

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

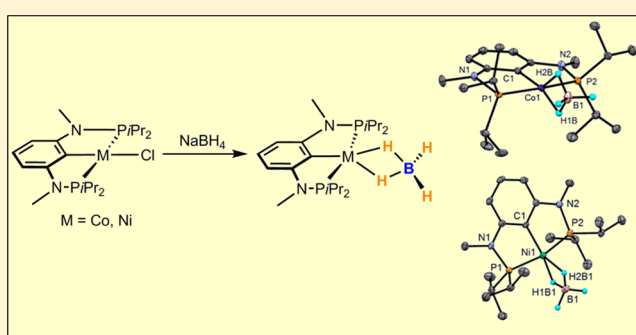
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## Supporting Information

**ABSTRACT:** The 15e square-planar complexes [Co(PCP<sup>Me</sup>-iPr)Cl] (**2a**) and [Co(PCP-*t*Bu)Cl] (**2b**), respectively, react readily with NaBH<sub>4</sub> to afford complexes [Co(PCP<sup>Me</sup>-iPr)( $\eta^2$ -BH<sub>4</sub>)] (**4a**) and [Co(PCP-*t*Bu)( $\eta^2$ -BH<sub>4</sub>)] (**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  $\eta^2$ -fashion. These compounds are paramagnetic with effective magnetic moments of 2.0(1) and 2.1(1)  $\mu_B$  consistent with a d<sup>7</sup> low-spin system corresponding to one unpaired electron. None of these complexes reacted with CO<sub>2</sub> to give formate complexes. For structural and reactivity comparisons, we prepared the analogous Ni(II) borohydride complex [Ni(PCP<sup>Me</sup>-iPr)( $\eta^2$ -BH<sub>4</sub>)] (**5**) via two different synthetic routes. One utilizes [Ni(PCP<sup>Me</sup>-iPr)Cl] (**3**) and NaBH<sub>4</sub>, the second one makes use of the hydride complex [Ni(PCP<sup>Me</sup>-iPr)H] (**6**) and BH<sub>3</sub>·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  $\eta^2$ -mode. [Ni(PCP<sup>Me</sup>-iPr)( $\eta^2$ -BH<sub>4</sub>)] (**5**) loses readily BH<sub>3</sub> at elevated temperatures in the presence of NEt<sub>3</sub> to form **6**. Complexes **5** and **6** are both diamagnetic and were characterized by a combination of <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR, IR spectroscopy, and elemental analysis. Additionally, the structure of these compounds was established by X-ray crystallography. Complexes **5** and **6** react with CO<sub>2</sub> to give the formate complex [Ni(PCP<sup>Me</sup>-iPr)(OC(C=O)H)] (**7**). The extrusion of BH<sub>3</sub> from [Co(PCP<sup>Me</sup>-iPr)( $\eta^2$ -BH<sub>4</sub>)] (**4a**) and [Ni(PCP<sup>Me</sup>-iPr)( $\eta^2$ -BH<sub>4</sub>)] (**5**) with the aid of NH<sub>3</sub> to yield the respective hydride complexes [Co(PCP<sup>Me</sup>-iPr)H] and [Ni(PCP<sup>Me</sup>-iPr)H] (**6**) and BH<sub>3</sub>NH<sub>3</sub> 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(PCP<sup>Me</sup>-iPr)( $\eta^2$ -BH<sub>4</sub>)] (**4a**) and [Ni(PCP<sup>Me</sup>-iPr)( $\eta^2$ -BH<sub>4</sub>)] (**5**) were established by DFT computations.



## INTRODUCTION

Complexes containing the borohydride anion BH<sub>4</sub><sup>-</sup> are known for almost all transition metals and are the focus of much research over the last decades.<sup>1</sup> They exhibit an extensive and diverse coordination chemistry where, in the case of mononuclear complexes, the BH<sub>4</sub><sup>-</sup> ligand is coordinated in  $\eta^1$ -,  $\eta^2$ -, or  $\eta^3$ -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.<sup>2–11</sup> Moreover, since BH<sub>4</sub><sup>-</sup> and CH<sub>4</sub> are isoelectronic, it has been suggested that borohydrides can serve as structural models for the activation of C–H bonds in saturated hydrocarbons.<sup>12,13</sup>

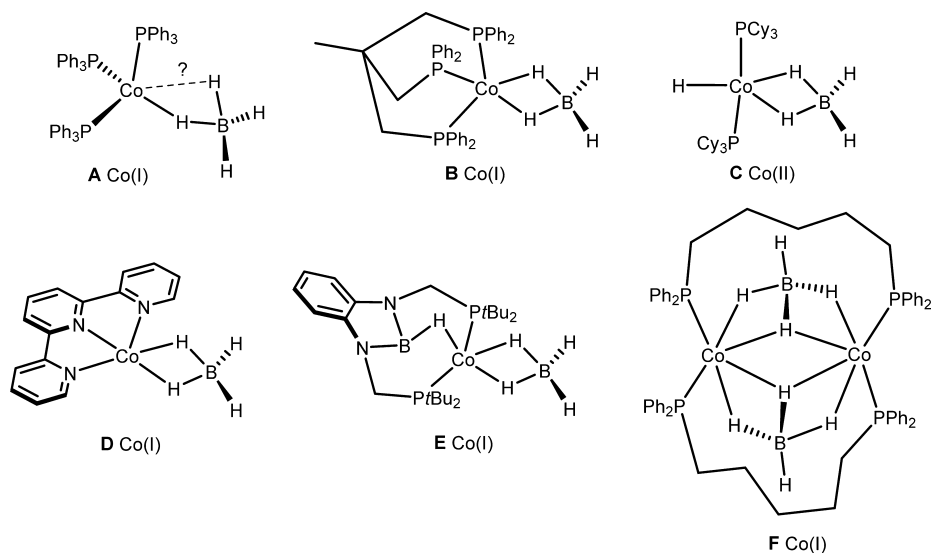
We are currently focusing on the chemistry of cobalt PCP pincer complexes based on the 1,3-diaminobenzene scaffold.<sup>14</sup> A few PCP pincer complexes featuring a direct cobalt–carbon single bond were reported in the literature,<sup>15–19</sup> but none of

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),<sup>20–25</sup> 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(PPh<sub>3</sub>)<sub>3</sub>X] (X = Cl, Br, I), while, in the case of B–F, their molecular structures and thus the bonding mode of the BH<sub>4</sub><sup>-</sup> ligands were unequivocally established by X-ray crystallography or neutron diffraction. Noteworthy, the complex *trans*-[Co(H)( $\eta^2$ -BH<sub>4</sub>)(PCy<sub>3</sub>)<sub>2</sub>] (Cy = cyclohexyl) (C) is the only known Co(II) borohydride complex which adopts a d<sup>7</sup> low-spin configuration. In the dinuclear complex F, the mode of BH<sub>4</sub><sup>-</sup> coordination is unusual in that each BH<sub>4</sub><sup>-</sup> unit chelates to two adjacent Co

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Scheme 1



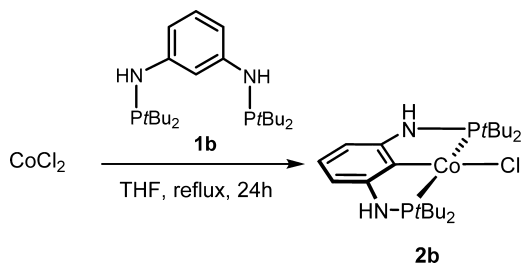
atoms as well as directly bridges these two Co atoms with a shared hydrogen.

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,  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-}i\text{Pr})\text{Cl}]$  (**2a**), was obtained by the reaction of anhydrous  $\text{CoCl}_2$  and  $\text{PCP-}i\text{Pr}$  (**1a**) in the presence of  $n\text{BuLi}$  as reported previously.<sup>14</sup> The analogous complex  $[\text{Co}(\text{PCP-}t\text{Bu})\text{Cl}]$  (**2b**), where the PCP ligand features acidic NH protons, had to be prepared via a different methodology. Refluxing a solution of anhydrous  $\text{CoCl}_2$  with the ligand  $\text{PCP-}t\text{Bu}$  (**1b**) in THF afforded directly **2b**, albeit in moderate isolated yield (32%) (Scheme 2). In

Scheme 2. Synthesis of Complex  $[\text{Co}(\text{PCP-}t\text{Bu})\text{Cl}]$  (**2b**)



analogy to **2a**,  $[\text{Co}(\text{PCP-}t\text{Bu})\text{Cl}]$  (**2b**) is a  $d^7$  low-spin complex with a solution magnetic moment  $\mu_{\text{eff}}$  of  $1.8(1) \mu_{\text{B}}$  (Evans method).<sup>26</sup> 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  $\text{C1-Co1-Cl1}$  angle deviates slightly from linearity, being  $176.80(7)^\circ$ . The  $\text{P(1)-Co1-P2}$  angle is  $165.92(3)^\circ$ .

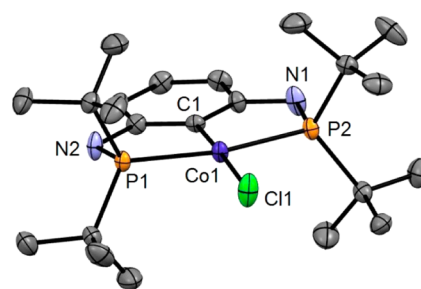
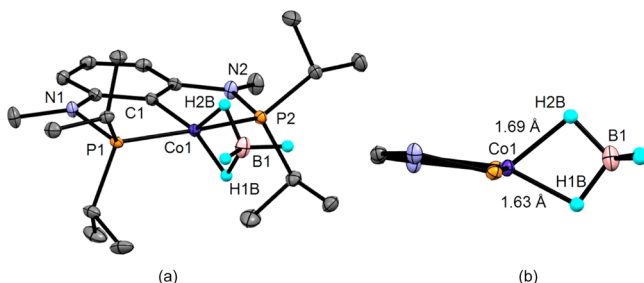
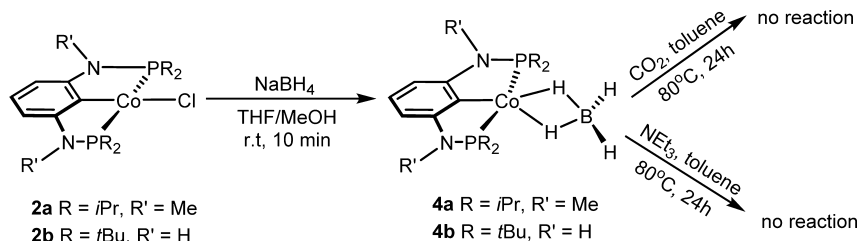


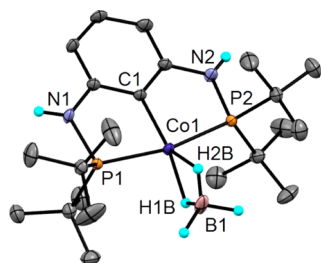
Figure 1. Structural view of  $[\text{Co}(\text{PCP-}t\text{Bu})\text{Cl}]$  (**2b**) showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg):  $\text{Co1-Cl1}$  2.260(1),  $\text{Co1-P1}$  2.2209(7),  $\text{Co1-P2}$  2.2343(7),  $\text{Co1-C1}$  1.935(2);  $\text{Cl1-Co1-P1}$   $96.67(3)$ ,  $\text{Cl1-Co1-P2}$   $97.12(3)$ ,  $\text{Cl1-Co1-C1}$   $176.80(7)$ ,  $\text{P1-Co1-P2}$   $165.92(3)$ ,  $\text{P1-Co1-C1}$   $82.90(7)$ ,  $\text{P2-Co1-C1}$   $83.48(7)$ .

Treatment of the 15e complexes  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-}i\text{Pr})\text{Cl}]$  (**2a**) and  $[\text{Co}(\text{PCP-}t\text{Bu})\text{Cl}]$  (**2b**) with 2 equiv of  $\text{NaBH}_4$  in THF/MeOH (1:1) for 5 min afforded the borohydride complexes  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-}i\text{Pr})(\eta^2\text{-BH}_4)]$  (**4a**) and  $[\text{Co}(\text{PCP-}t\text{Bu})(\eta^2\text{-BH}_4)]$  (**4b**) in 94% and 91% isolated yields, respectively (Scheme 3). These Co(II) complexes display large paramagnetic shifted and very broad  $^1\text{H}$  NMR signals and were thus not very informative.  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra could not be detected at all. The solution magnetic moments of  $2.0(1)$  and  $2.1(1) \mu_{\text{B}}$  are consistent with a  $d^7$  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.<sup>27</sup> The  $\eta^2$ -coordination mode of the  $\text{BH}_4^-$  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  $2415\text{--}2312 \text{ cm}^{-1}$ , which are attributed to terminal hydrogen–boron stretch  $\nu_{\text{B-H}_t}$ . The bridging boron–hydrogen stretching bands  $\nu_{\text{B-H}_b}$  are very broad and located in the region of  $1975\text{--}1825 \text{ cm}^{-1}$ .

The solid-state structures of **4a** and **4b** were determined by X-ray diffraction, unequivocally establishing the  $\eta^2$ -bonding mode of the  $\text{BH}_4^-$  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

Scheme 3. Synthesis of Co(II) Borohydride Complexes  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-}i\text{Pr})(\eta^2\text{-BH}_4)]$  (**4a**) and  $[\text{Co}(\text{PCP-}t\text{Bu})(\eta^2\text{-BH}_4)]$  (**4b**)

**Figure 2.** (a) Structural view of  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-}i\text{Pr})(\eta^2\text{-BH}_4)]$  (**4a**) showing 50% thermal ellipsoids (most H atoms omitted for clarity). (b) Inner part of **4a** showing the slightly asymmetric bonding of the  $\text{BH}_4^-$  ligand. Selected bond lengths (Å) and bond angles (deg): Co1–C1 1.933(1), Co1–P1 2.1752(5), Co1–P2 2.1860(5), Co1···B1 2.149(2), Co1–H1B 1.63(2), Co1–H2B 1.69(2); C1–Co1–B1 167.73(7), C1–Co1–P1 83.12(4), C1–Co1–P2 83.57(4), P1–Co1–P2 165.67(2).



**Figure 3.** Structural view of  $[\text{Co}(\text{PCP-}t\text{Bu})(\eta^2\text{-BH}_4)]$  (**4b**) showing 50% thermal ellipsoids (most H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Co1–C1 1.945(2), Co1–P1 2.2265(5), Co1–P2 2.2288(6), Co1···B1 2.157(3), Co1–H1B 1.66(3), Co1–H2B 1.78(3); P1–Co1–P2 165.24(2), P1–Co1–C1 82.72(6), P2–Co1–C1 82.93(6), C1–Co1–B1 174.0(1).

complexes are presented in Table 1. Cobalt borohydrides 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*- $[\text{Co}(\text{PCy}_3)_2(\text{H})(\eta^2\text{-BH}_4)]$ , which was also structurally characterized.<sup>22</sup> In **4a** and **4b**, cobalt is in a 5-fold coordination by one C, two P, and two H atoms furnished by the  $\eta^3\text{P,C,P}$ -bonded pincer ligand and by the  $\eta^2$ -bonded  $\text{BH}_4^-$  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-bipyramidal geometry,  $\tau = 1$ .<sup>28</sup> 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  $\text{H}_b$  and  $\text{H}_t$  of the  $\text{BH}_4^-$  ligand 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  $\text{BH}_4^-$  moiety is essentially symmetrically bound in  $\eta^2$ -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  $[\text{Co}(\text{terpy})(\eta^2\text{-BH}_4)]$ , which displays Co– $\text{H}_b$  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  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-}i\text{Pr})(\eta^2\text{-BH}_4)]$  (**5**) via two different routes. First, treatment of  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-}i\text{Pr})\text{Cl}]$  (**3**) with an excess of  $\text{NaBH}_4$  in THF/MeOH (1:1) yields **5** in 91% isolated yield (Scheme 4). The second approach makes use of the hydride complex  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-}i\text{Pr})\text{H}]$  (**6**), which was obtained from the reaction of **3** with  $\text{LiAlH}_4$ . Treatment of **6** with  $\text{BH}_3\cdot\text{THF}$  at room temperature led to the clean formation of **5** in 93% isolated yield. In contrast to the analogous cobalt complexes,  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-}i\text{Pr})(\eta^2\text{-BH}_4)]$  (**5**) loses readily  $\text{BH}_3$  at elevated temperatures. Heating a toluene solution of **5** at 80 °C for 24 h in the presence of  $\text{NEt}_3$  yields **6** in 93% isolated yield (Scheme 4). Complexes **5** and **6** are both diamagnetic and were characterized by a combination of  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  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.

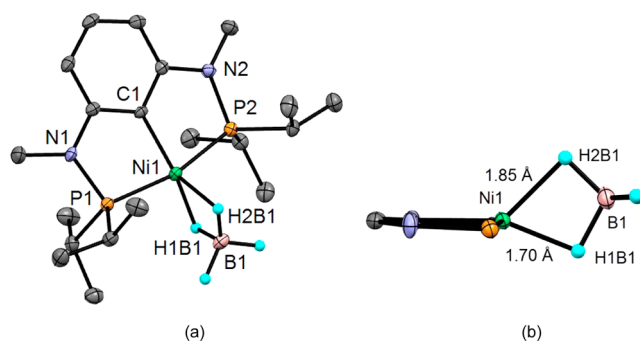
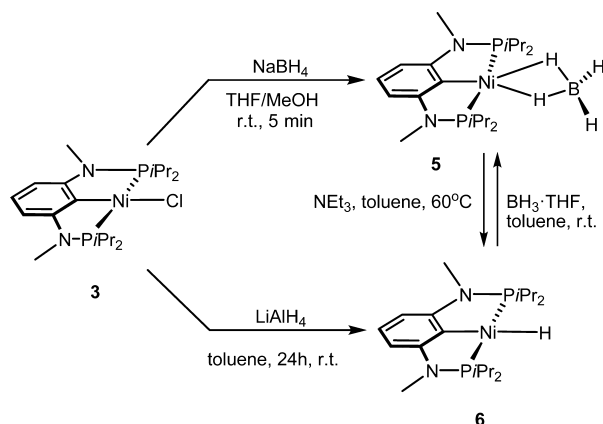
The IR spectrum of **5** shows a strong intensity absorption in the terminal boron–hydrogen stretching region (2384 and 2321  $\text{cm}^{-1}$ ) and a broad medium vibration in the bridging borohydride stretching region (2107–1845  $\text{cm}^{-1}$ ), which support an  $\eta^2$ -bonding mode of the  $\text{BH}_4^-$  ligand. In the  $^1\text{H}$  NMR spectrum, the  $\text{BH}_4^-$  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 ( $J_{\text{HB}} = 75.0$  Hz) (*cf.* the free  $\text{BH}_4^-$  anion gives rise to a sharp 1:1:1:1 quartet with a  $J_{\text{HB}}$  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  $^1\text{H}$  NMR spectra suggests that these hydrogens are fluxional on the NMR time scale, possibly involving  $\eta^1$ - or  $\eta^3\text{-BH}_4$  intermediates. The  $^1\text{H}$  NMR spectrum of **6** confirmed the presence of one hydride ligand, which appeared at  $-8.26$  ppm as a well-resolved triplet with a  $^2J_{\text{HP}}$  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-H <sub>b</sub> , Å	ref
Co(II)	$S = 1/2$	[Co(PCP <sup>Me</sup> -iPr)( $\eta^2$ -BH <sub>4</sub> )] ( <b>4a</b> )	2.149(2)	1.63(2), 1.69(2)	this work
Co(II)	$S = 1/2$	[Co(PCP-tBu)( $\eta^2$ -BH <sub>4</sub> )] ( <b>4b</b> )	2.156(3)	1.78(3), 1.66(3)	this work
Co(I)	$S = 1$	[Co(ppp)( $\eta^2$ -BH <sub>4</sub> )] ( <b>B</b> )	2.21(3)	1.6(2), 1.5(2)	21
Co(II)	$S = 1/2$	<i>trans</i> -[Co(PCy <sub>3</sub> ) <sub>2</sub> (H)( $\eta^2$ -BH <sub>4</sub> )] ( <b>C</b> )	2.14(1)	1.87(9), 1.80(8)	22
Co(I)	$S = 0$	[Co(terpy)( $\eta^2$ -BH <sub>4</sub> )] ( <b>D</b> )	2.162	1.81(5), 1.80(5)	23
				1.71(1), 1.74(1) <sup>a</sup>	
Co(I)	$S = 0$	[Co( <sup>t</sup> BuDBP)( $\eta^2$ -BH <sub>4</sub> )] ( <b>E</b> )	2.131(2)	1.66(2), 1.73(2)	24
Ni(II)	$S = 0$	[Ni(PCP <sup>Me</sup> -iPr)( $\eta^2$ -BH <sub>4</sub> )] ( <b>5</b> )	2.218(3)	1.70(3), 1.85(2)	this work
Ni(II)	$S = 0$	[Ni(POCOP- <i>i</i> Pr)( $\eta^2$ -BH <sub>4</sub> )]	2.214(3)	1.78(3), 1.85(3)	5
Ni(II)	$S = 0$	[Ni(POCOP- <i>t</i> Bu)( $\eta^2$ -BH <sub>4</sub> )]	2.187(5)	1.77(4), 1.87(4)	5
Ni(II)	$S = 0$	[Ni(POCOP-C <sub>5</sub> H <sub>9</sub> )( $\eta^2$ -BH <sub>4</sub> )]	2.189(5)	1.78(5), 1.87(5)	5
Ni(I)	$S = 1/2$	[Ni(ppp)( $\eta^2$ -BH <sub>4</sub> )]	2.24	1.59(5), 1.83(5)	51
Ni(II)	$S = 0$	[Ni(cyclam)( $\eta^2$ -BH <sub>4</sub> )]BH <sub>4</sub> <sup>c</sup>	2.202(6)	1.736, 1.800	52
Ni(II)	$S = 0$	<i>trans</i> -[Ni(PCy <sub>3</sub> ) <sub>2</sub> (H)( $\eta^2$ -BH <sub>4</sub> )]	2.201(8)	1.73(5), 1.76(6)	53
Ni(II)	$S = 0$	[Ni(Tp*)( $\eta^2$ -BH <sub>4</sub> )] <sup>d</sup>	2.048(5)	1.87(4)–1.94(7)	54
Fe(II)	$S = 0$	[Fe(PNP <sup>CH<sub>3</sub></sup> -iPr)(H)( $\eta^2$ -BH <sub>4</sub> )]	2.095(3)	1.60(2), 1.68(2)	8

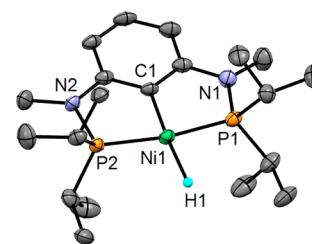
<sup>a</sup>Neutron diffraction data. <sup>c</sup>cyclam = 1,4,8,11-tetraazacyclotetradecane. <sup>d</sup>Tp\* = hydrotris(3,5-dimethylpyrazolyl)borate.

#### Scheme 4. Synthesis and Reactivity of Ni(II) Borohydride and Hydride Complexes [Ni(PCP<sup>Me</sup>-iPr)( $\eta^2$ -BH<sub>4</sub>)] (**5**) and [Ni(PCP<sup>Me</sup>-iPr)H] (**6**)



**Figure 4.** (a) Structural view of [Ni(PCP<sup>Me</sup>-iPr)( $\eta^2$ -BH<sub>4</sub>)]·0.5C<sub>6</sub>D<sub>6</sub> (**5**·0.5C<sub>6</sub>D<sub>6</sub>) 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 BH<sub>4</sub><sup>-</sup> ligand. Selected bond lengths (Å) and bond angles (deg): Ni1–C1 1.906(2), Ni1–P1 2.1675(8), Ni1–P2 2.1691(8), Ni1...B1 2.218(3), Ni1–H1B1 1.70(3), Ni1–H2B1 1.85(2); P1–Ni1–P2 165.19(3), P1–Ni1–C1 83.67(6), P2–Ni1–C1 83.54(6), C1–Ni1–B1 167.4(1).

55.8 Hz.<sup>29,30</sup> Complexes **5** and **6** exhibit a singlet at 136.0 and 144.5 ppm, respectively, in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum.



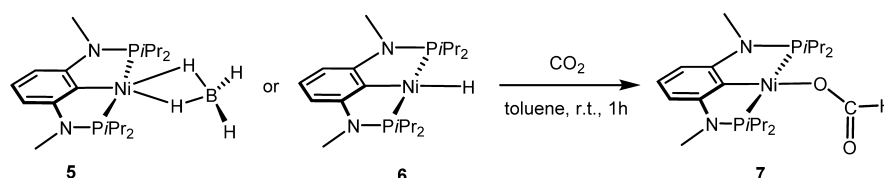
**Figure 5.** Structural view of [Ni(PCP<sup>Me</sup>-iPr)H] (**6**) showing 50% thermal ellipsoids (most H atoms and a second independent complex omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Ni1–P1 2.115(1), Ni1–P2 2.122(1), Ni1–C1 1.908(3); P1–Ni1–P2 169.97(3), P1–Ni1–C1 85.3(1), 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  $\tau$  value for **5** is 0.11, in agreement with a distorted square-pyramidal geometry. The nickel atom coordinates the BH<sub>4</sub> group in an  $\eta^2$ -fashion, but in a slightly asymmetrical fashion with Ni–H<sub>b</sub> distances of 1.70(3) and 1.85(2) Å. Similar Ni–H<sub>b</sub> 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.<sup>5</sup> 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 [Ni(POCOP-*i*Pr)( $\eta^2$ -BH<sub>4</sub>)] (1.901(2) Å), [Ni(POCOP-*t*Bu)( $\eta^2$ -BH<sub>4</sub>)] (1.898(4) Å), and [Ni(POCOP-C<sub>5</sub>H<sub>9</sub>)( $\eta^2$ -BH<sub>4</sub>)] (1.892(2) Å).<sup>5</sup> It is interesting to note that, in a related Pd PCP pincer complex based on ferrocene, the BH<sub>4</sub><sup>-</sup> moiety is coordinated in an unidentate mode with a Pd...B distance of 2.614(7) Å.<sup>31</sup>

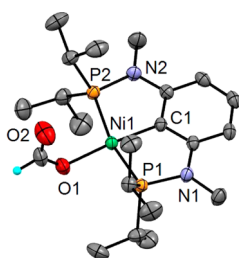
Guan and co-workers have recently shown<sup>5</sup> that both nickel hydride and borohydride PCP pincer complexes are able to reduce CO<sub>2</sub> to give formate complexes. Given the fact that **5** is also capable of liberating “BH<sub>3</sub>” as amine adduct to form a nickel hydride, we also explored the possibility of reducing CO<sub>2</sub>



**Scheme 5. Reaction of  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**5**) and  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})\text{H}]$  (**6**) with  $\text{CO}_2$  Giving the Formate Complex  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})(\text{OC}(\text{=O})\text{H})]$  (**7**)**



with complexes **5** and **6**. When exposed to 1 bar of  $\text{CO}_2$  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  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  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.

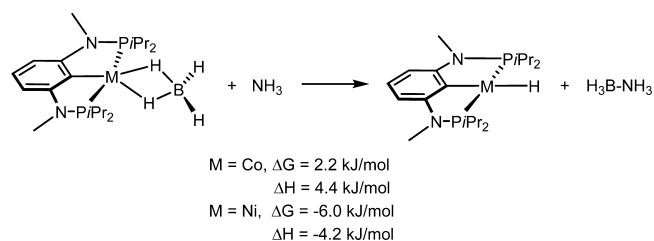


**Figure 6.** Structural view of  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})(\text{OC}(\text{=O})\text{H})]$  (**7**) showing 50% thermal ellipsoids (most H atoms and a second independent complex omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Ni1–P1 2.1712(7), Ni1–P2 2.1701(7), Ni1–O1 1.923(2), Ni1–C1 1.897(2); P1–Ni1–P2 166.49(2), P1–Ni1–O1 95.06(6), P1–Ni1–C1 84.05(7), P2–Ni1–O1 97.47(5), P2–Ni1–C1 84.12(7), O1–Ni1–C1 172.93(8).

On the basis of the above results with  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**5**) and  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})\text{H}]$  (**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.<sup>22,32,33</sup> Unfortunately, the reaction of  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})\text{Cl}]$  (**2a**) with  $\text{LiAlH}_4$  resulted in the formation of intractable materials together with the free protonated  $\text{PCP}^{\text{Me}}\text{-iPr}$  ligand. Likewise, treatment of **2a** with  $\text{Na}[\text{HBEt}_3]$  or  $n\text{BuLi}$  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  $\text{NEt}_3$  to give  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})\text{H}]$  nor react with  $\text{CO}_2$  to afford the formate complex  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})(\text{OC}(\text{=O})\text{H})]$  even at  $80^\circ\text{C}$  for 24 h (Scheme 3). For comparison, it was shown<sup>34</sup> that  $\text{BH}_3$  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  $\text{BH}_4$  unit and the thermodynamics for the reaction of  $\text{NH}_3$  with the Co- $\text{BH}_4$  and Ni- $\text{BH}_4$  moieties, we performed DFT calculations<sup>35</sup> on complexes **4a** and **5** (B3LYP functional; for details see the Experimental Section). This revealed that extrusion of  $\text{BH}_3$  with  $\text{NH}_3$  (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 ( $\text{NH}_3$ ) and the relatively small

**Scheme 6. DFT Calculated Thermodynamics of the Reaction of  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**4a**) and  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**5**) with  $\text{NH}_3$**

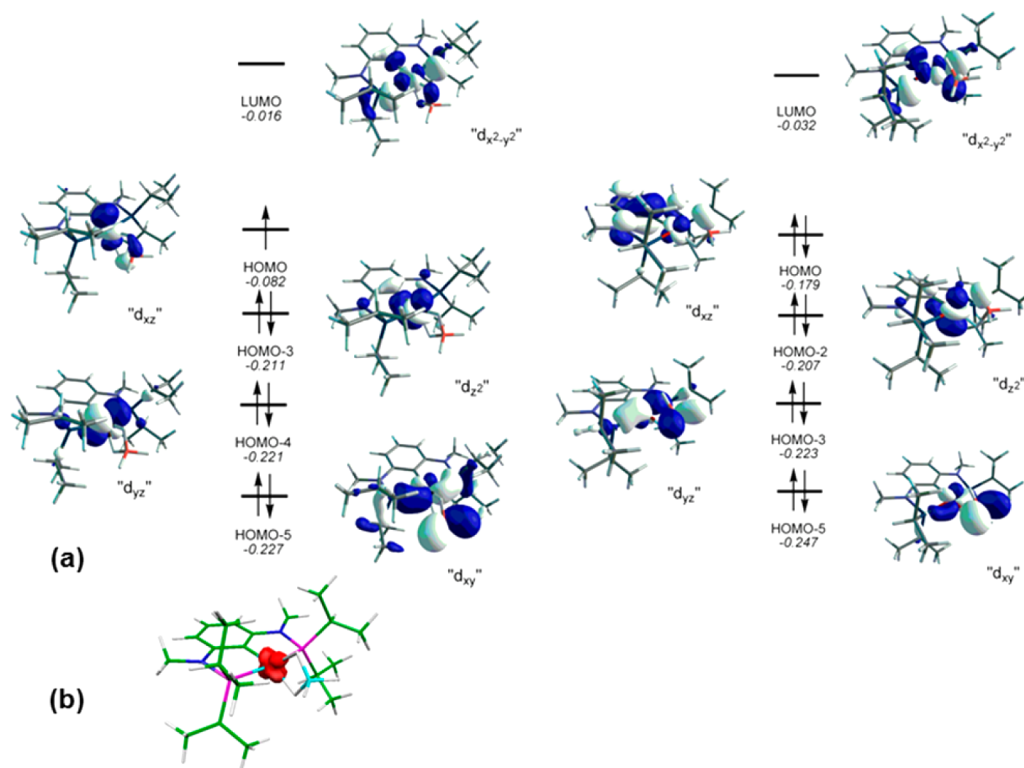


$\Delta G$  values obtained, indicate a clear trend and help explain why attempts to obtain the corresponding Co hydride complex from **4a** by removal of  $\text{BH}_3$  as an amine adduct were unsuccessful.

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 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  $\text{BH}_4^-$  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)<sup>36</sup> 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  $\text{BH}_4^-$  coordination is closer to  $\eta^2$ , 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  $\eta^1$ , 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  $d^8$  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;<sup>37</sup> see the Computational Details):  $C_{\text{PCP}} = 0.26$  (**4a**) and 0.24 (**5**),  $C_{\text{BH}_4} = -0.67$  (**4a**) and  $-0.73$  (**5**). This is reflected in an electron richer Co-atom in **4a** ( $C_{\text{Co}} = 0.42$ , compared with the Ni-atom in **5** ( $C_{\text{Ni}} = 0.49$ ) and indicates stronger coordination of the ligands in the case of the Co complex, in particular, a stronger M– $\text{BH}_4$  bond, in good accordance with the reactivity pattern observed for the reaction with  $\text{NH}_3$  (see Scheme 6).

## CONCLUSION

We have shown that the 15e square-planar complexes  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})\text{Cl}]$  (**2a**) and  $[\text{Co}(\text{PCP}\text{-}t\text{Bu})\text{Cl}]$  (**2b**), respectively, react readily with  $\text{NaBH}_4$  to afford complexes  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**4a**) and  $[\text{Co}(\text{PCP}\text{-}t\text{Bu})(\eta^2\text{-BH}_4)]$  (**4b**) in high yields. The  $\eta^2$ -bonding mode of the borohydride ligand



**Figure 7.** (a) DFT-computed frontier orbitals ( $d$ -splitting) for  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**4a**) (left) and for  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**5**) (right) and (b) spin density of  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**4a**). Energy values in italics (atomic units).

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)  $\mu_{\text{B}}$  consistent with a  $d^7$  low-spin system corresponding to one unpaired electron. None of these complexes react with  $\text{CO}_2$  to give formate complexes. For structural and reactivity comparisons, we prepared the analogous Ni(II) borohydride complex  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**5**) via two different routes. One utilizes  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})\text{Cl}]$  (**3**) and  $\text{NaBH}_4$ , the second one makes use of the hydride complex  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})\text{H}]$  (**6**) and  $\text{BH}_3\cdot\text{THF}$ . In both cases, **5** was obtained in high yields. While  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**5**) loses readily  $\text{BH}_3$  at elevated temperatures in the presence of  $\text{NEt}_3$  to form **6**, the Co(II) complex  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**4a**) did not react with  $\text{NH}_3$  to give a hydride complex. Complexes **5** and **6** react with  $\text{CO}_2$  to give the formate complex  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})(\text{OC}(\text{C}=\text{O})\text{H})]$  (**7**). DFT calculations revealed that 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  $\text{BH}_4^-$  coordination is closer to  $\eta^2$ , 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  $\eta^1$ , 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.<sup>38</sup> The deuterated solvents were purchased from Aldrich and dried over 4 Å

molecular sieves.  $N,N'$ -Bis(di-*tert*-butylphosphino)-1,3-diaminobenzene ( $\text{PCP-}t\text{Bu}$ ) (**1b**),<sup>39</sup>  $[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})\text{Cl}]$  (**2a**),<sup>14</sup> and  $[\text{Ni}(\text{PCP}^{\text{Me}}\text{-iPr})\text{Cl}]$  (**3**)<sup>14</sup> were prepared according to the literature.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on Bruker AVANCE-250, AVANCE-300 DPX, and AVANCE-400 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced internally to residual protio-solvent, and solvent resonances, respectively, and are reported relative to tetramethylsilane ( $\delta = 0$  ppm).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were referenced externally to  $\text{H}_3\text{PO}_4$  (85%) ( $\delta = 0$  ppm).

**$[\text{Co}(\text{PCP-}t\text{Bu})\text{Cl}]$  (**2b**).** A suspension of  $N,N'$ -bis(di-*tert*-butylphosphino)-1,3-diaminobenzene ( $\text{PCP-}t\text{Bu}$ ) (**1b**) (300 mg, 0.758 mmol) and anhydrous  $\text{CoCl}_2$  (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%). Anal. Calcd for  $\text{C}_{22}\text{H}_{41}\text{ClCoN}_2\text{P}_2$  (489.91): C, 53.94; H, 8.44; N, 5.72. Found: C, 53.89; H, 8.51; N, 5.78.  $\mu_{\text{eff}} = 1.8(1) \mu_{\text{B}}$  ( $\text{CH}_2\text{Cl}_2$ , Evans method).

**$[\text{Co}(\text{PCP}^{\text{Me}}\text{-iPr})(\eta^2\text{-BH}_4)]$  (**4a**).** To a suspension of **2a** (200 mg, 0.43 mmol) in THF/MeOH (1:1) (10 mL) was added  $\text{NaBH}_4$  (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%). Anal. Calcd for  $\text{C}_{20}\text{H}_{41}\text{-BCoN}_2\text{P}_2$  (441.25): C, 54.44; H, 9.37; N, 6.35. Found: C, 54.34; H, 9.41; N, 6.45. IR (ATR,  $\text{cm}^{-1}$ ): 1948–1825 (br,  $\nu_{\text{B-Hb}}$ ), 2387 (s,  $\nu_{\text{B-Ht}}$ ), 2312 (s,  $\nu_{\text{B-Ht}}$ ).  $\mu_{\text{eff}} = 2.0(1) \mu_{\text{B}}$  ( $\text{CH}_2\text{Cl}_2$ , Evans method).

**$[\text{Co}(\text{PCP-}t\text{Bu})(\eta^2\text{-BH}_4)]$  (**4b**).** This complex was prepared in an analogous fashion to **4a** with **2b** (100 mg, 0.204 mmol) and  $\text{NaBH}_4$  (17 mg, 0.408 mmol) as starting materials. Yield: 87 mg (91%). Anal. Calcd for  $\text{C}_{22}\text{H}_{43}\text{BCoN}_2\text{P}_2$  (469.31): C, 56.30; H, 9.67; N, 5.97. Found: C, 56.34; H, 9.73; N, 5.89. IR (ATR,  $\text{cm}^{-1}$ ): 1909 (br,  $\nu_{\text{B-Hb}}$ ), 1975 (br,  $\nu_{\text{B-Hb}}$ ), 2415 (s,  $\nu_{\text{B-Ht}}$ ), 2339 (s,  $\nu_{\text{B-Ht}}$ ).  $\mu_{\text{eff}} = 2.1(1) \mu_{\text{B}}$  ( $\text{CH}_2\text{Cl}_2$ , Evans method).

**[Ni(PCP<sup>Me</sup>-iPr)(η<sup>2</sup>-BH<sub>4</sub>)] (5). Method A.** A suspension of [Ni(PCP<sup>Me</sup>-iPr)Cl] (3) (200 mg, 0.435 mmol) and NaBH<sub>4</sub> (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<sub>3</sub>·THF adduct (469 μL, 0.469 mmol, 1.0 M solution in THF), and the mixture was stirred at room temperature for 30 min. The solvent was then evaporated under vacuum, and 5 was obtained as an orange-yellow solid. Yield: 192 mg (93%). Anal. Calcd for C<sub>20</sub>H<sub>41</sub>BN<sub>2</sub>NiP<sub>2</sub> (441.03): C, 54.47; H, 9.37; N, 6.35. Found: C, 54.45; H, 9.26; N, 6.41. <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 7.26 (t, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 1H), 6.09 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2H), 2.53 (vt, <sup>3,5</sup>J<sub>HP</sub> = 2.6 Hz, 6H, NCH<sub>3</sub>), 2.37 (m, 4H, CH), 1.40 (vq, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, <sup>3</sup>J<sub>HP</sub> = 7.5 Hz, 12H, CH<sub>3</sub>), 1.06 (vq, <sup>3</sup>J<sub>HH</sub> = 5.1 Hz, <sup>3,5</sup>J<sub>HP</sub> = 7.5 Hz, 12H, CH<sub>3</sub>), -0.75 (q, <sup>3</sup>J<sub>HB</sub> = 75.0 Hz, 4H, BH<sub>4</sub>). <sup>1</sup>H{<sup>31</sup>P} NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 7.15 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1H), 6.00 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2H), 2.43 (s, 6H, NCH<sub>3</sub>), 2.37 (m, 4H, CH), 1.40 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, CH<sub>3</sub>), 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 5.1 Hz, 12H, CH<sub>3</sub>), -0.75 (q, <sup>3</sup>J<sub>HB</sub> = 75.0 Hz, 4H, BH<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 160.7 (t, <sup>2</sup>J<sub>CP</sub> = 16.2 Hz, Ph), 126.5 (Ph), 100.8 (t, <sup>3</sup>J<sub>CP</sub> = 6.2 Hz, Ph), 31.7 (NCH<sub>3</sub>), 25.3 (t, <sup>2</sup>J<sub>CP</sub> = 11.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 17.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 17.4 (CH(CH<sub>3</sub>)<sub>2</sub>), the resonance of C<sub>ipso</sub> was obscured by the solvent peak. <sup>31</sup>P{<sup>1</sup>H} NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 136.0. IR (ATR, cm<sup>-1</sup>): 1845–2107 (br, ν<sub>B-Hb</sub>), 2321 (s, ν<sub>B-Ht</sub>), 2384 (s, ν<sub>B-Ht</sub>).

**[Ni(PCP<sup>Me</sup>-iPr)H] (6). Method A.** A suspension of [Ni(PCP<sup>Me</sup>-iPr)Cl] (3) (200 mg, 0.435 mmol) and LiAlH<sub>4</sub> (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% (156 mg). **Method B.** A suspension of 5 (200 mg, 0.453 mmol) and NEt<sub>3</sub> (1.26 mL, 9.06 mmol) in toluene (10 mL) was stirred at 80 °C for 24 h. After that, the solvent was removed under vacuum, and 6 was obtained as an orange-yellow solid. Yield: 180 mg (93%). Anal. Calcd for C<sub>20</sub>H<sub>38</sub>N<sub>2</sub>NiP<sub>2</sub> (427.19): C, 56.23; H, 8.97; N, 6.56. Found: C, 56.15; H, 9.03; N, 6.50. <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 7.31 (t, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 1H), 6.23 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2H), 2.65 (vt, <sup>3,5</sup>J<sub>HP</sub> = 2.7 Hz, 6H, NCH<sub>3</sub>), 2.06 (m, 4H, CH), 1.28 (m, 12H, CH<sub>3</sub>), 0.95 (m, 12H, CH<sub>3</sub>), -8.26 (t, <sup>2</sup>J<sub>HP</sub> = 55.8 Hz, 1H, Ni-H). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 160.6 (t, <sup>2</sup>J<sub>CP</sub> = 16.8 Hz, Ph), 139.3 (t, <sup>2</sup>J<sub>CP</sub> = 15.6 Hz, C<sub>ipso</sub> Ph), 127.0 (Ph), 100.2 (t, <sup>3</sup>J<sub>CP</sub> = 6.2 Hz, Ph), 31.5 (NCH<sub>3</sub>), 26.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 19.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 17.9 (CH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 144.5.

**[Ni(PCP<sup>Me</sup>-iPr)(OC(=O)H)] (7).** To a suspension of 6 (100 mg, 0.23 mmol) in pentane; the solution was stirred under 1 atm of CO<sub>2</sub> and the resulting solution immediately turned from orange-yellow to bright yellow. After 30 min, the solvent was removed under vacuum, and the bright yellow solid was obtained in good yield 90% (98 mg). Anal. Calcd for C<sub>21</sub>H<sub>38</sub>N<sub>2</sub>NiO<sub>2</sub>P<sub>2</sub> (471.19): C, 55.53; H, 8.13; N, 5.95. Found: C, 55.65; H, 8.23; N, 5.88. <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 8.61 (t, <sup>4</sup>J<sub>HP</sub> = 2.5 Hz, 1H, Ni formate) 7.18 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1H), 5.96 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H), 2.44 (vt, <sup>3,5</sup>J<sub>HP</sub> = 2.5 Hz, 6H, NCH<sub>3</sub>), 2.26 (m, 4H, CH), 1.45 (m, 12H, CH<sub>3</sub>), 1.14 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 167.1 (O(C=O)H), 161.7 (t, <sup>2</sup>J<sub>CP</sub> = 16.2 Hz, Ph), 127.2 (Ph), 117.1 (t, <sup>2</sup>J<sub>CP</sub> = 20.1 Hz, C<sub>ipso</sub> Ph), 100.7 (t, <sup>3</sup>J<sub>CP</sub> = 6.2 Hz, Ph), 31.5 (t, <sup>2</sup>J<sub>CP</sub> = 1.8 Hz, NCH<sub>3</sub>), 25.7 (t, <sup>1</sup>J<sub>CP</sub> = 10.0 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 17.6 (m, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (δ, C<sub>6</sub>D<sub>6</sub>, 20 °C): 117.1. IR (ATR, cm<sup>-1</sup>): 1614(s, ν<sub>CO</sub>).

**X-ray Structure Determination.** X-ray diffraction data of 2b, 4a, 4b, 5, and 6 were collected at T = 100 K in a dry stream of nitrogen on a Bruker Kappa APEX II diffractometer system using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) and fine sliced φ and ω-scans. Data of 7 were collected on a Bruker SMART APEX diffractometer at 190 K. Crystals of 6 were systematically twinned by 2-fold rotation around [001]. The reflections of both domains were separated using RLATT.<sup>40</sup> Data were reduced to intensity values with SAINT, and an absorption correction was applied with the multiscan

approach implemented in SADABS and TWINABS.<sup>35</sup> The structures were solved by charge flipping using SUPERFLIP<sup>41</sup> and refined against F with JANA2006.<sup>42</sup> The structure of 4a was solved by direct methods and refined against F<sup>2</sup> with the SHELX suite.<sup>43</sup> Non-hydrogen atoms were refined anisotropically. The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. H atoms connected to N and B were located in difference Fourier maps, and their positions were refined without restraints. Molecular graphics were generated with the program MERCURY.<sup>44</sup> Crystal data and experimental details are given in Tables S1 and S2 (Supporting Information).

**Computational Details.** All calculations were performed using the Gaussian 09 software package<sup>45</sup> on the Phoenix Linux Cluster of the Vienna University of Technology. The optimized geometries were obtained with the B3LYP functional,<sup>46</sup> without symmetry constraints. That functional includes a mixture of Hartree–Fock<sup>47</sup> exchange with DFT<sup>35</sup> exchange–correlation, given by Becke's three parameter functional with the Lee, Yang, and Parr correlation functional, which includes both local and nonlocal terms. The basis set used for the geometry optimizations consisted of the Stuttgart/Dresden ECP (SDD) basis set<sup>48</sup> to describe the electrons of the metal atoms, and a standard 6-31G(d,p) basis set<sup>49</sup> for all other atoms. A Natural Population Analysis (NPA)<sup>37</sup> and the resulting Wiberg indices<sup>36</sup> were used to study the electronic structure and bonding of the optimized species. The molecular orbitals of the Co complex presented in Figure 7 result from single point restricted open-shell calculations performed on the optimized structure. Three-dimensional representations of the orbitals were obtained with the program Chemcraft.<sup>50</sup>

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Complete crystallographic data, <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of all diamagnetic complexes, and technical details in CIF format for 2b, 4a, 4b, 5, 6, and 7 (CCDC entries 1044983–1044988). 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 interests.

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