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Cobalt-Mediated Vinylic C-H Functionalization of Alkenes

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Cobalt-Mediated Vinylic C–H Functionalization of Alkenes

By
Warren Christopher Boyd

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Chemistry
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Graduate Division
of the
University of California, Berkeley

Committee in charge:

Professor Robert G. Bergman, Co-chair
Professor F. Dean Toste, Co-Chair
Professor K. Peter C. Vollhardt
Professor Benito O. de Lumen

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Abstract

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Warren Christopher Boyd

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professors Robert G. Bergman and F. Dean Toste, Co-Chairs

Many organic reactions promoted or catalyzed by transition metals proceed *via* mechanisms in which bonds are formed and broken directly between the organic substrate and the metal center. Less common are reactions exhibiting ligand-based reactivity, in which the key bond formation and cleavage steps occur between the substrate and ligands attached to the active metal center. This dissertation describes the use of ligand-based reactivity of cobalt dinitrosyl complexes with alkenes to form vicinal dinitrosoalkane complexes of cobalt. In these complexes, the C–H bonds located α to the nitroso groups are significantly acidified relative to vinylic C–H bonds, allowing for these complexes to be deprotonated and functionalized with conjugate acceptors in Michael reactions. Removal of the cobalt dinitrosyl moiety from the functionalized complexes yields the product of a net vinylic C–H functionalization.

Chapter 1. Initial C–H functionalization was performed on cycloadducts of the $[Cp^tCo(NO)_2]$ moiety ($Cp^t = \eta^5\text{-}C_5Me_4H$) with cyclic alkenes. Electrophiles used in functionalization included α,β-unsaturated ketones, nitriles, nitro compounds, and sulfones. Functionalization was carried out under basic conditions using lithium bis(trimethylsilylamide) (LHMDS) and the Lewis-acid additive scandium(III) triflate. Heating of the functionalized Co complex in the presence of excess unfunctionalized alkene induced an alkene exchange reaction, which gave the functionalized alkene and unfunctionalized Co complex in high yields.

Chapter 2. Attempts were made to render the net vinylic C–H functionalization catalytic in cobalt, by carrying out the Michael addition and alkene exchange steps in a single reaction vessel at elevated temperature. Some level of catalysis was achieved using strong, neutral proazaphosphatrane or phosphazene bases, but undesirable side reactions limited the reaction's efficiency to four or five turnovers of the cobalt catalyst. The tin(IV) amide species bis(trimethylsilyl)(triphenylstannyl)amine was found to promote the functionalization reaction in the presence of the chloride ion, but gave lower yields than neutral phosphorus bases.

Chapter 3. The functionalization of cobalt dinitrosoalkane complexes was rendered enantioselective using a mixture of sodium bis(trimethylsilyl)amide (NaHMDS) and *N*-3,5-bis(trifluoromethyl)benzylquininium chloride as the base for deprotonation. The best combinations of yield and enantiomeric excess (e.e.) were obtained at -60 ºC on

cobalt dinitrosoalkanes bearing the bulky, highly directional Cp^{Si} ligand (Cp^{Si} = η^5-^{t}BuMe$_2$SiC$_5$H$_4$). The isomerization of functionalized complexes derived from norbornadiene, followed by further functionalization and alkene exchange, yielded C_2- or C_1-symmetric disubstituted norbornadienes with high e.e., which are competent chiral ligands for the enantioselective, rhodium(I)-catalyzed conjugate addition of phenylboronic acid to 2-cyclohexen-1-one.

Chapter 4. The Tp* (κ^3-hydridotris(3,5-dimethylpyrazolyl)borate) ligand, isolobal to Cp (η^5-C_5H_5) and its derivatives, was used in place of Cp derivatives to form cobalt dinitrosoalkane complexes derived from norbornene and norbornadiene. These complexes do not serve as Michael donors under the conditions explored, and the [Tp*Co(NO)$_2$] fragment undergoes less efficient alkene exchange than do the Cp analogs. The mononitrosyl complex [Tp*Co(NO)] is isolable, and does not form a bridged dimer analogous to [CpCo(μ-NO)]$_2$. Calculations on [Tp*Co(NO)] suggest that its electronic structure is best described as a quartet Co(II) center antiferromagnetically coupled to a triplet NO^- ligand, for an overall doublet ground state.

sunt lacrimae rerum et mentem mortalia tangunt.

- Vergil, *Aeneid* I.462

Cobalt-Mediated Vinylic C–H Functionalization of Alkenes

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ACKNOWLEDGMENTS

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I've long been grateful that I've been able to keep in touch as well as I have with my boon companions from Oberlin College, my baccalaureate *alma mater*. We may be scattered across the country, but your support has been a wonderful source of laughter and comfort during the arduous process of a Ph.D. Alex, Caitlin, Claire, Daniel, Erica, Glen, Peter, Matt, and Robin: you guys are the best.

Additional thanks, of course, are due to my parents, for supporting my curiosity and encouraging me in my education from day one. Without the encouragement you gave me to pursue my scientific interest, I would not be where I am today.

Finally, I want to thank Stephanie Johnson, my best friend and the light of my heart, for all the love and support you have given me throughout our years together. Here's to many more. *Te amo quam plurimum, mea carissima*.

Chapter 1

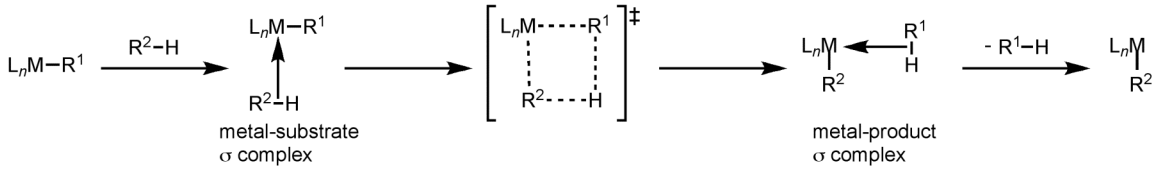
Functionalization and Alkene Exchange of Cobalt(I) Dinitrosoalkane Complexes

Portions of this chapter have been published as:
Schomaker, J. M.; Boyd, W. C.; Stewart, I. C.; Toste, F. D.; Bergman, R. G. Cobalt Dinitrosoalkane Complexes in the C–H Functionalization of Olefins. *J. Am. Chem. Soc*. **2008,** *130,* 3777-3779.

Introduction

Many organic reactions catalyzed or mediated by transition metals proceed *via* mechanisms in which bond formation and cleavage occurs between the organic substrate(s) and product(s) and the active metal center. These reactions often involve oxidative addition and reductive elimination as key mechanistic steps; for instance, the homogenous hydrogenation of alkenes by Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, involves an Rh(I)/Rh(III) cycle,[1] and a wide variety of palladium-catalyzed cross-coupling reactions are believed to proceed through a Pd(0)/Pd(II) cycle.[2] Another reaction pathway, frequently undergone by complexes of d^0 transition metals and *f*-block elements, is that of σ-bond metathesis, consisting of a metal-substrate σ complex is converted to a metal-product σ complex *via* a four-membered transition state (Scheme 1.1).[3]

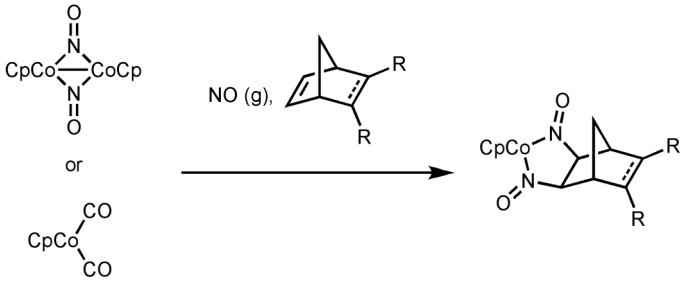
Scheme 1.1. C–H activation *via* σ-bond metathesis. R^1, R^2 = hydrocarbyl.



Other metal-catalyzed or mediated reactions involve what might be termed ligand-based reactivity, *i.e.* their mechanisms involve bond formation and cleavage between organic substrates and products and the ligands on the active metal center, in addition to, or instead of, direct substrate/metal reactions. Examples of this type of reactivity can be redox-neutral at the metal center, such as Toste's rhenium(V)-catalyzed hydrosilylation of aldehydes and ketones, involving the addition of silane across a Re–O double bond,[4] and Noyori's ruthenium(II)-catalyzed hydrogenation of ketones, in which the hydrogen atoms donated are present as a hydride ligand on Ru and a protic, N-bound hydrogen on an amine ligand.[5] Other examples of ligand-based reactivity involve changes in the relevant metal's oxidation state, as in the osmium-catalyzed dihydroxylation of alkenes to vicinal diols,[6] in which osmium(VIII) oxide reacts with an alkene to form an osmate(VI) diester.[6,7]

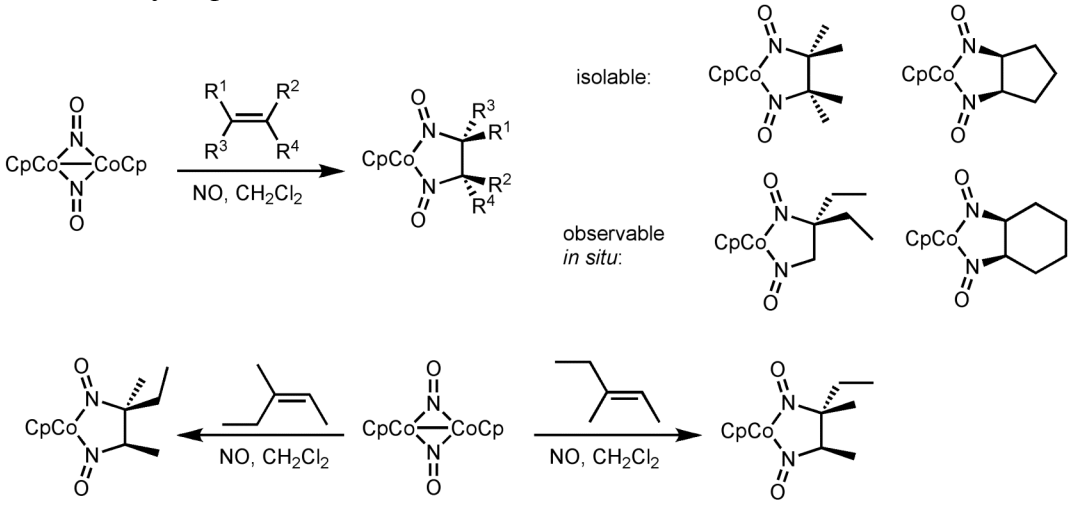
A ligand-based reaction involving the attachment of metal-bound nitrogen to organic substrates was discovered by Brunner, who reported[8] that treatment of the cobalt carbonyl complex $[CpCo(CO)_2]$ or the dinuclear dinitrosyl $[CpCo(\mu\text{-}NO)]_2$ (Cp = η^5-C_5H_5) with norbornene, norbornadiene, or their derivatives under a nitric oxide atmosphere yielded cobalt dinitrosoalkane complexes, with the $[CpCo(NO)_2]$ moiety in the *exo*-position of the bicyclic system (Scheme 1.2).

Scheme 1.2. Formation of cobalt dinitrosoalkane complexes.



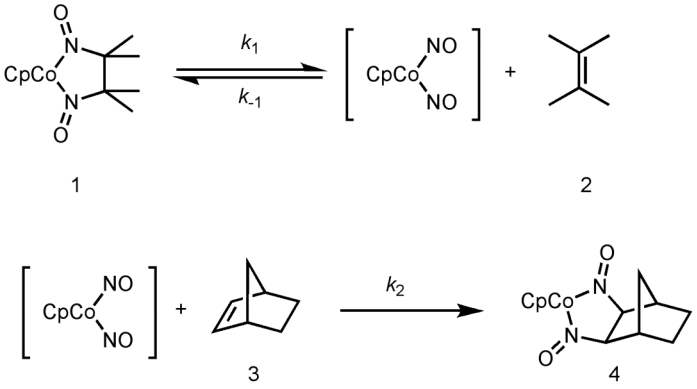
Bergman and Becker expanded the scope of this reaction to include alkenes less strained than the bicyclic alkenes studied by Brunner, including several acyclic alkenes.[9] However, some alkenes formed unstable cobalt dinitrosoalkane complexes that could be observed by infrared (IR) spectroscopy in THF solution, but not isolated. In general, cyclic alkenes with greater ring strain and more highly substituted acyclic alkenes yielded more stable cobalt dinitrosoalkanes. Complex formation was established to be stereoselective, involving *syn* addition of the [$CpCo(NO)_2$] moiety to the alkene double bond, as seen in the different products formed from the *E* and *Z* diastereomers of 3-methyl-pent-2-ene (Scheme 1.3).

Scheme 1.3. Expansion of cobalt dinitrosoalkane complex scope and stereoselectivity of product formation.



Further work by Becker and Bergman demonstrated that the [$CpCo(NO)_2$] moiety could be transferred from a less to a more highly strained alkene upon heating.[10] Based on kinetic studies, they proposed the following mechanism (Scheme 1.4):

Scheme 1.4. Proposed mechanism for alkene exchange of $[CpCo(NO)_2]$.

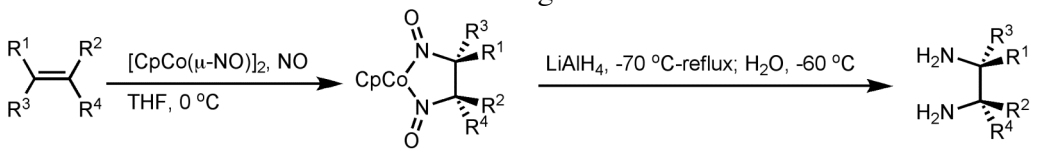


The kinetics of this reaction follow the rate law $\frac{-d[1]}{dt} = \frac{k_1 k_2 [1][3]}{k_{-1}[2] + k_2[3]}$, which reduces to $\frac{-d[1]}{dt} = k_1[1]$ when a large excess of the entering alkene **3** is used, so that $k_2[3] >> k_{-1}[2]$. This is kinetically equivalent to an organic S_N1 reaction,[11] with the entering alkene **3** and leaving alkene **2** taking the place of nucleophile and nucleofuge, respectively. The intermediate $[CpCo(NO)_2]$, while not stable enough to be isolated, can be observed in solution by nuclear magnetic resonance (NMR), IR, and UV-visible spectroscopy, though these techniques do not permit the assignment of its nitrosyl ligands as bent or linear. Based on the stereospecificity of the cycloaddition of $[CpCo(NO)_2]$ to alkenes, as well as the relative insensitivity of reaction rate to solvent polarity, Becker and Bergman proposed that the cycloaddition proceeds in a concerted, pericyclic fashion, without diradical or zwitterionic intermediates. This proposal has been supported by a theoretical analysis by Jørgensen and Hoffmann, who drew parallels between this cycloaddition and that of OsO_4 to alkenes.[7]

Cobalt-Bound Nitrosoenolates

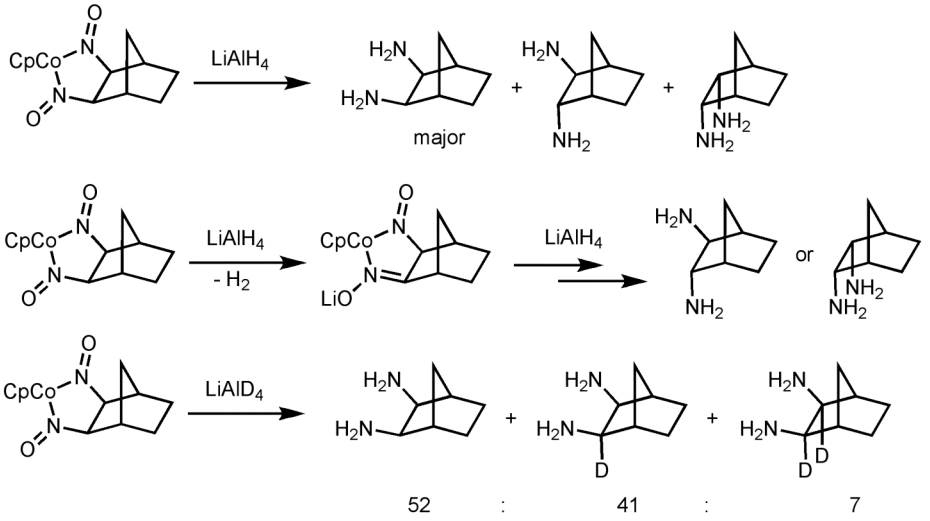
One synthetically useful reaction of cobalt dinitrosoalkanes is their ability to be reduced to vicinal diamines, completing an overall vicinal diamination reaction of alkenes. Becker and Bergman demonstrated that a wide variety of alkenes could be diaminated by formation of their corresponding cobalt dinitrosoalkane, followed by reduction with lithium aluminum hydride, either following isolation of the cobalt dinitrosoalkane or *in situ* (Scheme 1.5).[9]

Scheme 1.5. Vicinal diamination through cobalt dinitrosoalkanes.



While the cycloaddition of $[CpCo(NO)_2]$ to alkenes is stereospecifically *syn*, the diamines formed by the reduction of cobalt dinitrosoalkanes with hydrogen atoms α to the nitrosyl groups were isolated as mixtures of diastereomers. Becker and Bergman proposed that this loss of stereochemical purity was due to the deprotonation of the cobalt dinitrosoalkane, yielding an intermediate with nitrosoenolate character with a planar α carbon. Support for this hypothesis was provided by the results of a reduction using lithium aluminum deuteride; the major (*cis-exo*) diastereomer of the diamine product had deuterium incorporated into its α positions (Scheme 1.6).[9]

Scheme 1.6. Proposed origin of diamine diastereomers.

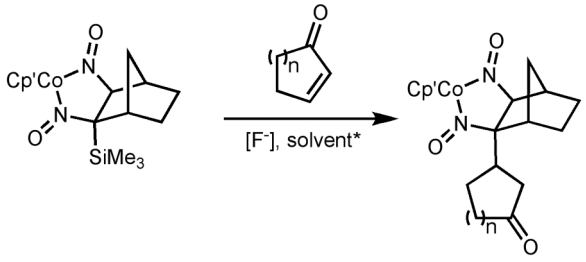


The likelihood of the formation of nitrosoenolate anions during the reduction of cobalt dinitrosoalkanes suggested the possibility of the controlled formation of these anions, and their use as nucleophiles in a C–H functionalization reaction of cobalt dinitrosoalkanes by electrophiles. Loss of $[CpCo(NO)_2]$ from a functionalized complex would yield a substituted alkene, with net C–H functionalization at the vinylic position.

Cobalt Dinitrosoenolate Formation from α-Silyl Complexes

Initial efforts toward the formation of cobalt nitrosoenolates as nucleophiles involved the generation of the nitrosoenolate anion not through deprotonation, but through treatment of a cobalt complex derived from 2-(trimethylsilyl)norbornene with fluoride. Treatment of the complex with either the Cp or Cp* ligand (Cp* = η^5-C_5Me_5) with the fluoride sources TBAF ($[Bu_4N]F$) or TASF ($[(Me_2N)_3S][Me_3SiF_2]$) in the presence of the conjugate acceptor electrophiles 2-cyclopenten-1-one or 2-cyclohexen-1-one yielded electrophilic substitution products in which the trimethylsilyl group has been replaced by the conjugate acceptor (Table 1.1).[12]

Table 1.1. Conjugate addition reactions from the desilylation of a cobalt dinitrosoalkane complex.



Cp'	n	F^- source	yield
Cp	1	TBAF	65%
Cp*	1	TASF	61%
Cp	2	TBAF	76%
Cp*	2	TBAF	32%
Cp*	2	TASF	65%

*THF for reactions using TBAF,
1,2-dimethoxyethane for reactions using TASF

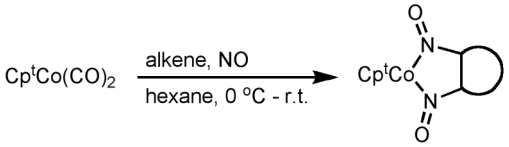
This reaction proceeded in moderate to good yield, with the anhydrous salt TASF giving higher yields than commercial, non-anhydrous solutions of TBAF when Cp*, as opposed to Cp, was used as the spectator ligand on cobalt. The more electron-donating nature[13] of Cp* compared with Cp may render the intermediate nitrosoenolate anion more Brønsted-basic and thus more vulnerable to adventitious moisture than the analogous Cp-containing anion.

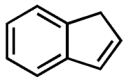
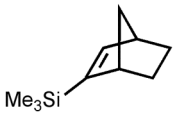
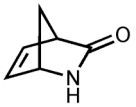
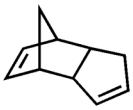
C–H Functionalization of Cobalt Dinitrosoalkane Complexes

The use of fluoride to effect the replacement of trimethylsilyl groups with conjugate acceptors demonstrated the viability of the nitrosoenolate anions as synthetically useful intermediates. The requirement of a silyl group, however, limits the scope of the reaction; consequently, we sought to perform a similar reaction using as substrates cobalt dinitrosoalkanes derived from unfunctionalized alkenes, with the nitrosoenolate anion formed *via* deprotonation as opposed to desilylation.

For these reactions, we used cobalt complexes with the Cp^t ligand ($Cp^t = \eta^5$-Me_4C_5H) in place of Cp or Cp*, for the utility of its ring-bound hydrogen atom as an NMR "handle." Treatment of the dicarbonyl complex [$Cp^tCo(CO)_2$] with excess alkene and NO allowed for the formation of a range of cyclic alkene adducts in useful yields (Table 1.2).[12]

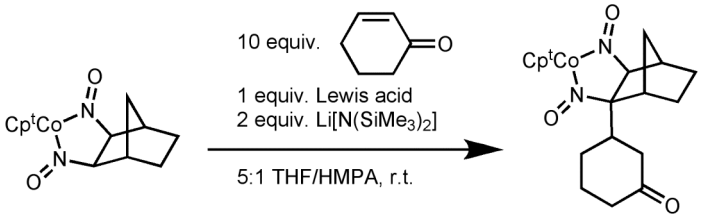
Table 1.2. Formation of cobalt dinitrosoalkanes with the Cp^t ligand.



alkene	yield	alkene	yield
	89%		77%
	77%		66%
	87%		92%
	44%		72%
	78%		19%
	74%		64%

The conjugate addition reaction of the $[Cp^tCo(NO)_2]$/norbornene adduct and 2-cyclohexen-1-one was examined using $Li[N(SiMe_3)_2]$ as base and a variety of Lewis-acidic compounds as additives (Table 1.3).[12] While the reaction proceeded in only 39% yield in the absence of a Lewis-acidic additive, the use of 1 equivalent of scandium(III) trifluoromethanesulfonate, $Sc(OTf)_3$, allowed isolation of the conjugate addition product in 82% yield (Table 1.3).[12]

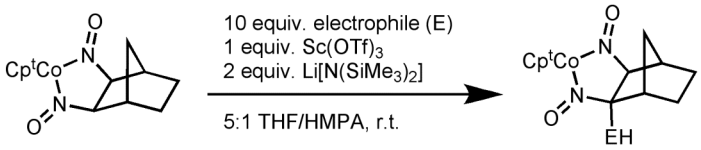
Table 1.3. Screening of Lewis acids as additives for conjugate addition.

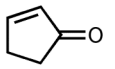
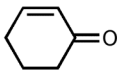
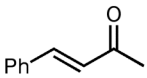
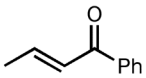
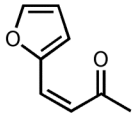
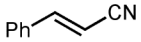
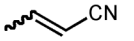
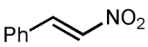
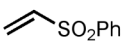


Lewis acid	yield	Lewis acid	yield
none	39%	$Hf(OTf)_4$	61%
$B(OMe)_3$	57%	$Sc(OTf)_3$	82%
$B(O^iPr)_3$	66%	$Y(OTf)_3$	39%
$B(OPh)_3$	18%	$Yb(OTf)_3$	61%
$BF_3{\cdot}OEt_2$	0%	$Zn(OTf)_2$	70%
$Cu(OTf)_2$	34%	$ZnCl_2$	52%

The scope of this addition reaction with respect to electrophile was examined with a variety of conjugate acceptors, and the $[Cp^tCo(NO)_2]$/norbornene adduct was found to add to α,β-unsaturated ketones, nitriles, nitro compounds, and sulfones. (Table 1.4).[12]

Table 1.4. Scope of electrophile in conjugate addition reaction.

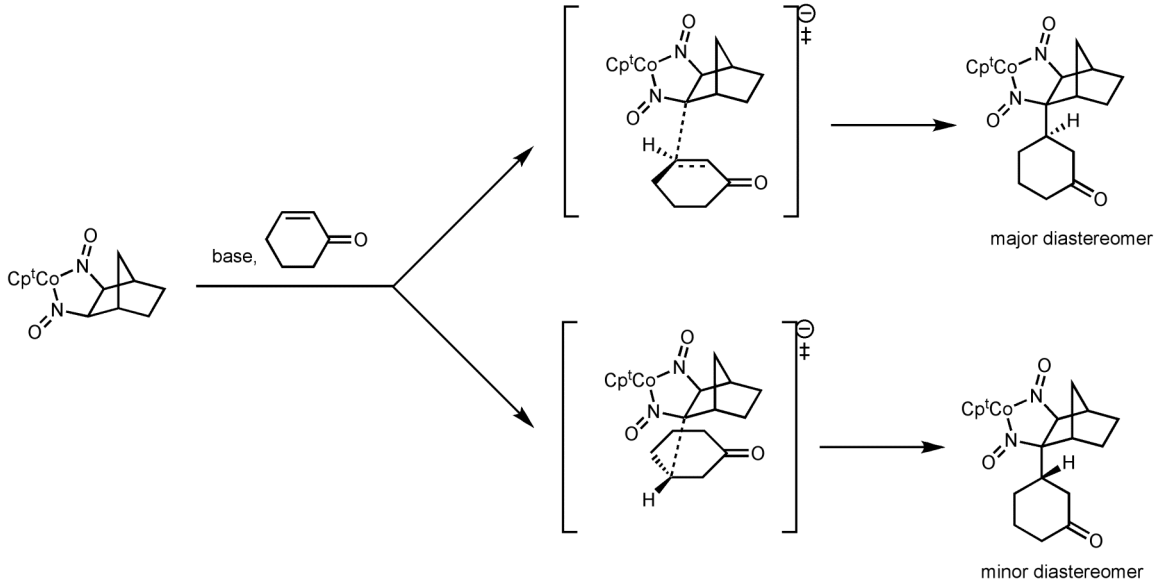


electrophile	yield	d.r.
	69%*	>9:1
	75-82%	>9:1
	70%	3:1
	81%	1:1
	74%	2.4:1
	31%	>9:1
	65%	4:1
	99%*	>9:1
	53% (disubstituted)	N/A

*yield based on recovered starting material.

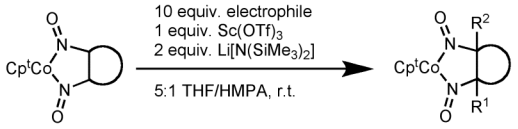
The electrophiles used, with the exception of phenyl vinyl sulfone, are prochiral, leading to the possibility of two diastereomeric products of conjugate addition. While some diastereomeric pairs were formed in comparable amounts, other reactions had diastereomeric ratios of over 9:1. A model that accounts for the diastereoselectivity of reaction, with 2-cyclohexen-1-one as the electrophile, is shown below (Scheme 1.7). According to this model, the transition state leading to the major diastereomer allows for dipole minimization between the carbonyl group of the electrophile and the nitroso groups of the cobalt complex, while also minimizing steric clashes between the two reaction partners. Crystallographic evidence that the major diastereomer depicted in Scheme 1.7 is, in fact, the one preferentially formed was obtained in connection with a study on rendering these conjugate additions enantioselective,[14] and will be discussed further in Chapter 3 of this dissertation. The fact that two equivalents of $Li[N(SiMe_3)_2]$ were required for substantial conversion may be due to reaction of the first equivalent with $Sc(OTf)_3$; this possibility and its implications are discussed further in Chapter 2 of this work.

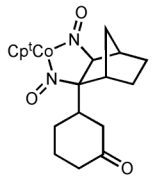
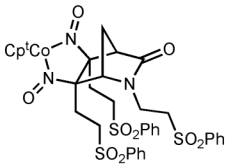
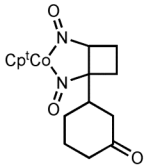
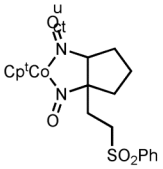
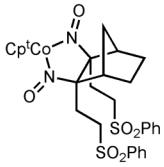
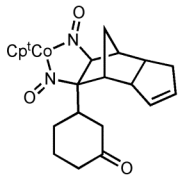
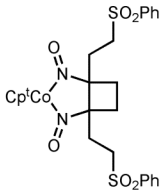
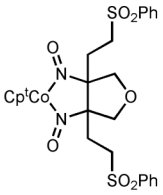
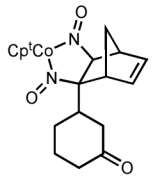
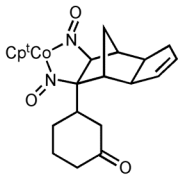
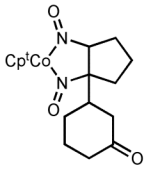
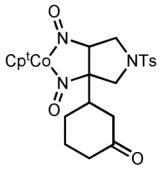
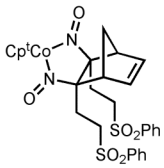
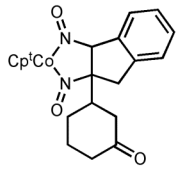
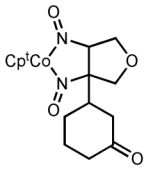
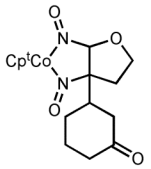
Scheme 1.7. Model for diastereoselectivity of conjugate addition.



Cobalt dinitrosoalkane complexes derived from cyclic alkenes other than norbornene also added to 2-cyclohexen-1-one or phenyl vinyl sulfone (Table 1.5) upon deprotonation.[12]

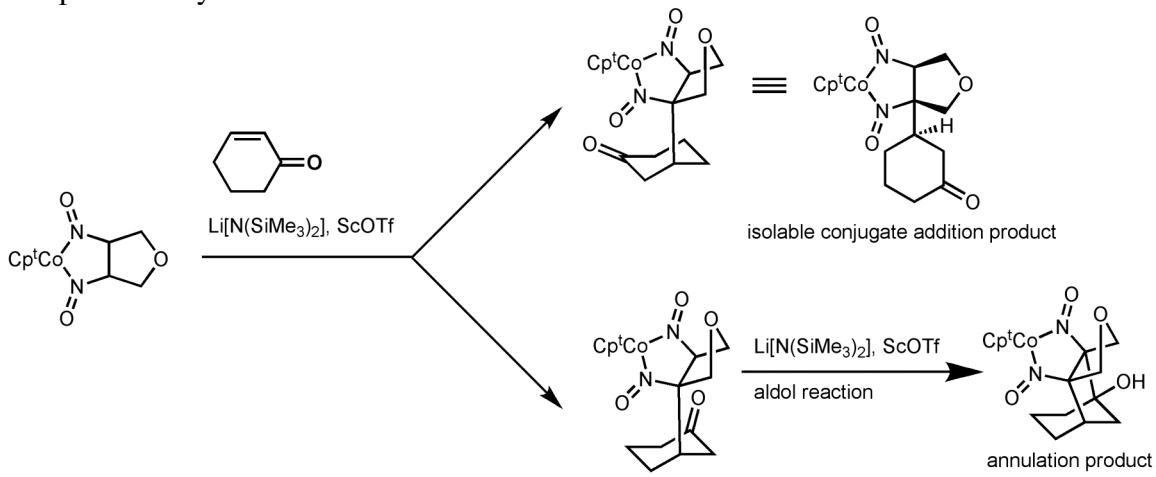
Table 1.5. Scope of cobalt dinitrosoalkane complex in conjugate addition reaction.



product	yield	product	yield	product	yield	product	yield
	82%		50%		79%		17%
	56%		0%		51%		40%
	69%	 + regioisomer	73%		48%		37%
	61%		15%		57%		61%

Later work in the Bergman and Toste groups demonstrated that cobalt dinitrosoalkane complexes derived from some smaller cyclic alkenes reacted with 2-cyclohexen-1-one to form two diastereomers of the conjugate addition product. One of each pair of disastereomers did not undergo further reactivity, and was readily isolated as in Table 1.5, but the other underwent an additional α-deprotonation and intramolecular aldol reaction, leading to an overall [3+2] annulation product, an example of which is shown in Scheme 1.8.[15]

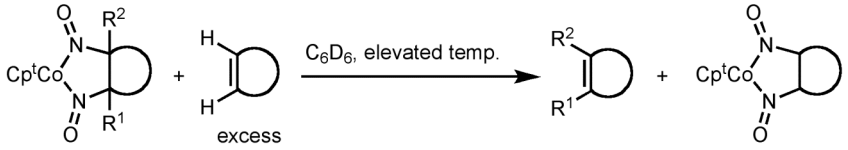
Scheme 1.8. Diastereomer-specific sequential addition of a cobalt dinitrosoalkane complex to 2-cyclohexen-1-one.

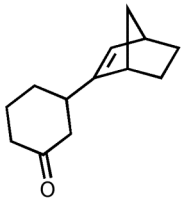
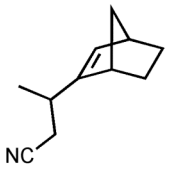
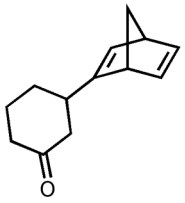
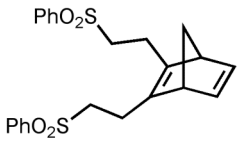
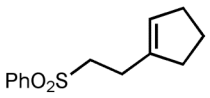


Cycloreversion and Alkene Exchange of Functionalized Cobalt Dinitrosoalkanes

To complete an overall vinylic C–H functionalization, the products of the conjugate additions shown in Tables 1.4 and 1.5 may be heated in the presence of excess parent alkene. Under these conditions, the [Cp^{t}Co(NO)$_2$] moiety was transferred from the more sterically-hindered functionalized cobalt dinitrosoalkane to the unsubstituted alkene, yielding the C–H functionalized alkene with regeneration of the parent cobalt dinitrosoalkane (Table 1.6).[12]

Table 1.6. Alkene exchange of functionalized cobalt dinitrosoalkanes.



product alkene	reaction temp. (°C)	yield
	90	95%*
	75-85	90%*
	120	80
	86	>90%*
	75	92%*

*yield determined by ^{1}NMR with mesitylene internal standard

The alkene reactions proceeded readily and cleanly under elevated temperature, with lower temperatures necessary to induce the cycloreversion of complexes derived from less strained alkenes, *e.g.* cyclopentene compared to norbornene. This observation is consistent with the alkene exchange trends previously noted by Becker and Bergman.[10]

Conclusion

The stepwise vinylic C–H functionalization of alkenes has been demonstrated by the cycloaddition of [Cp^{t}Co(NO)$_2$] to form cobalt dinitrosoalkane complexes, the

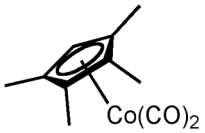
deprotonation and functionalization of these complexes, and finally the loss of the [$Cp^t(NO)_2$] moiety *via* thermolytic exchange with the unfunctionalized parent alkene. While the alkene exchange step proceeded cleanly and in high yield, the range of alkenes suitable for cobalt dinitrosoalkane formation was largely limited to cycloalkenes with significant ring strain. Chapter 2 of this dissertation will describe efforts to carry out the functionalization and alkene exchange in one reaction vessel, in a process catalytic in cobalt. Chapter 3 describes the successful development of an enantioselective conjugate addition reaction of cobalt dinitrosoalkanes, and the application of this reaction to the formation of C_2- and C_1-symmetric diene ligands.

Experimental Section

General experimental procedures. All air- and moisture-sensitive compounds were manipulated using standard Schlenk techniques. Reactions were carried out under a nitrogen atmosphere in glassware that was either oven-dried at 150 ºC overnight or flame-dried under nitrogen immediately prior to use. Pentane, hexane, diethyl ether, benzene, toluene, tetrahydrofuran (THF) and dichloromethane were dried and purified by passage through a column of activated alumina (type A2, 12 x 32, UOP LLC) under a stream of dry nitrogen. Hexamethylphosphoramide (HMPA) was dried over calcium hydride overnight, distilled under high vacuum and stored over properly activated molecular sieves. All other solvents were purified in accordance with *Purification of Laboratory Chemicals*.[16] Unless otherwise specified, all other reagents were purchased from commercial sources and used without further purification. Crotononitrile was purchased from Aldrich as a mixture of *cis* and *trans* isomers, and was determined by ^{1}H NMR to consist of roughly 62% the *cis* isomer and 38% the *trans*.

Reaction mixtures were magnetically stirred, with the exception of reactions performed in sealed NMR tubes. The majority of reactions were monitored by thin-layer chromatography (TLC) using 0.25 mm pre-coated silica gel plates from Silicycle (TLG-R10011B-323) or EMD (60 F_{254}), containing a fluorescent indicator for visualization by UV light. Various stains were used to visualize reaction products, including *p*-anisaldehyde, potassium permanganate, and phosphomolybdic acid in ethanol. Silica gel for flash chromatography was obtained from Silicycle (R12030B, particle size 40-63 μm, surface area 500 $m^2 \cdot g^{-1}$, 60 Å pore diameter) or MP Biomedicals (SiliTech gel, 32-63D, 60 Å pore diameter).

All NMR spectra were obtained at ambient temperature using Bruker AV-300, AVQ-400, or AVB-400 spectrometers. ^{1}H NMR chemical shifts are reported relative to residual solvent peaks (δ 7.24 ppm for $CDCl_3$, 7.15 ppm for C_6D_6). ^{13}C NMR chemical shifts are also reported relative to solvent peaks (δ 77.0 ppm for $CDCl_3$, 128.0 ppm for C_6D_6). NMR experiments were performed by flame-sealing medium-walled NMR tubes under vacuum after 3 freeze-pump-thaw cycles and placing the tubes in a bath of silicone oil set to the desired temperature. IR spectra were recorded on a Nicolet® Avatar® FT-IR spectrometer. Low-resolution mass-spectral data were obtained on an Agilent 6890N/5973 GC-MS equipped with a J&W Scientific DB-5MS capillary column (30 m x 0.25 mm, 0.50 μm). Both low- and high-resolution mass-spectral data were obtained from the Micromass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

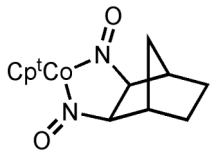


Dicarbonyl(tetramethylcyclopentadienyl)cobalt(I). To a 100-mL Schlenk flask was added 75 mL dichloromethane, and the solvent was sparged with nitrogen for 5 min. The flask was covered with aluminum foil and kept under a steady stream of nitrogen. Tetramethylcyclopentadiene (10.0 g, 82.6 mmol, 2.0 equiv. as a mixture of isomers) and octacarbonyl dicobalt(0) (14.0 g, 40.9 mmol, 1.0 equiv.) were added quickly. The flask

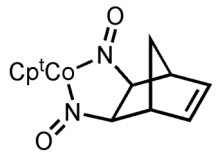
was fitted with a reflux condenser and the dark red-orange solution was heated to reflux for 48 h. The reaction mixture was cooled and the dichloromethane was carefully removed under vacuum at ambient temperature. The dark red-black residue was then distilled under reduced pressure through a 6-in Vigreaux column. The product distilled as a dark red-orange liquid that rapidly solidified in the receiver (b.p. 82-83 ºC at 1.0 torr). The product was obtained as dark red-orange crystals in 58% yield and exhibited spectroscopic properties consistent with literature data.[17]

Alkenes. Norbornene, norbornadiene, 2-azabicyclo[2.2.1]hept-5-en-3-one, *endo*-dicyclopentadiene, indene, cyclopentene, 2,5-dihydrofuran, and 2,3-dihydrofuran were obtained from commercial sources and used as received. Alkenes 2-(trimethylsilyl)norbornene, *exo*-dicyclopentadiene, and cyclobutene were prepared according to literature procedures,[18-20] while *N*-tosyl-3-pyrroline was prepared by standard tosylation of commercially available 3-pyrroline.

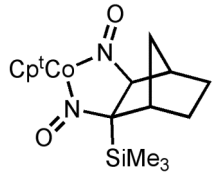
General procedure for the preparation of cobalt dinitrosoalkane complexes. An oven-dried Schlenk flask was charged with enough dry hexane to prepare a 0.1-0.2 M solution of [$Cp^tCo(CO)_2$]. The hexane was deoxygenated by sparging with nitrogen for 5 min, then [$Cp^tCo(CO)_2$] (1.0 equiv.) and the alkene (10 equiv. unless otherwise noted) were added quickly in one portion. The resulting dark red solution was cooled to 0 ºC by immersion in an ice water bath, and NO was bubbled slowly through the solution at a rate of approximately 1 bubble·s^{-1} using a silicone oil bubbler. A dark brown solid gradually precipitated from the dark red-black solution as the reaction progressed. The reaction was closely monitored by TLC until no starting material was seen (generally about 30-40 min. for reactions using less than 1.0 g of [$Cp^tCo(CO)_2$]). At this point, the NO addition was halted and nitrogen bubbled through the reaction mixture for 5 min to ensure removal of any remaining NO gas. The entire reaction mixture was loaded onto a silica gel column packed with hexanes, and the column was eluted with hexanes until all the excess alkene and starting material had been removed (the alkene generally eluted first as a light yellow band, and any remaining starting material as an orange band). The polarity of the mobile phase was then increased to 4:1 hexanes/ethyl acetate to elute the desired cobalt dinitrosoalkane complex. These complexes proved air- and moisture-stable and could be stored on the benchtop.



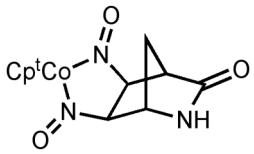
*(*cis-*2,3-Dinitrosonorbornane)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 89% yield as dark black, shiny microcrystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.48 (s, 1H), 2.68 (d, 2H, *J* = 0.8 Hz), 1.62 (s, 6H), 1.51 (s, 6H), 1.63-1.50 (m, 2H), 1.25 (m, 2H), 1.17 (d, 1H, *J* = 10.4 Hz), 0.76 (d, 1H, *J* = 10.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 100.2, 98.8, 91.5, 89.3, 42.2, 30.7, 26.6, 9.5, 7.7. HRMS $[M]^+$ calculated: 334.1092, observed: 334.1089.



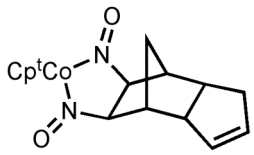
*(*cis-*5,6-Dinitrosonorbornene)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 77% yield as dark brown crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.2 (s, 2H), 4.5 (s, 1H), 3.1 (s, 2H), 2.98 (s, 2H), 1.74 (d, 1H, *J* = 9.2 Hz), 1.63 (s, 6H), 1.55 (s, 6H), 1.47 (d, 1H, *J* = 9.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ138.7, 100.1, 98.7, 91.0, 89.2, 47.0, 41.8, 9.5, 7.7. IR [neat, ν_{max} (cm^{-1})]: 2940 (w), 1482 (w), 1398 (m), 1313 (s). HRMS $[M]^+$ calculated: 332.0935, observed: 332. 0930.



*(*cis-*2,3-Dinitroso-2-trimethylsilylnorbornane)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 87% yield as dark black, shiny microcrystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.41 (s, 1H), 2.86 (br s, 1H), 2.81 (s, 1H), 2.61 (d, 1H, *J* = 4.4 Hz), 1.65 (s, 6H), 1.58 (m, 1H), 1.42 (m, 2H), 1.24 (m, 2H), 0.68 (d, 1H, *J* = 11.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 99.2, 98.2, 96.1, 96.0, 89.0, 46.7, 43.6, 32.5, 27.0, 25.3, 9.6, 7.7, 7.6, -1.6. HRMS $[M]^+$ calculated: 406.1487, observed: 406.1481.

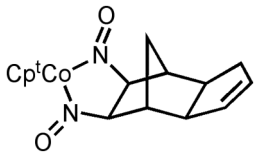


*(*cis-*5,6-Dinitroso-2-azabicyclo[2.2.1]heptan-3-one)(tetramethylcyclopentadienyl)cobalt(I)*. Only 2 equiv. of alkene were used in this reaction. The product was obtained in 44% yield as a dark brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.3 (br s, 1H), 4.5 (s, 1H), 4.1 (s, 1H), 3.2 (br s, 2H), 3.1 (br s, 1H), 1.7-1.8 (m, 2H), 1.59 (s, 6H), 1.5 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 100.9, 99.54, 99.47, 91.4, 89.7, 85.0, 57.0, 49.7, 34.4, 9.5, 7.62, 7.60. IR [neat, ν_{max} (cm^{-1})]: 3182 (br, w), 3082 (br, w), 1709 (s), 1316 (s). HRMS $[M]^+$ calculated: 349.0837, observed: 349.0831.

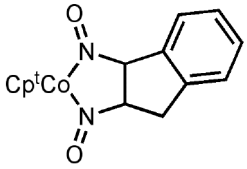


*(*cis-*5,6-Dinitroso-5,6-dihydro-*endo-*dicyclopentadiene)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 78% yield as a black microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.62-5.56 (m, 2H), 3.10 (br s, 1H), 2.79 (d, 1H, *J* = 5.2 Hz), 2.66 (m, 2H), 2.52 (m, 2H), 2.30-2.21 (m, 2H), 1.56 (s, 15H), 1.15 (d, 1H, *J* = 10.0 Hz), 0.94 (d, 1H, *J* = 10.2 Hz). ^{13}C NMR (100

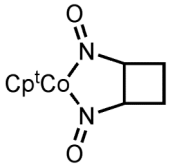
MHz, $CDCl_3$) δ 131.4, 131.1, 98.3, 88.3, 86.0, 52.5, 46.8, 45.2, 41.6, 33.7, 31.9, 7.9. HRMS $[M]^+$ calculated: 386.1405, observed: 386.1401.



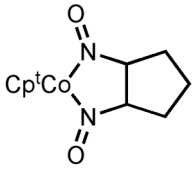
*(*cis-*5,6-Dinitroso-5,6-dihydro*-exo-*dicyclopentadiene)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 74% yield as a black microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 (d, 1H, *J* = 3.6 Hz), 5.42 (d, 1H, *J* = 3.2 Hz), 4.48 (s, 1H), 2.76 (dd, 2H, *J* = 14.0, 5.6 Hz), 2.69 (br d, 1H), 2.60 (dd, 1H, *J* = 17.2, 10.0 Hz), 2.48 (s, 1H), 2.40 (s, 1H), 2.23 (br m, 1H), 1.88 (d, 1H, *J* = 17.2 Hz), 1.63 (s, 6H), 1.54 (s, 6H), 0.96 (overlapping signals, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.9, 130.4, 100.2, 98.8, 91.8, 91.4, 89.3, 53.5, 48.3, 46.2, 41.5, 38.7, 24.6, 9.5, 7.6. HRMS $[M]^+$ calculated: 372.12480, observed: 372.12388.



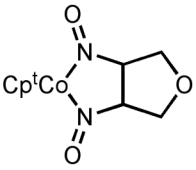
*(*cis-*1,2-Dinitrosoindane)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 77% yield as a brown, slightly crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 1H, J = 7.6 Hz), 7.33-7.21 (2 overlapping dd, 2H), 7.14 (d, 1H, *J* = 7.6 Hz), 4.49 (s, 1H), 4.34 (d, 1H, *J* = 6.4 Hz), 3.58 (dd, 1H, *J* = 11.6, 6.4 Hz), 3.41 (m, 2H), 1.62 (s, 3H), 1.61 (s, 3H), 1.54 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 137.9, 129.5, 126.7, 124.9, 124.6, 100.6, 100.5, 98.9, 92.7, 89.2, 87.0, 37.0, 9.4, 7.7. IR [neat, ν_{max} (cm^{-1})]: 2914 (w), 1481 (w), 1332 (s), 1319 (s). HRMS $[M+H]^+$ calculated: 357.1013, observed: 357.1019.



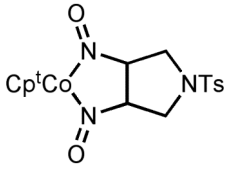
*(*cis-*1,2-Dinitrosocyclobutane)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 66% yield as a black microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.53 (s, 1H), 3.31 (dd, 2H, *J* = 3.6, 3.6 Hz), 2.51 (d, 2H, *J* = 4.0 Hz), 1.75 (d, 2H, *J* = 6.4 Hz), 1.66 (s, 6H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 100.2, 98.7, 89.1, 81.5, 26.0, 9.4, 7.6. HRMS $[M]^+$ calculated: 294.0779, observed: 294.0779.



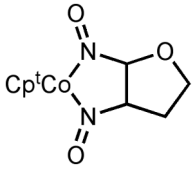
*(*cis-*1,2-Dinitrosocyclopentane)(tetramethylcyclopentadienyl)cobalt(I).* The product was obtained in 92% yield as a black microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.49 (s, 1H), 3.18 (d, 2H, *J* = 7.2 Hz), 2.17 (dd, 2H, *J* = 13.0, 5.4 Hz), 1.81 (m, 2H), 1.64 (s, 6H), 1.54 (s, 6H), 1.34 (m, 1H), 1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 100.2, 98.7, 89.6, 89.1, 32.8, 22.2, 9.5, 7.7. HRMS $[M]^+$ calculated: 308.0935, observed: 308.0932.



*(*cis-*3,4-Dinitrosotetrahydrofuran)(tetramethylcyclopentadienyl)cobalt(I).* The product was obtained in 72% yield as a black microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.5 (br s, 1H), 4.27 (d, 2H, *J* = 10.0 Hz), 3.65 (br m, 2H), 3.32 (br s, 2H), 1.61 (s, 6H), 1.53 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 100.9, 99.2, 89.5, 88.1, 71.7, 9.4, 7.7. IR [neat, ν_{max} (cm^{-1})]: 2919 (w), 2862 (m), 1398 (m), 1324 (s), 1278 (m), 1089 (s). HRMS $[M]^+$ calculated: 310.0728, observed: 310.0729.

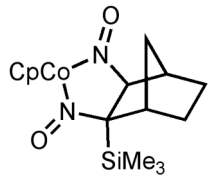


*(*cis-*3,4-Dinitroso-1-tosylpyrrolidine)(tetramethylcyclopentadienyl)cobalt(I).* Only 2 equiv. of alkene were used in this reaction. The product was obtained in 19% yield as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.2 Hz), 4.53 (s, 1H), 3.78 (d, 2H, *J* = 10.8 Hz), 3.17 (br s, 2H), 3.05 (dd, 2H, *J* = 11.2, 7.2 Hz), 2.43 (s, 3H), 1.60 (s, 6H), 1.51 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 131.8, 129.7, 127.9, 101.2, 99.7, 89.8, 85.2, 51.4, 21.5, 9.5, 7.6. IR [neat, ν_{max} (cm^{-1})]: 2881 (w), 1337 (m), 1160 (m). HRMS $[M+Na]^+$ calculated: 486.0874, observed: 486.0883.

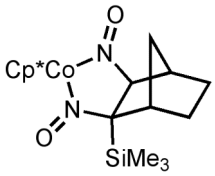


*(*cis-*2,3-Dinitrosotetrahydrofuran)(tetramethylcyclopentadienyl)cobalt(I).* The product was obtained in 64% yield as a black microcrystalline solid. An impurity was present that could not be cleanly separated from the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.54 (s, 1H), 4.34 (d, 1H, *J* = 4.8 Hz), 3.76 (m, 1H), 3.57 (m, 1H), 3.30 (m, 1H), 2.37 (m, 1H), 2.18 (m, 1H), 1.61 (s, 6H), 1.51 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$):

δ 106.7, 101.1, 99.5, 89.6, 86.3, 66.1, 32.4, 9.5, 7.7. HRMS $[M]^+$ calculated: 310.0728, observed: 310.0728.

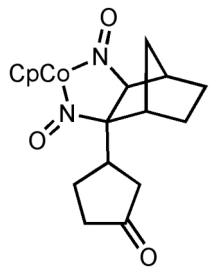


*(*cis-*2,3-Dinitroso-2-trimethylsilylnorbornane)(cyclopentadienyl)cobalt(I)*. The product was obtained in 65% yield as a black microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.9 (s, 5H), 2.81 (s, 2H), 2.59 (br s, 1H), 1.1-1.6 (several m, 5H), 0.78 (d, 1H, *J* = 10.4 Hz), 0.06 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 99.7, 98.0, 89.4, 48.6, 46.9, 43.6, 32.9, 26.7, 25.0, -1.7. HRMS $[M]^+$ calculated: 350.0861, observed: 350.0857.



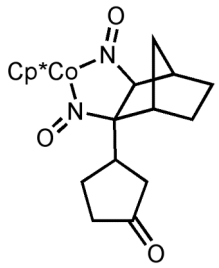
*(*cis-*2,3-Dinitroso-2-trimethylsilylnorbornane)(pentamethylcyclopentadienyl)cobalt(I)*. The product was obtained in 76% yield as a black microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.9 (1H), 2.83 (1H), 2.61 (1H), 1.6 (s, 15H), 1.46 (2H), 1.29 (1H), 1.12 (1H), 0.69 (1H), 0.2 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 97.8, 95.5, 95.3, 46.7, 43.6, 32.4, 27.1, 25.4, 7.9, -1.5. HRMS $[M]^+$ calculated: 420.1643, observed: 420.1636.

General procedure for the preparation of conjugate adducts of silylated cobalt dinitrosoalkane complexes. The cobalt dinitrosoalkane complex (25.0 mg) was dissolved in 7 mL dry THF under a stream of nitrogen. The conjugate acceptor (10.0 equiv.) was added in one portion and the dark red solution stirred at ambient temperature for 5 min. TBAF ($[Bu_4N]F$, 1.4 equiv.) was added in one portion, and the reaction was stirred until the starting material was consumed as judged by TLC (< 30 min). The solvent was removed under reduced pressure and the residue purified by column chromatography, with a hexane/ethyl acetate gradient. The reaction was performed in the same manner using TASF ($[(Me_2N)_3S][Me_3SiF_2]$) as the fluoride source, except that dry 1,2-dimethoxyethane was used as the reaction solvent.

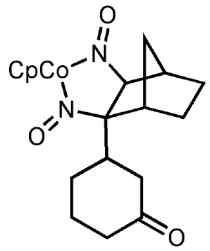


*{*cis-*2,3-Dinitroso-2-(3-oxocyclopentyl)norbornane}(cyclopentadienyl)cobalt(I)*. The product was obtained in 65% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$):

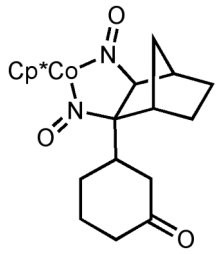
δ 4.97 (s, 5H), 2.72 (dd, 1H, *J* = 18.4, 9.4 Hz), 2.62-2.50 (m, 2H), 2.28-2.01 (m, 4H), 1.84-1.59 (several m, 6H), 1.38 (m, 1H), 1.28 (m, 1H), 0.94 (d, 1H, *J* = 10.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.4, 101.2, 98.1, 90.0, 44.8, 43.5, 40.2, 40.2, 38.0, 33.6, 26.9, 24.1, 23.8.



*{*cis-*2,3-Dinitroso-2-(3-oxocyclopentyl)norbornane}(pentamethylcyclopentadienyl)cobalt(I)*. The product was obtained in 61% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.87 (dd, 1H, *J* = 17.2, 6.8 Hz), 2.67 (br s, 1H), 2.57 (d, 1H, *J* = 4.4 Hz), 2.55 (s, 1H), 2.29 (d, 1H, *J* = 8.0 Hz), 2.22 (m, 1H), 2.09-1.94 (m, 2H), 1.56-1.38 (m, 5H), 1.30 (m, 1H), 1.16 (d, 1H, *J* = 10.4 Hz), 0.79 (d, 1H, *J* = 9.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.3, 98.8, 98.6, 98.5, 97.4, 94.4, 47.4, 44.6, 43.4, 40.4, 38.0, 33.1, 27.2, 23.9, 7.9. HRMS $[M+H]^+$ calculated: 431.1745, observed: 431.1754.



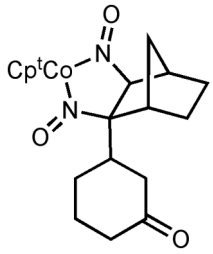
*{*cis-*2,3-Dinitroso-2-(3-oxocyclohexyl)norbornane}(cyclopentadienyl)cobalt(I)*. The product was obtained in 76% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.97 (s, 5H), 2.77-1.25 (several m, 17H), 0.92 (d, 1H, *J* = 9.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.5, 101.4, 99.6, 90.0, 43.7, 43.3, 43.1, 41.7, 41.1, 33.5, 27.1, 26.6, 25.2, 23.2. HRMS $[M]^+$ calculated: 374.1041, observed: 374.1034.



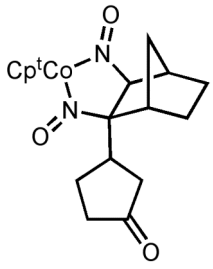
*{*cis-*2,3-Dinitroso-2-(3-oxocyclohexyl)norbornane}(pentamethylcyclopentadienyl)cobalt(I)*. The product was obtained in 65% yield as a brown solid. 1H NMR (400 MHz, $CDCl_3$): δ 2.94 (m, 1H), 2.68 (br s, 1H), 2.53-1.29 (m, 3H), 2.33-2.14 (m, 2H), 1.92 (m, 1H), 1.68-1.33 (overlapping signals, 6H), 1.57 (s, 15H), 1.27 (m, 1H), 1.18 (d, 1H, *J* = 9.6 Hz), 1.01 (m,

1H), 0.79 (d, 1H, *J* = 10.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.9, 99.2, 98.4, 95.7, 43.5, 43.4, 43.2, 42.3, 41.2, 33.2, 27.5, 26.7, 25.4, 23.4, 7.1. HRMS $[M]^+$ calculated: 444.1823, observed: 444.1829.

General procedure for the preparation of conjugate adducts of cobalt dinitrosoalkane complexes. The cobalt dinitrosoalkane complex (25.0 mg) was dissolved in a mixture of 2.5 mL dry THF and 0.5 mL dry HMPA under a stream of nitrogen. Scandium(III) triflate (1.0 equiv.) was added at ambient temperature, and the reaction mixture stirred briefly. The conjugate acceptor (10.0 equiv.) was added in one portion, followed by $Li[N(SiMe_3)_2]$ (2.0 equiv. as a 1.0 M solution in THF/ethylbenzene). The reaction mixture was stirred for 15 min and examined by TLC. If the reaction was not complete, small aliquots of additional $Li[N(SiMe_3)_2]$ were added until TLC indicated the disappearance of the starting material (generally < 30 min). The solvent was removed under reduced pressure, and the residue purified by column chromatography with a hexane/ethyl acetate gradient.

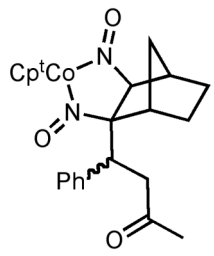


*{*cis*-2,3-Dinitroso-2-(3-oxocyclohexyl)norbornane}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 82% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.49 (s, 1H), 2.92 (dd, 1H, *J* = 13.6 Hz), 2.68 (br s, 1H), 2.55-2.52 (m, 3H), 2.31 (br d, 1H, *J* = 12.4 Hz), 2.19 (t of d, 1H, *J* = 13.8. 6.4 Hz), 1.95 (m, 2H), 1.65 (s, 3H), 1.64 (s, 3H), 1.57 (s, 6H), 1.5-1.35 (m, 4H), 1.46-1.41 (m, 3H), 1.1 (m, 1H), 0.83 (d, 1H, *J* = 10.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.9, 100.1, 100.06, 99.6, 98.9, 98.8, 96.3, 89.5, 43.5, 43.3, 43.2, 42.0, 41.1, 33.2, 27.4, 26.7, 25.3, 23.4, 9.6, 7.65, 7.57. HRMS $[M]^+$ calculated: 430.1667, observed: 430.1659.

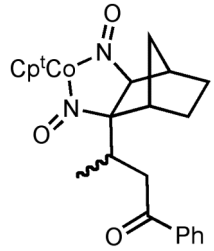


*{*cis*-2,3-Dinitroso-2-(3-oxocyclopentyl)norbornane}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 59% yield (69% yield based on recovered starting material) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.51 (s, 1H), 2.89 (dd, 1H, *J* = 17.4, 7.8 Hz), 2.71 (s, 1H), 2.68-2.54 (m, 2H), 2.34-1.99 (several m, 4H), 1.8 (m, 1H), 1.67 (s, 3H), 1.65 (s, 3H), 1.65-1.2 (m, 6H), 1.56 (s, 6H), 0.88 (d, 1H, *J* = 9.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ

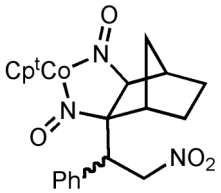
218.1, 100.3, 99.35, 99.03, 95.1, 89.5, 44.8, 43.5, 40.43, 40.39, 38.1, 33.3, 27.2, 24.04, 23.96, 9.6, 7.68, 7.60. HRMS $[M]^+$ calculated: 416.1510, observed: 416.1508.



*{*cis-*2,3-Dinitroso-2-(3-oxo-1-phenylbutyl)norbornane}(tetramethylcyclopentadienyl)cobalt(I)*. The brown solid was obtained in 70% yield as a 3:1 mixture of diastereomers. *Major diastereomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-6.91 (aromatic signals, 5H), 4.13 (s, 1H), 3.55 (dd, 1H, *J* = 17.6, 11.2 Hz), 3.22 (d, 1H, *J* = 9.6 Hz), 2.94 (d, 1H, *J* = 17.6 Hz), 2.76-2.52 (m, 3H), 2.50 (m, 1H), 1.99 (s, 3H), 1.6-1.3 (m, 3H), 1.55 (s, 3H), 1.50 (s, 3H), 1.47 (s, 3H), 1.46 (s, 3H), 0.87 (d, 1H, *J* = 9.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 138.4, 129.6, 127.9, 126.7, 100.0, 99.9, 99.7, 98.6, 97.7, 96.0, 90.0, 44.7, 44.6, 43.5, 43.4, 33.6, 31.0, 27.1, 23.6, 9.6, 9.2, 7.6, 7.4. HRMS $[M]^+$ calculated: 480.1823, observed: 480.1825.

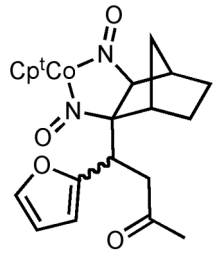


*{*cis-*2,3-Dinitroso-2-(3-oxo-3-phenyl-1-methylpropyl)norbornane}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 81% yield as a 1:1 mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (m, 1H), 7.8 (m, 1H), 7.62-7.38 (aromatic signals, 3H), 4.50 and 4.495 (2 s, 1H total), 3.39 (dd, 0.5H, *J* = 18.4, 10.2 Hz), 3.20 (d, 0.5H, *J* = 18.4 Hz), 2.80 and 2.74 (2 br s, 1H total), 2.65-2.53 (m, 3H), 2.38-2.33 (m, 1H), 1.69 (s, 1.5H), 1.68 (s, 1.5H), 1.67 (s, 1.5H), 1.64 (s, 1.5H), 1.60 (s, 1.5H), 1.59 (s, 1.5H), 1.56 (s, 3H), 1.68-1.35 (m, 5H), 1.19 (d, 1.5H, *J* = 6.8 Hz), 0.87 (d, 1H, *J* = 10.4 Hz), 0.63 (d, 1.5H, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 198.8, 137.3, 133.1, 128.5, 128.1, 127.8, 100.0, 99.5, 99.1, 98.1, 97.7, 89.5, 89.2, 44.0, 43.9, 43.5, 41.0, 40.5, 33.6, 33.5, 32.7, 31.9, 27.4, 27.2, 23.6, 23.3, 15.6, 15.2, 9.6, 7.7, 7.6. HRMS $[M]^+$ calculated: 480.1823, observed: 480.1815.

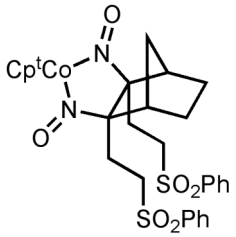


*{*cis-*2,3-Dinitroso-2-(2-nitro-1-phenylethyl)norbornane}(tetramethylcyclopentadienyl)cobalt(I)*. The product was

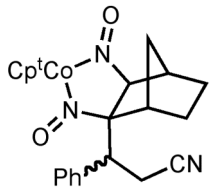
obtained in 53% yield (99% based on recovered starting material) as a brown solid. The product was one major diastereomer as indicated by NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (m, 3H), 6.93 (m, 2H), 5.35 (dd, 1H, *J* = 13.4, 11.8 Hz), 4.88 (dd, 1H, *J* = 13.6, 2.8 Hz), 4.19 (s, 1H), 3.53 (dd, 1H, *J* = 11.6, 2.8 Hz), 2.75 (br s, 1H), 2.65 (s, 1H), 3.51 (d, 1H, *J* = 2.8 Hz), 1.83-1.74 (m, 2H), 1.56 (s, 3H), 1.51 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.6-1.4 (m, 3H), 0.94 (d, 1H, *J* = 10.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.2, 129.4, 128.0, 127.9, 100.3, 100.2, 99.2, 99.1, 96.9, 94.7, 90.2, 46.4, 44.6, 43.3, 33.7, 27.0, 23.7, 9.4, 9.2, 7.5, 7.3. HRMS $[M+H]^+$ calculated: 484.1647, observed: 484.1643.



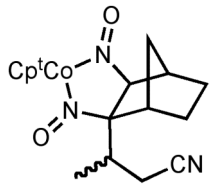
*(*cis-*2,3-Dinitroso-2-{3-oxo-1-(2-furyl)butyl}norbornane)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 61% yield as one major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 1H), 6.07 (d, 1H, *J* = 1.6 Hz), 5.80 (d, 1H, *J* = 2.8 Hz), 4.23 (s, 1H), 3.54-3.42 (overlapping signals, 2H), 2.95 (s, 1H), 2.85 (d, 1H, *J* = 16.8 Hz), 2.70 (br s, 1H), 2.57 (br s, 1H), 2.12 (s, 3H), 1.6-1.2 (m, 5H), 1.51 (s, 3H), 1.50 (s, 3H), 1.40 (s, 6H), 0.84 (d, 1H, *J* = 10.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8, 153.2, 141.0, 109.7, 106.8, 100.0, 98.7, 98.3, 96.1, 89.4, 44.0, 43.3, 42.5, 37.0, 33.3, 30.6, 27.2, 23.4, 9.5, 9.4, 7.53, 7.45. HRMS $[M+H]^+$ calculated: 471.1694, observed: 471.1693.



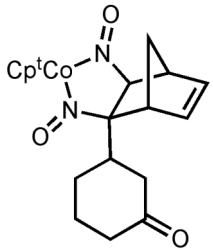
*(*cis-*2,3-Dinitroso-2,3-bis{2-(phenylsulfonyl)ethyl}norbornane)(tetramethylcyclopentadienyl)cobalt(I)* The product was obtained in 56% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.22 (aromatic signals, 10H), 4.43 (s, 1H), 3.33 (m, 2H), 3.02 (m, 2H), 2.48 (2H), 2.04 (m, 3H), 1.67 (m, 3H), 1.33-0.66 (several signals, 6H), 1.49 (s, 6H), 1.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 133.9, 129.4, 127.9, 100.7, 99.1, 96.0, 89.8, 52.4, 46.2, 32.4, 25.0, 24.3, 9.3, 7.3. HRMS $[M+Na]^+$ calculated: 693.1479, observed: 693.1476.



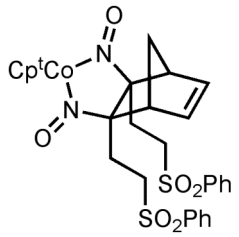
*{*cis-*2,3-Dinitroso-2-(2-cyano-1-phenylethyl)norbornane}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 31% yield as one major diastereomer. ^{1}H NMR (400 MHz, C_6D_6): δ 0.55 (d, 1H, *J* = 10 Hz), 0.794-1.194 (m, 5H), 1.268 and 1.292 (overlapping singlets, 6H total), 1.386 (s, 3H), 1.475 (s, 3H), 2.486-2.585 (m, 5H), 3.20 (dd, 1H, *J* = 16.8, 11.2 Hz), 3.988 (s, 1H), 6.682-6.93 (aromatic signal, 5H). ^{13}C NMR (100 Mz, C_6D_6): δ 7.35, 7.51, 9.21, 9.52, 19.28, 23.98, 27.18, 30.23, 33.84, 43.83, 44.51, 45.21, 90.22, 94.26, 97.78, 98.41, 98.56, 99.89, 118.30, 127.43, 129.59, 136.47. HRMS $[M]^+$ calculated: 463.1670, observed: 463.1668.



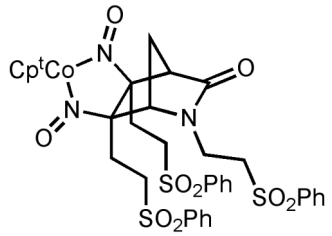
*{*cis-*2,3-Dinitroso-2-(2-cyano-1-methylethyl)norbornane}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 65% yield as a 4:1 mixture of diastereomers. ^{1}H NMR (400 MHz, C_6D_6): δ 0.49 (dd, 1H, *J* = 10.4, 1.2 Hz), 0.64 (d, 2H, *J* = 6.8 Hz), 0.66-0.92 (m, 4H), 1.067-1.160 (m, 2H), 1.370-1.401 (m, 7H), 1.539-1.548 (two singlets, 3H total), 1.562-1.571 (two singlets, 3H total), 2.14 (dd, 1H, *J* = 17.2, 3.2 Hz), 2.255 (s, 1H), 2.373 (d, 1H, *J* = 2.4 Hz), 2.464-2.623 (m, 2H), 4.264 (s, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 7.54, 7.60, 9.55, 15.08, 19.77, 20.59, 23.44, 27.11, 30.23, 33.66, 43.62, 43.79, 89.51, 95.21, 98.61, 98.69, 98.94, 100.04, 100.15, 118.89. HRMS $[M+H]^+$ calculated: 402.1592, observed: 402.1592.



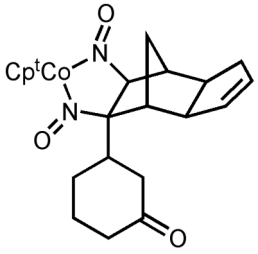
*{*cis-*5,6-Dinitroso-5-(3-oxocyclohexyl)norbornene}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 69% yield as one major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24 (s, 2H), 4.55 (s, 1H), 3.12 (br s, 2H), 2.94 (t, 1H, *J* = 13.8 Hz), 2.74 (s, 1H), 2.51-2.18 (several m, 4H), 2.02 (m, 1H), 1.82 (d, 1H, *J* = 9.2 Hz), 1.68 (d, 3H, *J* = 0.8 Hz), 1.7-1.5 (m, 2H), 1.65 (s, 3H), 1.56 (s, 6H), 1.47-1.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 138.6, 137.5, 99.6, 99.5, 98.9, 97.5, 89.3, 48.3, 48.1, 44.3, 44.0, 43.4, 41.1, 26.7, 25.1, 9.6, 7.7, 7.6. IR [neat, ν_{max} (cm^{-1})] 2920 (m), 2880 (w), 1711 (m), 1329 (s), 1298 (m). HRMS $[M]^+$ calculated: 428.1510, observed: 428.1501.



*(*cis-*5,6-Dinitroso-5,6-bis{2-(phenylsulfonyl)ethyl}norbornene)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 61% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.58 (aromatic signals, 10H), 5.97 (s, 2H), 4.48 (s, 1H), 3.36 (t of d, 2H, *J* = 13.2, 4.4 Hz), 3.00 (t of d, 2H, *J* = 13.1, 3.7 Hz), 2.92 (s, 2H), 1.94 (t of d, 2H, *J* = 13.2, 3.5 Hz), 1.65 (t of d, 2H, *J* = 13.1, 4.0 Hz), 1.47 (s, 6H), 1.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 137.4, 133.8, 129.4, 128.0, 100.7, 99.1, 98.4, 89.7, 52.6, 51.5, 44.1, 27.4, 9.3, 7.3. HRMS $[M+Na]^+$ calculated: 691.1323 observed: 691.1307.



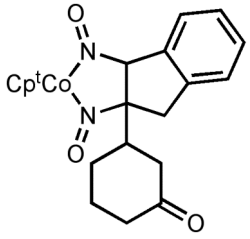
*(*cis-*5,6-Dinitroso-2,5,6-tris{2-(phenylsulfonyl)ethyl}-2-azabicyclo[2.2.1]heptan-3-one)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 50% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.9-7.56 (aromatic signals, 15H), 4.57 (s, 1H), 4.00 (s, 1H), 3.66-3.51 (2 m, 3H), 3.31-3.26 (m, 2H), 3.07-2.99 (m, 2H), 2.88 (s, 1H), 2.27 (m, 2H), 1.93 (m, 2H), 1.76-1.71 (m, 3H), 1.49 and 1.488 (2 s, 6H), 1.38 and 1.37 (2 s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 138.5, 134.2, 134.17, 133.66, 129.64, 129.59, 128.48, 129.2, 128.3, 128.0, 127.8, 101.5, 99.9, 99.8, 98.4, 66.6, 54.4, 52.8, 52.1, 51.4, 37.0, 36.2, 26.7, 25.0, 9.3, 7.26, 7.21. HRMS $[M+Na]^+$ calculated: 876.1469, observed: 876.1464.



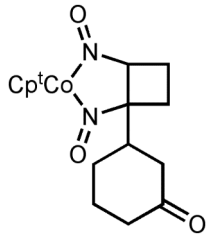
+ regioisomer

*{*cis-*5,6-Dinitroso-5-(3-oxacyclohexyl)-6-hydro*-exo-*dicyclopentadiene)(tetramethylcyclopentadienyl)cobalt(I) and regioisomer*. The product was obtained as a mixture of regioisomers in 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65 (m, 1H), 5.39 (m, 1H), 4.48 (s, 1H), 2.98-1.41 (several m, 16H), 1.639 (s, 3H), 1.630 (s, 3H), 1.53 (s, 6H), 1.16-0.92 (2 m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.9, 210.8, 133.1, 132.8, 130.5, 130.4, 100.1, 100.0, 99.7, 99.4, 98.93, 98.85, 96.7, 96.6, 89.5, 54.2,

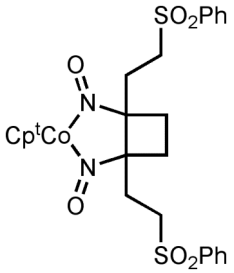
49.9, 49.4, 49.1, 47.9, 46.6, 43.2, 43.1, 42.3, 41.5, 41.4, 41.1, 39.1, 39.0, 38.1, 37.5, 26.8, 26.7, 26.6, 25.3, 9.6, 7.62, 7.55. HRMS $[M+H]^+$ calculated: 469.1901, observed: 469.1904.



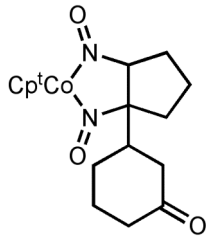
*{*cis-*1,2-Dinitroso-2-(3-oxocyclohexyl)indane}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 15% yield as a brown solid contaminated with small amounts of impurities. *Major product*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.08 (aromatic signals, 4H), 4.44 (s, 1H), 3.99 (d, 1H, *J* = 18 Hz), 3.23 (d, 1H, *J* = 18 Hz), 2.67 (m, 1H), 2.34 (s, 1H), 1.85-1.3 (overlapping m, 7H), 1.58-1.45 (several s, 12H total). The material decomposed before a ^{13}C NMR spectrum could be obtained. IR [neat, ν_{max} (cm^{-1})] 2927 (m), 2862 (w), 1708 (m), 1458 (w), 1328 (s), 1314 (s). HRMS $[M]^+$ calculated: 452.1510, observed: 452.1523.



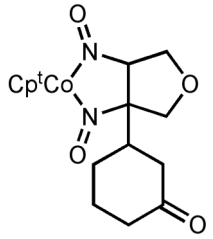
*{*cis-*1,2-Dinitroso-1-(3-oxocyclohexyl)cyclobutane}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 79% yield as a mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.53 and 4.51 (2 s, 1H total), 3.39 (dd, 0.3H from the minor diastereomer, *J* = 9.0, 4.6 Hz), 3.0 (m, 0.3H from the minor diastereomer), 2.60 (m, 0.7H from major diastereomer), 2.45-1.5 (several overlapping signals, 13H), 1.64-1.48 (several s, 12H total). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.3, 210.1, 99.90, 99.85, 98.7, 98.57, 94.6, 91.3, 89.4, 89.2, 84.9, 74.7, 46.3, 44.8, 43.2, 42.2, 41.3, 41.2, 39.3, 38.7, 37.6, 36.8, 30.6, 29.1, 27.0, 26.2, 26.0, 25.0, 24.9, 24.7, 24.5, 24.0, 22.7, 20.2, 9.45, 9.29, 7.62, 7.51, 7.27, 7.23. A second fraction appeared to be the alcohol from reduction of the ketone. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.53 and 4.52 (2 s, 1H), 2.60 (m, 1H), 2.39-2.3 (br s, 2H), 2.20 (s, 1H), 2.18-1.98 (2 m, 2H), 1.81-1.68 (m, 2H), 1.67-1.5 (m, 4H), 1.643 and 1.639 (2 s, 6H), 1.523 and 1.518 (2 s, 6H), 1.41-1.2 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 99.90, 98.8, 98.7, 94.6, 89.4, 74.8, 44.8, 39.3, 36.8, 29.1, 27.0, 24.0, 20.2, 9.29, 9.27, 7.27, 7.23. HRMS $[M]^+$ calculated: 390.1354, observed: 390.1349.



(cis-1,2-Dinitroso-1,2-bis{2-(phenylsulfonyl)ethyl}cyclobutane)(tetramethylcyclopentadienyl)cobalt(I). The product was obtained in 51% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.60 (aromatic signals, 10H), 4.50 (s, 1H), 3.19 (d of t, 2H, *J* = 13.1, 4.7 Hz), 3.00 (m, 2H), 2.23 (m, 2H), 1.95-1.84 (m, 4H), 1.64 (dd, 2H, *J* = 12.6, 6.2 Hz), 1.53 (s, 6H), 1.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 133.9, 129.5, 128.0, 100.9, 99.2, 90.2, 89.6, 51.6, 28.0, 25.5, 9.3, 7.3. HRMS $[M]^+$ calculated: 630.1269, observed: 630.1284.

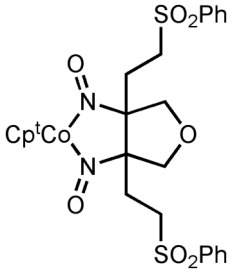


*{*cis-*1,2-Dinitroso-1-(3-oxocyclohexyl)cyclopentane}(tetramethylcyclopentadienyl)cobalt (I)*. The product was obtained in 48% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.50 (s, 1H), 2.69 (d, 1H, *J* = 9.2 Hz), 2.40 (ddd, 1H, *J* = 13.00, 6.2, 2.4 Hz), 2.32 (br m, 1H), 2.24-2.03 (overlapping signals, 3H), 1.7-1.2 (m, 10H), 1.67 (s, 3H), 1.65 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.35, 210.25, 100.3, 99.42, 99.35, 98.9, 93.4, 93.1, 89.4, 44.29, 44.21, 43.1, 41.2, 41.0, 35.5, 35.2, 33.7, 33.5, 27.2, 26.0, 24.8, 23.0, 22.8, 9.5, 7.7, 7.6. IR [neat, ν_{max} (cm^{-1})]: 2926 (w), 2869 (w), 1708 (m), 1331 (s). HRMS $[M]^+$ calculated: 404.1510, observed: 404.1517.

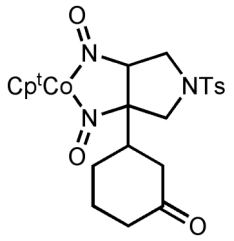


*{*cis-*3,4-Dinitroso-3-(3-oxocyclohexyl)tetrahydrofuran}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.58 (s, 1H), 4.33 (d, 1H, *J* = 9.6 Hz), 4.24 (d, 1H, *J* = 10.4 Hz), 4.01 (d, 1H, *J* = 10.4 Hz), 3.46 (d, 1H, *J* = 9.6 Hz), 2.5-2.2 (several m, 5H), 2.01 (m, 1H), 1.66 (s, 3H), 1.63 (s, 3H), 1.58 (s, 3H), 1.49 (s, 3H), 1.4-1.2 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 100.9, 99.4, 98.1, 92.4, 89.7, 74.0, 72.1, 42.8, 41.8, 40.9, 27.3, 24.6, 9.5, 7.7. IR [neat, ν_{max} (cm^{-1})]: 3513 (w), 2923 (m), 2862 (w), 1712 (m), 1309 (s), 1286 (m), 1192 (s), 1123 (s). HRMS $[M]^+$ calculated:

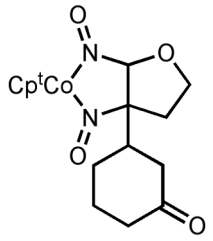
406.1303, observed: 406.1304.



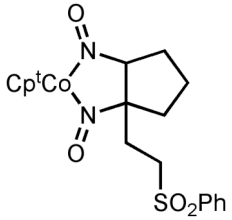
*(*cis-*3,4-Dinitroso-3,4-bis{2-(phenylsulfonyl)ethyl}tetrahydrofuran)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 40% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.62 (aromatic signals, 10H), 4.54 (s, 1H), 4.50 (s, 1H), 4.19-4.15 (2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.44, 134.1, 129.6, 128.0, 101.5, 99.9, 96.1, 90.1, 75.6, 53.8, 51.8, 25.6, 18.5, 9.4, 7.5.



*{*cis-*3,4-Dinitroso-1-tosyl-3-(3-oxocyclohexyl)pyrrolidine}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 37% yield as a mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62, 7.58 (2 d, 2H, *J* = 8.0 Hz), 7.32, 7.27 (2 d, 2H, *J* = 7.8 Hz), 4.55, 4.53 (2 s, 1H), 3.99 and 3.65 (2d, 1H, *J* = 10.4 Hz), 3.85 and 3.44 (d, 1H, *J* = 14.0 Hz), 3.25 and 3.00 (d, 2H, *J* = 10.8 Hz), 2.65 (d, 1H, *J* = 10.4 Hz), 2.43 (s, 3H), 2.4-1.2 (several m, 9H), 1.61 (6H), 1.49 (6H). HRMS $[M]^+$ calculated: 559.1551, observed: 559.1556.

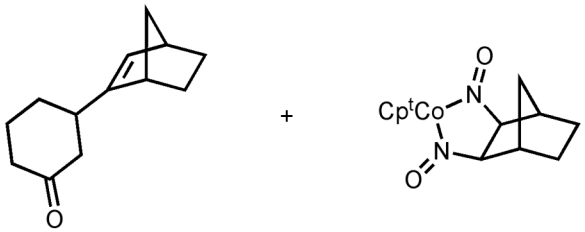


*{*cis-*2,3-Dinitroso-3-(3-oxocyclohexyl)tetrahydrofuran}(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 61% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.57 (s, 1H), 4.25 (s, 1H), 3.78 (dd, 1H, *J* = 8.2, 8.2 Hz), 3.58 (m, 1H), 2.45-1.25 (several m, 9H), 1.61 and 1.51 (2 s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.6, 110.3, 100.2, 99.7, 96.7, 89.8, 66.9, 44.1, 43.0, 41.2, 34.8, 26.5, 24.7, 9.5, 7.7. HRMS $[M]^+$ calculated: 406.1303; observed: 406.1305.

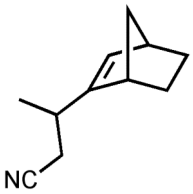


*(*cis-*1,2-Dinitroso-1-{2-(phenylsulfonyl)ethyl}cyclopentane)(tetramethylcyclopentadienyl)cobalt(I)*. The product was obtained in 17% yield as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.59 (aromatic signals, 5H), 4.51 (s, 1H), 3.02 (d, 1H, *J* = 8.4 Hz), 2.82-2.78 (m, 2H), 2.45-2.39 (m, 1H), 2.26 (m, 1H), 2.09-2.06 (m, 1H), 1.90-1.83 (br m, 2H), 1.62 (s, 3H), 1.60 (s, 3H), 1.51 (s, 3H), 1.50 (s, 3H), 1.4-1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 135.0, 129.4, 128.0, 100.5, 100.4, 99.1, 95.0, 94.5, 89.5, 51.9, 37.8, 33.2, 29.9, 22.8, 9.5, 7.7, 7.6. HRMS $[M+H]^+$ calculated: 477.1258, observed: 477.1256.

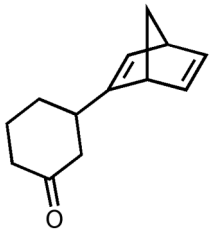
General procedure for the cycloreversion/alkene exchange reactions of cobalt dinitrosoalkane complexes. A medium-walled NMR tube was charged with 5.0 mg cobalt dinitrosoalkane complex, 10.0 equiv. parent alkene and 0.3 mL deuterated benzene containing mesitylene (approximately 0.5 mg) as an internal standard. The NMR tube was subjected to three freeze-pump-thaw cycles and then flame-sealed under vacuum. The sealed tube was placed in a constant temperature bath at the desired temperature and monitored periodically by ^{1}H NMR spectroscopy. Larger-scale reactions were performed in thick-walled sealed glass tubes. When TLC analysis indicated that the reaction was complete, the volatile materials were removed under reduced pressure and the residue purified by column chromatography with a hexane/ethyl acetate gradient to give a mixture of the desired functionalized alkene and the cobalt dinitrosoalkane complex of the parent alkene.



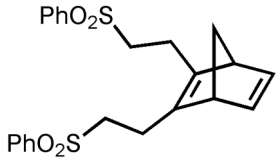
2-(3-Oxocyclohexyl)norbornene. The reaction mixture was heated at 75 °C for 16 h and then heated at 90 ºC for 6 h. A 95% NMR yield was obtained based on the use of mesitylene as the internal standard. Data are given for a mixture of the organic product and the parent $[Cp^tCo(NO)_2]$/norbornene adduct. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.57 (s, 1H), 4.44 (s, 1H), 2.75 (d, 2H, *J* = 11.2 Hz), 2.64 (br s, 2H), 2.59 (br s, 2H), 2.5 (m, 2H), 2.4-2.21 (m, 4H), 2.05-1.86 (m, 3H), 1.60 (s, 6H), 1.50 (s, 6H), 1.7-0.97 (several m, 11H), 0.72 (d, 1H, *J* = 13.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.9, 152.2, 127.7, 100.4, 99.0, 91.8, 89.5, 49.2, 46.7, 44.1, 42.4, 42.3, 41.7, 40.1, 31.0, 30.2, 26.9, 26.4, 25.3, 9.8, 7.9.



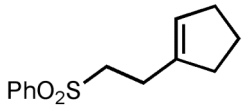
2-(2-Cyano-1-methylethyl)norbornene. The reaction mixture was heated at 75 °C for 15 h and 85 °C for 20 h. A 90% NMR yield was obtained based on the use of mesitylene as the internal standard. This reaction was performed preparatively in 4 mL benzene, using 63.2 mg (0.16 mmol) functionalized cobalt complex and 7.5 equiv. norbornene, with the reaction mixture heated for 9 min at 130 °C in a Biotage Initiator™ Eight microwave reactor. Every 3 min, reaction progress was examined by TLC, using chloroform as the developing solvent. After solvent was removed, the crude product was chromatographed on silica gel using 1:1 pentane/chloroform, followed by pure chloroform, as eluent. The product was isolated in 65% yield as a yellow oil. ^{1}H NMR (400 MHz, C_6D_6): δ 5.40 (br s, 1H), 2.64 (d, 1H, *J* = 1.6 Hz), 2.37 (s, 1H), 2.04-1.96 (m, 1H), 1.67-1.39 (m, 4H), 1.33-1.29 (m, 1H), 0.99-0.91 (m, 2H), 0.81 (s, 2H), 0.79 (s, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 150.96, 128.57, 118.39, 49.08, 43.74, 42.46, 31.45, 26.27, 25.29, 23.02, 18.18. HRMS $[M]^+$ calculated: 161.1204, observed: 161.1200.



2-(3-Oxocyclohexyl)norbornadiene. The reaction mixture was heated in a sealed tube at 120 °C for 36 h. The isolated yield based on recovered starting material was 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66 (m, 2H), 6.11 (m, 1H), 3.45 (m, 1H), 3.28 (m, 1H), 2.69 (m, 1H), 2.42 (dd, 1H, *J* = 14.4, 4.4 Hz), 2.28-2.10 (m, 3H), 1.98-1.82 (m, 3H), 1.67 (d, 1H, *J* = 9.2 Hz), 1.42 (d, 1H, *J* = 9.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.4, 160.6, 143.7, 142.1, 134.2, 73.3, 52.4, 49.9, 45.8, 41.4, 40.0, 28.6, 24.2.



2,3-Bis{2-(phenylsulfonyl)ethyl}norbornadiene. The reaction mixture was heated in a sealed NMR tube at 75 °C for 15 h (approximately 50% conversion), then heated at 86 °C for 26 h. The product was obtained in a >90% NMR yield using mesitylene as the internal standard. ^{1}H NMR (400 MHz, C_6D_6): δ 7.88 (d, 4H, *J* = 8.0 Hz), 7.07-7.04 (m, 6H), 6.46 (m, 2H), 2.94-2.89 (m, 4H), 2.82-2.75 (m, 2H), 2.51-2.43 (m, 2H), 2.35-2.23 (m, 2H), 1.82 (m, 1H), 1.46 (m, 1H).



1-{2-(Phenylsulfonyl)ethyl}cyclopentene. The reaction mixture was heated in a sealed NMR tube at 75 °C for 15 h. The product was obtained in a 92% NMR yield using mesitylene as the internal standard. ^{1}H NMR (400 MHz, C_6D_6): δ 7.83 (d, 2H, J = 8.0 Hz), 7.06-6.9 (m, 3H), 5.01 (br s, 1H), 2.95 (m, 4H), 2.4-1.4 (6H), 1.56 and 1.53 (2 s, 12H).

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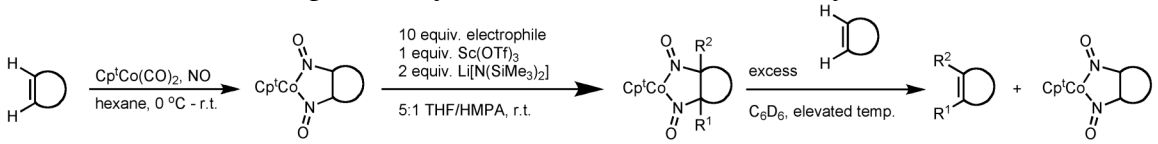
Chapter 2

Progress Towards the Cobalt(I)-Catalyzed Vinylic C–H Functionalization of Alkenes

Catalysis: Goals and Challenges

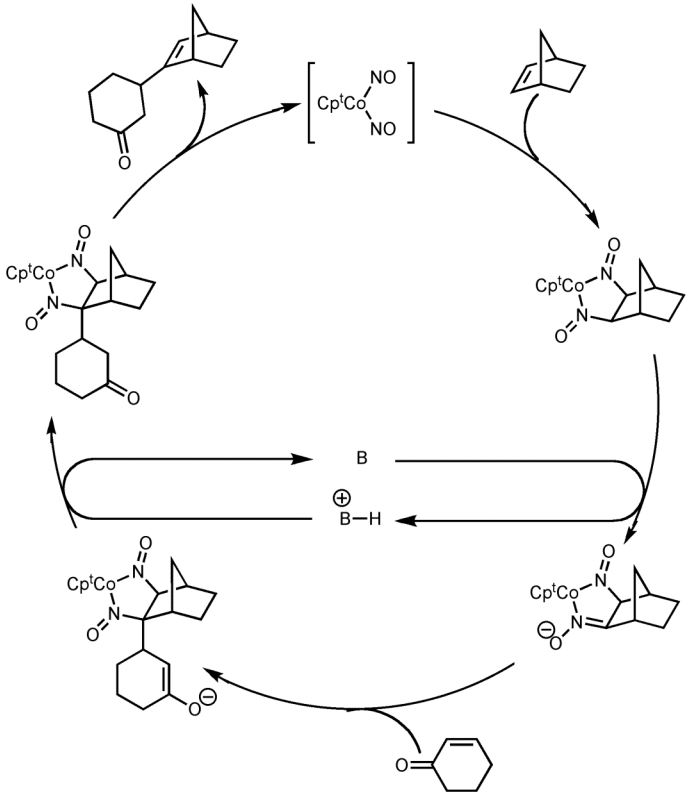
The preceding chapter describes the vinylic C–H functionalization of cycloalkenes *via* a stepwise process: formation of a cobalt(I) dinitrosoalkane complex acidifies the formerly vinylic hydrogen atoms, now α to the nitroso groups of the complex. These complexes, once deprotonated, add as nucleophiles to α,β-unsaturated ketones, nitriles, nitro compounds and sulfones in a conjugate fashion, yielding functionalized cobalt complexes. Finally, thermolysis of the functionalized complexes in the presence of the unfunctionalized parent alkene results in the [Cp^{t}Co(NO)$_2$] moiety migrating to the parent alkene, regenerating the initial cobalt dinitrosoalkane and yielding a functionalized alkene as the organic product (Scheme 2.1).[1]

Scheme 2.1. Stepwise vinylic C–H functionalization of cycloalkenes.



The stepwise success of this C–H functionalization strategy raised the possibility that the functionalization and alkene exchange could be made to occur in the same reaction vessel, and that a catalytic amount of cobalt could be used. The proposed catalytic cycle is shown below (Scheme 2.2), with norbornene and 2-cyclohexen-1-one as the alkene and electrophile respectively.

Scheme 2.2. Proposed catalytic cycle for the cobalt-catalyzed C–H functionalization of alkenes.



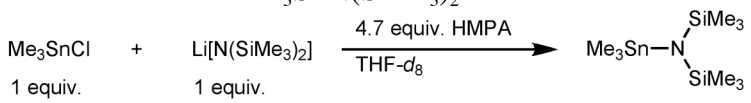
The cycle shown in Scheme 2.2 depicts a reaction catalytic with respect to the Brønsted base as well as to cobalt. In principle, the one-pot, catalytic reaction could be developed using stoichometric quantities of base. The fact that elevated temperatures are required for the alkene exchange reaction which releases the organic product, however, suggested that the use of stoichiometric amounts of the base might be overly harsh under these one-pot conditions. This is especially a concern for cobalt dinitrosoalkanes derived from five-membered cycloalkenes; the stoichiometric functionalization of such complexes required rapid handling, as they tended to decompose if left in basic solution.[1]

Tin(IV) Amides as Sub-Stoichiometric Bases

Initial design of a catalytic system focused on one source of complexity in the stoichiometric system, namely, the presence of a Lewis acid in addition to a Brønsted base in the conjugate addition step. Lewis acids such as $Sc(OTf)_3$ have (at least) two possible roles in the mechanism of conjugate addition: acidification of the cobalt dinitrosoalkanes by coordination to the nitroso oxygen, and coordination to the conjugate acceptor to increase its electrophilicity. Additionally, Brønsted bases like $[N(SiMe_3)_2]^-$ have the potential to act as Lewis bases and form adducts with the Lewis acids used. For example, the amido complex $Sc[N(SiMe_3)_2]_3$ can be formed from the salt metathesis reaction of $Li[N(SiMe_3)_2]$ and $ScCl_3$,[2] and similar reactivity between $Li[N(SiMe_3)_2]$ and $Sc(OTf)_3$ may occur under reaction conditions. Further supporting this possibility was the observation that two equivalents of $Li[N(SiMe_3)_2]$ are required for significant conversion in the conjugate addition shown in Scheme 2.1,[1] suggesting that the first equivalent may be rendered less basic by such adduct formation.

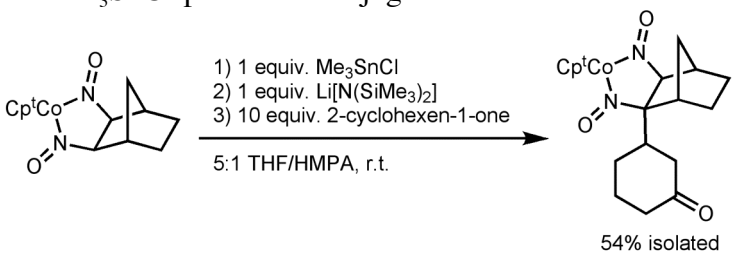
Reasoning that a Lewis acid with only one labile ligand might provide a reaction that is easier to study mechanistically or tune for optimal synthetic results, an NMR-scale reaction was conducted between equimolar amounts of $Li[N(SiMe_3)_2]$ and chlorotrimethylstannane, Me_3SnCl, in the presence of HMPA. This reaction proceeded fairly cleanly, yielding the mixed silylamine/stannylamine $Me_3SnN(SiMe_3)_2$ *in situ* (Scheme 2.3).

Scheme 2.3. Formation of $Me_3SnN(SiMe_3)_2$.



Following this result, Me_3SnCl was examined as a Lewis acid in the conjugate addition reaction of cobalt dinitrosoalkanes (Scheme 2.4). Notably, only one equivalent of $Li[N(SiMe_3)_2]$ was required to effect complete conversion of the starting cobalt complex as judged by thin layer chromatrography (TLC).

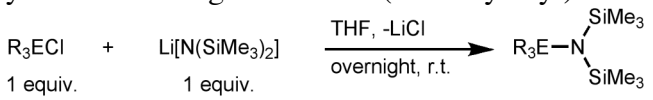
Scheme 2.4. Me_3SnCl-promoted conjugate addition.



The reaction in Scheme 2.4 also proceeded with $Li[N(SiMe_3)_2]$ added as the final reagent to a mixture of cobalt complex, Me_3SnCl, and 2-cyclohexen-1-one, as in conjugate additions performed with other Lewis acids, but in this case 1.2 equiv. base were necessary to effect complete conversion by TLC, and the isolated yield fell to 43%.

Given the competency of a $Me_3SnCl/Li[N(SiMe_3)_2]$ mixture at promoting conjugate addition, and NMR evidence for the formation of the potentially active species $Me_3SnN(SiMe_3)_2$, $Me_3SnN(SiMe_3)_2$ and other triorganotetrel bis(trimethylsilyl)amides were synthesized on a preparative scale *via* salt metathesis (Table 2.1).

Table 2.1. Synthesis of triorganotetrel bis(trimethylsilyl)amides.

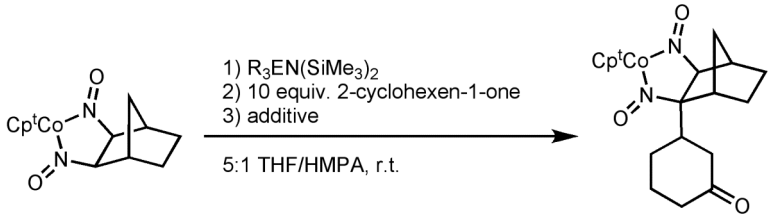


E	R	yield
Sn	Me	89%
Sn	Ph	89%
Ge	Ph	90%

Preparations of the tin compounds listed in Table 2.1 have previously been reported in the literature,[3] but the germane $Ph_3GeN(SiMe_3)_2$ has not, to the best of my knowledge.

The tetrel amides were screened for their competence in the conjugate addition reaction of a cobalt dinitrosoalkane to 2-cyclohexen-1-one (Table 2.2).

Table 2.2. Triorganotetrel amide-promoted conjugate addition reactions.



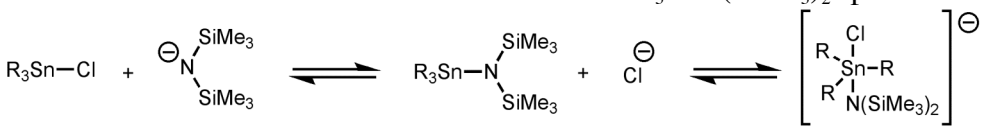
entry	R	E	equiv. $R_3EN(SiMe_3)_2$	additive	equiv. additive	yield
1	Me	Sn	1	LiCl	1	59%
2	Ph	Sn	1	LiCl	1.5	*ca.* 73%*
3	Ph	Sn	0.5	LiCl	2	84%†
4	Ph	Sn	0.3	LiCl	2.5	83%
5	Ph	Sn	1	LiCl	1.5	0%‡
6	n/a	n/a	0	LiCl	2	0%#
7	Ph	Sn	0.3	LiBr	3.1	trace
8	Ph	Sn	0.3	$[Bu_4N]Cl$	2.5	79%
9	Ph	Sn	0.3	$[Bu_4N]Cl$	2.5	57%‡
10	Ph	Sn	0.3	$[Bu_4N]F$	2.5	43%
11	Ph	Ge	0.3	$[Bu_4N]Cl$	2.5	0%

*Product contaminated with unidentified phenyl-containing impurity
†21 equiv. 2-cyclohexen-1-one used
‡Reaction performed in THF without HMPA cosolvent
#2 equiv. $HN(SiMe_3)_2$ added in place of $R_3EN(SiMe_3)_2$ species

Notably, none of the tetrel amides was capable of promoting the conjugate addition without a further additive. LiCl was found to be an effective additive, consistent with its presence as a byproduct of the *in situ* formation of $Me_3SnN(SiMe_3)_2$ from Me_3SnCl and $Li[N(SiMe_3)_2]$ (*cf.* Scheme 2.4). These conditions allowed for the use of substoichiometric quantities of the tin amide $Ph_3SnN(SiMe_3)_2$ while maintaining good yield (entries 3 and 4). Initially, this was suspected to be due to the Li^+ ion acting as a Lewis acid to further promote the reaction. The failure of LiBr to yield more than trace product (entry 7) argued against this hypothesis, however, as did the failure of the reaction in the absence of HMPA (entry 5), given that HMPA strongly coordinates Li^+ and would be expected to, if anything, reduce its Lewis acidity.[4] The ability of the salt $[Bu_4N]Cl$, with its non-Lewis acidic cation, to promote the reaction (entry 8) suggests that the Cl^- anion enables $Ph_3SnN(SiMe_3)_2$ to act as a base in this reaction; this salt allows the reaction to proceed, albeit in lower yield, in the absence of HMPA (entry 9), presumably because HMPA is no longer required to break up a $[Li^+][Cl^-]$ ion pair.

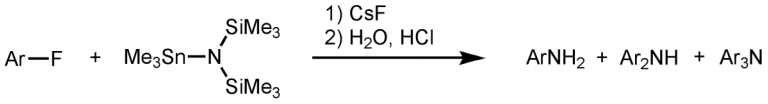
The role of Cl^- in rendering $R_3SnN(SiMe_3)_2$ species sufficiently basic to deprotonate cobalt dinitrosoalkanes is not unambiguously clear, but two plausible mechanisms are shown in Scheme 2.5 below.

Scheme 2.5. Possible reactions between Cl^- and $R_3SnN(SiMe_3)_2$ species.



The Cl^- ion can be imagined to displace $[N(SiMe_3)_2]^-$ from the Sn center, transiently forming the more basic anion, or to add to form the pentacoordinate stannate ion $[R_3Sn(Cl)N(SiMe_3)_2]^-$, which could prove more basic than the neutral $R_3SnN(SiMe_3)_2$. Miller and Furin propose a mechanism involving displacement of $[N(SiMe_3)_2]^-$ from $Me_3SnN(SiMe_3)_2$ by F^- in the amination of polyfluorinated arenes by nucleophilic aromatic substitution (Scheme 2.6), though they acknowledge that F^- attack on the silyl centers may proceed through pentacoordinate silicate species.[5]

Scheme 2.6. Fluoride-promoted amination of polyfluoroarenes by $Me_3SnN(SiMe_3)_2$.

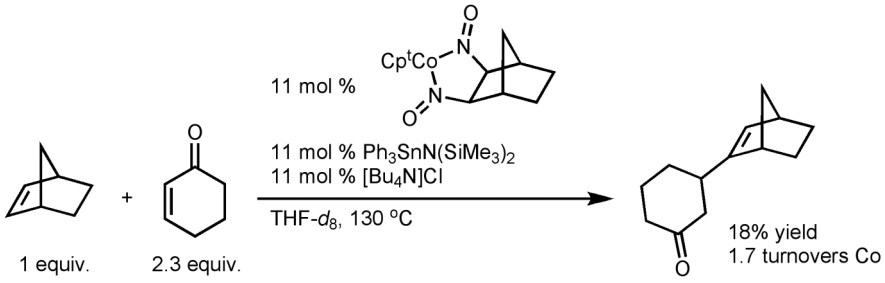


One-Pot Vinylic C–H Functionalization of Norbornene

The relatively mild nature of the $Ph_3SnN(SiMe_3)_2/Cl^-$ base mixture, the ability of its basic component to be used in sub-stoichiometric amounts, and the lack of a required Lewis acid suggested that this system might be amenable for cobalt dinitrosoalkane C–H functionalization and cycloreversion in one reaction mixture at elevated temperatures, for a reaction overall catalytic in cobalt.

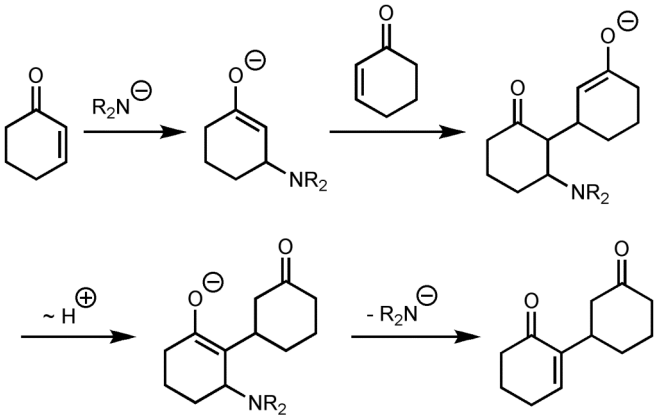
The addition of norbornene to 2-cyclohexen-1-one was examined with $Ph_3SnN(SiMe_3)_2$ and a norbornene-derived cobalt complex as cocatalysts (Scheme 2.7).

Scheme 2.7. Cobalt- and tin-catalyzed conjugate addition of norbornene to 2-cyclohexen-1-one.



This reaction is technically catalytic in both cobalt and tin, in that the yield based on either of these reagents, as opposed to norbornene, would be greater than 100%. The synthetic utility, however, of a catalytic system which turned over less than twice is low. One factor limiting catalysis is the gradual, irreversible degradation of $Ph_3SnN(SiMe_3)_2$; monitoring of the reaction by ^1H NMR showed loss of $Ph_3SnN(SiMe_3)_2$ and formation of $HN(SiMe_3)_2$. Additionally, 2-cyclohexen-1-one was consumed in side reactions, one of which appears to be the formation of a dimer, likely *via* a Rauhut-Currier reaction[6] (Scheme 2.8, R = $SiMe_3$).

Scheme 2.8. Rauhut-Currier dimerization of 2-cyclohexen-1-one.

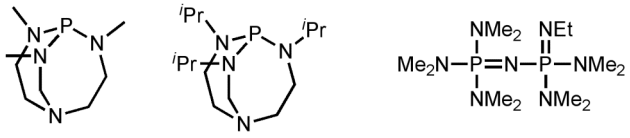


The reason for the degradation of $Ph_3SnN(SiMe_3)_2$ is not entirely clear. It is fairly thermally stable; heating of a THF-d_8 solution to 130 °C for 115 min caused minor formation of $HN(SiMe_3)_2$, but the ratio of $Ph_3SnN(SiMe_3)_2$ to $HN(SiMe_3)_2$ was still approximately 5:1 after that time. It is possible that $(Me_3Si)_2N^-$ deprotonates either the desired product or dimers/oligomers of 2-cyclohexen-1-one irreversibly, in a reaction whose rates are competitive with its attack on transiently-formed Ph_3SnCl. Additionally, $(Me_3Si)_2N^-$ may act as a base in the irreversible E2 reaction of Bu_4N^+, releasing butene and tributylamine; this hypothesis is supported by the observation by GC-MS of tributylamine in the reaction mixture. No trimethylsilyl chloride was observed in the reaction mixture; attack of Cl^- on the Si centers of $Ph_3SnN(SiMe_3)_2$ did not seem to be a problem.

The inefficiency of $Ph_3SnN(SiMe_3)_2$ as the base in the cobalt-catalyzed C–H functionalization suggested that a further variety of bases be explored. Strong, neutral

"superbases," lacking a potentially Lewis acidic countercation, were sought, in hopes of minimizing the degradation of cobalt species or Rauhut-Currier reactions of 2-cyclohexen-1-one. Species explored included the proazaphosphatrane bases of Verkade[7] and the phosphazenes of Schwesinger[8] (Figure 2.1).

Figure 2.1. Strong, neutral bases and their conjugate acid pK_a values.[7c, 8]



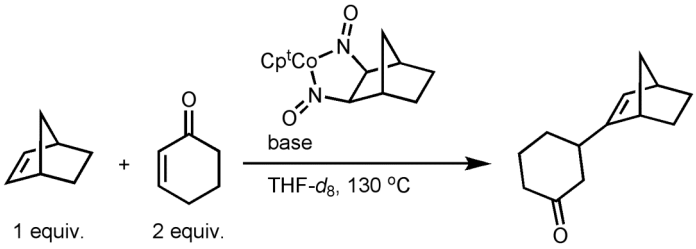
V-Me
32.9 (MeCN)

V-^{i}Pr
33.6 (MeCN)

P_2-Et
32.9 (MeCN)
21.1 (DMSO)

The performance of strong, neutral bases in the cobalt-catalyzed C–H functionalization is shown in Table 2.3 below.

Table 2.3. Cobalt-catalyzed C–H functionalization with neutral "superbases."



entry	mol % Co	base	mol % base	yield*	turnovers Co
1	9.6	V-Me	13.5	49%	5.1
2†	6.2	V-^{i}Pr	9.5	25%	4.1
3	8	V-Me	4	34%	4.1
4	0	V-Me	5	0%	n/a
5	10	V-Me	1	12%	1.2
6	9	P_2-Et	10	34%	3.7
7	8	P_2-Et	4	44%	5.2
8	9	P_2-Et	1	22%	2.3
9	10	P_2-Et	2.4	37%	3.9
10	10	P_2-Et	5	22%	2.3

Entries 1-9: [Co] = 12-13 mM
Entry 10: [Co] = 3.8 mM
*NMR yield, with ferrocene internal standard
†1.3 equiv. 2-cyclohexen-1-one used

Both Verkade's proazaphosphatrane V-Me and Schwesinger's phosphazene P_2-Et perform significantly better than the $Ph_3SnN(SiMe_3)_2/Cl^-$ mixture, each yielding about 5 turnovers of cobalt (entries 1 and 7). Rauhut-Currier dimerization of 2-cyclohexen-1-one still occurred, but not as quickly as with $Ph_3SnN(SiMe_3)_2/Cl^-$. Yields of the dimer are difficult to estimate, as the amount of dimer decreases after an initial increase, probably

due to the formation of higher oligomers by a continuation of the mechanism proposed in Scheme 2.8. Qualitatively, 2-cyclohexen-1-one side reactions seem to proceed more quickly with P_2-Et than with V-Me, and lower loadings of P_2-Et than of V-Me are preferable (*cf.* entries 1 and 3 *vs.* 6 and 7). Several weaker bases, such as tetramethylguanidine, 1,8-bis(dimethylamino)naphthalene ("Proton-sponge"), and the iminophosphoranes $(Me_3N)_2PNH$ and $(Me_2N)_3PN^tBu$, did not catalyze the reaction illustrated in Table 2.3. Phosphazenes analogous to P_2-Et, but with three or more phosphorus atoms, were not explored in this reaction. The self-condensation of acetonitrile is known to be catalyzed by these higher phosphazenes,[8] and these bases thus seemed likely to participate in unwanted side reactions if used in this chemistry.

The control experiment entry 4 confirms the expected result that V-Me was not capable of catalyzing the conjugate addition of norbornene to 2-cyclohexen-1-one in the absence of cobalt. It appears, however, that V-Me was involved in side reactions with the cobalt dinitrosoalkane complex, especially in the absence of electrophile; a control experiment with norbornene, 10 mol % cobalt dinitrosoalkane, and 5 mol % V-Me, but no 2-cyclohexen-1-one, heated to 130 °C showed a half-life of roughly 3 h for the cobalt species under basic conditions. The degradation of cobalt species is supported by the observation of modest peak broadening in the NMR spectra of reaction mixtures after extended reaction times, and the formation of a dark brown to black precipitate. Peak broadening appears to be the result of the formation of paramagnetic species, perhaps cobalt(II), and not solely precipitation, as it was not ameliorated by centrifugation of sealed NMR tubes containing reaction mixtures.

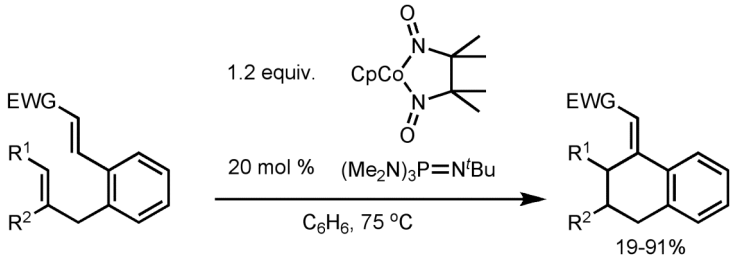
In addition to basic degradation of cobalt dinitrosoalkanes, there may be a decomposition pathway, or pathways, starting from the $[Cp^tCo(NO)_2]$ intermediate. Becker and Bergman[9] noted that precipitation of degradation products occurred when a benzene or THF solution of $[CpCo(NO)_2]$, generated *in situ*, was left to stand. In the reactions of Table 2.3, after several turnovers, the concentration of norbornene in the reaction mixtures may have fallen to a point where decomposition of $[Cp^tCo(NO)_2]$, if it proceeds by a unimolecular pathway, became competitive with trapping of this intermediate by unfunctionalized norbornene.

Conclusion

The sequential C–H functionalization of cobalt dinitrosoalkane complexes and alkene exchange to release a functionalized organic product have been explored in a one-pot context, with the goal of developing a cobalt-catalyzed C–H functionalization. With norbornene and 2-cyclohexen-1-one as coupling partners, it was found that the use of bases in catalytic amounts enabled the cobalt-catalyzed reaction to proceed in modest yield. While the use of the mixed stannyl-/silylamine $Ph_3SnN(SiMe_3)_2$, activated by chloride ion, gave poor results, neutral "superbases" such as Verkade's proazaphasphotrane and Schwesinger's P_2-phosphazene allowed for several turnovers of cobalt. Higher yields are prevented by basic dimerization and oligomerization of 2-cyclohexen-1-one, basic degradation of cobalt dinitrosoalkanes, and possibly decomposition of the $[Cp^tCo(NO)_2]$ intermediate.

The general one-pot methodology was later used by Zhao, Bergman, and Toste in the cobalt-mediated intramolecular C–H functionalization of alkenes (Scheme 2.9).[10]

Scheme 2.9. Cobalt-mediated intramolecular C–H functionalization.



In this system, the adduct of 2,3-dimethyl-but-2-ene with $[CpCo(NO)_2]$ was used as the starting cobalt reagent, with alkene exchange onto the substrate occurring *in situ*. This method was general for a wide variety of electron-withdrawing substituents on the conjugate acceptor portion of the substrate, but still generally required stoichiometric amounts of cobalt to obtain high yields. Only in one case (R^1, R^2 = $-(CH_2)_3-$, EWG = COPh) did the reaction proceed with catalytic amounts of cobalt (20 mol % catalyst loading, 60% yield, 3 turnovers), with basic and thermal decomposition of cobalt species thwarting higher turnover. Nonetheless, this illustrates the utility of the one-pot reaction strategy, in spite of inefficient catalysis.

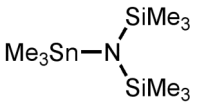
Experimental Section

General experimental procedures. All air- and moisture sensitive compounds were manipulated using Schlenk techniques as noted in Chapter 1, or in a VAC Atmospheres glovebox. Non-deuterated solvents were dried and purified as described in Chapter 1; THF-d_8, obtained from Cambridge Isotope Laboratories, was dried and deoxygenated by addition of sodium metal and benzophenone, and vacuum-transferred after a purple color of ketyl indicator was obtained. Such dry, deoxygenated THF-d_8 was stored over properly activated molecular sieves in the glovebox.

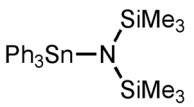
2-Cyclohexen-1-one was obtained from Sigma-Aldrich, dried over anhydrous magnesium sulfate overnight, distilled under high vacuum, and stored in the glovebox. Lithium chloride was dried at 160 °C under high vacuum for 2 days, and tetrabutylammonium chloride was dried at 150 °C under high vacuum for 3 days. All other reagents were purchased from commercial sources (Sigma-Aldrich, Strem) and used without further purification.

Reaction mixtures were stirred and monitored, and products purified and analyzed, as described in Chapter 1. When air-sensitive reagents were employed in reactions carried out in sealed NMR tubes, the reaction mixtures were prepared in the glovebox and removed attached to a Cajon adapter. ^{1}H and ^{13}C NMR chemical shifts in THF-d_8 are reported relative to solvent peaks (^{1}H: δ 1.72 and 3.58 ppm, ^{13}C: δ 25.31 and 67.21 ppm).

General procedure for the preparation of triorganotetrel bis(trimethylsilyl)amides. The reaction and work-up are both performed under anaerobic and anhydrous conditions in the glovebox. The triorganotetrel chloride (3.10 mmol) was added as a solid to a solution of 519.5 mg Li[N(SiMe$_3$)$_2$] (3.10 mmol) in 10 mL THF in a 20-mL scintillation vial, with stirring. The vial was sealed and the reaction mixture stirred at ambient temperature overnight. The disappearance of starting material was confirmed by ^{1}H NMR spectroscopy of a 0.1-mL aliquot of reaction mixture diluted with THF-d_8, after which point solvent was removed from the reaction mixture using the glovebox's internal pump. The resulting solid was extracted into a second solvent (diethyl ether or benzene), and the extract was filtered through a Pasteur pipet packed with glass fiber. Removal of solvent from the filtered extract yielded the product.

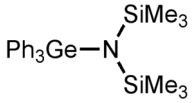


(Trimethylstannyl)bis(trimethylsilyl)amine. The product was isolated in 89% yield as a pale brown liquid. Benzene was used as the extraction solvent. ^{1}H NMR (400 MHz, THF-d_8): δ 0.34 (s, 9H), 0.11 (s, 18H). ^{13}C NMR (100 MHz, THF-d_8): δ 5.8, -0.7.



(Triphenylstannyl)bis(trimethylsilyl)amine. The product was isolated in 89% yield as a flaky white solid. Diethyl ether was used as the extraction solvent. ^{1}H NMR (400

MHz, THF-d_8): δ 7.66-7.63 (aromatic signals, 6H), 7.39-7.30 (aromatic signals, 9H, 0.07 (s, 18H). ^{13}C NMR (100 MHz, THF-d_8): δ 143.0, 137.6, 130.2, 129.6, 6.1. This material was compared spectroscopically with a sample of authentic $Ph_3SnN(SiMe_3)_2$ kindly provided by Prof. Manfred Bochmann[3b] and found to have identical chemical shifts.



(Triphenylgermyl)bis(trimethylsilyl)amine. The product was isolated in 90% yield as a flaky white solid. Diethyl ether was used as the extraction solvent. ^{1}H NMR (400 MHz, THF-d_8): δ 7.67-7.60 (aromatic signals, 6H), 7.40-7.29 (aromatic signals, 9H), 0.029 (s, 18H). ^{13}C NMR (100 MHz, THF-d_8): δ 140.9, 136.1, 130.2, 129.0, 6.0.

General procedure for the functionalization of a cobalt dinitrosoalkane complex with 2-cyclohexen-1-one. In the glovebox, a Schlenk flask was charged with 50 mg (0.15 mmol) of the [Cp^{t}Co(NO)$_2$]/norbornene cycloadduct,[1] 10-20 equiv. 2-cyclohexen-1-one, and the tin or germanium species, in a mixture of 5 mL THF and 1 mL HMPA. The reaction mixture was removed from the glovebox and pumped onto a Schlenk line. After confirming a lack of initial reaction by TLC after 15 min, a solution of additive (Li[N(SiMe$_3$)$_2$] or LiCl) in THF was added to the reaction mixture *via* syringe. In cases where [Bu$_4$N]Cl was used as an additive, its relative insolubility in THF rendered it difficult to add *via* syringe. In such cases, the reaction mixture was itself transferred *via* syringe into a septum-sealed scintillation vial containing [Bu$_4$N]Cl under nitrogen. The stirred reaction mixture was examined by TLC until consumption of starting material was complete, at which point the solvent removed under reduced pressure, and the residue purified by flash column chromatography with a hexanes/ethyl acetate gradient.

General procedure for the NMR-monitored catalytic functionalization of norbornene by 2-cyclohexen-1-one. A solution containing the desired concentration of cobalt complex, 2-cyclohexen-1-one, norbornene, ferrocene internal standard, and tin species (if applicable) in THF-d_8 was prepared and added to a separately weighed portion of base or [Bu$_4$N]Cl. Generally, a total of 1 mL THF-d_8 was used for each experiment. The resulting solution was added to a medium-walled NMR tube. In reactions utilizing [Bu$_4$N]Cl, this less soluble reagent was weighed directly into the NMR tube. The NMR tube was attached to a Cajon adapter, removed from the glovebox, and flame-sealed under vacuum follwing 3 freeze-pump-thaw cycles. After an initial ^{1}H NMR spectrum was taken, the sealed tube was immersed in an stirred silicone oil bath heated to the desired temperature and periodically removed and immersed in ice water prior to taking additional spectra. Reaction progress was monitored by the disappearance of the vinyl peak of norbornene at δ 5.97 ppm (s) and the vinyl peaks of 2-cyclohexen-1-one at 5.87 ppm (d, J = 10 Hz) and 6.94 ppm (d of t, J = 10.4, 4.1 Hz), and the appearance of the vinyl peak of the organic product, 2-(3-oxocyclohexyl)norbornene, at 5.61 ppm (br s). The Rauhut-Currier dimerization product of 2-cyclohexen-1-one was conveniently observed in the reaction mixtures by its vinyl signal at 6.92 ppm (t, J = 4.0 Hz).

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Chapter 3

Cobalt-Mediated, Enantioselective Synthesis of C_2- and C_1-Symmetric Norbornadiene Derivatives and Their Use in Rhodium-Catalyzed Conjugate Addition

Portions of this chapter have been published as:
Boyd, W. C.; Crimmin, M. R.; Rosebrugh, L. E.; Schomaker, J. M.; Bergman, R. G.; Toste, F. D. Cobalt-Mediated, Enantioselective Synthesis of C_2 and C_1 Dienes. *J. Am. Chem. Soc.* **2010,** *132,* 16365-16367.

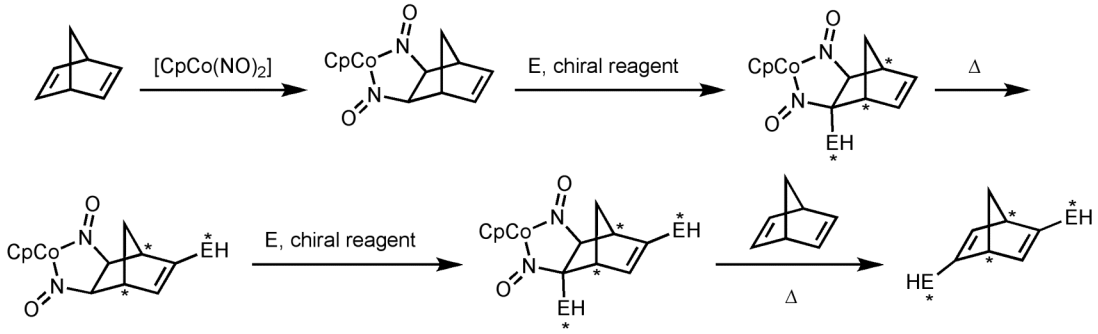
Chiral Norbornadiene Derivatives and Their Use in Enantioselective Catalysis

Alkenes have long been known to behave as ligands for transition metals, coordinating to the metal center through the carbon-carbon π system, as in the early ethene complex $K_2[PtCl_3(\eta^2\text{-}C_2H_4)]\cdot H_2O$ (Zeise's salt).[1] Many coordinated alkenes are readily displaced by more strongly-binding ligands, allowing metal-alkene complexes to serve as precatalysts for enantioselective metal-catalyzed reactions, in which the alkenes are replaced *in situ* by chiral, enantiopure ligands to form the catalytically-active metal complex. Dienes capable of coordinating a metal center by two carbon-carbon π systems, however, are frequently significantly less labile as ligands than monoalkenes, and can thus serve as "spectator ligands" in catalytically active species. In recent years, research has focused on the use of enantiopure C_2- and C_1-symmetric dienes as ligands for late transition metal-catalyzed enantioselective reactions.[2]

Several research groups,[3-7] most prominently those of Hayashi[3] and Carreira,[4] have reported the use of chiral ligands featuring a bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) or bicyclo[2.2.2]octa-2,5-diene framework in metal-catalyzed organic reactions, such as enantioselective 1,2- or 1,4-additions, arylative cyclizations, and kinetic resolutions. Some such ligands are themselves derived from molecules in the biological chiral pool; others are prepared from racemic starting materials *via* reaction sequences involving chiral auxiliaries, oxazaborolidine organocatalysts, enzymes, or palladium catalysts with chiral ligands.

The cobalt-mediated C–H functionalization developed by the Bergman and Toste groups[8] presented an alternative strategy for the enantioselective desymmetrization of norbornadine, one which avoids the use of chiral auxiliaries, enzymes, or precious metals. While the functionalizations discussed thus far in this dissertation have involved only one carbon-carbon double bond per alkene substrate, one can envision sequential functionalization of both alkene moieties in norbornadiene. This strategy would yield chiral centers at the bridgehead positions of the norbornadiene framework, as well as on any prochiral electrophiles used (Scheme 3.1).

Scheme 3.1. Sequential asymmetric double functionalization of norbornadiene.

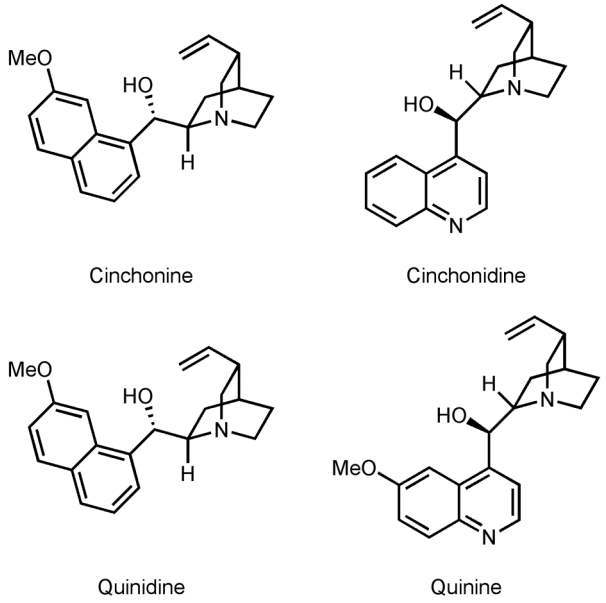


The key questions for this goal are the choice of chiral reagent to effect enantioinduction, and whether the third reaction of Scheme 3.1, namely, the migration of the $[CpCo(NO)_2]$ moiety from the more to the less substituted double bond in a monofunctionalized norbornadiene would proceed in high yield without an excess of unfunctionalized alkene present as in Table 1.5.

A Chiral Base Mixture for Cobalt-Mediated C–H Functionalization

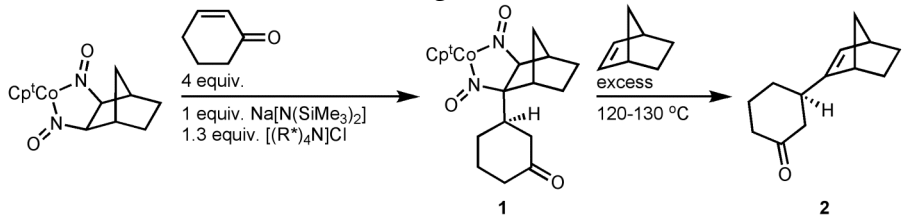
The initial screening of enantioselective reaction conditions focused on the monofunctionalization of norbornene, as opposed to norbornadiene. The chiral additives explored were derived from cinchona alkaloids, a class of natural products derived from the bark of trees in the *Cinchona* genus. In addition to their medicinal importance,[9] cinchona alkaloids and their derivatives have found wide use in synthetic organic chemistry, acting as a source of chiral information in enantioselective dihydroxylation, cycloaddition, halogenation, aldol, Mannich, Morita-Bayliss-Hilman, and other reactions.[10] An attractive feature of this family of products is the existence of the "pseudoenantiomeric" pairs of cinchonine and cinchonidine and quinine and quinidine (Figure 3.1).

Figure 3.1. Commonly used cinchona alkaloids.

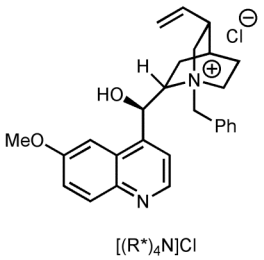


Initial screening of enantioselective reaction conditions involved the functionalization of the $[Cp^tCo(NO)_2]$/norbornene adduct with 2-cyclohexen-1-one, using a mixture of $Na[N(SiMe_3)_2]$ and *N*-benzylquininium chloride (Table 3.1).[11]

Table 3.1. Initial screening of enantioselective reaction conditions.



entry	temp. (°C)	solvent	time	yield of **1**	d.r. of **1**	e.e. of **2**[a]
1	r.t.	THF/HMPA[b]	3 h	89%	14.1:1	18%
2[c]	r.t.	THF/HMPA[b]	4 h	81%	6.1:1	2%
3[d]	r.t.	THF/HMPA[b]	2.5 h	17%	1.1:1	6%
4	-60	THF/HMPA[b]	41.5 h	40%	50:1	65%
5	r.t.	Et_2O	27 h	58%	>99:1	2%
6	r.t.	MeCN	21 h	64%	25:1	16%
7	r.t.	THF	17.5 h	75%	33:1	36%
8	-60 to 0	THF	6 days (14 h at 0 °C)	74%	>99:1	58%



$[(R^*)_4N]Cl$

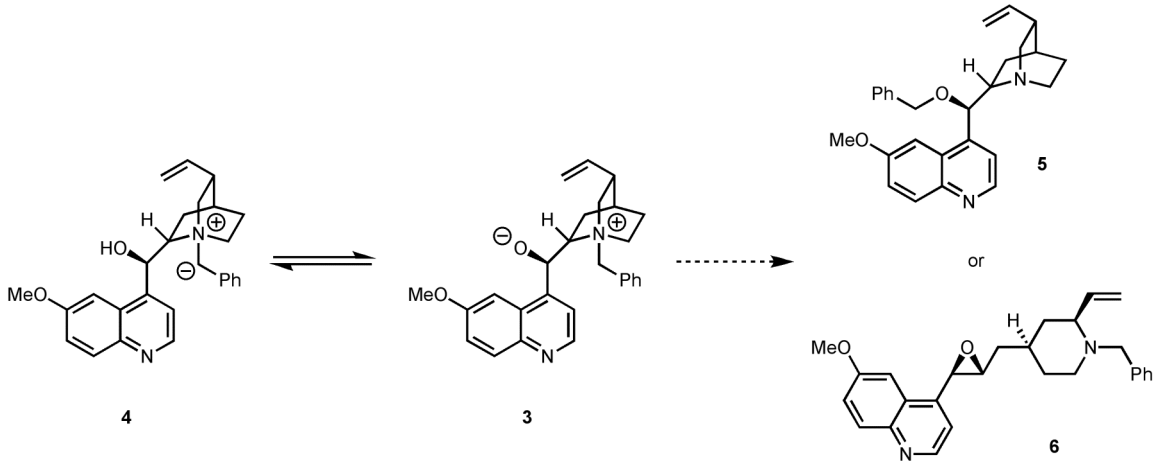
[a] $Na[N(SiMe_3)_2]$ and $[(R^*)_4N]Cl$ premixed and filtered, e.e. of major diastereomer only.
[b] 5.3:1 THF to HMPA.
[c] $Na[N(SiMe_3)_2]$ added to mixture of substrates and $[(R^*)_4N]Cl$.
[d] Quinine used in place of $[(R^*)_4N]Cl$.

The mixture of $Na[N(SiMe_3)_2]$ and *N*-benzylquininium chloride yielded the conjugate addition product **1** in high yield with high diastereoselectivity; analysis of the cycloreversion product **2** by chiral gas chromatography showed that this reaction also proceeds with low but significant enantioselectivity (entry 1). Greater enantiomeric excess (e.e.) was obtained by the use of THF without HMPA cosolvent, at the price of a significantly increased reaction time (entry 7). At lower temperatures, the reaction proceeded even more slowly, but with still greater enantio- and diastereoselectivity (entries 4 and 8).

The order of reagent addition proved crucial to enantioinduction; when a control experiment was performed with $Na[N(SiMe_3)_2]$ added to a mixture of the remaining reagents, the adduct **1** was formed in good yield, but with low diastereoselectivity and as an essentially racemic mixture (entry 2). As $Na[N(SiMe_3)_2]$ is sufficiently basic to promote the conjugate addition in the absence of a chiral additive, the low stereoselectivity observed in entry 2 is likely due to this racemic background reaction. The use of quinine in place of its quaternized salt gave **1** in low yield with almost no enantio- or diastereoselectivity (entry 3).

Given these results, it is likely that $Na[N(SiMe_3)_2]$ and $[(R^*)_4N]Cl$ reacted to form a chiral base responsible for enantioinduction; a plausible candidate is the zwitterionic ammonium alkoxide **3** (Scheme 3.2).

Scheme 3.2. Proposed structure and degradation pathways of chiral base species.



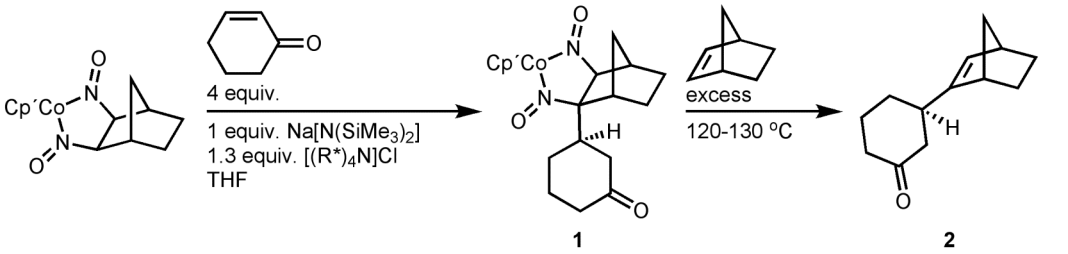
When a light yellow solution of $Na[N(SiMe_3)_2]$ was added to the white powder $[(R^*)_4N]Cl$, a bright red mixture was initially formed, which turned yellow after a few seconds of agitation. The initial red color may be due to a kinetic deprotonation to form the nitrogen ylide **4** (whose carbanionic center is conjugated with an aromatic ring), which then isomerizes to **3**. The observation that reactions conducted at low temperatures seem to stall after initial slow conversion may be due to decomposition of **3**, perhaps to benzyl transfer product **5** or epoxide **6**, neither of which would be sufficiently basic to promote the conjugate addition. This hypothesis is supported by the observation that the reaction depicted in Table 3.1 did not proceed when a THF/HMPA solution of $[(R^*)_4N]Cl$ and $Na[N(SiMe_3)_2]$ was allowed to sit for 1.75 days in the glovebox before being added to the reaction mixture.

Zwitterions of this sort have previously been proposed as being involved in the reactions of chiral ammonium ions bearing hydroxyl groups. Soai and Watanabe proposed such a zwitterion derived from (+)-*N*-methylephedrine as being involved in the asymmetric addition of diethylzinc to aldehydes.[12] Hughes and Dolling propose that *N*-benzylchinchoninium bromide forms a complex with its zwitterion in the asymmetric phase-transfer methylation of an indanone, based on elemental analysis and basicity measurements of a toluene extract,[13] while O'Donnell and coworkers suggest that the same zwitterion participates in an unwanted side reaction to partially racemize products from an enantioselective Schiff-base alkylation.[14]

Enantioselective Monofunctionalization of Norbornene and Norbornadiene

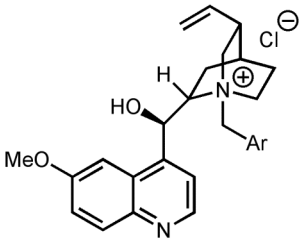
The promising results of Table 3.1 were improved upon by modifying the Cp ligand on the cobalt complex used and the benzyl group on the quininium salt. Variants of *N*-benzylquininium chloride bearing trifluoromethyl substituents on their phenyl rings improved enantioselectivity and shortened reaction times, allowing the use of THF as a pure solvent at reduced temperatures. In addition, the use of Cp ligands with bulky, monodirectional substituents such as *tert*-butyl or *tert*-butyldimethylsilyl led to greater enantioselectivities (Table 3.2).[11]

Table 3.2. Optimization of the enantioselective conjugate addition reaction.



temp (°C)	Cp´[a]	Ar	time (h)	yield of **1**[b]	e.e. of **2**[c]
0	Cp^{tBu}	Ph	22	35%	72%
-45	Cp^{tBu}	4-CF_3-C_6H_4	17	53%	74%
-58	Cp^{Si}	3,5-$(CF_3)_2$-C_6H_3	15	73%	83%

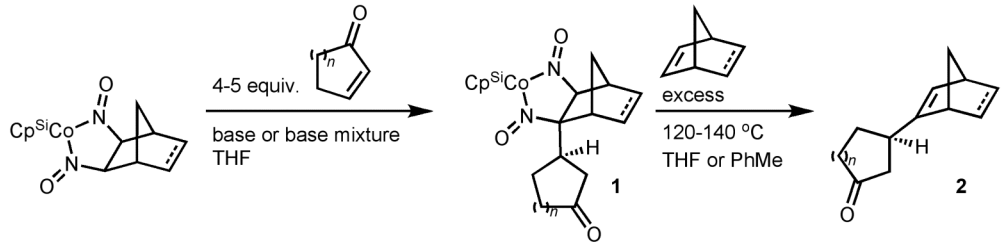
[a] Cp^{tBu} = η^5-^{t}BuC_5H_4, Cp^{Si} = η^5-^{t}Bu$Me_2SiC_5H_4$.
[b] **1** formed in all cases with >99:1 d.r.
[c] $Na[N(SiMe_3)_2]$ and $[(R^*)_4N]Cl$ premixed and filtered.



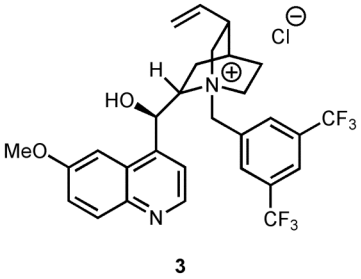
$[(R^*)_4N]Cl$

With the optimum conditions identified (THF, -58 °C, Cp´ = Cp^{Si}, Ar = 3,5-$(CF_3)_2$-C_6H_3), enantioselective monofunctionalizations of norbornene and norbornadiene were performed with five-, six-, and seven-membered cyclic electrophiles (Table 3.3).[11] Yields are compared with those obtained under racemic conditions using Verkade's base $P[NMe(CH_2)_2]_3N$.

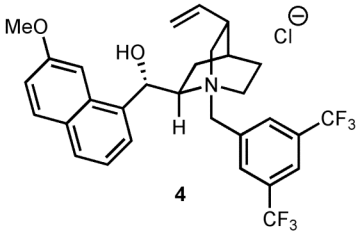
Table 3.3. Enantioselective and racemic monofunctionalization of norbornene and norbornadiene.



conditions[a]	parent alkene	*n*	time (h)	yield of **1**[b]	yield of **2**[c]	e.e. of **2**
racemic	norbornene	1	0.5	53%	39%	n/a
chiral	norbornene	1	16	66%	---	55%
racemic	norbornene	2	0.5	59%	99%[d]	n/a
chiral	norbornene	2	15	73%	---	83%
racemic	norbornene	3	0.5	60%	60%	n/a
chiral	norbornene	3	48	90%	---	54%
racemic	norbornadiene	1	0.5	83%	87%	n/a
chiral	norbornadiene	1	48	85%	---	43%
racemic	norbornadiene	2	0.5	53%	51%[d]	n/a
chiral	norbornadiene	2	12	78%	---	81%
chiral[e,f]	norbornadiene	2	48	90%	---	-85%
racemic	norbornadiene	3	0.5	70%	51%	n/a
chiral[e]	norbornadiene	3	72	88%	---	69%



3



4

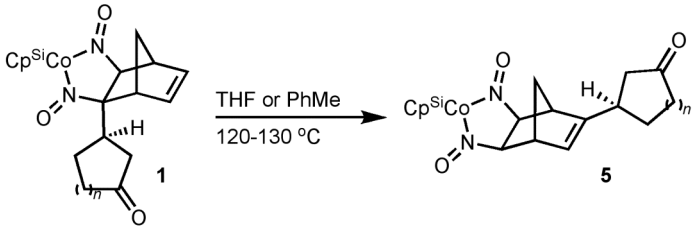
[a] Racemic conditions: 20 mol % Verkade's base. r.t.
Chiral conditions: 1 equiv. $Na[N(SiMe_3)_2]$, 1.3 equiv. **3**, premixed and filtered.
[b] All racemic reactions yield **1** with >9:1 d.r.; all chiral reactions give >99:1 d.r.
[c] Alkene exchange yields only measured for reactions run with racemic **1**.
[d] Alkene exchange reaction performed with Cp^t (= η^5-Me_4C_5H) version of **1**.
[e] Reaction performed at -75 °C.
[f] Reaction performed using salt **4** in place of **3**.

For monofunctionalization of norbornene and norbornadiene, e.e. values ranged from modest (43%) to good (85%). Use of the salt **4**, derived from the quinine pseudoenantiomer quinidine, allowed for the opposite sense of enantioinduction.

Enantioselective Difunctionalization of Norbornadiene

Extending the enantioselective monofunctionalization of norbornene to difunctionalization, as outlined in Scheme 3.1, requires the isomerization of functionalized norbornadiene adducts **1**, transferring the $[Cp^{Si}Co(NO)_2]$ moiety from the more substituted (and thus more sterically encumbered) to the less substituted double bond. While previous alkene exchange reactions (*cf.* Table 1.5)[8a] were run with a significant excess of the alkene to which the $[CpCo(NO)_2]$ moiety was transferred, this isomerization proceeded cleanly to give isomers **5**, despite the lack of any excess of the entering alkene (Table 3.4).[11]

Table 3.4. Isomerization of monofunctionalized norbornene adducts.

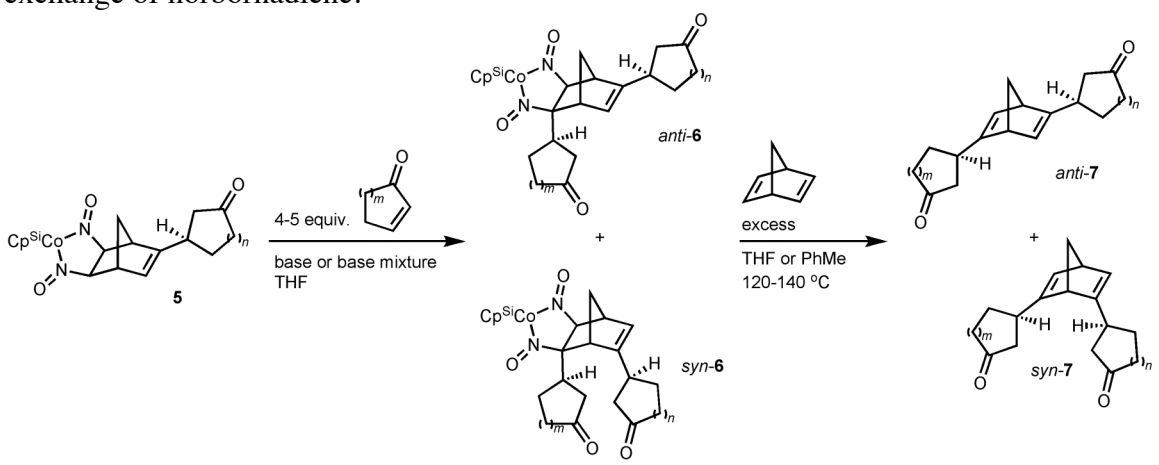


n	[**1**] (M)	temp. (°C)	yield of **5**
1	0.15	130	80%
2	0.10	120	92%
3	0.12	120	93%

The second functionalization of isomerized adducts **5** proceeded readily under both racemic and enantioselective conditions (Table 3.5).[11] While the racemic reactions yield difunctionalized adduct **6** with poor regioselectivity, the ratio of *anti*:*syn* **6** was significantly improved under the enantioselective conditions. Alkene exchange proceeded in high yield to give C_2- or C_1-symmetric norbornadiene derivatives *anti*-**7** with high e.e. (90-96%). As with the monofunctionalization of norbornadiene, the opposite sense of enantioinduction was effected by the use of quinidinium salt **4**.

Recrystallization of *anti*-**7** with $n = m = 2$ from pentane allowed for the removal of small amounts of *syn*-**7** and the increase of e.e. to 99%. The absolute configuration was determined to be (*R*,*R*,*R*,*R*) by single-crystal X-ray diffraction analysis (Figure 3.2).[11]

Table 3.5. Racemic and enantioselective second functionalization and alkene exchange of norbornadiene.



n	*m*	conditions[a]	yield of **6**	*anti*:*syn*	yield of **12**	e.e. of **12**
1	1	racemic	71%	1.5:1	87%	n/a
1	1	chiral	42%	3.7:1	92%	90%
2	2	racemic	90%	1.7:1	43%	n/a
2	2	chiral	67%	20:1	84-94%	96%
2	2	chiral[b,c]	73%	10:1	93%	-94%
3	3	racemic	86%	1.3:1	87%	n/a
3	3	chiral	87%	11:1	87%	91%
2	3	racemic	63%	2.7:1	85%	n/a
2	3	chiral[b]	84%	11:1	n.r.[d]	96%

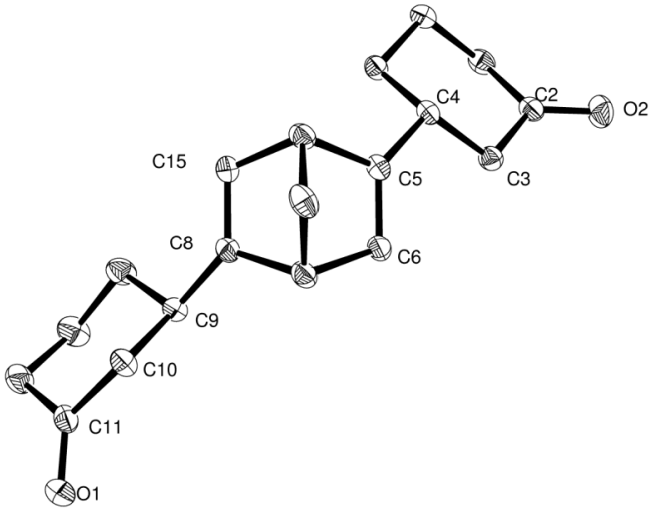
[a] Racemic conditions: 10-25 mol % Verkade's base, 2-20 equiv. conjugate acceptor, racemic **5**, r.t. Chiral conditions: 1 equiv. $Na[N(SiMe_3)_2]$, 1.3 equiv. **3** premixed and filtered, 4 equiv. conjugate acceptor, enantioenriched **5**, -58 °C

[b] Reaction conducted at -75 °C.

[c] Salt **4** used in place of **3**.

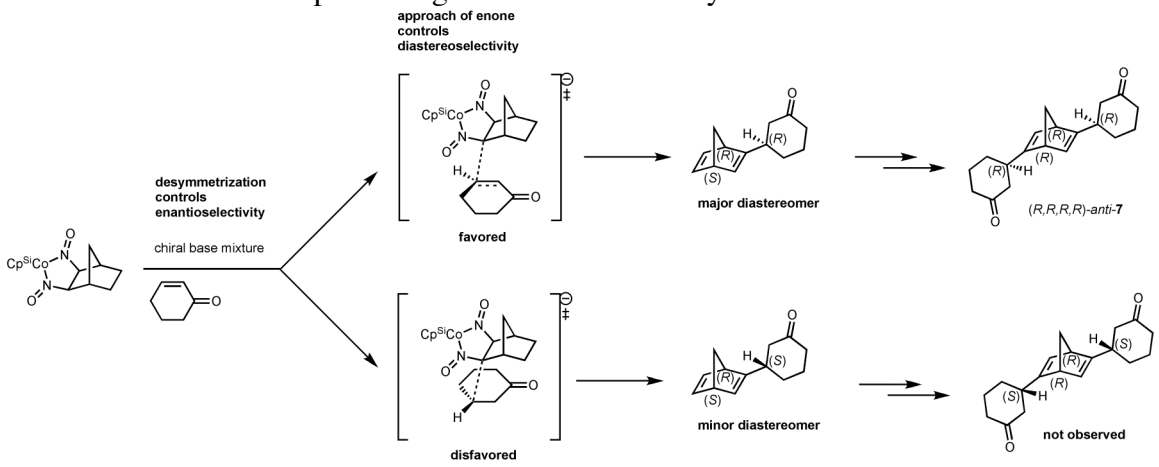
[d] Alkene exchange yield reported for reaction of the raemic complex only.

Figure 3.2. ORTEP representation of (*R*,*R*,*R*,*R*)-*anti*-**7**, $n = m = 2$. Hydrogen atoms are omitted for clarity. Flack parameter = 0.1451(0.1655). Selected bond lengths (Å): C(5)-C(6): 1.332(2), C(5)-C(4): 1.502(2), C(2)-O(2): 1.216(2).



The high stereoselectivity in this double functionalization sequence is proposed to be due to two orthogonal stereoselection events: desymmetrization of the nucleophile controls enantioselectivity, while the approach of the prochiral electrophile controls diastereoselectivity (Figure 3.3). In this fashion, two pairs of noncontiguous stereocenters are set with excellent control in the enantioselective synthesis of the *anti*-**7** regioisomers. The minor regioisomeric products, *syn*-**7**, are *meso*-symmetric (C_s point group) when $n = m$, and arise from imperfect regiocontrol in the second carbon–carbon bond-forming step (Scheme 3.3).[11]

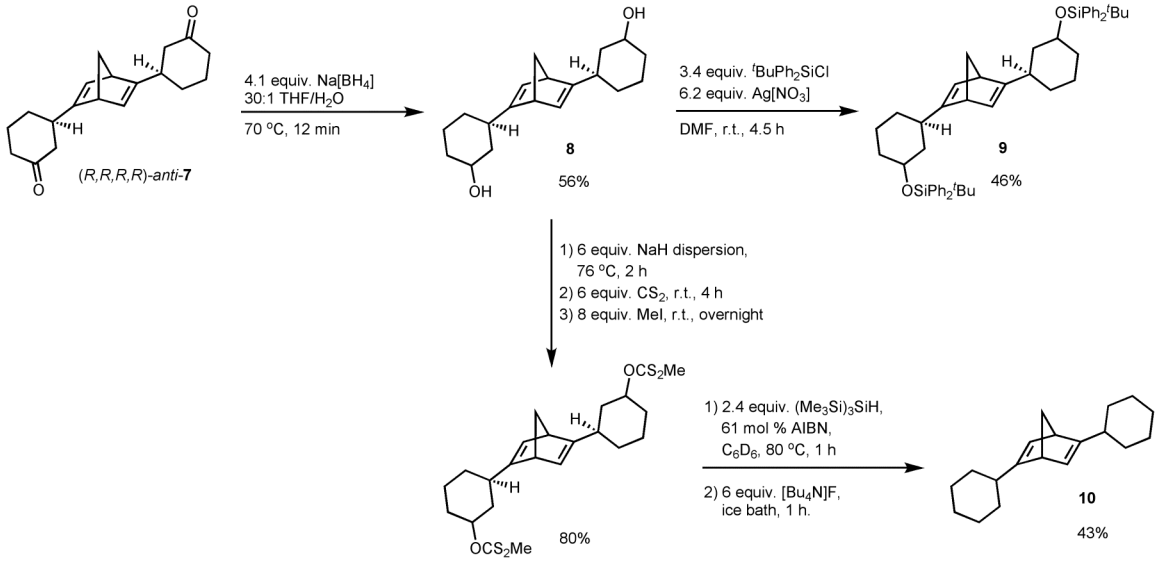
Scheme 3.3. Proposed origin of stereoselectivity.



Functional Group Manipulation of a C_2-Symmetric Diene

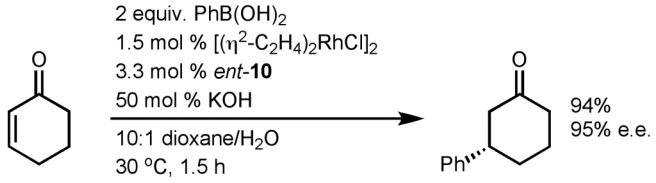
An immediate demonstration of the utility of this method of enantioselective diene formation consists of the functional group manipulation of the ketone moieties of (*R*,*R*,*R*,*R*)-*anti*-**7** ($n = m = 2$). Reduction of the carbonyl groups with sodium borohydride[15] yielded diol **8**, which was silylated to diether **9**[16] or deoxygenated *via* the dixanthate[17] to yield the hydrocarbon **10** (Scheme 3.4).

Scheme 3.4. Functional group manipulation of a C_2 diene.



The enantiomer of **10** has been shown by Van der Eycken to be an effective ligand for the highly enantioselective conjugate addition of phenylboronic acid to 2-cyclohexen-1-one (Scheme 3.5).[5]

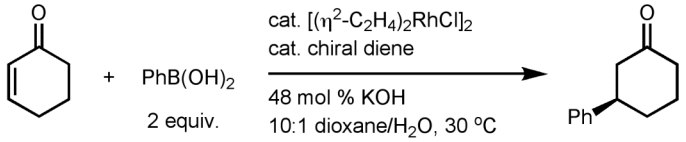
Scheme 3.5. *Ent*-**10** as a ligand for enantioselective conjugate addition.

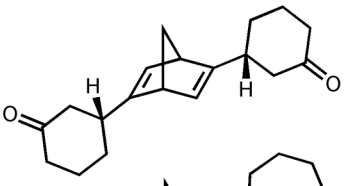
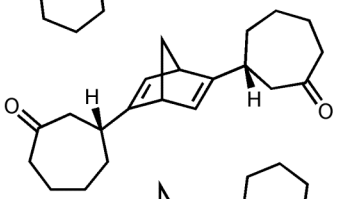
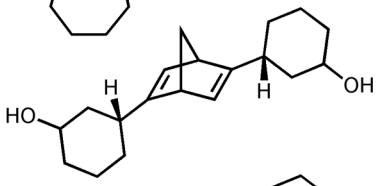
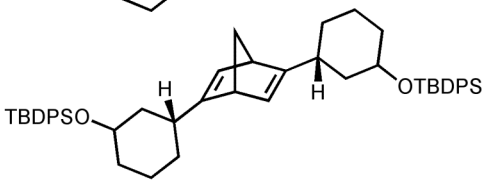


Novel C_2-Symmetric Dienes as Ligands for Rhodium-Catalyzed, Enantioselective Conjugate Addition

The methodology of Table 3.5 and the functional group manipulation of Scheme 3.4 provide for the synthesis of several novel, C_2-symmetric dienes with the potential to act as ligands for rhodium(I). To assess this ability, several of these ligands were screened in the rhodium(I)-catalyzed enantioselective conjugate addition of phenylboronic acid to 2-cyclohexen-1-one, following the general reaction conditions of Hayashi[3b] (Table 3.6).

Table 3.6. Use of novel C_2 dienes for enantioselective conjugate addition.



Chiral diene	mol% Rh dimer	mol% diene	Yield	e.e.
	1.6	3.4	76%	77%
	1.6	3.6	76%	75%
	1.7	3.8	67%	87%
	1.7	4.0	73%	86%

The novel C_2 dienes screened provided for moderate yields and moderate to high enantioselectivity in the conjugate addition reaction, but both yields and e.e. values were lower than those reported for similar reactions.[3-7] While these results demonstrate the competence of these chiral products as chiral ligands, they suggest that their greater utility may be found in their potential as a source of chiral frameworks with functional group "handles" for further modification.

Conclusion

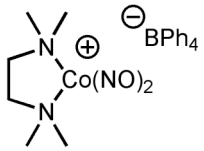
The use of a chiral base mixture, composed of a quinine-derived quaternary ammonium salt and the strong amide base $Na[N(SiMe_3)_2]$, allowed for the monofunctionalization of $[Cp^{Si}Co(NO)_2]$ and norbornene or norbornadiene with conjugate acceptors in good yield with modest e.e. Applying the same methodology to a double functionalization of norbornadiene, which utilized an unprecedented isomerization *via* alkene exchange, allowed for the formation of C_2- and C_1-symmetric norbornadiene derivatives in high yield with high e.e. These dienes were readily subjected to functional group manipulation, and used in a modestly enantioselective rhodium(I)-catalyzed conjugate addition reaction.

Experimental Section

General experimental procedures. Unless otherwise indicated, reactions were performed under anhydrous and anaerobic conditions as described in previous chapters. Solvents were dried and purified as previously described. Reaction mixtures were stirred and monitored, and products purified and analyzed, as described in previous chapters, with the exception that infrared spectra were obtained on a Thermo Scientific Nicolet iS10 spectrometer fitted with a Smart OMNI-transmission or Smart iTR device as either KBr discs, neat solids, or thin films. Additionally, optical rotation values were measured on a Perkin-Elmer 241 polarimeter using a cell with a path length of 1 dm. Elemental analyses were recorded by the University of California, Berkeley micro-mass facility.

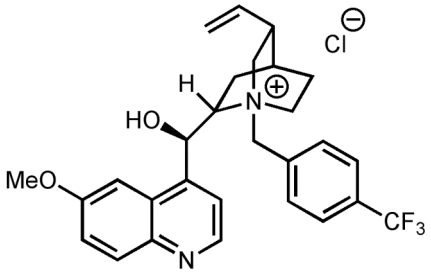
Chiral gas chromatography data were collected on an HP 6850 series GC fitted with Supelco™ chiral columns and a flame ionization detector (FID). Chiral high-performance liquid chromatography data were collected on a Shimadzu system, with a SIL-10AF autosampler, CTO-20A column oven, and SPD-M20A diode array detector fitted with a Chiralpak™ IA column. All single-crystal X-ray diffraction experiments were conducted at the University of California, Berkeley CheXray facility using a MicroSTAR-H X8 Apex II diffractometer equipped with a microfocus rotating anode, Cu K/α source, and Bruker APEX-II CCD detector. No absorption correction was applied. While structures were solved with SIR-97 and refined in SHELXL-97, the absolute configuration of the chiral 2,5-bis(3-oxocyclohexyl)norbornadiene ligand was determined by anomalous diffraction techniques.

Cobalt(II) chloride was dried prior to use by heating at 120 ºC at 0.1 torr for 12 hours. Volatile alkenes and *N*,*N*,*N*´,*N*´-tetramethylethylenediamine (TMEDA) were dried over calcium hydride, distilled under nitrogen, and degassed by 3 freeze-pump-thaw cycles. Methanol was heated to reflux under magnesium turnings under nitrogen for several hours and then distilled. Gaseous nitric oxide was purified by passage through a trap at -78 ºC before use. [(^{t}BuMe$_2$Si)C$_5$H$_4$]Li and (^{t}BuC$_5$H$_4$)Li were prepared by literature procedures.[18-19] The conjugate acceptors 2-cyclopenten-1-one and 2-cyclohexen-1-one were degassed by 3 freeze-pump-thaw cycles, dried overnight over anhydrous magnesium sulfate, and distilled under vacuum, while 2-cyclohepten-1-one, obtained in 80% "technical grade" purity from Aldrich, was chromatographed on silica gel with a 9:1, then 7:1 hexanes/ethyl acetate gradient before being degassed, dried over anhydrous magnesium sulfate, and filtered through glass fiber in the glovebox. Commercially available *N*-benzylquininium chloride was dried under vacuum overnight at 40 ºC. All other reagents were obtained from commercial suppliers (Sigma-Aldrich, Strem, Fluka) and used without further purification.

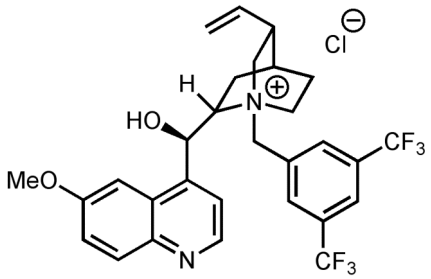


*(*N,N,N´,N´*-Tetramethylethylenediamine)dinitrosylcobalt tetrafluoroborate*. This compound was prepared by a modification of the literature procedure.[20] Under an argon atmosphere, $CoCl_2$ (4.75 g, 36.5 mmol, 1 equiv.) was dissolved in 150 mL methanol. Under an argon purge, TMEDA (8.3 mL, 73.1 mmol, 2 equiv.) was added *via* syringe. The argon gas flow was then replaced by nitric oxide gas. The gaseous NO was passed through a -78 ºC trap and applied to the reaction mixture *via* a manifold connected to an oil bubbler. Over a period of 8 h, a series of color changes occurred and the reaction mixture eventually turned a deep green/black. At this point the NO was stopped and the reaction mixture degassed, and a solution of sodium tetraphenylborate (27.4 g, 80.3 mmol, 2.2 equiv.) in 50 mL methanol was added dropwise *via* cannula transfer. After stirring for an additional 6 h, the resulting green precipitate was collected by filtration, washed with methanol (2 x 25 mL) and dried under vacuum. The isolated solid was extracted with 100 mL dichloromethane using a Soxhlet apparatus. The extraction was continued until the extracts were colorless, and the resulting black solution was concentrated to approximately 40 mL. Crystallization of the products was induced by the additon of 200 mL absolute ethanol. Two products crystallized as two distinct sets of crystals: black crystals of $[(TMEDA)Co(NO)_2][BPh_4]$ were separated from white crystals of $[TMEDA\text{-}H][BPh_4]$ by filtration followed by washing with hot ethanol (10 x 100 mL). The $[(TMEDA)Co(NO)_2][BPh_4]$ thus obtained (14.37 g, 25.9 mmol, 71%) provided satisfactory elemental analysis results. ^{1}H NMR (400 MHz, acetone-d_6): δ 3.01 (s, 12H), 3.28 (s, 4H), 6.78-6.82 (m, 4H, aromatic signals), 6.93-6.97 (m, 8H, aromatic signals), 7.35-7.36 (m, 8H, aromatic signals). ^{13}C NMR (100 MHz, acetone-d_6): δ 55.6, 62.4, 122.6, 126.3, 126.4, 137.4. IR [KBr disc, ν_{max} (cm^{-1})]: 1862, 1787. Elemental analysis for $C_{30}H_{36}O_2BCo$ calculated: C, 64.99; H, 6.49; N, 10.11; found: C, 65.15; H, 6.67; N, 9.98.

General procedure for the preparation of N*-benzylated* Cinchona *alkaloids*. On the benchtop, a 0.17-0.18 M suspension of quinine in acetone with 1.2 equiv. of the relevant benzyl chloride was put in a Schlenk tube with Kontes Teflon stopcock or a round-bottomed flask with condenser, flushed with nitrogen for 5 min, and heated to 65 ºC with stirring at least overnight. The reaction progress was monitored by ^{1}H NMR ($CDCl_3$) of concentrated aliquots. To accelerate reaction progress, more of the benzyl chloride was added periodically, with a total of 1.5-2.4 equiv. typically used. When NMR analysis of aliquots indicated that the reaction had proceeded to a ratio of at least 5:1 salt:quinine, acetone was removed from the reaction mixture under reduced pressure, and precipitation was performed (see each salt for conditions). While trifluoromethyl group-substituted ammonium salts derived from *Cinchona* alkaloids have been previously reported in asymmetric catalysis,[21] a detailed analysis of these salts has not been presented. Characterization is thus provided for each salt below.

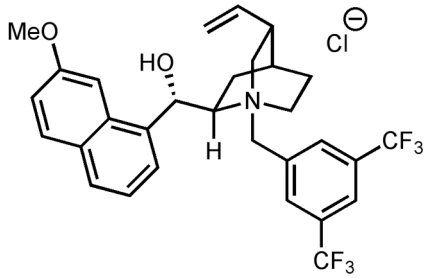


N-*(4-Trifluoromethylbenzyl)quininium chloride*. The crude reaction product was dissolved in minimal benzene to make a viscous solution, which gave some precipitate upon stirring for 2 h. Addition of hexane gave further precipitation of a light pink powder, which was isolated in 46% yield by suction filtration followed by washing with further hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, 1H, *J* = 4.5 Hz), 7.82 (d, 3H, *J* = 9.4 Hz), 7.64 (d, 1H, *J* = 4.5 Hz), 7.46 (d, 2H, *J* = 8.1 Hz), 7.29 (d, 1H, *J* = 6.7 Hz), 7.14-7.11 (m, 3H), 6.46 (d, 1H, *J* = 6.4 Hz), 6.10 (d, 1H, *J* = 12.0 Hz), 5.47-5.39 (m, 1H), 5.06-5.01 (m, 2H), 4.90 (d, 2H, *J* = 10.3 Hz), 3.77 (s, 3H), 3.40-3.35 (m, 1H), 3.22 (t, 1H, *J* = 11.6 Hz), 2.94-2.87 (m, 1H), 2.44 (br s, 1H), 2.19-2.11 (br m, 1H), 2.05 (t, 1H, *J* = 10.5 Hz), 1.90 (d, 1H, *J* = 3.0 Hz), 1.59 (t, 1H, *J* = 10.1 Hz), 1.29 (t, 1H, *J* = 11.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 147.5, 144.1, 142.9, 136.1, 134.4, 132.1, 128.3, 126.0, 120.5, 118.2, 102.0, 69.7, 64.7, 62.3, 61.1, 56.3, 51.0, 38.0, 26.5, 24.9, 22.0, remaining carbons not observed. ^{19}F NMR (376.5 MHz, $CDCl_3$) -62.2. IR [solid, ν_{max} (cm^{-1})]: 2980, 1621, 1508, 1323.



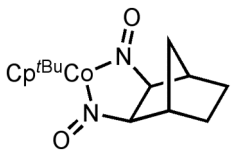
N-*[3,5-Bis(trifluoromethyl)benzyl]quininium chloride*. The crude reaction product was redissolved in minimal acetone, and a small amound of THF (roughly twice the amount of acetone by volume) was added with stirring, yielding some yellow precipitate. Further precipitation was induced by the slow addition of diethyl ether with stirring, until no further precipitation could be observed. The precipitate was isolated by suction filtration and washed several times with diethyl ether. If NMR analysis of the resulting powder showed any quinine or 3,5-bis(triflluoromethyl)benzyl chloride remaining, the powder was washed again with diethyl ether and a small amount of THF, and refiltered until observed pure by ^{1}H NMR. The pure product was obtained as a yellow powder in 59-65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 3H), 7.87-7.83 (m, 2H), 7.61 (d, 1H, *J* = 3.5 Hz), 7.18-7.14 (m, 3H), 6.49 (d, 1H, *J* = 3.5 Hz), 6.20 (d, 1H, *J* = 11.8 Hz), 5.57-5.45 (m, 2H), 5.12 (d, 1H, *J* = 16.9 Hz), 4.98 (m, 1H), 4.87 (d, 1H, *J* = 10.4 Hz), 4.20 (br d, 1H, *J* = 10.9 Hz), 4.06 (m, 1H), 3.89 (s, 3H), 3.20 (t, 1H, *J* = 11.2 Hz), 2.88 (m, 1H), 2.52 (m, 1H), 2.26 (m, 1H), 2.17-2.13 (m, 1H), 1.97 (s, 1H), 1.74-1.68 (m, 1H), 1.47-1.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 147.1, 144.0, 142.7, 135.9, 134.3, 132.5, 132.1, 131.7, 130.6, 125.8, 124.1, 121.3, 121.3, 120.4, 118.0, 101.4, 69.6,

64.3, 60.7, 60.5, 56.2, 51.2, 37.9, 26.7, 24.8, 21.7, remaining carbons not observed. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -61.9. IR [solid, ν_{mas} (cm^{-1})]: 2982 (broad), 1622, 1509, 1473, 1374, 1278, 1241, 1172, 1128. HRMS (ESI) [M^-] calculated for $C_{29}H_{29}F_6N_2O_2$: 551.2128, observed: 551.2117.



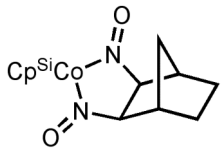
N-*[3,5-Bis(trifluoromethyl)benzyl]quinidinium chloride*. The crude material, a crystalline solid, was redissolved in 20 mL dichloromethane. Addition of this solution to 500 mL diethyl ether gave the product as a pure white solid (3.10 g, 83%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.56-8.42 (m, 3H), 7.93 (s, 1H), 7.75 (d, 1H, *J* = 9.2 Hz), 7.63 (dd, 1H, *J* = 12.4, 6.0 Hz), 7.32 (s, 1H), 7.06 (dd, 1H, *J* = 9.2, 2.4 Hz), 6.40 (d, 1H, *J* = 4.4 Hz), 6.06 (d, 1H, *J* = 12.4 Hz), 5.99-5.90 (m, 1H), 5.79 (d, 1H, *J* = 12.4 Hz), 5.21-5.18 (m, 2H), 4.65-4.63 (m, 2H), 4.05 (dd, 1H, *J* = 8.4, 8.4 Hz), 3.90 (s, 3H), 3.17 (dd, 1H, *J* = 10.8, 10.8 Hz), 2.72 (dd, 1H, *J* = 10.4, 10.4 Hz), 2.42-2.33 (m, 2H), 1.83 (s, 1H), 1.72-1.71 (m, 2H), 0.92-0.91 (m, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 158.5, 147.5, 144.6, 143.0, 136.2, 134.8, 132.7, 132.,4 132.0, 131.5, 124.8, 121.5, 120.9, 118.3, 102.3, 69.1, 66.1, 60.8, 57.0, 56.8, 38.7, 27.7, 24.3, 22.1. ^{19}F NMR (376.5 MHz, CD_2Cl_2): δ -62.3; IR [solid, ν_{max} (cm^{-1})]: 3083, 1623, 1512, 1371, 1277. HRMS (ESI) [M^+] calculated for $C_{29}H_{29}F_6N_2O_2$: 551.2128, observed: 551.2117.

General procedure for the synthesis of cobalt dinitrosoalkane complexes. Under a nitrogen or argon atmosphere, a solution of a lithium or sodium cyclopentadienyl salt (0.54 mmol, 1.2 equiv.) in 10 mL THF was added *via* cannula transfer to a slurry of $[(TMEDA)Co(NO)_2][BPh_4]$ (250 mg, 0.45 mmol, 1 equiv.) and alkene (4.5 mmol, 10 equiv.) in 10 mL THF at -78 ºC. After stirring for 5 min at -78 ºC, the reaction mixture was allowed to warm to ambient temperature and stirred for several hours or overnight. The reaction was monitored by TLC on silica gel, with a developing solvent mixture of 3:1 hexanes/ethyl acetate. Once the reaction was complete, the THF was removed under reduced pressure and the crude product dissolved in a minimal amount of dichloromethane and purified by flash column chromatography on silica gel with 9:1 hexanes/ethyl acetate as the eluent. Products isolated in this manner proved air- and moisture-stable in the solid state, and can be handled on the benchtop.

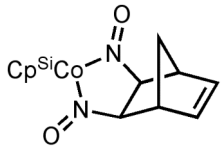


*(*cis*-2,3-Dinitrosonorbornane)(*tert*-butylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.87 (t, 2H, *J* = 2.0 Hz), 4.68 (t, 2H, *J* = 2.0 Hz), 2.71-2.72 (m, 2H), 2.61-2.63 (m, 2H), 1.50-1.53 (m,

3H), 1.18-1.17 (m, 1H), 1.16 (s, 9H), 0.84 (d, 2H, J = 10.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 93.6, 88.5, 87.2, 42.1, 31.4, 31.0, 30.9, 26.4. IR [solid, ν_{max} (cm^{-1})]:2960, 1408, 1342, 1260. MS (FAB, positive ion): 335 (35%, $[M+H]^+$), 240 (30%, $[M+H-C_7H_{10}]^+$), 210 (50%, $[M+H-C_7H_{10}-NO]^+$). HRMS (ESI, positive ion) calculated for $C_{16}H_{24}O_2N_2{}^{59}Co$: 335.1164, observed: 335.1151. The HRMS data were obtained in a later publication.[21]



*(*cis-*2,3-Dinitrosonorbornane)(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.15 (s, 2H), 4.73 (s, 2H), 2.68-2.69 (m, 2H), 2.60-2.61 (m, 2H), 1.45-1.51 (m, 1H), 1.16-1.18 (m, 2H), 0.85-0.87 (m, 1H), 0.85 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 95.8, 94.2, 93.7, 92.9, 42.2, 30.9, 26.3, 26.2, 17.1, -5.9. IR [solid, ν_{max} (cm^{-1})]: 2953, 2926, 2855, 1403, 1357, 1352, 1265, 1251. MS (FAB, positive ion): 393 (100 %, $[M+H]^+$), 335 (55%, $[M+HC_4H_9]^+$). HRMS (ESI, positive ion) calculated for $C_{18}H_{30}O_2N_2{}^{59}Co^{28}Si$: 393.1403, observed: 393.1387. The HRMS data were obtained in a later publication.[21]



*(*cis-*5,6-Dinitrosonorbornene)(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (s, 2H), 5.17 (s, 2H), 4.71 (s, 2H), 3.08-3.09 (m, 2H), 3.00-3.01 (m, 2H), 2.00 (d, 1H, J = 9.2 Hz), 1.52-1.58 (m, 3H), 0.86 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 95.6, 94.3, 93.2, 92.8, 58.4, 47.1, 26.3, 18.3, -5.9. IR [solid, ν_{max} (cm^{-1})]: 2951, 2924, 2856, 1412, 1343, 1280, 1250. MS (FAB, positive ion): 391 (35%, $[M+H]^+$), 333 (35%, $[M+H-C_4H_9]^+$).

General procedure for room-temperature enantioselective functionalization of cobalt dinitrosoalkane complexes with 2-cyclohexen-1-one. In the glovebox, a Schlenk tube was charged with a solution of 0.075 mmol cobalt dinitrosoalkane complex in 1 mL solvent (THF in the case of a THF/HMPA mixture). Separately, a solution of 1 equiv. $Na[N(SiMe_3)_2]$ in 2 mL solvent (THF in the case of a THF/HMPA mixture) was added to 1.3 equiv. chiral quaternary ammonium salt (or quinine, in the case of entry 3 of Table 3.1). To this suspension was added 0.6 mL additional solvent (HMPA in the case of a THF/HMPA mixture) and the mixture was agitated briefly and filtered through a pipet charged with glass fiber. The filtrate was added to the solution of cobalt dinitrosoalkane complex, followed immediately by 4 equiv. 2-cyclohexen-1-one in 0.2 mL solvent (THF in the case of a THF/HMPA mixture). Reactions were monitored by TLC on silica gel (3:1 hexanes/ethyl acetate as developing solvent), and when judged complete, the reaction mixture was opened to air, the solvent removed under reduced pressure, and the product flash chromatographed on silica gel using a 100:0 to 6:1 hexanes/ethyl acetate

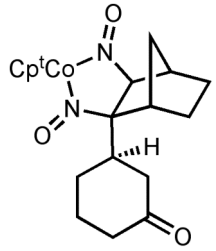
gradient to yield a product bench-stable in the solid state.

A control experiment was performed by dissolving the cobalt complex, 2-cyclohexen-1-one, and *N*-benzylquininium chloride in 1 mL THF and 0.6 mL HMPA, and adding $Na[N(SiMe_3)_2]$, dissolved in 2.2 mL THF, to begin the reaction (entry 2 in Table 3.1). An additional control experiment was performed using the conditions of entry 1 in Table 3.1, but adding the mixture of *N*-benzylquininium chloride and $Na[N(SiMe_3)_2]$ mixture without filtration; this reaction yielded similar results (89% yield, 12.4:1 d.r., 12% e.e.).

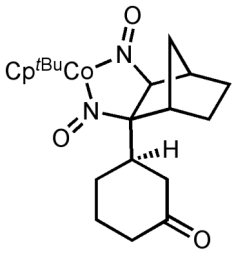
General procedure for low-temperature enantioselective functionalization of cobalt dinitrosoalkane complexes with 2-cyclohexen-1-one. In the glovebox, a Schlenk tube was charged with a solution of 0.075 mmol cobalt dinitrosoalkane complex and 4 equiv. 2-cyclohexen-1-one in 1.2 mL solvent (THF in the case of a THF/HMPA mixture). Separately, a chiral base mixture was prepared as follows: a solution of 1 equiv. $Na[N(SiMe_3)_2]$ in 2 mL solvent (THF in the case of a THF/HMPA mixture) was added to 1.3 equiv. chiral quaternary ammonium salt. To this suspension was added 0.6 mL additional solvent (HMPA in the case of a THF/HMPA mixture), and the mixture was agitated briefly and filtered through a pipet charged with glass fiber into a separate Schlenk tube or Schlenk flask. Both Schlenk tubes were flushed onto a nitrogen- or argon-filled Schlenk line and cooled to the desired temperature, and the chiral base mixture was added to the cobalt species and conjugate acceptor *via* cannula transfer. In the case of reactions performed at -45 to -60 ºC, the chiral base mixture was cooled to -78 ºC in a dry ice/acetone bath, and transferred to the cobalt-containing reaction vessel, which was maintained at the desired temperature in a Dewar containing methanol or acetone attached to a Neslab CryoCool apparatus. Reactions were monitored and products isolated as in the room-temperature case.

Alkene exchange and measurement of enantiomeric excess of 2-(3-oxocyclohexyl)norbornene. The functionalized cobalt complex and a large excess of norbornene (typically 15-40 equiv.) were dissolved in 3 mL THF and sealed in a Biotage microwave tube. If the reaction was set up outside the glovebox, the reaction mixture was flushed for about 5 min with nitrogen with a needle inlet and outlet in the microwave tube's septum before heating. The mixture was microwaved at 130 ºC and reaction progress was monitored by TLC. The THF was removed under reduced pressure and the residue dissolved in hexanes and passed through a small pipet column (5 cm silica in a Pasteur pipet above a small abount of sand, glass wool, and cotton), eluting with a mixture of approximately 3 drops ethyl acetate per pipetful of hexanes. Fractions were examined by TLC for the desired product, being visualized by $KMnO_4$ stain, and those containing the product were injected onto a chiral GC column without further purification, with an assay previously developed for pure 2-(3-oxocyclohexyl)norbornene using a Supelco β-Dex 120 column of dimensions 30 m x 0.25 mm x 0.25 μm: the oven temperature was set to 70 ºC for 25 min, increased to 180 ºC at a rate of 0.25 ºC·min^{-1}, then held at 180 ºC for 20 min. The inlet gas pressure was set at 12.54 psi with a flow rate of 1.0 mL·min^{-1} and average velocity of 25 cm·s^{-1}. Runs were made in constant-pressure mode, so flow decreases with increasing temperature. As the alkene exchange reaction was previously shown to proceed in high yield,[8a] the 2-(3-oxocyclohexyl)norbornene

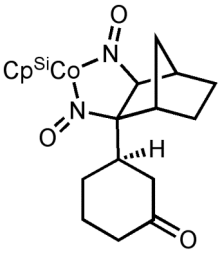
products were not isolated nor were their yields measured for this screen of enantioselectivity.



*{*cis-*2,3-Dinitroso-2-(3-oxocyclohexyl)norbornane}(tetramethylcyclopentadienyl)cobalt(I)*. This compound has been previously reported and fully characterized[8a] (see also Chapter 1 of this dissertation).



*{*cis-*2,3-Dinitroso-2-(3-oxocyclohexyl)norbornane}(*tert-*butylcyclopentadienyl)cobalt(I)*. The product was isolated as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.88 (dd, 1H, *J* = 4.4, 2.7 Hz), 4.80 (dd, 1H, *J* = 4.4, 2.7 Hz), 4.68-4.67 (m, 1H), 4.61-4.60 (m, 1H), 2.77 (t, 1H, *J* = 13.6 Hz), 2.59 (br s, 1H), 2.51 (d, 1H, *J* = 4.3 Hz), 2.48 (s, 1H), 2.44-2.39 (m, 1H), 2.31-2.27 (m, 1H), 2.23-2.15 (m, 1H), 2.03-1.97 (m, 1H), 1.69 (d, 1H, *J* = 10.6 Hz), 1.63-1.46 (m, 4H), 1.44-1.40 (m, 1H), 1.38-1.32 (m, 2H), 1.22-1.17 (m, 1H), 1.14 (s, 9H), 0.89 (dd, 1H, *J* = 10.5, 1.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.5, 122.2, 101.1, 99.0, 88.7, 88.1, 87.3, 87.2, 43.6, 43.2, 43.1, 41.7, 41.0, 33.5, 31.2, 30.9, 27.1, 26.9, 25.1, 23.3.

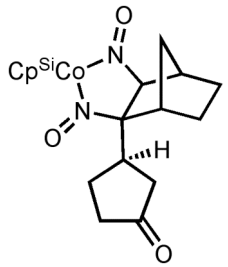


*{*cis-*2,3-Dinitroso-2-(3-oxocyclohexyl)norbornane}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19-5.17 (m, 1H), 5.13-5.11 (m, 1H), 4.75-4.74 (m, 1H), 4.70-4.68 (m, 1H), 2.76 (t, 1H, *J* = 13.4 Hz), 2.61 (br s, 1H), 2.53 (d, 1H, *J* = 4.2 Hz), 2.48 (s, 1H), 2.46-2.40 (m, 1H), 2.35-2.29 (m, 1H), 2.24-2.16 (m, 1H), 2.03-1.99 (m, 1H), 1.67 (br d, 1H, *J* = 10.7 Hz), 1.63-1.31 (m, 7H), 1.24-1.15 (m, 1H), 0.91 (dd, 1H, *J* = 10.5, 1.1 Hz), 0.85 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

210.5, 101.4, 99.5, 96.1, 96.0, 95.1, 93.1, 92.8, 43.8, 43.5, 43.2, 41.8, 41.2, 33.6, 27.3, 27.0, 26.4, 25.3, 23.4, 17.4, -6.0, -6.1; IR [solid, ν_{max} (cm^{-1})]: 2952, 1704, 1409, 1336, 1303, 1250. MS (FAB, positive ion): 489 (100%, $[M+H]^+$). HRMS calculated for $C_{24}H_{38}O_3N_2{}^{59}Co^{28}Si$: 489.1986, observed: 489.1978.

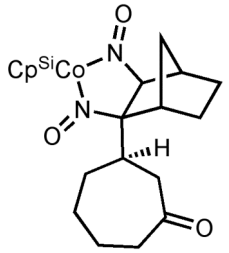
Racemic reaction conditions for the synthesis of monofunctionalized cobalt dinitrosoalkane complexes. A Schlenk tube was charged with a solution of cobalt dinitrosoalkane complex and conjugate acceptor in THF. To this mixture was added a solution of Verkade's proazaphosphatrane base in the same volume of THF in the glovebox. The total volume of solvent used resulted in the formation of a solution 8-12 mL in cobalt dinitrosoalkane. The Schlenk tube was sealed and removed from the glovebox. Reactions were monitored by silica gel TLC (3:1 hexanes/ethyl acetate eluent). When the reaction was complete, the reaction mixture was opened to an aerobic atmosphere, concentrated under reduced pressure, and flash chromatographed on silica gel, eluting with a 100:0 to 3:1 hexanes/ethyl acetate gradient. In the case of reactions performed using 2-cyclopenten-1-one as the conjugate acceptor, the products were sufficiently base-sensitive that they decomposed when concentrated before chromatography. In these cases, crude reaction mixtures were first chromatographed directly on a small silica gel column with 3:1 hexanes ethyl acetate eluent to quench remaining base. The eluate was then concentrated and rechromatographed rigorously.

Enantioselective reaction conditions for the synthesis of monofunctionalized cobalt dinitrosoalkane complexes. In the glovebox, a Schlenk tube was charged with a solution of 0.075 mmol cobalt dinitrosoalkane complex and 4 equiv. conjugate acceptor in 1.2 mL THF. Separately, a chiral base mixture was prepared as follows: a solution of 1 equiv. $Na[N(SiMe_3)_2]$ in 2 mL THF was added to 1.3 equiv. quaternary ammonium salt. To this suspension was added 0.6 mL additional THF, and the mixture was agitated briefly and filtered through a pipet charged with glass fiber into a separate Schlenk tube. Both Schlenk tubes were flushed onto a Schlenk line, and the cobalt and conjugate acceptor solution was cooled to -58 ºC using a Neslab CryoCool apparatus attached to a Dewar filled with acetone or methanol or -78 ºC using a dry ice/acetone bath, while the chiral base solution was cooled to -78 ºC in a dry ice/acetone bath. The chiral base solution was then added to the mixture of cobalt and conjugate acceptor *via* cannula transfer. Reactions were monitored and products isolated as in the racemic, ambient-temperature case; as in that case reactions mixtures containing 2-cyclopenten-1-one were passed directly through a short silica column with 3:1 hexanes/ethyl acetate eluent before the eluent was concentrated and subjected to rigorous chromatography.

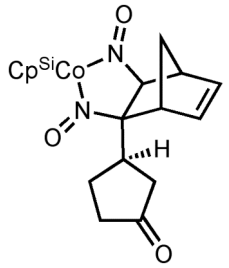


*{*cis-*2,3-Dinitroso-2-(3-oxocyclopentyl)norbornane}(*tert-

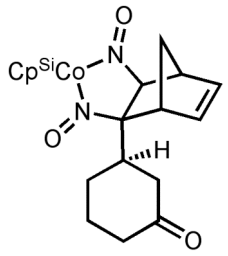
butyldimethylsilylcyclopentadienyl)cobalt(I). The product was isolated as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.18-5.16 (m, 1H), 5.10-5.09 (m, 1H), 4.75-4.74 (m, 1H), 4.68-4.67 (m, 1H), 2.74-2.67 (m, 1H), 2.60 (s, 1H), 2.57-2.55 (m, 2H), 2.26-2.17 (m, 2H), 2.14-1.99 (m, 2H), 1.81-1.75 (m, 2H), 1.69-1.58 (m, 2H), 1.40-1.35 (m, 2H), 1.25-1.18 (m, 1H), 0.92 (dd, 1H, J = 10.5, 1.1 Hz), 0.84 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.5, 101.3, 98.0, 96.2, 96.0, 95.2, 93.2, 92.7, 44.9, 43.7, 40.4, 40.3, 38.2, 33.7, 27.1, 26.4, 24.3, 24.0, 17.3, -5.9, -6.1; IR [solid, ν_{max} (cm^{-1})]: 2950, 2924, 1737, 1402, 1339, 1297, 1250. MS (FAB, positive ion): 475 (100%, $[M+H]^+$). HRMS calculated for $C_{23}H_{36}O_3N_2{}^{59}Co^{28}Si$: 475.1829, observed: 475.1822.



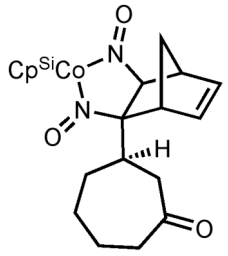
*{*cis-*2,3-Dinitroso-2-(3-oxocycloheptyl)norbornane}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.15-5.14 (m, 1H), 5.12-5.11 (m, 1H), 4.73-4.72 (m, 1H), 4.68-4.67 (m, 1H), 2.79-2.76 (dd, 1H, *J* = 11.2, 13.6 Hz), 2.62-2.61 (m, 2H), 2.54-2.51 (m, 1H), 2.39 (s, 1H), 2.32 (ddd, 1H, *J* = 16.2, 12.4, 4.4 Hz), 1.97-1.83 (m, 2H), 1.69 (d, 1H, *J* = 10.4 Hz), 1.61-1.52 (m, 3H), 1.40-1.24 (m, 4H), 1.23-1.08 (m, 3H), 0.92 (d, 1H, *J* = 10.4 Hz), 0.84 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.0, 101.1, 100.8, 96.1, 96.0, 95.2, 93.2, 92.9, 44.9, 44.4, 43.9, 43.7, 40.1, 33.8, 32.9, 28.9, 27.1, 26.5, 23.4, 23.3, 17.4, -5.9, -6.0. IR [solid, ν_{mas} (cm^{-1})]: 2922, 1695, 1415, 1340, 1309. MS (FAB, positive ion): 503 (100 %, $[M+H]^+$). HRMS calculated for $C_{25}H_{40}O_3N_2{}^{59}Co^{28}Si$: 503.2142, observed: 503.2135.



*{*cis-*5,6-Dinitroso-5-(3-oxocyclopentyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid. ^{1}H NMR (400 MHz, C_6D_6): δ 5.61 (dd, 1H, *J* = 5.2, 3.2 Hz), 5.48 (dd, 1H, *J* = 5.6, 3.2 Hz), 4.87-4.85 (m, 2H), 4.64-4.63 (m, 1H), 4.57-4.56 (m, 1H), 2.94 (s, 1H), 2.75 (s, 1H), 2.55-2.48 (m, 2H), 2.21 (d, 1H, *J* = 9.2 Hz), 1.97-1.87 (m, 2H), 1.60-1.53 (m, 2H), 1.46-1.34 (m, 2H), 1.25-1.20 (m, 1H) 0.83 (s, 9H), 0.20 (s, 3H), 0.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.2, 138.5, 138.2, 101.1, 98.5, 95.9, 95.8, 95.3, 93.2, 92.7, 50.0, 48.6, 45.0, 42.7, 40.7, 38.3, 26.4, 25.0, 17.4, -5.9, -6.0. IR [solid, ν_{mas} (cm^{-1})]: 2953, 1724, 1360, 1345, 1310, 1250. MS (FAB, positive ion): 473 (100%, $[M+H]^+$). HRMS calculated for $C_{23}H_{33}O_3N_2{}^{59}Co^{28}Si$: 472.1587, observed: 472.1587.



*{*cis-*5,6-Dinitroso-5-(3-oxocyclohexyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17-6.16 (br, 2H), 5.20-5.19 (m, 1H), 5.15-5.13 (m, 1H), 4.74-4.73 (m, 1H), 4.67-4.65 (m, 1H), 3.05 (s, 1H), 3.02-3.01 (br, 1H), 2.78-2.71 (m, 2H), 2.40-2.29 (m, 2H), 2.24-2.17 (m, 1H), 2.15 (d, 1H, *J* = 9.4 Hz), 2.03-1.97 (m, 1H), 1.62-1.58 (m, 2H), 1.51-1.36 (m, 3H), 0.85 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 210.5, 138.7, 137.7, 102.7, 99.4, 95.8, 95.2, 93.2, 92.8, 48.6, 48.5, 44.5, 44.0, 43.3, 41.2, 27.0, 26.4, 25.0, 17.4, -6.0, -6.1. IR [solid, ν_{max} (cm^{-1})]: 2925, 2854, 1708, 1410, 1335, 1300, 1251. MS (FAB, positive ion): 487 (100%, $[M+H]^+$). HRMS calculated for $C_{24}H_{35}O_3N_2{}^{59}Co^{28}Si$, 486.1749, observed: 486.1743.

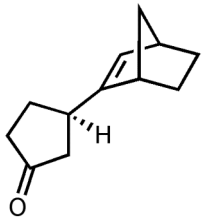


*{*cis-*5,6-Dinitroso-5-(3-oxocycloheptyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24-6.22 (m, 1H), 6.15-6.13 (m, 1H), 5.14 (dd, 1H, *J* = 3.8, 2.4 Hz), 5.11 (dd, 1H, *J* = 3.9, 2.5 Hz), 4.70-4.69 (m, 1H), 4.64 (m, 1H), 3.04 (br s, 2H), 2.78 (dd, 1H, *J* = 13.8, 11.1 Hz), 2.62 (s, 1H), 2.59 (br d, 1H, *J* = 13.8 Hz), 2.46 (dt, 1H, *J* = 16.8, 3.9 Hz), 2.31-2.23 (m, 1H), 2.16 (d, 1H, *J* = 9.3 Hz), 1.93-1.80 (m, 2H), 1.71-1.67 (m, 1H), 1.61-1.55 (m, 2H), 1.32-1.18 (m, 2H), 1.16-1.03 (m, 1H), 0.83 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.5, 138.3, 138.0, 104.2, 99.2, 95.8, 95.7, 95.1, 93.1, 92.8, 49.3, 48.6, 45.1, 44.4, 43.5, 42.0, 32.7, 28.7, 26.4, 23.8, 17.3, -6.0, -6.1. IR [solid, ν_{max} (cm^{-1})]: 2924, 2854, 1686, 1409, 1340, 1320, 1250. MS (FAB, positive ion): 501 (90%, $[M+H]^+$). HRMS calculated for $C_{25}H_{37}O_3N_2{}^{59}Co^{28}Si$: 500.1905, observed: 500.1900.

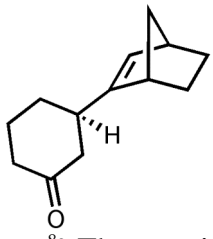
Thermal conditions for the alkene exchange of monofunctionalized cobalt dinitrosoalkane complexes. In a glovebox, the cobalt complex was weighed into a thick-walled Schlenk bomb. Norbornene or norbornadiene (20 equiv.) was weighed into a small vial and dissolved in toluene, and the soution was transferred to the bomb. The bomb was sealed and removed from the glovebox, then heated to 120-140 ºC. The reaction was monitored by TLC, and when complete, the crude products were purified by flash column chromatography on silica gen using a 100:0-1:1 hexanes/ethyl acetate gradient or a neat chloroform eluent, or by short-path vacuum distillation.

Microwave conditions for the alkene exchange of monofunctionalized cobalt dinitrosoalkane complexes. The functionalized cobalt complex and a large excess of norbornene or norbornadiene (typically 15-100 equiv.) were dissolved in 3 mL THF and sealed in a Biotage microwave tube. If the reaction was set up outside the glovebox, the reaction mixture was flushed for about 5 min with nitrogen with a needle inlet and outlet in the microwave tube's septum before heating. The mixture was microwaved at 130 ºC and reaction progress monitored by TLC. Once the reaction was complete, the THF was removed under reduced pressure and the crude product purified by flash column chromatography.

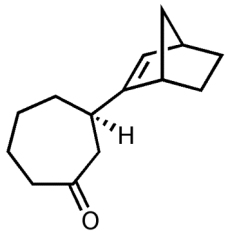
Measurement of enantiomeric excess of monofunctionalized alkenes. Yields reported below are for racemic samples. For the alkene exchange of enantioenriched cobalt complexes, the crude product was not rigorously isolated; rather, the THF was removed under reduced pressure and the residue dissolved in hexanes and passed through a small pipet column (5 cm silica in a Pasteur pipet above a small abount of sand, glass wool, and cotton), eluting with a mixture of approximately 3 drops ethyl acetate per pipetful of hexanes. Fractions were examined by TLC for the desired product, being visualized by $KMnO_4$ stain, and those containing the product were injected onto a chiral GC column without further purification, with assays previously developed for pure racemic samples of the functionalized alkenes. All GC-FID runs used the following method: the oven temperature was set to 70 ºC for 25 min, increased to 180 ºC at a rate of 0.25 ºC·min^{-1}, then held at 180 ºC for 20 min. The inlet gas pressure was set at 12.54 psi with a flow rate of 1.0 mL·min^{-1} and average velocity of 25 cm·s^{-1}. Runs were made in constant-pressure mode, so flow decreases with increasing temperature. The columns used are described for each analyte below.



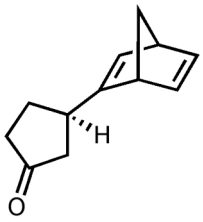
2-(3-Oxocyclopentyl)norbornene. The reaction was performed under thermal conditions with [Co] = 0.02 M, with the Cp^{Si} ligand present on cobalt in the initial complex. The product was isolated as a colorless oil in 39% yield by short-path distillation. ^{1}H NMR (400 MHz, C_6D_6): δ 5.38 (broad s, 1H), 2.67-2.66 (m, 1H), 2.43-2.41 (m, 1H), 2.33-2.27 (m, 1H), 2.02 (dd, 1H, J = 17.6, 6.8 Hz), 1.92 (ddd, 1H, J = 18.0, 8.0, 3.6 Hz), 1.79-1.65 (m, 3H), 1.57-1.44 (m, 2H), 1.34-1.22 (m, 2H), 0.99-0.94 (m, 2H), 0.84-0.82 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 215.7, 151.1, 78.6, 49.0, 44.2, 43.4, 42.3, 37.7, 37.3, 27.9, 26.5, 25.3. IR[thin film, ν_{max} (cm^{-1})]: 2960, 2869, 1743, 1403. MS (EI, positive ion): 190 (50%, $[M]^+$), 162 (100%, $[M\text{-}CO]^+$). HRMS calculated for $C_{12}H_{16}O$: 176.1201, observed: 176.1200. The compound was resolved by chiral GC on a Supelco™ β-Dex 120 column of dimensions 30 m x 0.25 mm x 0.25 μm, with t_R = 252.1, 253.1 min for a racemic sample (minor diastereomer at 250.5 min).



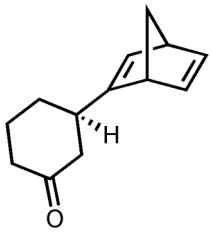
2-(3-Oxocyclohexyl)norbornene.[8a] The reaction was performed under microwave conditions with [Co] = 0.04 M, with the Cp^t ligand present on cobalt in the initial complex. The product was isolated as a light yellow oil in 99% yield by column chromatography using neat chloroform as eluent. ^{1}H NMR (400 MHz, C_6D_6): δ 5.45-5.44 (m, 1H), 2.70-2.69 (m, 1H), 2.49-2.48 (m, 1H), 2.38 (ddt, 1H, *J* = 13.6, 4.0, 1.6 Hz), 2.18-2.13 (m, 2H), 1.93-1.82 (m, 2H), 1.54-1.44 (m, 4H), 1.35-1.33 (m, 1H), 1.23-1.19 (m, 1H), 1.08-0.97 (m, 3H), 0.88-0.81 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 208.7, 152.7, 127.7, 49.6, 46.7, 44.5, 42.8, 41.7, 40.1, 30.3, 26.8, 25.6, 25.4. IR [thin film, ν_{max} (cm^{-1})]: 2958, 2867, 1712, 1447. MS (EI, positive ion): 190 (50%, $[M]^+$), 162 (100%, $[M-CO]^+$). HRMS calculated for $C_{13}H_{18}O$: 190.1358, observed: 190.1354. The compound was resolved by chiral GC on a Supelco™ β-Dex 120 column of dimensions 30 m x 0.25 mm x 0.25 μm, with t_R = 303.9, 305.3 min for a racemic sample (minor diastereomer at 301.7, 303.4 min).



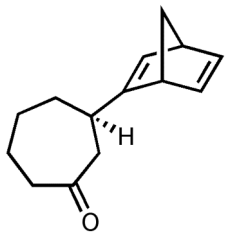
2-(3-Oxocycloheptyl)norbornene. The reaction was performed under thermal conditions with [Co] = 0.06 M, with the Cp^{Si} ligand present on cobalt in the initial complex. The product was isolated as a light yellow oil in 60% yield by column chromatography using neat chloroform as eluent. ^{1}H NMR (400 MHz, C_6D_6): δ 5.45-5.43 (m, 1H), 2.70-2.69 (m, 1H), 2.59-2.58 (m, 1H), 2.50 (dt, 1H, *J* = 14.0, 2.0 Hz), 2.31 (dd, 1H, *J* = 13.6, 11.2 Hz), 2.24-2.13 (m, 3H), 1.69-1.64 (m, 1H), 1.57-1.48 (m, 3H), 1.45-1.36 (m, 2H), 1.24-1.09 (m, 2H), 1.06-0.98 (m, 3H), 0.94-0.89 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 211.3, 154.0, 127.0, 49.6, 48.6, 44.8, 44.2, 42.8, 37.9, 36.1, 29.1, 27.0, 25.9, 24.5. IR [thin film, ν_{max} (cm^{-1})]: 2929, 2867, 1699, 1478. MS (EI, positive ion): 204 (50%, $[M]^+$), 176 (55%, $[M-CO]^+$). HRMS calculated for $C_{14}H2_0O$ 204.1514, observed: 204.1517. The compound was resolved by chiral GC on a Supelco™ β-Dex 120 column of dimensions 30 m x 0.25 mm x 0.25 μm, with t_R = 337.3, 339.4 min for a racemic sample.



2-(3-Oxocyclopentyl)norbornadiene. The reaction was performed under thermal conditions with [Co] = 0.2 M, with the Cp^{Si} ligand present on cobalt in the initial complex. The product was isolated as a colorless oil in 87% yield by column chromatography using a hexanes/ethyl acetate gradient as eluent. ^{1}H NMR (400 MHz, C_6D_6): δ 6.59-6.57 (m, 2H), 5.90 (s, 1H), 3.28 (s, 1H), 2.97 (s, 1H), 2.49-2.42 (m, 1H), 1.91-1.68 (m, 7H), 1.47-1.45 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 215.5, 159.5, 143.5, 141.8, 133.5, 73.0, 52.4, 50.0, 42.6, 37.7, 36.6, 26.2. IR [thin film, ν_{max} (cm^{-1})]: 2967, 2933, 1741, 1600, 1404. MS (CI, positive ion) 175 (70%, $[M+H]^+$), 174 (7%, $[M]^+$). HRMS calculated for $C_{12}H_{14}O$: 174.1045, observed: 174.1042. The compound was resolved by chiral GC on a Supelco™ β-Dex 225 column of dimensions 30 m x 0.25 mm x 0.25 μm, with t_R = 225.5, 231.7 min for a racemic sample.



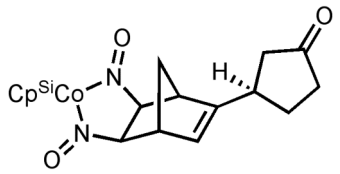
2-(3-Oxocyclohexyl)norbornadiene.[8a] The reaction was performed under microwave conditions with [Co] = 0.04 M, with the Cp^t ligand present on cobalt in the initial complex. The product was isolated as a light yellow oil in 51% yield by short-path distillation. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71-6.70 (m, 2H), 6.18 (s, 1H), 3.50-3.48 (m, 1H), 3.32 (s, 1H), 2.73-2.70 (m, 1H), 2.49-2.44 (ddt, 1H, J = 14.0, 4.4, 1.2 Hz), 2.34-2.19 (m, 3H), 1.92-1.82 (m, 4H), 1.68-1.60 (m, 1H), 1.53-1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 160.8, 144.0, 142.4, 134.4, 73.6, 52.7, 50.2, 46.0, 41.7, 40.3, 28.8, 24.4; IR [thin film, ν_{max} (cm^{-1})]: 2932, 2864, 1711, 1600, 1417. MS (EI, positive ion): 188 (100%, $[M]^+$). HRMS calculated for $C_{13}H_{16}O$: 188.1201, observed: 188.1204. The compound was resolved by chiral GC on a Supelco™ β-Dex 225 column of dimensions 30 m x 0.25 mm x 0.25 μm, with t_R = 255.9, 258.7 min for a racemic sample.



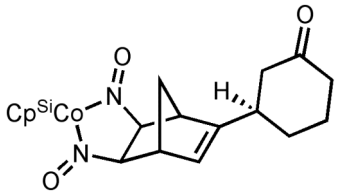
2-(3-Oxocycloheptyl)norbornadiene. The reaction was performed under thermal conditions with [Co] = 0.2 M, with the Cp^{Si} ligand present on cobalt in the initial complex. The product was isolated as a colorless oil in 51% yield by column

chromatography using a hexanes/ethyl acetate gradient as eluent. ^{1}H NMR (400 MHz, C_6D_6): δ 6.64-6.63 (m, 2H), 5.96 (s, 1H) 3.32 (s, 1H), 3.07 (s, 1H), 2.42-2.17 (m, 6H), 1.95-1.89 (m, 2H), 1.60-1.22 (m, 4H), 1.22-1.11 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 211.3, 162.3, 144.1, 142.7, 33.2, 73.7, 53.2, 50.6, 48.0, 44.3, 38.5, 35.3, 29.1, 24.6. IR [thin film, ν_{max} (cm^{-1})]: 2930, 2863, 1699, 1617, 1447. MS (CI, positive ion): 202 (50%, $[M]^+$), 185 (50%, $[M\text{-}OH]^+$). HRMS calculated for $C_{14}H_{18}O$: 202.1358, observed: 202.1355. The compound was resolved by chiral GC on a Supelco™ β-Dex 225 column of dimensions 30 m x 0.25 mm x 0.25 μm, with t_R = 327.8, 329.3 min for a racemic sample.

General procedure for the isomerization of monofunctionalized, norbornadiene-derived cobalt dinitrosoalkane complexes. In a glovebox, a solution of the functionalized cobalt complex (0.10-0.15 M) was prepared in THF or toluene in a thick-walled Schlenk bomb. The bomb was sealed and removed from the glovebox, and then heated to the desired temperature. The reaction was monitored by TLC or by the examination of aliquots by ^{1}H NMR, and once complete, crude products were purified by flash column chromatography on silica gel, using a 100:0-1:1 hexanes/ethyl acetate gradient as eluent.

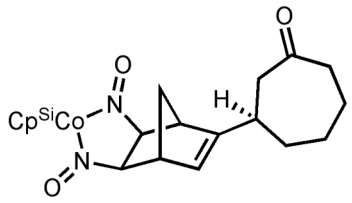


*{*cis-*5,6-Dinitroso-2-(3-oxocyclopentyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The reaction was performed at 130 ºC with [Co] = 0.15 M, and monitored by the examination of aliquots by ^{1}H NMR. The product was isolated as a black solid in 80% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 5.02-5.01 (m, 3H), 4.74-4.72 (m, 2H), 2.94 (s, 1H), 2.78 (s, 1H), 2.75 (d, 1H, *J* = 5.6 Hz), 2.68 (d, 1H, *J* = 5.6 Hz), 2.13 (d, 1H, *J* = 8.8 Hz), 1.95-1.90 (m, 1H), 1.79-1.71 (m, 2H), 1.62-1.45 (m, 2H), 1.35-1.26 (m, 3H), 0.88 (s, 9H), 0.27 (s, 3H), 0.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.6, 154.6, 130.2, 95.8, 94.6, 94.1, 93.1, 93.0, 92.9, 49.5, 47.3, 43.1, 42.8, 38.1, 38.0, 27.7, 26.5, 17.3, -5.7, -5.7. IR [solid, ν_{max} (cm^{-1})]: 2927, 2854, 1732, 1411, 1340, 1280. MS (FAB, positive ion): 473 (80%, $[M+H]^+$). HRMS calculated for $C_{23}H_{33}O_3N_2{}^{59}Co^{28}Si$: 472.1587, observed: 472.1592.



*{*cis-*5,6-Dinitroso-2-(3-oxocyclohexyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The reaction was performed at 120 ºC with [Co] = 0.10 M, and monitored by TLC. The product was isolated as a black solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.72-5.71 (m, 1H), 5.15-5.13 (m, 2H), 4.71-4.69 (m, 2H), 3.04-2.95 (m, 4H), 2.57-2.52 (m, 1H), 2.42-2.35 (m, 2H), 2.22-2.18 (m, 2H), 2.03-1.98 (m, 2H), 1.66-1.62 (m, 2H), 1.54-1.42 (m, 2H), 0.85 (s, 9H), 0.09 (s, 3H), 0.08

(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.4, 155.7, 130.1, 95.9, 95.8, 94.6, 94.1, 93.2, 93.1, 93.0, 49.3, 47.5, 45.8, 42.4, 41.4, 40.0, 29.5, 26.5, 25.1, 17.4, -5.7, -5.7. IR [solid, ν_{max} (cm^{-1})]: 2927, 2854, 1712, 1416, 1340, 1250. MS (FAB, positive ion): 487 ($[M+H]^+$). HRMS calculated for $C_{24}H_{35}O_3N_2{}^{59}Co^{28}Si$: 486.1743, observed: 486.1749.

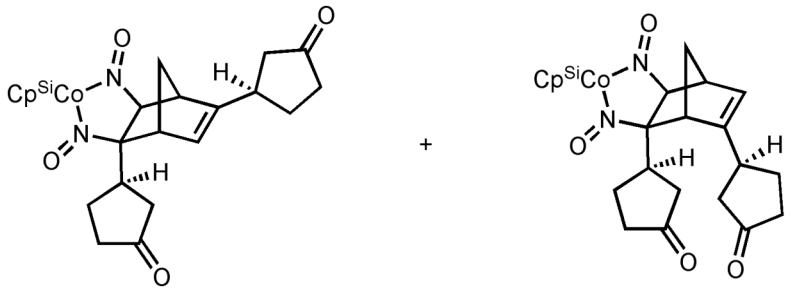


*{*cis-*5,6-Dinitroso-2-(3-oxocycloheptyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The reaction was performed at 120 °C with [Co] = 0.12 M, and monitored by TLC. The product was isolated as a black solid in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.68-5.67 (m, 1H), 5.14-5.11 (m, 2H), 4.69-4.68 (m, 2H), 3.01-2.96 (m, 4H), 2.53-2.40 (m, 5H), 2.03-1.91 (m, 4H), 1.62-1.49 (m, 2H), 1.41-1.34 (m, 2H), 0.84 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.2, 156.9, 129.5, 95.9, 95.8, 94.6, 94.2, 93.3, 93.1, 93.0, 49.6, 47.7, 47.4, 44.1, 42.4, 37.7, 35.2, 28.6, 26.5, 24.1, 17.4, -5.7, -5.7. IR [solid, ν_{max} (cm^{-1})]: 2926, 1698, 1340, 1258. MS (FAB, positive ion): 501 (90%, $[M+H]^+$). HRMS calculated for $C_{25}H_{37}O_3N_2{}^{59}Co^{28}Si$: 500.1905, observed: 500.1900.

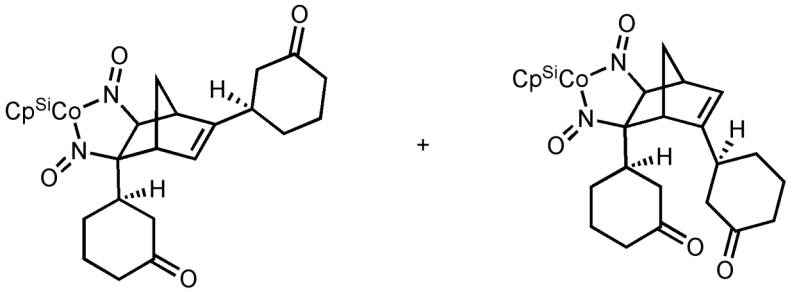
Racemic conditions for the second functionalization of cobalt dinitrosoalkane complexes. In the glovebox, a Schlenk tube was charged with a solution of racemic, monofunctionalized cobalt dinitrosoalkane (7.5-15 mM) and conjugate acceptor (2-20 equiv.) in THF (solution A). To this solution was added a solution of Verkade's proazaphosphatrane base (~20 mM, 10-25 mol%) at room temperature. For reactions employing 2-cyclopenten-1-one as the conjugate acceptor, low base and conjugate acceptor concentrations were used to minimize deleterious side reactions. The reactions were monitored by TLC on silica plates (3:1 hexanes/ethyl acetate eluent). When judged complete, the reaction mixture was opened to the laboratory atmosphere, concentrated under reduced pressure, and flash chromatographed on silica gel using a 100:0-3:1 hexanes/ethyl acetate gradient. In the case of reactions performed using 2-cyclopenten-1-one, the crude reaction mixture were first chromatographed directly on a small silica column with 3:1 hexanes/ethyl acetate eluent to quench remaining base, without prior concentration. The eluate was then concentrated and subjected to rigorous chromatography.

Enantioselective conditions for the second functionalization of cobalt dinitrosoalkane complexes. In the glovebox, a Schlenk tube was charged with a solution of 0.075 mmol enantioenriched, monofunctionalized cobalt dinitrosoalkane and 4 equiv. conjugate acceptor in 1.2 mL THF. Separately, a chiral base mixture was prepared as follows: a solution of 1 equiv. $Na[N(SiMe_3)_2]$ in 2 mL THF was added to 1.3 equiv. quaternary ammonium salt. To this suspension was added 0.6 mL additional THF, and the mixture was agitated briefly and filtered through a pipet charged with glass fiber into a separate Schlenk tube. Both Schlenk tubes were flushed onto a Schlenk line, and the cobalt and conjugate acceptor solution was cooled to -58 °C using a Neslab CryoCool

apparatus attached to a Dewar filled with acetone or methanol or -78 ºC using a dry ice/acetone bath, while the chiral base solution was cooled to -78 ºC in a dry ice/acetone bath. The chiral base solution was then added to the mixture of cobalt and conjugate acceptor *via* cannula transfer. Reactions were monitored and products isolated as in the racemic, ambient-temperature case; as in that case reactions mixtures containing 2-cyclopenten-1-one were passed directly through a short silica column with 3:1 hexanes/ethyl acetate eluent before the eluent was concentrated and rechromatographed.

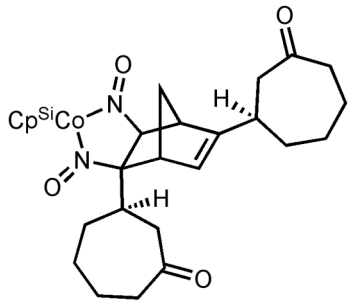


*{*cis-*5,6-Dinitroso-2,5-bis(3-oxocyclopentyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I) (*anti *regioisomer) and {*cis-*5,6-dinitroso-2,6-bis(3-oxocyclopentyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I) (*syn *regioisomer)*. The two regioisomers were isolated as a mixture. *Anti* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 (s, 1H), 5.16 (s, 1H), 5.11 (s, 1H), 4.73 (s, 1H), 4.65 (s, 1H), 2.98-2.88 (m, 3H), 2.75 (s, 1H), 2.59 (dd, 1H, *J* = 18.0, 10.0 Hz), 2.40 (dd, 1H, *J* = 18.0, 7.2 Hz), 2.31-2.12 (m, 7H), 2.07-2.02 (m, 3H), 1.82-1.72 (m, 3H), 1.60 (d, 1H, *J* = 8.8 Hz), 0.83 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.2, 217.0, 154.0, 129.4, 101.8, 98.2, 95.9, 95.8, 95.4, 93.1, 92.8, 50.7, 50.0, 44.9, 43.0, 42.8, 40.6, 38.2, 38.1, 37.5, 27.6, 26.4, 24.9, 17.3, -5.9, -6.0. *Syn* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (s, 1H), 5.12-5.10 (m, 1H), 4.73-4.72 (m, 1H), 4.65-4.63 (m, 1H), 3.01-2.86 (m, 4H), 2.75-2.67 (m, 1H), 2.51 (dd, 1H, *J* = 18.0, 10.0 Hz), 2.31-2.11 (m, 7H), 2.09-1.99 (m, 3H), 1.84-1.74 (m, 3H), 1.62-1.59 (m, 1H), 0.82 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.0, 216.9, 155.0, 129.8, 100.8, 99.2, 95.9, 95.8, 95.4, 53.6, 52.3, 48.1, 46.0, 43.8, 43.0, 41.7, 41.1, 37.7, 26.8, 26.4, 24.7, 17.3, -6.1, -6.2. IR [thin film, ν_{max} (cm^{-1})]: 2950, 1739, 1405, 1336, 1306. MS (FAB, positive ion): 555 (100%, $[M+H]^+$). HRMS calculated for $C_{28}H_{40}O_4N_2{}^{59}Co^{28}Si$: 555.2084, observed: 555.2097.

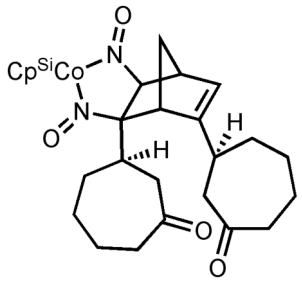


*{*cis-*5,6-Dinitroso-2,5-bis(3-oxocyclohexyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I) (*anti *regioisomer) and {*cis-*5,6-dinitroso-2,6-bis(3-oxocyclohexyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*

*(*syn *regioisomer)*. The two regioisomers were isolated as a mixture. *Anti* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (s, 1H), 5.19-5.18 (m, 1H), 5.14-5.13 (m, 1H), 4.74 (s, 1H), 4.66 (s, 1H), 2.97-2.95 (m, 2H), 2.80-2.75 (m, 1H), 2.66 (s, 1H), 2.51-2.48 (s, 1H), 2.42-2.39 (m, 3H), 2.30-2.12 (m, 5H), 2.06-1.91 (m, 3H), 1.71-1.57 (m, 3H), 1.47-1.37 (m, 4H), 0.85 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.4, 210.0, 155.4, 128.6, 103.2, 99.4, 95.9, 95.3, 93.2, 92.8, 50.2, 48.6, 45.7, 44.5, 44.2, 43.3, 41.2, 41.1, 40.1, 29.7, 27.0, 26.4, 25.3, 25.1, 17.4, -6.0, -6.1. *Syn* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88-5.87 (m, 1H), 5.19-5.18 (m, 1H), 5.15-5.14 (m, 1H), 4.75-4.74 (m, 1H), 4.67-4.66 (m, 1H), 2.98-2.96 (m, 2H), remaining peaks obscured by the major (*anti*) regioisomer. ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.7, 209.5, 155.8, 130.1, 102.6, 99.2, 95.1, 95.0, 93.0, 92.6, 49.9, 47.7, 46.6, 45.8, 44.3, 44.2, 41.2, 41.1, 39.2, 29.8, 28.6, 27.5, 24.8, 24.3, 17.2, -6.1, -6.2. MS (FAB, positive ion): 583 (100%, $[M+H]^+$). HRMS calculated for $C_{30}H_{43}O_4N_2{}^{59}Co^{28}Si$: 582.2319, observed: 582.2327.

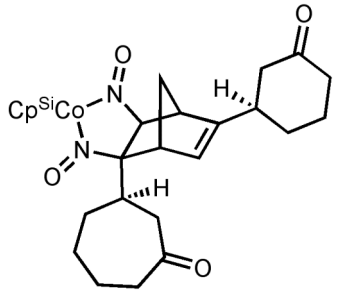


*{*cis-*5,6-Dinitroso-2,5-bis(3-oxocycloheptyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I) (*anti *regioisomer)*. The product is separable from its *syn* isomer by chromatography, and isolated as the more polar black solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (s, 1H), 5.14-5.13 (m, 1H), 5.11-5.10 (m, 1H), 4.71-4.70 (m, 1H), 4.65-4.64 (m, 1H), 3.00 (s, 1H), 2.93 (s, 1H), 2.80 (dd, 1H, *J* = 13.6, 10.8 Hz), 2.61-2.43 (m, 8H), 2.30 (ddd, 1H, *J* = 16.4, 12.0, 8.9 Hz), 2.13 (d, 1H, *J* = 9.2 Hz), 1.94-1.82 (m, 5H), 1.65-1.55 (m, 5H), 1.41-1.35 (m, 2H), 1.26-1.18 (m, 2H), 1.11-1.05 (m, 1H), 0.84 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.6, 213.0, 156.1, 128.4, 104.9, 99.2, 95.8, 95.7, 95.2, 93.1, 92.9, 50.9, 49.4, 47.5, 45.0, 44.5, 44.0, 43.6, 42.5, 37.6, 35.3, 32.6, 28.7, 28.5, 26.4, 24.0, 23.7, 17.3, -6.0, -6.1; IR [thin film, ν_{max} (cm^{-1})]: 2925, 1696, 1411, 1338, 1259. MS (FAB, positive ion): 611 (100%, $[M+H]^+$). HRMS calculated for $C_{32}H_{47}O_4N_2{}^{59}Co^{28}Si$: 610.2632, observed: 610.2645.

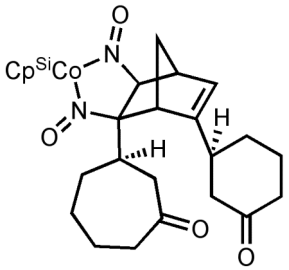


*{*cis-*5,6-Dinitroso-2,6-bis(3-oxocycloheptyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I) (*syn *regioisomer)*. The product is separable from its *anti* isomer by chromatography, and isolated as the less polar black solid. ^{1}H

NMR (400 MHz, $CDCl_3$): δ 5.78 (s, 1H), 5.16-5.15 (m, 1H), 5.13-5.12 (m, 1H), 4.72-4.71 (m, 1H), 4.67-4.66 (m, 1H), 3.04 (s, 1H), 2.94-2.91 (m, 2H), 2.79-2.64 (m, 5H), 2.53-2.42 (m, 3H), 2.27-2.16 (m, 3H), 1.92-1.87 (m, 4H), 1.65-1.56 (m, 5H), 1.46-1.24 (m, 2H), 1.17-1.10 (m, 2H), 0.85 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.7, 213.5, 157.2, 129.0, 104.1, 99.7, 95.9, 95.8, 95.1, 93.1, 92.8, 51.0, 48.6, 48.0, 45.7, 45.4, 43.9, 43.7, 41.8, 35.8, 34.2, 33.8, 28.4, 28.2, 24.7, 23.3, 17.4, -6.0, -6.1; IR [thin film, ν_{max} (cm^{-1})]: 2926, 2855, 1694, 1412, 1338, 1301 MS (FAB, positive ion): 611 (100%, $[M+H]^+$). HRMS calculated for $C_{32}H_{48}O_4N_2{}^{59}Co^{28}Si$: 611.2710, observed: 611.2720.



*{*cis-*5,6-Dinitroso-5-(3-oxocycloheptyl)-2-(3-oxocyclohexyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I) (*anti *regioisomer)*. The product is separable from its *syn* isomer by chromatography, and isolated as the more polar black solid. ^1H NMR (400 MHz, C_6D_6): δ 5.67 (s, 1H), 4.96-4.95 (m, 2H), 4.70-4.67 (m, 2H), 2.99 (s, 1H), 2.90 (s, 1H), 2.88 (dd, 1H, J = 10.8 and 2.0 Hz), 2.69-2.66 (m, 2H), 2.30-2.01 (m, 5H), 1.94-1.76 (m, 2H), 1.67-1.55 (m, 3H), 1.40-1.36 (m, 4H), 1.29-1.23 (m, 3H), 1.10-1.00 (m, 1H), 0.87 (s, 9H), 0.87-0.85 (m, 1H), 0.80-0.71 (m, 1H), 0.25 (s, 3H), 0.24 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 211.1, 207.2, 155.0, 129.0, 104.8, 99.3, 95.7, 95.6, 94.6, 93.0, 92.9, 50.8, 40.8, 45.5, 45.1, 44.5, 43.4, 43.1, 40.9, 39.8, 33.0, 29.6, 28.8, 26.5, 25.1, 23.8, 17.4, -5.8, -5.8. IR [thin film, ν_{max} (cm^{-1})]: 2929, 1698, 1412, 1337, 1299. MS (FAB, positive ion): 597 (100%, $[M^+]$). HRMS calculated for $C_{31}H_{45}O_4N_2{}^{59}Co^{28}Si$: 596.2475, observed: 596.2482.



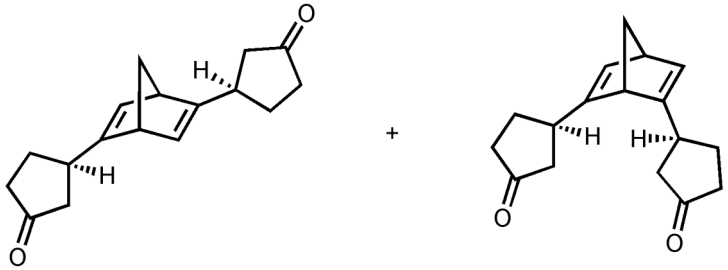
*{*cis-*5,6-Dinitroso-6-(3-oxocycloheptyl)-2-(3-oxocyclohexyl)norbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I) (*syn *regioisomer)*. The product is separable from its *anti* isomer by chromatography, and isolated as the less polar black solid. ^1H NMR (400 MHz, C_6D_6): δ 5.33 (s, 1H), 4.96-4.95 (m, 2H), 4.71-4.67 (m, 2H), 3.11-3.06 (m, 1H), 2.97-2.94 (m, 2H), 2.69 (s, 1H), 2.64-2.56 (m, 3H), 2.30-2.28 (m, 2H), 1.99-1.92 (m, 2H), 1.85-1.81 (m, 2H), 1.62-1.49 (m, 5H), 1.28-1.26 (m, 4H), 1.22-1.16 (m, 2H), 1.08-1.01 (m, 1H), 0.87 (s, 9H), .63-0.53 (m, 1H), 0.26 (s, 3H), 0.24 (s, 3H). ^{13}C

NMR (100 MHz, C_6D_6): δ 211.5, 207.3, 157.1, 128.9, 104.0, 99.6, 95.6, 94.5, 93.0, 92.7, 50.8, 48.4, 46.8, 45.9, 44.6, 43.7, 42.6, 41.2, 38.7, 33.9, 28.8, 26.4, 27.8, 26.5, 24.5, 23.2, 17.4, -5.9, -5.9. IR [thin film, ν_{max} (cm^{-1})]: 2929, 1698, 1412, 1337, 1299 MS (FAB, positive ion) 597 (100%, $[M+H]^+$). HRMS calculated for $C_{31}H_{45}O_4N_2{}^{59}Co^{28}Si$: 596.2475, observed: 596.2482.

Microwave preparation of disubstituted norbornadiene ligands by alkene exchange. In the glovebox, the difunctionalized cobalt complex (0.03-0.18 mmol) and a large excess (50-100 equiv.) of norbornadiene were dissolved in 3 mL THF and added to a microwave tube. The tube was capped and sealed and removed from the glovebox, then microwaved at 120-140 ºC. Following cooling of the reaction mixture to room temperature, the reaction was monitored by removing an aliquot by syringe under a nitrogen flow and examining it by silica gel TLC (3:1 hexanes, ethyl acetate eluent). Upon completion of the reaction, the THF was removed under reduced pressure and the crude product purified by flash column chromatography on silica gel, using a 100:0-3:1 hexanes/ethyl acetate gradient.

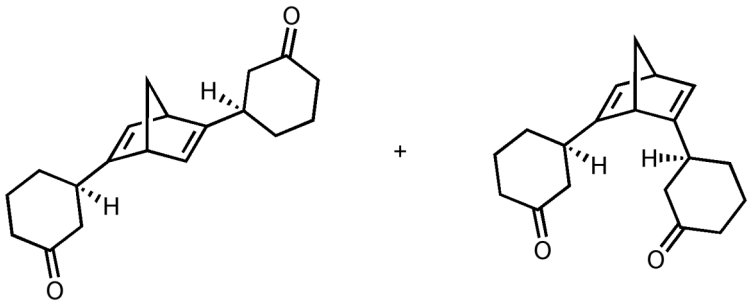
Thermal preparation of disubstituted norbornadiene ligands by alkene exchange. In the glovebox, the difunctionalized cobalt complex was weighed into a thick-walled Schlenk bomb. Separately, 20 equiv. norbornadiene was weighed into a small vial, dissolved in 1 mL toluene, and the solution transferred to the bomb. Additional toluene was then added to reach a solvent volume of 2.5 mL. The bomb was sealed, removed from the glovebox, and heated to 120-140 ºC in a silicone oil bath. Reactions were monitored and products purified as in the microwave case.

Analysis of enantioenriched disubstituted norbornadiene ligands. Chiral, enantioenriched products were analyzed by chiral HPLC, using a Shimadzu HPLC system fitted with a Chiralpak™ IA column and D2+W lamp. The flow rate was set at 1 $mL \cdot min^{-1}$ and a mixture of hexanes and isopropanol used as eluent; methods were developed on racemic samples of all chiral species before being used to measure enantiomeric excess. Detection occurred by absorption over a range of 190-800 nm, with intervals of 1 nm. Peaks were integrated at multiple wavelengths (190, 220, and 235 nm) to confirm clean peak separation. Complete separation of enantiomers was observed in all cases.



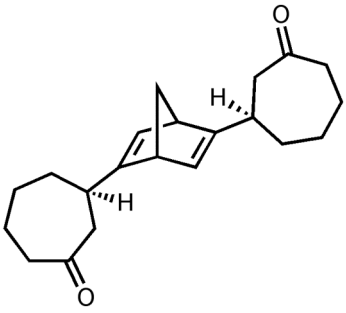
*2,5-Bis(3-oxocyclopentyl)norbornadiene (*anti *regioisomer) and 2,6-bis(3-oxocyclopentyl)norbornadiene (*syn *regioisomer)*. A mixture of the two products were isolated as a yellow oil. *Anti* isomer: ^{1}H NMR (400 MHz, C_6D_6): δ 5.87 (dd, 2H, J = 4.0, 1.6 Hz), 2.93-2.92 (m, 2H), 2.48-2.45 (m, 2H), 2.02-1.97 (m, 2H), 1.87-1.78 (m, 5H),

1.78-1.65 (m, 3H), 1.52-1.44 (m, 2H), 1.26-1.17 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 215.9, 160.6, 132.7, 71.6, 52.8, 43.2, 38.2, 37.2, 27.0. Enantioenriched samples were analyzed on HPLC using a 98.5:1.5 hexanes/isopropanol eluent mixture, with t_R = 45.6, 50.0 min for a racemic sample. $[\alpha]_D^{21}$= +16° (0.0067 g·mL^{-1}, $CHCl_3$, sample with 90% e.e.). *Syn* isomer: ^{1}H NMR (400 MHz, C_6D_6): δ 5.97-5.96 (m, 2H), 3.21-3.20 (m, 1H), 2.69-2.68 (m, 1H), 2.48-2.44 (m, 2H), 2.14 (dd, 2H, *J* = 7.6, 17.6 Hz) remaining peaks obscured by major isomer. ^{13}C NMR (100 MHz, C_6D_6): δ 216.0, 159.7, 134.6, 73.6, 55.5, 49.7, 44.3, 38.4, 37.9. Using the chiral HPLC method used to resolve the *anti* regioisomer, this *meso* compound has t_R = 52.5 min. IR [thin film, ν_{max} (cm^{-1})]: 2961, 2935, 2866, 1736, 1603, 1462, 1402, 1359. MS (ESI, positive ion) 257 (100%, $[M+H]^+$). HRMS calculated for $C_{17}H_{21}O_2$: 257.1526, observed: 257.1530.

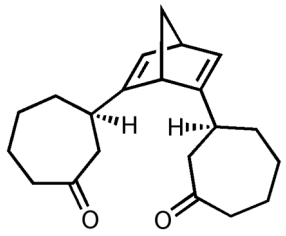


*2,5-Bis(3-oxocyclohexyl)norbornadiene (*anti *regioisomer) and 2,6-bis(3-oxocyclohexyl)norbornadiene (*syn *regioisomer)*. A mixture of the two products was isolated as a white solid. When prepared under enantioselective conditions, the *anti*:*syn* isomer ration was 20:1, and the *syn* isomer could be removed by recrystallization from hot pentane. *Anti* isomer: 1H NMR (400 MHz, $CDCl_3$): δ 6.18-6.16 (m, 2H), 3.30-3.29 (m, 2H), 2.81-2.74 (m, 2H), 2.45 (ddt, 2H, *J* = 14.4, 4.8, 1.6 Hz), 2.32-2.23 (m, 6H), 1.93-1.88 (m, 4H), 1.84-1.76 (m, 2H), 171-1.62 (m, 2H), 1.55-1.46 (m, 2H). ^{1}H NMR (400 MHz, C_6D_6): δ 6.02 (dd, 2H, *J* = 4.1, 1.8 Hz), 2.98-2.96 (m, 2H), 2.37-2.32 (m, 2H), 2.26 (broad dd, 2H, *J* = 13.9, 4.7 Hz), 2.09-2.02 (m, 4H), 1.93-1.87 (m, 2H), 1.86 (t, 2H, *J* = 1.5 Hz), 1.44-1.32 (m, 4H), 1.31-1.20 (m, 2H), 1.14-1.06 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6): 208.5, 161.5, 133.7, 71.9, 52.9, 46.0, 41.7, 40.1, 28.9, 24.5. Enantioenriched samples were analyzed on HPLC using a 97:3 hexanes/isopropanol eluent mixture, with t_R = 16.6, 26.8 min for a racemic sample. $[\alpha]_D^{21}$ = -18° [0.020 g·mL^{-1}, $CHCl_3$, sample with 98% e.e. of the (*R,R,R,R*) enantiomer]. $[\alpha]_D^{21}$ = +18° [0.037 g·mL^{-1}, $CHCl_3$, sample with 94% e.e. of the (*S,S,S,S*) enantiomer, with ~9% *syn* isomer impurity]. Selected collection parameters and data for single-crystal X-ray diffraction experiment: crystal system: triclinic, space group: P_1, *a* (Å): 6.4289(2), *b* (Å): 9.9793(3), *c* (Å): 12.8331(4), α (°): 18.995(2), β (°): 85.672(2), γ (°): 74.704(2), *V* (Å^3): 785.77(4), *Z*: 2, μ (mm^{-1}): 0.594, ρ (g·cm^{-3}): 1.202, θ range (°): 3.48 to 67.60, R_1, wR_2 [$I > 2\sigma(I)$]: 0.0293, 0.0737, R_1, wR_2 (all data): 0.0318, 0.0804, Measured/independent reflections/R_{int}: 15489/5016/0.0262, absolute structure parameter: 0.15(17). *Syn* isomer: ^{1}H NMR (400 MHz, C_6D_6): δ 6.09 (s, 2H), 3.24 (s, 1H), 2.83 (s, 1H), 2.48-2.44 (m, 2H), 2.34-2.23 (m, 2H), 2.14-2.03 (m, 2H), 1.95-1.81 (m, 4H), 1.46-1.33 (m, 8H), 1.15-1.06 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 208.4, 160.7, 135.2, 73.8, 54.7, 49.9, 47.0, 41.6, 40.5, 30.2, 24.9. Using the chiral HPLC

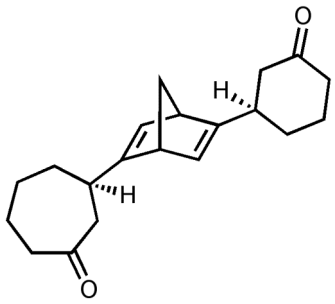
method used to resolve the *anti* regioisomer, this *meso* compound has t_R = 15.5 min. IR [thin film, ν_{max} (cm^{-1})]: 2954, 2930, 2861, 1705, 1604, 1448. MS (ESI, positive ion): 285 (35%, $[M+H]^+$). HRMS calculated for $C_{19}H_{25}O_2$: 285.1849, observed: 285.1853.



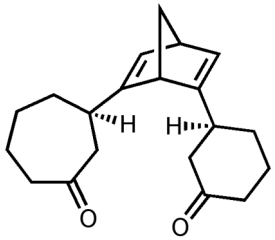
*2,5-Bis(3-oxocycloheptyl)norbornadiene (*anti *regioisomer)*. The product was isolated as a white solid. ^{1}H NMR (300 MHz, C_6D_6): δ 5.96 (d, 2H, *J* = 1.9 Hz), 3.04 (t, 2H, *J* = 1.9 Hz), 2.49-2.28 (m, 6H), 2.26-2.14 (m, 4H), 1.89 (t, 2H, *J* = 1.5 Hz), 1.68-1.59 (m, 2H), 1.55-1.47 (m, 2H), 1.43-1.35 (m, 2H), 1.26-1.11 (m, 2H), 1.08-1.00 (m, 4H). ^{13}C NMR (75 MHz, C_6D_6): δ 211.0, 162.2, 131.9, 71.5, 52.5, 47.8, 44.0, 38.1, 35.1, 28.8, 24.3. Enantioenriched samples were analyzed on HPLC using a 97:3 hexanes/isopropanol eluent mixture, with t_R = 19.0, 24.3 min for a racemic sample. $[\alpha]_D^{21}$ = +18° (0.051 $g \cdot mL^{-1}$, $CHCl_3$, sample with 92% e.e.). IR [solid, ν_{max} (cm^{-1})]: 2980, 2922, 2854, 1690, 1604, 1440, 1404 MS (ESI, positive ion): 313 (100 %, $[M+H]^+$). HRMS calculated for $C_{21}H_{29}O_2$: 313.2162, observed: 313.2157.



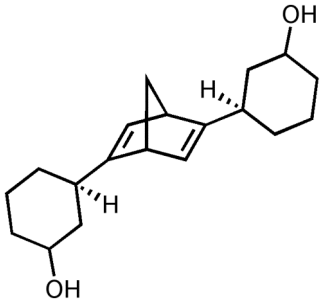
*2,6-Bis(3-oxocycloheptyl)norbornadiene (*syn *regioisomer)*. The product was isolated as a colorless oil. ^{1}H NMR: (400 MHz, C_6D_6): δ 6.08 (d, 2H, *J* = 3.2 Hz), 3.29-3.25 (m, 1H), 3.13-3.10 (m, 1H), 2.54-2.49 (m, 2H), 2.39-2.34 (m, 4H), 2.20-2.15 (m, 4H), 1.94 (dd, 2H, *J* = 1.2, 1.2 Hz), 1.67-1.62 (m, 2H), 1.54-1.51 (m, 2H), 1.39-1.34 (m, 2H), 1.21-1.16 (m, 3H), 1.10-1.01 (m, 2H), 0.92-.088 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 210.9, 161.4, 134.5, 73.4, 55.1, 49.5, 48.5, 43.9, 38.3, 35.9, 28.3, 24.1. Using the chiral HPLC method used to resolve the *anti* regioisomer, this *meso* compound has t_R = 12.7 min. IR [thin film, ν_{max} (cm^{-1})]: 2925, 2857, 1696, 1407. MS (EI, positive ion): 312 (20 %, $[M^+]$).



*2-(3-Oxocycloheptyl)-5-(3-oxocyclohexyl)norbornadiene (*anti *regioisomer)*. The product was isolated as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ 6.04-6.03 (m 1H), 5.91-5.90 (m, 1H), 3.02 (s, 1H), 2.96 (s, 1H), 2.43-2.40 (m, 1H), 2.35-2.18 (m, 6H), 2.09-1.99 (m, 2H), 1.92-1.85 (m, 3H), 1.62-1.57 (m, 1H), 1.48-1.47 (m, 1H), 1.40-1.34 (m, 3H), 1.23-1.17 (m, 2H), 1.09-0.99 (m, 3H). ^{13}C NMR (100 MHz, C_6D_6): 211.0, 208.3, 162.3, 161.0, 133.3, 131.8, 71.5, 52.6, 52.4, 47.8, 45.8, 44.0, 41.4, 40.0, 38.9, 35.0, 28.8, 28.7, 24.3. Enantioenriched samples were analyzed on HPLC using a 93:7 hexanes/isopropanol eluent mixture, with t_R = 10.3, 11.2 min for a racemic sample. $[\alpha]_D^{21}$ = +40° (0.0075 g·mL^{-1}, $CHCl_3$, sample with 96% e.e.). IR [thin film, ν_{max} (cm^{-1})]: 2930, 2861, 1698, 1446. MS (EI, positive ion): 298 (70%, [M$^+$]). HRMS calculated for $C_{20}H_{26}O_2$: 298.1933, observed: 298.1934.

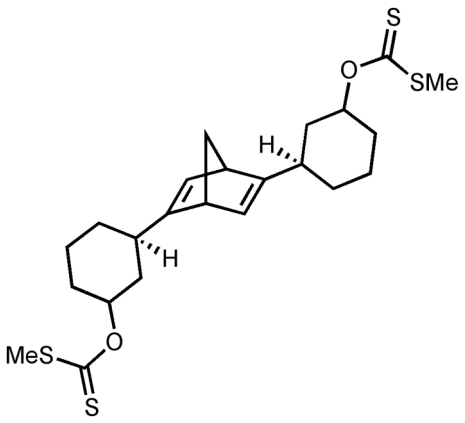


*2-(3-Oxocycloheptyl)-6-(3-oxocyclohexyl)norbornadiene (*syn *regioisomer)*. The product was isolated as a colorless solid. ^{1}H NMR (400 MHz, C_6D_6): δ 6.13 (s, 1H), 6.04 (s, 1H), 3.24 (s, 1H), 2.99 (s, 1H), 2.52 (d, 1H, J = 12.0 Hz), 2.45-2.19 (m, 6H), 2.10-2.00 (m, 2H), 1.90-1.82 (m, 3H), 1.62-1.06 (m, 10 H). ^{13}C NMR (100 MHz, C_6D_6): δ 211.2, 208.5, 161.5, 160.9, 135.5, 134.4, 73.8, 55.2, 49.9, 48.9, 46.9, 44.1, 41.7, 40.4, 38.7, 36.1, 30.5, 28.6, 24.9, 24.5. IR [thin film, ν_{max} (cm^{-1})]: 2931, 2862, 1710, 1701,1618, 1449, 1329. MS (EI, positive ion): 298 (70%, [M$^+$]). HRMS calculated for $C_{20}H_{26}O_2$: 298.1933, observed: 298.1936.



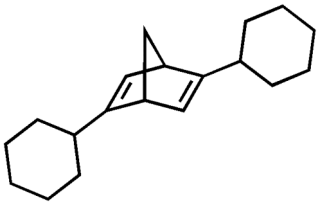
Synthesis of 2,5-bis(3-hydroxycyclohexyl)norbornadiene. A variation of the procedure of Zeynizadeh[15] was employed; this reaction is performed entirely on the

benchtop, with no attempt made to exclude atmospheric oxygen or carbon dioxide: a Schlenk tube with a Kontes Teflon stopcock was charged with a solution of 36.7 (0.129 mmol) (*R,R,R,R*)-2,5-bis(3-oxocyclohexyl)norbornadiene in a mixture of 0.78 mL THF and 26 μL deionized water, and 20.0 mg (0529 mmol, 4.1 equiv.) Na[BH_4] was added with stirring. The Schlenk tube was sealed and heated to 70 ºC for 12 min, after which point the reaction was judged complete by silica gel TLC and ^{1}NMR of an aliquot in $CDCl_3$. After addition of 1.2 mL deionized water to the reaction mixture with stirring, the product was extracted with dichloromethane (8 x 8 mL). The dichloromethane layers withere dried over sodium sulfate to afford the crude product (37.1 mg), which was flash chromatographed on a silica gel column with 1:1 hexanes/ethyl acetate eluent to yield 20.8 mg pure diol (0.072 mmol, 56%). ^{1}H NMR (400 MHz, C_6D_6): δ 6.10 (dd, 2H, *J* = 4.0, 1.6 Hz), 3.36 (m, 2H), 3.23-3.21 (m, 2H), 2.06-1.96 (m, 6H), 1.83-1.78 (m, 2H), 1.61-1.54 (m, 4H), 1.13-0.99 (m, 6H), 0.94 (br s, 2H), 0.85-0.73 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 163.1, 131.7, 71.6, 70.4, 52.1, 40.8, 38.8, 36.1, 30.4, 24.3. IR [thin film, ν_{max} (cm^{-1})]: 3316, 2926, 2854, 1603, 1448, 1360, 1281. MS (EI, positive ion): 288 ([M^+]) HRMS calculated for $C_{19}H_{28}O_2$: 288.2089, observed: 288.2094.



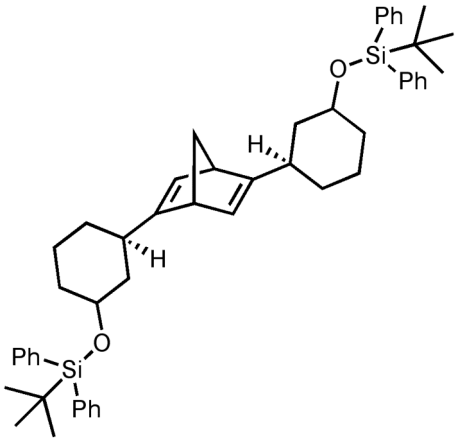
Synthesis of of 2,5-bis(3-hydroxycyclohexyl)norbornadiene dixanthate. A variation of the xanthate formation procedure previously used by the Toste group in the total synthesis of ventricosene was employed.[17] In the glovebox, a solution of 22.0 mg (0.076 mmol) of the preceding diol in 1.5 mL THF was added to a suspension of 18.2 mg of a 60 wt. % dispersion of sodium hydride in mineral oil (0.455 mmol NaH, 6.0 equiv.) in 1 mL THF. The mixture was transferred to a Schlenk tube with a Kontes Teflon stopcock and heated at 76 ºC with stirring for 4 h. The mixture was cooled to room temperature and 0.23 mL of a 2.04 M solution of carbon disulfide in dry THF (0.47 mmol CS_2, 6.2 equiv.) was added slowly *via* syringe, with stirring. The solution was stirred for 4 h at room temperature, at which point 0.24 mL of a 2.56 M solution of iodomethane in dry THF (0.62 mmol MeI, 8.1 equiv.) was added slowly *via* syringe, with stirring. The reaction mixture was stirred for 14.5 h at room temperature, at which point the Schlenk tube was cooled in an ice water bath and opened to the atmosphere. To the reaction mixture was added 5 mL saturated aqueous ammonium chloride with stirring, followed by 5 mL diethyl ether after removal from the ice bath. The organic layer was separated from the aqueous, and the aqueous layerwas extracted with diethyl ether (8 x 10 mL). The organic layers were combined, washed with saturated aqueous sodium bicarbonate (1 x 10 mL) and brine (1 x 10 mL), dried over magnesium sulfate, and concentrated. The

concentrate was flash chromatographed on a silica gel column with 9:1 hexanes/ethyl acetate as eluent to yield 28.7 mg (0.061 mmol, 80%) dixanthate, contaminated with a small amount of the *syn* regioisomeric product. ^{1}H NMR (400 MHz, C_6D_6): δ 5.94-5.92 (m, 2H), 5.71-5.65 (m, 2H), 3.08-3.07 (m, 2H), 2.30-2.27 (m, 2H), 2.19 (s, 6H), 1.91-1.90 (m, 2H), 1.50-1.43 (m, 4H), 1.31-1.18 (m, 2H), 1.08-1.03 (m, 2H), 0.73-0.66 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 215.8, 162.2, 132.1, 83.0, 71.8, 52.0, 38.4, 36.0, 31.4, 30.1, 23.8, 18.8. This compound was converted directly to 2,5-dicyclohexylnorbornadiene without further analysis (*vide infra*).



Synthesis of 2,5-dicyclohexylnorbornadiene by Barton deoxygenation. A variant of the deoxygenation procedure previously used by the Toste group in the total synthesis of ventricosene was employed.[17] To a solution of 26.5 mg dixanthate (0.057 mmol, 1 equiv.) in 1.75 mL of a 0.02 M solution of AIBN in C_6D_6 (0.034 mmol AIBN, 0.61 equiv.) was added 42 μL tris(trimethylsilyl)silane (0.136 mmol, 2.4 equiv.). The reslution solution was degassed by three freeze-pump-thaw cycles and put under nitrogen, then heated at 80 ºC for 1 h. Examination of an aliquot of the reaction mixture by ^{1}H NMR confirmed reaction completion. The reaction mixture was cooled in an ice bath, and 0.325 mL of 1 M $[Bu_4N]F$ in THF (0.325 mmol $[Bu_4N]F$, 2.4 equiv.) was added with stirring. After 1 h of stirring, 5.5 mL pentane was added to the reaction mixture, and the organic phase was washed with deionized water (2 x 35 mL) followed by brine (1 x 17.5 mL). The aqueous extracts were back-extracted with pentane (2 x 20 mL) and the combined organic layers were dried over magnesium sulfate and filtered, washing with pentane. The crude product was concentrated under reduced pressure, and 10.9 mg ferrocene was added. ^{1}H NMR analysis of this mixture showed 0.024 mmol hydrocarbon product (43%), integrating the vinyl 2H peak with respect to the ferrocene signal. The crude product was further purified by chromatography on a silica plug (1.75 in silica in a large pipet with 1 cm diameter), loading and eluting with pentane yielding the product contaminated with a small amount of its *syn* regioisomer, as well as with a peak in the silyl region derived from a byproduct of the silane reduction. Before optical rotation was measured, further purification was performed by preparative TLC with pentane eluent, on an EMD TLC silica gel 60 F_{254} plate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03-6.01 (m, 2H), 3.26-3.25 (m, 2H), 2.08-2.05 (m, 2H), 1.85 (s, 2H), 1.30-1.28 (m, 12H), 1.19-1.08 (m, 5H), 1.00-0.94 (m,n3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 130.8, 71.2, 51.8, 39.9, 31.3, 31.3, 26.3, 26.3. MS (EI, positive ion): 256 ($[M]^+$, 25 %), 173 (30%, $[M\text{-}C_6H_{11}]^+$). . $[\alpha]_D^{21}$ = +64º [0.0007 g·mL^{-1}, $CHCl_3$, sample derived from the diketone (*R,R,R,R*)-2,5-bis(3-oxocyclohexyl)norbornadiene with 95% e.e.]. The concentration of the hydrocarbon in the optical rotation sample was calculated by ^{1}H NMR of the material used in the measurement with a ferrocene internal standard. NMR-spectroscopic and mass-spectral data match those reported by Van der Eycken,[5] and the $[\alpha]_D^{21}$ value is close

in magnitude to $[\alpha]_D^{25}$= -58°, reported by Van der Eycken for the enantiomer of this compound.[5]



*Synthesis of 2,5-bis(3-*tert*-butyldiphenylsiloxycyclohexyl)norbornadiene*. The silylation procedure of Hardinger and Wijaya[16] was employed. In the glovebox, a solution of 13.2 mg of the diol 2,5-bis(3-hydroxycyclohexyl)norbornadiene (0.046 mmol, 1 equiv.) and 47.8 mg silver(I) nitrate (0.281 mmol, 6.2 equiv.) in 0.46 mL dry DMF was sealed in a Schlenk tube. The Schlenk tube was flushed onto a vacuum line, and 40 μL *tert*-butyldiphenylsilyl chloride (0.15 mmol, 3.4 equiv.) was added *via* syringe under nitrogen at room temperature with stirring, to yield an immediate white precipitate from the amber-colored starting solution. The completion of the reaction was confirmed by ^{1}H NMR spectroscopy of aliquots in C_6D_6, and after 4.5 h, the reaction mixture was opened to air, diluted with 4 mL deionized water, and extracted with diethyl ether (8 x 6 mL). The diethyl ether layers were washed with saturated aqueous sodium bicarbonate (1 x 7 mL), and this wash was back-extracted with diethyl ether (2 x 7 mL). The combined organic layers were dried over magnesium sulfate, and the solvent removed under reduced pressure. Initial flash column chromatography of the crude mixture using a 9:1-4:1 hexanes/ethyl acetate gradient as eluent yielded the product contaminated with what appears to be *tert*-butyldiphenylsilanol; this product was rechromatographed using a 9:1-3:1 pentane/chloroform gradient to yield a purer product as a white solid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.87-7.83 (m, 8H), 7.26-7.40 (m, 14H), 6.02 (dd, 2H, *J* = 3.9, 1.7 H), 3.82-3.73 (m, 2H), 3.08 (br t, 2H, *J* = 1.9 Hz), 2.18 (br d, 2H, *J* = 12.4 Hz), 1.94 (br s, 3H), 1.84 (br t, 2H, *J* = 12.0 Hz), 1.53-1.30 (overlapping peaks, 9H), 1.23 (s, 18H), 0.98-0.85 (m, 3H), 0.74 (m, 2H). The integrals sum to 67H as opposed to the 64; this appears to be because of a minor impurity, visible in the ^{1}H NMR spectrum, which overlaps with signals from the desired product. ^{13}C NMR (100 MHz, C_6D_6): δ 163.0, 136.3, 135.3, 135.2, 131.6, 129.9, 72.8, 71.3, 52.2, 41.0, 38.7, 36.4, 30.5, 30.4, 27.3, 24.2, 19.5.

Rhodium-catalyzed, enantioselective conjugate addition of phenylboronic acid to 2-cyclohexen-1-one. The general conditions of Hayashi[3b] were employed. In the glovebox, a solution of 0.01 mmol chiral diene ligand and 0.005 mmol $[(\eta^2\text{-}C_2H_4)_2RhCl]_2$ in 1 mL dry 1,4-dioxane was prepared and stirred for 1-2 h in a Schlenk flask. Separately, a 1.5 M aqueous solution of KOH was degassed by sparging with nitrogen for at least 15 min. To the rhodium/ligand solution was added 0.1 mL of the KOH solution (0.15 mmol

KOH, 48 mol%), and the resulting mixture was stirred for at least 15 min, at which point 75 mg phenylboronic acid (0.62 mmol, 2 equiv.) and 30 μL 2-cyclohexen-1-one (0.31 mmol, 1 equiv.) were added in rapid succession. The reaction mixture was heated to 30 ^{o}C in an oil bath with stirring, and the progress of the reaction was monitored by TLC (3:1 hexanes/ethyl acetate). Full conversion of 2-cyclohexen-1-one was in no case observed, but when the reaction appeared to have stopped, the mixture was allowed to cool to room temperature and opened to air. The mixture was passed through a silica plug, eluting with diethyl ether, and the eluate was analyzed by chiral gas chromatography on a Supelco^{TM} β-Dex 225 column of dimensions 30 m x 0.25 mm x 0.25 μm, with the oven temperature set to 70 ºC for 25 min, increased to 180 ºC at a rate of 0.25 ºC·min^{-1}, then held at 180 ºC for 20 min. The inlet gas pressure was set at 12.54 psi with a flow rate of 1.0 mL·min^{-1} and average velocity of 25 cm·s^{-1}. Runs were made in constant-pressure mode, so flow decreases with increasing temperature. This method was developed for a racemic sample of 3-phenylcyclohexanone, prepared using the platinum-catalyzed method of Hayashi and Sasaki,[22] t_R = 277.6, 280.5 min. Yields of the enantioenriched 3-phenylcyclohexanone were determined by ^{1}H NMR spectroscopy ($CDCl_3$) of the eluate (with diethyl ether removed under reduced pressure) with a known amount of ferrocene standard added.

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Chapter 4

Nitrosyl and Dinitrosoalkane Complexes of Cobalt with the κ^3-Hydridotris(3,5-dimethylpyrazolyl)borate Ligand

Portions of this chapter have been published as:

Crimmin, M. R.; Rosebrugh, L. E.; Tomson, N. C.; Weyhermüller, T.; Bergman, R. G.; Toste, F. D.; Wieghardt, K. [(TMEDA)Co$(NO)_2$][BPh_4]: A versatile synthetic entry point to four and five coordinate $\{Co(NO)_2\}^{10}$ complexes. *J. Organomet. Chem.* **2011,** *696,* 3974-3981

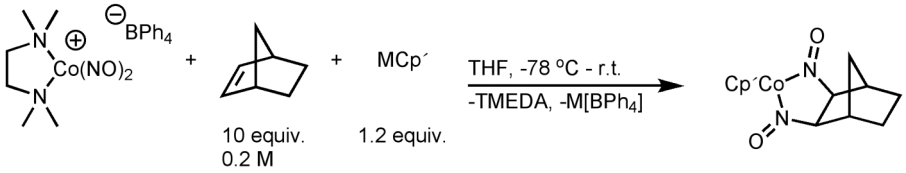
and

Tomson, N. C.; Crimmin, M. R. Petrenko, T.; Rosebrugh, L. E.; Sproules, S.; Boyd, W. C.; Bergman, R. G.; DeBeer, S.; Toste, F. D.; Wieghardt, K. A. A Step beyond the Feltham–Enemark Notation: Spectroscopic and Correlated *ab Initio* Computational Support for an Antiferromagnetically Coupled M(II)–$(NO)^-$ Description of Tp*M(NO) (M = Co, Ni). *J. Am. Chem. Soc.* **2011,** *133,* 18785-18801.

A Salt Metathesis Route to Cobalt Dinitrosoalkane Complexes

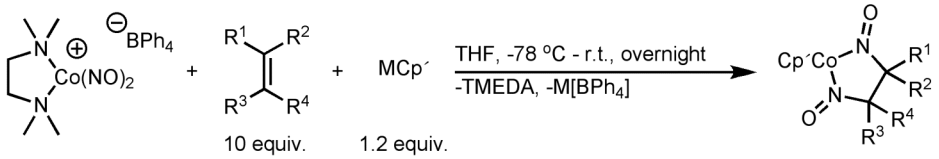
One disadvantage to the formation of $[CpCo(NO)_2]$/alkene adducts by treatment of $[CpCo(\mu\text{-}NO)]_2$ or $[CpCo(CO)_2]$ and the relevant alkene with NO gas[1,2] is that the incorporation of each Cp ligand requires the prior formation of a separate cobalt-containing starting material. In addition, both the alkene and the Cp ligand are exposed to the NO radical, which is potentially problematic for alkenes or ligands containing bonds with low homolytic bond dissociation enthalpies. An alternative synthetic scheme involves a common cobalt dinitrosyl precursor, the salt $[(TMEDA)Co(NO)_2][BPh_4]$ ($TMEDA = Me_2NCH_2CH_2NMe_2$),[3] which forms $[CpCo(NO)_2]$ upon treatment with MCp salts (M = Li, Na), liberating TMEDA and $M[BPh_4]$. If this salt metathesis reaction is conducted in the presence of an excess of an alkene, cobalt dinitrosoalkane complexes are readily formed (Tables 4.1 and 4.2).[4]

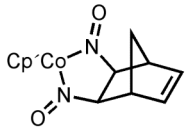
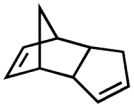
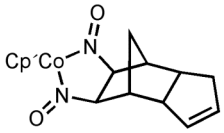
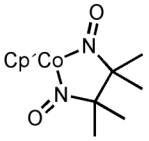
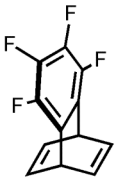
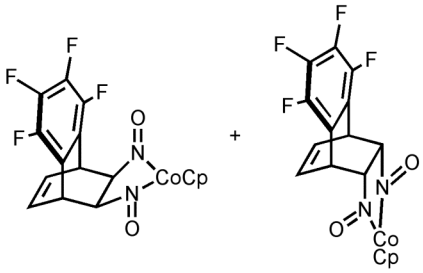
Table 4.1. Formation of $[Cp'Co(NO)_2]$/norbornene adducts *via* salt metathesis.



MCp´	time (h)	yield
NaCp	4	57%
$Li[\eta^5\text{-}MeC_5H_4]$	12	66%
$Li[\eta^5\text{-}C_5Me_5]$	12	67%
$Li[\eta^5\text{-}^tBuC_5H_4]$	0.5	74-94%
$Li[\eta^5\text{-}(Ph_2CH)C_5H_4]$	4	31%
$Li[\eta^5\text{-}Me_3SiC_5H_4]$	0.5	75%
$Li[\eta^5\text{-}^tBuMe_2SiC_5H_4]$	0.5-12	63-93%
$Li[\eta^5\text{-}^iPr_3SiC_5H_4]$	12	63%
$Li[\eta^5\text{-}1,3\text{-}(^iPr_3Si)_2C_5H_3]$	12	86%

Table 4.2. Formation of adducts between [Cp´Co(NO)$_2$] and other alkenes.



MCp´	alkene	product	yield
Li[η^5-^{t}BuMe$_2$SiC$_5$H$_4$]			86%
Li[η^5-^{t}BuMe$_2$SiC$_5$H$_4$]			88%
Li[η^5-^{t}BuMe$_2$SiC$_5$H$_4$]			67%[a]
LiCp		 1:1 *exo:endo*	77%[b]

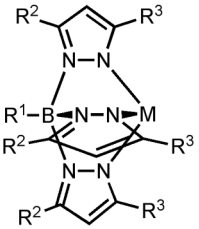
[a] Reaction conducted at r.t. for 1 h.

[b] Reaction quenched at -78 ºC after 0.5 h.; 2 equiv. alkene used.

Preparation and Reactivity of [Tp*Co(NO)$_2$]/Alkene Adducts

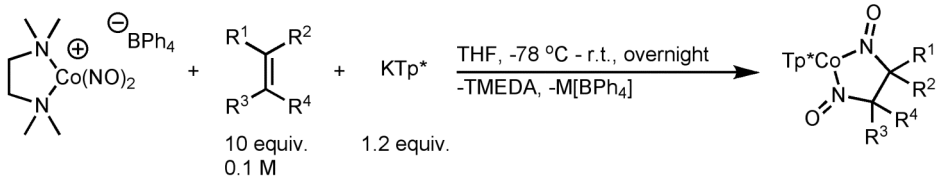
The flexibility of both ligand and alkene choice shown in Tables 4.1 and 4.2 suggested the possibility of forming cobalt dinitrosoalkane complexes with spectator ligands analogous to the Cp family. Tris(pyrazolyl)borates or "scorpionates," L_3^- anionic ligands with three dative nitrogen donor groups, bear some similarities in their coordination chemistry to the the L_2X Cp ligand and its derivatives, binding to metal centers in a κ^3 fashion (Figure 4.1).[5]

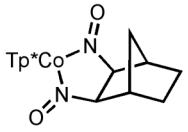
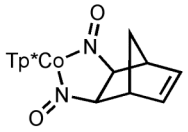
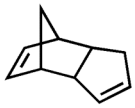
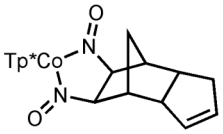
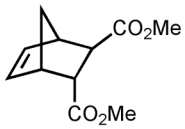
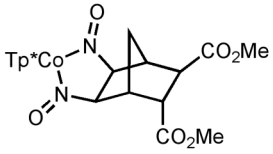
Figure 4.1. The structures of tris(pyrazolyl)borates and their κ^3 binding mode.



Common tris(pyrazolyl)borate ligands include the parent species Tp, where $R^1 = R^2 = R^3 = H$, and Tp*, where $R^1 = H$, $R^2 = R^3 = Me$, though many variants have been prepared. Tp ligands were pioneered by Trofimenko,[6] and their coordination chemistry with cobalt has been explored extensively by Theopold.[7] The salt metathesis methodology of Tables 4.1 and 4.2 can be used with the salt KTp* to prepare dinitrosoalkane complexes of the Tp* ligand (Table 4.3).[4]

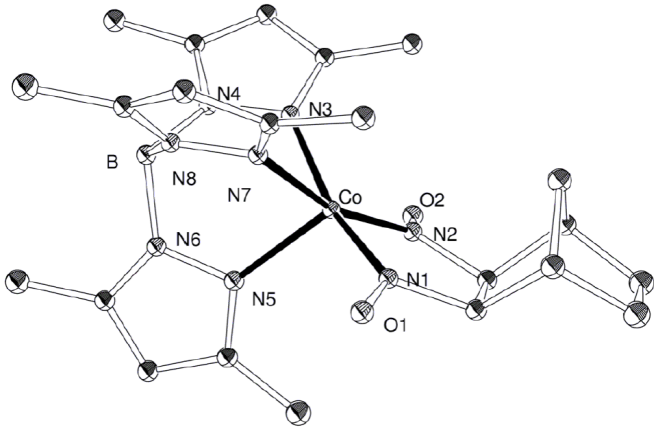
Table 4.3. Formation of Tp* dinitrosoalkane complexes.



alkene	product	yield
		65%
		62%
		56%
		31%

X-ray quality crystals of the [Tp*Co(NO)$_2$]/norbornene adduct were obtained by slow diffusion of pentane into a concentrated dichloromethane solution of the complex; the structure is shown in Figure 4.2.[4]

Figure 4.2. ORTEP representation of the [Tp*Co(NO)$_2$]/norbornene adduct.

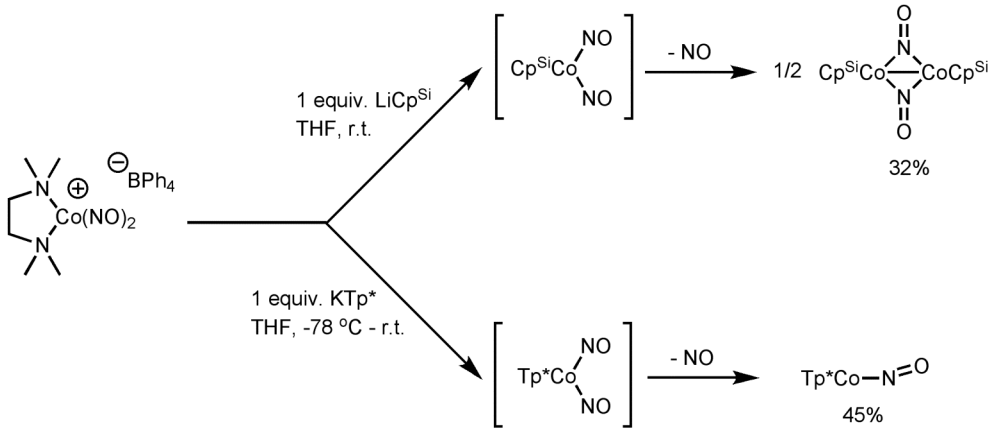


While this air- and moisture-stable complex appears to have C_s symmetry in the solid state, room-temperature ^{1}H NMR spectra in $CDCl_3$, C_6D_6, and toluene-d_8 show its three pyrazolyl ligands to be equivalent. At 193 K in toluene-d_8, however, the ^{1}H NMR spectrum shows decoalescence of both the aromatic and methyl signals, consistent with C_s symmetry.

While [Tp*Co(NO)$_2$] adducts of [2.2.2] bicyclic systems were readily formed, the salt metathesis reaction of Table 4.4 failed with less strained alkenes, such as cyclopentene, 2,5-dihydrofuran, and 2,3-dimethyl-but-2-ene. Additionally, this reaction failed when the parent ligand source KTp was used in place of KTp*, with the formation of the cobalt(II) species Tp$_2$Co observed instead of a dinitrosoalkane complex. The success of dinitrosoalkane complex formation using KTp* may be a result of the greater size of the Tp* ligand, which makes the formation of the side product (Tp*)$_2$Co less competitive for steric reasons. Adducts of [Tp*Co(NO)$_2$] and norbornene appear also to be significantly more base-sensitive then their Cp and Cp derivative analogs; attempts to functionalize them with 2-cyclohexen-1-one using Na[N(SiMe$_3$)$_2$] or Verkade's base led to decomposition, with no desired product observed.

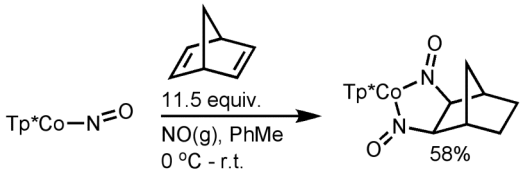
Perhaps the most notable difference in reactivity between the [CpCo(NO)$_2$] and [Tp*Co(NO)$_2$] moieties is their primary mode of decomposition in the absence of an alkene trap. The salt metathesis reaction of [(TMEDA)Co(NO)$_2$][BPh$_4$] with LiCp^{Si} (Cp^{Si} = η^5-^{t}BuMe$_2$SiC$_5$H$_4$) in the absence of alkene yields the bridged dimer [Cp^{Si}Co(μ-NO)]$_2$ with 18 electrons in each cobalt center's coordination sphere, presumably through dimerization of the 17-electron [Cp^{Si}Co(NO)] intermediate.[4] The analogous reaction with KTp* yields the paramagnetic, mononuclear species [Tp*Co(NO)] (Scheme 4.1).[4,8]

Scheme 4.1. Formation of Cp^{Si} and Tp* cobalt nitrosyl complexes.



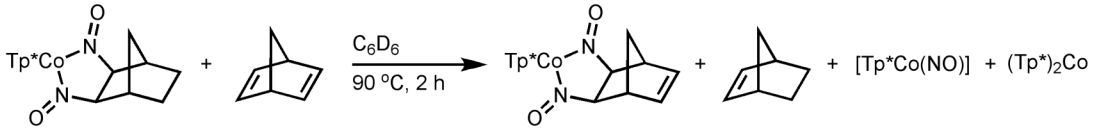
[Tp*Co(NO)] was characterized *via* X-ray crystallography, which showed it to be close to a linear nitrosyl complex, with a Co–N–O bond angle of 173.5° and a B–Co–NO angle of 173.5°. It was competent as a precursor to the [Tp*Co(NO)$_2$]/norbornene adduct when treated with NO gas and excess norbornene (Scheme 4.2),[8] showing similar reactivity to [CpCo(NO)]$_2$.[1]

Scheme 4.2. Reactivity of [Tp*Co(NO)] with NO and norbornene.



The alkene exchange reactions of the [Tp*Co(NO)$_2$] moiety were also explored. While alkene exchange reactions of [CpCo(NO)$_2$] proceeded most readily when [CpCo(NO)$_2$] migrated from a less to a more strained alkene,[2b] no adducts of [Tp*Co(NO)$_2$] and an alkene with little strain were isolable as starting materials in such a reaction. Thus, alkene exchange was explored between the norbornene adduct and the even more strained alkene norbornadiene (Table 4.4).

Table 4.4. Alkene exchange of the [Tp*Co(NO)$_2$] moiety.



1 **2** **3** **4** **5** **6**

0.1 M

[**2**] (M)	[**2**]/[**1**]	yield **3**	yield **4**	yield **5**	yield **6**
0.1	1	42.0%	70.5%	23.3%	2.8%
0.2	2	57.1%	83.4%	21.5%	3.3%
0.7	7	52.1%	78.4%	16.0%	3.3%
0.7	7	56.0%	85.6%	16.3%	3.7%
3.4	34	60.5%	67.0%	6.3%	1.3%
3.7	37	64.7%	74.6%	5.7%	0.6%

While the alkene exchange reaction of [Tp*Co(NO)$_2$] certainly proceeded, it was distinctly less clean than analogous reactions with [CpCo(NO)$_2$], or analogous moieties with Cp derivatives. Loss of NO to form [Tp*Co(NO)] was a competitive reaction without large excesses of norbornadiene, and formation of the cobalt(II) species (Tp*)$_2$Co was a minor, but notable, side reaction.

Electronic Structure of [Tp*Co(NO)$_2$]

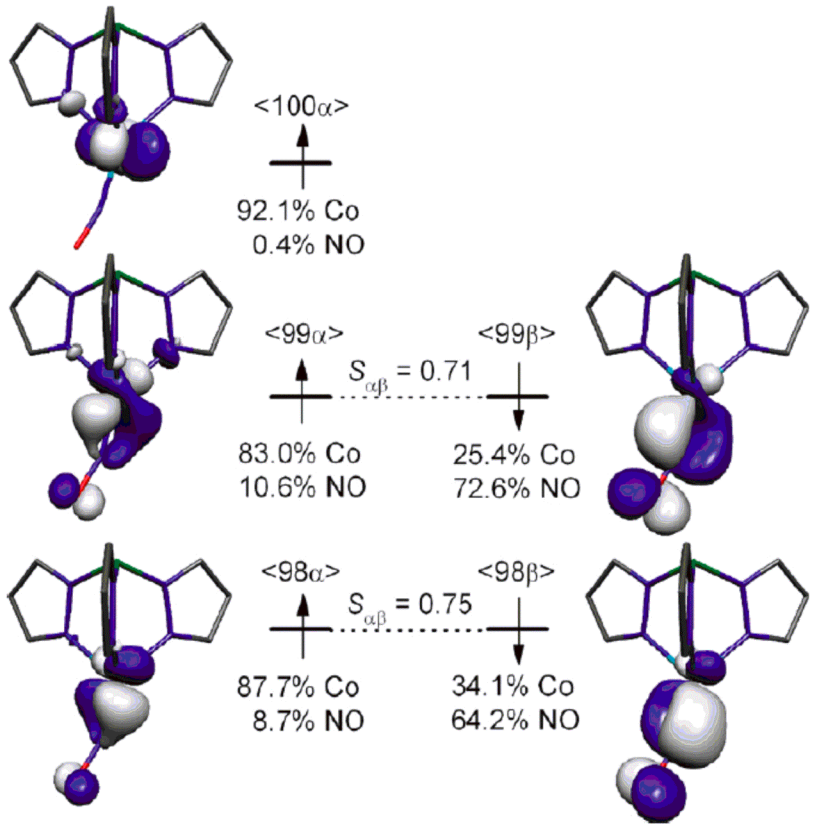
The synthesis of the paramagnetic mononitrosyl complex [Tp*Co(NO)] encouraged us to carry out a spectroscopic and computational investigation of its electronic structure. The standard electron-counting and oxidation-state rules apply differently to bent and linear nitrosyl ligands, with bent NO considered a one-electron ligand by the covalent model and a two-electron anionic $(NO)^-$ ligand by the ionic model, while linear NO is considered a three-electron ligand by the covalent model and a two-electron cationic $(NO)^+$ ligand by the ionic model.[9] Alternatively, the intentionally vague notation of Enemark and Feltham[10] classifies mononuclear metal nitrosyl complexes as $\{M(NO)_y\}^x$, where y is the number of nitrosyl ligands (whether linear or bent) and x the sum of the metal d electrons (assuming neutral NO ligands) and the NO π* electrons (one per NO).

By the standard rules of assigning oxidation states, [Tp*Co(NO)] would be assigned as a cobalt(0), d^9 complex, with the anionic $(Tp^*)^-$ and cationic $(NO)^+$ ligands. By the Enemark-Feltham notation, it is a $\{Co(NO)\}^9$ complex. Spectroscopic investigations of this complex, done in collaboration with the Wieghardt and DeBeer groups,[8] suggest that it is a cobalt(II) complex, with a doublet (S_{total} = 1/2) ground state whose spin is centered on Co. The simplest electronic structure model fitting these data would be that of a complex with a single unpaired electron associated with the cobalt center and a closed-shell $(NO)^-$ ligand, *i.e.* $S_{Co} = 1/2$, $S_{NO} = 0$.

A different electronic structure, however, is suggested by time-dependent density functional theory (TD-DFT) and the *ab initio* complete active space self-consistent field/multi-reference configuration interaction (CASSCF/MRCI) method, though the more rigorous latter used the simpler compound [TpCo(NO)] as a model (see Figure

4.1).[8] Both methods suggest that [Tp*Co(NO)] has five unpaired electrons in its ground state, with a quartet Co center (S_{Co} = 3/2) and triplet $(NO)^-$ ligand (S_{NO} = 1). An overall doublet ground state for the complex, however, is obtained *via* antiferromagnetic coupling between the cobalt center and the nitrosyl ligand, giving the experimentally observed value of S_{total} = 1/2. The calculated singly occupied molecular orbitals (SOMOs) of [Tp*Co(NO)] are displayed in Figure 4.3.[8]

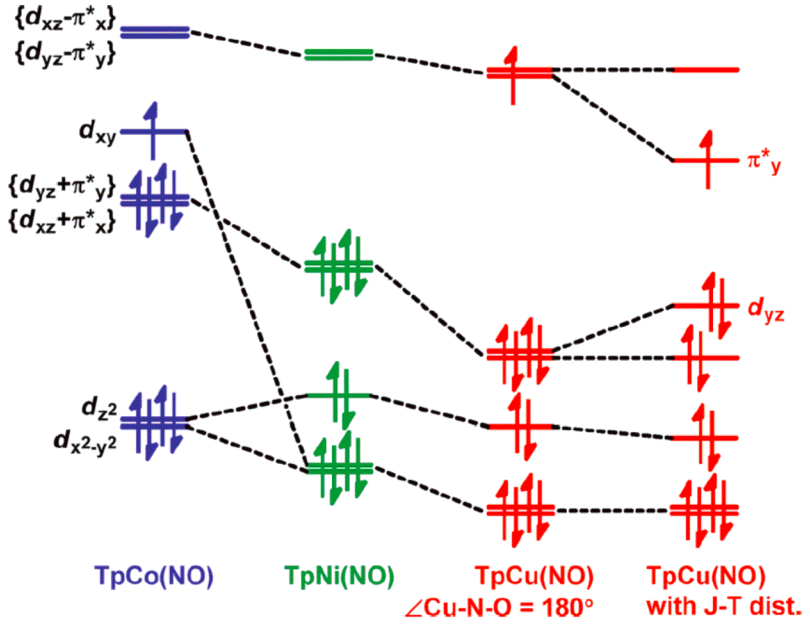
Figure 4.3. Frontier unrestricted corresponding orbitals (UCOs) of [Tp*Co(NO)], calculated from a geometry optimized using the B3LYP functional. $S_{\alpha\beta}$ denotes the spatial overlap between antiferromagnetically coupled orbitals. Methyl groups and hydrogen atoms have been removed for clarity.



These results are in contrast to spectroscopic and computational work by Tolman and coworkers,[11] whose analysis of the $\{Cu(NO)\}^{11}$ [Tp´Cu(NO)] complexes suggest a copper(I) center with S_{Cu} = 0 and a neutral, radical NO ligand with S_{NO} = 1/2. The computational methodology used to explore [Tp*Co(NO)] was extended to the $\{Ni(NO)\}^{10}$ complex [Tp*Ni(NO)], whose singlet ground state was found to be due to antiferromagnetic coupling between an S_{Ni} = 1 nickel(II) center and a S_{NO} = 1 nitrosyl anion, similar to the results with [Tp*Co(NO)]. More contribution from the minor Ni(I)/neutral $(NO)^0$ structure, however, was observed than from the analogous Co(I)/anionic $(NO)^-$ structure. Comparison of both of these complexes to [Tp´Cu(NO)] species suggest that the Co and Ni complexes have more M–NO double-bond character, while the Cu–NO linkage is closer to a single bond. A qualitative molecular orbital

scheme comparing the order of frontier orbitals in [TpM(NO)] (M = Co, Ni, Cu) is illustrated in Figure 4.4.[8]

Figure 4.4. Qualitative frontier orbital diagram of [TpM(NO)], M = Co, Ni, Cu. The Jahn-Teller distortion of [TpCu(NO)] consists of bending the Cu–N–O angle to 163°.



Conclusion

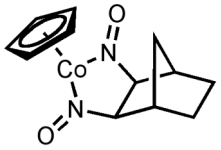
The Tp* ligand has been shown to be broadly analogous to Cp and its derivatives in the formation *via* salt metathesis of [Tp*Co(NO)$_2$]/alkene adducts. Notable differences in reactivity, however, include the inability to isolate adducts of alkenes whose [CpCo(NO)$_2$] adducts are readily isolated and characterized, and the decomposition of [Tp*Co(NO)$_2$]/alkene adducts under conditions used for the C–H functionalization of their Cp counterparts. Additionally, [Tp*Co(NO)$_2$] decomposes in the absence of alkenes to yield the paramagnetic, mononuclear species [Tp*Co(NO)], in contrast to the dimeric [Cp´Co(μ-NO)]$_2$ species. Spectroscopic and computational studies of [Tp*Co(NO)] suggest that its electronic structure consists of an S = 3/2 Co(II) center antiferromagnetically coupled to an S = 1 $(NO)^-$ anion, for an overall doublet ground state.

Experimental Section

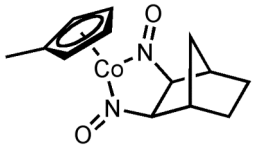
General experimental procedures. Unless otherwise indicated, reactions were performed under anhydrous and anaerobic conditions as described in previous chapters. Solvents were dried and purified as previously described. Reaction mixtures were stirred and monitored, and products purified and analyzed, as in previous chapters. Infrared spectra were obtained as described in Chapter 3.

Cobalt(II) chloride, volatile alkenes, TMEDA, methanol, and gaseous nitric oxide were dried and/or purified as described in Chapter 3. The cobalt species $[(TMEDA)Co(NO)_2][BPh_4]$ was prepared using a previously reported modification[12] (see also Chapter 3, Experimental Section) of the procedure of Caulton and coworkers.[3b] 5,6,7,8-Tetrafluoro-1,4-dihydro-1,4-ethenonapthalene was synthesized by the literature procedure.[13] The lithium salts $Li[\eta^5\text{-}MeC_5H_4]$, $Li[\eta^5\text{-}C_5Me_5]$, $Li[\eta^5\text{-}{}^tBuC_5H_4]$, $Li[\eta^5\text{-}(Ph_2CH)C_5H_4]$, $Li[\eta^5\text{-}Me_3SiC_5H_4]$, $Li[\eta^5\text{-}{}^tBuMe_2SiC_5H_4]$, $Li[\eta^5\text{-}{}^iPr_3SiC_5H_4]$, and $Li[\eta^5\text{-}1,3\text{-}({}^iPr_3Si)_2C_5H_3]$ were prepared by literature procedures.[14] All other reagents were obtained from commercial suppliers (Sigma-Aldrich, Strem) and used without further purification.

General procedure for the synthesis of cyclopentadienylcobalt dinitrosoalkane complexes. Under a nitrogen or argon atmosphere, a solution of a lithium or sodium cyclopentadienyl salt (0.54 mmol, 1.2 equiv.) in 10 mL THF was added *via* cannula transfer to a slurry of $[(TMEDA)Co(NO)_2][BPh_4]$ (250 mg, 0.45 mmol, 1 equiv.) and alkene (4.5 mmol, 10 equiv.) in 10 mL THF at -78 ºC. After stirring for 5 min at -78 ºC, the reaction mixture was allowed to warm to ambient temperature and stirred for several hours or overnight. The reaction was monitored by TLC on silica gel, with a developing solvent mixture of 3:1 hexanes/ethyl acetate. Once the reaction was complete, the THF was removed under reduced pressure and the crude product dissolved in a minimal amount of dichloromethane and purified by flash column chromatography on silica gel with 9:1 hexanes/ethyl acetate as the eluent. Products isolated in this manner proved air- and moisture-stable in the solid state, and can be handled on the benchtop.

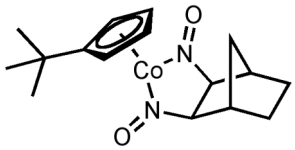


*(*cis*-2,3-Dinitrosonorbornane)(cyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 57% yield. Analytical data match those previously reported.[1,15]

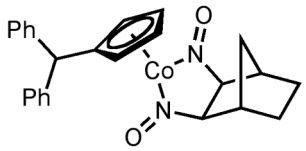


*(*cis*-2,3-Dinitrosonorbornane)(methylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 66% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 4.82-4.83 (m, 2H), 4.69-4.71 (m, 2H), 2.70-2.71 (m, 2H), 2.62-2.63 (m, 2H), 1.80 (s, 3H), 1.18-1.21

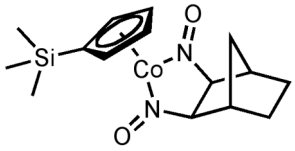
(m, 2H), 0.83 (d, 1H, J = 10.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 93.5, 90.9, 89.1, 42.4, 31.1, 26.6, 11.0. IR [solid, ν_{max} (cm^{-1})]: 2966, 1408, 1343, 1258, 1019. HRMS (ESI, positive ion): calculated for $C_{13}H_{18}O_2N_2Co$: 293.0695, observed: 293.0696.



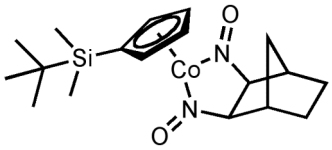
*(*cis-*2,3-Dinitrosonorbornane)(*tert-*butylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 94% yield. Analytical data match those previously reported[12] (see also Chapter 3 of this dissertation).



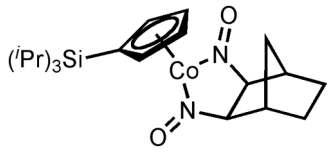
*(*cis-*2,3-Dinitrosonorbornane){(diphenylmethyl)cyclopentadienyl}cobalt(I)*. The product was isolated a black solid in 31% yield, contaminated with ~5% of an unknown impurity. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.26 (m, 10H), 5.18 (s, 1H), 4.88-4.89 (m, 2H), 4.58-4.59 (m, 2H), 2.72-2.73 (m, 2H), 2.63-2.64 (m, 2H), 1.51-1.56 (m, 2H), 1.19-1.26 (m, 3H), 0.76 (d, 1H, J = 10.4 Hz) ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6, 31.3, 42.4, 47.0, 89.2, 91.1, 111.1, 126.6, 128.4, 128.9, 143.4. IR [solid, ν_{max} (cm^{-1})]: 2962, 1415, 1343, 1259. HRMS (ESI, positive ion): calculated for $C_{25}H_{26}O_2N_2Co$: 445.1312, observed: 445.1308.



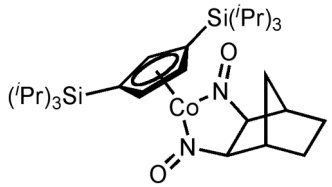
*(*cis-*2,3-Dinitrosonorbornane}(trimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, 9H), 0.43 (d, 1H, J = 10.0 Hz), 2.29-2.30 (m, 2H), 2.49-2.50 (m, 2H), 4.77 (s, 2H), 4.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.4, 26.3, 31.1, 42.4, 92.7, 93.7, 95.1, 96.6. IR [solid, ν_{max} (cm^{-1})]: 2954, 1411, 1344, 1282, 1038. HRMS (ESI, positive ion): calculated for $C_{15}H_{24}O_2N_2CoSi$: 351.0934, observed: 351.0921.



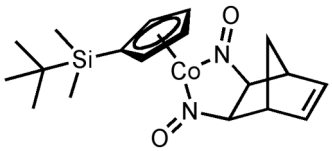
*(*cis-*2,3-Dinitrosonorbornane}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 84% yield. Analytical data match those previously reported[12] (see also Chapter 3 of this dissertation).



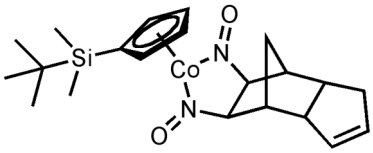
*(*cis-*2,3-Dinitrosonorbornane}(triisopropylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82 (d, 1H, *J* = 10.8 Hz), 1.01 (d, 18H, *J* = 6.8 Hz), 1.09-1.18 (m, 5H), 2.61-2.64 (m, 2H), 2.64-2.66 (m, 2H), 4.66-4.67 (m, 2H), 5.16-5.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.7, 18.7, 26.5, 31.2, 42.3, 91.5, 93.0, 93.9, 96.5. IR [solid, ν_{max} (cm^{-1})]: 2924, 2864, 1459, 1411, 1344, 1260. HRMS (ESI, positive ion): calculated for $C_{21}H_{36}O_2N_2CoSi$: 435.1873, observed: 435.1855.



*(*cis-*2,3-Dinitrosonorbornane}{1,3-bis(triisopropylsilyl)cyclopentadienyl}cobalt(I)*. The product was isolated as a black solid in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78 (d, 1H, *J* = 10.4 Hz), 1.00 (d, 18H, *J* = 7.2 Hz), 1.02 (d, 18H, *J* = 7.2 Hz), 1.11-1.16 (m, 4H), 1.38 (d, 1H, *J* = 10.4 Hz), 1.45-1.49 (m, 2H), 2.58-2.59 (m, 2H), 2.60-2.61 (m, 2H), 4.51-4.52 (m, 1H), 4.97-4.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 18.7, 18.9, 26.6, 31.2, 42.1, 93.9, 94.7, 100.8, 101.0. IR [solid, ν_{max} (cm^{-1})]: 2942, 2862, 1459, 1408, 1341, 1282, 1259. HRMS (ESI, positive ion): calculated for $C_{30}H_{56}O_2N_2CoSi$: 591.3207, observed: 591.3187.

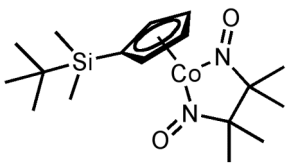


*(*cis-*5,6-Dinitrosonorbornene}(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 86% yield. Analytical data match those previously reported[12] (see also Chapter 3 of this dissertation).

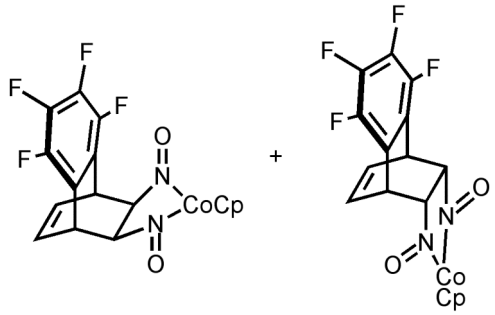


*(*cis-*5,6-Dinitroso-5,6-dihydro-*endo-*dicyclopentadiene)(*tert-*butydimethylsilylcyclopentadienyl)cobalt(I)*. The product was isolated as a black solid in 88% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 0.25 (s, 6H), 0.69 (d, 1H, *J* = 10.2 Hz), 0.88 (s, 9H), 1.67-1.84 (m, 3H), 1.97-2.00 (m, 1H), 2.49-2.54 (m, 2H), 2.61-2.54 (m, 2H), 2.73-2.75 (m, 1H), 4.76-4.77(m, 2H), 5.01-5.02 (m, 2H), 5.06-5.07 (m, 1H), 5.12-5.13 (m, 1H). ^{13}C NMR (75 MHz, C_6D_6): δ -5.5, 17.4, 26.6, 31.8, 34.1, 41.5, 45.7, 47.2, 52.6, 88.9, 91.2, 92.8, 92.9, 95.7, 130.8, 131.7. IR [solid, ν_{max} (cm^{-1})]: 2922, 2852, 1414, 1344, 1282.

HRMS (ESI, positive ion): calculated for $C_{21}H_{32}O_2N_2CoSi$: 431.1560, observed: 431.1566.



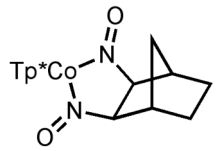
*Synthesis of (2,3-dinitroso-2,3-dimethylbutane)(*tert-*butyldimethylsilylcyclopentadienyl)cobalt(I)*. In the glovebox, a solution of 33.5 mg Li[η^5-^{t}BuMe$_2$SiC$_5$H$_4$] (0.18 mmol, 1.0 equiv.) in 10 mL THF was added to a slurry of 100 mg [(TMEDA)Co(NO)$_2$][BPh$_4$] (0.18 mmol, 1.0 equiv.) and 2,3-dimethylbut-2-ene (303 mg, 3.6 mmol, 20 equiv.) in 10 mL THF at ambient temperature and stirred for 1 h. After the reaction was complete, the reaction mixture was removed from the glovebox and opened to air. The THF was removed under reduced pressure and the crude product dissolved in minimum dichloromethane and purified by flash column chromatography on silica gel, using a 9:1 hexanes/ethyl acetate mixture as eluent. The product was isolated as a black solid in 67% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 0.21 (s, 6H), 0.88 (s, 9H), 0.94 (s, 12H), 4.70 (s, 2H), 5.01 (s, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ -5.6, 17.4, 24.2, 26.6, 92.9, 93.3, 93.8, 95.6. IR [solid, ν_{max} (cm^{-1})]: 2950, 2855, 1412, 1343, 1300. HRMS (ESI, positive ion): calculated for $C_{17}H_{32}O_2N_2CoSi$: 383.1560, observed: 383.1564.



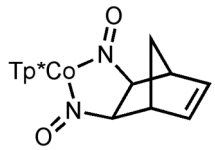
Synthesis of exo *and* endo *isomers of {5,6,7,8-tetrafluoro-1,4-dihydro-1,4-(*cis-*1,2-dinitrosoethano)naphthalene}(cyclopentadienyl)cobalt(I)*. Under an inert atmosphere, a solution of 11.7 mg LiCp (0.162 mmol, 0.9 equiv.) in 1 mL THF was added *via* cannula transfer to a slurry of 100 mg [(TMEDA)Co(NO)$_2$][BPh$_4$] (0.18 mmol, 1.0 equiv.) and 81.6 mg 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (0.36 mmol, 2.0 equiv.) in 1 mL THF at -78 °C. The reaction mixture was stirred for 30 min at -78 °C and transferred directly to a column packed with silica gel (5 cm depth, 4 cm diameter) to quench the reaction. The column was flushed with ethyl acetate until the washings were colorless. The solvent was removed under reduced pressure and the crude products purified by flash column chromatography on silica gel. The *exo* and *endo* isomers were separable in this manner. *Endo* isomer: the product was isolated in 36% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 5.80-5.78 (m, 2H), 4.75-4.70 (m, 2H), 4.66 (s, 5H), 2.49-2.48 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 131.4, 90.0, 87.9, 87.7, remaining carbons not observed. ^{19}F NMR (376.5 MHz, C_6D_6): δ -145.7, -157.4. IR [solid, ν_{max} (cm^{-1})]: 2917, 2848, 1497, 1411, 1331, 1281. R_f = 0.75 (3:1 hexanes/ethyl acetate). *Exo* isomer: the product was obtained in 41% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 5.55-5.34 (m, 2H),

4.58-4.56 (m, 2H), 4.32 (s, 5H), 2.53-2.51 (m, 2H). ^{19}F NMR (376.5 MHz, C_6D_6): δ -147.8, -159.6. IR [solid, ν_{max} (cm^{-1})]: 2916, 2848, 1496, 1340, 1330. HRMS (ESI, positive ion): calculated for $C_{17}H_{10}O_2N_2F_4Co$: 409.0005, observed: 409.0010. R_f = 0.40 (3:1 hexanes/ethyl acetate).

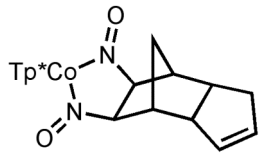
General procedure for the synthesis of {κ^3-hydridotris(3,5-dimethylpyrazolyl)borate}cobalt dinitrosoalkane complexes. Under an inert atmosphere, a solution of 72.6 mg KTp* (0.216 mmol, 1.2 equiv.) in 10 mL THF was added *via* cannula to a slurry of 100.4 mg [(TMEDA)Co(NO)$_2$][BPh$_4$] (0.181 mmol, 1 equiv.) and alkene (1.81 mmol, 10 equiv.) in 10 mL THF at -78 ºC. The reaction mixture was allowed to warm to room temperature and was stirred at room temperature overnight. When the reaction was judged complete by the analysis of aliquots by silica gel TLC, the THF was removed under reduced pressure and the crude product dissolved in minimum dichloromethane and purified by flash column chromatography on silica gel, using 9:1 hexanes/ethyl acetate as eluent. Products isolated in this manner proved air- and moisture-stable in the solid state and could be handled on the benchtop.



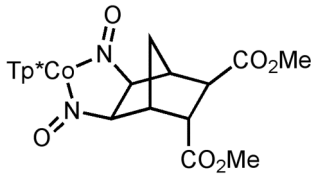
*(*cis*-2,3-Dinitrosonorbornane}{κ^3-hydridotris(3,5-dimethylpyrazolyl)borate}cobalt(I)*. The product was isolated as a brown solid in 65% yield. X-ray quality crystals were obtained by slow diffusion of pentane into a concentrated solution of the product in dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (d, 1H, *J* = 10.4 Hz), 1.21-1.28 (m, 2H), 1.36-1.47 (m, 2H), 1.53 (d, 1H, *J* = 10.4 Hz), 1.89 (s, 9H), 2.00 (m, 2H), 2.38 (s, 9H), 3.05 (m, 2H), 5.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.6, 13.8, 26.4, 31.6, 37.6, 93.5, 107.4, 145.0, 150.4. IR [KBr disk, ν_{max} (cm^{-1})]: 3050, 2967, 2927, 2525, 1544, 1364, 1340. MS (ESI, positive ion): 511 (100%, $[M+H]^+$), 416 (10%, $[M-C_7H_{10}]^+$), 386 (20%, $[M-C_7H_{10}-NO]^+$), 356 (95%, $M-C_7H_{10}-2NO]^+$). UV-vis [λ/nm (ε/$M^{-1}\cdot cm^{-1}$)]: 287 (22000), 455 (10000), 501 (sh, 9000). Elemental analysis calculated for $C_{22}H_{32}O_2N_8BCo$: 51.78, C; 6.32, H; 21.96, N, observed: 51.23, C; 6.26, H; 21.17, N. Selected collection parameters and data for single-crystal X-ray diffraction experiment: crystal system: triclinic, space group: *P*-1, *a* (Å): 10.7950(12), *b* (Å): 11.2263(13), *c* (Å): 12.6478(15), α (°): 102.699(2), β (°): 93.487(2), γ (°): 110.050(2), *V* (Å^3): 1389.0(3), *Z*: 2, μ (mm^{-1}): 0.847, ρ ($g\cdot cm^{-3}$): 1.423, θ range (°): 1.67 to 25.33, R_1, wR_2 [$I > 2\sigma(I)$]: 0.0362, 0.0909, R_1, wR_2 (all data): 0.0423, 0.0960, Measured/independent reflections/R_{int}: 7783/4524/0.0204. In toluene-d_8, the coalaescence temperature was measured to be T_c = 216 (± 3) K; at 193 K, the aryl signals of the Tp* ligand appear at δ 5.70 ppm (1H) and 5.77 ppm (2H), suggesting a structure with C_s symmetry.



*(*cis-*5,6-Dinitrosonorbornene}{κ³-hydridotris(3,5-dimethylpyrazolyl)borate}cobalt(I)*. The product was isolated as a brown solid in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.81 (d, 1H, *J* = 9.2 Hz), 1.89 (s, 9H), 2.29 (d, 1H, *J* = 9.2 Hz), 2.34 (m, 2H), 2.39 (s, 9H), 3.36 (m, 2H), 5.79 (s, 3H), 6.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.6, 13.7, 42.5, 42.7, 92.7, 107.5, 139.1, 145.2, 150.5. IR [KBr disk, ν_{max} (cm^{-1})]: 3050, 2964, 2924, 2505, 1544, 1365, 1341. MS (ESI, positive ion): 509 (100%, $[M+H]^+$). HRMS (ESI, positive ion): calculated for $C_{22}H_{31}O_2N_8BCo$: 509.1990, observed: 509.1982. Elemental analysis calculated for $C_{22}H_{30}O_2N_8BCo$: 51.99, C; 5.95, H; 22.05, N, observed: 52.42, C; 6.04, H; 21.74, N.



*(*cis-*5,6-Dinitroso-5,6-dihydro-*endo-*dicyclopentadiene){κ³-hydridotris(3,5-dimethylpyrazolyl)borate}cobalt(I)*. The product was isolated as a brown solid in 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (d, 1H, *J* = 10.4 Hz), 1.40 (d, 1H, *J* = 10.4 Hz), 1.86 (s, 9H), 1.92 (s, 2H), 2.36 (s, 9H), 2.40 (s, 2H), 2.49-2.54 (m, 1H), 2.97-2.98 (m, 1H), 3.07-3.11 (m, 1H), 3.17-3.18 (m, 1H), 5.69-5.74 (m, 1H), 5.75-5.78 (m, 1H), 5.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.5, 13.7, 31.7, 34.8, 40.8, 41.1, 42.0, 52.4, 88.5, 90.8, 107.3, 130.9, 132.1, 144.8, 150.3. IR [KBr disk, ν_{max} (cm^{-1})]: 3047, 2958, 2920, 2510, 1546, 1363, 1340. MS (ESI, positive ion): 548 (100%, $[M^+]$). HRMS (ESI, positive ion): calculated for $C_{25}H_{34}O_2N_8BCo$: 548.2224, observed: 548.2232. Elemental analysis calculated for $C_{25}H_{34}O_2N_8BCo$: 54.76, C; 6.25, H; 20.44, N, observed: 53.98, C; 6.10, H; 19.60, N.

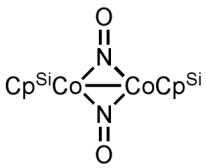


*{5,6-*cis-*Dinitroso-2,3-*trans-*bis(methoxycarbonyl)norbornane}{κ³-hydridotris(3,5-dimethylpyrazolyl)borate}cobalt(I)*. The product was isolated as a brown solid in 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (d, 1H, *J* = 10.8 Hz), 1.83 (s, 9H), 1.91 (d, 1H, *J* = 10.8 Hz), 2.06 (d, 1H, *J* = 8.4 Hz), 2.13 (d, 1H, *J* = 8.4 Hz), 2.38 (s, 9H), 2.95-2.96 (m, 1H), 3.21-3.23 (m, 1H), 3.48-3.50 (m, 2H), 3.76 (s, 3H), 3.83 (s, 3H), 5.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.5, 13.9, 31.5, 40.3, 41.3, 46.9, 47.4, 52.6, 52.7, 88.7, 91.6, 107.5, 145.2, 150.3, 172.4, 172.9. IR [KBr disk, ν_{max} (cm^{-1})]: 2954, 2927, 2522, 1738, 1728, 1546, 1451, 1433. MS (ESI, positive ion): 625 (40%, $[M-H]^+$). HRMS (ESI, positive ion): calculated for $C_{26}H_{35}O_6N_8BCo$: 625.2099, observed: 625.2104. Elemental analysis calculated for $C_{26}H_{36}O_2N_8BCo$: 49.86, C; 5.79, H; 17.89, N, observed: 48.87, C; 6.04, H; 15.92, N.

$Tp^*Co-N^{=O}$

*Synthesis of {κ^3-hydridotris(3,5-dimethylpyrazolyl)borate}nitrosylcobalt [Tp*Co(NO)].* In the glovebox, 553 mg [(TMEDA)Co(NO)$_2$][BPh$_4$] (1 mmol, 1 equiv.) was loaded into a Schlenk tube. Similarly, 336 mg KTp* (1 mmol, 1 equiv.) was weighed out and transferred into a separate Schlenk tube. The tubes were sealed, removed from the glovebox, and attached to a vacuum line. To each Schlenk tube was transferred 20 mL THF *via* cannula under a positive pressure of nitrogen. The slurry of [(TMEDA)Co(NO)$_2$][BPh$_4$] was cooled to -78 ºC with a dry ice/acetone bath, and the KTp* solution was tadded to it *via* cannula. A slow color change to green was observed upon warming to room temperature. After an additional 30 min of stirring at room temperature, the solvent was removed under vacuum. The product could be isolated by extraction into 20 mL hot toluene; filtration and concentration of the resulting solution, followed by hot recrystallization, provided the product as a dark green, air-sensitive solid in 45% yield. ^{1}H NMR (400 MHz, C_6D_6): δ -22.3 (s, 9H), 11.7 (s, 3H), 28.5 (s, 9H). IR [KBr disk, ν_{max} (cm^{-1})]: 2921, 2522, 1732, 1540, 1180. MS (FAB, positive ion): 356 (100%, [M-NO]$^+$). Elemental analysis calculated for $C_{15}H_{22}ON_7BCo$: 46.66, C; 5.74, H; 25.39, N, observed: 46.17, C; 5.58, H; 24.20, N. Selected collection parameters and data for single-crystal X-ray diffraction experiment: crystal system: orthorhombic, space group: *Pmc*2$_1$, *a* (Å): 13.0809(108), *b* (Å): 7.9962(11), *c* (Å): 17.398(2), α (°): 90, β (°): 90, γ (°): 90, *V* (Å^3): 1819.8(4), *Z*: 4, μ (mm^{-1}): 0.961, ρ (g·cm^{-3}): 1.409, θ range (°): 1.56 to 5.36, R_1, wR_2 [$I > 2\sigma(I)$]: 0.0395, 0.0740, R_1, wR_2 (all data): 0.0591, 0.0827, Measured/independent reflections/R_{int}: 18814/3424/0.0662.

*Synthesis of (*cis-*2,3-dinitrosonorbornane}{κ^3-hydridotris(3,5-dimethylpyrazolyl)borate}cobalt(I) from [Tp*Co(NO)].* In the glovebox, 41.0 mg [Tp*Co(NO)] (0.106 mmol, 1 equiv.) and 115 mg norbornene (1.22 mmol, 11.5 equiv.) were weighed into a Schlenk tube. The tube was sealed, removed from the glovebox, and attached to a vacuum line. Under a positive pressure of nitrogen, 10 mL dry toluene was transferred into the Schlenk tube *via* cannula. The reaction mixture was cooled to 0 ºC and placed under a partial vacuum, and gaseous NO (1 atm) was introduced *via* the manifod. The reaction mixture was stirred at 0 ºC for 30 min, warmed to room temperature, and stirred for a further 30 min. After the reaction was complete as judged by TLC analysis of aliquots of the reaction mixture, the system was flushed with argon, and the solvent was removed under reduced pressure. The crude solid was purified and the purified material characterized as in the formation of this product by the salt-metathesis route (*vide supra*).



*Synthesis of (*tert-*butyldimethylsilylcyclopentadienyl)(μ-nitrosyl)cobalt dimer.* In the glovebox, 200 mg [(TMEDA)Co(NO)$_2$][BPh$_4$] (0.362 mmol, 1 equiv.) and 67.2 mg Li[η^5-^{t}BuMe$_2$SiC$_5$H$_4$] (0.362 mmol, 1 equiv.) were weighted into separate vials. A slurring of the cobalt complex was made in 4 mL THF and a solution of the

cyclopentadienyllithium reagent in 1 mL THF added dropwise. The reaction mixture was stirred for 30 min at room temperature and the solvent removed under vacuum. The crude product was extracted with 10 mL benzene and flushed through a short silica pad in the glovebox (5 cm depth, 4 cm diameter), eluting with 40 mL benzene. Benzene was removed under vacuum from the resulting black-green solution to yield the product as a black solid in 32% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.32 (m, 4H), 4.97 (m, 4H), 0.80 (s, 18H), 0.14 (s, 12H). ^{13}C NMR (100 MHz, toluene-d_8): δ 94.7, 89.6, 26.1, 1.0, -5.9. IR [solid, ν_{max} (cm^{-1})]: 2924, 2852, 1588, 1533, 1468, 1247. MS (EI, positive ion): 536 (60%, [M^+]).

Alkene exchange of {κ^3-hydridotris(3,5-dimethylpyrazolyl)borate}cobalt dinitrosoalkane complexes. Solutions of the desired concentrations of [Tp*Co$(NO)_2$]/norbornene adduct **1** and norbornadiene **2** were prepared in C_6D_6 and added to a medium-walled NMR tube attached to a Cajon adapter. The combination of tube and adapter was attached to a vacuum line, and the tube was degassed by three freeze-pump-thaw cycles and sealed under vacuum. Reactions were heated in an oil bath set to 90 °C, and reaction progress and side product formation monitored by ^{1}H NMR. Yields were determined by comparison with a mesitylene internal standard.

*Computational studies of [Tp*Co(NO)]*. Computational details of this work, performed in collaboration with the Wieghardt and DeBeer groups, are given in the literature report.[8]

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