Dihydrogen Binding to Isostructural $S = \frac{1}{2}$ and $S = 0$ Cobalt Complexes

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ABSTRACT: Two isostructural, nonclassical Co(H$_2$) complexes are prepared from their Co(N$_2$) precursors using tris(phosphino)silyl and tris(phosphino)borane ancillary ligands. Comproportionation of CoBr$_2$ and Co metal in the presence of TPB (tris-(o-diisopropylphosphinophenyl)borane) gives (TPB)-CoBr$_4$. One-electron reduction of 4 triggers N$_2$ binding to give (TPB)Co(N$_2$)(2-N$_2$) which is isostructural to previously reported [SiP$_3$]Co(N$_2$)(1-N$_2$) ([SiP$_3$] = tris-(o-diisopropylphosphinophenyl)silyl). Both 1-N$_2$ and 2-N$_2$ react with 1 atm H$_2$ to generate thermally stable H$_2$ complexes 1-H$_2$ and 2-H$_2$, respectively. Both complexes are characterized by a suite of spectroscopic techniques in solution and by X-ray crystallography. The H$_2$ and N$_2$ ligands in 2-H$_2$ and 2-N$_2$ are labile under ambient conditions and the binding equilibria are observable by temperature-dependent UV/vis. A van’t Hoff analysis allows for the ligand binding energetics to be determined (H$_2$: $\Delta H^\circ = -12.5(3)$ kcal mol$^{-1}$ and $\Delta S^\circ = -26(3)$ cal K$^{-1}$ mol$^{-1}$; N$_2$: $\Delta H^\circ = -13.9(7)$ kcal mol$^{-1}$ and $\Delta S^\circ = -32(5)$ cal K$^{-1}$ mol$^{-1}$).

INTRODUCTION

Cobalt-based coordination compounds are active catalysts for a number of H$_2$-producing and -consuming reactions, including H$^+$ reduction,$^1$ H$_2$ storage,$^2$ and hydroformylation.$^3$ In each of these processes, nonclassical Co(H$_2$) complexes are probable intermediates, and H$_2$ binding (or release) is likely an elementary mechanistic step. For example, interest in developing earth-abundant catalysts for H$^+$ reduction has prompted mechanistic investigations of several Co-based catalysts.$^4$ The three most plausible mechanisms (Scheme 1) invoke H$_2$ release from a transient Co(H$_2$) complex formed by protonation of a Co(II)H species (1), bimolecular coupling of two Co(II)H species (2), or protonation of a Co(III)H species (3). Although mechanisms (1) and (2) employ an $S = \frac{1}{2}$ Co(H$_2$) complex, such a complex has never been observed. In fact, reports of open-shell metal dihydrogen complexes are scant.$^5,6$ There are a few reports of closed-shell Co(H$_2$) complexes,$^7,8$ (Figure 1); in each case, the complexes’ thermal instability called for in situ characterization at low temperature. In addition, the energetics of H$_2$ binding to Co in any spin state or to any homogeneous, open-shell metal complex have not been experimentally ascertained. Given the broad scope of current research interest in the hydrogen chemistry of cobalt, we sought to develop model systems that fill this void. This work presents solution-state and structural studies of a pair of isostructural Co(H$_2$) complexes in two spin states, including the first example of an $S = \frac{1}{2}$ Co(H$_2$) complex. The thermal stability of the complexes allowed for single crystal X-ray diffraction$^9$ and equilibrium binding studies that are the first of their kind for well-characterized Co(H$_2$) complexes.

Homogeneous Co complexes with hard donors are not known to form stable H$_2$ complexes. In contrast, the recently reported $S = 0$ nonclassical Co(H$_2$) complex (pocop)Co(H$_2$) (pocop = k$^2$-C$_6$H$_3$-1,3-[OP('Bu)$_2$]$_2$)$^7e$ is stable in solution below 220 K and is supported by soft, polarizable phosphines; this feature likely promotes low-temperature H$_2$ binding and thwarts degradative pathways such as oxidative addition or heterolytic cleavage. In addition, its square planar geometry allows it to react with >1 equiv H$_2$. With these hypotheses in

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mind, we targeted highly covalent Co fragments of coordination number >3 in order to generate thermally robust Co(H₂) complexes. In particular, we utilize two tetradentate ligands: neutral TPB (tris-(o-diisopropylphosphinophenyl)borane), introduced by Bourissou, 10 and anionic SiP₃ tris-(o-diisopropylphosphinophenyl)silyl), introduced by our lab. 11 Group 10 complexes of the latter ligand have been demonstrated to bind weak σ-donors including H₂ and N₂ while providing minimal activation via π-backbonding. 12

### RESULTS AND DISCUSSION

**Preparation of Co(N₂) Synthons.** We previously reported the S = 0 [SiP₃]Co(N₂) complex (1-N₂) 11 and targeted the isostructural complex (TPB)Co(N₂) (2-N₂) as a precursor to an S = 1/2 Co(H₂) species. Installation of Co into TPB (3) was accomplished by metalation with CoBr₂ in the presence of excess Co powder (Scheme 2). Orange-brown (TPB)CoBr (4) has a solution magnetic moment of $\mu_{\text{eff}} = 3.0 \mu_B$ (298 K), consistent with an $S = 1$ spin state. Its solid-state geometry is between tetrahedral and trigonal bipyramidal with a Co–B distance of 2.4629(8) Å (Figure 2). Thus, 4 can be viewed analogously to Thomas’s Co–Zr heterobimetallic complexes supported by phosphinoamide ligands. 13

Reduction of 4 with NaC₁₀H₈ under N₂ yields yellow, S = 1/2 (TPB)Co(N₂) (2-N₂; $\mu_{\text{eff}} = 1.5 \mu_B$ 298 K). Its EPR spectrum shows a nearly axial signal ($g = [2.561, 2.077, 2.015]$) (Figure 3, top). In the solid state, 2-N₂ adopts a trigonal bipyramidal geometry with a Co–B bond length of 2.319(1) Å (Figure 2). The N₂ ligand of 2-N₂ is labile in solution as well as in the solid state (vide infra). An intense $\nu$(N–N) stretch is observed by IR spectroscopy at 2089 cm⁻¹. Compared with isostructural 2-N₂, 1-N₂ has one additional valence electron and has a correspondingly lower $\nu$(N–N) IR stretch of 2063 cm⁻¹. 11,14 A similar $\nu$(N–N) stretch (2081 cm⁻¹) has been recently reported for a topologically related cobalt alatrane complex. 15

**Characterization of [SiP₃]Co(H₂) and (TPB)Co(H₂).** Although 1-N₂ is stable to vacuum in solution, it converts over several hours to 1-H₂ under 1 atm H₂ at RT (Scheme 3).

Both 1-H₂ and 1-N₂ are orange and exhibit a single sharp resonance in their $^{31}$P NMR spectra (79.8 and 65.6 ppm, respectively), consistent with a C₃-symmetric structure in solution. The $^1$H NMR signals for the dihydrogen ligands of 1-H₂ and 1-HD appear at $-7.78$ ppm and $-7.80$ ppm ($J_{\text{HD}} = 30$ Hz), respectively (Scheme 3 inset). Temperature-dependent $T_1$ relaxation studies reveal $T_1(\text{min}) = 29$ ms (243 K, 500 MHz). The high $J_{\text{HD}}$ coupling constant and low $T_1(\text{min})$ value support

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**Scheme 2**

![Scheme 2](image)

**Figure 2.** Solid-state structures of 4 (left) and 2-N₂ (right). H atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level.

**Scheme 3**

![Scheme 3](image)

**Figure 3.** EPR spectra of 2-N₂ (top), 2 (middle), and 2-H₂ (bottom) recorded in toluene glass at 10 K and 9.38 GHz. Black traces: experiment; red traces: simulation.
the formulation of 1-H2 as a nonclassical H2 complex rather than a dihydride in solution.\textsuperscript{16}

Although 1-H2 is indefinitely stable in solution at RT under an H2 atmosphere, 1-N2 is slowly formed upon exposure of 1-H2 to 1 atm N2. The thermal stability of 1-H2 allowed us to obtain high-quality single crystals for an X-ray structure determination (Figure 4). The data reveal a coordination geometry of approximately C\texttextsuperscript{3} with Co–P and Co–Si distances slightly shorter than those observed in 1-N2. The apical H2 ligand could not be located in the difference map, though a globular disk of residual electron density is observed (\textit{vide infra}).

Unlike for 1-N2, application of vacuum to a toluene solution of 2-N2 results in formation of a new species. Dark brown 2 absorbs more strongly than 2-N2 in the entire visible region, with the former having characteristic absorption bands at 510–520 and 806 nm (\(g = 2.457, 2.123, 2.029\)). The EPR spectra of 2-H2 and 2-D2 are identical (see SI) and broad; as a result, no \(^1\)H hyperfine coupling can be gleaned. Raman spectra of 2-H2 and 2-D2 (in both solution and solid states) are identical; this observation precludes the presence of Co–H(D) bonds in 2-H2(D2) which are expected to have observable stretches that are subject to isotopic shifts approximated by the harmonic oscillator model. In contrast to M–H(D) stretches, H–H and D–D stretches often are too weak to observe or are obscured by resonances attributed to the other ligands.\textsuperscript{5,6}

Orange single crystals of 2-H2 were grown by slowly cooling a saturated solution of 2-H2 under 1 atm H2. The sample diffracted strongly to 0.58 Å, and the final solution (not including the H2 ligand) fits the data very satisfactorily (see SI). The (TPB)Co frameworks of 2-N2 and 2-H2 are similar, with the latter exhibiting slightly contracted Co–P and Co–B bonds (Figure 4 and Table 1). The analogous contraction in Co–P and Co–Si bond lengths also occurs between 1-H2 and 1-N2. Akin to 1-H2, a globular disk of residual positive electron density trans to the B atom is observed. The irregular shape may arise from static positional disorder of the H2 ligand or from dynamic tunneling between states separated by the rotational barrier of the H2 ligand as was postulated for the related complex [SiP\texttextsuperscript{3}]Fe(H2)\texttextsuperscript{5} 5-H2.\textsuperscript{6} A similarly shaped surface of the residual electron density is generated from the X-ray data of 5-H2 (see SI).

The non-H atom locations of 2-N2 and 2-H2 provide further support for formulating 2-H2 as an H2 complex rather than a dihydride. In particular, an octahedral cis-dihydride is expected to exhibit one wide P–Co–P angle to accommodate a bisecting hydride

![Figure 4. Solid-state structures of 1-H2 (top, left) and 2-H2 (top, right). H atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Positive residual electron density isosurfaces of 1-H2 (bottom, left) and 2-H2 (bottom, right) drawn at the +0.47 electrons Å\texttextsuperscript{-3} level.](image-url)

Table 1. Selected Bond Lengths and Angles

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Figure 5. Temperature-dependent UV/vis studies of H2 (left) and N2 (right) binding to 2 in toluene under 1 atm H2 or N2. The top traces in the UV/vis spectra are pure 2 in toluene under vacuum. Darker traces correspond to higher temperatures. Van’t Hoff plots of the equilibrium of H2 or N2 binding to 2 are derived from the concentration of 2 as indicated by the absorbance at 740 nm (see Experimental Section). The standard states for 2, 2-H2, 2-N2, H2, and N2 are defined as 1 M in toluene for all species at 25 °C. Caution should be exercised in directly comparing these thermodynamic values since the standard states may be defined differently.

Figure 5, left). A van’t Hoff analysis reveals the energetics of H2 binding to 2: ΔH° = −12.5(3) kcal mol−1 and ΔS° = −26(3) cal K−1 mol−1. These values may include contributions from a weak agostic interaction or interaction with solvent, depending on the solution structure of 2 (vide supra). This work is, to our knowledge, the first time the energetics of H2 binding to a homogeneous Co complex have been determined experimentally. These values are in line with representative examples of H2 binding energetics for other homogeneous metal complexes (ΔH°: −6.5 to −18 kcal mol−1; ΔS°: −19 to −44 cal K−1 mol−1).28 Caution should be exercised in directly comparing these thermodynamic values since the standard states may be defined differently.

An analogous study of N2 binding to 2 was undertaken between 30.2−86.3 °C (toluene, 1 atm N2; Figure 5, right), and the energetics of N2 binding to 2 were determined to be ΔH° = −13.9(7) kcal mol−1 and ΔS° = −32(5) cal K−1 mol−1. Compared with N2 binding H2 is slightly less favorable enthalpically and less disfavorably entropically. The more negative value of ΔS° for N2 binding is in part due to the higher absolute entropy of free N2. Similar observations have been made for Cr, Mo, and W complexes.20h,2f

Comparison with Related Trigonal Bipyramidal M(H2) Complexes. Isostructural 1-H2 and 2-H2 are themselves rare examples of Co(H2) complexes and, along with [SiP3]Fe(H2) (5-H2) and [[SiP3]Ni(H)]{BARF}6-H2),12a constitute a family of (M−E)4 and (M−E)10 H2 complexes that are well-suited for comparison (Table 2).21 For example, 2-H2 and 5-H2 are valence isoelectronic, thermally stable complexes. However, the M(H2) interaction is weaker in 2-H2 presumably due to the poorer π-backbonding ability of Co compared with Fe. This difference allows for the equilibrium of N2 and H2 binding to 2 to be observed at ambient conditions (1 atm H2 or N2 at RT), whereas S-N2 and S-H2 are stable to vacuum. On the other hand, 1-H2 and 2-H2 are neutral complexes of Co that vary by

ligand. The widest P−C−P angle in 2-H2 is 124.49(1)° which is significantly narrower than would be expected.18 Alternatively, if the H−H bond is cleaved in 2-H2 to give a trigonal bipyramidal species of the form Co(H)(TPB-H), the boron in 2-H2 would be expected to be tetrahedral with nearly linear B−H−Co bonding; this isomer would have a significantly longer Co−B distance than what is observed. The non-H atom positions in the DFT-optimized structure (see SI) are consistent with the X-ray structure; the intact H2 ligand in the optimized structure is not significantly elongated compared with free H2 (0.82 and 0.74 Å, respectively).

Although the spectroscopic and computational data support the formulations of 1-H2 and 2-H2 as nonclassical H2 complexes, it remains possible that dihydride structures and/or a hydride−borohydride structure for 2-H2 are thermally accessible. We have observed reversible H2 activation across a M−B bond in a related diphosphinoborane nickel systems to form a (B−H)Ni(H) motif.19 Both 1-H2 and 2-H2 facilitate scrambling of HD to give H2, D2, and HD; although this process may be mediated by transient hydrido species, it may also be accomplished by other conceivable mechanisms such as Lewis acidic H2 activation and deprotonation by trace exogenous base.

Thermochemistry of H2 and N2 Binding to 2. The lability of N2 and H2 from 2-N2 and 2-H2 under vacuum contrasts with the behavior of 1-N2 and 1-H2 (both of which are stable to vacuum). Additionally, the UV/vis spectra of 2-N2 and 2-H2 (1 atm N2 or H2, toluene, RT) show a small quantity of 2 which is readily identified by its characteristic band at 806 nm. This subtle feature prompted us to study the thermochemistry of H2 and N2 binding to 2 by UV/vis spectroscopy.

Gratifyingly, the temperature dependence of KΩ2 could be extracted by monitoring the concentration of 2 by UV/vis spectroscopy in the range 24.2−81.7 °C (toluene, 1 atm H2;
In conclusion, a pair of isostructural Co(H2) complexes have been prepared and characterized. 1-H2 and 2-H2 are notable for their thermal stability and are the first Co(H2) complexes to be characterized crystallographically. In addition, 2-H2 is the first reported S = 1/2 Co(H2) complex and one of very few well-characterized paramagnetic M(H2) complexes. The less electron-rich 2-H2 binds H2 (and N2) less strongly than the S = 0 complex 1-H2(N2). This attenuated binding strength allows for the solution equilibrium energetics of H2 and N2 binding to 2 to be observed. This work demonstrates that within a family of isostructural (M−E)910 H2 complexes, the valence electron count and the H2 binding affinity may be systematically tuned by adjusting the identity of the M−E unit.

**EXPERIMENTAL SECTION**

**General Considerations.** All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of dinitrogen. Solvents were degassed and dried by sparging with N2 gas and passage through an activated alumina column. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3 Å molecular sieves prior to use. Reagents were purchased from commercial vendors and used without further purification unless otherwise noted. 1-N23 and (TPB)24 were synthesized according to literature procedures. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN).

**Spectroscopic Measurements.** 1H, 13C, and 31P NMR spectra were collected at room temperature, unless otherwise noted, on Varian 300 MHz, 400 MHz, and 500 MHz NMR spectrometers. 1H and 13C spectra were referenced to residual solvent resonances. 31P spectra were referenced to external 85% phosphoric acid (δ = 0 ppm). T1(1H) values were determined by fitting the pulse-recovery 1H spectra at various temperatures using the T1 calculation protocols in either Varian’s VnmrJ software or Mestrelab Research S. L.’s Mestrenova version 6.2.1. EPR spectroscopy were recorded on a Bruker Ems spectrometer at ~1 mM concentrations. IR measurements were obtained in KBr pellets using a Bio-Rad Excalibur FTS 3000 spectrometer with Varian Resolutions Pro software. Solution-state Raman spectra were acquired using a coherent Innova 70 S-W Ar-ion laser, a Spex 750 M spectrophotograph with a 1200 gr/mm grating, and a Horiba Jобin Yvon Synapse TE cooled CCD detector. Solid-state Raman spectra were acquired on a Renishaw M1000 Micro Raman spectrometer system using an Ar ion laser and 514.5 nm excitation.

**X-ray Crystallography.** X-ray diffraction studies were carried out at the Caltech Division of Chemistry and Chemical Engineering X-ray Crystallography Facility on a Bruker three-circle SMART diffractometer with a SMART 1K CCD detector. Data were collected at 100 K using Mo Kα radiation (λ = 0.71073 Å). Structures were solved by direct or Patterson methods using SHELXS and refined against F2 on all data by full-matrix least-squares with SHELXL-97. All crystal hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at geometrically calculated positions and refined using a riding model except for those corresponding to H2 ligands. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 (1.5 for methyl groups) times the Ueq of the atoms to which they are bonded.

**Computational Details.** All calculations were performed using the Gaussian03 suite.16 The geometry optimizations were done without any symmetry restraints at the DFT level of theory using the B3LYP hybrid functional. The 6-31G(d) basis set was used for all atoms. The full ligand was used for each calculation, and the minimized structures were verified with frequency calculations. The starting coordinates for the metal and ligand were taken from the crystal structures. To model H2 adducts, hydrogen atoms were initially placed in the apical binding site at an arbitrary initial distance of 1.5 Å from the metal and 0.9 Å from each other. To model dihydrogen, hydrogen atoms were initially placed orthogonal to one another (one in the apical site and one bisecting a P−M−P angle) at a distance of 1.4 Å from the metal.

**Preparation of [SiP(Ir)2]Co(H2)(1-H2).** Under a dinitrogen atmosphere, 1-N2 (12 mg, 0.05 mmol) was dissolved in toluene-d8 transferred to a J. Young tube, and sealed. The sample was freeze−pump−thawed three times, then exposed to 1 atm H2 while frozen. No visible change occurred upon thawing the sealed tube. The reaction was complete after five days at room temperature, without agitation; the solution remained orange. The H2 adduct remained intact through three freeze−pump−thaw cycles, as well as 1.5 h under static vacuum in solution. Exposure to an N2 atmosphere, however, resulted in gradual displacement of the H2 and reversion to the starting N2 adduct. As such, elemental analysis was not performed. Single crystals were grown by slow concentration of a benzene solution. 1H NMR (toluene-d8; δ): 8.10 (d, J = 7 Hz, 3H), 7.23 (m, 3H), 7.20 (m, 3H), 7.05 (m, 3H), 2.22 (br s, 6H), 0.94 (s, 18H), 0.49 (br s, 18H), −7.78 (br s, 2H). T1(min) (∼30 °C, 500 MHz) = 29 ms. 13C(H) NMR (toluene-d8; δ): 157.2 (m), 147.9 (m), 132.4 (m), 128.5 (s), 127.7 (s, partially overlapping with solvent peak), 126.4 (s), 28.1 (br s), 19.2 (s), 18.7 (s). 31P(H) NMR (toluene-d8; δ): 79.8 (s).

**Preparation of [SiP(Ir)2]Co(HD)(1-HD).** A sample of [SiP(Ir)2]Co(N2) (8 mg, 11 mmol) dissolved in toluene-d8 in a J. Young tube was freeze−pump−thawed three times, then exposed to ~1 atm HD (generated from the reaction of excess LiAlH4 and D2O) while frozen. Upon thawing in the sealed tube and sitting at room temperature for 5 days, the solution remained orange, and the NMR spectra showed complete conversion to the HD adduct. 1H NMR (toluene-d8; δ): 8.10 (d, J = 6 Hz, 3H), 7.23 (m, 3H), 7.20 (m, 3H), 7.05 (m, 3H), 2.22 (br s, 6H), 0.94 (s, 18H), 0.49 (br s, 18H), −7.80 (br s, 1H). T1(1H) ∼30 Hz, T1(1H) HD = 6 Hz, 1H. 31P(H) NMR (toluene-d8; δ): 79.0 (s).

**Preparation of (TPB)CoBr(4).** A Schlenk tube was charged with TPB (3, 302.0 mg, 0.850 mmol), CoBr2 (185.9 mg, 0.850 mmol), Co powder (249.6 mg, 4.250 mmol), THF (20 mL), and a magnetic stirbar. The green solution was heated at 90 °C for 2 days. After cooling, the residue was transferred to a 500 mL filter flask in a glovebox. The solvent was removed from the resulting deep yellow-green solution in vacuo to give a dark residue. Residual THF was removed by adding benzene (5 mL) to the residue and evaporating to dryness under vacuum. Pentane (200 mL) was added and stirred vigorously for 5 min. This resulted in formation of a yellow solution with blue precipitate. The solution was decanted from the solids and filtered through a pad of Celite on a scinttered glass frit. The remaining solids were extracted with pentane (60 mL portions) until the extracts were colorless (four times); the extracts were filtered and combined with the first batch. Removal of the solvent in vacuo provided a yellow-brown solid that was dissolved in benzene (5 mL) and lyophilized to give an orange-brown solid (435 mg, 0.596 mmol, 70%). Single
crystals were grown by slow evaporation of an Et2O solution into HMDSO. 1H NMR (400 MHz, C6D6) δ 111.76, 29.58, 16.71, 15.99, 4.59, −0.03, −0.20, −1.01, −2.66, −8.34. Elemental analysis for C58H60BrCoPF3: calc. C 59.28 H 7.46, found C 58.90 H 7.17.

Preparation of (TPB)Co(N2) (2-N2). A solution of NaCp2H2 was prepared by stirring naphthalene (34.3 mg, 0.277 mmol) and sodium (23.7 mg, 1.03 mmol) in THF (3 mL) for 4 h. The resulting deep-green solution was filtered and added dropwise to a stirring solution of 4 [149.4 mg, 0.2056 mmol] in THF (2 mL). The resulting dark red-brown solution was allowed to stir for 6 h. Solvent was removed in vacuo and the resulting dark-red-brown residue was dissolved in benzene (2 mL). Solvent was again removed in vacuo, and the resulting solid was stirred in benzene (3 mL) for 5 min. The brown solution was filtered through a pad of Celite and lyophilized to give dark brown crystals.

Solid samples of 2 were stored under N2 turned bright yellow over several days, giving 2-N2 (106.0 mg, 0.1566 mmol, 76%). Single crystals were grown by slow evaporation of an Et2O solution into HMDSO. 2H NMR (400 MHz, C6D6) δ 26.95, 23.82, 16.28, 11.35, 5.09, 2.15, 1.56, −0.60, −1.35, −1.73. Elemental analysis shows low values for N which is consistent with the observed lability of the N2 ligand.

Generation of (TPB)Co(N2) (2-H2). A dark brown solution of 2 under vacuum was exposed to 1 atm H2, resulting in immediate formation of a yellow solution. The transformation is clean by 2H NMR and reversible by exposure to N2 atmosphere to reform 2-N2. 2H NMR (400 MHz, C6D6) δ 59.33, 14.93, 12.96, 10.31, 5.42, 3.88, 1.38, −0.10, −2.05, −3.97. Elemental analysis was not obtained due to the compound's propensity to bind ambient N2.

Generation of (TPB)Co(N2) (2-H2). A dark brown solution of 2 under vacuum was exposed to 1 atm H2, resulting in immediate formation of a yellow solution. The transformation is clean by 2H NMR and reversible by subjecting the solution to three freeze-pump-thaw cycles to reform 2. Single crystals were grown by slowly cooling a saturated HMDSO/methylcyclohexane (1:1) solution of 2-H2 under 1 atm H2. 2H NMR (400 MHz, C6D6) δ 27.48, 22.60, 15.17, 10.34, 5.52, 2.75, 1.21, 0.43, −0.84, −2.51. Elemental analysis was not obtained because the compound is only stable to H2 loss under H2 atmosphere.

Measurement of K(H2) as a Function of Temperature. A 0.00390 M solution of 2-N2 (23.8 mg, 0.0351 mmol) in toluene (9.00 mL) was generated in a glovebox. A two-necked glass tube with a 24/40 joint on top and a side arm with a 14/20 joint was charged with the solution and a stirbar. The 24/40 joint was equipped with a dip probe (Hellma Worldwide, 10 mm, 661.302-UV model), and the 14/20 joint was equipped with a dip probe (d) Baya, M.; Houghton, J.; Daran, J.-C.; Poli, R.; Male, L.; Albinati, S.; Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. J. Am. Chem. Soc. 1986, 108, 2552. (b) Wang, M.; Chen., L.; Sun, L. Energy Environ. Sci. 2012, advance article.


(9) A complex that is at least predominantly (if not fully) a dihydride in solution may be a dihydride complex in the solid state: Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. J. Am. Chem. Soc. 1992, 114, 5905–5906.


(18) A search of the Cambridge Structural Database (including the Nov. 2011 update) reveals that the narrowest such ∠P−M−P is 139° (where M is a first-row metal and ∠P−M−P is bisected by a hydride).


(21) The (M−E)n notation22a,b refers to the number of valence electrons, n, formally assigned to the metal (M = Fe, Co, or Ni) including those shared between the metal and the axially bound main group ligand (E = B or Si). Since the M−E bonds may be highly covalent and the M−E interactions are partially dictated by the cage structure of the tetradentate ligand and the M−E distance, the bonding electrons between M and E are often not reliably assigned to either atom.22c,d As such, the (M−E)n descriptor tracks the total number of valence electrons without implicit valence or oxidation number assignments


(26) Geometry optimized at the the B3LYP/6-31G(d) level using Gaussian03, revision D.01; Frisch, M. J. et al. Gaussian, Inc.: Wallingford, CT, 2004. Full reference in Supporting Information as ref 1.

