)	R1 = 0.0750, wR2 = 0.1055
Absolute structure parameter	0(2)
Extinction coefficient	0.021(2)
Largest diff. peak and hole	0.159 and -0.154 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3246(2)	7435(5)	2459(1)	40(1)
O(2)	5109(2)	-1373(5)	1135(1)	32(1)
C(1)	4200(4)	7345(7)	2700(2)	29(1)
C(2)	5066(3)	5605(7)	2461(2)	29(1)
C(3)	4639(3)	3980(7)	1942(2)	28(1)
C(4)	5241(3)	2194(7)	1699(2)	25(1)
C(5)	4710(3)	590(7)	1218(2)	25(1)
C(6)	3667(3)	1262(6)	835(2)	23(1)
C(7)	3564(3)	3383(7)	511(2)	26(1)
C(8)	2613(3)	3886(7)	130(2)	26(1)
C(9)	1735(3)	2290(7)	87(2)	28(1)
C(10)	1819(3)	199(7)	419(2)	29(1)
C(11)	2784(3)	-351(7)	785(2)	27(1)
C(12)	4528(3)	8994(7)	3239(2)	27(1)
C(13)	3793(3)	10819(7)	3389(2)	31(1)

	x	y	z	U(eq)
C(14)	4070(3)	12411(7)	3874(2)	34(1)
C(15)	5085(3)	12212(7)	4219(2)	36(1)
C(16)	5817(3)	10424(7)	4075(2)	33(1)
C(17)	5549(3)	8819(7)	3583(2)	32(1)
C(18)	6419(3)	1629(7)	1933(2)	31(1)

Table 3. Bond lengths [Å] and angles [°].

O(1)-C(1)	1.224(4)	O(2)-C(5)	1.238(4)
C(1)-C(12)	1.495(6)	C(1)-C(2)	1.510(6)
C(2)-C(3)	1.493(5)	C(3)-C(4)	1.344(5)
C(4)-C(5)	1.479(5)	C(4)-C(18)	1.500(5)
C(5)-C(6)	1.502(5)	C(6)-C(7)	1.393(5)
C(6)-C(11)	1.398(5)	C(7)-C(8)	1.388(5)
C(8)-C(9)	1.387(5)	C(9)-C(10)	1.384(5)
C(10)-C(11)	1.392(5)	C(12)-C(17)	1.392(5)
C(12)-C(13)	1.397(5)	C(13)-C(14)	1.380(5)
C(14)-C(15)	1.388(5)	C(15)-C(16)	1.375(5)
C(16)-C(17)	1.394(5)		

O(1)-C(1)-C(12)	119.9(4)	O(1)-C(1)-C(2)	121.3(4)
C(12)-C(1)-C(2)	118.8(4)	C(3)-C(2)-C(1)	114.5(3)
C(4)-C(3)-C(2)	124.1(3)	C(3)-C(4)-C(5)	119.8(3)
C(3)-C(4)-C(18)	122.6(4)	C(5)-C(4)-C(18)	117.4(3)
O(2)-C(5)-C(4)	120.1(3)	O(2)-C(5)-C(6)	118.5(4)
C(4)-C(5)-C(6)	121.4(3)	C(7)-C(6)-C(11)	119.2(3)
C(7)-C(6)-C(5)	122.6(3)	C(11)-C(6)-C(5)	118.2(3)
C(8)-C(7)-C(6)	120.9(4)	C(9)-C(8)-C(7)	119.8(4)
C(10)-C(9)-C(8)	119.7(4)	C(9)-C(10)-C(11)	120.9(4)
C(10)-C(11)-C(6)	119.5(4)	C(17)-C(12)-C(13)	118.7(4)
C(17)-C(12)-C(1)	122.7(4)	C(13)-C(12)-C(1)	118.6(4)

C(14)-C(13)-C(12)	120.6(4)	C(13)-C(14)-C(15)	120.2(4)
C(16)-C(15)-C(14)	119.7(4)	C(15)-C(16)-C(17)	120.4(4)
C(12)-C(17)-C(16)	120.2(4)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	25(2)	49(2)	47(2)	-13(2)	-9(2)	2(1)
O(2)	29(2)	33(2)	35(2)	0(2)	-1(1)	5(1)
C(1)	25(2)	38(3)	25(2)	0(2)	3(2)	2(2)
C(2)	23(2)	37(3)	27(2)	3(2)	-2(2)	-5(2)
C(3)	19(2)	35(3)	28(2)	5(2)	-3(2)	-2(2)
C(4)	19(2)	31(2)	26(2)	4(2)	0(2)	-3(2)
C(5)	18(2)	30(2)	27(2)	6(2)	5(2)	1(2)
C(6)	21(2)	25(2)	23(2)	-6(2)	5(2)	-1(2)
C(7)	22(2)	28(2)	27(2)	-5(2)	2(2)	-3(2)
C(8)	21(2)	34(3)	25(2)	0(2)	-2(2)	-2(2)
C(9)	19(2)	38(3)	26(2)	0(2)	-2(2)	6(2)
C(10)	18(2)	37(3)	32(2)	-5(2)	2(2)	-5(2)
C(11)	24(2)	29(2)	27(2)	0(2)	3(2)	3(2)
C(12)	22(2)	38(3)	21(2)	0(2)	4(2)	0(2)
C(13)	23(2)	38(3)	30(2)	1(2)	3(2)	0(2)
C(14)	28(2)	37(3)	36(2)	-6(2)	6(2)	-5(2)
C(15)	33(3)	46(3)	30(2)	-9(2)	3(2)	-8(2)
C(16)	28(2)	45(3)	24(2)	-3(2)	-3(2)	-10(2)
C(17)	26(2)	39(3)	33(2)	-1(2)	1(2)	1(2)
C(18)	18(2)	47(3)	28(2)	1(2)	2(2)	1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3).

	x	y	z	U(eq)
H(2A)	5728	6455	2281	35
H(2B)	5333	4688	2845	35
H(3)	3894	4223	1773	33
H(7)	4154	4499	550	31
H(8)	2563	5320	-99	32
H(9)	1079	2630	-170	33
H(10)	1208	-875	398	35
H(11)	2844	-1811	1000	32
H(13)	3095	10967	3156	37
H(14)	3563	13647	3971	40
H(15)	5273	13306	4553	44
H(16)	6511	10283	4313	39
H(17)	6064	7602	3483	39
H(18A)	6861	3060	1973	47
H(18B)	6787	594	1613	47
H(18C)	6378	863	2366	47