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Evaluation of Cobalt Complexes Bearing Tridentate Pincer Ligands for Catalytic C−H Borylation

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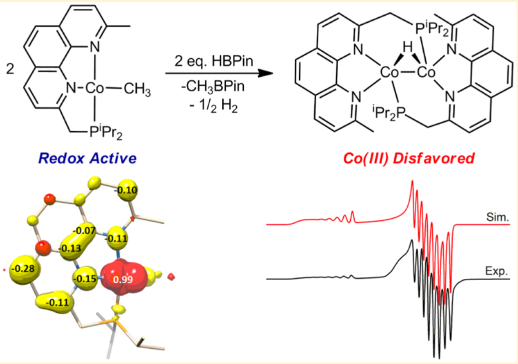
Ⓢ *Supporting Information*

ABSTRACT: Cobalt(II) dichloride complexes supported by a variety of neutral, tridentate pincer ligands have been prepared and, following in situ activation with $NaBEt_3H$, evaluated for the catalytic borylation of 2-methylfuran, 2,6-lutidine, and benzene using both HBPin and B_2Pin_2 (Pin = pinacolate) as boron sources. Preparation of well-defined organometallic compounds in combination with stoichiometric experiments with HBPin and B_2Pin_2 provided insight into the nature and kinetic stability of the catalytically relevant species. In cases where sufficiently electron donating pincers are present, such as with bis(phosphino)pyridine chelates, Co(III) resting states are preferred and catalytic C−H borylation is efficient. Introduction of a redox-active subunit into the pincer reduces its donating ability and, as a consequence, the accessibility of a Co(III) resting state. In these cases, unusual mixed-valent μ-hydride cobalt complexes have been crystallographically and spectroscopically characterized. These studies have also shed light on the active species formed during in situ activated cobalt alkene hydroboration catalysis and provide important design criteria in base metal catalyzed C−B bond forming reactions.



■ INTRODUCTION

The transition metal catalyzed borylation of C−H bonds of arenes and heteroarenes is now established as one of the most widely practiced methods of C−H functionalization, a result of efficient and selective catalyst technology coupled with the value and versatility of organoboronate esters in synthesis.[1−3] Most prominent of the noble metal catalysts are the iridium complexes generated from treatment of $[Ir(COE)_2Cl]_2$ or $[Ir(COD)OMe]_2$ (COE = cyclooctene; COD = 1,5-cyclooctadiene) and 4,4′-di-*tert*-butylbipyridine, owing to the relatively mild reaction conditions, use of stoichiometric quantities of reagents, broad functional group tolerance, and compatibility with high-throughput experimentation for reaction optimization.[4−7] Mechanistic[8] and computational studies[9] support an iridium(III) tris(boryl) active species that promotes C−H cleavage,[10] and catalysis occurs through an Ir(III)−Ir(V) couple. Silica-supported monophosphine rhodium and iridium catalysts[11] as well as iridium nanoparticles[12] also promote C−H borylation, often with selectivity distinct from the soluble organometallic iridium compounds.

There has been long-standing interest in using base metals in catalytic C−H borylation. Prior to the discovery and maturation of the precious metal catalyzed methods, photochemical activation of the iron-boryl complex FpBCat (Fp = η^5-$C_5H_5Fe(CO)_2$; Cat = catecholate) was reported for the stoichiometric borylation of arenes.[13] Mankad and co-workers have recently introduced copper and zinc complexes into the iron coordination sphere and exploited metal−metal cooperativity to enable catalytic turnover under irradiation.[14] These compounds complement thermal methods catalyzed by Fe_2O_3 nanoparticles[15] and a cyclopentadienyl iron N-heterocyclic carbene compound in the presence of sacrificial alkenes.[16]

Our laboratory has been exploring how the electronic structure of four-coordinate cobalt alkyl complexes bearing tridentate pincer ligands can be rationally manipulated to enable activation of strong bonds via oxidative addition. On the basis of insights from iron hydride chemistry,[17] the synthesis of $(^{R}PNP)CoR^1$ (PNP = bis(phosphino)pyridine; R = ^iPr, ^tBu; R^1 = alkyl, hydride) was targeted. Concurrent with reports from Milstein and co-workers,[18] these compounds proved to be a rich platform for the oxidative addition of H−H, Si−H, and C−H bonds.[19] Facile ligand modification by both heterolytic and homolytic pathways was also demonstrated, a consequence of benzylic C−H bonds that are both acidic and are prone to homolysis due to a thermodynamically accessible Co(I)−Co(II) redox couple.[20] The isopropyl-substituted variant, $(^{iPr}PNP)CoCH_2SiMe_3$, proved to be a highly active and selective precatalyst for the borylation of arenes and heterocycles.[21] Turnover numbers in excess of 5000 were observed at ambient temperature using stoichiometric quantities of HBPin (Pin = pinacolate). The cobalt catalysts proved tolerant of certain pyridine derivatives that are incompatible with common iridium precursors, highlighting the unique reactivity potential

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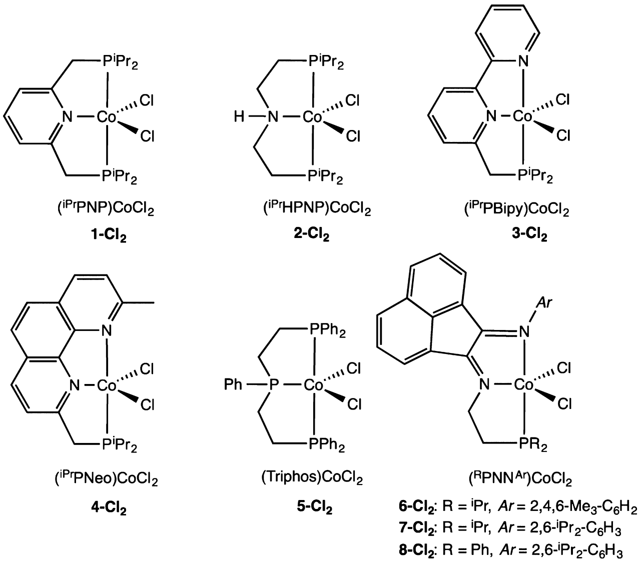
available with base metal catalysts. On the basis of these observations, we became interested in exploring the efficacy of other, related neutral tridentate pincer ligands in cobalt-catalyzed C−H borylation. Here we describe systematic evaluation of a family of neutral tridentate pincer ligands for the Co-catalyzed borylation of heteroarenes and arenes. Preparation of well-defined organometallic compounds and study of their stoichiometric reaction chemistry with HBPin and B$_2$Pin$_2$ have provided insight into the nature of the catalytically relevant compounds formed from in situ activation. In addition, the electronic properties of each pincer have also been correlated with the stoichiometric reaction chemistry and catalytic borylation performance.

■ RESULTS AND DISCUSSION

To assess various tridentate pincer types in cobalt-catalyzed C−H borylation, in situ activation methods were developed to expedite evaluation. Previous studies from our laboratory demonstrated that treatment of bis(imino)pyridine iron dihalides with NaBEt$_3$H is an effective method for generating active catalysts for alkene cycloaddition[22] and hydrosilylation.[23] Ritter and co-workers have also applied in situ activation methods in imino-pyridine iron-catalyzed hydroboration of 1,4-dienes,[24] an approach later extended to bis(imino)pyridine derivatives by Huang[25] and Thomas.[26] In situ activation has also been utilized for related cobalt-catalyzed alkene hydroborations,[27] and an enantioselective variant for selected 1,1-disubstituted aryl alkenes has recently been reported.[28] Caution must be exercised in evaluating structure−reactivity relationships involving specific metal−ligand combinations, as selectivity and activity are often inferior to catalytic reactions performed with isolated complexes.[22,28−30]

Presented in Figure 1 are the various cobalt(II) dichloride complexes evaluated for catalytic C−H borylation. To calibrate results with new cobalt precursors, in situ activation of (^{iPr}PNP)CoCl$_2$ (**1-Cl$_2$**) was also included. The amine-bridged cobalt dichloride, (^{iPr}HPNP)CoCl$_2$ (**2-Cl$_2$**), was selected due to its structural relationship to the PNP and demonstrated catalytic activity of the cyclohexyl variant in hydrogenation catalysis.[31] Phosphinobipyridinyl (^{iPr}PBipy)[27,28,32] and related phosphinoneocuproine (^{iPr}PNeo) supported complexes were also synthesized; the latter was added to the series as a less expensive alternative to the former. We also note that (^{iPr}PBipy)CoCl$_2$ is active for alkene hydroboration upon activation with NaBEt$_3$H.[27] Related (^{R}PNN^{Ar})CoCl$_2$ complexes (**6-Cl$_2$**, **7-Cl$_2$**, and **8-Cl$_2$**), compounds known to promote ethylene oligomerization upon activation with alkyl aluminoxanes,[33] were also synthesized due to their relationship to **3-Cl$_2$** and **4-Cl$_2$**. The cobalt dichloride bearing the commercially available tridentate phosphine, (Triphos)CoCl$_2$ (**5-Cl$_2$**), was also included in the study.



(^{iPr}PNP)CoCl$_2$ **1-Cl$_2$**

(^{iPr}HPNP)CoCl$_2$ **2-Cl$_2$**

(^{iPr}PBipy)CoCl$_2$ **3-Cl$_2$**

(^{iPr}PNeo)CoCl$_2$ **4-Cl$_2$**

(Triphos)CoCl$_2$ **5-Cl$_2$**

(^{R}PNN^{Ar})CoCl$_2$

6-Cl$_2$: R = ^{i}Pr, *Ar* = 2,4,6-Me$_3$-C$_6$H$_2$

7-Cl$_2$: R = ^{i}Pr, *Ar* = 2,6-^{i}Pr$_2$-C$_6$H$_3$

8-Cl$_2$: R = Ph, *Ar* = 2,6-^{i}Pr$_2$-C$_6$H$_3$

Figure 1. Cobalt dihalide complexes used in this study and their associated shorthand designations.

Catalytic C−H borylation performance was assayed using three representative substrates: 2-methylfuran, 2,6-lutidine, and benzene. Each was chosen to represent major classes of compounds typically evaluated in C−H borylation catalysis.[1] The standard catalytic procedure utilized 5 mol % of the desired cobalt dichloride complex and 10 mol % of NaBEt$_3$H in a 0.55 M THF solution of the desired substrate using either HBPin or B$_2$Pin$_2$ as the stoichiometric borylating agent. An excess of arene was used in the reaction with benzene, and conversion is reported relative to the boron reagent. The progress of each reaction was determined by gas chromatography, and the results of these experiments are reported in Table 1.

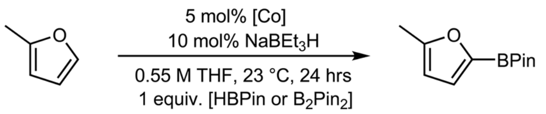
The majority of the cobalt dihalide complexes proved active for the borylation of 2-methylfuran with B$_2$Pin$_2$. Catalytic performance was significantly reduced using HBPin as the boron source. Poor performance was also observed with the traditionally more challenging substrates 2,6-lutidine and benzene. Only combinations of **1-Cl$_2$**/NaBEt$_3$H with B$_2$Pin$_2$ produced reasonable amounts of the desired product.

Stoichiometric experiments were performed with this platform to determine the identity of the cobalt compound formed during in situ activation. Addition of two equivalents of NaBEt$_3$H to a benzene-d_6 slurry of **1-Cl$_2$** and HBPin followed by filtration and analysis by ^{1}H and ^{31}P NMR spectroscopies established clean formation of previously characterized *trans*-(^{iPr}PNP)Co(H)$_2$(BPin). Previous studies from our laboratory have identified this compound as the resting state during the borylation of furan derivatives.[21]

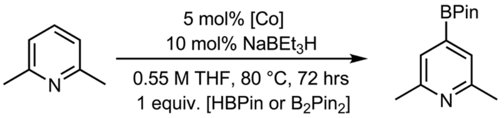
A series of experiments were conducted to explore why the other, related pincer platforms proved less effective in catalytic C−H borylation. The in situ activation procedure does not necessarily allow for true evaluation of structure−reactivity relationships, as the same organometallic cobalt active species may not form upon treatment of the cobalt dichloride with NaBEt$_3$H. Also of interest was determining the origin of the different reactivity observed with B$_2$Pin$_2$ versus HBPin. The preparation of well-defined organometallic complexes of the various chelates was therefore explored in an attempt to address these issues and gain insight into the nature of catalyst performance.

Because bis(phosphino)pyridine and bis(imino)pyridine cobalt alkyl complexes have been shown to be effective precatalysts for C−H borylation,[21] organometallic compounds of [(PBipy)Co], [(PNeo)Co], and [(^{R}PNN^{Ar})Co] were pursued. Treatment of a THF slurry of the appropriate cobalt dichloride complex with two equivalents of either LiCH$_3$ or LiCH$_2$SiMe$_3$ followed by evaporation, extraction into diethyl ether, and low-temperature recrystallization furnished each of the desired monoalkyl complexes in modest to good yields (Figure 2). Each product is diamagnetic and as such exhibits

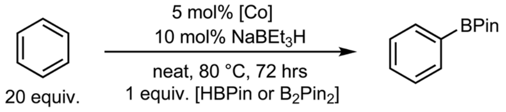
Table 1. Evaluation of Various Cobalt Dihalide Complexes for the Catalytic Borylation of 2-Methylfuran, 2,6-Lutidine, and Benzene[a]



	[Co] Precursor						
	1-Cl_2	**2-Cl_2**	**3-Cl_2**	**4-Cl_2**	**5-Cl_2**	**6-Cl_2**	**7-Cl_2**	**8-Cl_2**
HBPin	75	14	<5	<5	5	34	24	<5
B_2Pin_2	>98	42	95	30	85	48	<5	<5



	[Co] Precursor							
	1-Cl_2	**2-Cl_2**	**3-Cl_2**	**4-Cl_2**	**5-Cl_2**	**6-Cl_2**	**7-Cl_2**	**8-Cl_2**
HBPin	10	<5	<5	<5	18	<5	<5	<5
B_2Pin_2	73	6	26	<5	25	<5	<5	<5



	[Co] Precursor							
	1-Cl_2	**2-Cl_2**	**3-Cl_2**	**4-Cl_2**	**5-Cl_2**	**6-Cl_2**	**7-Cl_2**	**8-Cl_2**
HBPin	13	<5	<5	<5	5	<5	<5	<5
B_2Pin_2	63	6	14	<5	32	<5	<5	<5

[a] For 2-methylfuran and 2,6-lutidine yields were determined by GC using a cyclooctane standard; for benzene yields were determined by NMR spectroscopy with a ferrocene standard.

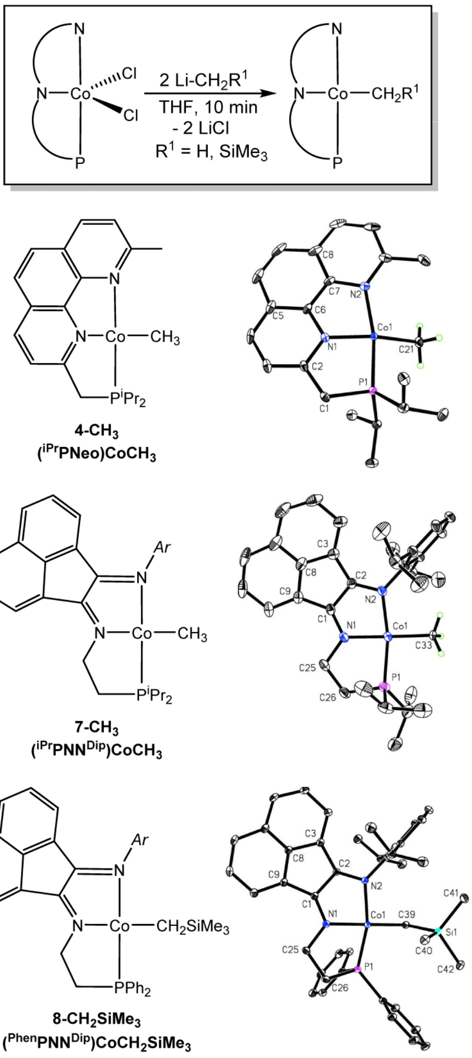


Figure 2. Synthesis of pincer-ligated cobalt alkyl complexes and representations of their solid-state structures at 30% probability ellipsoids. Hydrogen atoms except those attached to the cobalt methyl ligands are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4-CH_3, 7-CH_2SiMe_3, and 8-CH_3

	4-CH_3	7-CH_2SiMe_3	8-CH_3
Co(1)−N(1)	1.8516(16)	1.9820(15)	1.873(3)
Co(1)−N(2)	1.9856(16)	1.9031(15)	1.957(3)
Co(1)−P(1)	2.1317(6)	2.1238(5)	2.1455(10)
Co(1)−C(alkyl)	1.978(2)	1.9679(18)	1.906(3)
N(1)−C(1/6)	1.382(2)	1.323(2)	1.322(5)
N(2)−C(2/7)	1.389(3)	1.327(2)	1.331(5)
C(1/6)−C(2/7)	1.405(3)	1.435(2)	1.433(5)
N(1)−Co(1)−C(alkyl)	160.80(8)	171.57(7)	178.20(16)
P(1)−Co(1)−N(2)	166.69(5)	164.31(5)	167.74(9)

the number of resonances expected for C_s symmetric compounds. The solid-state structures of $(^{iPr}PNeo)CoCH_3$ (**4-CH_3**), $(^{iPr}PNN^{Dip})CoCH_3$ (**7-CH_3**), and $(^{Phen}PNN^{Dip})CoCH_2SiMe_3$ (**8-CH_2SiMe_3**) were determined by X-ray diffraction and are presented in Figure 2, while selected bond distances and angles are presented in Table 2. The overall molecular geometry for each four-coordinate compound is best described as distorted planar. The N(1)−Co(1)−C_{alkyl} bond angles are nearly linear, the largest distortion being 160.80(8)° in the [PNeo] variant. The P(1)−Co(1)−N(2) bond angles are comparably large, yet consistently demonstrate a slight lifting of the metal above the idealized metal−ligand plane.

Each of the chelates in the cobalt alkyl complexes contain a structural subunit, a bipyridine or diimine, that can be potentially redox-active.[34] Perturbations to bond distances in the chelate are often diagnostic of participation in the electronic structure of the metal complex.[35,36] To our knowledge the metric parameters for the radical anions of $[^{R}PNN^{Ar}]$ and [PNeo] chelates have not been established experimentally or computationally. The $[^{R}PNN^{Ar}]$ chelate is closely related to the well-studied bis(imino)acenaphthenequinone (BIAN) ligand, and metrical parameters for the neutral[37] and mono- and dianionic[38] forms of this derivative have been established and are presented in Table 3. Unfortunately, metrical parameters for the related 1,10-phenantholine ligand have yet to be established. However, data are available for the neocuproine ligand in its neutral state.

The bond distances in the chelates of both **7-CH_2SiMe_3** and **8-CH_3** alkyl complexes characterized in this study are most consistent with the monoanionic, radical form of the ligand. In **4-CH_3**, the chelate distance is consistent with one-electron

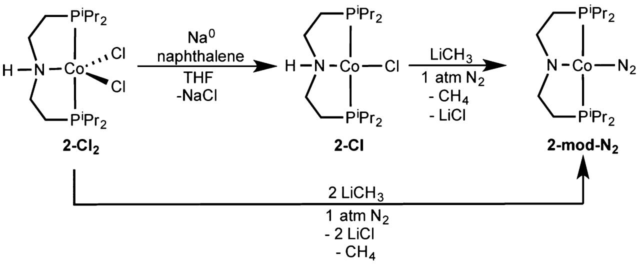
Table 3. Selected Bond Distances (Å) for Known Examples of Metal Complexes Bearing Neutral, Monoanionic, and Dianionic Bis(aryl)acenaphthenequinonediimine (BIAN) Chelates

	$(^{Dip}BIAN)NiBr_2$	$(^{Dip}BIAN)Na$	$(^{Dip}BIAN)Na_2$
M−N(1)	2.026(3)	2.2837(13)	
M−N(2)	2.036(3)	2.3411(14)	
N(1)−C(1)	1.286(5)	1.3239(18)	1.387(4)
N(2)−C(2)	1.286(5)	1.3326(19)	1.386(4)
C(1)−C(2)	1.511(6)	1.446(2)	1.402(4)

reduction. DFT calculations performed at the B3LYP level of theory[41−43] corroborate this assignment of the electronic structures. In each case, broken symmetry (1,1) solutions were preferred, corresponding to low-spin Co(II) centers engaged in antiferromagnetic coupling with chelate-centered radicals. As reported in the Supporting Information, the computed bond distances are in good agreement with the experimental values, with the largest deviations from the X-ray data being observed in the metal−ligand bond length, a typical feature of the B3LYP functional.[44]

The synthesis of cobalt alkyl complexes bearing the $[^{iPr}HPNP]$ chelate was also explored. In addition to preparing potential precatalysts for C−H borylation, these molecules are also of interest because the saturated ligand precludes the possibility of a redox-active chelate and authentic Co(I) alkyls would result. Unfortunately, addition of various alkyl lithium reagents ($LiCH_3$, $LiCH_2SiMe_3$) to either **2-Cl$_2$** or $(^{iPr}PN^{H}P)$-CoCl (**2-Cl**) resulted in isolation of the known cobalt dinitrogen complex $(^{iPr}PNP\text{-amide})CoN_2$ (**2-mod-N$_2$**) (Scheme 1), previously reported by Arnold and co-workers.[45]

Scheme 1. Synthesis of 2-mod-N$_2$ from Attempted Alkylation of 2-Cl$_2$ or 2-Cl

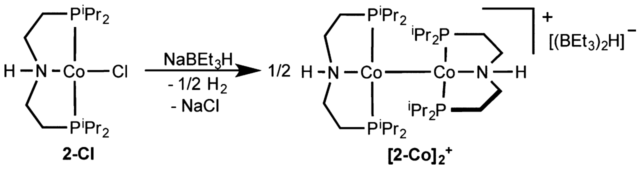


2-Cl$_2$ **2-Cl** **2-mod-N$_2$**

Importantly, isolated **2-mod-N$_2$** proved inactive for the catalytic borylation of methylfuran with either HBPin or B_2Pin_2 under standard catalytic conditions.

Despite the inability to isolate a Co(I) alkyl with the $[^{iPr}HPNP]$ chelate, studies were conducted to gain insight into the nature of a cobalt compound formed under in situ activated borylation conditions. Addition of two equivalents of a 1.0 M toluene solution of $NaBEt_3H$ to a stirring THF solution of **2-Cl$_2$** in the presence of 20 equivalents of HBPin produced a complex mixture of products. One product from this mixture was isolated in low yield following recrystallization and identified by single-crystal X-ray diffraction as the paramagnetic, bimetallic cobalt cation $[(^{iPr}HPNP)Co]_2[H(BEt_3)_2]$ $[\mathbf{2\text{-}Co}]_2^+$, generated from reduction of the cobalt dichloride precursor by $NaBEt_3H$ (Scheme 2).

Scheme 2. Isolation of $[\mathbf{2\text{-}Co}]_2^+$ from Treatment of 2-Cl$_2$ with NaBEt$_3$H



2-Cl **$[\mathbf{2\text{-}Co}]_2^+$**

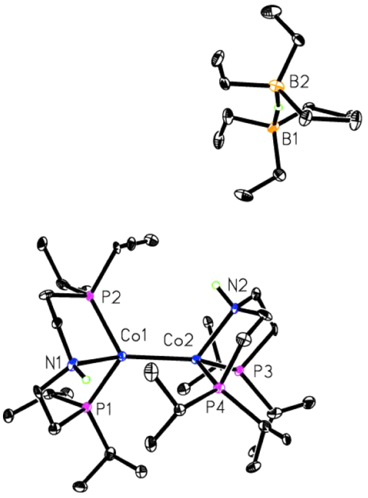


Figure 3. Molecular structure of $[\mathbf{2\text{-}Co}]_2^+$ with 30% probability ellipsoids. Hydrogen atoms except for the amides and borohydride counterion were omitted for clarity.

A representation of the molecular structure is presented in Figure 3, and selected bond distances and angles are presented in the SI. The Co−Co distance of 2.461(2) Å is within the range typically associated with a Co−Co single bond (2.46 Å). No close contacts were observed between the anion and the bimetallic cation. Notably, the metal−ligand bond distances differ significantly between the two cobalt subunits, consistent with a mixed-valent, Co(0)−Co(I) compound.

The X-band EPR spectrum of $[\mathbf{2\text{-}Co}]_2^+$ was recorded in toluene glass at 10 K (Figure 4). A rhombic signal was observed

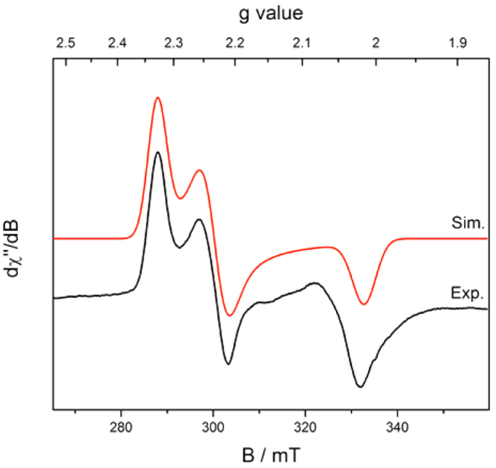


Figure 4. X-band EPR spectrum of $[\mathbf{2\text{-}Co}]_2^+$. The spectrum was recorded in toluene glass at 10 K. Conditions for $[\mathbf{2\text{-}Co}]_2^+$: microwave frequency = 9.380 GHz, power = 2.0 mW, modulation amplitude = 1 mT/100 kHz. Spectroscopic parameters for $[\mathbf{2\text{-}Co}]_2^+$: $g_x = 2.32$, $g_y = 2.23$, $g_z = 2.01$, $A_{xx} = 1$ MHz, $A_{yy} = 1$ MHz, $A_{zz} = 1$ MHz, $A_{strain} = (0, 0, 0)$, $g_{strain} = (0.001, 0.05, 0.05)$.

with relatively small g anisotropy ($g_x = 2.32$, $g_y = 2.23$, $g_z = 2.01$) and was readily simulated using the parameters reported in the caption of Figure 4. While the observed anisotropy suggests that the spin is metal centered, the lack of observed cobalt hyperfine interactions precludes further analysis of Co−Co interactions from EPR spectroscopic data. Unfortunately, even crystalline samples of the complex display significant contamination of other paramagnetic species in the ^{1}H and ^{31}P NMR spectra, likely due to decomposition of the complex in solution.

The remaining metal complexes generated vary in yield as a function of HBPin loading. When **2-Cl$_2$** was reduced in the presence of five equivalents of HBPin, the amount of [**2-Co**]$_2^+$ diminished and other diamagnetic cobalt complexes were formed. Three resonances consistent with cobalt hydrides were observed at −10.8, −18.5, and −20.7 ppm, respectively. Increasing the amount of added HBPin to 20 equivalents relative to cobalt also generated the mixture of putative cobalt hydrides and another diamagnetic cobalt complex. Unfortunately the complexity of the mixture and the inability to separate the various components prohibited full characterization of these products.

Reactivity of 4-CH$_3$ with HBPin. Our laboratory has previously reported that treatment of (^{iPr}PNP)CoCH$_2$SiMe$_3$ (**1**)-**CH$_2$SiMe$_3$** with excess HBPin resulted in loss of Me$_3$SiCH$_2$BPin with formation of *trans*-(^{iPr}PNP)CoH$_2$(BPin). The Co(III) product has been identified as the resting state during the catalytic borylation of methylfuran with HBPin.[21] To determine whether similar cobalt(III) complexes were accessible with other pincers, the addition of two equivalents of HBPin to **4-CH$_3$** was initially studied. Immediately following the addition, CH$_3$BPin was identified by ^{1}H NMR spectroscopy along with two new paramagnetic cobalt compounds. Over the course of 1 h at ambient temperature, one of the cobalt complexes completely converted to the other. The thermodynamic product was identified as [(^{iPr}PNeo)Co]$_2$(μ_2-H), [**4-Co**]$_2$(**μ_2-H**) based on NMR and EPR spectroscopies, X-ray diffraction, and combustion analysis.

The benzene-d_6 ^{1}H NMR spectrum of [**4-Co**]$_2$(**μ_2-H**) at 20 °C exhibits the number of resonances consistent with a C_s symmetric compound. A solution magnetic moment of $\mu_{\mathrm{eff}} = 1.9$ μ_B was measured in benzene-d_6 solution at 20 °C, consistent with an overall $S = 1/2$ spin state. This compound was most conveniently and rationally prepared from treatment of **4-Cl$_2$** with two equivalents of NaBEt$_3$H followed by filtration and low-temperature recrystallization (Scheme 3).

X-ray quality crystals of [**4-Co**]$_2$(**μ_2-H**) were obtained from a diethyl ether solution of the compound stored at −35 °C. A representation of the molecular structure is shown in Figure 5, and selected metrical parameters are reported in Table 4. The X-ray data confirmed a "flyover" structure where the phosphine from one [(^{iPr}PNeo)] chelate spans two metals. The hydride bridging the two cobalt centers was located and freely refined. The geometry about each cobalt center is best described as distorted trigonal bipyramidal, where the equatorial plane is defined by the metal hydride, the phosphine of the adjacent chelate, and one nitrogen donor from the neocuproine ligand. The axial positions are defined by the adjacent cobalt center and remaining nitrogen donor. The bond distortions to the neocuproine portion of the chelate suggest one electron reduction when compared to the metrical parameters of the neocuproine fragment in its neutral state.[39,40] For example, the N−C$_{\mathrm{ipso}}$ distances are elongated to 1.382(2) and 1.383(2) Å, and the interpyridine distance was contracted to 1.404(2) Å. The Co−Co bond of 2.3844(5) Å is significantly shorter than the accepted Co−Co single bond length of 2.46 Å[46] and similar bridging hydride dimers synthesized by Peters[47] (2.464 Å), Meek[48] (2.520 Å), Hanson[49] (2.637 Å), and Rix[50] (2.736 Å).

The electronic structure of dinuclear, $S = 1/2$ [**4-Co**]$_2$(**μ_2-H**) was further studied by X-band EPR spectroscopy. The toluene glass spectrum recorded at 10 K is presented in Figure 6. An axial signal was observed with one large g value at approximately $g = 3.1$, which is split into eight lines due to hyperfine coupling to the ^{59}Co nucleus ($I = 7/2$, 100% natural abundance). Two smaller g values appear near $g = 2.0$, which exhibit similar cobalt hyperfine coupling. The spectrum presented in Figure 6 was readily simulated using the parameters reported in the figure caption. Accurate reproduction of the line shapes was accomplished using a combination of g- and A-strain parameters to model a distribution of

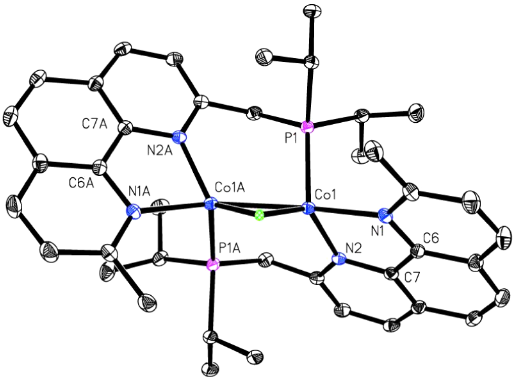
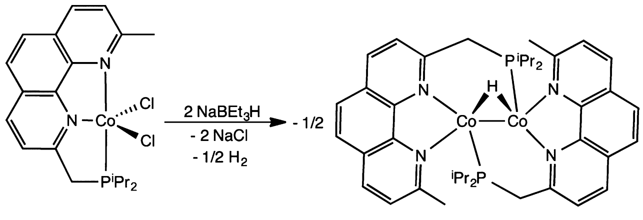


Figure 5. Molecular structure and selected bond distances for (**4**)-**Co$_2$(μ_2-H)** with 30% probability ellipsoids. Hydrogen atoms except for the bridging hydride are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [4-Co]$_2$(μ_2-H)

Co(1)−N(1)	2.0199(13)
Co(1)−N(2)	1.9542(13)
Co(1)−P(1)	2.1993(5)
Co(1)−H(0)	1.629(2)
Co(1)-Co(1A)	2.3844(5)
N(1)−C(6)	1.382(2)
N(2)−C(7)	1.383(2)
C(6)−C(7)	1.404(2)
P(1)−Co(1)−N(2)	111.35(4)
Co(1)−H(0)−Co(1A)	94.11(8)
N(1)−Co(1)−Co(1A)	151.84(4)
H(0)−Co(1)−P(1A)	110.81(4)
H(0)−Co(1)−N(2)	131.45(6)

Scheme 3. Synthesis of [4-Co]$_2$(μ_2-H)



4-Cl$_2$ **[4-Co]$_2$(μ_2-H)**

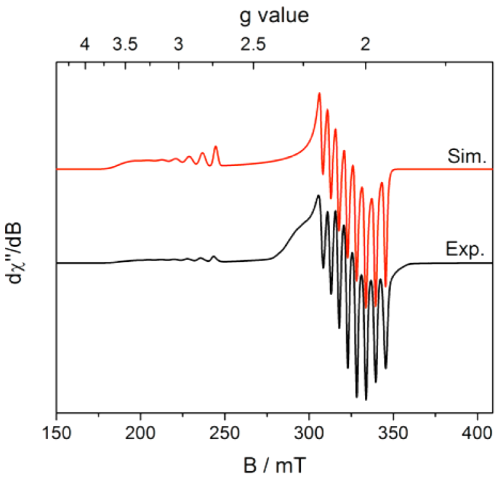


Figure 6. X-band EPR spectrum of [**4-Co**]$_2$(**μ_2-H**) recorded in toluene glass at 10 K. Microwave frequency = 9.380 GHz, power = 0.25 mW, modulation amplitude = 1 mT/100 kHz. Spectroscopic parameters for [**4-Co**]$_2$(**μ_2-H**): $g_x = 3.08$, $g_y = 2.05$, $g_z = 2.05$, $A_{xx} = 334$ MHz, $A_{yy} = 68$ MHz, $A_{zz} = 154$ MHz, $A_{\text{strain}} = (41, 0, 0)$, $g_{\text{strain}} = (0.13, 0.06, 0.001)$.

different molecular configurations frozen out upon sample glassing that give rise to anisotropic line broadening. A similar mixed-valent Co(I)−Co(II) bridging hydride complex supported by bis(phosphino)hydridoborane ligands has recently been prepared by Peters.[47] The EPR spectrum for their complex displays a rhombic signal with hyperfine interactions arising from a single ^{59}Co nucleus, similar to the spectral features of [**4-Co**]$_2$(**μ_2-H**).

DFT calculations were conducted at the B3LYP level of theory to gain additional insight into the electronic structure of [**4-Co**]$_2$(**μ_2-H**). The presence of four active spin centers in the molecule introduces significant complexity into interpretation of the computational output. The metrical data from the X-ray structure establish monoreduced chelates, thereby limiting the number of possibilities under consideration. Four possibilities were evaluated and are illustrated in Figure 7: high-spin Co(II)−high-spin Co(I), high-spin Co(II)−low-spin Co(I), low-spin Co(II)−high-spin Co(I), and low-spin Co(II)−low-spin Co(I). The relatively large g anisotropy as well as cobalt hyperfine interactions suggests that the unpaired electron is cobalt- rather than ligand-based. These observations argue against the possibility of low-spin complexes, as such configurations would likely result in a ligand-centered SOMO. Unfortunately, the remaining electronic structure descriptions cannot be distinguished based on the available experimental and computational data. While calculations of a variety of different electronic structure possibilities converged, the relative differences in single-point energy were too small (<5 kcal) to confidently assign the correct structure.

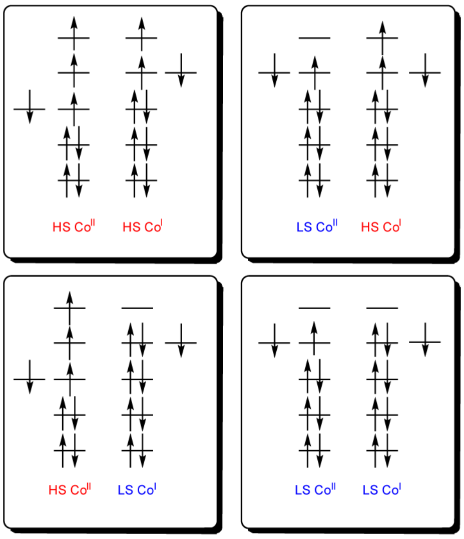


Figure 7. Possible electronic structures for [**4-Co**]$_2$(**μ_2-H**).

Spin projection analysis[51] was carried out, as it is a useful tool for determining the relative contributions from two coupled spin centers. The output provides coefficients for the g- and d-tensors of each spin center. The g-tensor coefficients of each spin center relate to one another in the same manner as the A values do. In this fashion one can determine the relative magnitudes of each A value operating on the system.[52] For [**4-Co**]$_2$(**μ_2-H**), it was assumed that the antiferromagnetic coupling interactions between the cobalt and the redox-active chelate are very strong in comparison to Co−Co interactions. This is often the case in transition metal complexes and has been used previously to successfully model multispin systems in reduced bis(aldimine)iron complexes.[53]

In the high-spin Co(II)−high-spin Co(I) case, spin projection analysis demonstrates that one metal center will have an A value with a magnitude 4 times larger than the other, as can be seen from the spin projection coefficients (1.333 vs 0.333). In this limit, contributions from one metal center could be sufficiently small such that they are masked by the natural line broadening observed in the spectrum. For the remaining two electronic structure possibilities, spin projection analysis suggests that one metal center would have no contribution to the overall spin, again consistent with the observed EPR behavior. While spin projection analysis does not discern which of these electronic structure descriptions is most appropriate, it does provide insight as to why hyperfine coupling from only one cobalt center was observed in the 10 K EPR spectrum.

The second paramagnetic species generated from the addition of HBPin to **4-CH$_3$** is likely an isomer of [**4-Co**]$_2$(**μ_2-H**). Support for this formulation derives from the observation that addition of hydrogen to **4-CH$_3$** in the absence of boron reagents generated CH_4 and the unknown paramagnetic product, thereby excluding a cobalt boryl compound. The benzene-d_6 ^{1}H NMR spectrum of the complex displays 13 broad, paramagnetically shifted resonances, establishing a lower symmetry than expected for the putative, monomeric cobalt hydride, **4-H**. Use of D_2 gas resulted in loss of CH_3D and generated the same paramagnetic cobalt product. In the presence of an H_2 or D_2 atmosphere, the lifetime of the complex was increased to approximately 8 h at ambient temperature. Removal of this atmosphere resulted in immediate conversion to [**4-Co**]$_2$(**μ_2-H**). Unfortunately attempts to obtain the EPR spectrum of the intermediate produced only the spectrum of [**4-Co**]$_2$(**μ_2-H**). It is possible that if this compound is an isomer of [**4-Co**]$_2$(**μ_2-H**), similar EPR spectra would be observed.

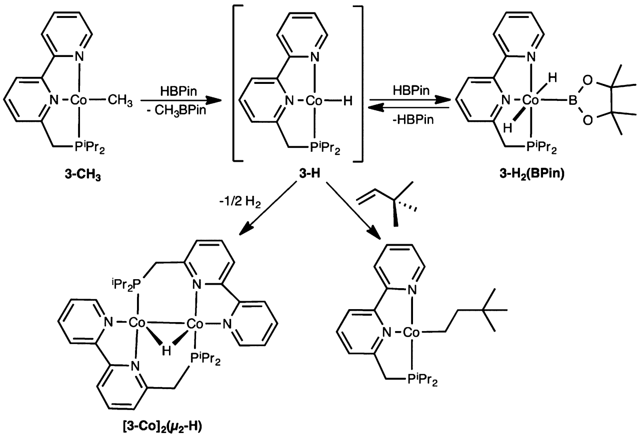
Isolated [**4-Co**]$_2$(**μ_2-H**) was evaluated as a precatalyst for the borylation of methylfuran using either HBPin or B_2Pin_2 as the boron source. In both cases, no turnover was observed, demonstrating that formation of the mixed-valent μ-hydrido dicobalt complex is an available deactivation pathway in borylation catalysis. Addition of HBPin or B_2Pin_2 to [**4-**

Co]$_2$(μ_2-H) was monitored by ^{1}H NMR spectroscopy, and in both cases an unidentified, complex mixture of paramagnetic cobalt complexes was obtained.

Addition of B$_2$Pin$_2$ to **4-CH$_3$** liberated CH$_3$BPin and generated a complex mixture of paramagnetic compounds from which the major product, **[4-Co]$_2$(μ_2-H)**, was identified. It is likely that the [PNeo] chelate is the source of the hydrogen atom required for the stoichiometry of the transformation and may be the origin of the other unidentified products in the mixture. The reduced catalytic efficiency of **4-CH$_3$** in catalytic borylation is traced to its propensity to form **[4-Co]$_2$(μ_2-H)** in the presence of boron reagents.

Reactivity of 3-CH$_3$ with HBPin. Addition of an excess (~10 equiv) of HBPin to a benzene-d_6 solution of **3-CH$_3$** resulted in formation of CH$_3$BPin along with a new diamagnetic cobalt(III) product identified as *trans*-(^{iPr}PBipy)-CoH$_2$(BPin), **3-H$_2$(BPin)**. The benzene-d_6 ^{1}H NMR spectrum of the compound displays 13 resolved resonances, one of which appears as a broad signal at −9.4 ppm, diagnostic for a cobalt hydride. Single ^{31}P and ^{11}B resonances were observed at 86.2 and 26.6 ppm, respectively, similar to what has been observed for *trans*-(^{iPr}PNP)CoH$_2$(BPin). NOESY experiments established exchange between free pinacolborane and the cobalt hydride on the NMR time scale at 20 °C, accounting for the observed broadness of the hydride signal and supporting rapid interconversion between Co(I) and Co(III) compounds. To further probe this equilibrium, 3,3-dimethylbutene was added to a benzene-d_6 solution of **3-CH$_3$** immediately following treatment with HBPin. Monitoring the outcome of the reaction by ^{1}H NMR spectroscopy established clean and quantitative formation of (^{iPr}PBipy)CoCH$_2$CH$_2$CMe$_3$, consistent with initial formation of the cobalt(I) hydride followed by immediate trapping by the terminal alkene (Scheme 4).

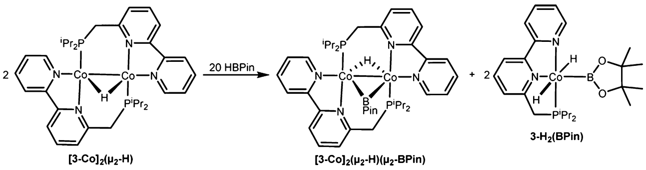
Scheme 4. Reactivity of 3-H and Its Equilibrium with 3-H$_2$(BPin)



In the absence of sufficient quantities of HBpin, the equilibrium between **3-H$_2$(BPin)** and **3-H** shifts toward the Co(I) complex, which undergoes loss of hydrogen to generate the mixed-valent cobalt hydride complex [(^{iPr}PBipy)Co]$_2$(μ_2-H), **[3-Co]$_2$(μ_2-H)**. Similar to **[4-Co]$_2$(μ_2-H)**, this product is also obtained from treatment of **3-Cl$_2$** with two equivalents of NaBEt$_3$H. The benzene-d_6 ^{1}H NMR spectrum of the purple product exhibited 15 well-resolved resonances, consistent with a C_s symmetric dicobalt compound. The X-band EPR spectrum recorded in a toluene glass at 10 K (Figure S25) exhibits an axial signal with g values of 2.24, 2.0, and 1.96, similar to the spectral features of **[4-Co]$_2$(μ_2-H)**. These results demonstrate that Co(III) complexes are accessible with this class of pincers, although formation of mixed-valent μ-hydride cobalt complexes is a significant decomposition pathway not previously observed with [(PNP)Co]-type complexes.[21]

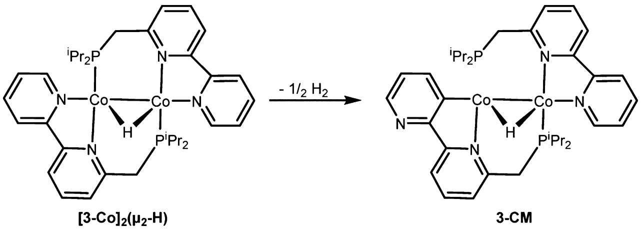
Treatment of **3-Cl$_2$** with NaBEt$_3$H was previously reported as a method for the generation of alkene hydroboration catalysts.[27] Because these experiments were conducted in the presence of a large excess of HBPin, our studies now clearly establish that both **3-H$_2$(BPin)** and **[3-Co]$_2$(μ_2-H)** are formed under these conditions and little of **3-H** is present due to its kinetic instability. To gain further insight into these processes and to determine the most relevant species to catalysis, additional experiments were conducted with **[3-Co]$_2$(μ_2-H)** and HBPin. Upon addition of 20 equivalents of borane, a 2:1 ratio of products was observed (Scheme 5). The major product was identified as **3-H$_2$(BPin)**, while the minor product exhibited a number of ^{1}H and ^{31}P NMR resonances consistent with a C_1 symmetric compound. A diagnostic doublet of doublets ($^2J_{PH}$ = 31, 64 Hz) was observed at 20.17 ppm, signaling the presence of a cobalt hydride that couples to two inequivalent ^{31}P nuclei. Accordingly, two singlets were observed at 62.2 and 115 ppm in the ^{31}P NMR spectrum, while a ^{11}B NMR experiment revealed a peak at 34.4 ppm, establishing a boron-containing product. On the basis of the spectroscopic data and the stoichiometry of the reaction, the minor product is likely the μ-hydride, μ-boryl product **[3-Co]$_2$(μ_2-H)(μ_2-BPin)**. Thus, three cobalt compounds, **3-H$_2$(BPin)**, **[3-Co]$_2$(μ_2-H)(μ_2-BPin)**, and **[3-Co]$_2$(μ_2-H)**, are plausible during both catalytic C−H borylation and alkene hydroboration.

Scheme 5. Reaction of [3-Co]$_2$(μ_2-H) with Excess HBPin



Notably, isolated **[3-Co]$_2$(μ_2-H)** proved inactive for the borylation of 2-methylfuran using HBPin as the stoichiometric borylating agent. With B$_2$Pin$_2$, >95% conversion of 2-methylfuran was observed, consistent with the in situ catalytic data reported in Table 1. Monitoring the borylation with B$_2$Pin$_2$ by ^{1}H NMR revealed the presence of a significant quantity of **[3-Co]$_2$(μ_2-H)** along with a new diamagnetic, C_1 symmetric dicobalt complex. Stirring a benzene-d_6 solution of **[3-Co]$_2$(μ_2-H)** in the absence of B$_2$Pin$_2$ also resulted in formation of this new diamagnetic product, thereby eliminating the possibility of a boron-containing cobalt compound. The benzene-d_6 ^{1}H NMR spectrum exhibited a doublet centered at −42 ppm ($^2J_{PH}$ = 40 Hz) consistent with a cobalt hydride coupling to a single phosphorus atom. Two ^{31}P resonances were observed at 56.7 and 92.2 ppm. All of the pincer resonances were located and identified by ^{1}H, ^{13}C, and multinuclear correlation NMR experiments with the exception of one. The symmetry of the compound and the spectroscopic data support formation of a μ-hydride cobalt product where one of the bipyridine subunits has undergone cyclometalation (Scheme 6). We note that one possibility consistent with the data is shown in Scheme 6, but other isomers are indeed plausible.

Scheme 6. Pincer Cyclometalation of $[\mathbf{3\text{-}Co}]_2(\mu_2\text{-}\mathbf{H})$



None of the complexes derived from the addition of HBPin to **$3\text{-}CH_3$** are competent for borylation when HBPin is used as the stoichiometric borylating agent. The data reported here suggest that B_2Pin_2 is the more effective borylating reagent due to its ability to avoid formation of inactive bridging hydride compounds.

Reactivity of $[(^{R}PNN^{Ar})Co]$ with HBPin and $NaBEt_3H$. A similar series of experiments were conducted with the $[(^{R}PNN^{Ar})Co]$ family of complexes. Unfortunately, treatment of the cobalt dihalides with $NaBEt_3H$ or addition of HBPin to the corresponding cobalt alkyls generated an unidentified complex mixture of products as judged by NMR spectroscopy. Analysis of these mixtures by EPR spectroscopy (see the SI) revealed signals similar to $[\mathbf{3\text{-}Co}]_2(\mu_2\text{-}\mathbf{H})$ and $[\mathbf{4\text{-}Co}]_2(\mu_2\text{-}\mathbf{H})$, suggesting that similar mixed-valent hydride complexes are formed with this pincer platform.

Evaluation of Pincer Electronic Properties. To gain additional insight into the role of pincer electronic properties on catalytic borylation activity and related stoichiometric chemistry, the corresponding series of iron dicarbonyl complexes was prepared and the CO stretching frequencies were determined by infrared spectroscopy. In each case, the iron dicarbonyl complex was prepared by straightforward reduction of the iron dichloride under an atmosphere of carbon monoxide.[57] Table 5 reports the CO stretching frequency for each compound. Also included in Table 5 is the bis(imino)pyridine derivative $(^{iPr}PDI)Fe(CO)_2$ for comparison.

Although the data in Table 5 were recorded in different media, the relative electron-donating properties of various pincer ligands are apparent. The most electron-donating in the series is the [PNP]-type chelate bearing the sp^3 nitrogen atom.

Table 5. Infrared CO Stretching Frequencies of Dicarbonyl Iron Compounds with Tridentate Pincer Ligands

Easier to access Co(III)
Increased Borylation Activity

Complex	ν(C≡O) (cm^{-1})
$(^{iPr}HPNP)Fe(CO)_2$	1838, 1767[a]
$(^{iPr}PNP)Fe(CO)_2$	1842, 1794[b]
$(^{iPr}PBipy)Fe(CO)_2$	1907, 1847[c]
$(^{iPr}PNeo)Fe(CO)_2$	1908, 1846[e]
$(Triphos)Fe(CO)_2$	1926, 1875[e]
$(^{iPr}PNN^{Mes})Fe(CO)_2$	1951, 1889[e]
$(^{Phen}PNN^{Dip})Fe(CO)_2$	1960, 1896[e]
$(^{iPr}PDI)Fe(CO)_2$	1974, 1914[d]

Harder to access Co(III)
Increased Hydroboration Activity

[a] Thin film on Nujol.[54] [b] Thin film on KBr.[17] [c] Thin film on NaCl.[56] [d] In pentane solution.[55] [e] In benzene-d_6 solution.

Replacing the tertiary amine with a pyridine donor results in a slight decrease in the electron-donating ability of the ligand when coordinated to iron.

Introduction of a redox-active diimine into the pincer such as a bipyridine, neocuproine, or α-diimine significantly reduces the electron-donating properties of the pincer. Nevertheless, studies with $[(^{iPr}PBipy)Co]$ demonstrate that oxidative addition to form Co(III) complexes is accessible under catalytic borylation conditions. However, it is the electron-withdrawing effect of the redox-active portion of the ligand (relative to the [PNP]-type pincers) that facilitates reductive elimination and opens pathways to mixed-valent dicobalt compounds with reduced efficacy for C−H borylation. Table 6 includes estimated equilibrium constants for the Co(I)−Co(III) couple and illustrates the effect of the type of ligand (strong field vs redox-active) on the ability to support cobalt(III). The values reported in Table 6 were estimated by integrations from ^1H NMR spectroscopy. Addition of two equivalents of HBPin to $(^{iPr}PNP)CoCH_3$ resulted in immediate formation of *trans*-$(^{iPr}PNP)CoH_2(BPin)$. No significant quantity of $(^{iPr}PNP)CoH$ or products derived from its formation were observed. This is in contrast to complexes supported by [PDI] or $[^{R}PNN^{Ar}]$ chelates, where formation of a cobalt(III) compound was not observed even upon addition of an excess of HBPin. Addition of two equivalents of HBPin to **$3\text{-}CH_3$** resulted in formation of **$3\text{-}H_2(BPin)$** as well as $[\mathbf{3\text{-}Co}]\mathbf{2}(\mu_2\text{-}\mathbf{H})$, indicating reversible oxidative addition of HBPin from **3-H**. Over the course of 15 min, the mixture converged to $[\mathbf{3\text{-}Co}]\mathbf{2}(\mu_2\text{-}\mathbf{H})$ as the sole metal product.

Table 6. Estimated Equilibrium Constants for Oxidative Addition of HBPin to Pincer Cobalt Alkyl Complexes

$$\begin{array}{c}LCo\text{-}R\\ +\ 2\ HBPin\end{array} \underset{\substack{23\ ^{\circ}C\\ \textit{fast}}}{\overset{K_{eq}}{\rightleftharpoons}} \begin{array}{c}LCo\text{-}H_2(BPin)\\ +\ R\text{-}Bpin\end{array}$$

L	K_{eq}
(^{iPr}PNP)	$>10^2$
$(^{iPr}PBipy)$	$\sim 10^1$
$(^{iPr}PNeo)$	<1
$(^{iPr}PNN^{Mes})$	<1
$(^{Phen}PNN^{Dip})$	<1
(^{iPr}PDI)	<1

Although the redox-active complexes are less effective for C−H borylation, these compounds, as reported by our group and Huang, are active for alkene hydroboration.[27,30] These observations suggest that Co(III) intermediates are less important during that cycle, in agreement with DFT computational studies on alkene hydrogenation that favor maintenance of the cobalt(II) oxidation state when catalysts containing redox-active bis(imino)pyridine pincers are used. Supporting these conclusions is the poor alkene hydroboration activity of **$1\text{-}CH_2SiMe_3$**. Under catalytic conditions, the presence of excess HBPin favors a Co(III) resting state and diminishes the concentration of the putative Co(I) hydride necessary for alkene insertion.

These data suggest that because of its electronics the $[^{iPr}PN^{H}P]$ platform should support a highly effective borylation catalyst; however deprotonation of the N−H position interferes with the ability to form the appropriate catalytically relevant intermediates required for sustained turnover. This observation

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reminds us that while electronics play an integral role in formation of an active catalyst, attention must also be paid to other chemical and physical properties of the ligand such as functional groups susceptible to deprotonation, ligand sterics, bite angle, and rigidity.

■ CONCLUDING REMARKS

A family of cobalt(II) dichloride complexes bearing neutral tridentate pincers were evaluated for catalytic C−H borylation using $NaBEt_3H$ as an in situ activator and with both HBPin and B_2Pin_2 as the stoichiometric boron source. Insights into the relative catalytic performance of each class of pincer were obtained from preparation of the corresponding organometallic compounds formed under catalytic conditions and assaying their relative stability during the course of turnover. In the case of the relatively electron donating pincer (^{iPr}PNP) high borylation activity was observed with a Co(III) resting state. Reduction of the electron-donating capability of the pincer decreases the stability of the Co(III) resting state and opens pathways to mixed-valent Co(I)−Co(0) compounds, accounting for the diminished catalytic activity. However, pincer ligands bearing redox-active subunits are more effective for catalytic alkene hydroboration, a consequence of Co(III) inhibiting turnover. In sum, these studies provide important insights for the design of base metal complexes for catalytic carbon−boron bond forming reactions.

■ EXPERIMENTAL SECTION

General Considerations. All reactions were carried out in an MBraun inert atmosphere (nitrogen) drybox unless otherwise stated. All glassware was stored in the oven before use. The solvents used in the drybox were dried and deoxygenated using literature procedures.[58] HBPin (Aldrich), sodium triethylborohydride (1.0 M in toluene, Aldrich), and bis(pinacolato)diboron (AllyChem) were used without further purification. Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Methylfuran and 2,6-lutidine were purchased from Aldrich and distilled from CaH_2 under reduced pressure before use. Cyclooctane (Acros Organics), used a standard for gas chromatography, was distilled from $LiAlH_4$ under reduced pressure before use. The following compounds were prepared as described previously: (^{iPr}PNP)$CoCl_2$,[18] (^{iPr}HPNP)$CoCl_2$,[59] (^{iPr}PBipy)$CoCl_2$,[27] (Triphos)$CoCl_2$,[60] (Triphos)$FeBr_2$,[61] and (^{Phen}PNN^{Dip})$FeCl_2$.[62]

^1H NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz. All chemical shifts are reported relative to $SiMe_4$ using ^1H (residual) chemical shifts of the solvent as a secondary standard. ^{13}C NMR spectra were recorded on a Bruker 500 spectrometer operating at 125.71 MHz. ^{13}C chemical shifts are reported relative to $SiMe_4$ using chemical shifts of the solvent as a secondary standard where applicable. ^{31}P NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 299.763 MHz and were referenced to 85% H_3PO_4 as an external standard. For all paramagnetic compounds, peak width at half-height is reported in hertz. Infrared spectroscopy was conducted on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc. (Ledgewood, NJ, USA).

GC analyses were performed using a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu AOC-20s autosampler and a Shimadzu SHRXI-5MS capillary column (15 m × 250 μm). The instrument was set to an injection volume of 1 μL, an inlet split ratio of 20:1, and inlet and detector temperatures of 250 and 275 °C, respectively. UHP-grade helium was used as carrier gas with a flow rate of 1.82 mL/min. The temperature program used for all the analyses is as follows: 60 °C, 1 min; 15 °C/min to 250 °C, 2 min.

Solution magnetic moments were determined by the method of Evans at 22 °C using a ferrocene standard unless otherwise noted.[63] Gouy magnetic susceptibility balance measurements were performed with a Johnson Matthey instrument that was calibrated with $HgCo(SCN)_4$. Continuous wave (CW) EPR spectra were recorded at 10 K on an Bruker X-band EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop, and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with molybdenum and copper X-ray tubes (λ = 0.710 73 and 1.541 84 Å, respectively). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

Quantum-Chemical Calculations. All DFT calculations were performed with the ORCA program package.[64] The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level[65−67] of DFT. The all-electron Gaussian basis sets were those developed by the Ahlrichs group.[68−70] Triple-ζ quality basis sets def2-TZVP with one set of polarization functions on cobalt and on the atoms directly coordinated to the metal center were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used that were of double-ζ quality in the valence region and contained a polarizing set of d-functions on the non-hydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX) approach[71−73] were chosen to match the orbital basis.[74,75,76] Numerical frequencies were calculated at the same level of theory to confirm the optimized geometries (no imaginary frequencies) and to derive thermochemical data. Throughout this paper we describe our computational results by using the broken-symmetry (BS) approach by Ginsberg[77] and Noodleman.[78] Because several broken symmetry solutions to the spin-unrestricted Kohn−Sham equations may be obtained, the general notation BS(m,n)[79] has been adopted, where m (n) denotes the number of spin-up (spin-down) electrons at the two interacting fragments. Canonical and corresponding orbitals, as well as spin density plots, were generated with the program Molekel.[80]

Preparation of [^{iPr}PNeo] (4). A thick-walled glass vessel was charged with a mixture of neocuproine (5.0 g, 24.0 mmol), diethyl ether (30 mL), and a stir bar. The reaction mixture was cooled to −78 °C before a diethyl ether (20 mL) solution of lithium diisopropylamide (2.57 g, 24.0 mmol) was slowly added. The resulting solution was warmed to room temperature and stirred for 2 h. After this time, the contents of the vessel were again cooled to −78 °C before chlorodiisopropylphosphine (3.66 g, 24.0 mmol) was slowly added. The resulting reaction mixture was stirred at 23 °C overnight. The crude product was washed with degassed water (3 × 40 mL), dried over sodium sulfate, and filtered through Celite. Upon evaporation of the diethyl ether in vacuo, a yellow-orange oil was obtained. Recrystallization from diethyl ether yielded 2.5 g (32%) of a white solid identified as the title compound. Anal. Calcd for $C_{20}H_{25}N_2P$: C, 74.05; H, 7.77; N, 8.63. Found: C, 74.08; H, 7.51; N, 8.53. ^1H NMR (300 MHz, C_6D_6, 23 °C): δ = 1.05 (m, 12H, ^{i}Pr CH_3), 1.77 (sd, $^2J_{PH}$ = 7.0 Hz, $^3J_{PH}$ = 1.6 Hz, 2H, ^{i}Pr CH), 2.69 (s, 3H, neocuproine CH_3), 3.36 (d, $^2J_{PH}$ = 1.9 Hz, 2H, P-CH_2), 6.92 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar), 7.30 (s, 2H, Ar), 7.58 (m, 3H, Ar). $^{13}C\{^1H\}$ NMR (125.71 MHz, C_6D_6, 23 °C): δ = 19.3 (m, P-$CHMe_2$), 20.2 (m, Ar-CH_3), 24.2 (m, P-$CHMe_2$), 34.1 (m, P-CH_2), 122.94 (Ar CH), 123.5 (m, Ar CH), 125.4 (Ar CH), 125.6 (Ar CH), 127.0 (m, Ar C) 135.6 (Ar CH), 135.7 (Ar CH), 146.5 (Ar C), 146.7 (Ar C) 158.8 (Ar C) 161.6 (Ar C) 161.7 (Ar C). $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 23 °C): δ = 13.36 (s) ppm.

Preparation of (^{iPr}PNeo)$CoCl_2$ 4-Cl_2. A 20 mL scintillation vial was charged with a stir bar, 0.200 g (1.54 mmol) of cobalt dichloride, 0.500 g (1.54 mmol) of ^{iPr}PNeo, and 10 mL of tetrahydrofuran. The resulting solution was stirred for approximately 16 h at ambient temperature. The resulting gray-blue solution was layered with pentane, and a gray precipitate was observed and collected on a glass frit. The solid was washed with 50 mL of pentane, followed by 50 mL of diethyl ether. The resulting solid was collected, and any remaining volatiles were removed in vacuo, yielding 0.643 g (92%) of an analytically pure solid identified as (^{iPr}PNeo)CoCl$_2$. Anal. Calcd for $C_{20}H_{25}Cl_2CoN_2P$: C, 52.88; H, 5.55; N, 6.17. Found: C, 53.02; H, 5.61; N, 5.94. ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = -47.77$ (3H, $\Delta\nu_{1/2}$ = 141 Hz), −17.21 (6H, $\Delta\nu_{1/2}$ = 79 Hz), −14.68 (6H, $\Delta\nu_{1/2}$ = 80 Hz), −13.32 (1H, $\Delta\nu_{1/2}$ = 40 Hz), −7.03 (1H, $\Delta\nu_{1/2}$ = 35 Hz), 12.32 (1H, $\Delta\nu_{1/2}$ = 36 Hz), 16.55 (1H, $\Delta\nu_{1/2}$ = 35 Hz), 21.97(1H, $\Delta\nu_{1/2}$ = 36 Hz), 52.02 (2H, $\Delta\nu_{1/2}$ = 194 Hz), 68.68 (1H, $\Delta\nu_{1/2}$ = 43 Hz), 80.13 (2H, $\Delta\nu_{1/2}$ = 207 Hz). Magnetic susceptibility (MSB): μ_{eff} = 4.3 μ_B.

Preparation of (^{iPr}PNeo)CoCH$_3$ 4-CH$_3$. A 20 mL scintillation vial was charged with a stir bar, 0.200 g (0.44 mmol) of (^{iPr}PNeo)CoCl$_2$, and 10 mL of tetrahydrofuran. The blue solution was chilled in the freezer to −35 °C, and a 1.6 M solution of LiCH$_3$ in diethyl ether (0.55 mL, 0.88 mmol) was then added dropwise. The resulting dark green solution was stirred for 15 min at room temperature, and then the votalies were removed in vacuo. The product was extracted from the solid residue with copious amounts of diethyl ether and filtered through a plug of Celite. Recrystallization of the crude material from a diethyl ether solution at −35 °C furnished 0.100 g of green-purple crystals suitable for X-ray diffraction. Anal. Calcd for $C_{21}H_{28}CoN_2P$: C, 63.32; H, 7.08; N, 7.03. Found: C, 63.40; H, 6.62; N, 6.75. ^{1}H NMR (300 MHz, C$_6$D$_6$, 23 °C): $\delta = -1.13$ (d, $^3J_{PH}$ = 8.2 Hz, 3H, Co-CH$_3$), 1.25 (m, 12H, ^{i}Pr CH$_3$), 2.16 (d, $^2J_{PH}$ = 11.0 Hz, 2H, P-CH$_2$), 2.96 (sept, $^3J_{HH}$ = 7.3 Hz, 2H, ^{i}Pr CH), 3.93 (s, 3H, neocuproine CH$_3$), 6.75 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Ar CH), 6.83 (d, $^3J_{HH}$ = 8.8 Hz, 1H, Ar CH), 7.11 (d, $^3J_{HH}$ = 9.0 Hz, 1H, Ar CH), 8.53 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar CH), 9.11 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ar CH), 12.56 (t, $^3J_{HH}$ = 6.9 Hz, 1H, Ar CH) ppm. ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$, 23 °C): δ = 17.5 (^{i}Pr CH$_3$), 19.2 (^{i}Pr CH$_3$), 19.9 (^{i}Pr CH), 30.0 (Ar-CH$_3$), 39.3 (P-CH$_2$), 122.5 (Ar-CH), 122.8(Ar-CH), 127.5(Ar-CH), 127.6, (Ar-CH), 128.3(Ar-CH), 132.8 (Ar-CH), 129.2 (Ar C), 141.7 (Ar C), 145.3 (Ar C), 152.1 (Ar C), 155.5 (Ar C), 173.4 (Ar-C) ppm. ^{31}P{^{1}H} NMR (300 MHz, C$_6$D$_6$, 23 °C): δ = 22.2 (br s) ppm.

Preparation of [(^{iPr}PNeo)Co]$_2$(μ_2-H), 4-Co$_2$(μ_2-H). A 20 mL scintillation vial was charged with a stir bar, 0.015 g (0.04 mmol) of (^{iPr}PNeo)CoCH$_3$, and 1 mL of benzene. To the stirring solution was added dropwise 0.010 g (0.08 mmol) of HBPin, and a color change from green to red-brown was observed. The resulting solution was stirred for 30 min at room temperature before the solution was filtered through Celite and the volitles were removed, furnishing 0.010 g of [(^{iPr}PNeo)Co]$_2$(μ_2-H). Anal. Calcd for $C_{40}H_{51}Co_2N_4P_2$: C, 62.58; H, 6.70; N, 7.30. Found: C, 62.41; H, 7.01; N, 7.56. ^{1}H NMR (300 MHz, C$_6$D$_6$, 23 °C): $\delta = -38.0$ (2H, $\Delta\nu_{1/2}$ = 56 Hz), −14.8 (6H, $\Delta\nu_{1/2}$ = 44 Hz), −3.88 (6H, $\Delta\nu_{1/2}$ = 17 Hz), −1.38 (6H, $\Delta\nu_{1/2}$ = 19 Hz), 1.64 (6H, $\Delta\nu_{1/2}$ = 9 Hz), 3.97 (2H, $\Delta\nu_{1/2}$ = 40 Hz), 8.57 (6H, $\Delta\nu_{1/2}$ = 36 Hz), 10.9 (d, 2H, P-CH$_2$), 12.7 (d, 2H, P-CH$_2$), 15.7 (2H, $\Delta\nu_{1/2}$ = 17 Hz), 16.8 (2H, $\Delta\nu_{1/2}$ = 24 Hz), 19.2 (2H, $\Delta\nu_{1/2}$ = 17 Hz), 29.2 (2H, $\Delta\nu_{1/2}$ = 17 Hz), 31.3 (2H, $\Delta\nu_{1/2}$ = 17 Hz); two peaks not located. Magnetic susceptibility (MSB): μ_{eff} = 1.9 μ_B.

Alternative Procedure for Preparation of [(^{iPr}PNeo)Co]$_2$(μ_2-H), 4-Co$_2$(μ_2-H). A 20 mL scintillation vial was charged with a stir bar, 0.100 g (0.22 mmol) of (^{iPr}PNeo)CoCl$_2$, and 5 mL of diethyl ether. A 1.0 M solution of NaBEt$_3$H in toluene (0.44 mL, 0.44 mmol) was then added dropwise to the solution of (^{iPr}PNeo)CoCl$_2$. The resulting mixture was stirred for 15 min at room temperature followed by filtration through Celite. Removal of the volatiles in vacuo furnished 0.068 g (79%) of the title [(^{iPr}PNeo)Co]$_2$(μ_2-H) as a dark brown solid.

Preparation of (^{iPr}PNeo)FeBr$_2$(THF), 4-FeBr$_2$(THF). A 20 mL scintillation vial was charged with a stir bar, 0.450 g (1.38 mmol) of ^{iPr}PNeo, 0.299 g (1.38 mmol) of FeBr$_2$, and 5 mL of tetrahydrofuran. The mixture was stirred for 18 h, after which time the solution was layered with pentane. The resulting red-orange precipitate was collected on a fine glass frit and washed with 50 mL of diethyl ether. The solid was dried in vacuo, yielding 0.643 g (86%) of an orange solid identified as (^{iPr}PNeo)FeBr$_2$(THF). Anal. Calcd for $C_{20}H_{25}Br_2FeN_2P$: C, 47.09; H, 5.43; N, 4.58. Found: C, 47.10; H, 5.22; N, 4.62. ^{1}H NMR (400 MHz, CDCl$_3$, 23 °C): $\delta = -27.34$ (1H, $\Delta\nu_{1/2}$ = 17 Hz, Ar-H), −4.12 (3H, $\Delta\nu_{1/2}$ = 188 Hz, Ar-CH$_3$), 1.89 (2H, $\Delta\nu_{1/2}$ = 15 Hz), 3.78 (2H, $\Delta\nu_{1/2}$ = 15 Hz), 6.93 (6H, $\Delta\nu_{1/2}$ = 83 Hz, ^{i}Pr CH$_3$), 10.34 (1H, $\Delta\nu_{1/2}$ = 18 Hz, Ar-H), 17.47 (6H, $\Delta\nu_{1/2}$ = 67 Hz, Ar-CH$_3$), 22.24 (1H, $\Delta\nu_{1/2}$ = 17 Hz, Ar-H), 31.94 (1H, $\Delta\nu_{1/2}$ = 17 Hz, Ar-H), 45.35 (2H, $\Delta\nu_{1/2}$ = 118 Hz), 51.90 (1H, $\Delta\nu_{1/2}$ = 17 Hz, Ar-H), 58.47 (1H, $\Delta\nu_{1/2}$ = 17 Hz, Ar-H), 124.58 (2H, $\Delta\nu_{1/2}$ = 207 Hz). Magnetic susceptibility (MSB): μ_{eff} = 4.5 μ_B

Preparation of (^{iPr}PNeo)Fe(CO)$_2$, 4-Fe(CO)$_2$. A thick-walled vessel was charged with 3.5 g of mercury, approximately 10 mL of THF, and a stir bar. Sodium (0.014 g, 0.615 mmol) was cut into small pieces and added slowly to the rapidly stirred slurry. The resulting amalgam was stirred for an additional 30 min to ensure complete dissolution. A slurry of (^{iPr}PNeo)FeBr$_2$ (0.166 g, 0.307 mmol) in 10 mL of THF was added to the reaction vessel, which was then sealed. The resulting mixture was cooled to −196 °C, and the vessel was evacuated. One atmosphere of CO was introduced, and the reaction mixture was stirred for 24 h. The resulting green mixture was then decanted away from the amalgam, and the volatiles were removed in vacuo. The resulting solid was dissolved in diethyl ether and passed through a pad of Celite. The solvent was removed in vacuo to yield 0.053 g (39%) of a green solid identified as (^{iPr}PNeo)Fe(CO)$_2$. Anal. Calcd for $C_{22}H_{27}FeN_2O_2P$: C, 60.57; H, 5.78; N, 6.42. Found: C, 60.68; H, 5.85; N, 6.33. ^{1}H NMR (300 MHz, C$_6$D$_6$, 23 °C): δ = 1.05 (m, 12H, P-CHMe$_2$), 2.05 (m, 2H, P-CHMe$_2$), 3.10 (d, 2H, P-CH$_2$), 3.59 (s, 3H, Ar-CH$_3$), 6.79 (d, 1H, Ar-CH), 6.92 (d, 1H, Ar-CH), 7.18−7.38 (m, 4H, Ar-CH) ppm. ^{13}C{^{1}H} NMR (125.71 MHz, C$_6$D$_6$, 23 °C): δ = 17.5 (d, P-CHMe$_2$), 27.9 (d, P-CHMe$_2$), 29.1 (Ar-CH$_3$), 36.2 (d, P-CH$_2$), 115.1 (d, Ar-CH), 118.8 (Ar-CH), 119.1 (Ar-CH), 125.4 (Ar-CH), 126.0 (Ar-CH), 126.7 (Ar-CH), 129.5 (Ar-C), 130.6 (Ar-C), 139.8 (Ar-C), 143.4 (Ar-C), 155.2 (Ar-C), 161.3 (Ar-C), 218.7 (d, carbonyl) ppm. ^{31}P{^{1}H} NMR (300 MHz, C$_6$D$_6$, 23 °C): δ = 119.0 (s) ppm. IR (benzene): νCO 1846, 1908 cm^{-1}.

Preparation of (^{iPr}PBipy)CoCH$_3$, 3-CH$_3$. A 20 mL scintillation vial was charged with 0.300 g (0.721 mmol) of (^{iPr}PBipy)CoCl$_2$ and 5 mL of tetrahydrofuran. The solution was chilled in the freezer to −35 °C, and a 1.6 M solution of LiCH$_3$ in diethyl ether (0.901 mL, 1.44 mmol) was then added dropwise. The resulting dark purple solution was stirred for 15 min at room temperature before the volatiles were removed in vacuo. The product was extracted from the solid residue with 10 mL of diethyl ether, which was then filtered through a plug of Celite and concentrated in vacuo and yielded 0.140 g (54%) of a purple solid identified as (^{iPr}PBipy)CoCH$_3$. Anal. Calcd for $C_{18}H_{26}CoN_2P$: C, 60.00; H, 7.27; N, 7.77. Found: C, 59.55; H, 7.19; N, 7.01. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): $\delta = -0.45$ (d, $^3J_{PH}$ = 8.00, 3H, CH$_3$), 0.77 (dd, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, P-CH*Me*$_2$), 1.27 (dd, $^3J_{PH}$ = 12.8 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, P-CH*Me*$_2$), 2.90 (sept, $^3J_{HH}$ = 7.1 Hz, 2H, P-*CH*Me$_2$), 4.77 (d, $^2J_{PH}$ = 9.6 Hz, 2H, P-CH$_2$), 5.40 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Ar-CH), 7.38 (d, $^3J_{HH}$ = 6.6 Hz, 1H, Ar-CH), 7.43 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-CH), 8.85 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Ar-CH), 9.82 (t, $^3J_{HH}$ = 6.6 Hz, 1H, Ar-CH), 11.09 (m, 1H, Ar-CH), 14.65 (m, 1H, Ar-CH). ^{13}C{^{1}H} NMR (125.71 MHz, benzene-d_6, 23 °C): δ 17.9 (P-CHMe$_2$), 18.8 (m, P-CHMe$_2$), 38.4 (m, P-CH$_2$), 113.4 (Ar-H), 121.1 (m, Ar-H), 124.5 (s, Ar-H), 132.5 (s, Ar-H), 133.4 (s, Ar-H); quaternary carbons, Co-CH$_3$ were not observed. ^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 13.58 (br s, P-CHMe$_2$).

Preparation of (^{iPr}PBipy)CoH$_2$(BPin), 3-H$_2$(BPin). A 20 mL scintillation vial was charged with 0.005 g (0.014 mmol) of (^{iPr}PBipy)CoCH$_3$ and 1 mL of benzene-d_6. To the solution was added 0.018 g (0.139 mmol) of HBPin. The resulting dark purple solution was filtered through Celite and analyzed by NMR. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): $\delta = -9.40$ (br s, 2H, Co-H), 0.85 (dd, $^3J_{PH}$ = 13.1, 7.1 Hz, 6H, P-CH*Me*$_2$), 1.01 (s, 12H, BPin), 1.17 (dd, $^3J_{PH}$ = 16.2, 7.32 Hz, 6H, P-CH*Me*$_2$), 2.19 (m, 2H, P-*CH*Me$_2$), 3.02 (d, $^2J_{PH}$ = 9.7 Hz, 2H, P-CH$_2$), 6.61 (d, $^3J_{HH}$ = 6.7 Hz, 1H, Ar-CH), 6.94 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar-CH), 7.02 (t, $^3J_{HH}$ = 6.5 Hz, 1H, Ar-CH), 7.09

(m, 1H, Ar-CH), 7.21 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Ar-CH), 7.29 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Ar-CH), 11.02 (d, $^3J_{HH}$ = 6.3 Hz, 1H, Ar-CH). ^{13}C{^{1}H} NMR (125.71 MHz, benzene-d_6, 23 °C): δ 17.3 (s, P-CHMe$_2$), 18.4 (s, P-CHMe$_2$), 23.7 (m, P-CHMe$_2$), 33.6 (m, P-CH$_2$), 113.8 (m, Ar-H), 117.0 (s, Ar-H), 118.5 (s, Ar-H), 120.4 (s, Ar-H), 122.0 (s, Ar-H), 127.4 (s, Ar-CH), 156.9 (s, Ar-CH) ppm. ^{31}P{^{1}H} NMR (benzene-d_6, 23 °C): δ 86.2 (br s, P-CHMe$_2$). ^{11}B NMR (benzene-d_6, 23 °C): δ = 22.0 (br s, Co-BPin) ppm.

Preparation of [(^{iPr}PBipy)Co]$_2$(μ_2-H), 3-Co$_2$(μ_2-H). A 20 mL scintillation vial was charged with a stir bar, 0.250 g (0.60 mmol) of (^{iPr}PBipy)CoCl$_2$, and 5 mL of diethyl ether. A 1.0 M solution of NaBEt$_3$H in toluene (1.20 mL, 1.20 mmol) was then added dropwise to a solution of (^{iPr}PBipy)CoCl$_2$. The resulting mixture was stirred for 15 min at room temperature followed by filtration through Celite. Removal of the volatiles in vacuo furnished 0.130 g (63%) of the title [(^{iPr}PBipy)Co]$_2$(μ_2-H) as a dark purple solid. Anal. Calcd for $C_{34}H_{47}Co_2N_4P_2$: C, 59.05; H, 6.85; N, 8.10. Found: C, 58.59; H, 6.83; N, 7.99. ^{1}H NMR: δ = −17.97 (2H, $\Delta\nu_{1/2}$ = 31 Hz), −11.54 (2H, $\Delta\nu_{1/2}$ = 56 Hz), −0.62 (2H, $\Delta\nu_{1/2}$ = 22 Hz), −0.14 (2H, $\Delta\nu_{1/2}$ = 17 Hz), 0.03 (2H, $\Delta\nu_{1/2}$ = 23 Hz), 3.84 (2H, $\Delta\nu_{1/2}$ = 31 Hz), 4.18 (2H, $\Delta\nu_{1/2}$ = 22 Hz), 5.01 (2H, $\Delta\nu_{1/2}$ = 38 Hz), 5.56 (2H, $\Delta\nu_{1/2}$ = 47 Hz), 8.39 (2H, $\Delta\nu_{1/2}$ = 19 Hz), 12.13 (2H, $\Delta\nu_{1/2}$ = 15 Hz), 14.72 (2H, $\Delta\nu_{1/2}$ = 17 Hz), 15.43 (2H, $\Delta\nu_{1/2}$ = 22 Hz), 20.94 (2H, $\Delta\nu_{1/2}$ = 19 Hz), 49.81 (2H, $\Delta\nu_{1/2}$ = 56 Hz) ppm. Magnetic susceptibility (MSB): μ_{eff} = 1.9 μ_B.

Preparation of (Triphos)Fe(CO)$_2$, 5-Fe(CO)$_2$. A thick-walled glass vessel was charged with 2.5 g of mercury, approximately 10 mL of THF, and a stir bar. Sodium (0.012 g, 0.53 mmol) was cut into small pieces and added slowly to the rapidly stirred slurry. The resulting amalgam was stirred for an additional 30 min to ensure complete dissolution. A slurry of (Triphos)FeBr$_2$ (0.200 g, 0.27 mmol) in 10 mL of THF was added to the reaction vessel, which was then sealed. The resulting mixture was cooled to −196 °C, and the vessel was evacuated. One atmosphere of CO was admitted to the vessel, and the reaction mixture was stirred for 24 h. The resulting yellow mixture was then decanted away from the amalgam, and the volatiles were removed in vacuo. The resulting solid was dissolved in diethyl ether and passed through a pad of Celite. The solvent was removed in vacuo to yield 0.134 g (78%) of a yellow solid identified as (Triphos)Fe(CO)$_2$. Anal. Calcd for $C_{36}H_{35}FeO_2P_3$: C, 66.68; H, 5.44. Found: C, 66.91; H, 5.17. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): δ = 1.47−2.25 (m, 8H, P-CH$_2$), 6.86−7.15 (m, 18H, Ar-CH), 7.23−7.36 (m, 1H, Ar-CH), 7.47−7.56 (m, 2H, Ar-CH), 8.03 (m, 4H, Ar-CH). ^{13}C{^{1}H} NMR (125.71 MHz, benzene-d_6, 23 °C): δ = 30.0 (m, P-CH$_2$), 32.0 (m, P-CH$_2$), 128.7 (m, Ar CH), 129.3 (Ar CH), 129.6 (Ar CH), 130.5 (m, Ar CH), 130.9 (m, Ar CH), 133.1 (m, Ar CH), 138.8 (m, P-Ar C), 141.5 (m, P-Ar C). ^{31}P{^{1}H} NMR (300 MHz, benzene-d_6, 23 °C): δ = 96.55 (d), 134.20 (t) ppm. IR (benzene): νCO 1875, 1926 cm^{-1}.

Preparation of (^{iPr}PNN^{Dip})FeBr$_2$, 7-FeBr$_2$. A thick-walled vessel was charged with a stir bar, 0.338 g (1.57 mmol) of iron dibromide, 0.253 g (1.57 mmol) of 2-(diisopropylphosphino)ethanamine, 0.536 g (1.57 mmol) of 2-((2,6-diisopropylphenyl)imino)acenaphthylene-1-one, and 10 mL of tetrahydrofuran. The solution was stirred for approximately 16 h at 60 °C. The solution was layered with pentane, and the resulting precipitate was collected on a glass frit and washed with 50 mL of pentane, followed by 50 mL of diethyl ether. The collected solid was collected and dried in vacuo, yielding 0.970 g (88%) of an analytically pure brown solid identified as (^{iPr}PNN^{Dip})-FeBr$_2$. Anal. Calcd for $C_{32}H_{41}Br_2FeN_2P$: C, 54.88; H, 5.90; N, 4.00. Found: C, 55.07; H, 6.32; N, 4.38. Magnetic susceptibility (MSB): μ_{eff} = 4.4 μ_B.

Preparation of (^{iPr}PNN^{Dip})Fe(CO)$_2$, 7-Fe(CO)$_2$. A thick-walled vessel was charged with 3 g of mercury, approximately 10 mL of THF, and a stir bar. Sodium (0.02 g, 0.857 mmol) was cut into small pieces and added slowly to the rapidly stirred slurry. The resulting amalgam was stirred for an additional 30 min to ensure complete dissolution. A solution of (^{iPr}PNN^{Dip})FeBr$_2$ (0.300 g, 0.428 mmol) in 10 mL of THF was added to the reaction vessel, which was then sealed. The resulting mixture was cooled to −196 °C, and the vessel was evacuated. One atmosphere of CO was admitted, and the reaction mixture was stirred for 24 h. The resulting purple mixture was then decanted away from the amalgam, and the volatiles were removed in vacuo. The resulting solid was dissolved in diethyl ether and passed through a pad of Celite. The solvent was removed in vacuo to yield 0.232 g (90%) of a purple solid identified as (^{iPr}PNN^{Dip})Fe(CO)$_2$. Anal. Calcd for $C_{34}H_{41}FeN_2O_2P$: C, 68.46; H, 6.93; N, 4.70. Found: C, 68.22; H, 7.18; N, 4.54. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): δ = 0.82 (dd, $^3J_{PH}$ = 14.2 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P-CHMe$_2$), 0.93 (dd, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, P-CHMe$_2$), 1.02 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Ar-CHMe$_2$), 1.60 (d, $^3J_{HH}$ = 6.9 Hz, 6H, Ar-CHMe$_2$), 1.79 (m, 2H, P-CHMe$_2$), 2.03 (m, 2H, P-CH$_2$), 3.67 (m, 2H, Ar-CHMe$_2$), 3.88 (m, 2H, N-CH$_2$), 6.40 (d, $^3J_{HH}$ = 7.0 Hz, 1H, Ar-CH), 6.84 (d, $^3J_{HH}$ = 6.9 Hz, 1H, Ar-CH), 6.87 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Ar-CH) 7.20−7.45 (m, 6H, Ar-H) ppm. ^{13}C{^{1}H} NMR (125.71 MHz, benzene-d_6, 23 °C): δ = 18.3 (P-CHMe$_2$), 18.7 (P-CHMe$_2$), 24.9 (Ar-CHMe$_2$), 25.1 (Ar-CHMe$_2$), 28.0 (Ar-CHMe$_2$), 28.2 (d, P-CHMe$_2$), 29.0 (d, P-CH$_2$), 53.4 (d, N-CH$_2$), 119.5 (Ar-CH), 120.1 (Ar-CH), 124.0 (Ar-CH), 124.5 (Ar-CH), 125.0 (Ar-CH), 125.4 (Ar-CH), 126.6 (Ar-CH), 127.6 (Ar-CH), 130.6 (Ar-C), 132.0 (Ar-C), 132.3 (Ar-C), 136.3 (Ar-C), 140.6 (Ar-C), 141.3 (Ar-C), 151.5 (Ar-C), 156.6 (Ar-C), 219.7 (carbonyl) ppm. ^{31}P{^{1}H} NMR (300 MHz, benzene-d_6, 23 °C): δ = 111.0 (s) ppm. IR (benzene): νCO 1889, 1951 cm^{-1}.

Preparation of (^{iPr}PNN^{Dip})CoCl$_2$, 7-Cl$_2$. A Schlenck tube was charged with a stir bar, 0.500 g (3.85 mmol) of cobalt dichloride, 0.621 g (3.85 mmol) of 2-(diisopropylphosphino)ethanamine, 1.315 g (3.85 mmol) of 2-((2,6-diisopropylphenyl)imino)acenaphthylene-1-one, and 10 mL of tetrahydrofuran. The solution was stirred for 16 h at 60 °C. The solution was cooled, then layered with pentane, and the resulting precipitate was collected on a glass frit and washed with 50 mL of pentane, followed by 50 mL of diethyl ether. The isolated solid was collected, and any remaining volatiles were removed in vacuo, yielding 2.10 g (89%) of an analytically pure green solid identified as (^{iPr}PNN^{Dip})CoCl$_2$. Anal. Calcd for $C_{32}H_{41}Cl_2CoN_2P$: C, 62.54; H, 6.72; N, 4.55. Found: C, 61.99; H, 6.34; N, 4.50. Magnetic susceptibility (MSB): μ_{eff} = 4.3 μ_B.

Preparation of (^{iPr}PNN^{Dip})CoCH$_3$, 7-CH$_3$. A 20 mL scintillation vial was charged with a stir bar, 0.200 g (0.325 mmol) of (^{iPr}PNN^{Dip})CoCl$_2$, and 10 mL of tetrahydrofuran. The mixture was chilled in the freezer to −35 °C, and a 1.6 M solution of LiCH$_3$ in diethyl ether (0.407 mL, 0.651 mmol) was then added dropwise. The resulting dark purple solution was stirred for 15 min at room temperature before the volatiles were removed in vacuo. The product was extracted from the solid residue with diethyl ether and filtered through a plug of Celite. Removal of the solvent in vacuo yielded 0.120 g of a purple solid. Recrystallization from a diethyl ether solution at −35 °C furnished crystals suitable for X-ray diffraction. Anal. Calcd for $C_{33}H_{34}CoN_2P$: C, 70.95; H, 7.94; N, 5.01. Found: C, 70.86; H, 7.66; N, 4.55. ^{1}H NMR (benzene-d_6, 23 °C): δ −7.75 (m, 2H, N-CH$_2$), −1.41 (d, $^3J_{PH}$ = 8.2 Hz, 3H, Co-CH$_3$), 0.52 (dd, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, P-CHMe$_2$), 1.38 (d, $^3J_{HH}$ = 7.2 Hz, 6H, Ar-CHMe$_2$), 1.43 (d, $^3J_{HH}$ = 7.2 Hz, 6H, Ar-CHMe$_2$), 1.58 (dd, $^3J_{PH}$ = 12.8 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, P-CHMe$_2$), 2.91 (sept, $^3J_{HH}$ = 7.2 Hz, 2H, P-CHMe$_2$), 4.54 (m, 2H, P-CH$_2$), 5.72 (sept, $^3J_{HH}$ = 7.2 Hz, 2H, Ar-CHMe$_2$), 6.06 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar CH), 6.62 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Ar CH), 7.64 (d, $^3J_{HH}$ = 6.9 Hz, 1H, Ar-CH), 7.81 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ar-CH), 8.10 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Ar-CH), 8.15 (t, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-CH), 8.82 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar CH), 9.63 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar CH). ^{13}C{^{1}H} NMR (125.71 MHz, benzene-d_6, 23 °C): δ = 16.9 (P-CHMe$_2$), 18.3 (Ar-CHMe$_2$), 19.6 (P-CHMe$_2$), 24.4 (P-CHMe$_2$), 25.0 (Ar-CHMe$_2$), 27.5 (P-CHMe$_2$), 30.0 (Ar-CHMe$_2$), 65.1 (N-CH$_2$), 111.2 (Ar-CH), 117.8 (Ar-CH), 119.7 (Ar-CH), 124.0 (Ar-CH), 124.4 (Ar-CH), 126.7 (Ar-CH), 132.4 (Ar-C), 132.7 (Ar-CH), 133.4 (Ar-C), 136.7 (Ar-CH), 142.7 (Ar-C), 147.6 (Ar-C), 153.6 (Ar-C), 154.2 (Ar-C), 167.9 (Ar-C), 187.0 (Ar-C) ppm. ^{31}P{^{1}H} (300 MHz, benzene-d_6, 23 °C): δ = −24.6 (br s) ppm. ^{31}P{^{1}H} NMR (300 MHz, benzene-d_6, 23 °C): δ = −24.6 (br s) ppm.

Preparation of (^{iPr}PNN^{Mes})FeBr$_2$, 6-FeBr$_2$. A Schlenck tube was charged with a stir bar, 0.334 g (1.55 mmol) of iron dibromide, 0.250 g (1.55 mmol) of 2-(diisopropylphosphino)ethanamine, 0.464 g (1.55 mmol) of 2-(mesitylimino)acenaphthylene-1-one, and 10 mL of tetrahydrofuran. The solution was stirred for 16 h at 60 °C. The resulting mixture was layered with pentane, and the precipitate was collected on a glass frit and washed with 50 mL of pentane, followed by 50 mL of diethyl ether. The isolated solid was collected, and any remaining volatiles were removed in vacuo, yielding 0.943 g (92%) of an analytically pure green-brown solid identified as (^{iPr}PNN^{Mes})FeBr$_2$. Anal. Calcd for $C_{29}H_{35}Br_2FeN_2P$: C, 52.92; H, 5.36; N, 4.25. Found: C, 52.64; H, 5.55; N, 3.92. Magnetic susceptibility (MSB): μ_{eff} = 4.6 μ_B.

Preparation of (^{iPr}PNN^{Mes})Fe(CO)$_2$, 6-Fe(CO)$_2$. A thick-walled vessel was charged with 3 g of mercury, approximately 10 mL of THF, and a stir bar. Sodium (0.021 g, 0.912 mmol) was cut into small pieces and added slowly to the rapidly stirred slurry. The resulting amalgam was stirred for an additional 30 min to ensure complete dissolution. A solution of (^{iPr}PNN^{Mes})FeBr$_2$ (0.300 g, 0.456 mmol) in 10 mL of THF was added to the reaction vessel, which was then sealed. The resulting mixture was brought to −196 °C, and the vessel was evacuated. One atmosphere of CO was introduced, and the reaction mixture was stirred for 24 h. The resulting purple mixture was then decanted away from the amalgam, and the volatiles were removed in vacuo. The resulting solid was dissolved in diethyl ether and passed through a pad of Celite. The solvent was removed in vacuo to give 0.202 g (80%) of a purple solid identified as (^{iPr}PNN^{Mes})Fe(CO)$_2$. Anal. Calcd for $C_{31}H_{35}FeN_2O_2P$: C, 67.15; H, 6.36; N, 5.05. Found: C, 67.22; H, 6.18; N, 4.94. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): δ = 0.84 (dd, 6H, P-CH*Me*$_2$), 0.92 (dd, 6H, P-CH*Me*$_2$), 1.79 (m, 2H, P-*CH*Me$_2$), 2.02 (m, 2H, P-CH$_2$), 2.27 (s, 3H, Aryl p-CH$_3$), 2.48 (s, 6H, aryl o-CH$_3$), 3.87 (m, 2H, N-CH$_2$), 6.56 (d, 1H, Ar-CH), 6.87 (m, 1H, Ar-CH), 7.01 (s, 2H, aryl m-CH), 7.24 (m, 1H, Ar-CH), 7.27 (m, 1H, Ar-CH), 7.31 (m, 1H, Ar-CH), 7.38 (m, 1H, Ar-CH). ^{13}C{^{1}H} NMR (125.71 MHz, benzene-d_6, 23 °C): δ = 18.2 (Aryl m-CH$_3$), 18.6 (P-CH*Me*$_2$), 18.8 (P-CH*Me*$_2$), 21.1 (aryl p-CH$_3$), 28.1 (d, P-*CH*Me$_2$), 28.9 (d, P-CH$_2$), 53.5 (N−CH$_2$), 118.8 (Ar-CH), 119.1 (Ar-CH), 125.1 (2C, Ar-CH), 127.6 (Ar-CH), 128.6 (Ar-CH), 129.6 (aryl m-CH), 130.4 (Ar-C), 130.7 (Ar-C), 132.1 (Ar-C), 132.3 (Ar-C), 134.4 (Ar-C), 136.4 (Ar-C), 152.2 (Ar-C), 155.8 (Ar-C), 220.1 (d, CO) ppm. ^{31}P{^{1}H} NMR (300 MHz, benzene-d_6, 23 °C): δ = 112.2 (s) ppm. IR (benzene): νCO 1889, 1951 cm^{-1}.

Preparation of (^{iPr}PNN^{Mes})CoCl$_2$, 6-Cl$_2$. A Schlenck tube was charged with a stir bar, 0.500 g (3.85 mmol) of cobalt dichloride, 0.621 g (3.85 mmol) of 2-(diisopropylphosphino)ethanamine, 1.153 g (3.85 mmol) of 2-(mesitylimino)acenaphthylene-1-one, and 10 mL of tetrahydrofuran. The solution was stirred overnight (∼16 h) at 60 °C. The resulting mixture was layered with pentane, and the precipitate was collected on a glass frit and washed with 50 mL of pentane, followed by 50 mL of diethyl ether. The resulting solid was collected, and any remaining volatiles were removed in vacuo, yielding 1.89 g (86%) of an analytically pure green solid identified as (^{iPr}PNN^{Mes})CoCl$_2$. Anal. Calcd for $C_{29}H_{35}Cl_2CoN_2P$: C, 60.84; H, 6.16; N, 4.89. Found: C, 60.50; H, 6.27; N, 4.76. Magnetic susceptibility (MSB): μ_{eff} = 4.1 μ_B.

Preparation of (^{iPr}PNN^{Mes})CoCH$_3$, 6-CH$_3$. A 20 mL scintillation vial was charged with a stir bar, 0.150 g (0.262 mmol) of (^{iPr}PNN^{Mes})CoCl$_2$, and 10 mL of tetrahydrofuran. The mixture was chilled in the freezer to −35 °C. A 1.6 M solution of LiCH$_3$ in diethyl ether (0.328 mL, 0.524 mmol) was then added dropwise to the chilled solution of (^{iPr}PNN^{Mes})CoCl$_2$. The resulting dark purple solution was stirred for 15 min at room temperature before the volatiles were removed in vacuo. The product was extracted from the solid residue with diethyl ether and filtered through a plug of Celite. Removal of the solvent in vacuo yielded 0.094 g (69%) of the title product. Recrystallization from a diethyl ether solution at −35 °C furnished crystals suitable for X-ray diffraction. Anal. Calcd for $C_{30}H_{38}CoN_2P$: C, 69.75; H, 7.41; N, 5.42. Found: C, 69.35; H, 7.55; N, 5.38. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): δ −7.70 (dd, 2H, N-CH$_2$), −1.28 (d, $^3J_{PH}$ = 7.47, 3H, Co-CH$_3$), 0.51 (dd, $^3J_{PH}$ = 7.35, 6H, P-CHMe$_2$), 1.58 (d, $^3J_{PH}$ = 7.40, 6H, P-CHMe$_2$), 2.66 (s, 3H, aryl p-CH$_3$), 2.91 (m, 2H, P-CHMe$_2$), 3.43 (s, 6H, aryl o-CH$_3$), 4.48 (m, 2H, P-CH$_2$), 6.07 (t, 1H, Ar CH), 6.64 (t, 1H, Ar CH), 7.43 (s, 2H, Aryl m-CH), 7.67 (d, 1H, Ar CH), 8.27 (d, 1H, Ar CH), 8.80 (d, 1H, Ar CH), 9.64 (d, 1H, Ar CH). ^{13}C{^{1}H} NMR (125.71 MHz, benzene-d_6, 23 °C): δ = 16.9 (d, ^{i}Pr CH$_3$), 18.3 (Ar CH$_3$), 19.6 (d, ^{i}Pr CH$_3$), 21.1 (Ar CH$_3$), 22.1 (^{i}Pr CH), 27.4 (d, P-CH$_2$), 64.9 (N-CH$_2$), 110.9 (Ar-CH), 117.5 (Ar-CH), 118.6 (Ar-CH), 120.9 (Ar-C), 124.0 (Ar-CH), 129.9 (Ar-CH), 133.1 (Ar-CH), 134.5 (Ar-C), 136.7 (Ar-CH), 142.6 (Ar-C), 147.3 (Ar-C), 153.3 (Ar-C), 154.2 (Ar-C), 168.1 (N═C), 187.0 (N═C) ppm. ^{31}P{^{1}H} NMR (300 MHz, benzene-d_6, 23 °C): δ = −21.5 (br s) ppm.

Preparation of (^{Phen}PNN^{Dip})Fe(CO)$_2$, 8-Fe(CO)$_2$. A thick-walled vessel was charged with 3.0 g of mercury, approximately 10 mL of THF, and a stir bar. Sodium (0.018 g, 0.78 mmol) was cut into small pieces and added slowly to the rapidly stirred slurry. The resulting amalgam was stirred for an additional 30 min to ensure complete dissolution. A solution of (^{Phen}PNN^{Dip})FeBr$_2$ (0.300 g, 0.39 mmol) in 10 mL of THF was added to the reaction vessel, which was then sealed. The resulting mixture was brought to −196 °C, and the vessel was evacuated. One atmosphere of CO was introduced, and the reaction mixture was stirred for 24 h. The resulting purple mixture was then decanted away from the amalgam, and the volatiles were removed in vacuo. The resulting solid was dissolved in diethyl ether and passed through a pad of Celite. The solvent was removed in vacuo to give 0.222 g (85%) of a purple solid identified as (^{Phen}PNN^{Dip})Fe(CO)$_2$. Anal. Calcd for $C_{40}H_{37}FeN_2O_2P$: C, 72.29; H, 5.61; N, 4.22. Found: C, 72.52; H, 5.87; N, 3.97. ^{1}H NMR (400 MHz, benzene-d_6, 23 °C): δ = 1.04 (d, $^3J_{HH}$ = 6.8 Hz, 6H, Ar-^{i}Pr), 1.59(d, $^3J_{HH}$ = 6.7 Hz, 6H, Ar-^{i}Pr), 2.81 (m, 2H, P-CH$_2$), 3.76 (m, 2H, ^{i}Pr CH), 3.80 (m, 2H, N-CH$_2$), 6.46 (d, $^3J_{HH}$ = 7.0 Hz 1H, Ar-H), 6.87 (t, $^3J_{HH}$ = 7.7 Hz 1H, Ar-H), 7.00 (br m, 6H, Ar-H), 7.17 (br m, 2H, Ar-H), 7.28 (d, $^3J_{HH}$ = 8.0 Hz 1H, Ar-H), 7.36 (br m, 4H, Ar-H), 7.51 (br m, 4H, Ar-H). ^{13}C{^{1}H} NMR (125.71 MHz, benzene-d_6, 23 °C): δ = 25.0 (^{i}Pr CH$_3$), 28.1 (^{i}Pr CH), 35.8 (m, P-CH$_2$), 51.4 (N-CH$_2$), 119.7 (Ar-CH), 120.3 (Ar-CH), 124.1 (Ar-CH), 125.2 (Ar-CH), 125.4 (Ar-CH), 126.8 (Ar-CH), 127.7 (Ar-CH), 128.4 (Ar-CH), 128.6 (Ar-CH), 128.8 (Ar-CH), 128.9 (Ar-CH), 130.3 (Ar-CH), 130.6 (Ar-C), 131.8 (Ar-C), 132.1 (Ar-C), 132.3 (Ar-CH), 132.4 (Ar-CH), 133.2 (m, Ar-CH), 135.7, 136.4, 139.7, 141.3, 145.0, 151.4, 152.0, 156.9, 218.2 (m, CO) ppm. ^{31}P{^{1}H} NMR (300 MHz, C_6D_6, 23 °C): δ = 89.5 (s) ppm. IR (benzene-d_6): νCO 1896, 1960 cm^{-1}.

Preparation of (^{Phen}PNN^{Dip})CoCl$_2$, 8-Cl$_2$. A Schlenck tube was charged with a stir bar, 0.500 g (3.85 mmol) of cobalt dichloride, 0.883 g (3.85 mmol) of 2-(diphenylphosphino)ethanamine, 1.315 g (3.85 mmol) of 2-((2,6-diisopropylphenyl)imino)acenaphthylene-1-one, and 10 mL of tetrahydrofuran. The solution was stirred overnight (∼16 h) at 60 °C. The resulting mixture was layered with pentane, and the precipitate was collected on a glass frit and washed with 50 mL of pentane, followed by 50 mL of diethyl ether. The resulting solid was collected, and any remaining volatiles were removed in vacuo, yielding 2.18 g (83%) of an analytically pure orange-brown solid identified as (^{Phen}PNN^{Dip})CoCl$_2$. Anal. Calcd for $C_{38}H_{37}Cl_2CoN_2P$: C, 66.87; H, 5.46; N, 4.10. Found: C, 66.46; H, 5.52; N, 3.73. Magnetic susceptibility (MSB): μ_{eff} = 4.1 μ_B.

Preparation of (^{Phen}PNN^{Dip})CoCH$_3$, 8-CH$_3$. A 20 mL scintillation vial was charged with a stir bar, 0.150 g (0.220 mmol) of (^{Phen}PNN^{Dip})CoCl$_2$, and 10 mL of tetrahydrofuran. The mixture was chilled in the freezer to −35 °C. A 1.6 M solution of LiCH$_3$ in diethyl ether (0.275 mL, 0.440 mmol) was then added dropwise to the chilled solution of (^{Phen}PNN^{Dip})CoCl$_2$. The resulting dark purple solution was stirred for 15 min at room temperature before the volatiles were removed in vacuo. The product was extracted from the solid residue with diethyl ether and filtered through a plug of Celite. Removal of the solvent in vacuo yielded 0.076 g (55%) of the title product. Anal. Calcd for $C_{39}H_{40}CoN_2P$: C, 74.75; H, 6.43; N, 4.47. Found: C, 75.00; H, 5.99; N, 4.21. ^{1}H NMR (300 MHz, benzene-d_6, 23 °C): δ = −6.60 (br s, 2H, N−CH$_2$), −1.01 (d, 3H, Co-CH$_3$), 1.36 (br s, 12H, ^{i}Pr CH$_3$), 4.88 (br s, 2H, P-CH$_2$), 5.67 (m, 2H, ^{i}Pr CH), 6.13 (br s, 1H, Ar), 6.67 (t, 1H, Ar), 7.04 (m, 4H, Ar), 7.57 (m, 6H, Ar), 7.76 (d, 2H, Ar), 8.10 (br s, 2H, Ar), 8.72 (d, 1H, Ar), 9.47 (d, 1H, Ar), 1H not located. ^{13}C{^{1}H} NMR (125.71 MHz, benzene-d_6, 23 °C): δ = 24.3 (Ar-CH*Me*$_2$), 25.1 (Ar-*CH*Me$_2$), 30.2 (P-CH2), 117.8 (Ar-CH), 120.1 (Ar-CH), 123.2 (Ar-CH), 124.5 (Ar-CH), 126.9 (Ar-CH), 127.5 (Ar-

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CH), 128.7 (Ar-CH), 128.8 (Ar-CH), 129.8 (Ar-CH), 132.6 (Ar-CH), 133.5 (Ar-CH) ppm; N-CH$_2$, Co-CH$_3$, and Ar−C not located. ^{31}P{^{1}H} NMR (300 MHz, benzene-*d*$_6$, 23 °C): $\delta = -37.8$ (br s) ppm.

Preparation of ($^{\text{Phen}}$PNN$^{\text{Dip}}$)CoCH$_2$SiMe$_3$, 8-CH$_2$SiMe$_3$. A 20 mL scintillation vial was charged with a stir bar, 0.100 g (0.147 mmol) of ($^{\text{Phen}}$PNN$^{\text{Dip}}$)CoCl$_2$, and 10 mL of tetrahydrofuran. The mixture was chilled in the freezer to −35 °C. A separate vial was charged with 0.027 g (0.293 mmol) of ((trimethylsilyl)methyl)lithium and 5 mL of diethyl ether. The lithium reagent was then added dropwise to the chilled solution of ($^{\text{Phen}}$PNN$^{\text{Dip}}$)CoCl$_2$. The resulting dark purple solution was stirred for 15 min at room temperature before the volatiles were removed in vacuo. The product was extracted from the solid residue with diethyl ether and filtered through a plug of Celite. Removal of the solvent in vacuo yielded 0.120 g of the title product. Recrystallization from a diethyl ether solution at −35 °C furnished crystals suitable for X-ray diffraction. Anal. Calcd for $C_{42}H_{48}CoN_2PSi$: C, 72.20; H, 6.92; N, 4.01. Found: C, 72.20; H, 6.80; N, 3.62. ^{1}H NMR (300 MHz, benzene-*d*$_6$, 23 °C): $\delta = -6.57$ (br s, 2H, N-CH$_2$), −1.00 (s, 9H, Co-CH$_2$SiMe$_3$), −0.11 (br s, 2H, Co-CH$_2$SiMe$_3$), 1.29 (d, 6H, ^{i}Pr CH$_3$), 1.64 (d, 6H, ^{i}Pr CH$_3$), 4.88 (br s, 2H, P-CH^2), 5.68 (m, 2H, ^{i}Pr CH), 6.08 (t, 1H, Ar), 6.64 (t, 1H, Ar), 7.47 (d, 1H, Ar), 7.80 (br s, 8H, Ar) 8.13 (t, 1H, Ar), 8.68 (d, 1H, Ar), 9.94 (d, 1H, Ar), 4H not located. ^{13}C{^{1}H} NMR (125.71 MHz, benzene-*d*$_6$, 23 °C): $\delta =$ 3.2 (s, Si-CH$_3$), 22.7 (s, P-CH$_2$), 24.7 (Ar CH*Me*$_2$), 26.1 (s, Ar CH*Me*$_2$), 30.01 (s, *CH*Me$_2$), 61.1 (N-CH$_2$), 111.6 (Ar-CH), 117.9 (Ar-CH), 120.5 (Ar-CH), 124.0 (Ar-CH), 124.9 (Ar-CH), 127.3 (Ar-CH), 128.8 (Ar-CH), 130.1 (Ar-CH), 131.8 (Ar-C), 132.4 (Ar-CH), 133.1 (Ar-C), 134.5 (Ar-CH), 136.2 (Ar-CH), 141.9 (Ar-C), 147.5 (Ar-C), 152.0 (Ar-C), 153.1 (Ar-C), 167.7 (N═C), 183.9 (N═C) ppm. ^{31}P{^{1}H} NMR (300 MHz, benzene-*d*$_6$, 23 °C): $\delta = -37.8$ (br s) ppm.

General Procedure for in Situ Activated Borylation with B$_2$Pin$_2$ or HBPin. A scintillation vial was charged with 0.140 g (0.55 mmol, 1 equiv) of B$_2$Pin$_2$, 0.45 g (0.55 mmol, 1 equiv) of 2-methylfuran, 0.062 g (0.55 mmol, 1 equiv) of cyclooctane, 0.2 mL of THF, 0.012 g (0.028 mmol, 0.05 equiv) of ($^{\text{iPr}}$PBipy)CoCl$_2$, and 0.055 mL (0.055 mmol, 0.1 equiv) of a 1 M solution of NaBEt$_3$H in toluene. The vial was then capped and its contents were stirred at 23 °C for 24 h. The reaction mixture was quenched by exposing the mixture to air, and the solvent removed in vacuo. The resulting residue was purified by extraction into hexane and passage through a silica plug. The isolated compound was analyzed by ^{1}H and ^{13}C NMR spectroscopy. An identical procedure was followed using HBPin as the stoichiometric boron source.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional NMR spectroscopic, X-ray crystallographic, and DFT outputs. Crystallographic data available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Mkhalid, I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.

(2) Hartwig, J. F. *Acc. Chem. Res.* **2011**, *45*, 864.

(3) (a) Hall, D. G. *Boronic Acids*; Wiley-VCH: Weinheim, Germany, 2005. (b) Dick, G. R.; Woerly, E. M.; Burke, M. D. *Angew. Chem., Int. Ed.* **2012**, *51*, 2667.

(4) (a) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (b) Takagi, J.; Sato, K.; Hartwig, J. F.; Ishiyama, T.; Miyaura, N. *Tetrahedron Lett.* **2002**, *43*, 5649. (c) Ishiyama, T.; Takagi, J.; Hartwig, J. F.; Miyaura, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 3056. (d) Ishiyama, T.; Nobuta, Y.; Hartwig, J. F.; Miyaura, N. *Chem. Commun.* **2003**, 2924.

(5) Tajuddin, H.; Harrisson, P.; Bitterlich, B.; Collings, J. C.; Sim, N.; Batsanov, A. S.; Cheung, M. S.; Kawamorita, S.; Maxwell, A. C.; Shukla, L.; Morris, J.; Lin, Z.; Marder, T. B.; Steel, P. G. *Chem. Sci.* **2012**, *3*, 3505.

(6) (a) Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 7534. (b) Kallepalli, V. A.; Shi, F.; Paul, S.; Onyeozili, E. N.; Maleczka, R. E.; Smith, M. R. *J. Org. Chem.* **2009**, *74*, 9199. (c) Ros, A.; Lopez-Rodriguez, R.; Estepa, B.; Alvarez, E.; Fernandez, R.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 4573.

(7) Preshlock, S. M.; Ghaffari, B.; Maligres, P. E.; Krska, S. W.; Maleczka, R. E.; Smith, M. R. *J. Am. Chem. Soc.* **2013**, *135*, 7572.

(8) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyuara, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 14263.

(9) (a) Vanchura, B. A.; Preshlock, S. M.; Roosen, P. C.; Kallepalli, V. A.; Staples, R. J.; Maleczka, R. E.; Singleton, D. A.; Smith, M. R. *Chem. Commun.* **2010**, *46*, 7724. (b) Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. *J. Am. Chem. Soc.* **2003**, *125*, 16114.

(10) Chotana, G. A.; Vanchura, B. A.; Tse, M. K.; Staples, R. J.; Maleczka, R. E.; Smith, M. R. *Chem. Commun.* **2009**, 5731.

(11) (a) Kawamorita, S.; Murakami, R.; Iwai, T.; Sawamura, M. *J. Am. Chem. Soc.* **2013**, *135*, 2947. (b) Kawamorita, S.; Miyzaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2012**, *134*, 12934. (c) Kawamorita, S.; Miyzaki, T.; Ohmiya, H.; Iwai, T.; Sawamura, M. *J. Am. Chem. Soc.* **2011**, *133*, 19310.

(12) Yinghuai, Z.; Chenyan, K.; Peng, A. T.; Emi, A.; Monalisa, W.; Louis, L. K.; Hosmane, N. S.; Maguire, J. A. *Inorg. Chem.* **2008**, *47*, 5756.

(13) (a) Waltz, K. M.; He, W.; Muhoro, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11357. (b) Waltz, K. M.; Muhoro, C. N.; Hartwig, J. F. *Organometallics* **1999**, *18*, 3383.

(14) Mazzacano, T. J.; Mankad, N. P. *J. Am. Chem. Soc.* **2013**, *135*, 17258.

(15) Yan, G.; Jiang, Y.; Kuang, C.; Wang, S.; Liu, H.; Zhang, Y.; Wang, J. *Chem. Commun.* **2010**, *46*, 3170.

(16) Hatanaka, T.; Ohki, Y.; Tatsumi, K. *Chem.—Asian J.* **2010**, *5*, 1657.

(17) Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2006**, *45*, 7252.

(18) Khaskin, E.; Diskin-Posner, Y.; Weiner, L.; Leitus, G.; Milstein, D. *Chem. Commun.* **2013**, *49*, 2771.

(19) Semproni, S. P.; Atienza, C. C. H.; Chirik, P. J. *Chem. Sci.* **2014**, *5*, 1956.

(20) Semproni, S. P.; Milsmann, C.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 9211.

(21) Obligacion, J. V.; Semproni, S. P.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 4133.

(22) Bouwkamp, M. W.; Bowman, A. C.; Lokbovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13340.

(23) Chirik, P. J.; Tondreau, A. M.; Delis, J. G. P.; Lewis, K. M.; Weller, K. J.; Nye, S. A. U.S. Patent Application 20120130106A1.

(24) Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915.

(25) Zhang, L.; Peng, D.; Leng, X.; Huang, Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 3676.

(26) Greenhalgh, M. D.; Thomas, S. P. *Chem. Commun.* **2013**, *49*, 11230.

(27) Zhang, L.; Zuo, Z.; Leng, X.; Huang, Z. *Angew. Chem., Int. Ed.* **2014**, *53*, 2696−2700.

(28) Zhang, L.; Zuo, Z.; Wan, X.; Huang, Z. *J. Am. Chem. Soc.* **2014**, *136*, 15501.

(29) Obligacion, J. V.; Chirik, P. J. *Org. Lett.* **2013**, *15*, 2680.
(30) Obligacion, J. V.; Chirik, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 19107.
(31) Zhang, G.; Scott, B. L.; Hanson, S. K. *Angew. Chem., Int. Ed.* **2012**, *51*, 12102−12106.
(32) Balaraman, E.; Gnanaprakasm, B.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 16756.
(33) Schmiege, B. M.; Carney, M. J.; Small, B. L.; Gerlach, D. L.; Halfen, J. A. *Dalton Trans.* **2007**, 2547−2562.
(34) Ray, K.; Petrenko, T.; Wieghardt, K.; Neese, F. *Dalton Trans.* **2007**, 1552−1566.
(35) Scarborough, C. C.; Wieghardt, K. *Inorg. Chem.* **2011**, *50*, 9773−9793.
(36) Kaim, W. *Inorg. Chem.* **2011**, *50*, 9752−9765.
(37) Kong, S.; Song, K.; Liang, T.; Guo, C.-Y.; Sun, W.-H.; Redshaw, C. *Dalton Trans.* **2013**, *42*, 9176−9187.
(38) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Fukin, G. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3294−3298.
(39) Baggio, S.; Baggio, R.; Mombrú, A. W. *Acta Crystallogr. C* **1998**, *54*, 1900−1902.
(40) Dehghani, A.; M. Amini, M.; Najafi, E.; Tadjarodi, A.; Notash, B. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2012**, *68*, m811−m811.
(41) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.
(42) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(43) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.
(44) Neese, F. *JBIC J. Biol. Inorg. Chem.* **2006**, *11*, 702−711.
(45) Rozenel, S. S.; Padilla, R.; Arnold, J. *Inorg. Chem.* **2013**, *52*, 11544−11550.
(46) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 4290.
(47) Lin, T. P.; Peters, J. C. *J. Am. Chem. Soc.* **2014**, *136*, 13672−13683.
(48) Chen, L.; Kountz, D. J.; Meek, D. W. *Organometallics* **1985**, *4*, 598.
(49) Hanson, B. E.; Fanwick, P. E.; Mancinila, J. S. *Inorg. Chem.* **1982**, *21*, 3811.
(50) Field, J. S.; Haines, R. J.; Rix, L. A. *J. Chem. Soc., Dalton Trans.* **1990**, 2311.
(51) Using the program Scoeff by Eckhard Bill.
(52) Bencini, A.; Gatteschi, D. *Electron Paramagnetic Resonance of Exchange Coupled Systems*; Springer Verlag: Berlin, 1990.
(53) Russell, S. K.; Milsmann, C.; Lobkovsky, E.; Weyhermüller, T.; Chirik, P. J. *Inorg. Chem.* **2011**, *50*, 3159.
(54) Koehne, I.; Schmeier, T. J.; Bielinski, E. A.; Pan, C. J.; Lagaditis, P. O.; Bernskoetter, W. H.; Takase, M. K.; Würtele, C.; Hazari, N.; Schneider, S. *Inorg. Chem.* **2014**, *53*, 2133.
(55) Bart, S. C.; Chłopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.
(56) Zell, T.; Milko, P.; Fillman, K. L.; Diskin-Posner, Y.; Bendikov, T.; Iron, M. A.; Leitus, G.; Ben-David, Y.; Neidig, M. L.; Milstein, D. *Chem.—Eur. J.* **2014**, *20*, 4403.
(57) Darmon, J. M.; Turner, Z. R.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2012**, *31*, 2275.
(58) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.
(59) Rozenel, S. S.; Kerr, J. B.; Arnold, J. *Dalton Trans.* **2011**, *40*, 10397.
(60) Grutters, M. M. P.; van der Vlugt, J. I.; Pei, Y.; Mills, A. M.; Lutz, M.; Spek, A. L.; Müller, C.; Moberg, C.; Vogt, D. *Adv. Synth. Catal.* **2009**, *351*, 2199−2208.
(61) Mukhopadhyay, T. K.; Feller, R. K.; Rein, F. N.; Henson, N. J.; Smythe, N. C.; Trovitch, R. J.; Gordon, J. C. *Chem. Commun.* **2012**, *48*, 8670−8672.
(62) Small, B. L.; Rios, R.; Fernandez, E. R.; Carney, M. J. *Organometallics* **2007**, *26*, 1744−1749.
(63) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.
(64) Neese, F. *Orca - an ab Initio, DFT and Semiempirical Electronic Structure Package*, Version 2.8, Revision 2287; Institut für Physikalische und Theoretische Chemie, Universität Bonn: Bonn, Germany, November 2010.
(65) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.
(66) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(67) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(68) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
(69) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.
(70) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
(71) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. *Chem. Phys.* **2009**, *356*, 98.
(72) Kossmann, S.; Neese, F. *Chem. Phys. Lett.* **2009**, *481*, 240.
(73) Neese, F. *J. Comput. Chem.* **2003**, *24*, 1740.
(74) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119.
(75) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283−S42.
(76) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652.
(77) Ginsberg, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 111.
(78) Noodleman, L.; Peng, C. Y.; Case, D. A.; Mouesca, J. M. *Coord. Chem. Rev.* **1995**, *144*, 199.
(79) Kirchner, B.; Wennmohs, F.; Ye, S.; Neese, F. *Curr. Opin. Chem. Biol.* **2007**, *11*, 134.
(80) *Molekel*, Advanced Interactive 3D-Graphics for Molecular Sciences, available at http://www.cscs.ch/molkel/.