Table IV. Fractional Atomic Coordinates and Isotropic Displacement Parameters (Å²) for 1[PF₆]

	x/a	*y/b*	*z/c*	U^a
Pt(1)	0.30279 (3)	0.09876 (2)	0.33122 (2)	0.027
Pt(2)	0.24673 (3)	0.13707 (2)	0.40280 (2)	0.028
Pt(3)	0.17853 (3)	0.08408 (2)	0.34727 (2)	0.028
Pt(4)	0.21659 (3)	0.15875 (2)	0.30775 (2)	0.028
P(1)	0.3342 (2)	0.0271 (1)	0.3605 (1)	0.035
P(2)	0.1926 (2)	0.0172 (1)	0.3879 (2)	0.036
P(3)	0.3692 (2)	0.1278 (1)	0.2807 (1)	0.031
P(4)	0.2839 (2)	0.2106 (1)	0.2785 (1)	0.036
P(5)	0.2608 (2)	0.1687 (1)	0.4683 (1)	0.033
P(6)	0.3493 (2)	0.2396 (2)	0.5184 (2)	0.047
P(7)	0.0831 (2)	0.0882 (1)	0.3150 (1)	0.035
P(8)	0.1194 (2)	0.1910 (1)	0.3067 (1)	0.033
O(1)	0.3833 (5)	0.1625 (4)	0.3870 (4)	0.052 (3)
O(2)	0.1046 (6)	0.1354 (4)	0.4162 (4)	0.53 (3)
C(1)	0.2775 (7)	0.0105 (4)	0.3994 (5)	0.030 (4)
C(2)	0.3670 (7)	0.1908 (5)	0.2836 (5)	0.036 (4)
C(3)	0.3141 (7)	0.2182 (5)	0.4676 (5)	0.037 (4)
C(4)	0.0569 (8)	0.1486 (5)	0.3173 (5)	0.045 (5)
C(5)	0.3334 (8)	0.1432 (5)	0.3800 (6)	0.046 (5)
C(6)	0.1543 (8)	0.1258 (5)	0.4020 (5)	0.036 (4)
H(1)	0.245 (6)	0.076 (4)	0.301 (4)	0.02 (4)

[a] For Pt, P, and F atoms, U is the equivalent isotropic displacement parameter defined as $U = {}^1/_3\sum_{i=1,3}^{3}\sum_{j=1,3}^{3}U_{ij}b_ib_j(\mathbf{a}_i\cdot\mathbf{a}_j)$, where b_i is the ith reciprocal cell edge and $\mathbf{a}_i$ is the ith direct cell vector.

was also refined as a rigid group in which the F atoms defined an octahedron centered on the P atom with P–F = 1.53 Å; (c) phenyl and methylene hydrogen positions were deduced geometrically, a fixed contribution for the scattering of these atoms was added to the structure factors, and U(H) = 0.050 Å² was assumed; (d) anisotropic displacement parameters were used only for Pt, P, and F atoms. All calculations were performed with use of the locally developed GX program package.[18]

Complex, neutral atom scattering factors were taken from ref 19. Function values in the final difference synthesis ranged from −0.83 to +0.97 e Å⁻³. Crystallographic data are given in Table III, fractional atomic coordinates and isotropic displacement parameters in Table IV, anisotropic displacement parameters in Table S1, calculated fractional coordinates and assumed isotropic displacement parameters (Å²) for phenyl and methylene H atoms in Table S2, and the structure amplitudes in Table S3 (Tables S1–S3 are in the supplementary material).

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Registry No. 1[PF$_6$], 118444-65-8; 4[PF$_6$], 136676-31-8; 5[PF$_6$], 136705-06-1; 6[PF$_6$], 136705-08-3; 7[PF$_6$]$_2$, 136705-10-7; 8[PF$_6$]$_2$, 136705-12-9; dppm, 2071-20-7; [Pt(O$_2$CCF$_3$)$_2$(dppm)], 99642-82-7; [Au(NO$_3$)(PPh$_3$)], 14897-32-6; ^{195}Pt, 14191-88-9.

Supplementary Material Available: Table S1 (anisotropic displacement parameters) and Table S2 (complete fractional coordinates for all atoms and calculated fractional coordinates and assumed isotropic displacement parameters (Å²) for phenyl and methylene H atoms) (6 pages); Table S3 (structure amplitudes) (31 pages). Ordering information is given on any current masthead page.

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New Routes to Co^{I}–Bis(diphenylphosphino)methane–Carbonyl Complexes Containing Monocoordinated and Chelating Ligands: Structure of [Co(η^2-dppm)$_2$(CO)][Co(CO)$_4$]

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The mechanism of reduction of Co^{II} by NaBH$_4$ in the presence of CO and dppm (Ph$_2$PCH$_2$PPh$_2$), which can give any one or more of several Co^{I}, Co^{0}, or Co^{I-} complexes depending upon experimental conditions, has been elucidated by detailed study of possible individual steps of the reaction. Reactions of CoX(η^1-dppm)$_3$ (X = Cl, Br) with CO lead in sequence to CoX(η^1-dppm)$_2$(CO)$_2$, [Co(η^2-dppm)(η^1-dppm)(CO)$_2$]X, and [Co(η^2-dppm)$_2$(CO)]X, all of which have been isolated and fully characterized, and the series of reactions can be reversed under CO at elevated temperatures. The related complex [Co(η^1-dppm)(CO)$_4$]Br is formed by a modification of the procedure. The synthesis and X-ray crystal structure of [Co(η^2-dppm)$_2$(CO)]-[Co(CO)$_4$] (1), formed in the direct reduction of the CoX$_2$/dppm/CO system by NaBH$_4$, are reported, and evidence for the reaction sequence whereby 1 is formed is presented. The heterobinuclear complex [CoRh(μ-dppm)$_2$(μ-CO)(CO)$_2$(μ-Cl)]Cl has been synthesized by reaction of CoCl(η^1-dppm)$_2$(CO)$_2$ with Rh$_2$(CO)$_4$Cl$_2$. An X-ray diffraction investigation showed that 1 crystallizes in space group $P2_1/a$ with a = 25.737 (6) Å, b = 11.129 (2) Å, c = 18.085 (3) Å, α = 99.06 (2)°, and Z = 4.

Introduction

Reactions of Co^{II} salts with NaBH$_4$ or NaBH$_3$CN in the presence of bis(diphenylphosphino)methane (dppm) have been shown[2] to give a variety of products depending upon the reaction conditions. These products include the tetrahedral Co^{I} species CoX(η^1-dppm)$_3$ (X = Cl, Br), Co^{III} complexes of the type [CoHX(η^2-dppm)$_2$]$^+$ (X = Cl, Br, I, BH$_3$CN), and the mixed oxidation state system

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(1) (a) Lakehead University. (b) University of Western Ontario. (c) University of Minnesota—Duluth.

(2) Elliot, D. J.; Holah, D. G.; Hughes, A. N.; Maciaszek, S.; Magnuson, V. R.; Parker, K. O. *Can. J. Chem.* **1988,** *66,* 81.

$Co_2X_3(dppm)_2$, for which the structure has not yet been established. If the reductions are carried out in an atmosphere of CO, any one or more of several Co-carbonyl–dppm complexes containing Co^I, Co^0, or Co^{I-} may be formed, with the nature of the major product being critically dependent upon the reaction conditions. Thus, if $NaBH_4$ is added to a Co^{II}/dppm/CO system in $EtOH/C_6H_6$ over 10–30 min, either or both of two solid products is initially obtained[3] depending upon the conditions. These are the Co^I–Co^{I-} species $[Co(\eta^2\text{-dppm})_2CO][(Co(CO)_4]$ (**1**)[4] and the binuclear complex $Co_2(\mu\text{-dppm})_2(CO)_4$ (**2**). The first of these can be converted[3] (with loss of CO) into a mixture of **2** and $Co_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(CO)_2$ (**3**) by stirring in dichloromethane/ethanol solution—a process similar to that recently observed[5] in a more general form in the synthesis of heterobimetallic dppm–CO complexes. This mixture of isomers can, in turn, be converted quantitatively into pure **3** by stirring a suspension in ethanol. This transformation can be reversed by crystallization of a solution of **3** in dichloromethane to give a mixture of **2** and **3**, and the solution equilibrium **2** $\rightleftharpoons$ **3** has been studied in detail.[6] If reaction conditions are modified slightly, a fourth product, $Co(\eta^1\text{-dppm})(\mu\text{-dppm-BH}_2)(CO)_2$ (which contains the first fully characterized example of a $Co–BH_2$ bond), is formed[7] as a minor product together with **2** and **3**. If, however, the basic reaction is carried out with very rapid addition (ca. 1 min) of $NaBH_4$ (but otherwise unmodified), the principal product is the diphenylphosphido-bridged system $Co_2(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-dppm})_2(CO)_2$.[8]

Clearly, although the above mentioned products are formed in one experimental step, several mechanistic steps must be involved. Furthermore, it is probable that those reactions leading to the formation of phosphido-bridged binuclear complexes follow a different mechanistic pathway from those leading to the other products. Thus, while the reduction of metal ions by $NaBH_4$ in the presence of CO has proved to be an extremely useful route to binuclear dppm-bridged carbonyl complexes, the mechanisms involved are poorly understood. It is clearly important to improve the mechanistic understanding if the application of this synthetic method is to be expanded in a rational way, particularly to the synthesis of heterobimetallic complexes. The cobalt system, as outlined above, is particularly rich and complex, and so an attempt has been made to determine the sequence of reactions that leads to each possible product. This paper reports the synthesis of several new Co^I–carbonyl–dppm complexes in the context of these reactions and also outlines the probable pathway for the formation of **1**, the apparent precursor of **2** and **3**. The crystal structure of **1** is also reported.

Experimental Section

Reagents and Solvents. Bis(diphenylphosphino)methane (dppm) was obtained from the Strem Chemical Co., Inc., and was used without further purification. $NaBH_4$ (Alfa) was stored under dry conditions, $CoX(\eta^1\text{-dppm})_3$ and $Co_2(dppm)_2X_3$ (X = Cl, Br) were prepared as previously reported,[2] and all solvents used were reagent grade and were degassed prior to storage under N_2 in a glovebox.

Physical Measurements. Samples and reagents were protected from atmospheric oxidation during weighing and data collection. Microanalyses for C and H were acquired in our laboratories by using a Control Equipment Corp. Model 240XA analyzer using V_2O_5 as a combustion aid. Infrared spectra (Nujol mulls) were recorded on a Beckman IR-4250 spectrophotometer. A Bruker AC-E 200 NMR spectrometer equipped with a variable-temperature controller (BVT-1000S) was used to record ^1H and ^{31}P spectra at 200 and 81.014 MHz, respectively. Chemical shifts are reported as δ values with positive shifts downfield of Me_4Si for ^1H and downfield of the signal of external 85% H_3PO_4 for ^{31}P. For the ^{31}P spectra, frequency lock was provided by either a deuterated solvent or, in the cases of reaction mixtures in which deuterated solvents were not used, a coaxial D_2O insert. Molecular weights were determined by vapor pressure osmometry using a Wescor Model 5500 instrument. Mass spectra were acquired with an Hitachi-Perkin-Elmer RMU-7 spectrometer.

Synthesis of the Compounds. Syntheses were carried out either under an atmosphere of CO followed by workup in a N_2-filled glovebox or directly in the glovebox. In general, it was found to be easier to isolate pure products in good yield from reactions using $CoBr_2$ than from those in which $CoCl_2$ was used. The syntheses recorded herein are therefore representative rather than comprehensive.

$CoX(\eta^1\text{-dppm})_2(CO)_2$ (X = Cl, Br; 4a, 4b). Carbon monoxide was passed into a solution of $CoCl(\eta^1\text{-dppm})_3$ (0.5 g, 0.58 mmol) in benzene (20 mL), with stirring, for 30 min. To the resulting solution was added hexane (20 mL), and the mixture was stored at 0 °C for 48 h. The yellow-orange crystalline product formed (a mixture of **5a** and **6a**, see Results and Discussion and Scheme I) was collected, washed with diethyl ether and hexane, and then dried. The solid was then dissolved in benzene (20 mL), the solution was heated to 50–60 °C, and CO was passed until most of the solvent had evaporated, at which time peroxide-free diethyl ether (10 mL) was added to the viscous residue. The yellow solid obtained was collected by filtration, washed with diethyl ether, and dried to give **4a** (0.25 g, 68%). Anal. Calcd for $C_{52}H_{44}O_2ClP_4Co$: C, 67.95; H, 4.82. Found: C, 67.69; H, 5.07. IR: ν_{CO} 1988 (s), 1927 (s) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.1 (m, vb, 4 H, $P–CH_2–P$). $^{31}P\{^1H\}$ NMR (C_6D_6): simplified AA′XX′ pattern, $\delta P_A = \delta P_{A'} = 54.8$ (dd), $\delta P_X = \delta P_{X'} = -24.8$ (dd), J = 41.7 and 29.5 Hz.

The corresponding bromo compound **4b** was prepared from $CoBr(\eta^1\text{-dppm})_3$ by a virtually identical procedure (yield, 72%). Anal. Calcd for $C_{52}H_{44}O_2BrP_4Co$: C, 64.81; H, 4.60. Found: C, 65.07; H, 5.14. IR: ν_{CO} 1988 (s), 1927 (s) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.1 (m, vb, 4 H, $P–CH_2–P$). $^{31}P\{^1H\}$ (C_6D_6). Simplified AA′XX′ pattern, $\delta P_A = \delta P_{A'} = 51.2$ (dd), $\delta P_X = \delta P_{X'} = 24.8$ (dd), J = 42.0 and 29.4 Hz. MW: calcd 963.65; found (vapor-pressure osmometry) 955.2, 978.8.

$[Co(\eta^2\text{-dppm})(\eta^1\text{-dppm})(CO)_2]X$ (X = Br, BPh_4; 5b, 5c). Treatment of $CoBr(\eta^1\text{-dppm})_3$ (0.5 g, 0.39 mmol) in benzene (20 mL) with CO followed by addition of hexane (15 mL) and storage at 0 °C for 48 h in the manner outlined above yielded an orange crystalline mixture of **5b** and **6b**. This was dissolved in benzene (10 mL) under CO, hexane (10 mL) was added, and the solution was heated to 70 °C under CO, after which it was cooled to room temperature and allowed to stand for 8 h. Pure crystalline **5b** (0.13 g, 35%) was obtained. Anal. Calcd for $C_{52}H_{44}O_2BrP_4Co$: C, 64.81; H, 4.60. Found: C, 64.95; H, 4.83. IR: ν_{CO} 1990 (s), 1925 (s), 1898 (sh) cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.2 (m, vb, 2 H, η^2-$P–CH_2–P$), 3.1 (m, vb, 2 H, η^1-$P–CH_2–P$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ambient temperature, fluxional system, δ): −3.44 (unresolved, η^2-$P_A–CH_2–P_B$), 50.35 (dt, $Co–P_C–CH_2–P_D$), −28.66 (d, $Co–P_C–CH_2–P_D$), $J_{AC} = J_{BC} = 24.5$, $J_{CD} = 50.1$ Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −85 °C): see Results and Discussion.

The corresponding BPh_4^- salt **5c** was prepared by a variation on the above method. A stirred solution of $CoBr(\eta^1\text{-dppm})_3$ (0.5 g, 0.39 mmol) in benzene (20 mL) was treated with CO for 30 min, and $NaBPh_4$ (0.2 g, 0.58 mmol) in tetrahydrofuran (2 mL) was added. The solution was allowed to stand at 0 °C for 48 h under CO, during which time red crystals (mainly **5c** with some **6c**) were deposited. These were collected and washed several times with diethyl ether followed by hexane. The crystals were then dissolved

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(4) This complex was originally formulated[3] as $Co_2(\eta^2\text{-dppm})_2(CO)_4$ and later corrected: Holah, D. G.; Hughes, A. N.; Elliot, D. J.; Puddephatt, R. J.; Moser, I. M.; Magnuson, V. R. *Abstr. Papers—Am. Chem. Soc.* **1990**, 199th, INOR 259. See also ref. 7.

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in a mixture of benzene (10 mL) and dichoromethane (10 mL) heated to boiling under CO. The solution was cooled and allowed to stand at room temperature for 8 h, after which the orange crystals of **5c** (0.2 g, 40%) were collected. IR (ν_{CO}) and NMR (^{1}H and ^{31}P) data are identical with those of **5b**.

The analogous complex **5a** (prepared from $CoCl_2 \cdot 6H_2O$) was characterized only spectroscopically.

[Co(η^2-dppm)$_2$(CO)] (X = Br, BPh$_4$; 6b, 6c). The initial steps in the syntheses of **6b** and **6c** are virtually identical with those recorded above for **5b** and **5c**. After the first filtration (removing mainly **5b** and **5c**, respectively), however, the *filtrates* were treated with additional hexane (10 mL) and the solutions were allowed to stand at 0 °C for a further 48 h under N_2. The resulting red crystals of **6b** and **6c** obtained respectively in the two syntheses were washed with diethyl ether followed by hexane several times (for **6b**) or benzene followed by hexane (for **6c**). The two products were recrystallized (benzene/hexane 1:1 for **6b**, and benzene/dichloromethane 1:1 for **6c**) and were obtained in yields of 37% and 39%, respectively. Anal. Calcd for $C_{51}H_{44}OBrP_4Co$ (**6b**): C, 65.47; H, 4.74. Found: C, 65.17; H, 5.06. Calcd for $C_{75}H_{64}OBP_4Co$ (**6c**): C, 76.68; H, 5.49. Found: C, 76.51; H, 5.25. IR: ν_{CO} 1930 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 2.1 (m, vb, 4 H, η^2-P–CH$_2$–P). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −6.78.

As with **5a**, **6a** (prepared similarly from $CoCl_2 \cdot 6H_2O$) was characterized only spectroscopically.

[Co(η^1-dppm)(CO)$_4$]Br·C$_6$H$_6$ (7). CoBr(η^1-dppm)$_3$ (1.3 g, 1 mmol) was dissolved in benzene (20 mL), and CO was passed (with stirring) for 5 min. A solution of $NaBH_4$ (0.04 g, 1 mmol) in ethanol (10 mL) was then added over a period of 10 min, after which the mixture was stirred for 1 h. Most of the solvent was then removed by passage of a slow stream of N_2/CO, and a red solid precipitated. This was removed by filtration, washed several times with peroxide-free ether and then hexane, and dried under reduced pressure to give pure **7** (0.16 g, 22%). Anal. Calcd for $C_{35}H_{28}O_4BrP_2Co$: C, 58.91; H, 3.93. Found: C, 59.03; H, 3.35. IR: ν_{CO} 2000 (s), 1950 (s), 1920 (s) cm^{-1}. ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 60 (d, Co–*P*–CH$_2$–P), −27 (d, Co–P–CH$_2$–*P*), J_{PP} = 74 Hz. The presence of benzene was confirmed by mass spectrometry.

Complex **7** can also be prepared (36% yield) by treating **4** (X = Br) with CO and $NaBH_4$ in a manner similar to that outlined above.

[Co(η^2-dppm)$_2$(CO)][Co(CO)$_4$]·0.5C$_2$H$_5$OH (1). $CoBr_2 \cdot xH_2O$ (0.88 g, ~2.7 mmol) and dppm (2.04 g, 5.31 mmol) were dissolved in benzene/ethanol (1:1, 30 mL), and CO was passed through the solution for 10 min. $NaBH_4$ (0.20 g, 5.29 mmol) suspended in ethanol (30 mL) was then added dropwise over 30 min, and the resulting red solution was stirred for a further 1 h. The mixture was filtered, and the volume of the filtrate was slowly reduced by passage of N_2. Red needles of **1** (0.56 g, 42%) were obtained. Anal. Calcd for $C_{56}H_{47}O_{5.5}P_4Co_2$: C, 64.07; H, 4.51. Found: C, 63.94; H, 4.43. IR: ν_{CO} 2010, 1998 (s), 1950 (s), 1855, 1835 cm^{-1}. ^{1}H and ^{31}P{^{1}H} NMR: identical with those of **6** except for the presence of ethanol signals in the ^{1}H spectrum.

[CoRh(μ-dppm)$_2$(μ-CO)(CO)$_2$(μ-Cl)]Cl (9). CoCl(η^1-dppm)$_2$(CO)$_2$ (**4a**) (0.213 g, 2.3 mmol) was dissolved in benzene (10 mL), and $Rh_2(CO)_4Cl_2$ (0.043 g, 0.11 mmol) in dichloromethane (5 mL) was added. The solution was stirred for 30 min, and hexane (10 mL) was added to precipitate crystals of **9** (0.1 g, 43%) identical in all respects with an authentic[9] sample.

Crystal Structure Determination for [Co(η^2-dppm)$_2$(CO)][Co(CO)$_4$] (1). Unsolvated crystals of **1** suitable for X-ray examination were obtained, as flat hexagonal plates elongated along one direction, by dissolving the crude product obtained from the synthetic procedure outlined earlier in C_2H_5OH/CH_2Cl_2 (1:1) followed by passage of a slow stream of nitrogen. A crystal with dimensions 0.34 × 0.17 × 0.06 mm was chosen for diffraction and mounted on the end of a glass rod. Data collection was carried out on a CAD4 diffractometer using Mo Kα radiation monochromatized with graphite. Cell constants were determined from 23 reflections found by an automatic search routine. Crystal data and structure refinement data are summarized in Table I. Calculations were carried out on an AT&T 6386 WGS computer with a PC version of NRCVAX.[10] Heavy atoms were found by direct methods. Successive cycles of least-squares refinement and Fourier or difference Fourier calculations led to the positions for the remaining atoms. Hydrogen atoms were included but not refined. All carbon atoms in the phenyl rings were refined isotropically. The final cycle of refinement included 355 variables

Table I. Summary of Crystal, Intensity Collection and Structure Refinement Data for [Co(η^2-dppm)$_2$(CO)][Co(CO)$_4$] (1)

formula	$Co_2P_4O_5C_{55}H_{44}$
fw	1026.3
cryst syst	monoclinic
space group	$P2_1/a$
cell params	
a, Å	25.737 (6)
b, Å	11.129 (2)
c, Å	18.085 (3)
α, deg	90
β, deg	99.06 (2)
γ, deg	90
V, Å^3	5043.1
cryst size, mm	0.34 × 0.17 × 0.06
no. of molecules/cell	4
d_{calc}, g/cm^3	1.352
d_{obs}, g/cm^3	1.31 (±0.02)
temp	ambient
abs coeff, cm^{-1}	8.2
diffractometer	CAD4
radiation	Mo Kα (λ = 0.7093 Å) graphite monochromatized
attenuation factor	17.60
scan type	ω
scan range 2θ, deg	0–48
no. of unique reflns	7899
measd region	$\pm h,+k,+l$
no. of obs reflns	2748 $I > 2.5\sigma(I)$
least squares no. of variables	355
R_F[a]	0.053
R_w[b]	0.062
GOF[c]	1.346
weighting	counter
k	$(0.03)^2$
max C/S	0.009
largest neg peak, e/Å^3	−0.280
largest pos peak, e/Å^3	0.410

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/[\sigma^2(|F_o|) + k|F_o|^2]$. [c] $\text{GOF} = [\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$.

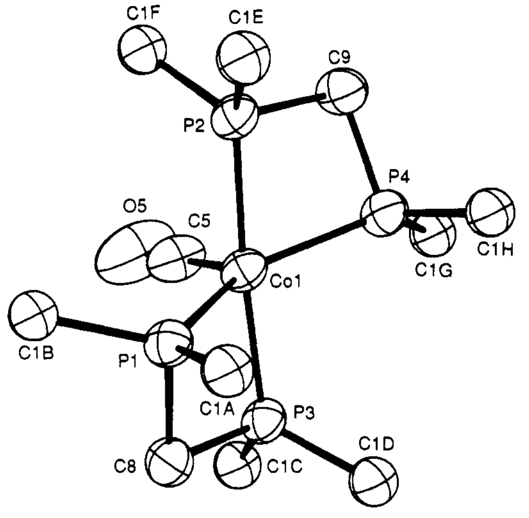

Figure 1. ORTEP drawing of [Co(η^2-dppm)$_2$(CO)]$^+$ with atoms shown as 30% probability ellipsoids. Phenyl rings have been omitted for clarity.

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and converged to $R = 0.053$ and $R_w = 0.062$.[11] The final positional and thermal parameters are given in Table II, and an ORTEP drawing of the cation, $[Co(\eta^2\text{-dppm})_2(CO)]^+$, is given in Figure 1.

Results and Discussion

Cationic–anionic complexes of the type $[Co(PR_3)_n(CO)_{5-n}][Co(CO)_4]$ are normally synthesized[12,13] from disproportionation reactions of phosphines or phosphites with $Co_2(CO)_8$, and the formation[3,4] of $[Co(\eta^2\text{-dppm})_2(CO)][Co(CO)_4]$ (1) in $Co^{II}/dppm/BH_4^-/CO$ reactions might, at first sight, be assumed to fall into this category. Indeed, it has recently been shown[13] that $Co_2(CO)_8$ reacts with dppm rapidly (a few minutes) to give the salt $[Co(dppm)(CO)_3][Co(CO)_4]$ and that this loses CO to give $Co_2(\mu\text{-dppm})(\mu\text{-CO})_2(CO)_4$. However, it is most unlikely that $Co_2(CO)_8$, which is normally formed from Co^{II} only under extremely forcing conditions,[14] could be formed in significant quantities under the mild conditions (room temperature, atmospheric pressure, short reaction times) of these reactions. Certainly, we have uncovered no evidence for the formation of $Co_2(CO)_8$ in our detailed studies[3,4,6-8] of this reaction system. Furthermore, the recent synthesis,[9] which is rapid and has good yields (40% after recrystallization), of $CoRh(\mu\text{-dppm})_2(CO)_3$ directly from the $Co^{II}/Rh^{III}/dppm/BH_4^-/CO$ system under similarly mild conditions, with $[Rh(\eta^2\text{-dppm})_2(CO)]^+$ (which appears to react with $[Co(CO)_4]^-$, also present, in the manner demonstrated[5] in a different approach to the synthesis of the Co–Rh complex) clearly characterized in the reaction mixture, indicates that the cation and anion could possibly be formed by independent routes. The following discussion explores and eliminates this possibility and shows that a disproportionation reaction of a Co^0 dimeric species, formed by an unusual route, is indeed involved in the formation of 1.

Table II. Positional[a] and Thermal Parameters for $[Co(\eta^2\text{-dppm})_2(CO)][Co(CO)_4]$ (1)

atom	x	y	z	B_{iso},[b] Å^2
Co2	0.16884 (6)	0.29312 (15)	0.19522 (9)	5.32 (9)
C1	0.1409 (5)	0.1641 (14)	0.2278 (8)	7.0 (9)
O1	0.1219 (4)	0.0794 (9)	0.2491 (8)	10.8 (8)
C2	0.2168 (5)	0.2428 (13)	0.1439 (7)	6.7 (8)
O2	0.2488 (4)	0.2052 (10)	0.1121 (6)	10.4 (7)
C3	0.1996 (5)	0.3760 (12)	0.2707 (8)	6.1 (8)
O3	0.2216 (4)	0.4303 (10)	0.3201 (6)	9.7 (7)
C4	0.1186 (6)	0.3800 (14)	0.1430 (8)	7.5 (8)
O4	0.0837 (4)	0.4368 (11)	0.1140 (7)	11.6 (8)
Co1	0.42608 (5)	0.72823 (12)	0.29942 (7)	3.28 (6)
P1	0.40828 (10)	0.54894 (24)	0.24811 (15)	3.32 (13)
P2	0.50059 (10)	0.7786 (3)	0.25854 (14)	3.44 (12)
P3	0.34652 (10)	0.6773 (3)	0.32377 (15)	3.50 (13)
P4	0.41420 (11)	0.91567 (24)	0.25696 (16)	3.71 (14)
C8	0.3541 (4)	0.5180 (9)	0.3029 (5)	3.8 (5)
C9	0.4869 (4)	0.9397 (9)	0.2579 (6)	4.2 (5)
C5	0.4569 (4)	0.7227 (11)	0.3921 (7)	5.1 (6)
O5	0.4766 (3)	0.7192 (10)	0.4535 (5)	9.3 (7)
C1A	0.3786 (4)	0.5257 (9)	0.1510 (5)	3.43 (21)[c]
C2A	0.3866 (4)	0.6104 (9)	0.0981 (6)	4.13 (23)
C3A	0.3637 (4)	0.5960 (10)	0.0227 (6)	5.2 (3)
C4A	0.3325 (4)	0.4958 (11)	0.0033 (6)	5.7 (3)
C5A	0.3244 (5)	0.4111 (11)	0.0539 (7)	6.0 (3)
C6A	0.3479 (4)	0.4248 (10)	0.1291 (6)	4.9 (3)
C1B	0.4553 (4)	0.4235 (8)	0.2677 (5)	3.41 (21)
C2B	0.4745 (4)	0.3950 (10)	0.3410 (6)	4.80 (25)
C3B	0.5125 (5)	0.3021 (11)	0.3569 (6)	6.0 (3)
C4B	0.5311 (4)	0.2428 (10)	0.3000 (6)	5.2 (3)
C5B	0.5112 (4)	0.2710 (10)	0.2274 (6)	4.83 (24)
C6B	0.4736 (4)	0.3611 (9)	0.2110 (5)	4.03 (23)
C1C	0.3304 (4)	0.6854 (10)	0.4179 (6)	4.37 (23)
C2C	0.3473 (5)	0.7845 (11)	0.4627 (7)	6.4 (3)
C3C	0.3316 (6)	0.7916 (13)	0.5363 (8)	8.1 (4)
C4C	0.3013 (5)	0.7026 (12)	0.5574 (7)	6.8 (3)
C5C	0.2837 (4)	0.6090 (11)	0.5147 (6)	5.6 (3)
C6C	0.2985 (4)	0.6007 (10)	0.4428 (6)	4.8 (3)
C1D	0.2857 (4)	0.7334 (9)	0.2673 (5)	4.01 (21)
C2D	0.2702 (4)	0.8470 (11)	0.2831 (6)	5.3 (3)
C3D	0.2227 (5)	0.8961 (12)	0.2420 (8)	7.3 (3)
C4D	0.1951 (5)	0.8270 (12)	0.1880 (7)	6.8 (3)
C5D	0.2081 (5)	0.7128 (13)	0.1722 (7)	7.4 (3)
C6D	0.2561 (5)	0.6645 (11)	0.2126 (6)	5.5 (3)
C1E	0.5138 (4)	0.7358 (9)	0.1655 (5)	4.01 (21)
C2E	0.5367 (4)	0.6258 (10)	0.1575 (6)	4.9 (3)
C3E	0.5456 (5)	0.5880 (11)	0.0874 (7)	6.0 (3)
C4E	0.5312 (5)	0.6587 (13)	0.0290 (7)	6.7 (3)
C5E	0.5083 (5)	0.7686 (12)	0.0323 (7)	7.2 (3)
C6E	0.4991 (4)	0.8097 (10)	0.1048 (6)	5.4 (3)
C1F	0.5646 (4)	0.7521 (9)	0.3161 (5)	4.04 (22)
C2F	0.6052 (4)	0.8364 (10)	0.3183 (6)	5.2 (3)
C3F	0.6560 (5)	0.8128 (11)	0.3612 (7)	6.0 (3)
C4F	0.6635 (5)	0.7104 (12)	0.4002 (6)	6.0 (3)
C5F	0.6242 (5)	0.6255 (11)	0.3980 (6)	6.0 (3)
C6F	0.5738 (4)	0.6481 (10)	0.3564 (6)	4.64 (24)
C1G	0.3917 (4)	1.0347 (9)	0.3150 (6)	4.16 (23)
C2G	0.3475 (4)	1.1039 (10)	0.2873 (6)	5.4 (3)
C3G	0.3285 (5)	1.1882 (12)	0.3342 (8)	7.1 (3)
C4G	0.3541 (5)	1.2014 (12)	0.4049 (7)	6.7 (3)
C5G	0.3983 (5)	1.1373 (12)	0.4348 (7)	6.7 (3)
C6G	0.4168 (5)	1.0501 (11)	0.3867 (7)	6.0 (3)
C1H	0.3824 (4)	0.9561 (9)	0.1628 (5)	3.64 (21)
C2H	0.3435 (4)	0.8818 (10)	0.1269 (6)	4.61 (24)
C3H	0.3186 (5)	0.9084 (12)	0.0545 (7)	6.8 (3)
C4H	0.3338 (5)	1.0104 (13)	0.0203 (7)	7.2 (3)
C5H	0.3718 (5)	1.0840 (12)	0.0545 (7)	7.0 (3)
C6H	0.3970 (5)	1.0593 (11)	0.1269 (7)	5.8 (3)

[a] Estimated standard deviations are given in parentheses. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(11) + b^2B(22) + c^2B(33) + ab(\cos\gamma)B(12) + ac(\cos\beta)B(13) + bc(\cos\alpha)B(23)]$. [b] B_{iso} is the mean of the principal axes of the thermal ellipsoid. [c] All phenyl carbon atoms were refined isotropically.

It has been established[15] for some time that Co^{II}–phosphine complexes can form unstable Co^{II}–phosphine–carbonyl derivatives upon exposure to CO at room temperature and that slow reduction to Co^I by CO can also occur.[15,16] Generally, however, the equilibrium

$$Co(PR_3)_2X_2 + CO \rightleftharpoons Co(PR_3)_2X_2(CO)$$

lies very far to the left[16] for bulkier, less basic, phosphines similar to dppm and the reduction process proceeds at a negligible rate for the case where X = Cl and PR_3 is a triarylphosphine. In the $Co^{II}/dppm/BH_4^-/CO$ reactions leading to the formation[3,4] of 1, the exposure of the Co^{II}/dppm mixture to CO is so brief (and the dppm is sufficiently bulky) that it is probable that some reduction of the phosphine-complexed Co^{II} by $NaBH_4$ occurs before significant interaction of CO with the metal center takes place. Accordingly, since the first products isolated from similar reactions in the absence of carbon monoxide are[2] the reduced species $Co_2X_3(dppm)_2$ and $CoX(\eta^1\text{-dppm})_3$ (X = Cl, Br) and since it is also well established[16,17] that CO interacts smoothly with Co^I–phosphine complexes, we have investigated the reactions of both of these products with

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(11) Atomic scattering factors were taken from: Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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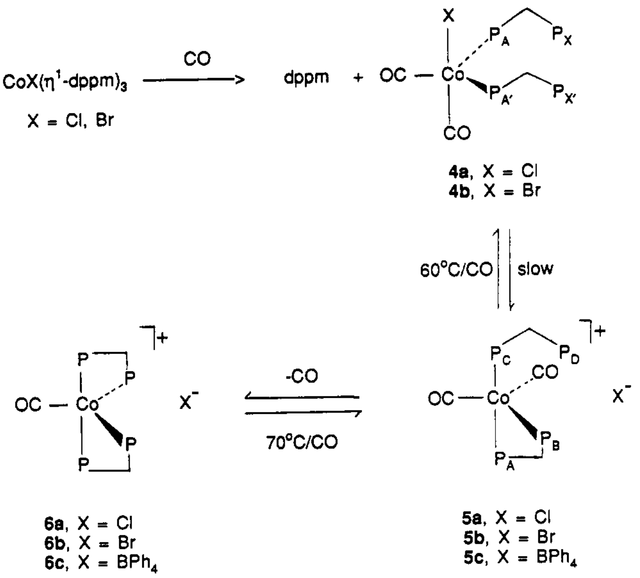
(13) Lisic, E. C.; Hanson, B. E. *Inorg. Chem.* **1986**, *25*, 812.

(14) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley Interscience: New York, 1988; p 1022.

(15) See, for example: Albertin, G.; Bordignon, E.; Orio, A. A.; Rizzardi, G. *Inorg. Chem.* **1975**, *14*, 944 and references cited therein.

(16) Bressan, M.; Corain, B.; Rigo, P.; Turco, A. *Inorg. Chem.* **1970**, *9*, 1733.

Scheme I



CO in the absence of $NaBH_4$.

Dealing first with $CoX(\eta^1\text{-dppm})_3$ for which the structure has been established,[2] these react rapidly and very cleanly with CO to give, in sequence and in quantitative yield, complexes **4**–**6**. All of these complex types can be isolated in pure form and have been fully characterized (see Experimental Section and later discussion). The second and third steps in the reaction sequence can be reversed under certain conditions, and both the forward and reverse reactions are summarized in Scheme I.

Thus, exposure of a benzene solution of the high-spin[2] $CoX(\eta^1\text{-dppm})_3$ to CO at ambient temperature and pressure leads to the very rapid formation of free dppm (^{31}P NMR) and a low-spin Co^I–dppm complex which, in the $^{31}P\{^1H\}$ NMR spectrum, shows a doublet of doublets for coordinated P centered on δ 54.8 (J = 41.7 and 29.5 Hz) coupled with a second doublet of doublets for uncoordinated P centered on δ −24.8. No other signals were observed in the spectrum, and the reaction therefore appears to be quantitative. Given the fact that free dppm is produced in the reaction and also that simple Co^I–phosphine complexes of the type $CoX(PEt_3)_3$ are known[17] to react with CO to give, initially, $CoX(PEt_3)_3(CO)$ and then $CoX(PEt_3)_2(CO)_2$, it seemed probable that the product is **4** or, less probably, the ionic species $[Co(\eta^1\text{-dppm})_2(CO)_3]X$, although attempts to precipitate a BPh_4^- salt were unsuccessful. The product cannot be isolated in a pure state from this reaction and attempts at crystallization under a variety of conditions lead to the formation of further reaction products (a mixture of **5** and **6**). However, a molecular weight determination on a pure sample (X = Br) obtained by a less direct route (Experimental Section and later discussion) confirmed that the compound is indeed the nonionic **4**. The ^{31}P NMR spectrum can therefore be interpreted as a simplified AA′XX′ spectrum of what is probably a fluxional five-coordinate system.

If the solution containing **4** is allowed to stand, it isomerizes to **5** through displacement of X by one of the uncoordinated P atoms. This compound, which can also be isolated in pure form (X = Br) by an indirect route (Experimental Section), shows, in $CDCl_3$, at room temperature a ^{31}P spectrum that is consistent with an A_2MX pattern arising from a fluxional five-coordinate system. Thus, signals are observed at δ −3.44 (unresolved hump, P_A and P_B), 50.35 (doublet of doublets, J = 24.5 and 49.4 Hz, P_C), and −28.7 (doublet, J = 49.4 Hz, P_D). At −85 °C, however, the fluxional process is slowed to the point that all P atoms (and their couplings) become clearly observable with P_A at δ 12.6, P_B at δ −21.0, P_C at δ 49.3, and P_D at δ −31.6 (J_{AB} = 113.0, J_{AC} = 109.0, J_{BC} = 58.0, J_{CD} = 50.7 Hz). The assignments are made on the assumption that the geometry of **5** at low temperatures is as shown in Scheme I. Thus, the chelated dppm would adopt the apical–equatorial arrangement to minimize strain and, while a value of J_{AC} of 109 Hz might seem to be low for a trans coupling, it is almost certainly much too high for the cis coupling, which would be observed if the monocoordinated dppm were to adopt the equatorial arrangement. It should be noted that the geometry shown is similar to that established[7] for $Co(\eta^1\text{-dppm})(\mu\text{-dppm-}BH_2)(CO)_2$.

Complex **5** is also formed as a minor product in several other reactions in which Co^{II} is reduced by $NaBH_4$ in the presence of CO and dppm. In each case, characterization was mainly by ^{31}P NMR spectroscopy and the syntheses are unreliable. Experimental details are not given here.

As with the transformation **4** → **5** described above, solutions of **5** slowly give **6** ($\delta(^{31}P)$ −6.78), easily isolable by crystallization as the Br^- or BPh_4^- salts, by displacement of a CO ligand by the remaining uncoordinated P atom.

As mentioned earlier, the complexes **4** and **5** are extremely difficult to isolate in pure form from the series of transformations outlined above. At best, mixtures of products are obtained. However, the process is reversible and it is by this route that pure **4** and **5** are obtained. Full details are given in the Experimental Section, but the essentials of the process are that treatment of **6b** or **6c** in benzene/hexane with CO at 70 °C followed by careful cooling and crystallization under CO produces pure crystalline **5b** or **5c**. A modification of this procedure produces **4a** or **4b**. The first step in this reverse process is clearly the displacement of one coordinated P atom by CO (**6** → **5**). The mechanism of the second step is less obvious since it is apparently not a simple matter of X^- directly displacing a second coordinated P atom. If this were the case, the forward reaction **4** → **5** would be unlikely to occur under the conditions observed and the presence of CO would not be necessary for the reverse reaction. It possible that in the transformation **5** → **4** under CO at ~60 °C, the first step is displacement of coordinated P by CO (to give the unstable species $[Co(\eta^1\text{-dppm})_2(CO)_3]X$) which is quickly followed by displacement of a CO ligand by X^-. An alternative explanation is that the large excess of CO displaces the **6** ⇌ **5** equilibrium strongly in favor of **5** (and, indeed, completely suppresses the forward reaction), allowing slow attack on **5** by halide ion.

While it is clear from the foregoing discussion that $[Co(\eta^2\text{-dppm})_2(CO)]^+$ is readily formed in high yield in the reaction of $CoX(\eta^1\text{-dppm})_3$ with CO, there is no evidence for the formation of $[Co(CO)_4]^-$. It seemed probable then that, in the formation of **1**, either $[Co(CO)_4]^-$ is formed as a result of the continued presence of $NaBH_4$ in the reaction mixture after $CoX(\eta^1\text{-dppm})_3$ has reacted with CO or an entirely different reaction pathway is followed.

The first of these possibilities can be discarded since treatment of a benzene solution of $CoBr(\eta^1\text{-dppm})_3$ under CO with ethanolic $NaBH_4$ leads only to the formation of $[Co(\eta^1\text{-dppm})(CO)_4]Br$ (**7**), which is readily isolated in a pure state as a benzene solvate and which has been fully characterized (Experimental Section). Similar results were obtained from the treatment of pure **4b** with $NaBH_4$. In neither case was any further reduction of Co^I observed. The steps involved in the transformations, which do not

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[17] Klein, H. F.; Karsch, H. H. *Inorg. Chem.* **1975**, *14*, 473.

occur under CO in the absence of $NaBH_4$, have not been established.

Since no trace of $[Co(CO)_4]^-$ was found (solution IR spectra) in any of the reactions reported above, the possibility that **1** (or $[Co(CO)_4]^-$) is formed from the less well-characterized[2] $Co_2X_3(dppm)_2$, which are apparently precursors of $CoX(\eta^1\text{-dppm})_3$ in the reduction of CoX_2/dppm mixtures with $NaBH_4$ in the absence of CO, was explored. Treatment of pure $Co_2Cl_3(dppm)_2$ with CO in ethanol/benzene gives a solution that shows unexpected NMR properties. Thus, at room temperature, the spectrum shows a broadened singlet at δ 6.0 due to the presence of **6a** and two broad and poorly resolved humps at δ −3.5 and +51.8. However, as the temperature is reduced, a new doublet appears at around δ −28 and the signal at −3.5 disappears to be replaced by two new signals at δ −19.5 (doublet of doublets) and +14.1 (triplet). At −68 °C, the spectrum is well resolved and virtually identical (apart from small chemical shift differences and the peak due to **6a**) with that of pure **5a** recorded under similar low-temperature conditions (see earlier discussion).

It appears then that the high-spin Co^I center in $Co_2X_3(dppm)_2$ reacts with CO to give, in addition to **6a**, the low-spin cation of **5** which, at room temperature, is weakly associated through the uncoordinated P atom with the unreacted high-spin Co^{II} center. As a result, the signal of this P atom is not observable because of the local paramagnetic environment that also causes considerable line broadening in the remainder of the spectrum. However, the rapid exchange between associated and nonassociated **5**, which apparently takes place at room temperature, is slowed as the temperature is decreased until the equilibrium (which favors the nonassociated form of **5**) is frozen and the unperturbed spectrum of **5** is observed. These temperature-dependent changes in the ^{31}P spectrum are fully reversible and it is worth noting also that addition of small amounts of free dppm to the solution at room temperature causes no change in the NMR spectrum—i.e., no signal for free dppm is observed presumably because of the effect of the Co^{II} species.

That this interpretation is correct was shown by treating a solution of pure **5b** in ethanol/benzene with an equimolar amount of $CoBr_2$. The resulting mixture possessed a ^{31}P spectrum identical with that of the mixture produced by direct treatment of $Co_2X_3(dppm)_2$ with CO in ethanol/benzene discussed above. Of even more interest is the fact that further treatment of this solution with $NaBH_4$ (in a Co:$NaBH_4$ ratio of 2:1) results in the reduction of the Co^{II} center to Co^I and the formation of the known[18] $[Co_2(\mu\text{-}Br)(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2]Br$ (**8**) (as ascertained by ^{31}P NMR examination of the reaction mixture and "spiking" the mixture with an authentic sample). Further addition, again under CO, of a similar amount of $NaBH_4$ leads to the reduction of both Co^I centers in **8** and the formation of the **2** $\rightleftharpoons$ **3** equilibrium system, as shown by the ^{31}P NMR spectrum and "spiking" with authentic[3] **2**. Exposure of this solution to an atmosphere of CO results in a disproportionation reaction and the formation of **1**. In this connection, it is worth noting that a similar disproportionation has been observed[5] for $CoRh(\mu\text{-dppm})_2(CO)_3$. It seems clear then that this is the route whereby **1** is formed in direct (Experimental Section) Co^{II}/dppm/BH_4^-/CO reactions, and the sequence of events is summarized in Scheme II.

Scheme II

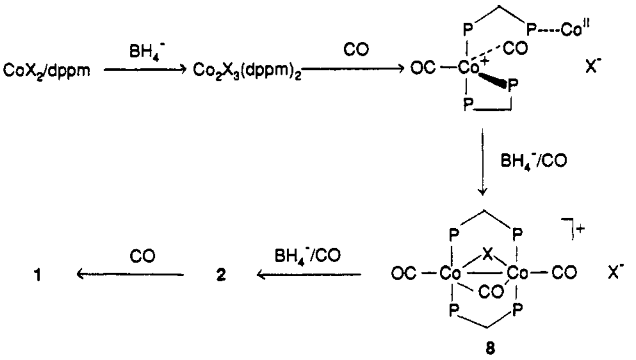

Table III. Bond Lengths (Å) and Angles (deg)[a] in the Coordination Sphere of the Cation $[Co(\eta^2\text{-dppm})_2(CO)]^+$

(a) Bond Lengths	
Co1–P1	2.217 (3)
Co1–P2	2.208 (3)
Co1–P3	2.207 (3)
Co1–P4	2.227 (3)
Co1–C5	1.735 (12)
C5–O5	1.145 (14)
P1–C8	1.849 (10)
P3–C8	1.829 (10)
P2–C9	1.826 (10)
P4–C9	1.862 (10)
(b) Bond Angles	
Axial to Equatorial	
P2–Co1–C5	93.1 (3)
P2–Co1–P1	102.53 (3)
P2–Co1–P4	73.93 (11)
P3–Co1–C5	94.9 (3)
P3–Co1–P1	73.73 (11)
P3–Co1–P4	103.37 (11)
Equatorial to Equatorial	
P1–Co1–P4	133.73 (12)
P1–Co1–C5	113.8 (4)
P4–Co1–C5	112.5 (4)
Axial to Axial	
P2–Co1–P3	172.05 (11)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

As already noted,[4] complex **1** was originally formulated[3] as an isomer of **2** and **3**—i.e., a complex of formula $Co_2(dppm)_2(CO)_4$. However, X-ray investigations of these three complexes have shown that complex **1** possesses one more CO ligand than **2** or **3** (for which the structures and reaction chemistry will form the basis of a separate paper[18]) and has the ion-pair formulation used throughout this paper. The cation in **1**, $[Co(\eta^2\text{-dppm})_2(CO)]^+$, shown in Figure 1, is nearly identical with that reported[19] for the complex $[Co(\eta^2\text{-dppm})_2(CO)]ClO_4$ prepared by an entirely different route. Bond lengths and angles for the cations in the two complexes agree within 0.02 Å and 2.0°, respectively. Selected bond lengths and angles for the coordination sphere of the cation of **1** are shown in Table III. The $[Co(CO)_4]^-$ anion exhibits tetrahedral geometry, as expected, with an average C–Co–C angle of 109.5°, and the overall structural characteristics are in good agreement with those of the tetracarbonylcobaltate anion reported previously.[20]

Finally, a very preliminary study of the potential of **4** as a convenient starting material in heterobimetallic syntheses was carried out. Thus, **4a** was treated in benzene

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solution with $Rh_2(CO)_4Cl_2$ in dichloromethane to give the known[9] $CoRh(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2(\mu\text{-Cl})]Cl$ (9) in 43% yield. Further such studies are in progress.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council of Canada (to D.G.H., A.N.H., and R.J.P.) is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles for 1 and ORTEP diagrams of 1 (5 pages); a listing of structure factors for 1 (20 pages). Ordering information is given on any current masthead page.

Notes

Imine-Transfer Reactions from Zirconium to Phosphorus and Boron. Synthesis of the First *C*-Phosphanyl-, *N*-Phosphanyl-, or *N*-Boranylimines

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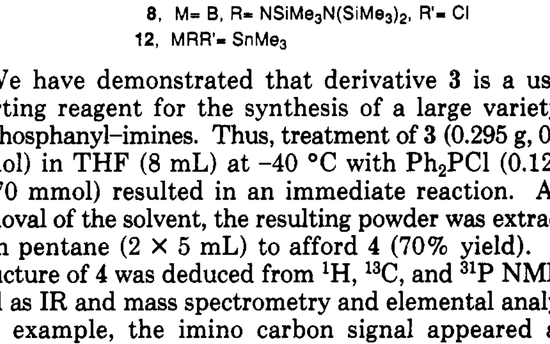
Summary: A "one-pot" reaction involving $(i\text{-}Pr_2N)_2PCN$ (**1**), the Schwartz reagent Cp_2ZrHCl (**2**), and halogenated phosphorus or boron species allows the synthesis of the first *C*-phosphanyl-, *N*-phosphanyl-, or *N*-boranylimines, **4–8**.

Organozirconium reagents have found widespread application in organic synthesis but less frequently in main-group element chemistry.[1] Our continuing interest in this area is to develop new routes to functionalized organic derivatives possessing one or more main-group elements. We have already provided examples of unusual neutral or cationic metallacycles obtained via hydrozirconation[2] of analogous phosphorus compounds of alkenes or imines, i.e., phospha-alkenes R—P=C< or iminophosphanes R—P=N–.

Here we report the use of the readily available *N*-zirconium–imino compound **3** for the facile preparation of the first *N*- and *C*-diphosphanyl- or *C*-phosphanyl-*N*-boranylimines, **4–6** or **7** and **8**. Until now only diphosphorylated species **9**, in which the two phosphorus atoms are tetracoordinated, were known.[3]

The *N*-zirconium–imino species **3** was conveniently prepared in near-quantitative yield by reacting bis(diisopropylamino)cyanophosphane (**1**)[4] with Cp_2ZrHCl (**2**) in THF.[5] Evidence for the formation of **3** was mainly given by ^1H NMR (δ $CH{=}N$ 9.66 ppm (d, $^2J_{PH}$ = 60.0 Hz)) and ^{13}C NMR spectroscopy ($\delta(C{=}N)$ 184.56 ppm (d, $^1J_{CP}$ = 13.7 Hz)).



4, M= P, R=R'= Ph
5, M= P, R= i-Pr2N, R'= Cl
6, M= P, R=R'= i-Pr2N
7, M= B, R=R'= i-Pr2N
8, M= B, R= NSiMe3N(SiMe3)2, R'= Cl
12, MRR'= SnMe3

We have demonstrated that derivative **3** is a useful starting reagent for the synthesis of a large variety of *C*-phosphanyl–imines. Thus, treatment of **3** (0.295 g, 0.570 mmol) in THF (8 mL) at –40 °C with Ph_2PCl (0.126 g, 0.570 mmol) resulted in an immediate reaction. After removal of the solvent, the resulting powder was extracted with pentane (2 × 5 mL) to afford **4** (70% yield). The structure of **4** was deduced from ^1H, ^{13}C, and ^{31}P NMR as well as IR and mass spectrometry and elemental analysis. For example, the imino carbon signal appeared as a doublet of doublets ($^1J_{CP}$ = 24.7 Hz, $^2J_{CP}$ = 4.0 Hz) centered at 178.21 ppm in the ^{13}C NMR spectrum, while a doublet of doublets at 8.62 ($^2J_{HP}$ = 56.7 Hz, $^3J_{HP}$ = 29.9 Hz) ppm was observed for the imino proton in the ^1H NMR spectrum. Lastly, the ^{31}P NMR spectrum exhibited two doublets (δ = 56.5 and 60.6 ppm, $^2J_{PP}$ = 26.2 Hz) corroborating the presence of two different phosphane groups.

The iminodiphosphane **5** was similarly prepared from **3** and (diisopropylamino)dichlorophosphane $(i\text{-}Pr_2N)PCl_2$.

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(1) See for example: (a) Fryzuk, M. D.; Bates, G. S.; Stone, C. *Tetrahedron Lett.* **1986**, *27*, 1537. (b) Muklenbernd, T.; Benn, R.; Rufinska, A. *Organometallics* **1986**, *5*, 1023. (c) Heisteeg, B. J. J.; Schat, G.; Akkermann, O. S.; Bickelhaupt, F. *Organometallics* **1986**, *5*, 1749. (d) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (e) Fryzuk, M. D.; Bates, G. S.; Stone, C. *J. Org. Chem.* **1988**, *53*, 4425. (f) Buchwald, S. L.; Fisher, R. A.; Foxman, B. M. *Angew. Chem., Int. Engl.* **1990**, *29*, 771. (g) Fisher, R. A.; Nielsen, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 165–171.

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(3) Levkova, L. N.; Alimov, P. I. *Izv. Akad. Nauk SSSR, Ser. Khim* **1966**, *12*, 2218.

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(5) (a) Hydrozirconation of *p*-tolunitrile with $Cp^*{}_2ZrH_2$ has been reported to provide the azomethine insertion product: Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (b) Hydrozirconation of R—C≡N (R = CH_3, C_6H_5, $CH_2C_6H_5$) with Cp_2ZrHCl led to formation of the corresponding metalla-imines: Frömberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 343.

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