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Reactions of Cobalt(II) with $NaBH_4$ in the Presence of Bidentate Phosphines: Crystal and Molecular Structures of $CoH[Ph_2P(CH_2)_3PPh_2]_2 \cdot C_6H_6$ and $[Co(BH_4)[Ph_2P(CH_2)_5PPh_2]]_2 \cdot 0.5C_6H_6$

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The reactions between Co(II) and $NaBH_4$ in the presence of the phosphines $Ph_2P(CH_2)_nPPh_2$ (n = 2–6) and *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$ lead, through a series of intermediates, to the formation of CoH(phosphine)$_2$ species, except in the case of the trans ligand, where hydrogenation occurs and $CoH[Ph_2P(CH_2)_2PPh_2]_2$ is formed. Single-crystal X-ray diffraction studies on $CoH[Ph_2P(CH_2)_3PPh_2]_2 \cdot C_6H_6$ show that the compound crystallizes in the monoclinic space group $P2_1/n$, with unit cell parameters a = 13.640 (6) Å, b = 15.794 (5) Å, c = 23.870 (9) Å, β = 101.04 (4)°, V = 5047.2 Å^3, Z = 4, and d_{calcd} = 1.267 g cm^{-3}. The structure converged to a conventional R factor of 0.042 for 4754 observations and showed a five-coordinated Co(I) atom with two chelating phosphines and a hydride group in a distorted-trigonal-bipyramidal arrangement. In addition, with two of the longer chain phosphines (n = 4, 5) it is possible to isolate Co(I)–BH_4 species shown, in the case of n = 5, to be $[Co(BH_4)[Ph_2P(CH_2)_5PPh_2]]_2 \cdot 0.5C_6H_6$. This compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 10.305 (3) Å, b = 14.990 (3) Å, c = 20.343 (5) Å, α = 107.87 (2)°, β = 90.72 (2)°, γ = 105.88 (2)°, V = 2861 (3) Å^3, Z = 2, and d_{calcd} = 1.240 g cm^{-3}. The structure converged to a conventional R factor of 0.052 for 4290 observations. The dimeric species consists of two Co(I) atoms bridged by both phosphine ligands and BH_4 ligands in a hitherto unknown way such that each BH_4 group chelates to each cobalt using one common hydrogen, leaving one terminal hydrogen uninvolved. Alternatively, the BH_4 group can be considered as a tridentate ligand to two cobalt atoms separated by 2.869 (1) Å. The cobalt and boron atoms are almost coplanar, but, since there is no obvious strain in the Co–P$(CH_2)_5$P–Co linkages, the steric and electronic requirements of the bridging tetrahydroborate groups apparently dictate the distorted coordination geometry about the Co atoms.

Introduction

Reactions between $NaBH_4$ and Co(II) have been studied in the presence of monodentate[2,3] and tridentate[4] phosphine ligands and have been found to lead to the formation of a variety of Co(II) and Co(I) complexes containing chloro, hydrido, or tetrahydroborato groups. In comparison, there is relatively little data available on similar reactions with bidentate phosphines and this, together with the fact that some interesting species have been isolated[5] from related Ni(II)–bidentate phosphine–$NaBH_4$ reactions, led us to study reactions between Co(II) and $NaBH_4$ in the presence of the phosphines $Ph_2P(CH_2)_nPPh_2$ (n = 2 (dppe), 3 (dppp), 4 (dppb), 5 (dpppe), 6 (dpph)) and *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$. The ready production of CoH(dppe)$_2$ and Co(dppe)$_2$ has been reported,[6] as has that of CoH(*cis*-$Ph_2PCH{=}CHPPh_2$)$_2$,[7] but until the publication of a preliminary report on part of this work,[8] no examples of tetrahydroborate coordinated to Co(I) in systems containing such bidentate phosphines had been found. We have also found that the bidentate phosphine ligand with n = 1 behaves so significantly differently from the other phosphines in the reactions reported here that results of these studies will be reported separately.[9]

Experimental Section

Reagents and Solvents. The phosphines were obtained from the Strem Chemical Co., Inc., and were used without further purification. $NaBH_4$ was obtained from the Alfa Division of Morton Thiokol, Inc., and was stored under dry conditions. All solvents used were reagent grade and were degassed and stored under N_2 in a glovebox.

Physical Measurements. All samples were protected from atmospheric oxidation during weighing and data collection. Microanalytical data for C and H were acquired on a Perkin-Elmer 240 analyzer using V_2O_5 as a combustion aid. Infrared spectra were recorded on a Beckman IR-12 or IR-4250 spectrophotometer as Nujol mulls. A Bruker WP-80 FT instrument equipped with an automatic temperature control device (B-VT 1000) was used to record ^1H and ^{31}P NMR spectra at 80 and 32.3 MHz, respectively. Chemical shifts are reported as δ values with positive shifts downfield of Me_4Si for ^1H and downfield of the signal of the external standard 85% H_3PO_4 (δ = 0) for ^{31}P. Magnetic susceptibility data were obtained by NMR[10] methods.

Syntheses of the Compounds. All syntheses were carried out under a flow of pure nitrogen in a glovebox. Yields were generally between 20 and 50%.

CoH(dppe)$_2$. CoH(dppe)$_2$ was prepared as previously described[2a] except that a mixture of $CoCl_2 \cdot 6H_2O$ and dppe was treated directly with $NaBH_4$. The crude red solid was recrystallized from a benzene–ethanol mixture. IR: ν(Co–H) = 1890 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (25 °C, $CHCl_3$): δ 72.0 (singlet). ^1H NMR in the hydride region (25 °C, C_6D_6): δ −15.3 (quintet, J_{P-H} = 23 Hz).

CoH(dppe)$_2$ was also formed in the stirred reaction, at 70–80 °C, between $CoCl_2 \cdot 6H_2O$ (0.19 g, 0.8 mmol) in ethanol (25 mL), *trans*-$Ph_2PCH{=}CHPPh_2$ (1.38 g, 3.5 mmol) in toluene (5 mL), and $NaBH_4$ (0.07 g, 1.7 mmol) in ethanol (10 mL), the sodium tetrahydroborate being added over a 20-min period. The stirring was continued for a further 20 min as the solution cooled, and the red precipitate was filtered off, recrystallized, and shown by infrared spectra and ^{31}P, ^1H, and ^{13}C NMR studies to be CoH(dppe)$_2$. At room temperature, this reaction slowly produced a fine black precipitate of cobalt boride.

CoH(*cis*-$Ph_2PCH{=}CHPPh_2$)$_2$ was prepared in a reaction similar to that described above for the trans phosphine, except that room temperature was maintained. The molar ratios between $CoCl_2 \cdot 6H_2O$, the phosphine, and $NaBH_4$ were 1:4.5:1.2. The crude red product was filtered off, washed with ethanol, water, and ethanol, and, finally, recrystallized from an ethanol–toluene mixture. IR: ν(Co–H) = 1892 cm^{-1}. $^{31}P\ \{^1H\}$ NMR (25 °C, $CHCl_3$): δ 80.2 (singlet). ^1H NMR in the hydride region (25 °C, C_6D_6): δ −15.0 (quintet, J_{P-H} = 22 Hz). Anal. Calcd for CoH($Ph_2PCH{=}CHPPh_2$)$_2$: C, 73.3; H, 5.3. Found: C, 73.3; H, 5.8.

CoH(dppp)$_2$ was prepared similarly to the cis-phosphine complex, described above, with use of molar ratios between $CoCl_2 \cdot 6H_2O$, the phosphine, and $NaBH_4$ of 1:3.3:1.5. The red product was again filtered off, washed with ethanol, water, 10% HNO_3 (to remove traces of cobalt boride), water, and ethanol, and then recrystallized from toluene–ethanol.

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IR: ν(Co–H) = 1965 cm^{-1}. $^{31}P\{^1H\}$ NMR (25 °C, $CHCl_3$): δ 32.5 (singlet). ^1H NMR in the hydride region (25 °C, C_6D_6): δ −14.6 (quintet, J_{P-H} = 25.0 Hz). Anal. Calcd for $CoH(dppp)_2$: C, 73.3; H, 6.0. Found: C, 73.0; H, 5.9.

Crystals suitable for X-ray work were obtained by very slow crystallization from benzene–ethanol, which produced the benzene solvate $CoH(dppp)_2 \cdot C_6H_6$.

$CoH(dppb)_2$ was prepared in the reaction, at 55–60 °C, between a stirred mixture of $CoCl_2 \cdot 6H_2O$ (0.25 g, 1.1 mmol) and dppb (1.8 g, 4.2 mmol) in ethanol–toluene (4:1, 50 mL) and a suspension of $NaBH_4$ (0.23 g, 6.1 mmol) in ethanol, with the latter added over a 10-min period. The mixture was cooled for 15 min and the resulting red solid filtered off and washed with ethanol, water, and then ethanol again. Final recrystallization was from toluene–ethanol. IR: ν(Co–H) = 1965 cm^{-1}. $^{31}P\{^1H\}$ NMR (25 °C, $CHCl_3$): δ 39.2 (singlet). ^1H NMR in the hydride region (25 °C, C_6D_6): δ −16.9 (quintet, J_{P-H} = 28 Hz). Anal. Calcd for $CoH(dppb)_2$: C, 73.7; H, 6.2. Found: C, 72.8; H, 6.1.

$CoH(dpppe)_2$ and $CoH(dpph)_2$ were not isolated in pure form, but fairly good evidence for their formation was obtained. Reactions between $CoCl_2 \cdot 6H_2O$, the appropriate phosphine, and $NaBH_4$ carried out in benzene–ethanol mixtures (as above) produced dark thick oils, but when benzene alone was used (dpppe, room temperature) or benzene with a few drops of ethanol added (dpph, room temperature or 50 °C), red solutions were obtained after 5–7 h. In the case of dpppe, the reaction filtrate was concentrated to a red oil that resisted attempts at crystallization. IR: ν(Co–H) = 2070 cm^{-1}. $^{31}P\{^1H\}$ NMR (25 °C, C_6H_6): δ 37.98 (singlet). A similar procedure for the dpph reaction also gave a red oil. IR: ν(Co–H) = 2080 cm^{-1}. $^{31}P\{^1H\}$ NMR (25 °C, C_6H_6): δ 38.17.

Hydroborate-Containing Products. The course of the reactions leading to products containing coordinated BH_4^- groups is critically dependent on bidentate phosphine chain length, reactant ratios, solvents, temperature, and, most of all, the rate of addition of the $NaBH_4$. Furthermore, even though the reaction described below for dpppe has been carried out many times, the desired product is, occasionally, not the one that is formed. It is essential that oxygen be excluded throughout the synthesis and purification of the product.

$[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$. To a stirred, clear, deep blue solution of $CoCl_2 \cdot 6H_2O$ (0.57 g, 2.37 mmol) and the phosphine (2.99 g, 6.79 mmol) in ethanol (18 mL) and toluene (14 mL) at room temperature was added dropwise under a slow N_2 flow a suspension of $NaBH_4$ (0.17 g, 4.5 mmol) in ethanol (5 mL) over a period of 30 min. The color changed rapidly, and a green precipitate formed. Filtration yielded a dark green solid, which was washed through the filter by benzene (~10 mL). A small amount of a blue residue may remain at this point. The benzene washings were combined with the original greenish yellow filtrate, to which was added ethanol (~50 mL). Dark green crystals grew from this solution over a 24-h period at 0 °C and were recrystallized from benzene–hexane (~60 mL, 1:1) over 2 days at 0 °C. Crystals suitable for X-ray work were grown over a period of 1 week by gradually lowering the temperature of a benzene–hexane solution of the complex to ~−18 °C. IR: $\nu(B\text{–}H_{terminal})$ = 2415 (s) cm^{-1}, $\nu(B\text{–}H_{bridging})$ = 2030 (s), 1985 (s) cm^{-1}. Anal. Calcd for $[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$: C, 67.7; H, 6.2. Found: C, 68.4; H, 7.1.

In a similar reaction involving dppb, a dark green product that appeared to contain coordinated BH_4 was obtained (IR: $\nu(B\text{–}H_{terminal})$ = 2385 cm^{-1}, $\nu(B\text{–}H_{bridging})$ = 2070 (b) cm^{-1}. Anal. Calcd for $Co(BH_4)(dppb)$: C, 67.3; H, 6.4. Found: C, 67.4; H, 6.1) but, in spite of considerable effort, the reaction could not be duplicated satisfactorily. Shorter phosphine chains appear to give only very short-lived BH_4-containing products.

Crystal Data and Intensity Measurements. Small crystals of $CoH(dppp)_2 \cdot C_6H_6$ and $[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$ were mounted in quartz capillaries in an inert-atmosphere box. Crystals suitable for data collection were selected on the basis of a polarizing microscope examination and preliminary precession photographs. A tabulation of the crystal and intensity data for both compounds is presented in Table I. $CoH(dppp)_2 \cdot C_6H_6$ was found to crystallize in the primitive monoclinic crystal class by use of the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing programs.[11] Delaunay reduction calculations did not support higher order symmetry. Systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, led to the unique choice of $P2_1/n$ as the space group. $[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$ was found to crystallize in the triclinic crystal class.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement for $CoH(dppp)_2 \cdot C_6H_6$ and $[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$

	$CoH(Ph_2P(CH_2)_3PPh_2)_2 \cdot C_6H_6$	$[Co(BH_4)(Ph_2P(CH_2)_5PPh_2)]_2 \cdot 0.5C_6H_6$
fw	884.8	1067.6
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
cell parameters		
a, Å	13.640 (6)	10.305 (3)
b, Å	15.794 (5)	14.990 (3)
c, Å	23.870 (9)	20.343 (5)
α, deg	90	107.87 (2)
β, deg	101.04 (4)	90.72 (2)
γ, deg	90	105.88 (2)
V, Å^3	5047.2	2861 (3)
cryst size, mm	0.2 × 0.2 × 0.2	0.10 × 0.25 × 0.45
molecules/cell	4	2
d_{calcd}, g cm^{-3}	1.267	1.240
temp	ambient	ambient
abs coeff, cm^{-1}	4.1	7.5
diffractometer	CAD4	CAD4
radiation	Mo K$\bar{\alpha}$ (λ = 0.710 69 Å), graphite monochromatized	Mo K$\bar{\alpha}$ (λ = 0.710 69 Å), graphite monochromatized
scan type	ω–2θ	ω–2θ
scan range, 2θ, deg	0–50	0–46
unique reflcns measd (region)	8846 ($+h,+k,\pm l$)	8085 ($h,\pm k,\pm l$)
obsd reflcns	4754 [$F_o^2 \geqslant 2.5\sigma(F_o^2)$]	4290 [$F_o^2 \geqslant 2\sigma(F_o^2)$]
least-squares no. of variables	589	595
R	0.042	0.052
R_w	0.041	0.049
GOF[a]	1.3	1.5
p	0.04	0.03

[a] The error in an observation of unit weight (GOF) is $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

Data collection, using Mo K$\bar{\alpha}$ radiation, was on the CAD-4 Nonius diffractometer using the ω–2θ scan. Background counts were measured on both ends of the scan range with use of the ω–2θ scan, equal, on each side, to one-fourth of the scan range of the peak. No decay in the intensity of three standard peaks measured every 1.5 h of exposure was noted for either compound. Intensity data were corrected for Lorentz, polarization, and background effects.[12] No absorption corrections were carried out for either compound.

Solution and Refinement of Structures. Both structures were solved by conventional heavy-atom techniques. Metal atoms were located by Patterson synthesis. For $CoH(dppp)_2 \cdot C_6H_6$, successive full-matrix least-squares refinement and difference-Fourier maps were used to reveal the positions of the P and C atoms in the coordination complex as well as the H atom bonded to cobalt and the benzene solvent C atoms. For $[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$, these techniques revealed the P, C, and B atom positions as well as the hydrogen atoms attached to the boron. Atomic scattering factors were taken from tabulated values;[13] scattering was corrected for the real and imaginary components of anomalous dispersion with use of ref 14.

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(11) A CAD-4 Enraf-Nonius diffractometer was used for preliminary analysis and for data collection. Enraf-Nonius CAD4-SDP programs on PDP 8A, PDP 11/34, and CDC CYBER 815 computers were used in calculations. The crystallographic computing package is described by: Frenz, B.A. In "Computing in Crystallography"; Schenk, H., Oelof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. "CAD4 and SDP User's Manual"; Enraf-Nonius: Delft, Holland, 1978.

(12) The intensity data were processed as described in: "CAD4 and SDP User's Manual"; Enraf-Nonius: Delft, Holland, 1978. The net intensity I is given as $I = [K/(NPI)](C - 2B)$, where K = 20.1166 × (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $[\sigma(I)]^2 = (K/(NPI))^2[C + 4B + (\rho I)^2]$, where ρ is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by a $\sigma(F_o) = {}^1/_2[\sigma(I)/I]F_o$.

(13) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromer, D. T. *Ibid.*, Table 2.3.1.

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Table II. Positional and Equivalent Isotropic Temperature Factors (Å^2) for CoH(dppp)$_2$·C_6H_6

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
Co	0.41524 (4)[a]	0.17371 (3)	0.15580 (2)	2.540	C5D	0.6388 (3)	−0.0285 (3)	0.0672 (2)	5.068
P1	0.47599 (7)	0.16592 (7)	0.24679 (4)	3.051	C6D	0.5529 (3)	0.0061 (3)	0.0800 (2)	3.961
P2	0.40821 (8)	0.03927 (7)	0.14518 (4)	2.811	C1E	0.1931 (3)	0.2056 (3)	0.2035 (2)	3.239
P3	0.27699 (7)	0.24089 (7)	0.15578 (4)	2.964	C2E	0.1578 (3)	0.1227 (3)	0.1983 (2)	4.421
P4	0.50148 (8)	0.27557 (7)	0.12825 (4)	2.974	C3E	0.1004 (3)	0.0899 (3)	0.2345 (2)	5.490
C11	0.4156 (3)	0.0846 (3)	0.2839 (2)	4.115	C4E	0.0759 (3)	0.1385 (3)	0.2769 (2)	5.653
C12	0.4326 (3)	−0.0053 (3)	0.2643 (2)	4.228	C5E	0.1075 (3)	0.2207 (3)	0.2827 (2)	5.512
C13	0.3771 (3)	−0.0259 (3)	0.2038 (2)	3.734	C6E	0.1662 (3)	0.2540 (3)	0.2464 (2)	4.022
C21	0.2936 (3)	0.3546 (3)	0.1752 (2)	3.838	C1F	0.1836 (3)	0.2540 (2)	0.0889 (2)	3.310
C22	0.3576 (3)	0.4013 (3)	0.1393 (2)	4.090	C2F	0.0832 (3)	0.2682 (3)	0.0884 (2)	5.124
C23	0.4690 (3)	0.3802 (3)	0.1536 (2)	3.741	C3F	0.0152 (3)	0.2772 (4)	0.0378 (2)	6.559
C1A	0.6067 (3)	0.1343 (2)	0.2728 (2)	3.237	C4F	0.0469 (4)	0.2736 (3)	−0.0134 (2)	6.821
C2A	0.6474 (3)	0.1319 (3)	0.3311 (2)	4.534	C5F	0.1460 (4)	0.2616 (3)	−0.0142 (2)	5.807
C3A	0.7433 (3)	0.1051 (3)	0.3501 (2)	5.780	C6F	0.2136 (3)	0.2523 (3)	0.0363 (2)	4.277
C4A	0.8014 (3)	0.0790 (3)	0.3117 (2)	5.670	C1G	0.4879 (3)	0.2967 (2)	0.0508 (2)	3.293
C5A	0.7628 (3)	0.0810 (3)	0.2544 (2)	5.103	C2G	0.4793 (3)	0.2314 (3)	0.0131 (2)	4.424
C6A	0.6654 (3)	0.1075 (3)	0.2349 (2)	3.851	C3G	0.4745 (3)	0.2431 (3)	−0.0451 (2)	4.793
C1B	0.4727 (3)	0.2581 (3)	0.2940 (2)	3.638	C4G	0.4765 (4)	0.3208 (3)	−0.0659 (2)	6.509
C2B	0.5472 (3)	0.3188 (3)	0.2987 (2)	4.515	C5G	0.4811 (7)	0.3868 (4)	−0.0300 (2)	11.982
C3B	0.5438 (4)	0.3920 (3)	0.3308 (2)	6.031	C6G	0.4875 (6)	0.3751 (3)	0.0281 (2)	9.321
C4B	0.4669 (4)	0.4037 (3)	0.3594 (2)	7.101	C1H	0.6398 (3)	0.2806 (3)	0.1446 (2)	3.612
C5B	0.3937 (4)	0.3447 (3)	0.3558 (2)	6.334	C2H	0.6938 (3)	0.3420 (3)	0.1785 (2)	5.054
C6B	0.3957 (3)	0.2710 (3)	0.3237 (2)	4.757	C3H	0.7974 (3)	0.3413 (4)	0.1899 (2)	7.318
C1C	0.3138 (3)	−0.0074 (2)	0.0871 (2)	2.957	C4H	0.8477 (3)	0.2785 (4)	0.1675 (2)	7.820
C2C	0.2318 (3)	0.0384 (3)	0.0620 (2)	3.647	C5H	0.7963 (3)	0.2176 (4)	0.1335 (2)	6.031
C3C	0.1571 (3)	0.0049 (3)	0.0203 (2)	4.747	C6H	0.6929 (3)	0.2183 (3)	0.1219 (2)	4.521
C4C	0.1647 (3)	−0.0770 (3)	0.0024 (2)	5.098	C1	0.3490 (6)	0.0047 (4)	0.5151 (4)	13.630
C5C	0.2458 (3)	−0.1241 (3)	0.0267 (2)	4.913	C2	0.2966 (6)	0.0617 (4)	0.5362 (3)	12.298
C6C	0.3196 (3)	−0.0905 (3)	0.0690 (2)	4.047	C3	0.2496 (5)	0.1203 (4)	0.5023 (3)	10.302
C1D	0.5197 (3)	−0.0158 (2)	0.1294 (2)	3.132	C4	0.2567 (5)	0.1249 (4)	0.4484 (3)	10.085
C2D	0.5751 (3)	−0.0749 (3)	0.1652 (2)	5.038	C5	0.3117 (5)	0.0683 (4)	0.4255 (2)	9.963
C3D	0.6619 (4)	−0.1091 (3)	0.1521 (2)	6.824	C6	0.3577 (5)	0.0061 (5)	0.4605 (3)	11.638
C4D	0.6935 (3)	−0.0857 (3)	0.1032 (2)	6.557	H	0.385 (2)	0.160 (2)	0.096 (1)	3.550[b]

[a] Numbers in parentheses here and in succeeding discussions are estimated standard deviations in the least significant digits. [b] Actual isotropic temperature factor.

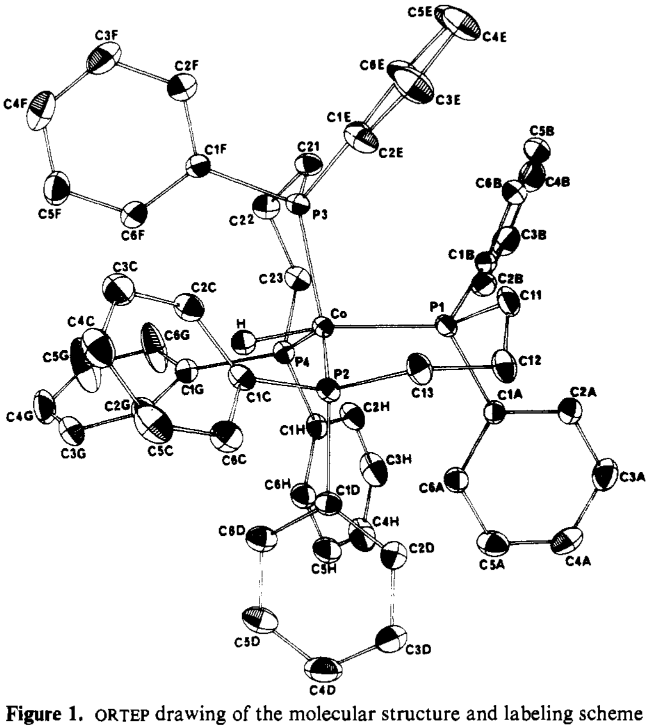

Figure 1. ORTEP drawing of the molecular structure and labeling scheme for CoH(dppp)$_2$. The atoms are represented by their 30% probability ellipsoids for thermal motion. Hydrogen atoms on carbon are omitted for clarity.

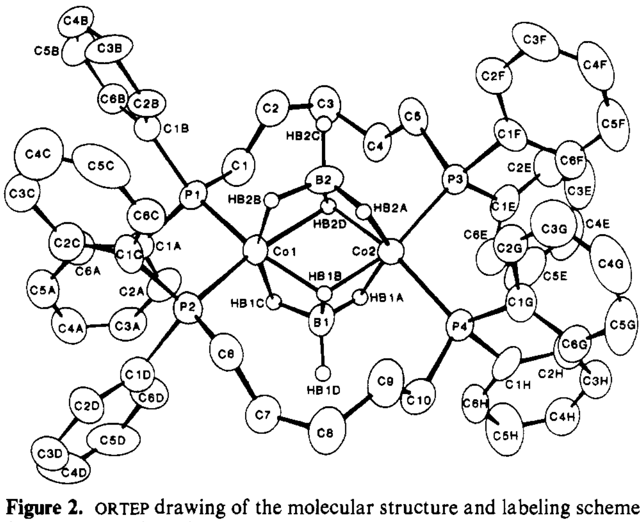

Figure 2. ORTEP drawing of the molecular structure and labeling scheme for [Co(BH$_4$)(dpppe)]$_2$. The atoms are represented by their 30% probability ellipsoids for thermal motion. Hydrogen atoms on carbon are omitted for clarity.

For CoH(dppp)$_2$·C_6H_6, all non-hydrogen atoms and the hydride hydrogen were refined by full-matrix least-squares techniques. The function minimized was $\sum w(|F_o| - F_c|)^2$, where $w = 1/[\sigma(F_o^2)]^2$. Anisotropic thermal parameters were refined for Co, P, and C atoms; an isotropic thermal parameter was used for the hydride hydrogen but not refined. Other hydrogen positions were calculated but not refined; C–H distances were set at 0.95 Å. The final difference map was featureless, the largest peak being 0.165 e/Å^3. The final residuals R and R_w were 0.042 and 0.041, respectively.[15] Final positional and thermal parameters of the refined atoms are given in Table II, and the atom-labeling scheme is shown in Figure 1.

For [Co(BH$_4$)(dpppe)]$_2$·0.5C_6H_6, positional parameters and anisotropic thermal parameters for all non-hydrogen atoms in the complex were refined. Hydrogen atoms attached to carbon in the dpppe ligand were fixed at appropriate locations and not refined. Positional parameters for the hydrogen atoms attached to B were refined, but isotropic thermal parameters were not. The solvent molecule, benzene, was disordered.

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[15] The unweighted and weighted residuals are defined as $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2}$.

Table III. Positional and Equivalent Isotropic Temperature Factors ($Å^2$) for $[Co(BH_4)(dpppe)]_2{\cdot}0.5C_6H_6$

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
Co1	0.30533 (8)	0.30313 (5)	0.23133 (4)	2.543	C6B	0.3136 (7)	0.0227 (4)	0.0293 (3)	9.886
Co2	0.24217 (8)	0.47989 (5)	0.23644 (4)	2.540	C1C	0.1914 (7)	0.1107 (4)	0.2887 (3)	11.801
P1	0.3702 (2)	0.2015 (1)	0.13862 (8)	2.683	C2C	0.2425 (7)	0.0316 (4)	0.2613 (3)	10.136
P2	0.3007 (2)	0.2356 (1)	0.31723 (9)	3.168	C3C	0.1543 (9)	−0.0633 (5)	0.2328 (4)	15.735
P3	0.1883 (2)	0.5297 (1)	0.14713 (9)	2.745	C4C	0.0180 (9)	−0.0816 (5)	0.2302 (4)	22.592
P4	0.2283 (2)	0.6009 (1)	0.33356 (9)	3.096	C5C	−0.0306 (8)	−0.0033 (6)	0.2577 (4)	21.774
B1	0.4333 (8)	0.4593 (5)	0.2753 (4)	3.564	C6C	0.0524 (7)	0.0930 (5)	0.2873 (3)	11.166
B2	0.1193 (8)	0.3234 (5)	0.1901 (4)	3.471	C1D	0.4525 (7)	0.2262 (4)	0.3586 (3)	9.204
HB1A	0.427 (5)	0.503 (3)	0.243 (2)	5 (1)[a]	C2D	0.4467 (8)	0.1722 (5)	0.4030 (4)	16.094
HB1B	0.308 (5)	0.420 (3)	0.282 (2)	6 (1)[a]	C3D	0.5664 (9)	0.1667 (5)	0.4323 (4)	22.100
HB1C	0.475 (4)	0.393 (3)	0.244 (2)	4 (1)[a]	C4D	0.6879 (8)	0.2152 (6)	0.4171 (4)	25.216
HB1D	0.505 (4)	0.503 (3)	0.327 (2)	4 (1)[a]	C5D	0.6959 (8)	0.2715 (6)	0.3751 (4)	13.532
HB2A	0.093 (4)	0.386 (3)	0.237 (2)	4 (1)[a]	C6D	0.5767 (7)	0.2764 (5)	0.3452 (3)	12.472
HB2B	0.127 (5)	0.263 (3)	0.224 (2)	5 (1)[a]	C1E	0.2903 (6)	0.6443 (4)	0.1356 (3)	9.936
HB2C	0.050 (5)	0.282 (3)	0.141 (2)	5 (1)[a]	C2E	0.2459 (7)	0.6857 (4)	0.0915 (4)	17.173
HB2D	0.236 (4)	0.371 (3)	0.183 (2)	4 (1)[a]	C3E	0.3264 (8)	0.7682 (5)	0.0807 (4)	27.483
C1	0.4213 (6)	0.2610 (4)	0.0724 (3)	9.807	C4E	0.4554 (8)	0.8100 (5)	0.1151 (4)	25.188
C2	0.3042 (7)	0.2564 (4)	0.0231 (3)	9.439	C5E	0.5019 (7)	0.7701 (5)	0.1578 (4)	12.107
C3	0.3358 (7)	0.3407 (4)	−0.0071 (3)	14.390	C6E	0.4208 (7)	0.6873 (4)	0.1699 (3)	11.163
C4	0.3335 (6)	0.4377 (4)	0.0465 (3)	13.057	C1F	0.0150 (6)	0.5408 (4)	0.1421 (3)	10.051
C5	0.1903 (6)	0.4430 (4)	0.0613 (3)	9.547	C2F	−0.0910 (7)	0.4614 (4)	0.1050 (3)	10.628
C6	0.2220 (7)	0.2914 (5)	0.3931 (3)	16.002	C3F	−0.2242 (7)	0.4677 (5)	0.1054 (4)	14.218
C7	0.3111 (7)	0.3893 (5)	0.4411 (3)	14.596	C4F	−0.2484 (7)	0.5530 (5)	0.1414 (4)	25.896
C8	0.2311 (8)	0.4586 (5)	0.4792 (3)	18.876	C5F	−0.1449 (7)	0.6317 (5)	0.1779 (4)	22.945
C9	0.1717 (7)	0.5016 (4)	0.4318 (3)	17.805	C6F	−0.0140 (7)	0.6260 (4)	0.1782 (4)	12.288
C10	0.2755 (7)	0.5823 (4)	0.4146 (3)	8.916	C1G	0.0652 (6)	0.6255 (4)	0.3521 (3)	9.664
C1A	0.5292 (6)	0.1796 (4)	0.1606 (3)	7.541	C2G	−0.0524 (7)	0.5546 (4)	0.3173 (3)	12.143
C2A	0.6478 (6)	0.2566 (4)	0.1751 (3)	8.243	C3G	−0.1774 (7)	0.5652 (5)	0.3317 (4)	15.719
C3A	0.7694 (7)	0.2455 (5)	0.1956 (4)	7.529	C4G	−0.1878 (7)	0.6485 (5)	0.3809 (4)	26.156
C4A	0.7741 (7)	0.1602 (5)	0.2024 (4)	14.113	C5G	−0.0745 (7)	0.7192 (5)	0.4167 (4)	25.058
C5A	0.6580 (7)	0.0832 (5)	0.1895 (4)	13.524	C6G	0.0513 (7)	0.7079 (4)	0.4033 (3)	10.212
C6A	0.5360 (6)	0.0926 (4)	0.1676 (3)	8.625	C1H	0.3475 (6)	0.7204 (4)	0.3426 (3)	6.638
C1B	0.2660 (6)	0.0801 (4)	0.0857 (3)	7.125	C2H	0.3134 (7)	0.7964 (4)	0.3295 (3)	9.187
C2B	0.1365 (6)	0.0443 (4)	0.1001 (3)	7.636	C3H	0.4132 (8)	0.8827 (4)	0.3344 (4)	12.934
C3B	0.0557 (7)	−0.0479 (5)	0.0600 (4)	11.445	C4H	0.5462 (8)	0.8920 (5)	0.3493 (4)	13.429
C4B	0.1029 (8)	−0.1026 (5)	0.0052 (4)	10.412	C5H	0.5824 (8)	0.8177 (5)	0.3616 (5)	18.344
C5B	0.2318 (8)	−0.0685 (5)	−0.0105 (4)	10.509	C6H	0.4858 (7)	0.7332 (4)	0.3578 (4)	13.736

[a] Actual isotropic temperature factor.

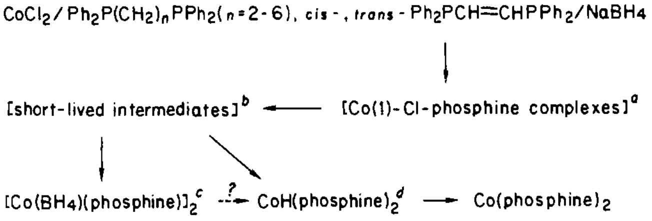
The largest peak in the final difference-Fourier map was 0.326 e/$Å^3$. No chemically significant peaks were found in the final difference-Fourier map in the BH_4^- region, indicating that the hydrogens on the boron atoms were refined satisfactorily. Final R and R_w values are 0.052 and 0.049, respectively. Final positional and thermal parameters are given in Table III, and the atom-labeling scheme is shown in Figure 2.

For both compounds, tables of observed and calculated structure factors and anisotropic thermal parameters are available.[16]

Results and Discussion

In general, the hydride species $CoH(phosphine)_2$ are easily recognized and isolated from these reactions (see Scheme I), although difficulties were experienced in obtaining pure samples of products containing the longer chain dpppe and dpph ligands. There is no doubt, however, from the IR and NMR data recorded in the Experimental Section that these last two compounds exist, but they appear oily and resisted attempts at crystallization. It is important in these reactions that at least a 1:2 molar ratio of Co:phosphine be maintained to prevent the rapid production of dark precipitates of cobalt boride. Clearly, *trans*-$Ph_2PCH{=}CHPPh_2$ is unable to protect the Co from further reduction by occupying what appears to be a minimum requirement of four coordination sites on the cobalt, and it is therefore not unreasonable to see, when this phosphine is used, the slow production of cobalt boride even when a 1:2 ratio is maintained. What is more surprising is that the same reaction carried out at higher temperatures resulted in hydrogenation of the ligand and the isolation of $CoH(dppe)_2$. Whether this is a homogeneous reaction, or whether the hydrogenation is catalyzed by solid cobalt boride,[17] has not yet been investigated.

Scheme I



[a] Green products with dppp (n = 3) and dppb (n = 4). [b] Number of products seen in ^{31}P NMR depends on phosphine used; see text. [c] dpppe (n = 5) and (nonreproducibly) dppb (n = 4). [d] All phosphines except for *trans*-$Ph_2PCH{=}CHPPh_2$; see text.

The ^1H NMR spectra of the red hydrides all show an upfield quintet due to coupling of the hydride with four apparently equivalent phosphorus atoms. The proton-decoupled ^{31}P NMR spectra all show a single signal, which again indicates that the P atoms of the complexes are equivalent in solution. The downfield positions of the signals are consistent with chelating phosphines, with the biggest downfield (δ 70–80) shifts associated with the five-membered ring systems. For the six-membered ring, the signal moves upfield (δ 32) but shifts back downfield (δ 39.2) for the seven-membered ring. These trends for chelating bis(phosphines) have been discussed extensively elsewhere.[18] The longer chain phosphines may or may not be chelating. The positions of ν(Co–H) in the IR spectra show a steady increase with ring size, over the range 1890–2080 cm^{-1}.

The crystal structure of the dppp compound consists of molecular $CoH(dppp)_2$ units and benzene solvent molecules. As

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(16) Supplementary material; see end of paper.

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Table IV. Selected Interatomic Distances and Angles in $CoH(dppp)_2 \cdot C_6H_6$

	Distances, Å		
Co–P1	2.175 (1)	P4–C1H	1.853 (4)
Co–P2	2.138 (1)	C11–C12	1.527 (5)
Co–P3	2.164 (1)	C12–C13	1.531 (5)
Co–P4	2.168 (1)	C21–C22	1.526 (5)
Co–H	1.42 (3)	C22–C23	1.529 (5)
P1–C11	1.843 (4)	C–C[a]	1.377 (6)
P1–C1A	1.841 (4)	H–P1	3.57 (3)
P1–C1B	1.847 (4)	H–P2	2.23 (3)
P2–C13	1.849 (4)	H–P3	2.58 (3)
P2–C1C	1.854 (4)	H–P4	2.44 (3)
P2–C1D	1.853 (4)	P1–P2	3.143 (1)
P3–C21	1.858 (4)	P1–P3	3.351 (1)
P3–C1E	1.848 (4)	P1–P4	3.392 (1)
P3–C1F	1.853 (4)	P2–P3	3.685 (1)
P4–C23	1.844 (4)	P2–P4	3.989 (1)
P4–C1G	1.853 (4)	P3–P4	3.298 (1)
	Angles, deg		
H–Co–P1	167 (1)	Co–P1–C11	113.6 (1)
H–Co–P2	74 (1)	P1–C11–C12	113.0 (3)
H–Co–P3	90 (1)	C11–C12–C13	114.2 (3)
H–Co–P4	83 (1)	C12–C13–P2	116.8 (3)
P1–Co–P2	93.56 (4)	C13–P2–Co	118.3 (1)
P1–Co–P3	101.15 (4)	Co–P3–C21	114.2 (1)
P1–Co–P4	102.69 (4)	P3–C21–C22	112.5 (3)
P2–Co–P3	117.88 (4)	C21–C22–C23	114.8 (3)
P2–Co–P4	135.68 (4)	C22–C23–P4	114.4 (3)
P3–Co–P4	99.17 (4)	C23–P4–Co	112.8 (1)

[a] Average distance in phenyl rings.

shown in Figure 1, the coordination complex consists of a central Co atom attached to a hydrogen atom and four phosphorus atoms (two from each of the two chelating bidentate dppp ligands). The coordination polyhedron of $CoH(dppp)_2$ can be derived from a trigonal bipyramid with phosphorus atoms P2, P3, and P4 occupying the equatorial positions and the hydride ligand and P1 occupying the axial positions. The polyhedron is distorted such that the Co atom lies 0.307 Å from the plane defined by the three equatorial phosphorus atoms in the direction of the P1 atom; that is, the P2, P3, and P4 atoms are displaced toward the hydride ligand. Co, P1, P2, and H are nearly planar, with atom to plane distances of less than 0.053 Å.

Selected distances and angles are reported in Table IV. The Co–H distance of 1.42 (3) Å compares favorably with reported literature values varying from 1.34 (8) to 1.65 (2) Å for a variety of cobalt–hydride complexes.[19] The average Co–P distance of 2.161 (1) Å is considered normal. The P3–Co–P4 angle of 99.17 (4)° is larger than the P1–Co–P2 angle of 93.56 (4)°, consistent with the P3 and P4 atoms and associated dppp ligand chelating across the equatorial position with P1 and P2 and the associated dppp ligand chelating across the one equatorial and one axial position of the trigonal bipyramid. The short equatorial P–H distances of 2.23 (3), 2.58 (3), and 2.44 (3) Å and the small H–Co–equatorial P atom angles of 74 (1), 90 (1), and 83 (1)° indicate that the hydride is effectively shielded from the environment.

A quantitative measure of the amount of distortion of the coordination polyhedron of $CoH(dppp)_2$ from a trigonal bipyramid can be estimated by the method of Whitfield et al.,[20] who proposed that a half-open cone angle, ϕ, of approximately 80° suggests a geometry midway between that of a distorted trigonal bipyramid and a distorted monocapped tetrahedron. With use of the calculated value of ϕ of 81.3°, this coordination polyhedron can best be described as a distorted trigonal bipyramid.

The structure is basically similar to that of $IrH(dppe)_2$ although, in the latter, the hydride hydrogen was not located, and insufficient data were presented[21] to allow a detailed comparison between the distortions in the two structures.

It is clear that the P atoms in the Co compound are not equivalent in the solid state, and so the fact that only a single ^{31}P NMR signal is seen must mean that fast ligand reorganization processes take place in solution to create an average environment for the P atoms.

The steric requirements of the ligands (dppe, *cis*-$Ph_2PCH{=}CHPPh_2$) forming five-membered chelate rings in these trigonal-bipyramidal systems would be such that each of the two such rings resulting from chelation in the species CoH(bis(phosphine))$_2$ would prefer the axial–equatorial arrangement. This would require the hydride hydrogen to occupy an equatorial site. On the other hand, the best that could be achieved for the six- and seven-membered rings resulting from dppp and dppb (which would prefer diequatorial coordination to minimize ring strain) chelation is for three P atoms to occupy equatorial sites, which therefore requires the hydrogen to locate in an axial position. This is, in fact, observed in the structure of the dppp compound as already described. One might therefore expect that, if the hydride ligand does indeed occupy an equatorial site in the dppe and *cis*-$Ph_2PCH{=}CHPPh_2$ compounds and an axial site in the dppp and dppb complexes, the two different types of complex should show significantly different Co–H stretching frequencies in their IR spectra. This also is observed. Thus, the dppe and *cis*-$Ph_2PCH{=}CHPPh_2$ complexes show ν(Co–H) at 1890 and 1892 cm^{-1}, respectively, while the dppp and dppb complexes both show ν(Co–H) at 1965 cm^{-1}. On the other hand, an equatorial Co–H bond in an ideal trigonal bipyramid should be shorter than an axial bond, and one would perhaps expect the equatorial vibration to show the higher frequency. However, the dppp complex is far from being an ideal trigonal bipyramid, and such arguments must be used very cautiously for such grossly distorted systems. A crystal structure of the dppe complex would, nevertheless, be of interest, and attempts to grow suitable crystals are now being made.

The hydrides appear to be the final Co(I) species to form in these reactions, the next step being the reduction to Co(0) and the formation of Co(phosphine)$_2$ species. However, the reactions are very complex (Scheme I) and yield a range of other products, some of which may be detected by ^{31}P NMR spectroscopy. In addition, the range of products and intermediates observed depends markedly upon the phosphine used. For example, in the case of the dpppe reactions, carried out over a narrow range of conditions, signals at δ 60, 48, 34, 32, 28, ~27 (doublet), 16, and −14, due to at least eight fairly short-lived products, have been observed. Furthermore, any paramagnetic intermediates would not exhibit clear and sharp ^{31}P signals. Reactions involving dppb are equally complex, while fewer intermediates were noticed in the dppe reactions.

In spite of considerable effort, we have been unable to isolate in pure form most of these transient species. In some reactions (e.g., dppp, dppb) the first isolable (but not fully characterized) compounds that we have seen are dark green, paramagnetic Co–phosphine–chloride species. Reflectance spectra show signals in the 6000–6500; 10000–11000; and 16000–17000-cm^{-1} regions, and these suggest the presence of tetrahedral Co(I).[22] In addition, two compounds of empirical formula $Co(BH_4)$(phosphine) (dppb and dpppe) were obtained and, since neither appears to show ^{31}P signals, it is difficult to say at what point these form relative to the other products observed, except to say that they are produced before CoH(phosphine)$_2$. It should be noted that only the longer chain phosphines appear to form the BH_4 compounds, and since the CoH(phosphine)$_2$ species form readily for all of the phosphines studied, it may well be that the two types of compounds form by independent routes and that the BH_4 compounds are not precursors to the hydrides. The complex $Co(BH_4)$(dppb) has not been obtained reproducibly, and even the more straightforward synthesis of the dpppe compound, which is now fully characterized (see

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Table V. Selected Interatomic Distances and Angles in $[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$

Distances, Å

Co1–Co2	2.869 (1)	Co2–P4	2.272 (2)	B1–HB1D	1.18 (6)	P2–C1C	1.810 (6)	C3–C4	1.532 (7)
Co1–P1	2.270 (2)	Co2–HB1A	1.84 (6)	B2–HB2A	1.22 (6)	P2–C1D	1.826 (7)	C4–C5	1.529 (7)
Co1–P2	2.267 (2)	Co2–HB1B	1.71 (6)	B2–HB2B	1.32 (6)	P3–C5	1.833 (6)	C6–C7	1.520 (8)
Co1–HB1B	1.73 (6)	Co2–HB2A	1.78 (5)	B2–HB2C	1.12 (6)	P3–C1E	1.838 (5)	C7–C8	1.533 (8)
Co1–HB1C	1.85 (5)	Co2–HB2D	1.64 (5)	B2–HB2D	1.26 (6)	P3–C1F	1.843 (6)	C8–C9	1.517 (8)
Co1–HB2B	1.76 (6)	Co2–B1	2.246 (7)	B1–B2	3.422 (9)	P4–C10	1.836 (6)	C9–C10	1.514 (8)
Co1–HB2D	1.88 (5)	Co2–B2	2.233 (6)	P1–C1	1.841 (6)	P4–C1G	1.836 (6)	C–C[a]	1.375 (9)
Co1–B1	2.239 (7)	B1–HB1A	1.08 (6)	P1–C1B	1.823 (5)	P4–C1H	1.828 (6)		
Co1–B2	2.215 (7)	B1–HB1B	1.29 (6)	P1–C1A	1.832 (6)	C1–C2	1.532 (7)		
Co2–P3	2.280 (2)	B1–HB1C	1.20 (5)	P2–C6	1.830 (6)	C2–C3	1.529 (7)		

Angles, deg

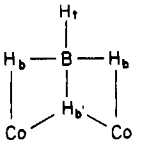
P1–Co1–P2	105.83 (6)	HB1C–Co1–HB1B	67 (3)	HB2A–Co2–HB1B	80 (3)	HB2B–B2–HB2D	110 (4)
P1–Co1–HB1C	89.28 (3)	B1–Co1–B2	100.4 (2)	HB2D–Co2–HB1A	85 (3)	HB2C–B2–HB2D	115 (4)
P1–Co1–HB2B	106.69 (3)	B1–Co2–B2	99.6 (3)	HB2D–Co2–HB1B	72 (3)	Co1–B1–Co2	79.6 (2)
P1–Co1–HB2D	97.25 (2)	P3–Co2–P4	104.33 (6)	HB1A–Co2–HB1B	63 (3)	Co1–B2–Co2	80.3 (2)
P1–Co1–HB1B	150.32 (1)	P3–Co2–HB2A	103.39 (2)	HB1A–B1–HB1B	104 (4)	Co1–HB2B–B2	91 (3)
P2–Co1–HB1C	106.27 (2)	P3–Co2–HB1A	106.24 (2)	HB1A–B1–HB1C	109 (4)	Co1–HB1C–B1	92 (3)
P2–Co1–HB2B	86.61 (2)	P3–Co2–HB2D	91.73 (2)	HB1A–B1–HB1D	113 (4)	Co2–HB2A–B2	95 (3)
P2–Co1–HB2D	151.58 (1)	P3–Co2–HB1B	160.59 (1)	HB1B–B1–HB1C	105 (4)	Co2–HB1A–B1	97 (4)
P2–Co1–HB1B	98.23 (2)	P4–Co2–HB2A	100.22 (2)	HB1B–B1–HB1D	115 (4)	Co1–HB1B–Co2	113 (3)
HB2B–Co1–HB2D	71 (2)	P4–Co2–HB1A	98.88 (3)	HB1C–B1–HB1D	108 (4)	Co1–HB2D–Co2	109 (3)
HB2B–Co1–HB1C	156 (3)	P4–Co2–HB2D	161.25 (1)	HB2A–B2–HB2B	98 (3)	Co1–P1–C1	111.0 (2)
HB2B–Co1–HB1B	91 (3)	P4–Co2–HB1B	93.72 (2)	HB2A–B2–HB2C	123 (4)	Co1–P2–C6	114.6 (2)
HB2D–Co1–HB1C	90 (2)	HB2A–Co2–HB2D	66 (3)	HB2A–B2–HB2D	99 (4)	Co2–P4–C10	113.6 (2)
HB2D–Co1–HB1B	66 (2)	HB2A–Co2–HB1A	139 (3)	HB2B–B2–HB2C	110 (4)	Co2–P3–C5	113.3 (2)

[a] Average distance in phenyl rings.

below), does not always yield the desired product (see Experimental Section).

The mode of coordination of the BH_4 group is of great interest in these two compounds in view of the fact that their IR spectra show a pattern that is not easily explained[23] in the context of the known modes of coordination, namely monodentate,[24] bidentate,[2,23] tridentate,[23] and bridging ("doubly bidentate").[25] Because of this and the somewhat surprising fact that we have been able to isolate BH_4-containing products from these reactions only when long-chain phosphines were used, a structural investigation of Co(BH_4)(dpppe) was undertaken.

From Figure 2, it is clear that the complex is dimeric and consists of two Co(I) atoms bridged by both phosphine and tetrahydroborate ligands. The mode of BH_4^- coordination is unprecedented in that each BH_4^- unit chelates to two different Co(I) atoms as well as directly bridges the two Co atoms with a common hydrogen. That is, for each BH_4^- unit, two hydrogen atoms, designated as H_b, bridge Co–H_b–B units, and one hydrogen atom, $H_{b'}$, bridges the Co–$H_{b'}$–Co unit as well as Co–$H_{b'}$–B:



The fourth hydrogen in each BH_4^- unit, H_t, is not involved in coordination with the Co. An important feature of the structure determination is that the dimer does not contain a crystallographic center of symmetry; accordingly, the successful refinement of the hydrogens in the two independent BH_4^- groups showing similar coordination is meaningful.

Selected interatomic distances and angles are given in Table V. The coordination geometry around the Co(I) atoms can best be described as distorted octahedral. This distortion is almost certainly due to the requirement that the two BH_4^- units act as bridging units in the mode described above and not to any steric requirements of the dpppe ligands. This is supported by the fact that the observed bond distances and angles in the bridging dpppe ligands are normal and strain free. Also, the only other BH_4-containing product obtained, Co(BH_4)(dppb), exhibits an IR spectrum similar to that of the dpppe compound, and thus presumably it too contains bridging dppb ligands. This may be further support for the argument that the distorted-octahedral geometry around Co is probably not due to the requirements of the bridging phosphines.

The four atoms Co1, Co2, B1, and B2 are nearly coplanar; see Table VI, plane 2. Likewise, the sets of atoms Co1, Co2, HB1B, HB2D and Co1, Co2, HB1A, HB1C, HB2A, HB2B are also nearly coplanar; see planes 1 and 3, respectively, in Table VI. The dihedral angle between planes 1 and 3 of 71.4° is a measure of the steric requirements of the BH_4^- unit; perfect octahedral coordination for Co would require a dihedral angle of 90°. In addition, the dihedral angle between plane 7 (P1, Co1, P2) and plane 8 (P3, Co2, P4) is 17.5°, and this is also indicative of the effect that the steric and electronic requirements of the BH_4^- units have upon the coordination geometry around Co.

The average Co–H_b distance of 1.74 (6) Å compares favorably with values of 1.740 (12) and 1.707 (12) Å as determined by neutron diffraction for bidentate BH_4^- in Co(terpy)(BH_4).[19b] The average value of the Co–$H_{b'}$ distance, the second type of Co–H distance, is 1.81 (6) Å. This is slightly longer than the average Co–H_b distance, as one would expect since $H_{b'}$ is bridging three atoms, Co1, Co2, and B1 or B2, while the H_b atoms are bridging only two atoms. Differences in these distances are also expected since $H_{b'}$ atoms are trans to ligand P atoms while hydrogen atoms of the type H_b are only trans to one another. The average H_b–Co–$H_{b'}$ angle, the internal angle in the chelating BH_4^- ligand, of 67 (5)° is within the range normally observed[23,26] for bidentate BH_4^- (56–74°).

Within the BH_4^- unit, three different types of B–H distances can be observed, H_t–B, H_b–B, and $H_{b'}$–B. From a molecular orbital point of view, these can be considered as H–B distances where the H atom is involved in two, three, and four-center bonding, respectively. The average values of the H_t–B, H_b–B, and $H_{b'}$–B distances are 1.15 (6), 1.20 (6), and 1.28 (6) Å, re-

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(23) See for example in: Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

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Table VI. Least-Squares Planes for $[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$

Least-Squares Planes

plane no.	atoms	dist from plane, Å	plane no.	atoms	dist from plane, Å
1	Co1	0.000 (1)	3	B1[a]	−0.687 (13)
	Co2	0.000 (1)		B2[a]	0.737 (12)
	HB1B	0.002 (86)		HB1B[a]	−0.904 (80)
	HB2D	0.023 (79)		HB2D[a]	0.972 (72)
	P1[a]	0.980 (3)			
	P2[a]	−0.966 (3)	4	B1	0.004 (12)
	P3[a]	0.426 (3)		B2	0.001 (12)
	P4[a]	−0.507 (3)		HB1B	−0.058 (85)
	B1[a]	1.279 (13)		HB1D	−0.057 (76)
	B2[a]	−1.216 (13)		HB2C	0.039 (84)
				HB2D	−0.114 (78)
2	Co1	0.000 (1)		HB1A[a]	−0.792 (80)
	Co2	0.000 (1)		HB1C[a]	1.062 (76)
	B1	0.033 (13)		HB2A[a]	−0.859 (76)
	B2	0.032 (12)		HB2B[a]	1.049 (81)
	HB1A[a]	0.701 (76)		Co1[a]	1.423 (1)
	HB1B[a]	−0.695 (81)		Co2[a]	−1.441 (1)
	HB1C[a]	0.657 (72)			
	HB1D[a]	−0.553 (74)	5	B1	
	HB2A[a]	−0.831 (73)		Co1	
	HB2B[a]	−0.695 (77)		B2	
	HB2C[a]	0.5[illegible] (80)			
	HB2D[a]	0.7[illegible] (73)	6	B1	
				Co2	
3	Co1	0.000 (1)		B2	
	Co2	0.000 (1)			
	HB1A	−0.024 (74)	7	P1	
	HB1C	−0.102 (70)		Co1	
	HB2A	−0.157 (71)		P2	
	HB2B	0.023 (75)			
			8	P3	
				Co2	
				P4	

Dihedral Angles between the Planes

plane	angle, deg	plane	angle, deg
1–3	71.4	3–4	87.2
1–4	87.7	5–6	2.6
2–3	24.6	7–8	17.5
2–4	86.8		

Equations of the Planes of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	0.8449	0.4724	−0.2509	1.7878
2	0.4063	0.2568	−0.8769	−2.4235
3	0.0457	0.0641	−0.9969	−4.1731
4	0.5047	−0.8594	−0.0817	−3.3082
5	0.4171	0.2365	−0.8775	−2.4647
6	0.3951	0.2765	−0.8760	−2.3194
7	−0.8406	−0.4453	−0.3083	−4.1936
8	−0.8649	−0.5019	−0.0101	−3.1435

[a] Atom not used in determining least-squares plane.

spectively. Although the location of hydrogen atoms by X-ray diffraction techniques is subject to considerable error, it is interesting to note that the average H–B bond distances follow the expected order. Also interesting is the observation that the B, H_b, and H_t atoms are nearly coplanar; see plane 4, Table VI. Dihedral angles between plane 2 (Co1, Co2, B1, B2) and plane 4 and plane 1 (Co1, Co2, HB1B, HB2D) and plane 4 are 86.8 and 87.8°, respectively. Likewise, the dihedral angle between plane 4 and plane 3 (Co1, Co2, HB1A, HB1C, HB2A, HB2B), 87.2°, is near 90°.

The average Co–B distance of 2.233 (7) Å is comparable to that observed in $CoP^3(BH_4)$ and $Co(terpy)(BH_4)$ of 2.21 (3) and 2.15 Å, respectively.[19a]

The structural data described above allow an interpretation of the IR spectrum of the dpppe complex in the BH_4 region. There is a strong, sharp $\nu(H_t\text{–}B)$ peak at 2410 cm^{-1} and two strong peaks in the region normally associated with M–H–B bridging stretches. The lower energy, broad peak at ~1980 cm^{-1} is assigned to the longer $B\text{–}H_{b'}$ bond and the sharper peak at 2030 cm^{-1} to the slightly shorter $B\text{–}H_b$ bond.

There are several examples[27] of what are formally Co(I)–Co(I)-bridged species with Co–Co distances of ~2.5 Å. The observed Co1–Co2 distance of 2.869 (1) Å in the BH_4 compound would, at first sight, appear to be too long for appreciable Co–Co bond formation. However, while $[Co(BH_4)dpppe]_2 \cdot 0.5C_6H_6$ is paramagnetic, the observed paramagnetism is very low (ca. 0.75 μ_B/Co, measured in solution[10]), indicating considerable spin interaction between the two cobalt atoms. It is possible that this low value for the paramagnetism is due to trace impurities, although it was fairly reproducible for several preparations of the complex in which the product had been recrystallized several times. This paramagnetism also accounts for the fact that no ^{31}P or ^{11}B NMR signals are observable for the compound even on very freshly prepared and rigorously purified samples.

In summary, it is clear that reactions of Co(II) with BH_4^- in the presence of bidentate phosphines are very complex and we have been able to isolate and characterize only a fraction of the numerous products that are formed under the quite narrow range of reaction conditions which we have studied. Coordinated BH_4^- complexes have been formed only from reactions with the longer chain phosphines and not with dppe or dppp. This suggests that the ability of BH_4^- to bridge, which has been discussed elsewhere[28] in the context of its isolobality with chloride and other species, is stable in these systems only when the longer chain bidentate phosphines assist in holding together the two metal centers.

We have clearly demonstrated[29] in reactions between Ni(II), $NaBH_3CN$, and either dppm or dppe that the course of the reactions is dependent on the phosphine, and that appears also to be the case here. In addition, we have isolated[9] a number of quite different (from those described above) intermediates from reactions between Co(II), BH_4^-, and dppm, and the nature of these products is further evidence for the profound effect of ligand chain length on reaction pathway. The stable, 18-electron $CoH(phosphine)_2$ complexes are particularly easy to isolate from these reactions, and this explains their easy characterization in other work.[6,7]

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Registry No. $CoH(dppe)_2$, 18433-72-2; $CoH(cis\text{-}Ph_2PCH{=}CHPPh_2)_2$, 70252-14-1; $CoH(dppp)_2 \cdot C_6H_6$, 98574-22-2; $CoH(dppb)_2$, 54497-49-3; $CoH(dpppe)_2$, 98482-09-8; $CoH(dpph)_2$, 98482-10-1; $[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$, 98482-12-3; $Co(BH_4)(dppb)$, 98482-13-4; $trans\text{-}Ph_2PCH{=}CHPPh_2$, 983-81-3.

Supplementary Material Available: Tables of positional and thermal parameters, complete bond lengths and angles, and structure factors for both $CoH(dppp)_2 \cdot C_6H_6$ and $[Co(BH_4)(dpppe)]_2 \cdot 0.5C_6H_6$ (54 pages). Ordering information is given on any current masthead page.

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