# Well-Defined Cobalt(I) Dihydrogen Catalyst: Experimental Evidence for a Co(I)/Co(III) Redox Process in Olefin Hydrogenation

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S *Supporting Information*

ABSTRACT: The synthesis of a cobalt dihydrogen Co^I-(H_2) complex prepared from a Co^I-(N_2) precursor supported by a monoanionic pincer bis(carbene) ligand, ^{Mes}CCC (^{Mes}CCC = bis(mesityl-benzimidazol-2-ylidene)phenyl), is described. This species is capable of H_2/D_2 scrambling and hydrogenating alkenes at room temperature. Stoichiometric addition of HCl to the Co^I-(N_2) cleanly affords the Co^{III} hydridochloride complex, which, upon the addition of Cp_2ZrHCl, evolves hydrogen gas and regenerates the Co^I-(N_2) complex. Furthermore, the catalytic olefin hydrogenation activity of the Co^I species was studied by using multinuclear and parahydrogen (p-H_2) induced polarization (PHIP) transfer NMR studies to elucidate catalytically relevant intermediates, as well as to establish the role of the Co^I-(H_2) in the Co^I/Co^{III} redox cycle.
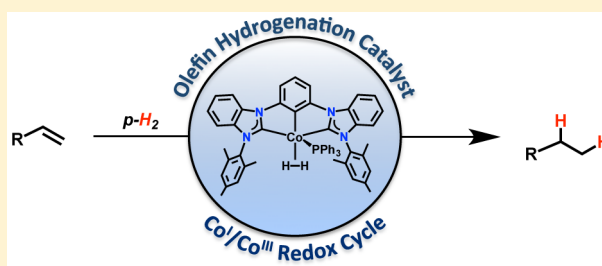
INTRODUCTION

Catalytic homogeneous hydrogenation is one of the most atom economical methods employed for the transformation of organic substrates. The abundant use of late second- and third-row transition metal systems in these reactions reflects the high activity, selectivity, and overall function conferred.[1] Detailed mechanistic studies elucidating oxidation state changes at the metal centers over the course of catalysis, as well as the nature of H_2 interaction and substrate binding, have enabled improvements to be made to these catalytic systems.[2]

More recently, there has been a wide interest in employing sustainable first-row transition metals in the hydrogenation of olefins. Work by Budzelaar,[3] Chirik,[4,5] Hanson,[6−8] and Peters[9,10] in this area clearly demonstrates the potential of ligand-assisted cobalt-based systems as hydrogenation catalysts. However, catalytic complexes featuring exclusively metal-centered reactivity with cobalt are rare.[11,12] As such, a detailed mechanistic study of such systems is necessary. Nonclassical transition-metal dihydride complexes, including those consisting of iron[13−16] and nickel,[17−20] are probable intermediates in a variety of catalytic H_2-producing and -consuming reactions, but further investigations are needed.[21−24]

Due to the inherent thermal instability of Co-(H_2) complexes, few can be studied in catalytic transformations. A recent example by the Peters group features a Co-(H_2) complex characterized by X-ray crystallography, and the thermal stability of the complex permitted equilibrium binding studies of the dihydrogen ligand.[25] Other Co-(H_2) complexes have been reported, but in these cases the thermal instability only allowed for *in situ* characterization at low temperature.[26−28] Interestingly, none of the reported Co-(H_2) complexes have proven to be effective catalysts. In fact, the only evidence of a Co-(H_2)

complex directly involved in catalysis was reported in a computational study of the $Co_2(CO)_8$-catalyzed oxo process developed by Ziegler and co-workers,[29,30] as well as an in NMR studies of phosphine derivatives of cobalt-hydroformylation catalysts employing parahydrogen (p-H_2) induced polarization (PHIP) transfer.[31,32]

We recently reported a series of cobalt pincer complexes featuring electron-rich monoanionic bis(carbene) ligands, ^{Mes}CCC and ^{DIPP}CCC (^{Mes}CCC = bis(mesityl-benzimidazol-2-ylidene)phenyl and ^{DIPP}CCC = bis(diisopropylphenyl-benzimidazol-2-ylidene)phenyl).[33] Cleavage of the strong aryl C−H bond was achieved in a one-pot metalation procedure to afford the Co^{III} complexes, whereby reduction of these species with the appropriate equivalents of reductant afforded the Co^{II} and Co^I complexes. Interested in further exploring low-valent cobalt catalysts to be employed in Co^I/Co^{III} catalysis,[34] we investigated the reactivity of our Co^I-(N_2) complex, (^{Mes}CCC)-CoN_2PPh_3 (**1-N_2**), to effect two-electron chemistry with dihydrogen. In doing so, we synthesized a Co^I-(H_2) complex that is catalytically active toward the hydrogenation of olefins under ambient conditions and have successfully identified various intermediates within the catalytic cycle using both multinuclear and PHIP transfer NMR studies. These studies provide strong evidence for a Co^I/Co^{III} redox in the catalytic cycle.

RESULTS AND DISCUSSION

Synthesis and Characterization of Co^I-(H_2) Complexes. The addition of H_2 (4 atm) to **1-N_2** at room
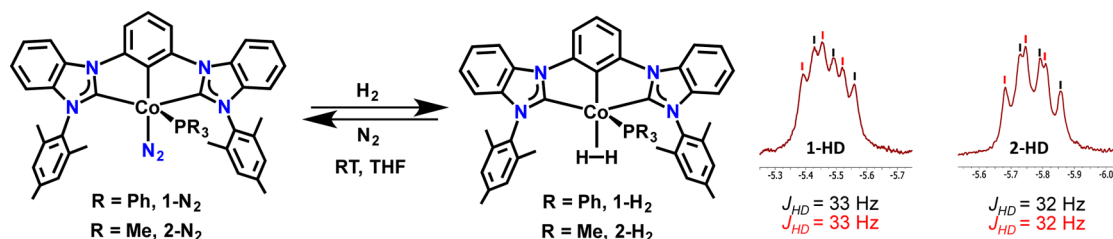
Figure 1. (Left) Synthesis of nonclassical Co^I-dihydride complexes ($1\text{-}H_2$ and $2\text{-}H_2$) from the Co^I-dinitrogen complexes. (Right) Truncated ^1H NMR spectrum showing the upfield region for **1-HD** and **2-HD**.
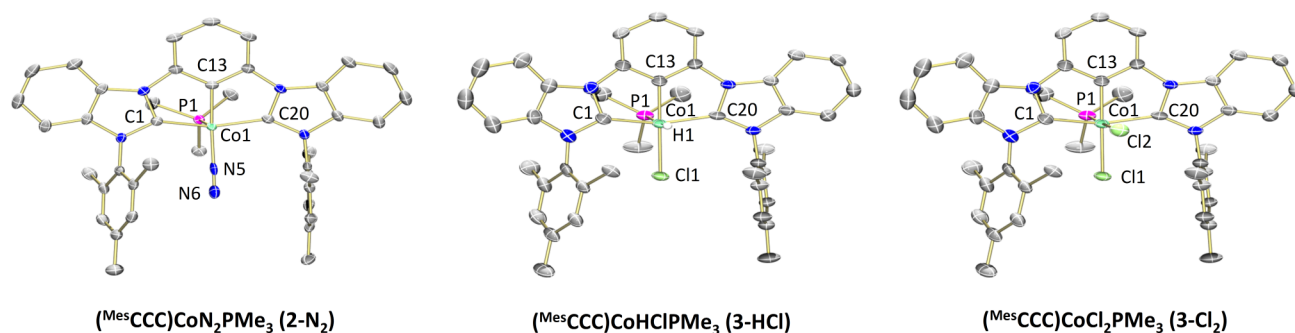

Figure 2. Molecular structures of $2\text{-}N_2$, $3\text{-}HCl$, and $3\text{-}Cl_2$ shown with 50% probability ellipsoids. Solvent molecules and H atoms have been omitted for clarity. Table of bond lengths and angles can be found in the SI (Table S1).

temperature in toluene-d_8 resulted in an immediate color change from dark red to red-orange (Figure 1). The ^1H NMR spectrum of the resulting species in toluene-d_8 revealed a new diamagnetic product (Figure S6). A shift of the three mesityl methyl resonances from 2.03, 1.92, and 1.62 ppm to 2.14, 1.82, and 1.30 ppm was observed and is consistent with a C_s-symmetric molecule in solution. An additional broad resonance at −5.56 ppm corresponding to 2H confirmed the addition of dihydrogen to yield ($^{Mes}CCC)Co(H_2)PPh_3$ ($1\text{-}H_2$). Subsequent exposure of $1\text{-}H_2$ to 1 atm of N_2 resulted in a color change back to dark red, indicating the formation of $1\text{-}N_2$ (Figure 1), which was verified by ^1H NMR spectroscopy.

To support our assignment of the resonance at −5.56 ppm as the added dihydrogen, the deuterium analogue of $1\text{-}H_2$ was prepared. Exposure of $1\text{-}N_2$ to 4 atm of D_2 in toluene-d_8 resulted in the formation of a red-orange diamagnetic species with identical pincer ligand resonances to those of $1\text{-}H_2$, as determined by ^1H NMR spectroscopy (Figure S7). Moreover, the absence of a broadened upfield resonance around −5.56 ppm in the ^1H NMR spectrum and observation of the corresponding resonance at −5.66 ppm in the ^2H NMR spectrum (Figure S8) confirmed that the dihydrogen gas was the source of this signal. Monitoring this solution over several days by ^2H NMR spectroscopy demonstrated that there was no incorporation of deuterium into the pincer ligand framework.

Given the facile and reversible nature of $1\text{-}H_2$ and $1\text{-}N_2$ formation, we next considered the possibility that $1\text{-}H_2$ was a nonclassical dihydrogen complex instead of a Co^{III}-dihydride. In order to determine the binding mode of H_2, T_1 relaxation studies on $1\text{-}H_2$ were performed. A T_1 study of the resonance at −5.56 ppm in a toluene-d_8 solution of $1\text{-}H_2$ from 203 to 343 K (Figure S1) gave the lowest T_1(min) value of 12 ms (253 to 313 K), supporting the formation of a nonclassical cobalt dihydride complex in solution, ($^{Mes}CCC)Co(H_2)PPh_3$ ($1\text{-}H_2$). The T_1 (min) value is consistent with other Co-(H_2) complexes reported in the literature.[25,26] Although this data is

consistent with a nonclassical bonding of H_2, Halpern and co-workers[35] reported that differentiating classical and nonclassical bonding of H_2 using the "T_1 criterion" requires a consideration of other NMR active nuclei. The high gyromagnetic ratio of ^{59}Co as well as the additional PPh_3 ligand in our complexes would naturally contribute to the relaxation rate of the bound H_2 ligand. Heinekey and co-workers have demonstrated upon a reinvestigation[36,37] that cationic nonclassical Co-(H_2) complexes[38,39] were more appropriately described as highly dynamic octahedral classical Co-$(H)_2$ molecules. They cited the absence of HD coupling and higher T_1 (min) measurements as a key part in their formulation.

In order to further understand the extent of H_2 coordination and activation, $1\text{-}N_2$ was reacted with HD gas. The resulting ^1H NMR spectrum of **1-HD** in toluene-d_8 displayed two sets of triplets at −5.56 and −5.60 ppm with a J_{HD} coupling constant of 33 Hz each (Figure S9). On the basis of previously reported correlations between J_{HD} and r_{HH} values by Morris,[40] the coupling constant corresponds to a r_{HH} of 0.87 Å, which is slightly shorter than other reported cobalt dihydrogen complexes ($r_{HH} = 0.95$[26] and 0.92[25] Å) and is consistent with a nonclassical binding mode of H_2 (d_{HH} of $H_2 = 0.74$ Å). Interestingly, the formation of free H_2 gas (4.50 ppm) was also observed in the ^1H NMR spectrum (Figures 1 and S9), suggestive of HD scrambling.

HD scrambling was probed further by adding a mixture of H_2 and D_2 (0.5 atm each) at 77 K to a degassed benzene-d_6 solution of $1\text{-}N_2$ (Figure S10). Within 10 min of warming to ambient temperature, the resulting ^1H NMR spectrum was consistent with the formation of **1-HD**, and, in addition, revealed a new triplet at 4.43 ppm ($J_{HD} = 43$ Hz), corresponding to the formation of HD as well as the expected singlet at 4.47 ppm for H_2. This result indicates that $1\text{-}N_2$ is capable of facilitating H_2/D_2 exchange, a process that is rare with cobalt,[25,41] and may be mediated by a transient Co^{III}-dihydrogen/dihydride species. However, Lewis acidic H_2
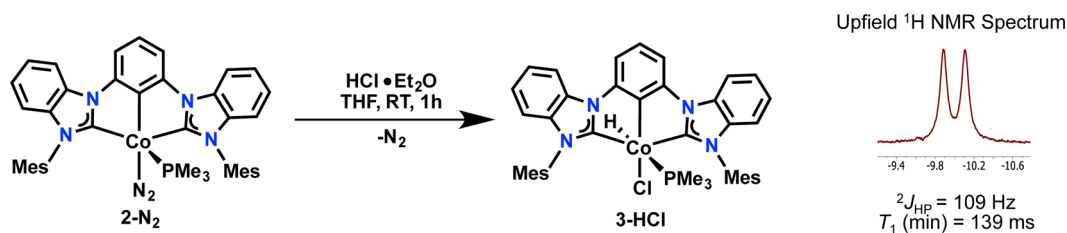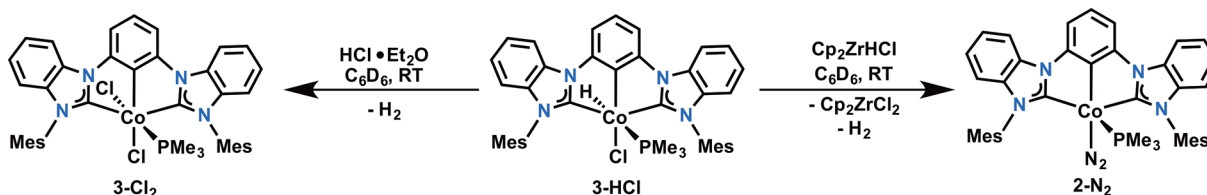
Figure 3. (Left) Synthesis of a Co^{III}−HCl molecule (**3-HCl**) via oxidative addition. (Right) Truncated ^{1}H NMR spectrum showing the upfield region for **3-HCl**.

Scheme 1

activation and deprotonation by exogenous base could not be ruled out as pathways for this scrambling process.[42]

Interested in understanding if the H−H bond was amenable to cleavage, a solution of **1-H$_2$** in toluene-d_8 was monitored by variable temperature ^{1}H NMR spectroscopy from −80 to 80 °C (Figures S24−S29). No changes suggesting H−H bond cleavage were observed in the ^{1}H NMR spectrum. Likewise, the dissociation of PPh$_3$ was not observed in either the ^{31}P or ^{1}H NMR spectrum over this temperature range.

These results prompted us to understand the role of the PPh$_3$ in H$_2$ binding and activation, and therefore, the substitution by a more basic phosphine, PMe$_3$, was targeted. Reduction of the previously published[33] (^{Mes}CCC)CoCl$_2$py with KC$_8$ in the presence of PMe$_3$ cleanly afforded the (^{Mes}CCC)CoN$_2$PMe$_3$ molecule (**2-N$_2$**) in good yields (see SI). Mesityl methyl resonances of **2-N$_2$** at 2.10, 2.09, and 2.02 ppm in the ^{1}H NMR spectrum establish a C_s coordination environment about the metal center and are slightly shifted downfield from that of **1-N$_2$**. X-ray crystallographic characterization (Figure 2) further established the connectivity of this square pyramidal ($\tau = 0.16$)[43] Co^I species. The two Co−C$_{NHC}$ bond lengths of 1.9033(19) and 1.9079(19) Å and the Co−C$_{aryl}$ bond length of 1.8734(19) Å are comparable to those in **1-N$_2$**. Similarly, the N$_2$ bond distance of 1.022(2) Å and an IR stretch (2114 cm^{-1}) (Figure S32) remain largely unactivated from free N$_2$ akin to that observed in **1-N$_2$**. In the presence of a more electron-donating phosphine, we hypothesized that the H−H bond may be more activated. The addition of H$_2$ (4 atm) to a degassed benzene-d_6 solution of **2-N$_2$** (Figure 1) resulted in the observation of a new species (**2-H$_2$**) by ^{1}H NMR spectroscopy, while 40% of the starting compound (**2-N$_2$**) remained unreacted. The mesityl methyl resonances are shifted slightly upfield to 2.02, 1.97, and 1.96 ppm, consistent with C_s-symmetry in solution. The presence of a broad resonance was observed at −5.77 ppm (Figure S13). Similar to **1-H$_2$**, a low T_1(min) value of 14 ms was observed for this resonance at 298 K, confirming σ-bound H$_2$ formulation, (^{Mes}CCC)Co(H$_2$)-PMe$_3$, **2-H$_2$**. A J_{HD} coupling constant of 32 Hz, obtained from treating **2-N$_2$** with a mixture of H$_2$ and D$_2$ (0.5 atm each) at 77 K, correlated[40] to an r_{HH} of 0.89 Å, demonstrating that the use of the more basic PMe$_3$ resulted in only a marginal elongation of the H−H bond (from 0.87 Å in **1-H$_2$**) (Figure S17). In

comparison to **1-H$_2$**, however, where the conversion to product was essentially quantitative, the use of the more electron-rich phosphine resulted in a lower conversion to **2-H$_2$**, indicating that H$_2$/N$_2$ exchange is slower or less favorable in the presence of the more basic phosphine.

Stoichiometric Reactivity of 2-N$_2$ with HCl. Since cleavage of the H−H bond is likely given the observed HD scrambling and Co-hydride species were not observed in variable temperature NMR studies, we sought a new synthetic pathway to understand H$_2$ reactivity with the cobalt center. The addition of 1 equiv of HCl·Et$_2$O to **2-N$_2$** resulted in the formation of an orange solution, and following workup, an orange solid, (^{Mes}CCC)CoHClPMe$_3$ (**3-HCl**), was isolated in good yields (Figure 3). Characterization of **3-HCl** by ^{1}H NMR spectroscopy in benzene-d_6 (Figure S18) revealed a similar ligand coordination environment to that observed in **2-N$_2$**. A doublet at −10.0 ppm corresponding to 1H with a T_1(min) value of 139 ms was assigned as a hydride and the large J value of this resonance ($^2J_{HP} = 109$ Hz) indicated a *trans* substitution of the hydride with respect to the phosphine. The observation of a similar resonance for the analogous reaction with DCl·Et$_2$O at −10.0 ppm ($^2J_{DP} = 16.4$ Hz) in the ^{2}H NMR spectrum (Figure S21) further established the source of the hydride was the added acid (no resonances indicative of the protonation of the carbene moiety or pincer framework were observed). The presence of an absorption band at 1828 cm^{-1} in the IR spectrum (Figure S33) was also consistent with a Co−H vibration mode, while the Co−D absorption band (calculated 1304 cm^{-1}) was not resolved in the fingerprint region of the IR spectrum.

Single crystals suitable for X-ray structure determination were grown from a concentrated diethyl ether solution of **3-HCl** and supported the oxidative addition of HCl onto **2-N$_2$**. The octahedral cobalt complex (Figure 2) has slightly elongated Co−C$_{NHC}$ (1.922(3) and 1.919(3) Å) and Co−P (2.2229(8) Å) bond lengths and a mildly shorter Co−C$_{aryl}$ bond length (1.857(3) Å) when compared to **2-N$_2$**. The Co−Cl bond distance of 2.3057(7) Å is longer than the two Co−Cl bond lengths in (^{Mes}CCC)CoCl$_2$py (2.2751(13) and 2.2651(12) Å), likely due to the C$_{aryl}$ trans influence. The hydride was found in the difference map with 88% occupancy and a bond length of 1.40(5) Å from the metal center. The

remainder of the electron density was modeled as a chloride atom with a bond length of 2.486(6) Å from the metal center, giving rise to a new Co^{III} species, (^{Mes}CCC)CoCl$_2$PMe$_3$, **3-Cl$_2$**. The formation of **3-Cl$_2$** likely coincided with the addition of a slight excess of 1 equiv of HCl to **2-N$_2$**. This was corroborated by the addition of another equivalent of HCl·Et$_2$O to a solution of **3-HCl** in benzene-d_6 (Scheme 1). The appearance of resonances corresponding to **3-Cl$_2$**, as well as H$_2$ gas observed in the ^{1}H NMR spectrum (Figure S31), supports that **3-Cl$_2$** is generated by the addition excess of HCl to **2-N$_2$**. Complex **3-Cl$_2$** was also independently prepared by the addition of 2 equiv of ClCPh$_3$ to complex **2-N$_2$** (see SI).

With complex **3-HCl** in hand, a hydride transfer reagent was added to the metal center to determine if the Co^{III}-(H$_2$) complex could be accessed. Under a dinitrogen atmosphere, the addition of Cp$_2$ZrHCl to a benzene-d_6 solution of **3-HCl** immediately resulted in the formation of **2-N$_2$** and Cp$_2$ZrCl$_2$ as well as H$_2$ gas, as assayed by ^{1}H NMR spectroscopy (Scheme 1 and Figure S30). The reaction likely proceeds through salt metathesis to generate a transient Co^{III}-cis(H)$_2$ species, followed by reductive coupling of dihydrogen and coordination of N$_2$ to yield **2-N$_2$**. This rapid reductive coupling suggests H$_2$/D$_2$ scrambling may in fact proceed via a Co^{III}-dihydride, but such a molecule is thermally unstable and, therefore, not easily detected via conventional characterization methods.
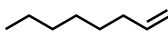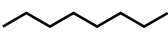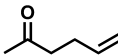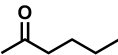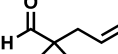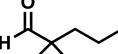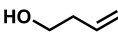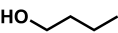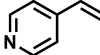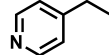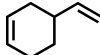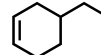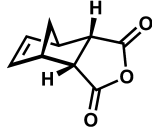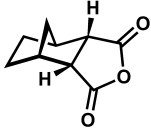
Olefin Hydrogenation with Co^{I}-(N$_2$) Complexes. Given the ability of the Co^{I}-(N$_2$) complexes to facilitate scrambling of H$_2$/D$_2$ as well as undergo oxidative addition and reductive elimination, we next probed the competency of the Co^{I}-(H$_2$) complexes toward catalytic hydrogenation of olefins, as transition metal dihydrogen complexes are often considered as transient intermediates in many catalytic hydrogenation reactions. In an effort to understand if **1-H$_2$** is catalytically relevant to the hydrogenation of olefins, a degassed benzene solution of **1-N$_2$** was exposed to H$_2$ (1 atm) for 10 min to generate **1-H$_2$** *in situ*. To this solution was added 50 equiv of styrene, and within 2 h at room temperature, the full conversion of styrene to ethylbenzene was observed by GC−MS. These hydrogenation studies were also monitored by ^{1}H and ^{13}C NMR spectroscopy (see SI). Upon addition of 4 atm of H$_2$ to a degassed benzene-d_6 solution of **1-N$_2$** or **2-N$_2$** (2 mol %) and styrene in a J. Young tube, the color of both of the mixtures changed from dark red to red-orange. Complete conversion to ethylbenzene was readily achieved within 2 h with **1-N$_2$**, while unsurprisingly **2-N$_2$** did not perform as well. Only 30% conversion was obtained when using **2-N$_2$**, likely the result of the lack of formation of **2-H$_2$** and phosphine−olefin exchange throughout catalysis. In the case of **1-N$_2$**, **1-H$_2$** was observed upon the completion of the reaction, indicating that **1-H$_2$** is the resting state of the catalytic cycle. To our knowledge this is the first example of a well-defined homogeneous cobalt dihydrogen complex that has been demonstrated to be an effective hydrogenation catalyst.

To better understand the nature of this catalysis, elemental mercury was added to a catalytic run, and no change in reactivity was observed indicating that this process is homogeneous.[44] Furthermore, we were curious about the role PPh$_3$ has in the catalysis, as dissociation of PPh$_3$ must occur given the electronic saturation of **1-N$_2$** and **1-H$_2$**. To this end, we examined the effect of adding excess PPh$_3$ to a catalytic reaction (Table S3). The addition of 5 mol equiv of PPh$_3$ with respect to **1-N$_2$** resulted in a diminished conversion of styrene to ethylbenzene (50%) after 2 h at room temperature.

Furthermore, the addition of 12.5 and 25 mol equiv of PPh$_3$ led to 12% and 6% conversion to ethylbenzene, respectively, as determined by ^{1}H NMR spectroscopy. This diminished conversion is consistent with dissociation of PPh$_3$ during catalysis.

Encouraged by the ability of **1-H$_2$** to effectively hydrogenate styrene, we expanded the substrate scope to include more sterically hindered olefins. Under catalytic conditions (2 mol % catalyst, 4 atm of H$_2$ in benzene-d_6 at room temperature) a variety of olefins bearing different functional groups were successfully hydrogenated (Table 1). Functionalities such as

Table 1. Olefin Hydrogenation Substrate Scope

Entry	Substrate	Product	conversion^a	time
1			>99%	3 h
2			>99%	2 h
3			>99%	22 h
4			>99%	2 h
5			>99%	2 h
6			>99%	21 h
7^b			>99%	2 h
8^c			>99%	22 h
9^c			>99%	17 h

^{a}Conversion was monitored by ^{1}H NMR. ^{b}Alkane product obtained after heating to 60 °C for 19 h. ^{c}Reaction was heated to 60 °C.

hydroxyl groups, ketones, anhydrides, and aldehydes did not inhibit catalytic activity and were not reduced. Interestingly, hydrogenation of cyclohexene did not proceed well at room temperature, but upon heating to 60 °C, complete conversion to cyclohexane was achieved (Table 1, entry 8). Selectivity toward terminal alkenes over internal alkenes was established with 4-vinylcyclohexene. At room temperature the terminal alkene was reduced (entry 7), and upon heating to 60 °C, the reduction of the internal C=C bond was achieved.

Mechanistic Studies. Having established that the reactivity of **1-N$_2$** with H$_2$ results in an arrested intermediate (**1-H$_2$**) in the oxidative addition of H$_2$ rather than a formal oxidation state change by the metal center and reasoning that catalytic activity

of these cobalt complexes likely proceeds through more than one oxidation state, we performed further mechanistic studies.

Toward this end, parahydrogen ($p\text{-}H_2$) was generated,[45] and parahydrogen induced polarization (PHIP) transfer NMR spectroscopy was performed in order to identify reaction intermediates.[46−48] This analytical technique has the possibility of selectively enhancing the signal of the reacting $p\text{-}H_2$ molecule by up to 5 orders of magnitude over the traditional Boltzmann distribution (10^{-5}). In order for the polarization to be observed, the $p\text{-}H_2$ molecules have to be transferred in a pairwise manner to magnetically distinctive positions on a substrate, while remaining mutually coupled. Furthermore, this transfer polarization process has to occur faster with respect to relaxation of the nuclear spin isomer of $p\text{-}H_2$.[49,50] The use of PHIP NMR spectroscopy has successfully allowed for the detection of organometallic reaction intermediates, especially those employed in hydrogenation reactions, which normally would have been "invisible" toward characterization by conventional methods.[49,51,52] The PHIP NMR data presented in this study were obtained by using a 45° pulse and with the use of a double quantum OPSY (only parahydrogen spectroscopy)[53] filter in the ^1H NMR spectrum following introduction of $p\text{-}H_2$ at low field (following ALTADENA[46] conditions, see SI).

The addition of $p\text{-}H_2$ (4 atm) to a solution of **1-N$_2$** in benzene-d_6 resulted in an identical ^1H NMR spectrum to that of **1-H$_2$**; no polarization of any signals was detected. If polarization did occur, then it would provide direct evidence that the H−H bond is broken and oxidative addition of H_2 on the metal center has occurred; however, since that is not the case, these results further support our initial formulation, in which **1-H$_2$** is best described as a dihydrogen complex (Figure 4).
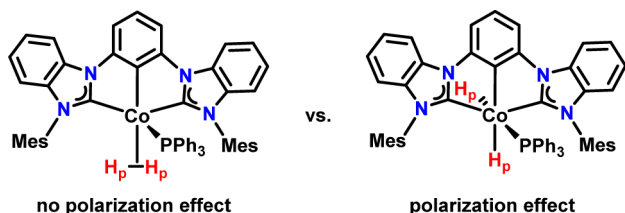

Figure 4. Expected PHIP effect of **1-H$_2$** (left) and the oxidative addition product of **1-H$_2$** (right).

We next explored PHIP studies under catalytic conditions. Upon the addition of $p\text{-}H_2$ (4 atm) to a solution of **1-N$_2$** (2 mol %) and styrene in benzene-d_6, polarization in the aliphatic and vinyl/aryl (sp^2 C−H) regions were observed in the ^1H and ^1H-OPSY NMR spectra (Figure S50 and Figure 5, respectively). Resonances at 1.07 and 2.44 ppm corresponding to the hydrogenation product of styrene (ethylbenzene) demonstrate that both H atoms of the H_2 molecule add to the substrate in a concerted fashion (Figure 5, known as ALTADENA). The polarization effect observed for resonances at 5.07, 5.59, 6.55, and 7.00−7.25 ppm suggests that a reversible exchange process in the hydrogenation reaction is operative (Figure 5, SABRE). SABRE (signal amplification by reversible exchange) occurs by polarizing a substrate using $p\text{-}H_2$ without any chemical transformation to the substrate.[54] Duckett and co-workers[54−56] have demonstrated the transfer of nuclear spin polarization to substrates without the incorporation of $p\text{-}H_2$, while citing the importance of the reversible binding of the substrate, and, in addition, have provided a theoretical
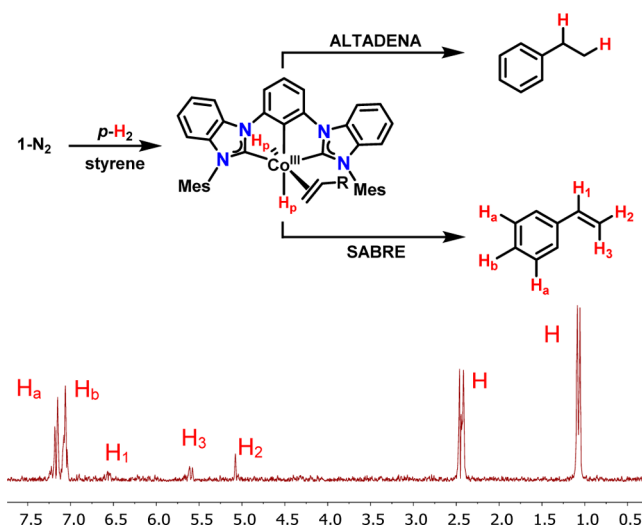

Figure 5. ^1H-OPSY NMR spectrum showing the hydrogenation of styrene using **1-N$_2$** with $p\text{-}H_2$.

understanding of this process.[57] In our case, only some of the nuclear spin polarization from $p\text{-}H_2$ transfers to styrene without hydrogenating the substrate. This indicates that the coordination of styrene and oxidative addition of H_2 onto the Co^I center proceeds in a joint manner, and that styrene coordination is reversible. Furthermore, this signal enhancement was also observed in the ^1H-OPSY NMR spectrum when using 4-vinylcyclohexene as the substrate, suggesting this effect is general and not specific to styrene (Figure S51).

In order to further investigate the reversible exchange process observed in the PHIP studies, we examined the feasibility of deuterium incorporation into styrene. Following the addition of D_2 (4 atm) to a benzene solution of **1-N$_2$** (2 mol %) and styrene, the incorporation of deuterium was observed in the olefinic region (5.05, 5.58, and 6.55 ppm) of styrene and the aliphatic region of the product (ethylbenzene) within 1 h at room temperature, as assayed in the ^2H NMR spectrum (Figure S46). The observation of **1-H$_2$**, **1-HD**, H_2, and HD gas in the ^1H NMR spectrum following the completion of the reaction (Figure S45), as well as HD gas in the ^2H NMR spectrum (Figure S46), are representative of another reversible reaction occurring over the course of catalysis. The observation of H_2 and HD likely occurs via β-hydride elimination from a Co-alkyl complex (*vide infra*). Deuterium labeling studies with cyclohexene revealed a similar scrambling process, indicating this process is general and not specific to styrene (Figures S47 and S48).

On the basis of data presented thus far, a comprehensive mechanistic picture of the catalytic hydrogenation process of **1-N$_2$** is proposed (Scheme 2). We have demonstrated through T_1 relaxation and HD labeling studies that a dihydrogen complex, **1-H$_2$**, is generated under an H_2 atmosphere by displacing the N_2 ligand from **1-N$_2$**. Next, PHIP NMR data supports that olefin displacement of the bound phosphine (***I-1***) must occur. No signal enhancements were observed upon the addition of $p\text{-}H_2$ to a solution containing only **1-N$_2$**; the olefin must be present for this enhancement to occur. Moreover, the addition of excess PPh$_3$ inhibits catalytic reactivity. Next, H_2 oxidatively adds onto the metal center to generate a Co^{III}-dihydride intermediate, ***I-2***. The polarization of styrene by SABRE indicates that the formations of ***I-1*** and ***I-2***, as well as ***I-1*** and **1-H$_2$**, are reversible and that oxidative addition of H_2 onto the

Scheme 2
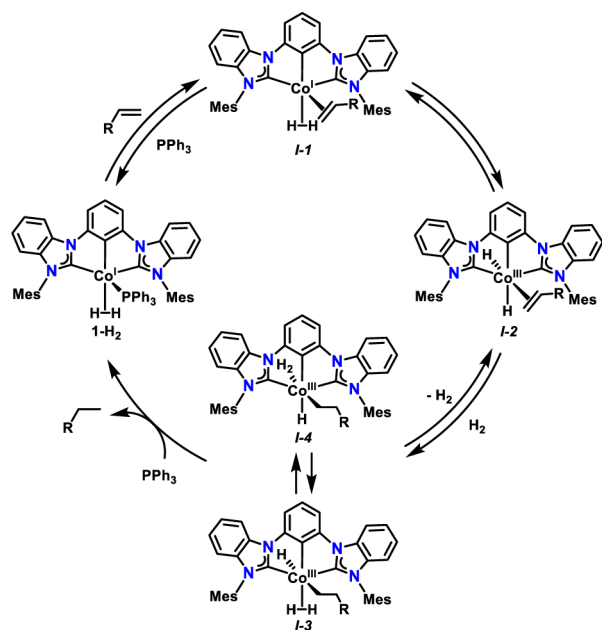
cobalt center does occur. Following *I-2* formation, migratory insertion generates a dihydrogen hydride, *I-3*. Detection of partially deuterated substrates is indicative of β-hydride elimination from *I-3* to generate *I-2*, accompanied by dissociation of H_2. The observation of HD and H_2 in deuterium studies strongly suggests that HD exchange occurs via complexes *I-3* and *I-4*, and further establishes that β-hydride elimination must be operative. Lastly, **1-H₂** is regenerated by reductive elimination of the alkane product and recoordination of PPh_3 to the cobalt complex.

CONCLUSION

In summary, a "Kubas-type" cobalt dihydrogen complex supported by a monoanionic bis(carbene) ligand platform was prepared and characterized in solution using multinuclear NMR studies. In the course of our studies, it was determined that Co^I-(N_2) precursors **1-N₂** and **2-N₂** exchange N_2 for H_2 and are able to facilitate the scrambling of H_2 and D_2. Stoichiometric examples of oxidative addition and reductive elimination with the CCC ligand platform demonstrate the viability of Co^I/Co^{III} redox couples in such scrambling processes and support the formation of a Co^{III}-$(H)_2$ intermediates. Furthermore, **1-N₂** is competent toward the hydrogenation of olefins in the presence of hydrogen gas. A number of studies suggest the dihydrogen complex, **1-H₂**, is the resting state of the active catalyst. Finally, the use of ^1H, ^2H, and PHIP NMR studies has enabled the identification of key reaction intermediates and established the role of the cobalt(I) dihydrogen complex, **1-H₂**, in the catalytic hydrogenation of olefins.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07066.

Crystallographic details for **2-N₂**, **3-HCl**, and **3-Cl₂** (CIF)

Spectral data and synthesis for complexes **1-H₂−3-Cl₂** and additional crystallographic data (PDF)

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Notes

The authors declare no competing financial interest.

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