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VIP **Cobalt Complexes**

Preparation of a Dihydrogen Complex of Cobalt**

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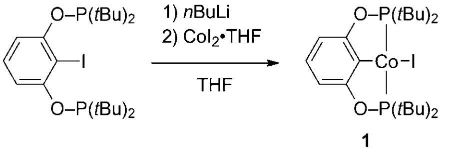
Ammonia borane (AB) is an attractive candidate for the chemical storage of hydrogen.[1] Recently, our research group reported that the complex [(pocop)IrH$_2$] (pocop = κ^3-C$_6$H$_3$-1,3-[OP(tBu)$_2$]$_2$) has facilitated the rapid release of H$_2$ from AB under mild conditions.[2] While this result is promising, iridium is too expensive for widespread application. Our efforts to extend the catalytic chemistry of [(pocop)IrH$_2$] to Co have led to several intriguing complexes. Direct analogues of the Ir catalyst were obtained, thereby demonstrating the unusual ligation of H$_2$ on a Co center. Herein we report the first cobalt–dihydrogen complex, which was characterized by NMR spectroscopy and studied by means of theoretical calculations.

The metalation of pocop–H with Co, achieved with a method similar to procedures developed for Ir or Ni, did not proceed in satisfactory yield.[3] An alternative approach that makes use of an iodinated pocop ligand was pursued, as described for a similar synthesis.[4] Complex **1** was prepared in good yield by activation of the ligand with nBuLi and the addition of CoI$_2$·THF (Scheme 1).



Scheme 1. Synthesis of **1** using an iodinated pocop proligand. THF = tetrahydrofuran.

The ^{1}H NMR spectrum of **1** (see the Supporting Information) exhibits three broad resonances outside the typical diamagnetic region with integral ratios of 36:2:1. The magnetic susceptibility of **1** was measured using the method of Evans[5] ($\mu_{\text{eff}} = 2.38$ BM, 297 K, [D$_8$]THF) and is consistent with a paramagnetic complex that contains one unpaired electron. The structure of **1** was determined by X-ray crystal structure analysis and is shown in Figure 1.[6] Similar Co complexes containing a Co center bound to a tris-chelating ligand have been reported, in which the arrangement of the ligand promotes a near planar environment around the metal center.[7]

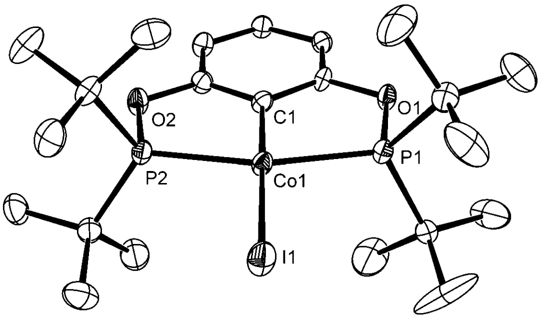


Figure 1. ORTEP diagram of **1**. Thermal ellipsoids are set at 50% probability and H atoms have been omitted for clarity. Relevant bond lengths [Å] and angles [°]: Co1–I1 2.5697(6), Co1–P1 2.2212(11), Co1–C1 1.924(4), Co1–P2 2.2207(11); P1-Co1-P2 162.81(4), C1-Co1-I1 179.60(11).

Reduction of **1** was accomplished using sodium amalgam. The isolated product is a mercury-bridged dicobalt species [{(pocop)Co}$_2$Hg] (**2**; Figure 2).[8] The ^{1}H NMR spectrum of **2** (see the Supporting Information) exhibits broad resonances outside the diamagnetic region with integral ratios of 36:2:1, thereby indicating a paramagnetic species. Density functional theory (DFT) calculations performed on [(pocop)Co] indicate that a triplet electronic configuration ($S = 1$, **triplet-[Co]**) is favored over the singlet state ($S = 0$, **singlet-[Co]**) by 18 kcal mol^{-1}. Similar calculations on **2** indicate that formation of a triplet dicobalt species from triplet [(pocop)Co] and singlet Hg is favorable in the gas phase ($\Delta H = -10.3$ kcal mol^{-1}).[9]

Introduction of H$_2$ gas to a solution of **2** at 195 K resulted in a new diamagnetic species **3** (Figure 3 for structure). The ^{1}H NMR spectrum in the high-field region exhibits a new resonance (with an integration of 2 versus other ligand resonances) at $\delta = -11.6$ ppm. Variable temperature ^{1}H NMR spectra were recorded at 500 MHz in [D$_{14}$]MeCy (see the Supporting Information). For the resonance at $\delta = -11.6$ ppm, the T_1 relaxation time was measured as a function of temperature. No well-defined T_1(min) value was found for

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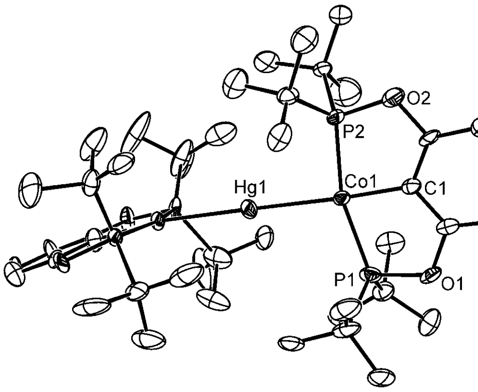

Figure 2. ORTEP diagram of **2**. Thermal ellipsoids are set at 50% probability and H atoms have been omitted for clarity. Relevant bond lengths [Å] and angles [°]: Co1–Hg1 2.623(2), Co1–P1 2.186(3), Co1–C1 1.946(11), Co1–P2 2.167(3); P1-Co-P2 162.63(14), C1-Co-Hg 175.7(3), Co1-Hg1-Co1 178.4(3).

3. A value of 30 ms was measured at 220 K, and the T_1 value continued to decrease with increasing temperature. Decomposition of **3** near ambient temperature prevented the collection of reliable data for T_1 above 220 K.

To better understand the nature of H_2 binding in **3**, deuterium was incorporated into the complex by using HD gas in place of H_2. This gave a 1:1:1 triplet resonance in the ^{1}H NMR spectrum at $\delta = -11.2$ ppm with $^1J_{HD} = 28$ Hz (Figure 3). Using a previously established correlation, this large HD coupling confirms that **3** is a dihydrogen complex of Co with $r_{HH} = 0.95$ Å.[10]

Studying solutions of **3** under increased hydrogen pressure allowed observation of a new diamagnetic product **4** (see Figure 3 for structure). With a H_2 pressure of 75 psi in the sample headspace, complex **4** was stable only below 220 K. The new resonance at $\delta = -9.3$ ppm integrated as four versus other ligand resonances. A T_1(min) value of 25 ms for the hydridic resonance of complex **4** was recorded at 180 K (500 MHz).

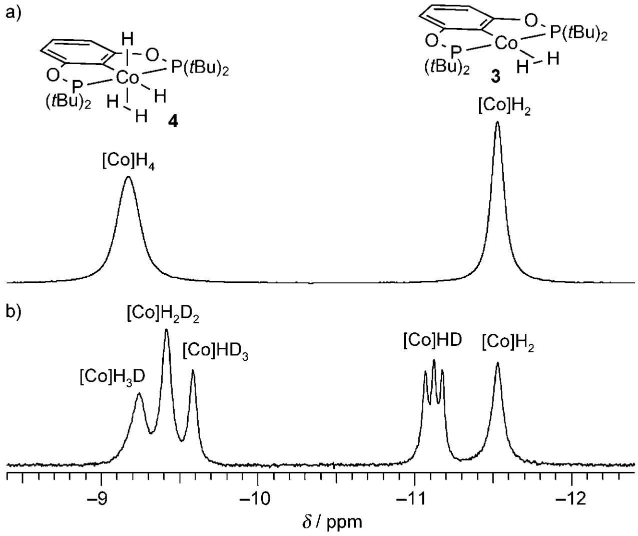

Figure 3. Partial ^{1}H NMR spectrum a) after introduction of H_2 gas and b) after introduction of HD gas to **2** (high-field region, 500 MHz, 190 K, [D$_{14}$]MeCy). Cy = cyclohexyl.

When HD gas was used in place of H_2, new resonances were observed just upfield of the resonance at $\delta = -9.3$ ppm, which correspond to the isotopomers of complex **4** (Figure 3). No HD coupling was observed in these resonances. The short T_1(min) value for **4** favors its formulation as a dihydrogen/dihydride.[11] Note that **3** and **4** are stable only at low temperature and in the presence of H_2 gas, and therefore were not isolable.

The chemical shifts of **3** and **4** as well as the chemical shifts and coupling constants of their isotopomers showed no significant temperature dependence. Also, no significant differences were noted when these spectra were recorded in [D$_8$]toluene.

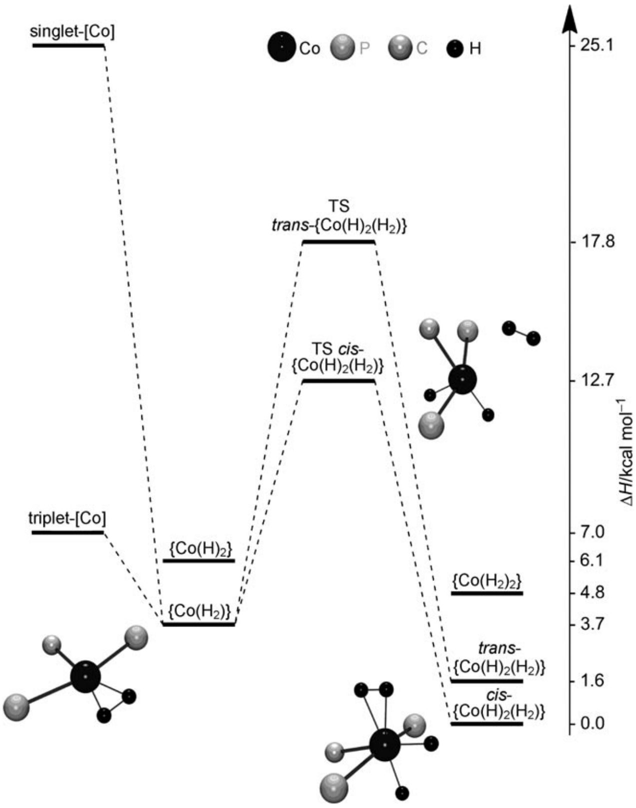

Figure 4. Energy profile diagram of all relevant species. Structures are shown for selected species. Only atoms directly coordinated to Co are shown. For computational details see the Supporting Information.

DFT calculations were performed to further investigate the reaction between **2** and H_2. It is assumed that complex **2** dissociates in solution to form a reactive three-coordinate species. The global minimum for **3** is a dihydrogen complex (**{Co(H$_2$)}**) that exists in two forms (both minima) with the H_2 perpendicular to, or lying in, the pocop plane (Figure 4). These structures have the same enthalpies, and the H_2 may be considered a free rotor in **3**. A square-pyramidal dihydride structure (**{Co(H)$_2$}**) is another minimum that exists for **3**, and is 2.4 kcal mol^{-1} higher in enthalpy. The addition of a second molecule of H_2 to **3** could give rise to several structures. The global minimum was found to be a *cis*-dihydrogen/dihydride complex, (***cis*-{Co(H)$_2$(H$_2$)}**). Two other minima were located that correspond to *trans*-dihydride dihydrogen (***trans*-{Co(H)$_2$(H$_2$)}**) and bis-dihydrogen (**{Co(H$_2$)$_2$}**) structures, 1.6 kcal mol^{-1} and 4.8 kcal mol^{-1} above the global minimum (***cis*-{Co(H)$_2$(H$_2$)}**), respectively. No minimum was found for a configuration containing only hydride ligands. Transition-state barriers for the loss of H_2 to form **{Co(H$_2$)}** were located 12.7 kcal mol^{-1} and 17.8 kcal mol^{-1} above ***cis*-{Co(H)$_2$(H$_2$)}** and ***trans*-{Co(H)$_2$(H$_2$)}**, respectively.

These calculations are in good agreement with the experimental results. The observation of a large J_{HD} value in complex **3** agrees with the assignment of the lowest energy structure as a dihydrogen complex of Co. The calculated r_{HH} value of 0.86 Å shows reasonable agreement with the experimentally determined value of 0.95 Å. For complex **4**, whose results are in agreement with the calculations, a formal $\mathrm{Co^V}$ complex with four hydride ligands (**{[Co]H$_4$}**) may be ruled out as a consequence of the short T_1(min) value.

There are limited examples of H_2 acting as a ligand to a cobalt center. Two reports describe the characterization of H_2 complexes of Co by using IR spectroscopic analysis after photoextrusion of a CO ligand at low temperature.[12] Brookhart and co-workers have reported the preparation and NMR spectra of $[Cp^*Co(PR_3)(H_2)(H)][B(Ar_F)_4]$, which is formulated as a dynamic dihydrogen/hydride complex ($Ar_F = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$).[13] This is the only report previous to ours of $\{Co(H_2)\}$ complexes observed by utilizing NMR spectroscopy.[14]

The reactivity of the {(pocop)Co} fragment resembles that of the analogous Ir fragment, which can bind one or two molecules of H_2 depending on temperature and H_2 pressure.[3a,15] While complex **3** was only observed at low temperature in non-coordinating solvents the Ir analogue binds hydrogen more strongly and is detectable at room temperature and low H_2 pressure, even in donor solvents, such as THF. The [(pocop)Ir] complex has been suggested as the active catalyst in alkane dehydrogenation reactions.[16] The reactivity of these interesting Co complexes is currently being explored for various catalytic applications.

Experimental Section

General considerations: All experiments were carried out under argon using Schlenk and glove box techniques. Solvents were dried and vacuum transferred immediately prior to use. NMR spectra were recorded at 298 K (unless otherwise noted) on Bruker AV300, AV500, or DRX500 spectrometers. ^{1}H NMR chemical shifts are reported relative to residual resonances of the solvent: [D$_6$]benzene ($\delta = 7.16$ ppm), [D$_8$]THF ($\delta = 1.73$ ppm), [D$_8$]toluene ($\delta = 2.09$ ppm), [D$_{14}$]MeCy ($\delta = 1.19$ ppm). ^{13}C{^{1}H} NMR chemical shifts are reported relative to the solvent: [D$_8$]THF ($\delta = 25.37$ ppm). ^{31}P{^{1}H} NMR chemical shifts are reported relative to H_3PO_4 (85% in H_2O) at $\delta = 0$ ppm. 2-Iodo-resorcinol[17] and $CoI_2{\cdot}THF$[18] were synthesized according to literature procedures. All other reagents were obtained from commercial sources and used as received. Solution magnetic moments were determined using the method of Evans.[5] Diamagnetic contributions were calculated using Pascal's constants.[19]

Preparation of (pocop)I: NaHMDS (10.31 g, 56.2 mmol) was dissolved in THF (200 mL) before $t\mathrm{Bu_2PCl}$ (11.1 mL, 58.4 mmol) was added by syringe. The reaction flask was cooled (273 K) and a solution of 2-iodo-resorcinol (6.56 g, 27.8 mmol in 200 mL THF) was added dropwise over 4 h. The flask was warmed to RT and stirring continued overnight. The light yellow slurry was filtered and the solvent was removed under vacuum. The resulting sticky solid was dissolved in pentane and filtered. The solution was cooled to 195 K for 3 h to precipitate the product and the supernatant was removed. Residual solvent was removed under vacuum, yielding 11.68 g of white solid. A second crop of product (1.20 g) was obtained after decreasing the original volume of the supernatant to one third. Total yield: 12.88 g (24.6 mmol; 88.5%); ^{1}H NMR (300 MHz, [D$_8$]THF): $\delta = 7.12$ (m, 1H, *p*-H), 7.02 (m, 2H, *m*-H), 1.21 ppm (d, 36H, ^3J(H,P) = 11.8 Hz, *t*Bu); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_8$]THF): $\delta = 160.7$ (d, ^2J(C,P) = 10.4 Hz, *o*-C), 129.7 (t, ^4J(C,P) = 1.9 Hz, *p*-C), 110.3 (dd, ^3J(C,P) = 25.0 Hz, ^5J(C,P) = 1.1 Hz, *m*-C), 82.8 (s, *i*-C), 36.5 (d, ^1J(C,P) = 26.6 Hz, $C(CH_3)_3$), 27.9 ppm (d, ^2J(C,P) = 15.9 Hz, $C(CH_3)_3$); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]THF): $\delta = 154.6$ ppm (s); ESI-MS: *m/z* 525.3 (100%, $[M+H]^+$). HMDS = bis(trimethylsilyl)amide.

Preparation of [(pocop)CoI] (**1**): (pocop)I (598 mg, 1.14 mmol) was dissolved in THF (50 mL) to give a colorless solution. While cooling in an ice-water bath, *n*BuLi (1.6 M in hexanes, 1.4 mL, 2.24 mmol) was added, thereby resulting in a light yellow solution. A blue solution of $CoI_2{\cdot}THF$ (881 mg, 2.29 mmol) in THF (100 mL) was immediately added, thereby resulting in a dark green solution. The reaction flask was removed from the bath and stirring was continued for 30 min. The reaction was opened to air and the solvent was removed under vacuum using a rotary evaporator. The dark green residue was dissolved in $CHCl_3$ (200 mL) and extracted with water (100 mL). The organic layer was collected and the solvent removed. Trituration with pentane and filtration gave a yellow/green solid. Yield: 555 mg (951 μmol, 83.4%); ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 12.8$ (s, 36H, fwhh = 380 Hz, *t*Bu), −8.3 (s, 1H, fwhh = 32 Hz, *p*-H), −23.1 ppm (s, 2H, fwhh = 110 Hz, *m*-H); magnetic moment ([D$_8$]THF, 297 K): 2.38 μ_B. fwhh = full width at half height.

Preparation of [{(pocop)Co}$_2$Hg] (**2**): Hexanes (25 mL) was vacuum transferred into a flask containing **1** (120 mg, 206 μmol). The reaction flask was cooled to 195 K and Na/Hg (Na 0.53%/w, 17.28 g, 4.0 mmol) was added by syringe under a strong flow of argon. The flask was degassed by freezing in liquid nitrogen, evacuating the headspace, and thawing in a dry ice/acetone bath at least nine times. The flask was warmed to 323 K and stirred vigorously for 5 h, which turned the bright yellow/green slurry into dark red/brown. After settling, the solution was cannula filtered. The solvent was removed under vacuum to yield a dark red/brown solid. Yield: 79 mg (140 μmol, 68%); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 4.55$ (s, 36H, fwhh = 30 Hz, *t*Bu), −0.25 (t, 1H, ^3J(H,H) = 7 Hz, *p*-H), −6.49 ppm (d, 2H, ^3J(H,H) = 7 Hz, *m*-H); elemental analysis calcd (%) for $C_{44}H_{78}Co_2HgO_4P_4$: C, 47.46; H, 7.06; found: C, 46.84; H, 7.07.

Preparation of [(pocop)CoH$_2$] (**3**) and [(pocop)CoH$_4$] (**4**): Complex **2** (4 mg, 9 μmol) was weighed into a double walled screw-cap NMR tube. [D$_{14}$]MeCy (0.3 mL) was added by vacuum transfer. The tube was frozen in liquid nitrogen and H_2 gas (75 psi) was introduced into the headspace. Thawing in a dry ice/acetone bath and gentle shaking resulted in a dark purple/brown solution containing both **3** and **4**. Characterization of **3**: ^{1}H NMR (500 MHz, [D$_{14}$]MeCy, 190 K): $\delta = 6.81$ (t, 1H, ^3J(H,H) = 8 Hz, *p*-H), 6.44 (d, 2H, ^3J(H,H) = 8 Hz, *m*-H), 1.32 (s, 36H, *t*Bu), −11.2 ppm (s, 2H, CoH); ^{31}P{^{1}H} NMR (202 MHz, [D$_{14}$]MeCy, 190 K) $\delta = 233$ ppm. Characterization of **4**: ^{1}H NMR (500 MHz, [D$_{14}$]MeCy, 190 K): $\delta = 6.72$ (t, 1H, ^3J(H,H) = 8 Hz, *p*-H), 6.32 (d, 2H, ^3J(H,H) = 8 Hz, *m*-H), 1.28 (s, 36H, *t*Bu),

−9.3 ppm (s, 4H, CoH); $^{31}P\{^{1}H\}$ NMR (202 MHz, [D_{14}]MeCy, 190 K): $\delta = 244$ ppm.

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