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Understanding the Mechanisms of Cobalt-Catalyzed Hydrogenation and Dehydrogenation Reactions

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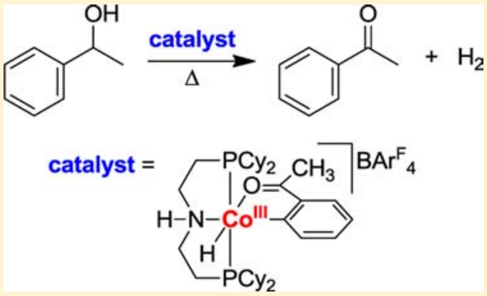
Ⓢ *Supporting Information*



ABSTRACT: Cobalt(II) alkyl complexes of aliphatic PNP pincer ligands have been synthesized and characterized. The cationic cobalt(II) alkyl complex $[(PNHP^{Cy})Co(CH_2SiMe_3)]BAr^F_4$ (**4**) ($PNHP^{Cy}$ = bis[(2-dicyclohexylphosphino)ethyl]amine) is an active precatalyst for the hydrogenation of olefins and ketones and the acceptorless dehydrogenation of alcohols. To elucidate the possible involvement of the N−H group on the pincer ligand in the catalysis via a metal−ligand cooperative interaction, the reactivities of **4** and $[(PNMeP^{Cy})Co(CH_2SiMe_3)]BAr^F_4$ (**7**) were compared. Complex **7** was found to be an active precatalyst for the hydrogenation of olefins. In contrast, no catalytic activity was observed using **7** as a precatalyst for the hydrogenation of acetophenone under mild conditions. For the acceptorless dehydrogenation of 1-phenylethanol, complex **7** displayed similar activity to complex **4**, affording acetophenone in high yield. When the acceptorless dehydrogenation of 1-phenylethanol with precatalyst **4** was monitored by NMR spectroscopy, the formation of the cobalt(III) acetylphenyl hydride complex $[(PNHP^{Cy})Co^{III}(\kappa^2\text{-}O,C\text{-}C_6H_4C(O)CH_3)(H)]BAr^F_4$ (**13**) was detected. Isolated complex **13** was found to be an effective catalyst for the acceptorless dehydrogenation of alcohols, implicating **13** as a catalyst resting state during the alcohol dehydrogenation reaction. Complex **13** catalyzed the hydrogenation of styrene but showed no catalytic activity for the room temperature hydrogenation of acetophenone. These results support the involvement of metal−ligand cooperativity in the room temperature hydrogenation of ketones but not the hydrogenation of olefins or the acceptorless dehydrogenation of alcohols. Mechanisms consistent with these observations are presented for the cobalt-catalyzed hydrogenation of olefins and ketones and the acceptorless dehydrogenation of alcohols.

■ INTRODUCTION

An important emerging goal of sustainable chemistry is the discovery of earth-abundant metal alternatives to precious metal catalysts.[1] The use of base-metal catalysts is particularly advantageous for large-scale and industrial applications, where the scarcity and cost of precious metals can be problematic. However, there are major challenges associated with the design of earth-abundant metal catalysts. The propensity of first-row transition metals to react by one-electron pathways unavailable to precious metals can make it difficult to predict and control catalytic reactivity. The paramagnetic nature of many earth-abundant metal complexes can also render identification and characterization of active catalysts and intermediates difficult.[2,3]

Nevertheless, significant recent advances have been made in the development of homogeneous earth-abundant metal hydrogenation catalysts.[4−8] Chirik and co-workers have designed iron catalysts of bis(imino)pyridine ligands capable of the rapid hydrogenation of olefins at ambient temperatures and pressures.[9] Enantioselective hydrogenation of *gem*-disubstituted alkenes was then achieved using a related cobalt analogue of a C_1 symmetric bis(imino)pyridine ligand.[10] Base metal hydrogenation catalysts are not limited to alkenes, as iron catalysts for the selective hydrogenation of ketones have also recently emerged.[11] Casey and co-workers developed a hydroxycyclopentadienyl iron hydride catalyst for the hydrogenation of ketones and aldehydes under mild conditions,[12] and more recent work by Milstein indicates that iron hydride complexes of a PNP pincer ligand are also highly effective catalysts for ketone hydrogenation.[13] For both iron systems, the catalytic hydrogenation of C═O bonds is proposed to proceed through mechanisms involving metal−ligand cooperativity, where the metal center delivers a hydride and a ligand delivers a proton to the substrate.[12,13] While promising, these previous examples of cobalt and iron catalysts have all been chemoselective, effective for the hydrogenation of either C═C or C═O bonds, but not both.

Recently, we reported a versatile cobalt(II) alkyl precatalyst $[(PNHP^{Cy})Co(CH_2SiMe_3)]BAr^F_4$ (**4**) for the hydrogenation of olefins, ketones, aldehydes, and imines.[14] The cobalt catalyst displayed high hydrogenation activities under mild conditions (25−60 °C, 1−4 atm H_2) and exhibited a broad functional group tolerance.[14] Whereas other earth-abundant metal catalysts are chemoselective, the cobalt catalyst is unique in that it is effective for the hydrogenation of a wide range of substrates.

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Subsequent studies found that the cobalt(II) alkyl complex **4** is also an active precatalyst for the acceptorless dehydrogenation of alcohols.[15] Acceptorless alcohol dehydrogenation has been gaining attention in a variety of important applications, including hydrogen production from biomass and the oxidant-free synthesis of ketones, esters, and amides.[16−18] However, previous catalysts for the acceptorless dehydrogenation of alcohols have been limited to precious metals, and complex **4** is the first example of a homogeneous earth abundant metal catalyst for this reaction.[19] A number of secondary alcohols were dehydrogenated in high yields using precatalyst **4** (5 mol %) (120 °C, 24−48 h).[15]

Despite the promise of cobalt complex **4** as a precatalyst, important details regarding the catalytic reactions remained unclear. The cobalt oxidation states and potential intermediates involved in the catalytic cycles were not well understood. We envisioned that hydrogenation and dehydrogenation reactions using **4** could proceed by metal−ligand cooperativity, as the aliphatic PNHP^{R} pincer ligand has been postulated to participate in catalytic reactions of related precious metal complexes.[20−22] Given the paucity of mechanistic information underlying this new class of catalysts, a better understanding of the fundamental steps involved in the catalytic hydrogenation and dehydrogenation reactions could greatly facilitate catalyst development and optimization.

This work presents details of the synthesis of cobalt(II) alkyl complexes and their use as precatalysts for hydrogenation and dehydrogenation reactions. The catalytic reaction mechanisms have been investigated in detail and the results suggest that the hydrogenation of olefins and ketones and the dehydrogenation of alcohols proceed by different pathways. In the acceptorless dehydrogenation of alcohols, a rare stable cobalt(III) aryl hydride product of C−H bond activation has been isolated and demonstrated to be a kinetically competent catalyst. In addition, our experiments provide surprising evidence that metal−ligand cooperativity is not required for the hydrogenation of olefins or the acceptorless dehydrogenation of alcohols. In contrast, metal−ligand bifunctional catalysis is implicated in the reduction of ketones. Mechanisms are proposed for the catalytic hydrogenation and dehydrogenation reactions, providing new insights for designing and enhancing the effectiveness of earth-abundant metal catalysts.

■ RESULTS

Synthesis and Characterization of Cobalt(II) Alkyl Precatalysts. In previous work, Fryzuk and co-workers reported the synthesis of the unusual square planar d^{7}-cobalt(II) alkyl complex $(N(SiMe_2CH_2PPh_2)_2)Co(CH_2SiMe_3)$ (**1**).[23] Complex **1** has a low-spin electronic configuration and a magnetic moment of $\mu_{eff} = 2.1\ \mu_B$.[23] The reaction of **1** with alkyl halides was studied to provide insight into the vitamin B_{12} active site,[23] but little else is known about the reactivity of **1**.

We were interested in further exploring the chemistry of this rare class of square planar d^{7}-cobalt(II) alkyl complexes and found that reaction of the aliphatic pincer ligand PNHP^{Cy} (PNHP^{Cy} = bis[(2-dicyclohexylphosphino)ethyl]amine) with $(pyr)_2Co(CH_2SiMe_3)_2$ afforded the neutral cobalt(II) alkyl complex $(PNP^{Cy})Co(CH_2SiMe_3)$ (**2**) (Figure 1).[14] The ^{1}H NMR spectrum of complex **2** displayed a broad signal at −5.26 ppm, corresponding to the $Si(CH_3)_3$ protons. Complex **2** has a square planar geometry in the solid state and a solution-state magnetic moment ($\mu_{eff} = 2.2\ \mu_B$) consistent with a low-spin d^{7} cobalt(II) center.[14,24,25]

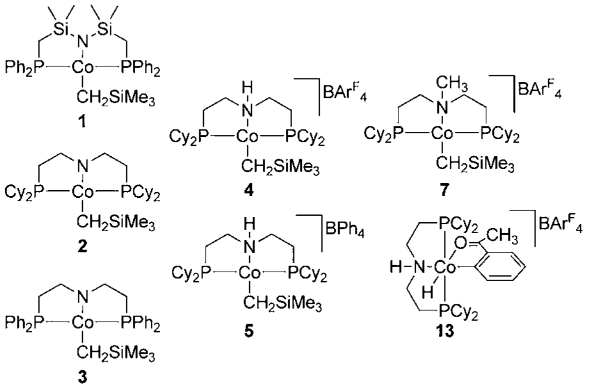


Figure 1. Cobalt(II) alkyl complex **1** reported by Fryzuk and co-workers[23] and cobalt precatalysts **2**−**5**, **7**, and **13**.

Using an analogous procedure, we prepared the phenyl-substituted derivative $(PNP^{Ph})Co(CH_2SiMe_3)$ (**3**) (PNHP^{Ph} = bis[(2-diphenylphosphino)ethyl]amine). Dark-red complex **3** was isolated in 72% yield and characterized by ^{1}H NMR and UV−vis spectroscopy and X-ray crystallography.

The solution state magnetic moment of **3** ($\mu_{eff} = 2.1\ \mu_B$) is quite similar to that of both complex **2** and Fryzuk's complex **1**.[23] The X-ray structure of complex **3** is shown in Figure 2. The distance between the cobalt center and the central nitrogen on the pincer ligand is 1.866(1) Å, close in value to that of **2** (1.880(3) Å) and consistent with an amido nitrogen.

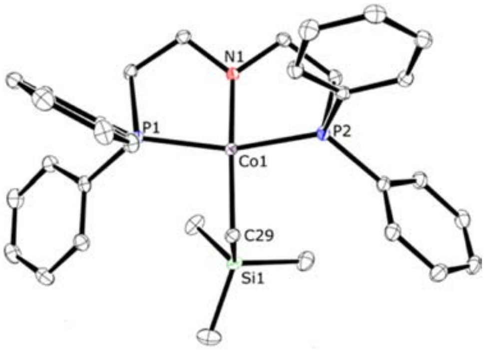


Figure 2. X-ray structure of complex **3** (thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): Co1−N1 = 1.866(1), Co1−C29 = 1.996(2), Co1−P1 = 2.195(1), Co1−P2 = 2.172(1), N1−Co1−C29 = 168.0(1), N1−Co1−P2 = 83.1(1), C29−Co1−P2 = 97.5(1), N1−Co1−P1 = 84.6(1), C29−Co1−P1 = 97.8(1), P2−Co1−P1 = 159.9(1).

Addition of $H[BAr^{F}_4]\cdot(Et_2O)_2$ (BAr^{F}_4 = $B(3,5\text{-}(CF_3)_2C_6H_3)_4$) to a solution of the neutral cobalt(II) complex **2** afforded the cationic alkyl complex $[(PNHP^{Cy})Co(CH_2SiMe_3)]BAr^{F}_4$ (**4**) in 85% yield.[14] The tetraphenylborate analogue $[(PNHP^{Cy})Co(CH_2SiMe_3)]BPh_4$ (**5**) was also prepared by the reaction of **2** with $[HNEt_3][BPh_4]$ in THF solution. Complexes **4** and **5** were characterized by ^{1}H NMR and IR spectroscopy, UV−vis spectroscopy, and X-ray crystallography. The ^{1}H NMR spectrum of **5** shows a broad signal at −21.12 ppm, corresponding to the $Si(CH_3)_3$ protons on the alkyl ligand. The X-ray structure of **5** is shown in Figure 3. In the solid state, both complexes **4** and **5** have distorted square planar structures. The distance between the cobalt

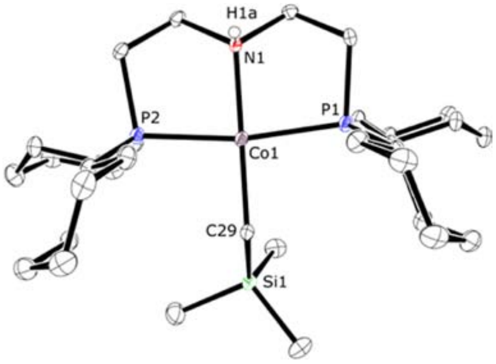


Figure 3. X-ray structure of complex **5** (molecular cation shown, thermal ellipsoids at 50% probability, hydrogen atoms except for H1a and cocrystallized THF omitted for clarity). Selected bond distances (Å) and angles (°): Co1–C29 = 1.989(3), Co1–N1 = 2.025(2), Co1–P1 = 2.249(1), Co1–P2 = 2.234(1), C29–Co1–N1 = 173.5(1), C29–Co1–P2 = 95.1(1), N1–Co1–P2 = 84.5(1), C29–Co1–P1 = 94.8(1), N1–Co1–P1 = 85.1(1), P2–Co1–P1 = 169.1(1).

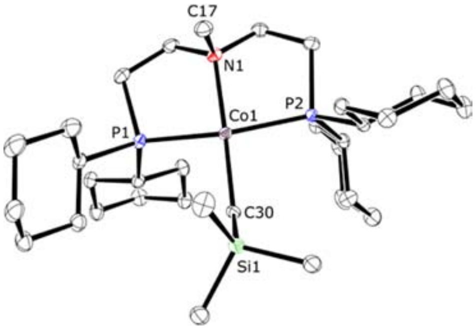
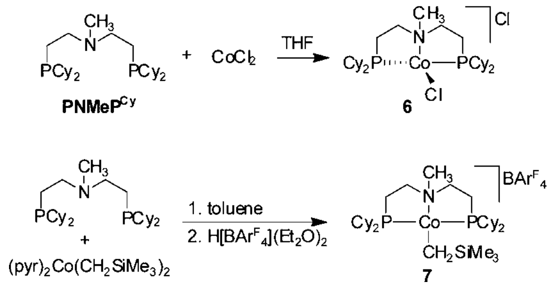


Figure 4. X-ray structure of complex **7** (molecular cation shown, thermal ellipsoids at 50% probability, hydrogen atoms and cocrystallized hexane omitted for clarity). The trifluoromethyl groups on the BAr^F_4 counterion were disordered. Selected bond distances (Å) and angles (°): Co1–C30 = 2.023(3), Co1–N1 = 2.064(3), Co1–P1 = 2.245(1), Co1–P2 = 2.249(1), C30–Co1–N1 = 177.7(1), C30–Co1–P1 = 93.3(1), N1–Co1–P1 = 85.2(1), C30–Co1–P2 = 96.4(1), N1–Co1–P2 = 85.4(1), P1–Co1–P2 = 164.2(1).

center and the pincer nitrogen in **5** (2.025(2) Å) is statistically identical to that of **4** (Co1–N1 = 2.030(5) Å).

In order to explore the influence of the N–H group on the $PNHP^{Cy}$ ligand on the reactivity of the cobalt complexes, we aimed to prepare related cobalt(II) alkyl compounds with the ligand $PNMeP^{Cy}$ ($PNMeP^{Cy}$ = bis[(2-dicyclohexylphosphino)-ethyl]methylamine), where the central nitrogen of the pincer ligand is substituted with a methyl group.[26] Reaction of $PNMeP^{Cy}$ with $CoCl_2$ afforded the cobalt(II) chloride complex $[(PNMeP^{Cy})Co(Cl)]Cl$ (**6**). Both the bright-blue color and solution state magnetic moment of **6** (μ_{eff} = 4.1 μ_B) are consistent with a high-spin tetrahedral cobalt(II) center.[23,27] The elemental analysis and insolubility of complex **6** (Scheme 1) in toluene and pentane support its formulation as $[(PNMeP^{Cy})Co(Cl)]Cl$. Unfortunately, no tractable cobalt products were obtained upon the reaction of complex **6** with $LiCH_2SiMe_3$ or MeLi (1 or 2 equiv) in THF or diethyl ether solution. A color change from blue to brown or black was observed, and only the free ligand $PNMeP^{Cy}$ was recovered from the reaction mixture.

Scheme 1. Synthesis of Cobalt(II) Complexes 6 and 7

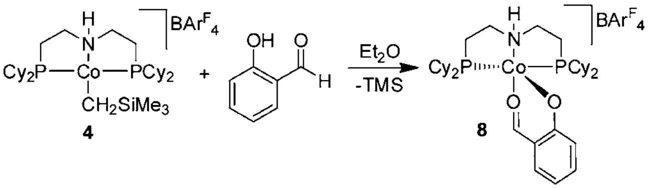


The cationic cobalt(II) alkyl complex $[(PNMeP^{Cy})Co(CH_2SiMe_3)]BAr^F_4$ (**7**) was instead prepared by the reaction of $PNMeP^{Cy}$ with $(pyr)_2Co(CH_2SiMe_3)_2$ in toluene, followed by reaction with $H[BAr^F_4]\cdot(Et_2O)_2$. Complex **7** (Scheme 1) was isolated by recrystallization from diethyl ether and pentane and characterized by ^1H NMR spectroscopy, elemental analysis, and X-ray crystallography. The X-ray structure of complex **7** is shown in Figure 4. Complex **7** has a distorted square planar structure which closely resembles that of **4** and **5**. The cobalt–carbon and cobalt–nitrogen bond distances in **7** (2.023(3) Å and 2.064(3) Å, respectively) are quite similar to those of **4** (2.001(7) Å and 2.030(5) Å).[14]

Catalytic Hydrogenation. As reported previously, the cationic cobalt(II) alkyl complex **4** is a precatalyst for the hydrogenation of olefins, ketones, aldehydes, and imines under mild conditions (25–60 °C, 1–4 atm H_2).[14] Complex **4** was generated in situ from the combination of **2** and $H[BAr^F_4]\cdot(Et_2O)_2$. An initial assessment of the functional group tolerance of the precatalyst **4** was communicated.[14] The cobalt catalyst was active in the presence of a carboxylic acid, with the hydrogenation of 4-pentenoic acid proceeding to afford pentanoic acid in 82% isolated yield after 24 h at 60 °C (1 atm H_2, 2 mol % **4**).[14] A tertiary amine functionality was also tolerated by the cobalt catalyst, with the hydrogenation of *N*-methyl-4-piperidone yielding 66% *N*-methyl-4-piperidinol after 24 h at 60 °C (1 atm H_2, 2 mol % **4**).[14]

Additional substrates were tested to further evaluate the substrate scope of precatalyst **4**. Hydrogenation of ethyl levinulate proceeded within 48 h at 60 °C, affording ethyl-3-hydroxypentanoate in high yield (>98%, as determined by NMR spectroscopy). No reaction was observed in the attempted hydrogenation of 2-hydroxybenzaldehyde, 2-acetyl-pyridine, or 4-hydroxy-3-methoxyacetophenone. This lack of hydrogenation activity may be due to the ability of these substrates to chelate to the cobalt center, suppressing further catalysis. Consistent with this idea, a new cobalt(II) complex $[(PNHP^{Cy})Co^{II}(\kappa^2\text{-}OC_6H_4CHO)]BAr^F_4$ (**8**) was obtained from the reaction of 2-hydroxybenzaldehyde with cobalt precatalyst **4**. Paramagnetic complex **8** was isolated in 89% yield (Scheme 2) and characterized by ^1H NMR and IR spectroscopy, elemental analysis, and X-ray crystallography.

Scheme 2. Isolation of Complex 8



The X-ray structure of **8** (Figure 5) reveals that the cobalt center has a trigonal bipyramidal geometry, binding both the $\mathrm{PNHP^{Cy}}$ ligand and the 2-hydroxybenzaldehyde substrate. The aldehyde oxygen is coordinated trans to the central nitrogen on the pincer ligand, and the length of the bond between the cobalt center and the aldehyde oxygen (2.010(3) Å) is significantly longer than that between the cobalt center and the phenolate oxygen (1.936(3) Å). In complex **8**, the P2−Co1−P1 angle is 123.5°, highlighting the conformational flexibility of the pincer ligand.

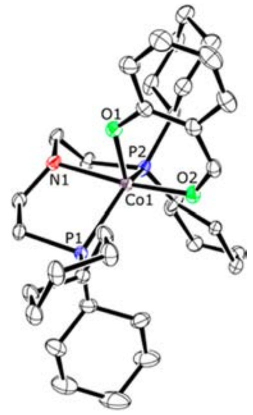
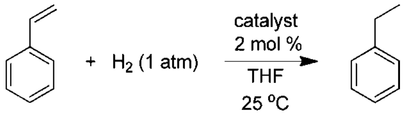


Figure 5. X-ray structure of **8** (molecular cation shown, thermal ellipsoids at 50% probability, hydrogen atoms and cocrystallized pentane omitted for clarity). The cyclohexyl substituents on P2 were disordered. Selected bond distances (Å) and angles (°): Co1−O1 = 1.936(3), Co1−O2 = 2.010(3), Co1−N1 = 2.288(3), Co1−P1 = 2.402(1), Co1−P2 = 2.416(1), O1−Co1−O2 = 92.8(1), O1−Co1−N1 = 80.6(1), O2−Co1−N1 = 172.9(1), O1−Co1−P1 = 109.5(1), O2−Co1−P1 = 104.6(1), N1−Co1−P1 = 80.1(1), O1−Co1−P2 = 118.5(1), O2−Co1−P2 = 101.3(1), N1−Co1−P2 = 80.0(1), P1−Co1−P2 = 123.5(1).

For the hydrogenation reactions, the impact of varying the substituents on the phosphorus of the cobalt(II) precatalyst was evaluated. The hydrogenation of styrene was carried out using a combination of 2 mol % of the phenyl-substituted cobalt complex $\mathrm{(PNP^{Ph})Co(CH_2SiMe_3)}$ (**3**) and 2 mol % of $\mathrm{H[BAr^F_4]\cdot(Et_2O)_2}$ in THF solution. No reaction was detected after 24 h at room temperature, conditions under which the analogous hydrogenation of styrene using cyclohexyl-substituted derivative **2** and $\mathrm{H[BAr^F_4]\cdot(Et_2O)_2}$ afforded quantitative conversion to ethylbenzene. Likewise, no reaction was observed in the attempted hydrogenation of acetophenone using 2 mol % **3** and 2 mol % $\mathrm{H[BAr^F_4]\cdot(Et_2O)_2}$ (1 atm H_2, 60 °C, 24 h). These results suggest that in combination with $\mathrm{H[BAr^F_4]\cdot(Et_2O)_2}$, the phenyl-substituted derivative **3** is significantly less effective than **2** for the hydrogenation of olefins and ketones (Tables 1 and 2).

Hydrogenation reactions were also tested using the isolated cobalt(II) precatalyst **5**, where the $\mathrm{BAr^F_4}$ counterion is replaced by $\mathrm{BPh_4}$. Use of the tetraphenylborate anion could be advantageous because it is considerably less expensive than the fluorinated analogue $\mathrm{BAr^F_4}$. However, a major drawback to the $\mathrm{BPh_4}$ anion is that it is more reactive than $\mathrm{BAr^F_4}$, having a reported tendency to transfer a phenyl group to metal centers.[28] The $\mathrm{BPh_4}$ anion also has the potential to coordinate to a metal center via a π-interaction with one of the phenyl rings.[28] Complex **5** (2 mol %) was a viable precatalyst for the hydrogenation of styrene, affording ethylbenzene in quantitative conversion after 24 h at room temperature (1 atm H_2). Complex **5** was also evaluated as a precatalyst for ketone hydrogenation. When the hydrogenation of acetophenone was carried out using precatalyst **5** (2 mol %), 1-phenylethanol was formed in 35% yield after 24 h at room temperature (1 atm H_2). Although these results indicate that the $\mathrm{BPh_4}$ derivative **5** is an effective precatalyst, higher activity was observed with the $\mathrm{BAr^F_4}$ analogue **4** (Table 2).

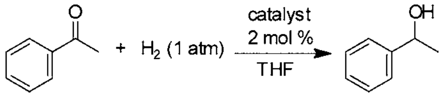
Table 1. Comparison of Cobalt Precatalysts for the Hydrogenation of Styrene[a]



precatalyst	% yield[b]
2	2
3 + $\mathrm{H[BAr^F_4]\cdot(Et_2O)_2}$	0
4	100
5	100
7	100
13	100

[a] Conditions: substrate (0.5 mmol), catalyst (0.01 mmol, 2 mol %) in THF (2 mL), 1 atm H_2, 25 °C, 24 h. [b] Yields of products were determined by GC analysis.

Table 2. Comparison of Cobalt Precatalysts for the Hydrogenation of Acetophenone[a]

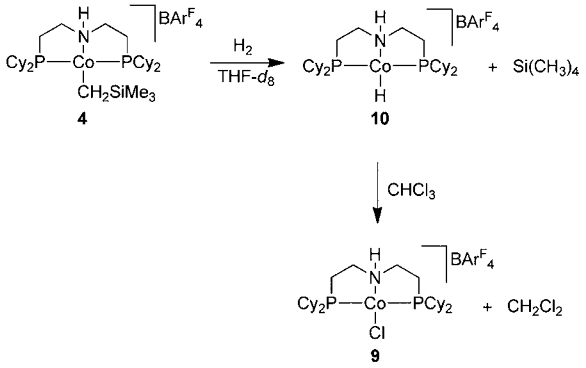


precatalyst	temperature	% yield[b]
2	25 °C	0
3 + $\mathrm{H[BAr^F_4]\cdot(Et_2O)_2}$	60 °C	0
4	25 °C	89 (98)[c]
5	25 °C	35
7	60 °C	0
13	60 °C	0

[a] Conditions: substrate (0.5 mmol), catalyst (0.01 mmol, 2 mol %) in THF (2 mL), 1 atm H_2, 24 h. [b] Isolated yields. [c] Yield determined by GC-MS.

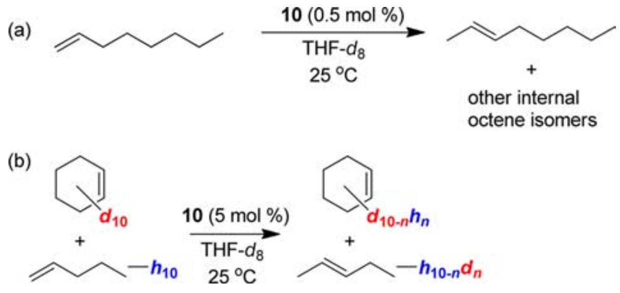
As previously communicated, in an attempt to gain insight into the alkene hydrogenation reaction, the reaction of cobalt(II) alkyl precatalyst **4** with hydrogen was carried out in THF-d_8 solvent and monitored by ^{1}H NMR spectroscopy.[14] Within 1 h at room temperature, signals corresponding to **4** disappeared from the ^{1}H NMR spectrum, and a new signal appeared at 0 ppm, corresponding to TMS. The solution was a clear yellow color, consistent with a homogeneous cobalt species. However, no signals that could be attributed to a cobalt product were detected in the ^{1}H NMR or ^{31}P NMR spectra.[14] When $CHCl_3$ was added to the reaction mixture, an immediate color change from yellow to red was observed, and the formation of CH_2Cl_2 was detected by ^{1}H NMR spectroscopy. The cobalt product of this reaction was identified as the cobalt(II) chloride complex $\mathrm{[(PNHP^{Cy})Co(Cl)]BAr^F_4}$ (**9**).[14] Complex **9** was isolated and characterized by UV−vis spectroscopy, elemental analysis, and X-ray crystallography.[14] The formation of **9** suggests that the initial product upon the reaction of **4** (Scheme 3) with hydrogen may be the cobalt(II) hydride complex $\mathrm{[(PNHP^{Cy})Co(H)]BAr^F_4}$ (**10**).[29]

Scheme 3. Reaction of Cobalt(II) Alkyl Complex 4 with Hydrogen



Further supporting the formation of a cobalt(II) hydride complex, solutions of **10** (generated by the reaction of **4** with H_2, followed by removal of the H_2 by repeated freeze pump thaw cycles) catalyzed rapid olefin isomerization at room temperature.[14] When 1-octene (200 equiv) was added to a THF-d_8 solution of **10**, complete isomerization to a mixture of internal octene isomers was observed within 20 min at room temperature.[14] A crossover experiment was also performed where a THF-d_8 solution of **10** was treated with a mixture of 1-pentene and cyclohexene-d_{10}.[14] Within 1 h at room temperature, complete isomerization of 1-pentene to 2-pentene was observed. In addition, H/D scrambling between the 2-pentene and the cyclohexene-d_{10} had occurred (Scheme 4).[14] The observed deuterium crossover is consistent with a pathway for olefin isomerization involving a cobalt-hydride intermediate.

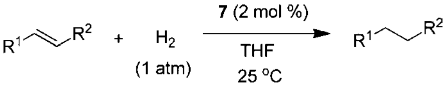
Scheme 4. (a) Isomerization of 1-Octene Catalyzed by 10[a] and (b) Deuterium Crossover Experiment

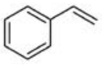
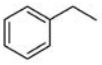
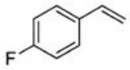
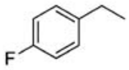
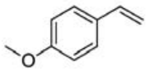
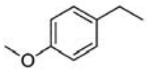


[a]Generated by addition of 1 atm H_2 to **4**, followed by removal of H_2.

Reactivity of [(PNMeP^{Cy})Co(CH$_2$SiMe$_3$)]BAr$^F_4$ (7): Possible Role of Metal–Ligand Cooperativity. To assess the potential participation of the N–H group on the PNHP^{Cy} pincer ligand in the hydrogenation reactions via metal–ligand bifunctional catalysis, we evaluated the hydrogenation of several alkenes using the cobalt(II) precatalyst [(PNMeP^{Cy})Co-(CH$_2$SiMe$_3$)]BAr$^F_4$ (**7**). Hydrogenation of styrene using precatalyst **7** proceeded smoothly at room temperature, affording ethylbenzene quantitatively within 24 h. Likewise, complex **7** proved to be an effective precatalyst for the hydrogenation of 4-fluorostyrene and 1-octene, producing 4-fluoroethylbenzene (100%) and *n*-octane (98%) after 24 h at room temperature (1 atm H_2). The internal olefins *cis*-cyclooctene and norbornene were also hydrogenated using **7**, affording cyclooctane and norbornane in nearly quantitative yields after 24 h (Table 3). These results suggest that a cooperative interaction involving the N–H group on the pincer ligand is not important for alkene hydrogenation by the cobalt catalyst.

Table 3. Alkene Hydrogenation Catalyzed by Complex 7[a]

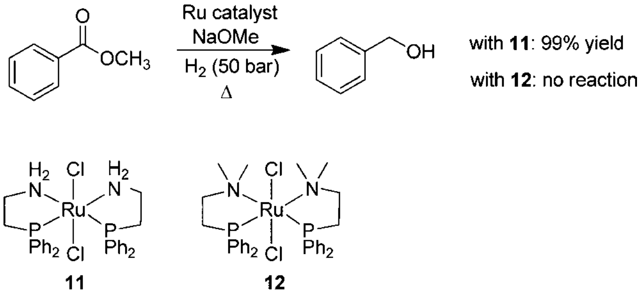


Entry	substrate	product	Yield[b] (%)
1			100
2			100
3			100
4			98
5			99
6			99

[a]Conditions: substrate (0.5 mmol), **7** (0.01 mmol, 2 mol %) in THF (2 mL), 1 atm H_2, 25 °C, 24 h. [b]Yields of products were determined by GC analysis.

In related Ru systems, where the hydrogenation of polar multiple bonds is proposed to proceed through metal–ligand bifunctional catalysis, replacement of N–H groups with N–Me groups has been found to have a detrimental impact on catalyst activity.[30] For example, Noyori and co-workers noted that substitution of ethylenediamine with *N*,*N*,*N′*,*N′*-tetramethylethylenediamine in a Ru catalyst system for the hydrogenation of ketones resulted in a completely ineffective catalyst.[31] In another example, Saudan and co-workers reported the ruthenium-based ester hydrogenation catalyst **11**, for which metal–ligand cooperativity was proposed to play a central role in the hydrogenation mechanism.[32] Catalytic activity was completely suppressed when N–Me substituted ruthenium derivative **12** was instead used in the reaction (Scheme 5).[32]

Scheme 5. Ester Hydrogenation Reaction Reported by Saudan and Co-workers (ref 32)[a]

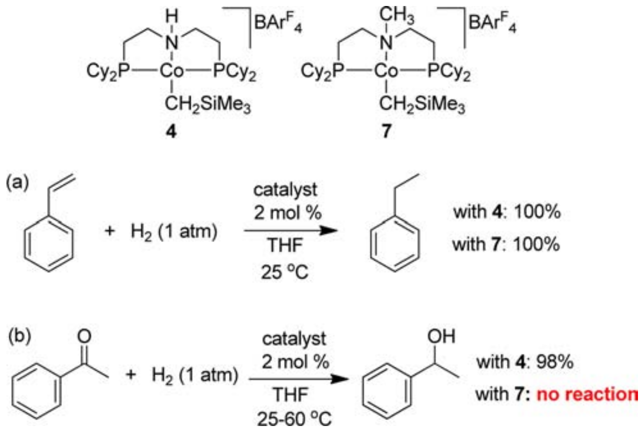


[a]Catalysis was completely inhibited for the N-Me substituted derivative **12**.

Thus, the comparable catalytic activities observed for alkene hydrogenation with cobalt precatalysts **4** and **7** are inconsistent with an alkene hydrogenation pathway requiring metal−ligand cooperativity, where diminished catalytic activity would be expected for the N−Me substituted derivative **7**.

We also tested cobalt(II) precatalyst **7** for the hydrogenation of ketones. No reaction was observed upon the attempted hydrogenation of acetophenone or 2,2,2-trifluoroacetophenone with **7** (2 mol %) after 24 h at room temperature. Even upon increasing the reaction temperature to 60 °C, no reaction was observed after 24 h with either substrate (Scheme 6). Finally, the hydrogenation of acetophenone was tested under a higher hydrogen pressure (4 atm H_2) using an increased loading of **7** (10 mol %). After 4 days at 60 °C, ca. 60% conversion of acetophenone to 1-phenylethanol was observed. In the ketone hydrogenation reactions, the activity of cobalt(II) precatalyst **7** is significantly less than that of **4**. For instance, the hydrogenation of acetophenone using **4** (2 mol %) was complete (98%, as determined by GC-MS analysis) within 24 h at room temperature (1 atm H_2). When precatalyst **4** (2 mol %) was used for the hydrogenation of acetophenone at a higher temperature (60 °C, 1 atm H_2), ~40% conversion was observed within 4 h. For the ketone hydrogenation reactions, the decreased catalytic activity observed upon the introduction of the N−Me group in the pincer ligand suggests a likely role for metal−ligand cooperativity in the reaction mechanism.

Scheme 6. Comparison of the Reactivity of 4 and 7: Hydrogenation of (a) Styrene and (b) Acetophenone

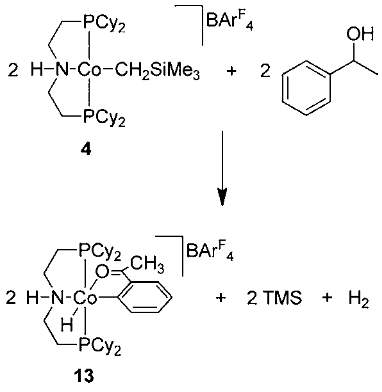


Cobalt-Catalyzed Alcohol Dehydrogenation: Isolation of a Cobalt(III)(acetylphenyl)hydride Complex. Previously, we found that the cationic cobalt(II) alkyl complex **4** serves as a precatalyst for the acceptorless dehydrogenation of secondary alcohols.[15] The dehydrogenation of several secondary benzylic alcohols, including 1-phenylethanol, *α*-isopropylbenzyl alcohol, and 1-(3-methoxyphenyl)ethanol, proceeded within 24−48 h at 120 °C using precatalyst **4** (5 mol %), affording the corresponding ketones as products in high isolated yields (81−95%).[15] In addition, complex **4** was found to be effective for the dehydrogenation of secondary aliphatic alcohols, affording 2-cyclohexanone (56%) and 2-hexanone (64%) upon the dehydrogenation of cyclohexanol and 2-hexanol, respectively.[15]

To gain insight into the alcohol dehydrogenation reaction, the dehydrogenation of 1-phenylethanol was carried out using **4** (10 mol %) in toluene-d_8 solvent and the reaction mixture monitored by NMR spectroscopy. Within 1 h of heating at 120 °C, the formation of a new diamagnetic cobalt product (**13**) was detected by ^{1}H and ^{31}P NMR spectroscopy. Complex **13** was the only diamagnetic cobalt product evident in the reaction mixture and was isolated in 71% yield and characterized by NMR and IR spectroscopy and elemental analysis.

The ^{31}P NMR spectrum of complex **13** displays a broad signal at 60.5 ppm (THF-d_8). The ^{1}H NMR spectrum of isolated complex **13** (THF-d_8) shows signals in the aryl region corresponding to the $\mathrm{BAr^F}_4$ counterion, as well as 4 additional aryl resonances (7.90, 7.49, 7.10, and 7.02 ppm), indicating a cobalt product containing a coordinated acetophenone molecule. A singlet at 2.83 ppm, integrating to 3H, further supports the presence of a coordinated acetophenone molecule. A broad triplet hydride signal is evident at −23.67 ppm ($^{2}J_{P-H}$ ~ 53 Hz), suggesting that the identity of the diamagnetic cobalt product is the cobalt(III)(acetylphenyl)hydride complex $[(\mathrm{PNHP^{Cy}})\mathrm{Co^{III}}(\kappa^2\text{-O,C-}C_6H_4C(O)CH_3)(H)]\mathrm{BAr^F}_4$ (**13**) (Scheme 7). In the NMR spectra, the broadening observed for both the phosphorus and hydride resonances is common for atoms bound directly to cobalt and is attributable to the quadrupolar ^{59}Co nucleus.[33]

Scheme 7. Proposed Balanced Reaction for the Formation of Cobalt(III) Complex 13



To confirm the identity of complex **13**, the reaction of **4** with 1-phenylethanol-$^{13}C_8$ was also carried out, affording the product **13**-$^{13}C_8$. Complex **13**-$^{13}C_8$ was isolated and characterized by NMR spectroscopy. The ^{13}C{^{1}H} NMR spectrum of **13**-$^{13}C_8$ (THF-d_8) shows a signal for the carbonyl carbon of the coordinated acetophenone-$^{13}C_8$ at 211.5 ppm, which appears as a doublet of doublets due to coupling to the two adjacent labeled carbons ($^{1}J_{C-C}$ = 55 Hz, $^{1}J_{C-C}$ = 43 Hz), shifted significantly downfield from the carbonyl signal of free acetophenone (197.2 ppm). The signals for the aryl carbons appear as multiplets at 146.8, 144.1, 132.5, 132.4, and 122.5 ppm (see Supporting Information). The cyclometalated carbon shows a broad signal at 187.1 ppm ($\Delta\nu_{1/2}$ = 120 Hz); due to the line width no coupling to phosphorus or carbon could be resolved. The chemical shift of the cyclometalated carbon is in the range of those reported by Crabtree and co-workers for cyclometalated *α*,*β*-unsaturated carbonyl ligands in a series of iridium phosphine complexes (159−199 ppm).[34] Crabtree and co-workers attributed the low-field chemical shifts of the Ir−C resonances to carbenoid character in the Ir−C bond.[34]

Providing further support for the identity of **13**, the related cobalt(III) complex $[(\mathrm{PNHP^{Cy}})\mathrm{Co^{III}}(\kappa^2\text{-O,C-3-}(OCH_3)\text{-}C_6H_3C(O)CH_3)(H)]\mathrm{BAr^F}_4$ (**14**) was prepared from the reaction of 1-(3-methoxyphenyl)ethanol with **4**. Complex **14** was characterized by NMR and IR spectroscopy, X-ray crystallography, and elemental analysis. The ^{31}P NMR spectrum of complex **14** displays a broad signal at 60.0 ppm, quite similar in chemical shift to that of **13**. The ^{1}H NMR spectrum of **14** also displays similar features to that of **13**, including signals in the aryl region (7.62, 7.06, and 6.65 ppm) corresponding to the coordinated 3-methoxyacetophenone molecule, a singlet at 2.84 ppm arising from the methyl group on the coordinated 3-methoxyacetophenone, and a Co−H signal at −22.10 ppm ($^2J_{P-H}$ = 54 Hz). The X-ray structure of complex **14** is shown in Figure 6. In complex **14**, the hydride ligand is located *trans* to the carbonyl group on the coordinated substrate, and the formation of a new Co−C bond is clearly observed, with a Co−C distance of 1.889(4) Å.

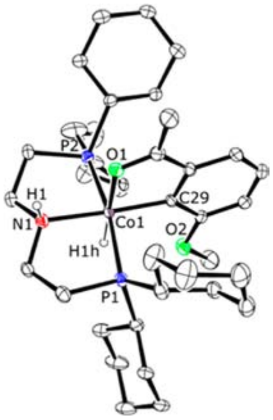
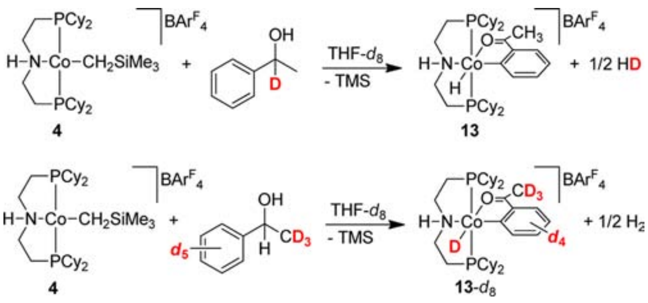


Figure 6. X-ray structure of complex **14** (molecular cation shown, thermal ellipsoids at 50% probability, hydrogen atoms except for H1 and H1h omitted for clarity). The trifluoromethyl groups on the BAr$^F_4$ counterion and a cyclohexyl substituent on P2 were disordered. Selected bond distances (Å) and angles (°): Co1−C29 = 1.889(4), Co1−O1 = 1.993(3), Co1−N1 = 2.020(3), Co1−P1 = 2.190(1), Co1−P2 = 2.205(1), C29−Co1−O1 = 83.9(2), C29−Co1−N1 = 173.1(2), O1−Co1−N1 = 89.4(1), C29−Co1−P1 = 92.8(1), O1−Co1−P1 = 100.7(1), N1−Co1−P1 = 87.0(1), C29−Co1−P2 = 94.5(1), O1−Co1−P2 = 92.8(1), N1−Co1−P2 = 87.3(1), P1−Co1−P2 = 165.3(1).

The formation of a cobalt(III) product in the alcohol dehydrogenation reaction was unexpected. One possible pathway for the formation of complex **13** would involve reduction of the initial cobalt(II) complex **4** to cobalt(I) by the alcohol 1-phenylethanol, generating acetophenone and tetramethylsilane as products. In support of this idea, although cobalt(I) complexes are typically prepared using stronger reducing agents like NaBH$_4$, NaBHEt$_3$, or alkali metals,[10,33] alcohols are well-known reducing agents for the synthesis of rhodium(I) and iridium(I) complexes.[35] The overall stoichiometry would be balanced by the dehydrogenation of a second molecule of 1-phenylethanol by cobalt(I), affording acetophenone and hydrogen. Finally, the C−H bond activation of acetophenone by the cobalt(I) species would generate the cobalt(III)(acetylphenyl)hydride complex **13**. A balanced reaction for the formation of **13** is shown in Scheme 7.

To confirm that the source of the hydride ligand in the cobalt(III)(acetylphenyl)hydride complex is the C−H bond activation of acetophenone, deuterium-labeling experiments were performed. The reaction of the cobalt(II) alkyl complex **4** with 1-phenylethanol-d_1 (prepared by the reduction of acetophenone with NaBD$_4$) was carried out in an NMR tube and monitored by NMR spectroscopy (Scheme 8). Formation of complex **13** was observed, and no deuterium incorporation into the hydride position occurred (the hydride signal integrated at full intensity). In contrast, when an analogous reaction of **4** with 1-phenylethanol-d_8 (prepared by the reduction of acetophenone-d_8 with NaBH$_4$) was monitored by ^{1}H NMR spectroscopy, formation of **13**-d_8 was observed (Scheme 8). The signals corresponding to the bound acetophenone and the hydride signal were all absent from the ^{1}H NMR spectrum. These results are consistent with the origin of the hydride ligand being the C−H bond activation of acetophenone.

Scheme 8. Deuterium-Labeling Experiments to Identify the Source of the Hydride Ligand in 13

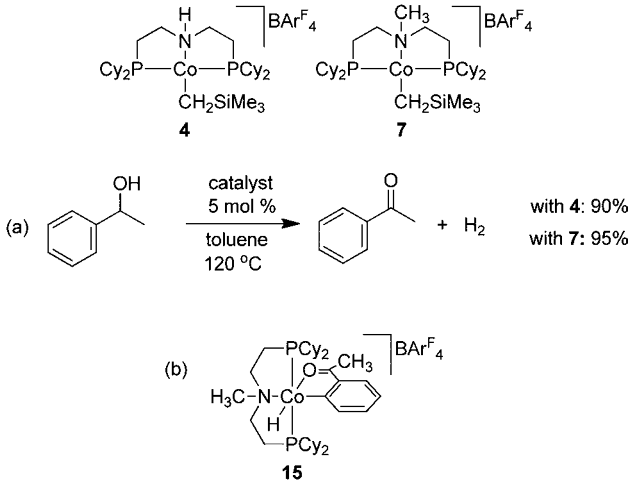


While examples of C−H bond activation by iridium(I) and rhodium(I) are ubiquitous, the activation of C−H bonds by cobalt(I) is less common.[36−38] Brookhart and co-workers demonstrated that the cobalt(I) ethylene complex Cp*Co-(C$_2$H$_4$)$_2$ (Cp* = pentamethylcyclopentadienyl) activated arene C−H bonds, noting H/D exchange between the ethylene ligands and benzene-d_6 or toluene-d_8 solvent upon thermolysis.[39] More recently, the same group reported the activation of sp^3 C−H bonds by the closely related cobalt(I) complex Cp*Co(VTMS)$_2$ (VTMS = vinyltrimethylsilane), which catalyzed the synthesis of enamines via an internal transfer hydrogenation reaction.[40] The cobalt(I) complex Co(CH$_3$)(PMe$_3$)$_4$ has also been observed to activate arene C−H bonds that are *ortho* to a ketone or imine functionality, affording methane and a cobalt(I) aryl-ligated product.[38] The formation of complex **13** is distinct from these prior examples in that C−H bond activation by cobalt(I) generates a cobalt(III) aryl hydride complex which is stable.

Although we are unaware of any prior examples of cobalt(III) aryl hydride complexes, a closely related iridium analogue has been reported by Goldman and co-workers.[41,42] The iridium(III) acetylphenyl hydride complex (PCP^{tBu})Ir(κ^2-O,C−C$_6$H$_4$C(O)CH$_3$)(H) (PCP^{tBu} = κ^3-C$_6$H$_3$-2,6-(CH$_2$P^{t}Bu$_2$)$_2$) was formed upon the C−H bond activation of acetophenone by the unsaturated iridum(I) fragment "(PCP^{tBu})Ir" (generated in situ by the reaction of (PCP^{tBu})IrH$_2$ with norbornene).[41] Notably, an isomer of the iridium complex where the aryl ligand is *trans* to the hydride was observed as the initial kinetic product upon C−H bond activation, with rearrangement to the thermodynamically preferred isomer where the hydride is *trans* to the carbonyl group occurring after thermolysis (135 °C).[41] At low temperature, several products of *meta* and *para* C−H bond activation were detected, implying that for d^8 metal centers, C−H bond activation at the less hindered *meta* and *para* positions may be kinetically preferred, while "chelateassisted" *ortho* C−H bond activation products arise due to their greater thermodynamic stability.[41]

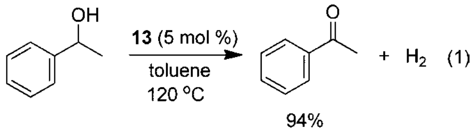
Alcohol Dehydrogenation with [(PNMeP^{Cy})Co(CH$_2$SiMe$_3$)]BAr$^F_4$ (7). The alcohol dehydrogenation reaction was also tested using the N−Me substituted cobalt(II) alkyl complex **7**. When a toluene solution of 1-phenylethanol was heated with **7** (5 mol %) at 120 °C for 24 h, acetophenone was formed in 95% isolated yield. The catalytic activity of **7** is quite similar to that observed for the cobalt(II) alkyl precatalyst **4**, demonstrating that the N−H group on the pincer ligand does not play a critical role in the alcohol dehydrogenation reaction (Scheme 9).

Scheme 9. (a) Dehydrogenation of 1-Phenylethanol Using Cobalt(II) Precatalysts 4 and 7 and (b) Proposed Structure of Complex 15



In the dehydrogenation of 1-phenylethanol using cobalt(II) precatalyst **7**, a cobalt(III) product, tentatively identified as the acetylphenyl hydride complex [(PNMeP^{Cy})Co^{III}(κ^2-O,C−C$_6$H$_3$C(O)CH$_3$)(H)]BAr$^F_4$ (**15**), was detected in the reaction mixture by ^{1}H and ^{31}P NMR spectroscopy. Repeated attempts to obtain crystals of **15** suitable for diffraction yielded only oil. However, the ^{1}H NMR spectrum of complex **15** displayed signals similar to those of **13**, including a signal for the CH$_3$ group on the coordinated acetophenone (s, 2.85 ppm), and a broad triplet hydride signal (−23.56 ppm, $^2J_{P-H}$ ~ 55 Hz). These results further suggest that the N−H group on the pincer ligand is not essential for the formation of the cobalt(III) acetylphenylhydride complex.

Reactivity of Co(III)(acetylphenyl)hydride Complex 13. To gain further insight into the role of **13** in the catalytic reactions, the isolated complex **13** was tested as a catalyst for the dehydrogenation of 1-phenylethanol. When a toluene solution of 1-phenylethanol was heated with **13** (5 mol %) for 24 h at 120 °C, acetophenone was isolated in 94% yield (eq 1).

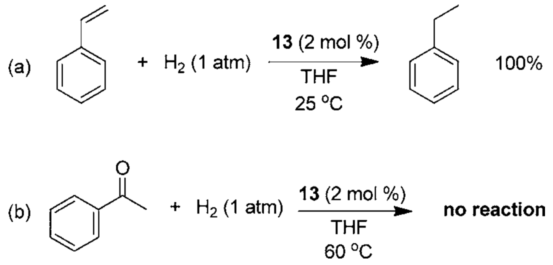


Both the detection of complex **13** in the catalytic reaction mixture by ^{1}H NMR spectroscopy and the ability of isolated complex **13** to catalyze the dehydrogenation of 1-phenylethanol point to **13** as a resting state of the cobalt catalyst in the dehydrogenation reaction.

A deuterium labeling experiment was performed where the dehydrogenation of a mixture of 1-phenylethanol-d_1 and α-isopropylbenzyl alcohol was carried out using cobalt catalyst **13** (5 mol %) and stopped prior to completion (~15% conversion). The starting alcohols were recovered from the reaction mixture and characterized by ^{1}H NMR spectroscopy. H/D scrambling was observed in the benzylic C−H positions of the alcohols, with ~22% of deuterium incorporated into the α-isopropylbenzyl alcohol and ~70% of protons incorporated into the 1-phenylethanol.[43] These results suggest that the alcohol dehydrogenation reaction is reversible and involves a cobalt hydride intermediate. A separate experiment confirmed the reversibility of the reaction; when acetophenone was heated with **13** (10 mol %) under 1 atm H$_2$ (120 °C, 40 h), 1-phenylethanol was formed in 15% yield.

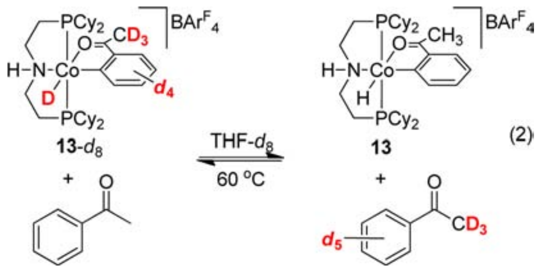
Cobalt(III) complex **13** was also tested as a catalyst for hydrogenation reactions at lower temperatures (Scheme 10, Tables 1 and 2). When a solution of styrene was treated with H$_2$ (1 atm) and **13** (2 mol %), ethylbenzene was formed in quantitative yield after 24 h at room temperature, as determined by GC-MS analysis. In contrast, no reaction was observed when the hydrogenation of acetophenone was attempted using catalyst **13** (2 mol %) after 24 h at room temperature. Even when the temperature was increased to 60 °C, no hydrogenation of acetophenone occurred after 24 h with **13** (2 mol %). Under increased hydrogen pressure (4 atm) and a higher catalyst loading (10 mol % **13**), slow hydrogenation of acetophenone was observed, with ~20% conversion to 1-phenylethanol occurring after 48 h at 60 °C.

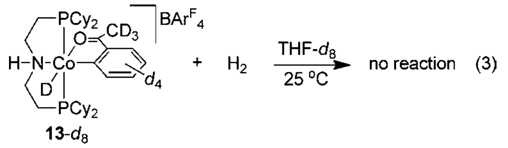
Scheme 10. (a) Hydrogenation of Styrene Using Cobalt(III) Complex 13 and (b) Attempted Hydrogenation of Acetophenone Using 13



Given the unusual nature of complex **13** as a stable cobalt(III) aryl hydride complex, additional experiments were carried out to further understand its reactivity. To investigate ligand exchange at the cobalt(III) center, complex **13**-d_8 was prepared via the reaction of **4** with 1-phenylethanol-d_8 (vide supra) and isolated. A THF-d_8 solution of **13**-d_8 was treated with acetophenone (6 equiv), and the reaction was monitored by NMR spectroscopy. After 1 h at room temperature, no exchange between **13**-d_8 and the added acetophenone was observed. However, exchange with acetophenone occurred rapidly when the reaction mixture was heated at 60 °C (eq 2). Resonances corresponding to the acetylphenyl and hydride ligands of **13** grew into the ^{1}H NMR spectrum, and exchange was complete within 1 h.

The reaction of **13**-d_8 with H$_2$ was also explored. A THF-d_8 solution of **13**-d_8 was treated with H$_2$ (1 atm), and the reaction mixture was monitored by ^{1}H NMR spectroscopy. After 24 h at



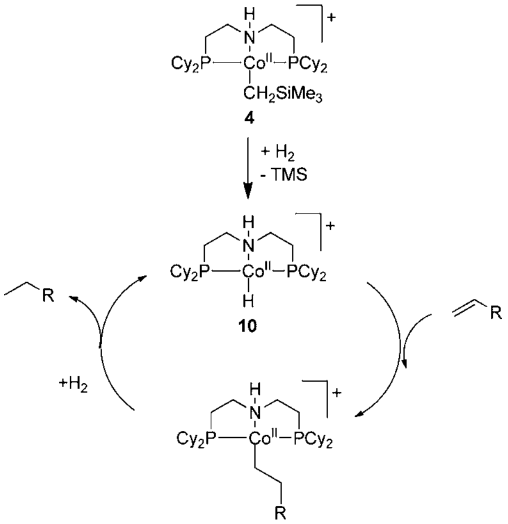


room temperature, no formation of H−D gas was observed, and no reaction of **13**-d_8 was detected (eq 3). Even upon increasing the reaction temperature to 60 °C, no reaction was observed between **13**-d_8 and hydrogen (1 atm) after 1 h. The lack of reactivity of **13**-d_8 with hydrogen is consistent with the observed inactivity of **13** in the hydrogenation of acetophenone at lower temperatures (25−60 °C). A very different observation was reported by Brookhart and co-workers for the cationic cobalt(III) alkyl complex [Cp*Co(PMe$_3$)(C$_2$H$_4$-μ-H)]BAr$^F_4$ (**16**), which formed the cobalt(III) hydride−dihydrogen complex [Cp*Co(PMe$_3$)(η^2-H$_2$)(H)]BAr$^F_4$ and ethane upon treatment with H$_2$ at −30 °C.[44] The major difference in reactivity between the two cationic cobalt(III) complexes may lie in the relative unsaturation of the formally 16-electron cobalt(III) center of **16**, which features a weak β-agostic interaction with one of the C−H bonds of the ethyl ligand.[44] The 18-electron cobalt center of **13** is coordinatively saturated, which may limit the binding of H$_2$ and subsequent reactions.

■ DISCUSSION

Mechanism of Cobalt-Catalyzed Alkene Hydrogenation. Based on our results, a catalytic cycle can be proposed for the hydrogenation of alkenes by the cobalt(II) alkyl precatalyst **4** (Scheme 11). Hydrogenolysis of the cationic cobalt(II) alkyl complex **4** generates cobalt(II) hydride complex **10** and tetramethylsilane. Subsequent alkene insertion into the Co−H bond of **10** affords a cobalt(II) alkyl intermediate. The observations of rapid olefin isomerization and H/D scrambling catalyzed by complex **10** at room temperature confirm the feasibility of this insertion step. Finally, reaction of the cobalt(II) alkyl intermediate with hydrogen releases the product and turns over the catalyst. Notably, the N−H group on the PNP pincer ligand is not required for the proposed catalytic cycle for the hydrogenation of alkenes. This is in agreement with the reactivity of the N−Me substituted complex [(PNMeP^{Cy})Co(CH$_2$SiMe$_3$)]BAr$^F_4$ (**7**), which was an equally effective precatalyst as **4** for the hydrogenation of alkenes.

Scheme 11. Proposed Mechanism of Cobalt-Catalyzed Olefin Hydrogenation



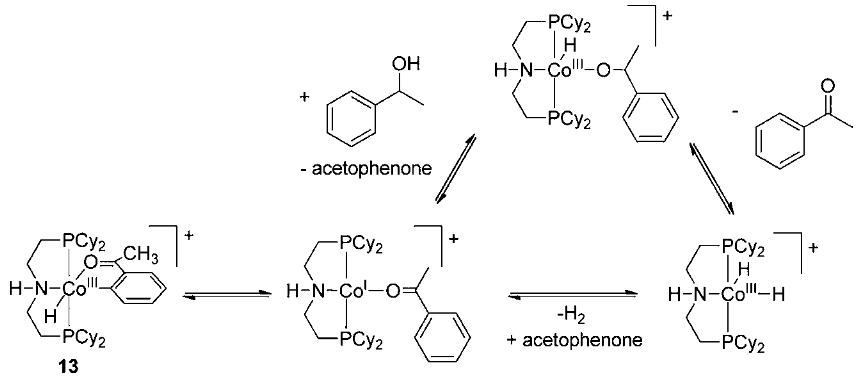
The proposed mechanism is consistent with previous work by Budzelaar and co-workers, which involved the development of a cobalt(I) catalyst of a bis(imino)pyridine ligand for the room temperature hydrogenation of olefins.[45] The catalytic reaction was proposed to proceed through a similar pathway involving the formation of a cobalt(I) hydride complex, olefin insertion to generate a cobalt alkyl intermediate, and subsequent σ-bond metathesis with H$_2$ to regenerate the cobalt hydride.[45] While the bis(imino)pyridine cobalt(I) complexes are diamagnetic, they have also been described as a low-spin cobalt(II) center that is antiferromagnetically coupled to a ligand radical anion.[46] More recently, Chirik and co-workers reported a cobalt catalyst of a C_1 symmetric bis(imino)pyridine ligand for the asymmetric hydrogenation of *gem*-disubstituted alkenes.[10] High enantioselectivities were observed, and the active catalyst is likely the cobalt hydride complex.[10]

Chirik and co-workers also studied the reactivity of the closely related cobalt(II) alkyl cation [(PDI)Co(CH$_3$)]BAr$^F_4$ (**17**) (PDI = 2,6-(2,6-^{i}Pr$_2$-C$_6$H$_3$N═CMe)$_2$C$_5$H$_3$N).[47] Complex **17** was characterized as a low-spin cobalt(II) center with a redox-neutral chelating ligand.[47] Cobalt(II) alkyl complex **17** was relatively unstable, undergoing bimolecular reductive elimination of ethane within ~12 h upon the addition of diethyl ether, forming the cobalt(I) product [(PDI)Co(OEt$_2$)]-BAr$^F_4$.[47] Chirik's cobalt(II) alkyl complex **17** was found to be a highly active catalyst for ethylene polymerization,[47] but its use as a precatalyst for the hydrogenation of olefins has not yet been reported.

The spontaneous change in oxidation state from cobalt(II) to cobalt(I) reported for Chirik's cobalt complex **17**[47] and the observation of a cobalt(III) species during the alcohol dehydrogenation reaction reveal that oxidation state changes in cobalt complexes can be facile. This casts some uncertainty on the true oxidation state of the cobalt center during the catalytic reactions. However, several observations appear to support a cobalt(II) valence during the catalytic hydrogenation of olefins. For instance, solution state magnetic moment measurements performed after the addition of hydrogen to **4** suggested the presence of paramagnetic species in solution, and no diamagnetic cobalt species were identified when the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. Moreover, unlike Chirik's cobalt(II) alkyl complex **17**,[47] complex **4** was stable in THF-d_8 solution at room temperature for at least 1 week. Finally, the cobalt(II) product [(PNHP^{Cy})Co(Cl)]BAr$^F_4$ (**9**) and CH$_2$Cl$_2$ were obtained upon trapping the reactive cobalt species formed from **4** and H$_2$ with CHCl$_3$.[14] Thus, for the olefin hydrogenation reactions, a cobalt(II) oxidation state seems most plausible.

Mechanism of Cobalt-Catalyzed Alcohol Dehydrogenation. In contrast to the olefin hydrogenation reactions, a

Scheme 12. Proposed Mechanism of Cobalt-Catalyzed Dehydrogenation of 1-Phenylethanol



diamagnetic cobalt product was formed during the alcohol dehydrogenation reactions. The isolation of cobalt(III) complex **13** and its effectiveness as a catalyst suggest that alcohol dehydrogenation proceeds through a cobalt(I)/(III) cycle. The cobalt-catalyzed alcohol dehydrogenation takes place under considerably more forcing conditions (120 °C) than the hydrogenation of olefins or ketones (25−60 °C) and likely involves a different reaction mechanism.

A mechanism consistent with these results is shown in Scheme 12. In the proposed catalytic cycle for the dehydrogenation of 1-phenylethanol, complex **13** is a catalyst resting state. Starting from **13**, reductive elimination of acetophenone generates a cobalt(I) intermediate and allows for ligand exchange at the cobalt center. Exchange of the bound acetophenone-d_8 in **13**-d_8 with free acetophenone occurred rapidly at 60 °C, verifying the possibility of such a reductive elimination step. Replacement of the coordinated acetophenone with 1-phenylethanol could occur by either associative or dissociative ligand substitution (associative substitution is shown in Scheme 12). Once the 1-phenylethanol has entered the cobalt(I) coordination sphere, oxidative addition of the O−H bond generates a cobalt(III) alkoxide complex. The cobalt(III) alkoxide complex undergoes *β*-hydride elimination to generate a cobalt(III) dihydride complex.[48,49] Loss of hydrogen and coordination of acetophenone or 1-phenylethanol completes the catalytic cycle. The overall reaction is reversible, as demonstrated experimentally (vide supra).

Although O−H bond oxidative addition is not a well-known reaction for cobalt(I), related rhodium(I) and iridium(I) complexes have been demonstrated to oxidatively add O−H bonds[50] as well as catalyze alcohol dehydrogenation reactions.[51−58] The catalytic cycle for cobalt-mediated alcohol dehydrogenation proposed here resembles that previously invoked for related pincer complexes of Ir and Ru.[52−54] For example, Jensen and co-workers proposed that the dehydrogenation of secondary alcohols using the iridium catalyst $(PCP^{tBu})IrH_2$ proceeds by oxidative addition of the O−H bond of the alcohol to the iridium(I) fragment "$(PCP^{tBu})Ir$", followed by *β*-hydride elimination to generate the iridium(III) dihydride complex.[53]

In other cases, alcohol dehydrogenation mechanisms involving metal−ligand cooperativity have been postulated.[55−57] Beller and co-workers proposed that the ruthenium complex $(PNP^{iPr})Ru(H)_2CO$ catalyzes the dehydrogenation of alcohols via an outer-sphere mechanism that requires participation of the central nitrogen on the pincer ligand.[58,59] For the cobalt system, an alcohol dehydrogenation pathway involving metal−ligand cooperativity is unlikely. Such a mechanism would conflict with the observed reactivity of the N−Me substituted cobalt(II) complex **7**, which was found to be an equally effective precatalyst as **4** for the acceptorless dehydrogenation of secondary alcohols.[60] Moreover, the detection of cobalt(III) complex **15** by NMR spectroscopy demonstrates that the N−H group on the pincer ligand is not required for the formation of a cobalt(III) species. Instead, these results implicate an alcohol dehydrogenation mechanism proceeding by a cobalt(I)/(III) redox cycle where the $PNHP^{Cy}$ chelate is a spectator ligand.

The possibility of such a two-electron cobalt(I)/(III) redox cycle has previously been investigated by Caulton and co-workers, who reported the synthesis of the unusual unsaturated cobalt(I) complex (PNP′)Co (**18**) (PNP′ = $^{-}N(SiMe_2CH_2P^tBu_2)_2$).[33] Paramagnetic complex **18** was found to have a high-spin triplet electronic configuration and a T-shaped geometry. When treated with hydrogen, complex **18** underwent oxidative addition, existing in equilibrium with the cobalt(III) dihydride complex $(PNP')Co(H)_2$.[61] Complex **18** was an active catalyst for the hydrogenation of ethylene, but its reactivity with other olefins was limited, likely due to the large steric bulk of the ligand impeding access to the metal center. While the reactivity of Caulton's cobalt(I) complex with alcohols or ketones has not yet been reported, the observation of catalytic hydrogenation of ethylene with complex **18** underscores the feasibility of a catalytic cycle based on a cobalt(I)/(III) redox couple.

Mechanism of Cobalt-Catalyzed Ketone Hydrogenation. The mechanism of the hydrogenation of ketones at lower temperatures may be distinct from that of the alkene hydrogenation and alcohol dehydrogenation reactions. Supporting this idea, the cobalt(III) aryl hydride complex **13** was an ineffective catalyst for the hydrogenation of ketones at low temperatures (25−60 °C), conditions under which rapid ketone hydrogenation was observed using cobalt(II) alkyl precatalyst **4**. Furthermore, the ketone hydrogenation activity was nearly completely suppressed using $[(PNMeP^{Cy})Co(CH_2SiMe_3)]BAr^F_4$ (**7**) as a precatalyst, confirming an important role for the N−H moiety of the pincer ligand in the reaction mechanism.

These results indicate that the ketone hydrogenation mechanism involves metal−ligand bifunctional catalysis, where the N−H group on the pincer ligand participates in the catalytic cycle. For related precious metal catalysts (Ru, Ir, Rh), metal−ligand cooperativity is most often proposed in the hydrogenation of polar multiple bonds; detailed studies of ruthenium catalysts have implicated an outer-sphere mechanism where the metal center delivers a hydride and the ligand delivers a proton to the substrate.[62,63] For instance, Casey and co-workers investigated the reduction of imines by Shvo's ruthenium catalyst, performing intramolecular trapping experiments that point to outer-sphere reduction of the imine and subsequent trapping of the unsaturated Ru intermediate by the amine product.[64,65] A slightly different pathway has been proposed for Noyori's hydrogenation catalyst *trans*-[Ru((*R*)-BINAP)(H)$_2$((*R*,*R*)-dpen)] (dpen =1,2-diphenylethylenediamine) by Bergens and co-workers, who detected a ruthenium-alkoxide complex at low temperatures by ^{1}H NMR spectroscopy.[66] Trapping experiments suggested that the alkoxide complex forms by delivery of the hydride from the Ru center to the alcohol, facilitated by hydrogen bonding involving the N−H group on the ligand.[67]

For the cobalt-catalyzed ketone hydrogenation, both outer-sphere reduction of the C═O bond and stepwise delivery of the hydride facilitated by hydrogen bonding with the N−H group of the pincer ligand are possible elementary pathways. A mechanism involving outer-sphere C═O bond reduction has been proposed in the recent example of iron-catalyzed ketone hydrogenation reported by Casey and co-workers, who performed trapping experiments to establish that the reaction proceeds via a concerted outer sphere delivery of the proton and the hydride to the substrate.[12] Metal−ligand bifunctional catalysis has also been implicated in the transfer hydrogenation of ketones by a class of highly effective iron catalysts developed by Morris and co-workers.[68] A stepwise hydride transfer, followed by a proton transfer, has been proposed for the active catalyst, an iron complex of a tetradentate PNNP ligand bearing both amido- and ene-amido functional groups.[69]

Ultimately, the oxidation state of the cobalt catalyst in the ketone hydrogenation reaction remains somewhat ambiguous. A catalytic cycle for ketone hydrogenation that entails a redox change at the cobalt center cannot be excluded, particularly given the observed formation of the diamagnetic cobalt(III) product **13** upon the reaction of **4** with 1-phenylethanol. On the other hand, the greater catalytic activity observed using cobalt(II) complex **4** as a precatalyst at lower temperatures (as compared to cobalt(III) complex **13**) may imply that the more active catalyst is a cobalt(II) hydride species. Consistent with this notion, the cobalt(II) complex **8**, where the cobalt(II) center is trapped by a chelating substrate, was isolated upon the attempted hydrogenation of 2-hydroxybenzaldehyde.

Overall, although some uncertainty remains as to the cobalt oxidation state(s) involved in the low-temperature hydrogenation of ketones, metal−ligand bifunctional catalysis is clearly implicated. These results suggest that the deliberate incorporation of cooperative ligands may be a promising strategy for the design of active earth abundant metal catalysts for the hydrogenation of polar multiple bonds.

■ SUMMARY AND CONCLUSIONS

The cationic cobalt(II) alkyl complex [(PNHP^{Cy})Co(CH$_2$SiMe$_3$)]BAr$^F{}_4$ (**4**) was found to be a highly effective precatalyst for the hydrogenation of olefins and ketones and the acceptorless dehydrogenation of alcohols. To investigate the potential role of metal−ligand cooperativity in the catalytic reactions, the reactivity of **4** was compared with the analogue [(PNMeP^{Cy})Co(CH$_2$SiMe$_3$)]BAr$^F{}_4$ (**7**), where the central nitrogen of the pincer ligand is substituted by a methyl group. The rapid room temperature hydrogenation of alkenes catalyzed by **7**, together with the isolation of [(PNHP^{Cy})Co(Cl)]BAr$^F{}_4$ upon trapping with CHCl$_3$, suggests that the olefin hydrogenation reaction proceeds through an insertion mechanism where the active catalyst is a cobalt(II) hydride complex.

For the alcohol dehydrogenation reaction, the stable diamagnetic cobalt(III)(acetylphenyl)hydride complex **13** was isolated and demonstrated to be a catalyst resting state. Comparable catalytic activities were obtained using cobalt complexes **4** and **7** as precatalysts; together, these experiments establish that the alcohol dehydrogenation reaction likely proceeds through a cobalt(I)/(III) redox cycle. In contrast, metal−ligand bifunctional catalysis is implicated in the low temperature hydrogenation of ketones using cobalt(II) alkyl precatalyst **4**, where catalytic activity was greatly diminished using the cobalt(II) alkyl precatalyst **7**.

The mechanisms of the cobalt-catalyzed hydrogenation and dehydrogenation reactions have major ramifications for future catalyst development, as a fundamental understanding of the elementary steps involved is necessary to rationally identify new ways to tune and control catalytic activity. The remarkable complexity of the cobalt-catalyzed reactions described here highlights the diversity of reaction pathways available for cobalt and other first-row transition-metal complexes. Notably, our studies suggest that both catalytic cycles based on cobalt(II) and cobalt(I)/(III) oxidation states are viable. The accessibility of each of these types of catalytic cycles will be an important consideration in the design of new earth abundant metal catalysts.

■ EXPERIMENTAL SECTION

General Considerations. Unless specified otherwise, all reactions were carried out under a dry argon atmosphere using standard glovebox and Schlenk techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Benzene-*d*$_6$, toluene-*d*$_8$, and THF-*d*$_8$ were dried over Na metal. Anhydrous grade THF, pentane, benzene, toluene, and diethyl ether were obtained from Aldrich or Acros and stored over 4 Å molecular sieves. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained at room temperature on a Bruker AV400 MHz spectrometer, with chemical shifts (δ) referenced to the residual solvent signal (^{1}H and ^{13}C) or referenced externally to H$_3$PO$_4$ (0 ppm). GC-MS analysis was obtained using a Hewlett-Packard 6890 GC system equipped with a Hewlett-Packard 5973 mass selective detector. UV−vis spectra were obtained on an Agilent 8453 UV−vis spectrophotometer equipped with a Peltier thermostatted single cell holder. IR spectra were obtained on a Perkin-Elmer Spectrum One instrument. Elemental analyses were performed by Midwest Microlab of Indianapolis, IN. Acetophenone-*d*$_8$ was purchased from C/D/N Isotopes, Inc., acetophenone-^{13}C$_8$ was purchased from Aldrich, and bis[(2-diphenylphosphino)ethyl]ammonium chloride was purchased from Strem Chemical. (PNP^{Cy})Co(CH$_2$SiMe$_3$),[14] PNMeP^{Cy},[26] (pyr)$_2$Co(CH$_2$SiMe$_3$)$_2$,[70] [HNEt$_3$][BPh$_4$],[71] and H[BAr$^F{}_4$]·(Et$_2$O)$_2$[72] were prepared according to previously published procedures.

1-Phenylethanol-*d*$_8$. In a vial, acetophenone-*d*$_8$ (0.500 g, 3.91 mmol) was dissolved in methanol (8 mL). NaBH$_4$ (0.148 g, 3.89 mmol) was added portionwise and vigorous bubbling occurred. The reaction mixture was allowed to stand at room temperature until the bubbling had ceased and then extracted with CH$_2$Cl$_2$ (20 mL) and H$_2$O (2 × 10 mL). The organic layer was dried over MgSO$_4$, filtered, and the solvent removed under vacuum. Yield: 0.476 g (94%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.91 (s, 2H, C*H*$_2$OH), 1.75 (br s, 1H, CH$_2$O*H*). ^{13}C{^{1}H} (100 MHz, CDCl$_3$): 145.8 (s), 128.2 (t, $^1J_{C-D}$ = 24 Hz), 127.2 (t, $^1J_{C-D}$ = 24 Hz), 125.2 (t, $^1J_{C-D}$ = 24 Hz), 70.4 (s), 24.5 (quintet, $^1J_{C-D}$ = 19 Hz). GC-MS (*m*/*z*): 130.

1-Phenylethanol-*d*$_1$. In a vial, acetophenone (0.152 g, 1.27 mmol) was dissolved in methanol (10 mL). NaBD$_4$ (0.053 g, 1.26 mmol) was added in portions, and then the reaction mixture was allowed to stand overnight until all bubbling ceased. The reaction was quenched by addition of H_2O (10 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent removed under vacuum. Yield: 0.128 g (82%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.30−7.28 (m, 4H, aryl), 7.24−7.20 (m, 1H, aryl), 1.42 (s, 3H, CH_3). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$): 145.9 (s), 128.6 (s), 127.6 (s), 125.6 (s), 70.1 (t, $^1J_{C-D}$ = 22 Hz), 25.1 (s). GC-MS (*m*/*z*): 123.

(PNP^{Ph})Co(CH_2SiMe_3) (3). In a vial, bis[(2-diphenylphosphino)-ethyl]ammonium chloride (42 mg, 0.088 mmol) and $LiCH_2SiMe_3$ (8.8 mg, 0.94 mmol) were suspended in diethyl ether (6 mL), and the suspension was stirred at room temperature for 24 h. The suspension was filtered through a plug of Celite, and the solvent removed under vacuum, affording a colorless oil consisting of PNP^{Ph} (bis[(2-diphenylphosphino)ethyl]amine), 26.7 mg (69%). The colorless oil was immediately used without further purification. To a vial containing PNP^{Ph} (26.7 mg, 0.0605 mmol) was added a solution of $(pyr)_2Co(CH_2SiMe_3)_2$ (23 mg, 0.059 mmol) in toluene (2 mL). The reaction mixture was allowed to stand at room temperature for 10 min, turning a dark-red color. The solvent was removed under vacuum. The red residue was extracted with diethyl ether (2 × 1 mL), filtered, and the solvent removed under vacuum, leaving a red solid. Yield: 25.6 mg (72% from PNP^{Ph}). ^1H NMR (400 MHz, THF-d_8): δ 9.01 (br s, PNP), 7.33 (br m, PNP), 6.45 (br s, PNP), −5.26 (br s, 9H, $SiMe_3$). UV−vis: 382 nm (ε = 3800 $M^{-1}cm^{-1}$), 443 nm (ε = 2100 $M^{-1}cm^{-1}$). μ_{eff} = 2.1 μ_B.

[(PNHP^{Cy})Co(CH_2SiMe_3)]BPh_4 (5). In a small vial, complex **2** (12.2 mg, 20 μmol) and $[HNEt_3][BPh_4]$ (8.4 mg, 20 μmol) were dissolved in THF (1.0 mL). The solution was layered carefully with pentane (3.0 mL), and the vial was sealed. The vial was then cooled to −25 °C for two days, during which time yellow needles formed. The supernatant was removed by pipet, and then the crystals were washed with pentane (1 mL) and dried under vacuum. Yield: 16.3 mg (90%). ^1H NMR (400 MHz, THF-d_8) δ 16.33 (br s, PNP), 15.33 (br s, PNP), 6.27 (br s, 8H, BPh_4), 6.20 (br s, PNP), 5.83 (br s, 8H, BPh_4), 5.75 (br s, 4H, BPh_4), 5.59 (br s, PNP), 4.19 (br s, PNP), 2.73 (br s, PNP), 1.30 (br s, PNP), −0.35 (br s, 2H, PNP), −1.74 (br s, 2H, PNP), −21.12 (br s, 9H, $Si(CH_3)_3$). UV−vis: 354 nm (ε = 2200 $M^{-1}cm^{-1}$), 444 nm (ε = 230 $M^{-1}cm^{-1}$). IR (thin film): ν_{N-H} = 3129 cm^{-1}.

[(PNMeP^{Cy})Co(Cl)]Cl (6). In a vial, PNMeP^{Cy} (25 mg, 0.0522 mmol) and $CoCl_2$ (6.8 mg, 0.053 mmol) were dissolved in THF (5 mL) and stirred for 5 h, forming a bright-blue solution. The solvent was removed under vacuum, and the blue solid washed with hexanes (3 × 3 mL). The solid was dried under vacuum. Yield: 23 mg (72%). ^1H NMR (400 MHz, THF-d_8) δ 8.37 (br s, PNP), 5.95 (br s, PNP), 0.68 (br s, PNP), 0.08 (br s, PNP), −0.21 (br s, PNP), −1.45 (br s, PNP), −7.10 (br s, PNP). UV−vis: 622 nm (ε = 530 $M^{-1}cm^{-1}$), 723 nm (ε = 330 $M^{-1}cm^{-1}$). μ_{eff} = 4.1 μ_B. Anal. calcd for $C_{29}H_{55}Cl_2CoNP_2$: C, 57.14; H, 9.09; N, 2.30. Found: C, 57.15; H, 9.21; N, 2.37.

[(PNMeP^{Cy})Co(CH_2SiMe_3)]BAr$^F_4$. (7). In each of two separate vials, PNMeP^{Cy} (191.8 mg, 0.400 mmol) and $(pyr)_2Co(CH_2SiMe_3)_2$ (156.5 mg, 0.400 mmol) were dissolved in toluene (5 mL), and the solutions were cooled to −25 °C. The two solutions were mixed and allowed to stir at ambient temperature for 30 min, during which time the reaction mixture turned a dark-brown color. The solvent was removed under vacuum, cold pentane (2 mL) was added and removed by a pipet rapidly, and the residue was dried under vacuum to give a brown sticky solid. The brown solid was then dissolved in diethyl ether (10 mL), and H[BAr$^F_4$]·$(Et_2O)_2$ (404.8 mg, 0.400 mmol) was added. The reaction mixture was stirred for 5 min, and then the solvent was removed under vacuum. The resulting brown solid was washed with pentane (3 mL) and dried under vacuum to give a pale-brown crude product (428.5 mg, ca. 72%). For recrystallization, the crude product (50.0 mg) was dissolved in diethyl ether (2 mL) in a small vial, the solution was layered carefully with pentane (5 mL), and the vial was sealed. The vial was then cooled to −25 °C for three days, during which time yellow blocks formed. The supernatant was removed by pipet, and then the crystals were washed with pentane (1 mL) and dried under vacuum. Recrystallization yield: 39.0 mg, 78%. ^1H NMR (400 MHz, THF-d_8) δ 18.05 (br s, PNP), 11.27 (br s, PNP), 10.60 (br s, PNP), 9.10 (br s, PNP), 4.53 (br s, PNP), −4.10 (br s, PNP), −4.32 (br s, PNP), −6.54 (br s, PNP), −17.81 (br s, 9H, $SiMe_3$). UV−vis: 354 nm (ε = 2500 $M^{-1}cm^{-1}$), 442 nm (ε = 330 $M^{-1}cm^{-1}$). Anal. calcd for $C_{65}H_{78}BCoF_{24}NP_2Si$: C, 52.43; H, 5.28; N, 0.94. Found: C, 51.99; H, 5.26; N, 0.86.

[(PNHP^{Cy})Co(κ^2-OC_6H_4CHO)]BAr$^F_4$ (8). In a small vial, complex **2** (6.1 mg, 10 μmol) and H[BAr$^F_4$]·$(Et_2O)_2$ (10.1 mg, 10 μmol) were dissolved in diethyl ether (0.5 mL), and 2-hydroxybenzaldehyde (12.2 mg, 0.1 mmol) was added. The solution was allowed to stand at room temperature for 30 min and layered carefully with pentane (1.0 mL). The vial was then cooled to −25 °C for three days, during which time dark-brown blocks formed. The solvent was removed by pipet, and then the crystals were washed with pentane (1 mL) and dried under vacuum. Yield: 13.4 mg (89%). ^1H NMR (400 MHz, THF-d_8) δ 41.70 (br s), 23.32 (br s), 3.78 (br s), 0.36 (br s), −0.43 (br s). UV−vis: 354 nm (ε = 4900 $M^{-1}cm^{-1}$), 441 nm (ε = 2500 $M^{-1}cm^{-1}$). IR (thin film): ν_{N-H} = 3178 cm^{-1}, $\nu_{C=O}$ = 1613 cm^{-1}. Anal. calcd for $C_{67}H_{70}BCoF_{24}NO_2P_2$: C, 53.33; H, 4.68; N, 0.93. Found: C, 53.06; H, 4.72; N, 0.91.

[(PNHP^{Cy})Co(κ^2-O,C−$C_6H_4C(O)CH_3$)(H)]BAr$^F_4$ (13). Complex **2** (12.1 mg, 20 μmol) and H[BAr$^F_4$]·$(Et_2O)_2$ (20.1 mg, 20 μmol) were dissolved in toluene (2.0 mL) in a 100 mL thick-walled glass vessel equipped with a Teflon stopcock and a stir bar. 1-Phenylethanol (24 μL, 0.2 mmol) was added, and the vessel was sealed. The sealed reaction vessel was heated in an oil bath at 120 °C for 18 h. At the end of the reaction, the reaction vessel was cooled to room temperature, and the reaction vessel was brought into the glovebox. The solvent was removed under reduced pressure and washed with pentane to give a yellow-brown solid. The crude product was recrystallized by diffusion of pentane into a diethyl ether solution at −25 °C, affording yellow needles, which were washed with pentane (2 × 0.5 mL) and dried under vacuum. Yield: 21.5 mg (71%). ^1H NMR (400 MHz, THF-d_8) δ 7.90 (d, 1H, *J* = 8.4 Hz, Co-aryl), 7.79 (br s, 8H, BAr$^F_4$), 7.57 (s, 1H, BAr$^F_4$), 7.49 (d, 1H, *J* = 8.0 Hz, Co-aryl), 7.10 (t, 1H, *J* = 7.2 Hz, Co-aryl), 7.02 (t, 1H, *J* = 7.2 Hz, Co-aryl), 4.71 (br s, 1H, N−H), 3.28−3.18 (m, 2H, PNP), 2.83 (s, 3H, CH_3), 2.35−2.25 (m, 4H, PNP), 2.00−1.85 (m, 10H, PNP), 1.58−1.24 (m, 22H, PNP), 1.06−0.83 (m, 12H, PNP), 0.59−0.51 (m, 2H, PNP), −23.67 (br t, 1H, $^2J_{P-H}$ ∼ 53 Hz, Co−H). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8) δ 60.5 (br s). UV−vis: 354 nm (ε = 5100 $M^{-1}cm^{-1}$), 462 nm (ε = 2800 $M^{-1}cm^{-1}$). IR (thin film): ν_{N-H} = 3184 cm^{-1}, $\nu_{C=O}$ = 1609 cm^{-1}. Anal. calcd for $C_{68}H_{73}BCoF_{24}NOP_2$: C, 54.16; H, 4.88; N, 0.93. Found: C, 54.08; H, 4.74; N, 1.11.

[(PNHP^{Cy})Co(κ^2-O,C-3-(OCH_3)$C_6H_4C(O)CH_3$)(H)]-BAr$^F_4$ (14). In the glovebox, complex **2** (12.1 mg, 20 μmol) and H[BAr$^F_4$]·$(Et_2O)_2$ (20.1 mg, 20 μmol) were dissolved in toluene (2.0 mL) in a 100 mL thick-walled glass vessel equipped with a Teflon stopcock and a stir bar. 1-(3-Methoxyphenyl)ethanol (30 mg, 0.2 mmol) was added, and the vessel was sealed. The sealed reaction vessel was heated in an oil bath at 120 °C for 18 h. At the end of the reaction, the reaction vessel was cooled to room temperature and brought into the glovebox. The solvent was removed under reduced pressure and washed with pentane to give an orange solid. Yellow-orange block-like crystals were obtained by recrystallization of the crude product by diffusion of pentane into a diethyl ether solution at −25 °C. Yield: 24.0 mg (78%). ^1H NMR (400 MHz, THF-d_8) δ 7.78 (br s, 8H, BAr$^F_4$), 7.62 (d, 1H, *J* = 7.2 Hz, Co-aryl), 7.57 (s, 4H, BAr$^F_4$), 7.06 (t, 1H, *J* = 7.2 Hz, Co-aryl), 6.65 (d, 1H, *J* = 7.2 Hz, Co-aryl), 4.72 (br s, 1H, N−H), 3.79 (s, 3H, -OCH_3), 3.27−3.16 (m, 2H, PNP), 2.84 (s, 3H, CH_3), 2.58−2.56 (m, 2H, PNP), 2.33−2.26 (m, 2H, PNP), 1.95−1.84 (m, 10H, PNP), 1.55−1.26 (m, 22H, PNP), 1.03−0.77 (m, 12H, PNP), 0.51−0.42 (m, 2H, PNP), −22.12 (br t, 1H, $^2J_{P-H}$ = 54 Hz, Co−H). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8) δ 60.0 (br s). UV−vis: 330 nm (ε = 4100 $M^{-1}cm^{-1}$), 440 nm (ε = 2200 $M^{-1}cm^{-1}$). IR (thin film): ν_{N-H} = 3142 cm^{-1}, $\nu_{C=O}$ = 1610 cm^{-1}. Anal. calcd for $C_{69}H_{75}BCoF_{24}NO_2P_2$: C, 53.88; H, 4.92; N, 0.91. Found: C, 54.05; H, 5.08; N, 1.09.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details, spectral data, X-ray crystallographic information and CIF files. 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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