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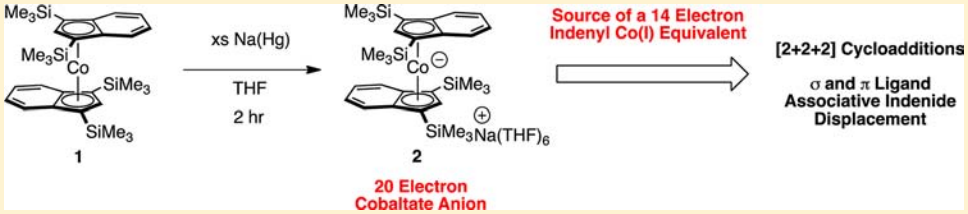
Synthesis of a Bis(indenyl) Co(I) Anion: A Reactive Source of a 14 Electron Indenyl Co(I) Equivalent

Fernando Hung-Low and Christopher A. Bradley*,†

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, United States

Ⓢ *Supporting Information*



ABSTRACT: Alkali metal reduction of (η^5-C_9H_5-1,3-$(SiMe_3)_2)_2$Co (**1**) in tetrahydrofuran (THF) permits isolation of the unusual and reactive 20 electron Co(I) anion $[Na(THF)_6]$[(η^5-C_9H_5-1,3-$(SiMe_3)_2)_2$Co] (**2**). Crystallographic characterization of both **1** and **2** provide support for the one electron reduction from Co(II) to Co(I). Reactivity studies of **2** are further consistent with a Co(I) equivalent, based on both one electron chemical oxidation to reform **1** and reaction with a variety of σ and π donors. Upon addition of pyridines or vinyltrimethylsilane to **2**, known dimer [(C_9H_5-1,3-$(SiMe_3)_2)_2Co_2$] (**3**) is formed, likely through 16 electron (η^5-C_9H_5-1,3-$(SiMe_3)_2$)Co(L) intermediates. Ethylene addition to **2** establishes an equilibrium between (η^5-C_9H_5-1,3-$(SiMe_3)_2$)Co(η^2-$H_2C{=}CH_2)_2$ (**8**) and **2**, suggestive of *reversible* ligand ejection from **2**. Crossover experiments between a related metal indenide salt and **2** confirm ligand extrusion from the anion, even in the absence of strong supporting donors. Reaction of **2** with PMe_3 results in formation of **3**, (η^5-C_9H_5-1,3-$(SiMe_3)_2$)Co$(PMe_3)_2$ (**13**), and a paramagnetic species, with the product ratios being highly dependent on the conditions of synthesis. Collectively, **2** demonstrates an alternative entry point into the chemistry of 14 electron Co(I) equivalents when compared to typical ligand loss from neutral 18 electron cyclopentadienyl cobalt bis(ligand) complexes, perhaps permitting generation of low electron count species more effective for small molecule activation.

■ INTRODUCTION

Cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) sandwich and piano stool metal complexes have been critical in the development of the field of organometallic chemistry, serving as important examples for structure, bonding, and reactivity studies with both early and late transition metals.[1−6] These and related ancillary ligands (i.e., indenyl and fluorenyl) have supported a wide variety of metal mediated transformations. Representative reactions include N_2 activation,[2] C−C bond coupling,[7] and olefin polymerization[4] with Group 4 metals, [2 + 2 + 2] cycloadditions with Co(I) fragments,[8] hydrosilation with Group 9 metals,[9] and Ni catalyzed olefin polymerization.[10] Regarding hydrocarbon activation, Cp and Cp* frameworks have been useful in accessing reactive Rh and Ir species capable of C−H bond oxidative addition.[11−15]

Notably lacking from studies of C−H bond activation of Group 9 metals are examples involving cobalt, which would be advantageous because of availability, lack of expense, and diminished toxicity. Though intramolecular activation of ligand sp^2 and sp^3 C−H bonds have been observed,[16−18] along with catalytic reports of sp^2 C−H activation which generally involve substrates containing directing groups or bulky substituents,[19−24] development of cobalt complexes capable of oxidatively adding aliphatic sp^3 C−H bonds have remained elusive.

Transitioning hydrocarbon activation to cobalt can introduce inherent issues of spin state which are often absent from second and third row analogues. For example, though 16 electron Cp*M(L) (M = Rh, Ir) intermediates readily activate sp^3 C−H bonds, the corresponding cobalt species are unreactive with alkanes.[25] Based on computational models of this system, the Cp*Co(L) intermediate is thought to exist as a spin triplet, in contrast to singlet Rh and Ir congeners, with lack of reactivity toward alkanes being attributed to a prohibitively high energy barrier to spin crossover.[26,27] Fundamental studies of the reactivity of pincer ligated PNPCo(I) triplets by Caulton and co-workers further suggest spin can often frustrate reactivity with alkanes.[28] However, recent catalytic activation of sp^3 C−H bonds by Co(I) has been achieved by Brookhart and co-workers, through use of the Cp*Co(η^2-$H_2C{=}CHSiMe_3)_2$ complex, mediating synthesis of enamines via transfer dehydrogenation,[29] suggesting concerns of spin state may not prevent C−H bond activation/functionalization using sources of low electron count cobalt(I).[30] The challenge then remains to generate singlet Co(I) species reactive enough to oxidatively

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add C−H bonds. Related reports of C−C bond coupling[31] and C−F activation[32] using Co provide promise that new strategies in ligand and complex[33] design can assist in mediating transformations typically associated with precious metals.

Interest in our group has focused on synthesis of new metastable Co(I) sources that, because of ring strain or use of more labile donor ligands, may provide transient access to 14 electron Co(I) fragments, in analogy to the key Ir intermediates implicated in alkane dehydrogenation.[34] Recently, we have improved synthetic access to $[(\mathrm{Cp^*Co})_2\text{-}\mu\text{-}(\eta^4{:}\eta^4\text{-arene})]$ complexes[35] and demonstrated that these compounds readily dissociate a Cp*Co(I) equivalent capable of transfer dehydrogenation of the same substrates popularized by Brookhart and co-workers under mild conditions.[36] The driving force of this dissociation likely results from arene rearomatization[37] and the strained metal-alkene bonding between cobalt and arene, leading to the enhanced reactivity of the sandwich complexes when compared to other known Cp*Co(I) surrogates.

Another approach to access low electron count Co(I) equivalents involves intramolecular appendage of donors to the Cp (or related) ancillary support.[38] In particular, we have recently synthesized indenyl Co(I) dimer $[(\mathrm{C_9H_5\text{-}1,3\text{-}(SiMe_3)_2})_2\mathrm{Co_2}]$ **3**, through reduction of bis(indenyl) cobalt(II) complex **1**, where the benzo portion of the indenyl ligand provides donor stabilization to Co,[39] and demonstrated that this complex serves as a source of an indenyl Co(I) equivalent (Figure 1).[40] The mechanism of formation of **3** was of interest, as the reaction could proceed through a formally 20 electron bis(indenyl) cobaltate anionic intermediate **2**. Though the corresponding $\mathrm{Cp_2Co}$ anion has been observed electrochemically[41] and such cobaltate species are proposed intermediates in the synthesis of $\mathrm{CpCoL_2}$ adducts, an anion of this type to our knowledge has not been isolated. Given the elusive nature of intermediates such as **2** and the importance of cobaltate and related anions in recent structural[42−44] and catalytic[45] studies, we thought it worthwhile to pursue isolation and utilization of **2** as an alternative source of a reactive 14 electron indenyl cobalt(I) equivalent, by indenide ligand ejection.

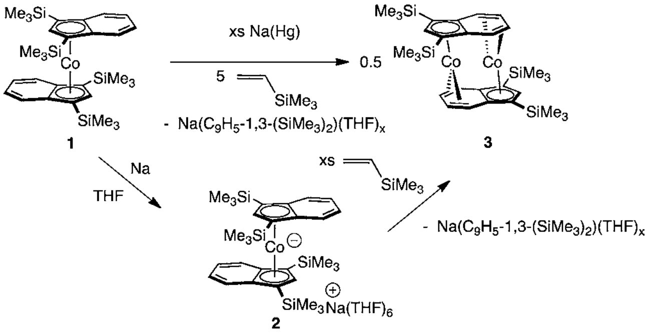


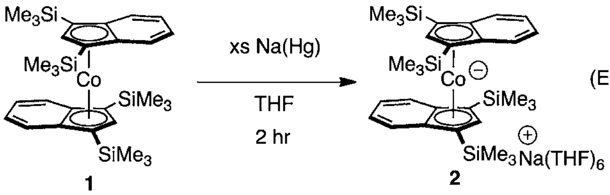
Figure 1. Synthesis of **3** by alkali metal reduction of **1** via proposed bis(indenyl) cobaltate anion intermediate **2**.

Here we present the isolation, structural characterization, and reactivity studies of the bis(indenyl) cobaltate anion **2**. Based on reactivity of the formally 20 electron complex, **2** behaves as a ready source of a 14 electron indenyl Co(I) fragment, via associative displacement of an indenide unit. This ligand extrusion even occurs in the presence of weak nucleophiles, such as other substituted indenide salts. In certain instances, the fine balance of ionic and covalent contributions to the bonding in **2** and neutral, 18 electron $(\eta^5\text{-}\mathrm{C_9H_5\text{-}1,3\text{-}(SiMe_3)_2})\mathrm{CoL_2}$ complexes unexpectedly permits facile reversibility between the two types of compounds. From these studies, anion **2** does provide entry into the chemistry of low valent cobalt in the absence of strong donors, hopefully permitting access to new and more reactive Co(I) species.

RESULTS AND DISCUSSION

Synthesis of the Substituted Bis(indenyl) Cobaltate Anion 2. Attempts to prepare the proposed bis(indenyl) cobaltate anion intermediate formed during the synthesis of **3** began with the reduction of **1** in the absence of strong donor ligands, both electrochemically and chemically. A cyclic voltammogram of **1** recorded in tetrahydrofuran (THF) using tetrabutylammonium hexafluorophosphate (TBAF) as the supporting electrolyte indicates both reversible oxidation, as expected to form an 18 electron cobaltocenium cation,[46] and reduction to form the presumed bis(indenyl) Co(I) anion, with $E_{1/2}$ values of −0.850 and −1.800 V relative to ferrocene/ferrocenium (Supporting Information).

Based on the reversible nature of electrochemical reduction of **1** in THF, chemical reduction using alkali metal reductants was pursued. Stirring **1** with excess sodium amalgam for 2 h gives good yields of anion **2** as a red solid (eq 1). A ^{1}H NMR spectrum of **1** recorded in benzene-d_6 displays only one broad, paramagnetic resonance, aside from THF peaks, at 5.69 ppm, tentatively assigned as the $\mathrm{SiMe_3}$ group (Supporting Information). Preparation of **2** is supported by solution magnetic susceptibility measurements in toluene-d_8, with a $\mu_{\mathrm{eff}} = 2.5(1)\ \mu_{\mathrm{B}}$ for **2** at −78 °C, indicating two unpaired electrons, as predicted based on the orbital splitting derived for a linear metallocene.[47] Electron paramagnetic resonance (EPR) spectra of **2** recorded in a 50:50 pentane: toluene mixture show no discernible signals, consistent with an $S = 1$ complex. The lack of an EPR signal suggests that paramagnetic Co(II) species, specifically **1**, are not present, given that the EPR spectrum of **1** resembles that of other characterized cobaltocene derivatives with a g value of 1.9713 (Supporting Information).[48]



(Eq 1)

X-ray quality crystals of **2** were obtained by slow evaporation of THF under light vacuum at ambient temperature, and an ORTEP representation of the structure is shown in Figure 2b. For metric comparisons, a structure of **1** was also obtained and is presented in Figure 2a. Both molecules adopt distinct rotational angles (44.7(1)° for **1** and 81.5(4)° for **2**), defined as the angle between the two planes generated from the metal, C(2), and the C(4)−C(9) midpoint for each of the indenyl ligands.[49] This difference in ring orientation is likely due to a subtle mixture of interring repulsion that minimizes contact between $\mathrm{SiMe_3}$ groups and spin effects (due to the different number of unpaired spins in each complex).[50] However, crystal packing effects cannot be completely discounted in leading to the observed conformations.

Aside from the presence of a Na counterion in **2**, cobalt−carbon bond distances elongate significantly in **2** relative to **1** (Table 1), indicative of reduction and increased electron

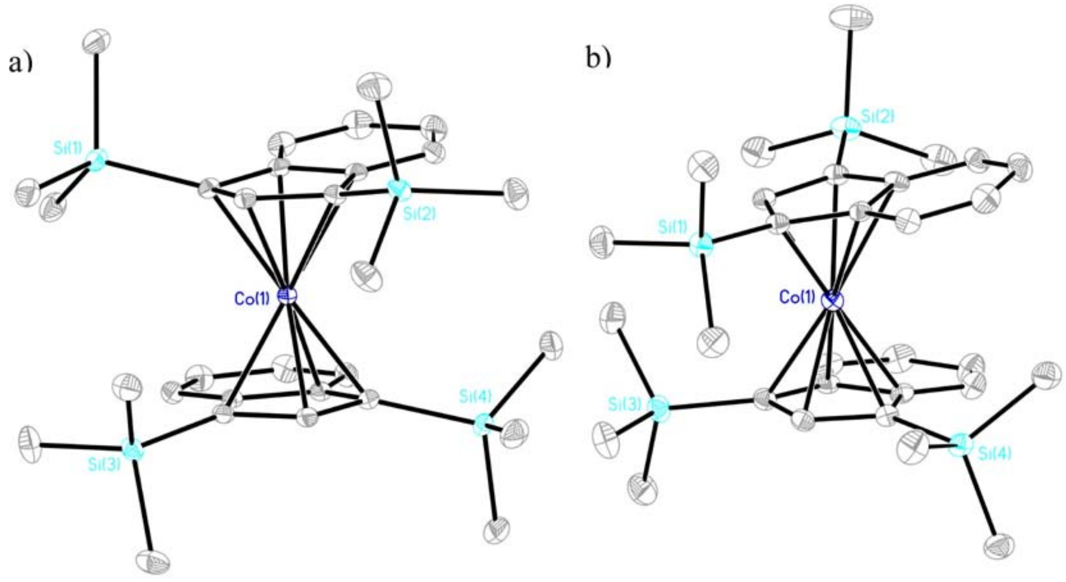


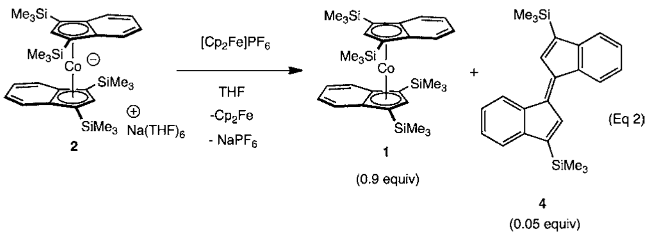
Figure 2. Molecular structures of (a) **1** and (b) **2** with 30% probability ellipsoids. Hydrogen atoms and the Na anion of **2** are omitted for clarity. Pertinent bond ranges (Å): Co(1)-C(indenyls), **1**: 2.06–2.25, **2**: 2.09–2.46. Rotational Angle (deg), **1**: 44.7(1), **2**: 81.5(4). Slip parameter (Δ): **1**: 0.154(3) Å, 0.090(6) Å, **2**: 0.240(3) Å, 0.229(5) Å; Hinge angle (deg): **1**: 3.6(5), 0.8(4), **2**: 4.6(3), 4.1(3); Fold angle (deg): **1**: 6.3(8), 4.4(8), **2**: 2.4(5), 2.2(6).

Table 1. Comparison of the Co−C(indenyl) Bond Distances (Å) in 1 and 2

	1	2		1	2
Co(1)−C(1)	2.1013(16)	2.298(4)	Co(1)−C(16)	2.1378(16)	2.294(4)
Co(1)−C(2)	2.0610(17)	2.092(4)	Co(1)−C(17)	2.0845(16)	2.092(4)
Co(1)−C(3)	2.1188(16)	2.156(4)	Co(1)−C(18)	2.1047(16)	2.154(4)
Co(1)−C(4)	2.2447(16)	2.387(4)	Co(1)−C(19)	2.1996(16)	2.365(4)
Co(1)−C(9)	2.2506(16)	2.456(4)	Co(1)−C(24)	2.1987(16)	2.451(4)

density at cobalt in **2**. Lack of dramatic changes in C−C bond lengths of the indenyl ligand further support the formulation for metal based reduction (Supporting Information). Slip-fold parameters, commonly used to evaluate η^5 versus η^3 hapticity,[49] support slight distortion from η^5 hapticity for **1** (Figure 1), with slip parameters ranging from 0.09 to 0.154 Å and hinge/fold angles varying between 0.8 and 6.4°, as also observed for $(\eta^5\text{-}C_9H_7)_2Co$.[49d] A greater slippage toward η^3 coordination is observed in **2**, but the complex is still within the higher range of parameters indicative of η^5 coordination in Group 9 complexes.[49] Interestingly, the formally 20 electron complex **2**, isoelectronic to nickelocene, does not show as significant a ring slippage toward η^3 coordination of the indenyl ligands as in its Group 10 congener.[51]

Further support of **2** as a Co(I) anion stems from electrochemical and chemical oxidation of the complex. A cyclic voltammogram of recrystallized **2** in THF displays reversible oxidation in two successive one electron steps, resembling the potentials found for electrochemical analysis of **1**, with $E_{1/2}$ values of −0.845 and −1.775 V with respect to ferrocene/ferrocenium (Supporting Information). Stirring **2** and 1 equiv of ferrocenium hexafluorophosphate in THF produces 0.9(1) equiv of **1** and 0.05(2) equiv of the organic byproduct **4**, as measured by integrations of the products by ^{1}H NMR spectroscopy, a possible result of oxidative coupling of indenyl units (eq 2).[52] The total mass balance, including formation of coupled ligand, implies chemical transfer of one electron from **2**, providing strong support for formulation of the compound as the bis(indenyl) cobaltate anion.



Though the cobaltocene anion has been generated electrochemically,[41] to our knowledge **2** represents the only isolable and structurally characterized cobaltate stabilized by cyclopentadienyl type (or related) ligands. As anions such as **2** are invoked as intermediates in the synthesis of a variety of 18 electron, cyclopentadienyl cobalt bis(ligand) adducts,[53−55] and these complexes are useful in a myriad of stoichiometric[56] and catalytic[8,57,58] reactions implicating 14 electron cyclopentadienyl Co(I) equivalents, we sought to examine reactivity of **2** to determine if the isolated material could behave as a complementary source of a low electron count indenyl Co(I) fragment.

Reactivity Studies of 2. *A. Thermal Stability of **2**.* The solution stability of **2** indicates the complex is quite robust, as heating for 24 h to 70 °C in benzene-d_6 results in minimal (10%) decomposition. Thermolysis of **2** in THF at the same temperature results in significant formation of **1** (25%) and free ligand (15%) over the course of 3 h. Similar conversion of **2** to **1** is observed when attempting to sublime **2** at a variety of temperatures. This decomposition via one electron oxidation is

Scheme 1. Reactivity of 2 with Vinyltrimethylsilane and Aromatic Amines under Various Conditions

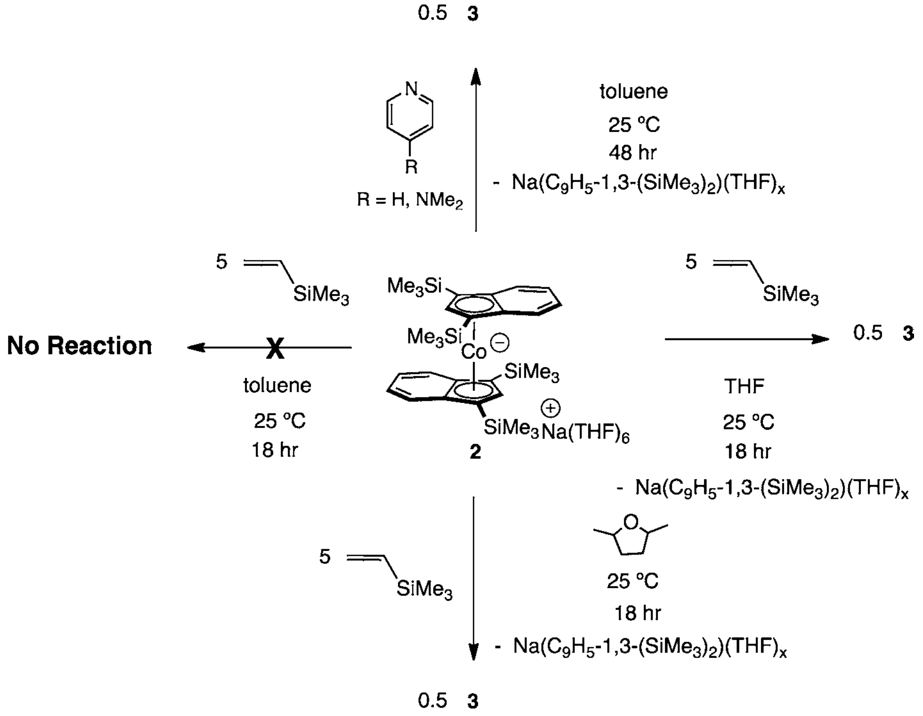
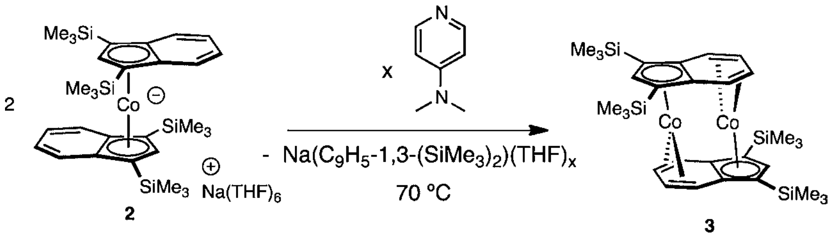


Table 2. Percent Conversion of 2 to 3 in the Presence of DMAP[a]



DMAP equivalents	% conversion
0.5	29
1.5	41
3	53

[a] Reaction performed in C_6D_6 and quenched with COD after 30 min to convert unreacted 2 to 5 prior to quantitation by ^{1}H NMR spectroscopy.

unusual; the source of the oxidant in the solution and solid state thermolyses is unclear.

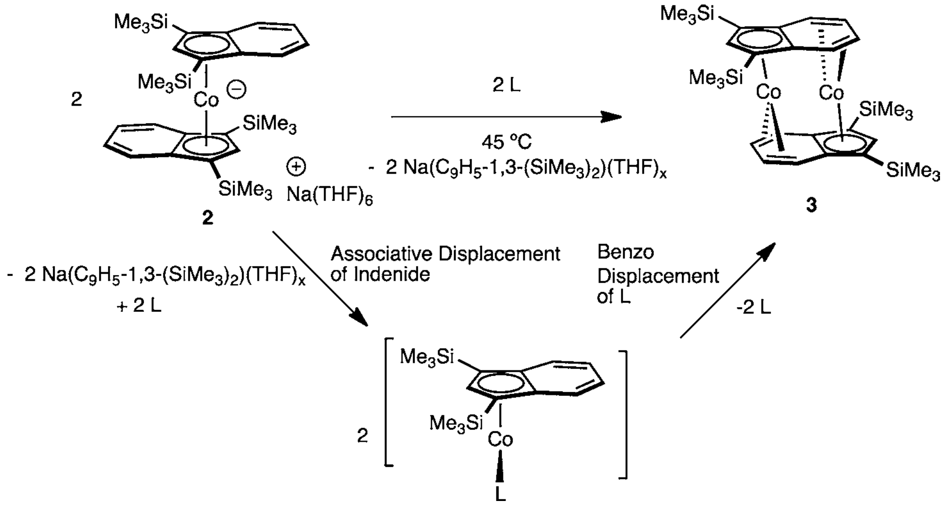
B. Formation of Dimer 3 from 2. As 2 was a proposed intermediate in the synthesis of 3, reaction of 2 with vinyltrimethylsilane was pursued. Stirring 2 in the presence of the bulky alkene in nonpolar solvents provides no conversion to 3 after 24 h. This was somewhat surprising, given that both reagents are soluble in alkanes or arenes. However, stirring 2 in THF, the solvent used in the synthesis of 3, at ambient temperature permits quantitative conversion to 3 over the time scale (typically 12–18 h) of the reduction used to prepare the dimer (Scheme 1). Conversion of 2 to 3 is also accomplished at ambient temperature using 2,5-dimethyl THF as the solvent, suggesting a polarity rather than ligand effect of the ethereal solvent.[59] Solvent polarity could affect ion pairing between the cobaltate unit and the sodium counterion, influencing the ability of indenide to be displaced by incoming ligands. In subsequent studies of the formation of 3, we found the dimer can also be formed cleanly from 2 in the presence of σ donors, such as pyridine or DMAP, in aromatic solvents over the course of hours (Scheme 1).

The mechanism of conversion of 2 to 3 was of interest, given that the reaction could proceed via associative or dissociative extrusion of a substituted sodium indenide unit. If the loss were dissociative in nature, this would suggest access to 14 electron indenyl Co(I) species from 2 was possible, even in the absence of strong supporting donors. Admittedly, this pathway seemed unlikely, given that 2 does not convert to 3 in the absence of supporting ligands.

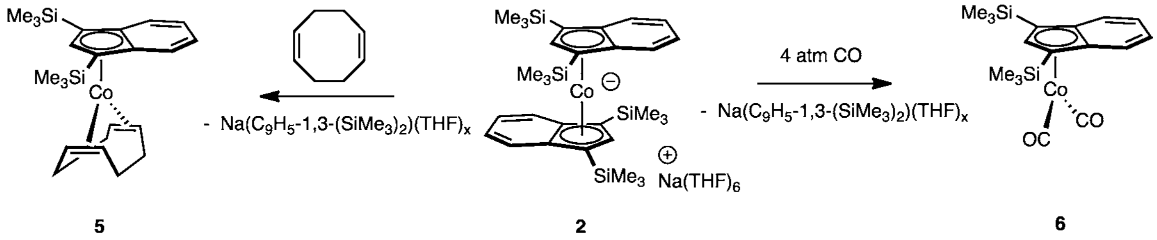
To examine ligand dependence on the reaction, conversion of 2 to 3 after 30 min was determined while varying the number of equivalents of DMAP present during the reaction at 70 °C in benzene-d_6. The higher temperature was used to facilitate conversion over the shorter time scale.

More rigorous kinetic studies were attempted, but were rendered difficult based on the need to quench each reaction because of the presence of unreacted (and paramagnetic) 2. To ensure mass balance during the reaction and to convert all species to diamagnetic products for more reliable integrations, a

Scheme 2. Proposed Mechanism for Conversion of 2 to 3 in the Presence of Vinyltrimethylsilane or Aromatic Amines



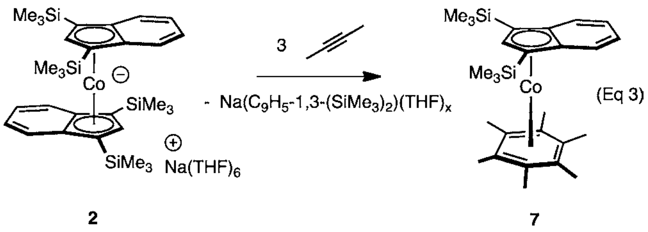
Scheme 3. Reaction of COD and Carbon Monoxide with 2



ferrocene standard was used and 1,4-cyclooctadiene (COD) was added prior to quantitation by ^{1}H NMR spectroscopy, which converted any unreacted **2** to the previously reported (η^5-C_9H_5-1,3-$(SiMe_3)_2$)Co(COD) (**5**) (vide infra).[40] The percent conversion to **3** as a function of DMAP equivalents after 30 min are shown in Table 2 and indicate a strong dependence on DMAP, suggesting ligand induced extrusion of the indenide salt is necessary to form **3**. Based on these results, we believe a reasonable mechanism for dimer formation proceeds through associative displacement of indenide, likely through an unobserved ring slipped intermediate,[60,61] followed by formation of a 16 electron adduct (η^5-C_9H_5-1,3-$(SiMe_3)_2$)-Co(L) (L = vinyltrimethylsilane or aromatic amine) which undergoes loss of L through benzo displacement and subsequent dimerization to **3** (Scheme 2). Such 16 electron intermediates are active species in C−H bond breaking events with related cyclopentadienyl Rh systems.[11] Here, much as observed in earlier studies with the cyclopentadienyl cobalt congeners,[25] the related Co analogue appears unreactive with C−H bonds. Whether this is due to the spin state of the intermediate or because the less electron donating silyl indenide[62] does not generate an electron rich cobalt center capable of oxidatively adding C−H bonds is difficult to determine.

C. Reaction of ***2*** *with π Ligands.* Given the conversion of **2** to **3** in the presence of both σ and π type ligands, reactivity of **2** was examined further with other donors from each ligand class. Reaction of **2** with less bulky π donors gives expected products for a source of a 14 electron indenyl Co(I) fragment. For example, addition of COD to **2** at ambient temperature provides the known complex **5**, based on ^{1}H and ^{13}C NMR spectroscopy (Scheme 3, vide supra).[40] The presumed substituted sodium indenide equivalent extruded during the reaction is difficult to identify directly by NMR spectroscopy, perhaps because of the THF present in the reaction mixture which likely coordinates the salt.[63] To detect the indenide equivalent for mass balance, after addition of COD to form **2**, a slight excess of methanol was added to protonate the sodium indenide salt. As **5** is stable in the presence of small amounts of methanol, quantitation of the amount of **5** and free ligand formed could be determined using an internal standard (i.e., ferrocene). Over three independent trials, 0.9(1) equiv of free ligand were liberated per 1 equiv of **5** formed, further supporting the structure of **2**. As CpCo(alkene)$_2$ complexes have been prepared from Cp_2Co reductions in the presence of alkene,[58] the conversion of **2** to **5** demonstrates that an indenyl analogue of the presumed anionic intermediate is competent for the proposed transformation. Given that metal carbonyl complexes are typically synthesized by reductions of higher valent metal compounds,[62] we explored the reactivity of **2** with carbon monoxide. Addition of 4 atm of CO to **2** at ambient temperature results in facile formation of the terminal dicarbonyl (η^5-C_9H_5-1,3-$(SiMe_3)_2$)Co(CO)$_2$ (**6**) (Scheme 3), based on comparison of NMR and IR data to previous literature reports.[40]

Addition of 3 equiv of 2-butyne to **2** results in a significant downfield shifting of the paramagnetic resonance to 7.86 ppm in benzene-d_6. Solution magnetic susceptibility measurements in toluene-d_8 reveal a μ_{eff} = 2.3(1) μ_B at 25 °C, indicative that the new complex still contains more than one unpaired electron. Addition of COD to the new compound in benzene-d_6 followed by heating to 70 °C for 4 days results in formation of **5** and 0.85(5) equiv of hexamethylbenzene based on integration against a ferrocene internal standard. These results, in conjunction with mass spectral data and an X-ray structure of the product, support formation of the paramagnetic hexamethylbenzene complex (η^5-C_9H_5-1,3-$(SiMe_3)_2$)Co(η^6-C_6Me_6) (7) (eq 3).[64]



X-ray quality crystals of 7 were grown from pentane at −35 °C and further support the synthesis of the [2 + 2 + 2] cycloaddition product (Figure 3). Pertinent cobalt-indenyl carbon bond distances and slip parameters indicate η^5 coordination of the indenide ligand (Figure 3). The arene in 7 remains essentially planar and the cobalt atom is displaced symmetrically over the center of the bound hexamethylbenzene. The C−C bonds in the aromatic ligand are elongated moderately relative to the free arene.

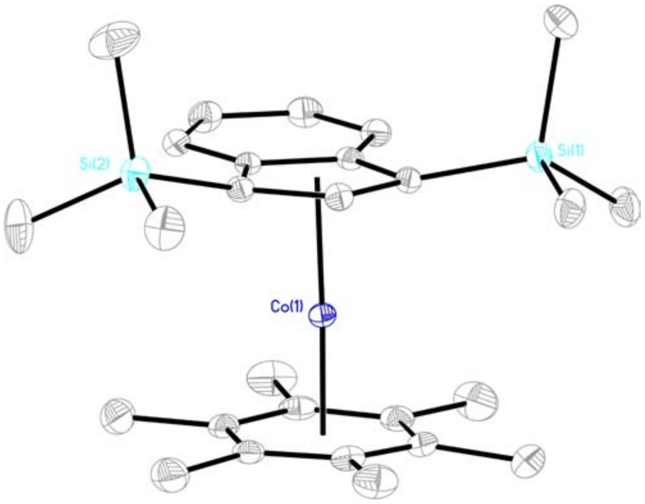
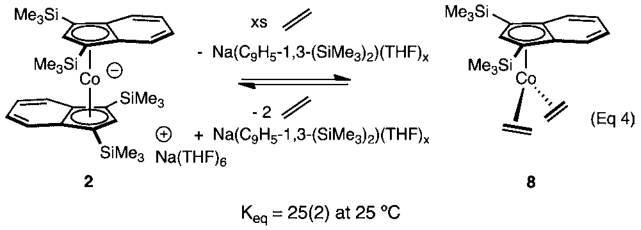


Figure 3. Molecular structure of 7 with 30% probability ellipsoids. Hydrogen atoms omitted for clarity. Pertinent bond ranges (Å): Co(1)-C(indenyls), 2.17−2.35; Co(1)-C(hexamethylbenzene), 2.17−2.24; C−C(hexamethylbenzene), 1.41−1.42. Slip parameter (Δ): 0.100(3) Å; Hinge angle (deg): 2.0(1); Fold angle (deg): 1.1(3).

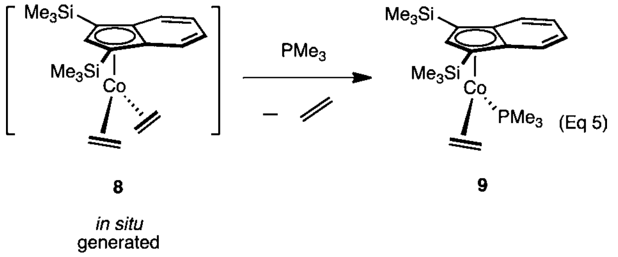
From a Co(I) equivalent, the [2 + 2 + 2] cycloaddition is an expected reaction, as related CpCo complexes have been utilized in arene and heteroarene formation.[8] With 2 or 7, addition of excess 2-butyne does result in catalytic hexamethylbenzene formation, though forcing conditions (70 °C over 10 h, 5 mol % loading of 2 or 7) are necessary to observe reasonable rates of catalytic turnover. This likely results from the need to displace bound arene with incoming alkyne and may also be complicated by spin issues with triplet 7.

Addition of cyclooctene to 2 results in no observable reaction, even upon heating to 70 °C in benzene-d_6. This lower affinity for alkene binding to Co relative to Rh or Ir congeners has been previously documented.[21,29] The diminished reactivity of alkenes would bode well for Co complexes competent to perform C−H bond oxidative addition, as the desired alkane to alkene transformation requires olefin release upon β-hydrogen elimination.[65] In the case of Rh and Ir, catalysts which perform alkane dehydrogenation have shown alkene binding can inhibit turnover.[65] Such an unproductive pathway would then likely not be as significant of a concern in cobalt based systems.

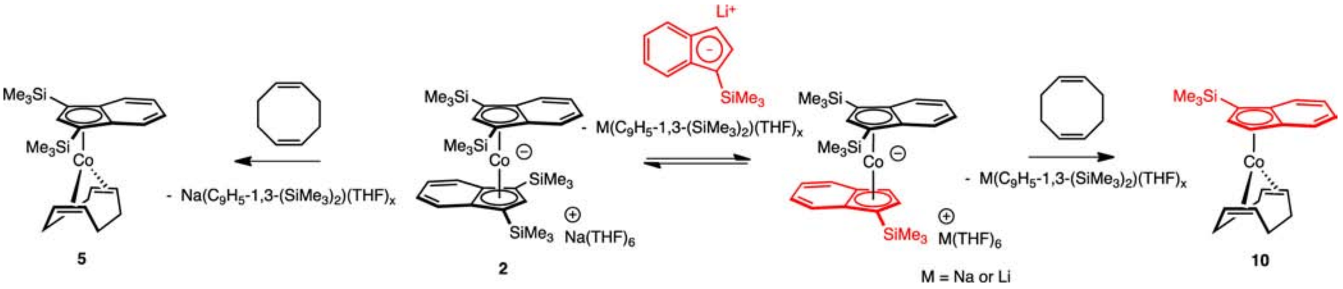
Excess ethylene addition to 2 results in formation of a C_s symmetric product, based on ^1H and ^{13}C NMR data, consistent with the bis(ethylene) adduct (η^5-C_9H_5-1,3-$(SiMe_3)_2$)Co(η^2-$H_2C{=}CH_2$)$_2$ (8) (eq 4). Somewhat surprisingly, upon removal of the excess ethylene, formation of 2 is again observed, indicating an equilibrium between 2 and 8. Upon addition of 2 equiv of ethylene, a K_{eq} = 25(2) was measured at 25 °C in benzene-d_6. Because of this equilibrium, the alkene resonances in the ^1H and ^{13}C NMR spectra of 8 were not located, even when cooling a solution of the compound to −78 °C in toluene-d_8, presumably because of facile exchange with free olefin. The reversibility of this reaction is unexpected, given that the product formed is a relatively sterically unhindered 18 electron adduct in a solvent favoring charge neutral species. However, the parent (η^5-C_9H_7)Co(η^2-$H_2C{=}CH_2$)$_2$ complex exhibits related thermal instability.[53c] The thermodynamic stability of 2 may stem from the strong ionic component to the bonding in the molecule, which would be less prevalent in neutral 8. Such strong ionic character has been observed previously in related magnesocene derivatives.[66] It is interesting to note that solutions of 8 do not convert to 3, even when heated for prolonged periods of time, suggesting significant differences in stability and reactivity of the presumed (η^5-C_9H_5-1,3-$(SiMe_3)_2$)Co(η^2-$H_2C{=}CH_2$) intermediate.



In an effort to better characterize the ethylene reaction product, 1 equiv of PMe_3 was vacuum transferred onto a frozen solution of 8, resulting in formation of the stable mixed ethylene trimethylphosphine adduct (η^5-C_9H_5-1,3-$(SiMe_3)_2$)-Co(η^2-$H_2C{=}CH_2$)(PMe_3) (9) and loss of an equivalent of ethylene (eq 5) upon warming to ambient temperature. The ^{31}P NMR resonance at 18.83 ppm for 9 in benzene-d_6 resembles the shift of other characterized mixed CpCo alkene/phosphine complexes.[67] In 9, the CH_2 resonances are now easily discerned, based on 2D HSQC data, at 1.05 and 1.21 ppm in the ^1H and ^{13}C NMR spectra recorded in toluene-d_8 at −70 °C, respectively. Though 9 can be prepared from 2 using this method, other synthetic strategies permit higher yielding, large scale preparation of the molecule (vide infra).



Scheme 4. Crossover Experiment between 2 and Li[C_9H_5-1-$SiMe_3$] Followed by Trapping with COD to form 5 and 10



The equilibrium between **2** and **8** provides direct evidence for the unusual *reversible* indenide dissociation and coordination at cobalt.[68−71] To further probe this exchange experimentally, in the absence of strong donor ligands, a crossover experiment between **2** and Li[C_9H_5-1-($SiMe_3$)] was performed in THF (Scheme 4), a solvent used primarily to ensure solubility of the ionic salt. Stirring the two compounds for 5 min followed by addition of COD and subsequent workup results in formation of both the expected adduct **5** and (η^5-C_9H_5-1-$SiMe_3$)Co-(COD) (**10**), based on comparison to ^{1}H and ^{13}C NMR spectra of independently prepared **10** (Supporting Information). X-ray quality crystals of **10** were grown from the crude crossover reaction mixture in pentane at −35 °C (Figure 4), further establishing formation of the adduct drived from indenide exchange.

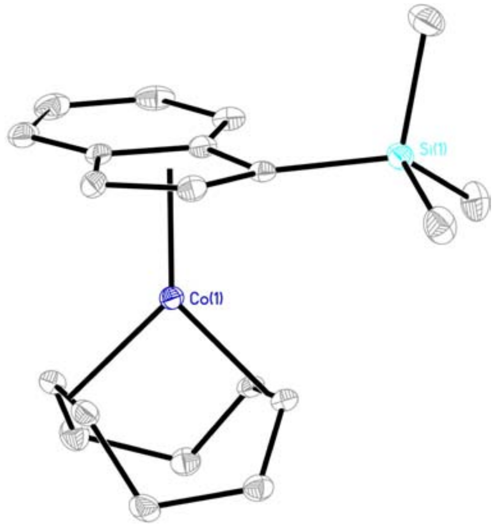
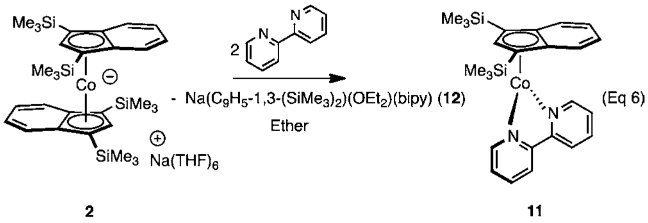


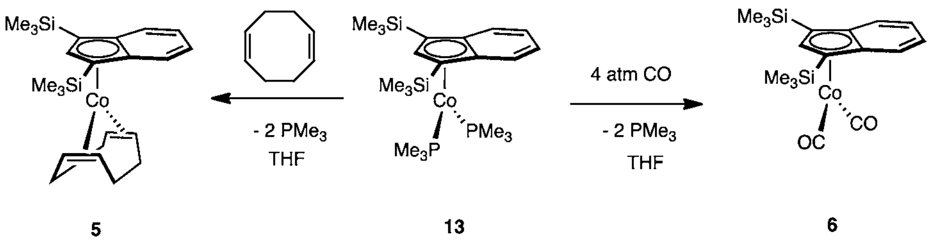
Figure 4. Molecular structure of **10** with 30% probability ellipsoids. Hydrogen atoms omitted for clarity. Pertinent bond ranges (Å): Co−C(indenyls), 2.06−2.19; Co−C(COD), 2.02−2.04. Slip parameter (Δ): 0.109(1) Å; Hinge angle (deg): 1.6(2); Fold angle (deg): 5.5(3).

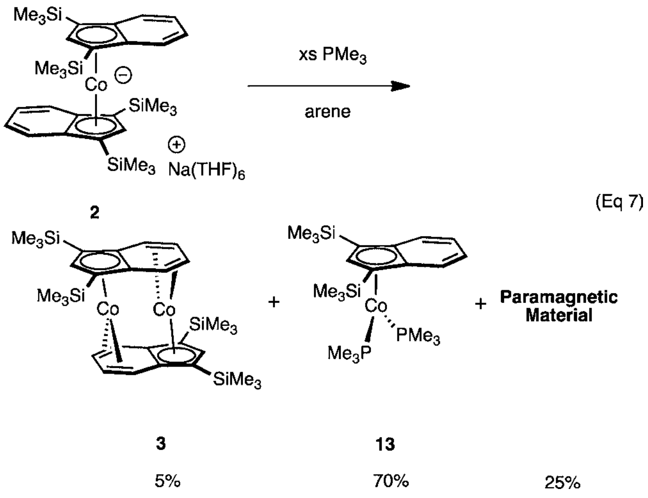
As a control, stirring **5** with Li[C_9H_5-1-$SiMe_3$] for 18 h results in no formation of **10**, suggesting the anion exchange is not influenced by the presence of COD and that the 18 electron adduct **5** is stable in the presence of indenide salts. Thus, based on the crossover experiment, we believe rapid exchange of indenide units in **2** is possible in polar solvents, resulting in the observation of both COD complexes upon facile ligand trapping (Scheme 4). This experiment further suggests even weak and hindered donors such as an indenide anion can displace the 1,3-disilyl-indenide, providing some hope that access of 14 electron equivalents might be possible through **2** or related complexes with unactivated substrates at elevated temperatures. The noted thermal stability of **2** in arene also proves promising in this regard.



D. Reaction of 2 with Other σ Ligands. Aromatic amines result in no isolable ligand adducts when added to **2**, but mediate conversion to **3** (vide supra). However, addition of a chelating aromatic amine, 2,2′-bipyridine (bipy), in diethyl ether results in formation of the diamagnetic adduct (η^5-C_9H_5-1,3-($SiMe_3$)$_2$)Co(bipy) (**11**) (eq 6), based on ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.[72] The C_s symmetry of **11** is discernible from both the ^{1}H and the ^{13}C NMR spectra of the compound, while the coordinated bipy unit is observed in the 6.93−9.30 ppm range in the ^{1}H NMR spectrum of **11**. The sodium indenide salt extruded during the reaction can be isolated from the product mixture when 2 equiv of bipy are added to **2** as the bipy/ether adduct (η^5-C_9H_5-1,3-($SiMe_3$)$_2$)-Na(OEt_2)(bipy) (**12**), based on NMR spectroscopy and an X-ray crystal structure obtained of **12** (Supporting Information). Quantitation of the free ligand upon methanol addition to the

Scheme 5. Reaction of 13 with COD and Carbon Monoxide





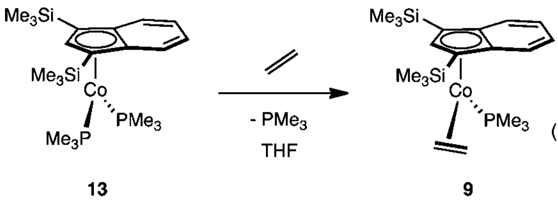
(Eq 7)

reaction mixture yields 0.9(1) equiv of ligand per molecule of formed **12**.

Addition of trimethylphosphine to **2** in alkane or arene solvents results in formation of multiple products, heavily dependent on the amount of PMe_3 present. When excess phosphine (>10 equiv) is added to **2**, small amounts of **3** (5%) and an unidentified paramagnetic species are formed (25%), along with precipitation of the primary reaction product (70% yield) as a green solid (eq 7). Though insoluble in alkane and aromatic solvents, the major compound produced is soluble in THF-d_8. The ^1H, ^{13}C, and ^{31}P NMR spectra of the complex are consistent with formation of the bis(trimethylphosphine) adduct $(\eta^5\text{-}C_9H_5\text{-}1,3\text{-}(SiMe_3)_2)Co(PMe_3)_2$ (**13**) (Supporting Information).[73] Combustion analysis of **13** further corroborates the proposed structure of the major product.

The identity of **13** was also established based on reactivity with other donor ligands. For instance, addition of either COD[74] or carbon monoxide to **13** in THF results in facile formation of the previously prepared adducts **5** and **6** (Scheme 5). Monitoring the addition of COD to **13** in THF-d_8, free trimethylphosphine can be detected by both ^1H and ^{31}P NMR spectroscopy after vacuum transfer from the reaction mixture. To mass balance the reaction of **13** with COD, methanol protonolysis after the reaction gives no free ligand and two molecules of PMe_3 liberated per molecule of **5** formed (Supporting Information), both consistent with the proposed structure of **13**.

Addition of excess ethylene to **13** in THF results in loss of 1 equiv of PMe_3 and formation of the mixed ligand adduct **9** (eq 8), previously prepared by addition of PMe_3 to **8** (eq 5). For large scale preparation, this method is preferable rather than addition of PMe_3 to **8**, as excess ethylene can be used. NMR spectroscopic data match those collected using the alternative synthetic procedure. X-ray quality crystals of **9** were grown from ether at −35 °C (Figure 5); structural parameters are consistent with an η^5 bound indenyl ligand (Figure 5), with a slip parameter of 0.042 Å and hinge/fold angles of less than 1°.[49]



(Eq 8)

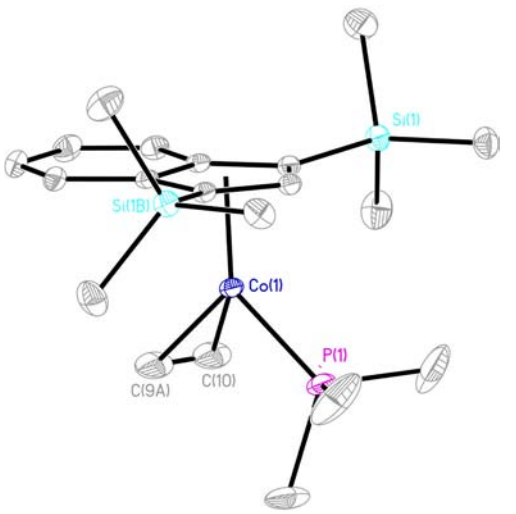
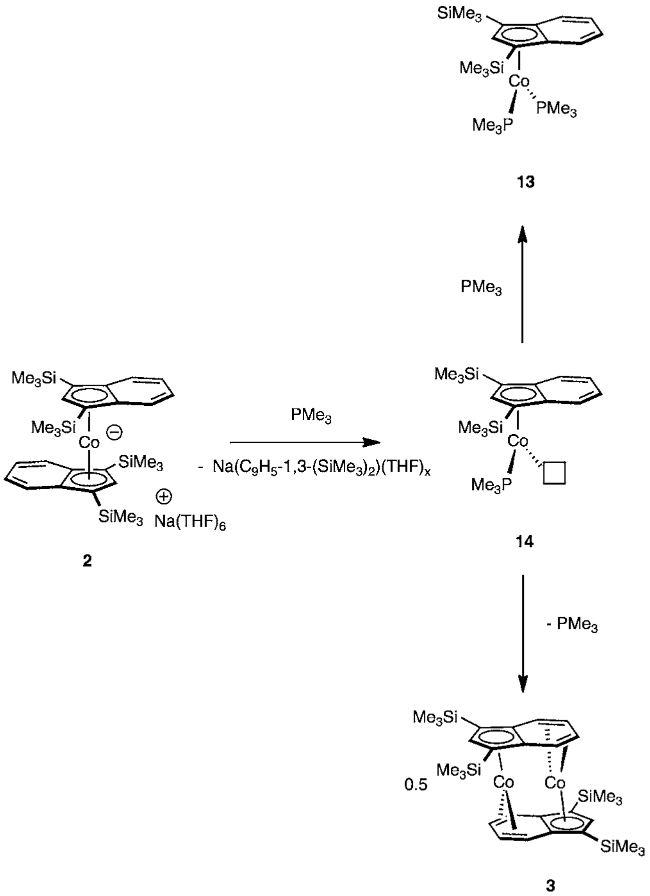


Figure 5. Molecular structure of **9** with 30% probability ellipsoids. Hydrogen atoms omitted for clarity. Pertinent bond ranges (in Å): Co(1)-C(indenyls), 2.06–2.16; Co(1)−C(9), 1.99; Co(1)−C(10), 2.03; Co(1)−P(1), 2.13. Slip parameter (Δ): 0.042(3) Å; Hinge angle (deg): 0.3(1); Fold angle (deg): 0.82(2).

The ratio of diamagnetic products observed during reaction of **2** with PMe_3 can be rationalized using one general mechanistic scheme (Scheme 6). In the presence of PMe_3,

Scheme 6. Proposed Pathway to Form 3 and 13 from 2



associative loss of an indenide ligand would permit formation of a 16 electron intermediate (η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)Co(PMe$_3$) (**14**), in analogy to reactions involving DMAP or vinyltrimethylsilane (vide supra). As with those presumed intermediates, no C−H activation is observed with **14**. Two equivalents of **14** could then release PMe$_3$ to give **3**, or the intermediate could be trapped by another equivalent of PMe$_3$ to produce adduct **13**. Based on the better σ donating ability of PMe$_3$, the stability of **14** may be greater than in the case of pyridine or DMAP, resulting in a higher ratio of **13** to **3**. The need for high concentrations of PMe$_3$ to provide optimal yields of **13** provides some support for the trapping of a reactive intermediate by excess ligand.

The identity of the paramagnetic product generated during the reaction with PMe$_3$ was also of interest. Unfortunately, the oily nature of the compound and the inability to isolate the complex in the absence of **3** has led to difficulty in isolating and fully characterizing the compound. Given that the formation of this product (with an upfield shift of the paramagnetic trimethylsilyl resonance to 4.29 ppm relative to **2** in benzene-*d*$_6$) occurs only in the presence of PMe$_3$, we currently propose formation of a ligand exchanged cobaltate anion, [Na(PMe$_3$)$_4$][(η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)$_2$Co]. Solution magnetic susceptibility measurements of the complex in benzene-*d*$_6$ support this formulation, with a μ_{eff} = 2.7(2) μ_B at 25 °C, indicating two unpaired electrons. LIFDI mass spectra of the unknown product are further consistent with the presence of the intact (η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)$_2$Co core, given a peak observed at 577 *m*/*z*. Current efforts are directed toward optimization of synthesis and definitive characterization of the complex.

■ CONCLUSIONS

Synthesis of the bis(indenyl) cobaltate anion **2** has been accomplished and the complex has been examined structurally and through reactivity studies. Though much of the chemistry associated with **2** is reminiscent of reactivity expected for such anions, the reversible ligand ejection and fine thermodynamic balance between the 20 electron triplet relative to 18 electron adduct **8** were surprising and point to significant stability imparted by the ionic bonding character in **2**. With respect to alkane activation, these studies suggest new potential sources of low valent Co fragments for study, specifically anionic Co(I) complexes which could extrude a ligand to provide 14 electron equivalents. The potential reversibility of the anion ejection and the triplet nature of the cobaltate anion may serve as stabilizing factors preventing complex degradation at the elevated temperatures (given the thermal stability of **2**) that will likely be required for reactivity with hydrocarbons.

The silyl substituents of **2**, because of steric bulk and less electron donating character, likely assist in stabilizing the cobaltate anion, so exploring access to more electron rich cobaltate analogues and their reactivity with small molecules are in progress. The relative robustness of **2** in alkanes and arenes suggests high temperature reactions of these complexes with hydrocarbons are worth continued investigation. Furthermore, methods of avoiding stable aggregates such as **3**, by appending substituents on the benzo ring to destabilize metal-alkene binding, are also being pursued.

■ EXPERIMENTAL SECTION[75]

Synthesis of [Na(THF)$_6$][(η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)$_2$Co] (2). A 50 mL round-bottomed flask was charged with 15.83 g (78.92 mmol) of mercury and approximately 5 mL of THF. While stirring, 0.080 g (3.48 mmol) of sodium metal was added, followed by 0.503 g (0.87 mmol) of **1**. The resulting reaction mixture was stirred vigorously for 3 h, and the dark solution was decanted from the amalgam and filtered through Celite. Removal of the THF in vacuo and recrystallization in diethyl ether at −35 °C afforded 0.724 g (77%) of **2** as a dark red solid. Single crystals suitable for X-ray diffraction studies were grown under light vacuum from THF at ambient temperature. Anal. Calcd for C$_{54}$H$_{94}$O$_6$Si$_4$Co: C, 64.18; H, 9.38. Found: C, 63.87; H, 9.12. ^{1}H NMR (benzene-*d*$_6$): δ = 1.40 (br, 24H, bound THF), 3.58 (br, 24H, bound THF), 5.69 (br s, 78 Hz, Si*Me*$_3$). Magnetic susceptibility (toluene-*d*$_8$, −78 °C): μ_{eff} = 2.5(1).

Synthesis of Dimer 3 from 2. A reaction vial was charged with 0.200 g (0.18 mmol) of **2**, 0.072 g (0.72 mmol) of vinyltrimethylsilane (4 equiv with respect to **2**), and then dissolved in 5 mL of THF. The resulting solution was stirred vigorously for 18 h at ambient temperature followed by removal of the solvent in vacuo. The resulting product was redissolved in pentane and filtered through Celite to afford 0.044 g (78%) of **3** as a dark red solid. NMR characterization of **3** matched previous literature reports.[40] Similar conversion of **2** to **3** was observed when using 2,5-dimethyl tetrahydrofuran over the same time period at ambient temperature.

Synthesis of (η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)Co(η^6-C$_6$Me$_6$) (7). A reaction vial was charged with 0.400 g (0.37 mmol) of **2**, 0.060 g (1.11 mmol) of 2-butyne (3 equiv with respect to **2**), and 10 mL of benzene. The reaction mixture was stirred vigorously for 6 h followed by removal of the solvent in vacuo. The resulting product was redissolved in pentane and filtered through Celite. Subsequent solvent removal and recrystallization in pentane at −35 °C afforded 0.135 g (76%) of **7** as a red solid. EI Mass spectrum for C$_{27}$H$_{41}$CoSi$_2$: calcd. 480 *m*/*z*; found 480 *m*/*z*. ^{1}H NMR (benzene-*d*$_6$): δ = 7.90 (br s, 78 Hz, Si*Me*$_3$). Solution magnetic susceptibility (toluene-*d*$_8$, −78 °C): μ_{eff} = 2.3(2).

Observation of (η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)Co(η^2-H$_2$C=CH$_2$)$_2$ (8). A J. Young NMR tube was charged with 0.015 g (0.014 mmol) of **2** and then dissolved in 0.5 mL of benzene-*d*$_6$. The tube was then charged with excess ethylene (dried in a liquid N$_2$ cooled trap) and the reaction mixture monitored by ^{1}H and ^{13}C NMR spectroscopy. Removal of ethylene resulted in the reversible formation of **2**. ^{1}H NMR (benzene-*d*$_6$): δ = 0.50 (s, 18H, Si*Me*$_3$), 3.78 (s, 1H, Cp), 6.75 (m, 2H, Benzo), 7.25 (m, 2H, Benzo). The two ethylene resonances were not observed. ^{13}C NMR (benzene-*d*$_6$): δ = 0.52 (Si*Me*$_3$), 83.55, 99.18, 109.76, 125.45, 126.88 (Cp/Benzo). One ethylene resonance not observed.

Synthesis of (η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)Co(η^2-H$_2$C=CH$_2$)(PMe$_3$) (9). A J. Young tube was charged with 0.050 g (0.046 mmol) of **2** and then dissolved in 0.5 mL of benzene-*d*$_6$. The tube was then charged with excess of ethylene (previously dried in a liquid N$_2$ cooled trap) and the reaction mixture was monitored by ^{1}H NMR spectroscopy as a function of time until conversion to **8** was complete. Excess PMe$_3$ (0.070 g, 0.92 mmol) was then vacuum transferred onto the reaction mixture via calibrated gas bulb addition. After 18 h, the solvent was removed in vacuo, and the resulting solid dissolved in pentane and filtered through Celite. Solvent removal followed by recrystallization from pentane at −35 °C yields 0.016 g (84%) of **9** as a dark red solid. ^{1}H NMR (toluene-*d*$_8$, −70 °C): δ = 0.51 (s, 18H, Si*Me*$_3$), 0.60 (s, 9 H, P*Me*$_3$), 1.05 (br, 2H, C*H*$_2$=CH$_2$), 1.21 (br, 2H, CH$_2$=C*H*$_2$), 4.79 (d, 1H, Cp), 6.77 (m, 2H, Benzo), 7.20 (m, 2H, Benzo). ^{13}C NMR (toluene-*d*$_8$, −70 °C): δ = 1.00 (Si*Me*$_3$), 19.10 (P*Me*$_3$), 34.31 (CH$_2$=CH$_2$), 97.31, 107.55, 123.47, 126.92, 145.62 (Cp/Benzo). ^{31}P NMR (toluene-*d*$_8$, −70 °C): δ = 41.41 ppm.

Synthesis of (η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)Co(bipy) (11). A reaction vial was charged with 0.102 g (0.094 mmol) of **2** and then dissolved in 5 mL of diethyl ether, followed by addition of 0.029 g (0.188 mmol) of bipy. The reaction mixture was vigorously stirred for 12 h, followed by removal of the solvent in vacuo. The resulting solid was redissolved in diethyl ether and filtered through Celite. Subsequent solvent removal and recrystallization in diethyl ether at −35 °C afforded 0.032 g (71%) of **11** as a violet solid. Crystals corresponding to the secondary product (η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)Na(OEt$_2$)(bipy) (**12**) were obtained from an additional recrystallization of the mother liquor. Toepler pump analysis of the addition of 2 equiv of bipy to **2** reveals no formation of gas byproduct during the reaction, suggesting no cobalt hydride species are present and further corroborating the structure of **2**. EI Mass spectrum for $C_{25}H_{31}CoN_2Si_2$: calcd. 474 *m/z*; found 474 *m/z*. ^{1}H NMR (benzene-d_6): δ = 0.38 (s, 18H, SiMe_3), 4.95 (s, 1H, Cp), 6.45 (m, 2H, Benzo/Bipy), 6.93 (m, 4H, Benzo/Bipy), 7.16 (m, 2H, Benzo), 7.46 (m, 2H, Benzo), 9.30 (d, 7 Hz, 2H, Benzo/Bipy). ^{13}C NMR (benzene-d_6): δ = 0.89 (SiMe_3), 76.69, 94.95, 103.32, 116.08, 121.56, 122.27, 125.11, 128.63, 142.45, 155.38 (Cp/Benzo/Bipy).

Synthesis of (η^5-C_9H_5-1,3-$(SiMe_3)_2$)Co$(PMe_3)_2$ (13). A reaction vial was charged with 0.301 g (0.278 mmol) of **2** and 0.211 g (2.78 mmol) of PMe_3 dissolved in 5 mL of benzene. The reaction mixture was stirred for 12 h, followed by filtration of the benzene solution and subsequent removal of the solvent in vacuo. The resulting solid was rinsed with 20 mL of pentane to afford 0.094 g (72%) of **13** as an analytically pure green solid. Anal. Calcd for $C_{21}H_{41}CoP_2Si_2$: C, 53.60; H, 8.78. Found: C, 53.30; H, 8.55. ^{1}H NMR (THF-d_8): δ = 0.29 (s, 18H, SiMe_3), 1.20 (br, 18H, PMe_3), 6.50 (br, 2H, Benzo), 7.00 (s, 1H, Cp), 7.53 (br, 2H, Benzo). ^{13}C NMR (THF-d_8): δ = 2.19 (SiMe_3), 101.78, 114.58, 120.95, 135.65, 139.95 (Cp/Benzo). The PMe_3 resonance was not located. ^{31}P NMR (THF-d_8): δ = 8.75 ppm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details, CV of **1** and **2**, NMR spectra of new compounds, selected mass spectra, and fully labeled views and X-ray data tables for **1**, **2**, **7**, **9**, **10**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 301 447 5285. Fax: 301 447 5021. E-mail: cbradley@msmary.edu.

Present Address

†Department of Science, Mount St. Mary's University, 16300 Old Emmitsburg Road, Emmitsburg, MD 21727.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For a general treatment of metallocene complexes and their applications, see: *Metallocenes*; Halterman, R. L., Togni, A., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

(2) For recent ancillary support of Zn(I) metal-metal bonds by Cp*, see: Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136.

(3) For use of substituted Cp ligands as supports of stoichiometric dinitrogen reduction with Zr, see: (a) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527. (b) Knobloch, D. J.; Lobkovsky, E.; Chirik, P. J. *Nat. Chem.* **2010**, *2*, 30. (c) Hirotsu, M.; Fontaine, P. P.; Zavalij, P. Y.; Sita, L. R. *J. Am. Chem. Soc.* **2007**, *129*, 12690.

(4) For general treatment of Group 4 metallocene catalyzed olefin polymerization, see: (a) Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science: Sausalito, CA, 2010. (b) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.

(5) For use of Cp*Ru complexes as supramolecular building blocks, see: Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

(6) For recent use of Cp metal complexes as precursors for chemical vapor deposition, see: Xia, A.; Heeg, M. J.; Winter, C. H. *J. Am. Chem. Soc.* **2011**, *124*, 11264.

(7) For use of stoichiometric Zr(II) equivalents in organic synthesis, see: (a) Negishi, E.-i.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755. (b) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884.

(8) (a) Heller, B.; Hapke, M. *Chem. Soc. Rev.* **2007**, *36*, 1085. (b) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860. (c) Geny, A.; Agenet, N.; Ianazzo, L.; Malacria, M.; Aubert, C.; Gandon, V. *Angew. Chem., Int. Ed.* **2009**, *48*, 1810.

(9) (a) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151. (b) Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 4385. (c) Bohm, V.; White, P. W.; Brookhart, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4694. (d) Roy, A. H.; Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, *129*, 2082.

(10) For representative use of indenyl ligands as supports for early and late transition metal catalysis, see: (a) Sui-Seng, C.; Castonguay, A.; Chen, Y.; Gareau, D.; Grouz, L. F.; Zargarian, D. *Top. Catal.* **2006**, *37*, 81.

(11) (a) Bergman, R. G. *Science* **1984**, *223*, 902. (b) Bergman, R. G. *Adv. Chem. Ser.* **1992**, *230*, 211.

(12) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (b) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81.

(13) (a) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140. (b) Jones, W. D. *Inorg. Chem.* **2005**, *44*, 4475.

(14) For representative photochemical C-H bond oxidative addition or observation of alkane complexes see: (a) Perutz, R. N. *Pure Appl. Chem.* **1990**, *62*, 1103. (b) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125.

(15) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995.

(16) For representative sp^2 ligand C-H activation with Co, see: Liu, N.; Li, X.; Sun, H. *J. Organomet. Chem.* **2011**, *696*, 2537.

(17) For representative sp^3 ligand C-H activation with Co, see: Xu, G.; Sun, H.; Li, X. *Organometallics* **2009**, *28*, 6090.

(18) For recent stoichiometric sp^3 ligand activation in NHC Co, see: Mo, Z.; Chen, D.; Leng, X. *Organometallics*, ASAP.

(19) Thompson, M. R.; Day, V. W.; Tau, K. D.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1237.

(20) For sp^2 C-H activation of aldehydes, see: (a) Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 3165. (b) Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 6965.

(21) Lenges, C. P.; Brookhart, M. *J. Organomet. Chem.* **1997**, *528*, 199.

(22) Li, L.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, *129*, 10707.

(23) For recent C-H activation of olefins using Cp*Co complexes, see: Schomaker, J. M.; Boyd, W. C.; Stewart, I. C.; Toste, F. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2008**, *130*, 3777.

(24) Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2011**, *133*, 17283.

(25) Bengali, A. A.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1995**, *117*, 3879.

(26) (a) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1996**, *118*, 1487. (b) Poli, R.; Smith, K. M. *Eur. J. Inorg. Chem.* **1999**, 877.

(27) For more recent treatment of Rh mediated C-H activation of cyclic alkanes, see: George, M. W.; Hall, M. B.; Portius, P.; Renz, A. L.; Sun, X. Z.; Towrie, M.; Zhang, X. Z. *Dalton Trans.* **2011**, *40*, 1751.

(28) (a) Ingleson, M. J.; Pink, M.; Fan, H.; Caulton, K. G. *Inorg. Chem.* **2007**, *46*, 10321. (b) Ingleson, M. J.; Pink, M.; Fan, H.; Caulton, K. G. *J. Am. Chem. Soc.* **2008**, *130*, 4262.

(29) Bolig, A. D.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, *129*, 14544.

(30) For recent related solvent dependent spin state equilibrium of CpCo(CO)(solvent) intermediates, see: Lomont, J. P.; Nguyen, S. C.; Schlegel, J. P.; Zoerb, M. C.; Hill, A. D.; Harris, C. B. *J. Am. Chem. Soc.* **2012**, *134*, 3120.

(31) Smith, A. L.; Hardcastle, K. I.; Soper, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 14358.

(32) Dugan, T. R.; Sun, X.-R.; Rybak-Akimova, E. V.; Olatunji-Ojo, O.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 12418.

(33) For strategies involving access of Co containing early/late transition metal heterobimetallic complexes for use in small molecule activation, see: (a) Krogman, J. P.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2011**, *133*, 14582. (b) Thomas, C. M. *Comments Inorg. Chem.* **2011**, *32*, 14.

(34) Krogh-Jespersen, K.; Czerw, M.; Summa, N.; Renkema, K. B.; Achord, P. D.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 11404.

(35) Schneider, J. J.; Denninger, U.; Heinemann, O.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 592.

(36) Hung-Low, F.; Tye, J. W.; Bradley, C. A. *Chem. Commun.* **2012**, *48*, 368.

(37) For reviews of complexes involving dearomatized ligands and their relevance to catalysis, see: (a) Harman, W. D. *Top. Organomet. Chem* **2004**, *7*, 95. (b) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588.

(38) For representative reports of Cp based ligands containing other linked donors, see: (a) Okuda, J.; Zimmermann, K. H. *Chem. Ber.* **1989**, *122*, 1645. (b) Ackroyd, N. C.; Katzenellenbogen, J. A. *Organometallics* **2010**, *29*, 3669.

(39) For previous reports of mono and bimetallic binding of the benzo ring of an indenyl ligand, see: (a) Jonas, K.; Rüsseler, W.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 928. (b) Gauvin, F.; Britten, J.; Samuel, E.; Harrod, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 1489. (c) Bradley, C. A.; Keresztes, I.; Lobkovsky, E.; Young, V. G.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 16937.

(40) Hung-Low, F.; Bradley, C. A. *Organometallics* **2011**, *30*, 2636.

(41) For electrochemical generation of the related $Cp_2Co(I)$ anion, see: Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2632.

(42) (a) Brennessel, W. W.; Young, V. G., Jr.; Ellis, J. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 7268. (b) Klaüi, W.; Kunz, P. C. *Inorg. Synth.* **2010**, *35*, 125. (c) Margulieux, G. W.; Weidemann, N.; Lacy, D. C.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 5033.

(43) For recent chemistry of the related Fp anion, see: Theys, R. D.; Dudley, M. E.; Hossain, M. M. *Coord. Chem. Rev.* **2009**, *253*, 180.

(44) For chemistry of related Mn anions, see: (a) Alvarez, C. S.; Bashall, A.; McInnes, E. J. L.; Layfield, R. A.; Mole, R. A.; McPartlin, M.; Rawson, J. M.; Wood, P. T.; Wright, D. S. *Chem.—Eur. J.* **2006**, *12*, 3053. (b) Stewart, M. A.; Moore, C. E.; Ditri, T. B.; Labios, L. A.; Rheingold, A. L.; Figueroa, J. S. *Chem. Commun.* **2011**, *47*, 406.

(45) For a review of cobaltate catalysts used in carbonylation of heterocycles, see: Church, T. L.; Getzler, D. Y. L.; Byrne, C. M.; Coates, G. W. *Chem. Commun.* **2007**, 657.

(46) For representative electrochemistry of cobaltocene derivatives, see: El Murr, N.; Dabard, R.; Laviron, E. *J. Organomet. Chem.* **1973**, *47*, C13.

(47) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley & Sons: New York, 1985; pp 392−394.

(48) (a) Ammeter, J. H.; Swalen, J. D. *J. Chem. Phys.* **1972**, *57*, 678. (b) Robbins, J. L.; Edelsten, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882. (c) Zoller, L.; Moser, E.; Ammeter, J. H. *J. Phys. Chem.* **1986**, *90*, 6632.

(49) For representative articles detailing these parameters, see: (a) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929. (b) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839. (c) Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012. (d) Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777. (e) Huber, T. A.; Bayrakdarian, M.; Dion, S.; Dubuc, I.; Belanger-Gariepy, F.; Zargarian, D. *Organometallics* **1997**, *16*, 5811. (f) Calhorda, M. J.; Félix, V.; Veiros, L. F. *Coord. Chem. Rev.* **2002**, *230*, 49.

(50) For conformational effects on spin state in related bis(indenyl) Cr complexes, see: Brady, E. D.; Overby, J. S.; Meredith, M. B.; Mussman, A. B.; Cohn, M. A.; Hanusa, T. P.; Yee, G. T.; Pink, M. *J. Am. Chem. Soc.* **2002**, *124*, 9556.

(51) Zargarian, D. *Coord. Chem. Rev.* **2002**, *233*−*234*, 157.

(52) Stradiotto, M.; Hazendonk, P.; Bain, A. D.; Brook, M. A.; McGlinchey, M. J. *Organometallics* **2000**, *19*, 590.

(53) (a) Lee, W. S.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *209*, 401. (b) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem.* **1983**, *95*, 729. (c) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.

(54) Hapke, M.; Weding, N.; Spannenberg, A. *Organometallics* **2010**, *29*, 4298.

(55) Salzer, A.; Täschler, C. *J. Organomet. Chem.* **1985**, *294*, 261.

(56) Witherell, R. D.; Ylijoki, K. E. O.; Stryker, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 2176.

(57) Lee, B. Y.; Chung, Y. K.; Jeong, N.; Lee, Y.; Hwang, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 8793.

(58) Cammick, J. K.; Jalisatgi, S.; Matzger, A. J.; Negrón, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1996**, *61*, 4798.

(59) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

(60) For kinetic studies related to late metal η^3 indenyl intermediates, see: (a) Rerek, M. E.; Ji, N.-L.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. (b) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. (c) Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198*−*200*, 219.

(61) For observation of indenyl ring slippage in related Rh and Ir complexes, see: (a) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329. (b) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778. (c) Frazier, J. F.; Anderson, F. E.; Clark, R.; Merola, J. S. *Inorg. Chim. Acta* **1994**, *222*, 135. (d) Westcott, S. A.; Kakkar, A. K.; Taylor, N. J.; Roe, D. C.; Marder, T. B. *Can. J. Chem.* **1999**, *77*, 205.

(62) Bradley, C. A.; Flores-Torres, S.; Lobkovsky, E.; Abruña, H. D.; Chirik, P. J. *Organometallics* **2004**, *23*, 5332.

(63) Jones, J. N.; Cowley, A. H. *Chem. Commun.* **2005**, 1300.

(64) For characterization of related Co(I) arene complexes,see: (a) Lee, W.-S.; Koola, J. D.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *206*, C4. (b) Boennemann, H.; Brijoux, W. *New J. Chem.* **1987**, *11*, 549. (c) Schneider, J. J. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 1055. (d) Wadepohl, H.; Borchert, T.; Pritzkow, H. *Chem. Commun.* **1995**, 1447.

(65) (a) Goettker-Schnetmann, I.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 9330. (b) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761.

(66) (a) Wilkinson, G.; Cotton, F. A.; Birmingham, J. M. *J. lnorg. Nucl. Chem* **1956**, *2*, 95. (b) Switzer, M. E.; Rettig, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 687. (c) Layfield, R. A. *Chem. Soc. Rev.* **2008**, *37*, 1098. (d) Crisp, J. A.; Meier, R. M.; Overby, J. S.; Hanusa, T. P.; Rheingold, A. L.; Brennessel, W. W. *Organometallics* **2010**, *29*, 2322.

(67) (a) Werner, H.; Heiser, B.; Klingert, B.; Doelfel, R. *J. Organomet. Chem.* **1982**, *240*, 179. (b) Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212.

(68) For *ansa*-Cp ligand epimerization mediated by solvent in Group 3 complexes, see: Yoder, J. C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1998**, *17*, 4946.

(69) For rac/*meso* interconversion in phosphine substituted indenyl iron compounds, see: Curnow, O. J.; Fern, G. M.; Hamilton, M. L.; Jenkins, E. M. *J. Organomet. Chem.* **2004**, *689*, 1897.

(70) For *ansa*-Cp ligand epimerization mediated by chloride ions in Group 4 metallocenes, see: Buck, R. M.; Vinayavekhin, N.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 3468.

(71) For recent studies of amide exchange between related $Cp^{Rn}FeNR_2$ and $LiNR'_2$, see: Walter, M. D.; White, P. S. *Inorg. Chem.* **2012**, *51*, 11860.

(72) For characterization of the related Cp*Co(bipy), see: Lenges, C. P.; White, P. S.; Marshall, W. J.; Brookhart, M. *Organometallics* **2000**, *19*, 1247.

(73) For characterization of $Cp^*Co(PMe_3)_2$, see: Koelle, U.; Khouzami, F.; Fuss, B. *Angew. Chem.* **1982**, *94*, 132.

(74) For related synthetic protocols of Cp/Indenyl Co(COD) complexes, see: (a) Gutnov, A.; Drexler, H.-J.; Spannenberg, A.; Oehme, G.; Heller, B. *Organometallics* **2004**, *23*, 1002. (b) Hapke, M.; Weding, N.; Spannenberg, A. *Organometallics* **2010**, *29*, 4298.

(75) General experimental details and additional syntheses are included in the Supporting Information.