Synthesis, Structure, and Reactivity of Co(II) and Ni(II) PCP Pincer Borohydride Complexes

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Supporting Information

ABSTRACT: The 15e square-planar complexes [Co(PCPMe-iPr)Cl] (2a) and [Co(PCP-iBu)Cl] (2b), respectively, react readily with NaBH4 to afford complexes [Co(PCPMe-iPr)(η2-BH4)] (4a) and [Co(PCP-iBu)(η2-BH4)] (4b) in high yields, as confirmed by IR spectroscopy, X-ray crystallography, and elemental analysis. The borohydride ligand is symmetrically bound to the cobalt center in η2-fashion. These compounds are paramagnetic with effective magnetic moments of 2.0(1) and 2.1(1) μB consistent with a d7 low-spin system corresponding to one unpaired electron. None of these complexes reacted with CO2 to give formate complexes. For structural and reactivity comparisons, we prepared the analogous Ni(II) borohydride complex [Ni(PCPMe-iPr)(η2-BH4)] (5) via two different synthetic routes. One utilizes [Ni(PCPMe-iPr)Cl] (3) and NaBH4, the second one makes use of the hydride complex [Ni(PCPMe-iPr)H] (6) and BH3·THF. In both cases, 5 is obtained in high yields. In contrast to 4a and 4b, the borohydride ligand is asymmetrically bound to the nickel center but still in an η2-mode. [Ni(PCPMe-iPr)(η2-BH4)] (5) loses readily BH3 at elevated temperatures in the presence of NEt3 to form 6. Complexes 5 and 6 are both diamagnetic and were characterized by a combination of 1H, 13C{1H}, and 31P{1H} NMR, IR spectroscopy, and elemental analysis. Additionally, the structure of these compounds was established by X-ray crystallography. Complexes 5 and 6 react with CO2 to give the formate complex [Ni(PCPMe-iPr)(OC(C==O)H)] (7). The extrusion of BH3 from [Co(PCPMe-iPr)(η2-BH4)] (4a) and [Ni(PCPMe-iPr)(η2-BH4)] (5) with the aid of NH3 to yield the respective hydride complexes [Co(PCPMe-iPr)H] and [Ni(PCPMe-iPr)H] (6) and BH3·NH3 was investigated by DFT calculations showing that formation of the Ni hydride is thermodynamically favorable, whereas the formation of the Co(II) hydride, in agreement with the experiment, is unfavorable. The electronic structures and the bonding of the borohydride ligand in [Co(PCPMe-iPr)(η2-BH4)] (4a) and [Ni(PCPMe-iPr)(η2-BH4)] (5) were established by DFT computations.

INTRODUCTION

Complexes containing the borohydride anion BH4− are known for almost all transition metals and are the focus of much research over the last decades.† They exhibit an extensive and diverse coordination chemistry where, in the case of mononuclear complexes, the BH4− ligand is coordinated in η1-, η2-, or η3-fashion featuring thus one, two, or three M-H-B bridges, respectively. Borohydride complexes are useful starting materials for the preparation of organometallic compounds, in particular hydride and dihydrogen complexes, and are active catalysts, for instance, in hydrogenation reactions.2–11 Moreover, since BH4− and CH3 ligands are isoelectronic, it has been suggested that borohydrides can serve as structural models for the activation of C–H bonds in saturated hydrocarbons.12,13 We are currently focusing on the chemistry of cobalt PCP pincer complexes based on the 1,3-diaminobenzene scaffold.14 A few PCP pincer complexes featuring a direct cobalt–carbon single bond were reported in the literature,15–19 but none of these contain a borohydride ligand. It has to be noted that, in general, cobalt borohydride complexes are very scarce. An overview of all complexes known to date (A–F),20–25 mostly based on the Co(I) oxidation state, is depicted in Scheme 1. The borohydride hapticity in A was inferred only on the basis of electronic spectroscopy comparisons to [Co(PPh3)2X] (X = Cl, Br, I), while, in the case of B–F, their molecular structures and thus the bonding mode of the BH4− ligands were unequivocally established by X-ray crystallography or neutron diffraction. Noteworthy, the complex trans-,[Co(H)(η2-BH4)- (PCy3)2] (Cy = cyclohexyl) (C) is the only known Co(II) borohydride complex which adopts a d1 low-spin configuration. In the dinuclear F mode, the bond of BH4− coordination is unusual in that each BH4− unit chelates to two adjacent Co.

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atoms as well as directly bridges these two Co atoms with a shared hydrogen.

Here, we report on the synthesis and reactivity of low-spin cobalt PCP pincer borohydride complexes in the oxidation state +II. For comparison, the synthesis and reactivity of an analogous low-spin Ni(II) PCP borohydride complex are also reported. A combination of structural, spectroscopic, and computational methods is presented to address the bonding in these new complexes.

**RESULTS AND DISCUSSION**

The starting material for the present study, [Co(PCPMe-iPr)Cl] (2a), was obtained by the reaction of anhydrous CoCl2 and PCP-iPr (1a) in the presence of nBuLi as reported previously.14 The analogous complex [Co(PCP-tBu)Cl] (2b), where the PCP ligand features acidic NH protons, had to be prepared via a different methodology. refluxing a solution of anhydrous CoCl2 with the ligand PCP-tBu (1b) in THF afforded directly 2b, albeit in moderate isolated yield (32%) (Scheme 2). In analogy to 2a, [Co(PCP-tBu)Cl] (2b) is a d7 low-spin complex with a solution magnetic moment \( \mu_{\text{eff}} \) of 1.8(1) \( \mu_B \) (Evans method).25 The solid-state structure of this complex was determined by X-ray diffraction, and a representation of the molecule is shown in Figure 1 with selected metrical parameters given in the caption. The molecular structure shows the metal in a typical slightly distorted square-planar configuration. The C1–Co1–Cl1 angle deviates slightly from linearity, being 176.80(7)°. The P(1)–Co1–P2 angle is 165.92(3)°.

Treatment of the 15e complexes [Co(PCPMe-iPr)Cl] (2a) and [Co(PCP-tBu)Cl] (2b) with 2 equiv of NaBH4 in THF/MeOH (1:1) for 5 min afforded the borohydride complexes [Co(PCPMe-iPr)(η2-BH4)] (4a) and [Co(PCP-tBu)(η2-BH4)] (4b) in 94% and 91% isolated yields, respectively (Scheme 3). These Co(II) complexes display large paramagnetic shifted and very broad \(^1\)H NMR signals and were thus not very informative. \(^{13}\)C{\(^1\)H} and \(^{31}\)P{\(^1\)H} NMR spectra could not be detected at all. The solution magnetic moments of 2.0(1) and 2.1(1) \( \mu_B \) are consistent with a d7 low-spin system corresponding to one unpaired electron. This value is higher than the one expected for the spin-only approximation and is explained by a spin orbit coupling contribution, being consistent with a low-spin square-planar complex. These \( \eta^2 \)-coordination mode of the BH\(_4^-\) ligand was first established by IR spectroscopy. Attenuated total reflectance IR spectra of the solid samples of 4a and 4b show two strong bands in the range of 2415–2312 cm\(^{-1}\), which are attributed to terminal hydrogen–boron stretch \( \nu_{\text{B–H}} \). The bridging boron–hydrogen stretching bands \( \nu_{\text{B–H}} \) are very broad and located in the region of 1975–1825 cm\(^{-1}\).

The solid-state structures of 4a and 4b were determined by X-ray diffraction, unequivocally establishing the \( \eta^2 \)-bonding mode of the BH\(_4^-\) ligand. Structural views are presented in Figures 2 and 3. Selected metrical parameters are given in the captions. Comparisons with related cobalt, nickel, and iron
Co(II) borohydride complexes are rare and typically found for Co(I) rather than Co(II). In fact, there is as yet only one report of a Co(II) borohydride complex, trans-[Co(PCy)₃(H)(η²-BH₄)], which was also structurally characterized. In 4a and 4b, cobalt is in a 5-fold coordination by one C, two P, and two H atoms furnished by the η²P,C,P-bonded pincer ligand and by the η²-bonded BH₄⁻ anion. The coordination sphere of the cobalt can be described as a strongly distorted square pyramid with P1, C1, P2, and H1B as the basal atoms and H2B as the apical atom. In pentacoordinated systems, the actual geometry of the complex can be described by the structural index parameter \( \tau = (\beta - \alpha) / 60 \), where \( \beta \) and \( \alpha \) are the two largest angles (\( \beta > \alpha \)). For an ideal square-pyramidal geometry, \( \tau = 0 \), while, for an ideal trigonal-bipyraramidal geometry, \( \tau = 1 \). According to this model, the \( \tau \) values for 4a and 4b are 0.11 and 0.25, in agreement with distorted square-pyramidal geometries. The disposition of the atoms C1, P1, P2, and B1 is slightly distorted square-planar. The boron atom in 4a and 4b is located about 0.59 and 0.31 Å above the plane of the aryl ring. The positions of the bridging and terminal hydrides H2 and H3 of the BH₄⁻ anion could be located in the difference Fourier map and refined isotropically. From this, Co1–H1B and Co1–H2B distances of 1.63(2) and 1.69(2) Å (4a) and 1.66(3) and 1.78(3) Å (4b), respectively, were derived, clearly showing that the BH₄⁻ moiety is essentially symmetrically bound in η²-fashion, which is in contrast to related Ni(II) PCP complexes (vide infra). Moreover, the Co–B distances of 2.149(2) and 2.157(3) Å are also consistent with this binding mode. One of the few known compounds is the closely related terpyridine Co(I) complex [Co(terpy)(η²-BH₄)], which displays Co–H₈ and Co–B distances of 1.71(1), 1.74(1), and 2.162 Å, respectively.

For structural and reactivity comparisons, we also prepared the analogous Ni(II) borohydride complex [Ni(PCPMe-iPr)(η²-BH₄)] (5) via two different routes. First, treatment of [Ni(PCPMe-iPr)Cl] (3) with an excess of NaBH₄ in THF/MeOH (1:1) yields 5 in 91% isolated yield (Scheme 4). The second approach makes use of the hydride complex [Ni(PCPMe-iPr)H] (6), which was obtained from the reaction of 3 with LiAlH₄. Treatment of 6 with BH₃THF at room temperature led to the clean formation of 5 in 93% isolated yield. In contrast to the analogous cobalt complexes, [Ni(PCPMe-iPr)(η²-BH₄)] (5) loses readily BH₃ at elevated temperatures. Heating a toluene solution of 5 at 80 °C for 24 h in the presence of NET₃ yields 6 in 93% isolated yield (Scheme 4). Complexes 5 and 6 are both diamagnetic and were characterized by a combination of ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR, IR spectroscopy, and elemental analysis. Additionally, the structure of these compounds was established by X-ray crystallography. Structural views are illustrated in Figures 4 and 5 with the main bond lengths and angles given in the captions.

The IR spectrum of 5 shows a strong intensity absorption in the terminal boron–hydrogen stretching region (2384 and 2321 cm⁻¹) and a broad medium vibration in the bridging borohydride stretching region (2107–1845 cm⁻¹) which support an η²-bonding mode of the BH₄⁻ ligand. In the ¹H NMR spectrum, the BH₄⁻ ligand gives rise to a broad low-field resonance quartet with an intensity ratio of approximately 1:1:1:1 centered at ~0.75 ppm (J_{HH} = 75.0 Hz) (cf. the free BH₄⁻ anion gives rise to a sharp 1:1:1:1 quartet with a J_{HH} coupling constant of 50 Hz). The resonance integrates as four hydrogens with respect to one pincer unit. The magnetic equivalence of terminal and bridging hydrogens observed in the ¹H NMR spectra suggests that these hydrogens are fluxional on the NMR time scale, possibly involving η¹- or η²-BH₄ intermediates. The ¹H NMR spectrum of 6 confirmed the presence of one hydride ligand, which appeared at ~8.26 ppm as a well-resolved triplet with a J_{HH} coupling constant of about...
Table 1. Selected Bond Distances (Å) for the Co(II) and Ni(II) PCP Borohydride Complexes 4a, 4b, 5 and Comparisons with Some Related Borohydride Co(I), Co(II), Ni(I), Ni(II), and Fe(II) Complexes

| Metal | Spin State | Compound | M−B, Å | M−H₂, Å |
|-------|------------|----------|--------|---------|
| Co(II) | $S = \frac{1}{2}$ | $[\text{Co}((\text{PCP})_{5}(\eta^5-\text{BH}_4))]$ (4a) | 2.149(2) | 1.63(2), 1.69(2) |
| Co(II) | $S = \frac{1}{2}$ | $[\text{Co}((\text{PCP})_{5}(\eta^5-\text{BH}_4))]$ (4b) | 2.156(3) | 1.78(3), 1.66(3) |
| Co(I)  | $S = 1$    | $[\text{Co}(\text{PCP})_{5}(\eta^5-\text{BH}_4)](\text{B})$ | 2.21(3) | 1.6(2), 1.5(2) |
| Co(I)  | $S = \frac{1}{2}$ | $\text{trans-}[\text{Co}((\text{PCP})_{5}(\eta^5-\text{BH}_4))](\text{C})$ | 2.14(1) | 1.87(9), 1.80(8) |
| Co(I)  | $S = 0$    | $[\text{Co}(\text{terpy})(\eta^5-\text{BH}_4)](\text{D})$ | 2.162 | 1.81(5), 1.8(5) |
| Ni(I)  | $S = \frac{1}{2}$ | $[\text{Ni}(\text{PCP})_{5}(\eta^5-\text{BH}_4)]$ | 2.202(6) | 1.736, 1.800 |
| Ni(II) | $S = 0$    | $[\text{Ni}(\text{PCP})_{5}(\eta^5-\text{BH}_4)](\text{E})$ | 2.201(8) | 1.73(5), 1.76(6) |
| Ni(II) | $S = 0$    | $[\text{Ni}(\text{PCP})_{5}(\eta^5-\text{BH}_4)](\text{F})$ | 2.048(5) | 1.87(4)−1.94(7) |
| Fe(II) | $S = 0$    | $[\text{Fe}(\text{PCP})_{5}(\eta^5-\text{BH}_4)]$ | 2.095(3) | 1.60(2), 1.68(2) |

*Neutron diffraction data. cyclam = 1,4,8,11-tetraazacyclotetradecane. aTp* = hydrotris(3,5-dimethylpyrazolyl)borate.

55.8 Hz. Complexes 5 and 6 exhibit a singlet at 136.0 and 144.5 ppm, respectively, in the $^{31}$P{H} NMR spectrum.

Figure 4. (a) Structural view of $[\text{Ni}((\text{PCP})_{5}(\eta^5-\text{BH}_4))]_{0.5} \cdot \text{D}_{2} \cdot (0.5 \cdot \text{D}_{2} \cdot \text{H}_{2})$ showing 50% thermal ellipsoids (most H atoms, solvent molecule, and a second independent complex omitted for clarity). (b) Inner part of 5 showing the asymmetric bonding of the BH₄⁻ ligand. Selected bond lengths (Å) and bond angles (deg): Ni1−C1 1.906(2), Ni1−P1 2.1675(6), Ni1−P2 2.1691(8), Ni1−B1 2.218(3), Ni1−H1Bi 1.703(3), Ni1−H2Bi 1.85(2), P1−Ni1−P2 165.19(3), P1−Ni1−C1 83.57(6), P2−Ni1−C1 83.54(6), C1−Ni1−B1 167.4(1).

Figure 5. Structural view of $[\text{Ni}((\text{PCP})_{5}(\eta^5-\text{BH}_4))](\text{H})$ (6) showing 50% thermal ellipsoids (most H atoms and a second independent complex omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Ni1−P1 2.115(1), Ni1−P2 2.122(1), Ni1−C1 1.908(3), P1−Ni1−P2 1.699(7), P1−Ni1−C1 85.3(1), P2−Ni1−C1 84.7(1), Ni1−H1 1.99(2).

The structural features of complex 5 are similar to those of complexes 4a and 4b. The r value for 5 is 0.11, in agreement with a distorted square-pyramidal geometry. The nickel atom coordinates the BH₄⁻ group in an $\eta^5$-fashion, but in a slightly asymmetrical fashion with Ni−H₂ distances of 1.70(3) and 1.85(2) Å. Similar Ni−H₂ distances were found in several other Ni(II) borohydride complexes, as shown in Table 1. Despite the similar covalent radii of Co and Ni, the Ni−B distance of 2.218(3) Å in 5 is larger than that in the corresponding paramagnetic Co(II) complexes 4a and 4b, but is comparable to those of related Ni(II) PCP complexes. The opposite trend is observed for the metal−carbon bond distances. The Co−C distances in 4a and 4b are 1.933(1) and 1.945(2) Å, respectively, whereas, in 5, the Ni−C distance is shorter, being 1.906 Å. Similar Ni−C distances are found in $[\text{Ni}((\text{POCOP})(\eta^5-\text{BH}_4))](1.901(2) \text{ Å})$, $[\text{Ni}((\text{POCOP})(\eta^5-\text{BH}_4))](1.898(4) \text{ Å})$, and $[\text{Ni}((\text{POCOP})_{2}(\eta^5-\text{BH}_4))](1.892(2) \text{ Å})$. It is interesting to note that, in a related Pd PCP pincer complex based on ferrocene, the BH₄⁻ moiety is coordinated in an unidentate mode with a Pd−B distance of 2.614(7) Å.

Guan and co-workers have recently shown that both nickel hydride and borohydride PCP pincer complexes are able to reduce CO₂ to give formate complexes. Given the fact that 5 is also capable of liberating “BH₄⁻” as amine adduct to form a nickel hydride, we also explored the possibility of reducing CO₂...
with complexes 5 and 6. When exposed to 1 bar of CO2 at room temperature for 1 h, 5 and 6 are fully converted to the nickel formate complex 7 (Scheme 5). This complex was again fully characterized by a combination of 1H, 13C{1H}, and 31P{1H} NMR, IR spectroscopy, and elemental analysis. Additionally, the solid-state structure of 7 was determined by single-crystal X-ray diffraction. A structural view is depicted in Figure 6 with selected bond distances given in the caption.

On the basis of the above results with [Ni(PCPMe2-iPr)(OC(==O)H)] (5) and [Ni(PCPMe2-iPr)H] (6), we also attempted to obtain Co(II) hydride as well as Co(II) formate complexes. It has to be mentioned that monomeric Co(II) hydride complexes are rather rare.2,3,33 Unfortunately, the reaction of [Co(PCPMe2-iPr)Cl] (2a) with LiAlH4 resulted in the formation of intractable materials together with the free protonated PCPMe2-iPr ligand. Likewise, treatment of 2a with Na[HBEt3] or nBuLi led to recovery of the starting material or decomposition with no evidence for the formation of a hydride complex. Moreover, 4a did neither react with NEt3 to give [Co(PCPMe2-iPr)H] nor react with CO2 to afford the formate complex [Co(PCPMe2-iPr)(OC(==O)H)] even at 80 °C for 24 h (Scheme 3). For comparison, it was shown34 that BH4 liberation from a Rh(I) bis-iminopyridine pincer borohydride with quinuclidine was strongly endothermic and attempts to obtain a Rh(I) hydride complex were unsuccessful.

DFT Calculations. To address the binding mode of the BH4 unit and the thermodynamics for the reaction of NH3 with the Co-BH4 and Ni-BH4 moieties, we performed DFT calculations35 on complexes 4a and 5 (B3LYP functional; for details see the Experimental Section). This revealed that extrusion of BH4 with NH3 (as model for amines) from the cobalt complex 4a is an endergonic process (2.2 kcal/mol), whereas, in the case of 5, the process is exergonic by −6.0 kcal/mol (Scheme 6). These results, although taken with due care giving the simplicity of the amine used (NH3) and the relatively small ΔG values obtained, indicate a clear trend and help explain why attempts to obtain the corresponding Co hydride complex from 4a by removal of BH3 as an amine adduct were unsuccessful.

The electronic structures of complexes 4a and 5 were evaluated by DFT calculations, and the relevant frontier orbitals (metal d-splitting), as well as the spin density of complex 4a, are presented in Figure 7. The orbitals are the expected ones for pseudo-square-pyramidal molecules, and the spin density of complex 4a is centered in the metal atom. Moreover, the calculations indicate a clear difference in the coordination of the BH4− ligand in the two complexes. In the Co species 4a, two comparable Co−H bonds exist, with distances of 1.84 and 1.72 Å. The corresponding Wiberg indices (WI)36 of 0.09 and 0.13 also indicate interactions of similar magnitude. On the other hand, for the Ni complex 5, there is a clear asymmetry in the two Ni−H interactions, with a normal bond (d = 1.65 Å, WI = 0.15) and a much weaker interaction (d = 2.06 Å, WI = 0.02). In other words, for the Co complexes, the BH4− coordination is closer to π2, and the overall geometry can be envisaged as in between square-planar and square-pyramidal. In complex 5, the borohydride ligand coordination is closer to π2, and the molecule overall geometry is nearer a normal square-planar, reflecting the tendency of Ni(II) to form complexes with that geometry, as expected for a d8 metal. Interestingly, the overall electron donation from the ligands to the metal is stronger in the case of the Co species, as shown by the ligand charges (NPA)37 see the Computational Details): CCoP = 0.26 (4a) and 0.24 (5), CBH4 = −0.67 (4a) and −0.73 (5). This is reflected in an electron richer Co-atom in 4a (CCo = 0.42, compared with the Ni-atom in 5 (CCo = 0.49) and indicates stronger coordination of the ligands in the case of the Co complex, in particular, a stronger M−BH4 bond, in good accordance with the reactivity pattern observed for the reaction with NH3 (see Scheme 6).

■ CONCLUSION

We have shown that the 15e square-planar complexes [Co(PCPMe2-iPr)Cl] (2a) and [Co(PCP-iBu)Cl] (2b), respectively, react readily with NaBH4 to afford complexes [Co(PCPMe2-iPr)(η2-BH4)] (4a) and [Co(PCP-iBu)(η2-BH4)] (4b) in high yields. The η2-bonding mode of the borohydride ligand
was confirmed by IR spectroscopy and X-ray crystallography. These compounds are paramagnetic with effective magnetic moments of 2.0(1) and 2.1(1) $\mu_B$ consistent with a $d^1$ low-spin system corresponding to one unpaired electron. None of these complexes react with CO$_2$ to give formate complexes. For structural and reactivity comparisons, we prepared the analogous Ni(II) borohydride complex [Ni(PCPMe$_3$-iPr)(η$^2$-BH$_4$)] (5) via two different routes. One utilizes [Ni(PCPMe$_3$-iPr)Cl] (3) and NaBH$_4$, the second one makes use of the hydride complex [Ni(PCPMe$_3$-iPr)H] (6) and BH$_3$·THF. In both cases, 5 was obtained in high yields. While [Ni(PCPMe$_3$-iPr)(η$^2$-BH$_4$)] (5) loses readily BH$_3$ at elevated temperatures in the presence of NEt$_3$ to form a hydride complex. Complexes 5 and 6 react with CO$_2$ to give the formate complex [Ni(PCPMe$_3$-iPr)(η$^2$-BH$_4$)] (4a) did not react with NH$_3$ to give a hydride complex. Complexes 5 and 6 do not react with NH$_3$, whereas the formation of the Ni hydride is thermodynamically favorable, whereas the formation of the Co(II) hydride, in agreement with the experiment, is unfavorable. From the calculations, it is apparent that, for the Co complexes, the BH$_3$ coordination is closer to $\eta^1$, and the overall geometry can be envisaged as in between square-planar and square-pyramidal. In complex 5, the borohydride ligand coordination is closer to $\eta^5$, and the overall geometry of the molecule is closer to normal square-planar, reflecting the tendency of Ni(II) to form complexes with that geometry, as expected for a $d^8$ metal.

**EXPERIMENTAL SECTION**

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques or in an MBraun inert-gas glovebox. The solvents were purified according to standard procedures. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. N,N'-Bu$_2$(di-tert-butylphosphino)-1,3-diaminobenzene (PCP-tBu) (1b),$^{39}$ [Co(PCPMe$_3$-iPr)Cl] (2a),$^{14}$ and [Ni(PCPMe$_3$-iPr)Cl] (3)$^{14}$ were prepared according to the literature. $^1$H, $^13$C($^1$H), and $^{31}$P($^1$H) NMR spectra were recorded on Bruker AVANCE-250, AVANCE-300 DPX, and AVANCE-400 spectrometers. $^1$H and $^13$C($^1$H) NMR spectra were referenced internally to residual proto-solvent, and solvent resonances, respectively, and are reported relative to tetramethylsilane ($\delta = 0$ ppm). $^{31}$P($^1$H) NMR spectra were referenced externally to H$_3$PO$_4$ (85%) ($\delta = 0$ ppm).

[Co(PCPMe$_3$-Bu)Cl] (2b). A suspension of N,N’-bis(di-tert-butylphosphino)-1,3-diaminobenzene (PCP-tBu) (1b) (300 mg, 0.758 mmol) and anhydrous CoCl$_2$ (104 mg, 0.796 mmol) in THF (40 mL) was refluxed for 24 h. After that, the solvent was removed under vacuum. The resulting crude product was dissolved in toluene, insoluble materials were removed by filtration, and the solvent was evaporated under vacuum to afford 2b as an orange solid. Yield: 118 mg (32%).

Calcd for C$_{22}$H$_{41}$CoN$_2$P$_2$ (441.25): C, 54.44; H, 9.37; N, 6.35. Found: C, 54.34; H, 9.41; N, 6.45. IR (ATR, cm$^{-1}$): 1948–1825 (br, $\nu_{\text{NH}}$), 2312 (s, $\nu_{\text{B-H}}$), $\mu_{\text{eff}} = 1.80(1) \mu_B$ (CH$_2$Cl$_2$, Evans method).

[Co(PCPMe$_3$-iPr)(η$^2$-BH$_4$)] (4a). To a suspension of 2a (200 mg, 0.43 mmol) in THF/MeOH (1:1) (10 mL) was added NaBH$_4$ (34 mg, 0.87 mmol), and the reaction mixture was stirred for 5 min. The solvent was then removed under reduced pressure, and the crude product was dissolved in toluene. Insoluble materials were removed by filtration, and the solvent was evaporated under vacuum to afford 4a as a dark red solid. Yield: 180 mg (94%).

Calcd for C$_{20}$H$_{42}$BCoN$_2$P$_2$ (489.91): C, 53.94; H, 8.44; N, 5.72. Found: C, 53.89; H, 8.51; N, 5.78. $\nu_{\text{B-H}}$, 2415 (s, $\nu_{\text{B-H}}$), 2312 (s, $\nu_{\text{B-H}}$), $\mu_{\text{eff}} = 2.0(1) \mu_B$ (CH$_2$Cl$_2$, Evans method).

[Co(PCPMe$_3$-Bu)(η$^2$-BH$_4$)] (4b). This complex was prepared in an analogous fashion to 4a with 2b (100 mg, 0.204 mmol) and NaBH$_4$ (17 mg, 0.408 mmol) as starting materials. Yield: 87 mg (91%).

Calcd for C$_{20}$H$_{41}$BCoN$_2$P$_2$ (469.31): C, 56.30; H, 9.73; N, 5.89. IR (ATR, cm$^{-1}$): 1909 (br, $\nu_{\text{B-H}}$), 1975 (br, $\nu_{\text{B-H}}$), 2415 (s, $\nu_{\text{B-H}}$), 2339 (s, $\nu_{\text{B-H}}$), $\mu_{\text{eff}} = 2.10(1) \mu_B$ (CH$_2$Cl$_2$, Evans method).
Method A. A suspension of [Ni\(\text{PCP}^{\text{Me}}\text{Pr}^2\text{BH}_4\)] (5). Method A. A suspension of [Ni(\text{PCP}^{\text{Me}}\text{Pr}^2\text{Cl})] (3) (200 mg, 0.435 mmol) and NaBH\(_4\) (38 mg, 0.87 mmol) in THF/MeOH (1:1) (10 mL) was stirred at room temperature for 5 min. The solvent was then removed under vacuum. The crude product was dissolved in toluene and filtered through a short plug of Celite to give an orange-yellow solution. After removal of the solvent under vacuum, the desired complex was isolated as an orange-yellow solid. Yield: 91% (175 mg).

Method B. To a suspension of 6 (200 mg, 0.469 mmol) in pentane (20 mL) was added the BH\(_3\) adduct (200 mg, 0.453 mmol) and LiAlH\(_4\) (330 mg, 8.7 mmol) in toluene (25 mL) was stirred at room temperature for 24 h. The mixture was then filtered through a short plug of Celite to give a clear yellow solution. After the solvent was evaporated under vacuum, the desired complex was isolated as an orange-yellow solid. Yield: 90% (98 mg).
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