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Synthesis of Di-*tert*-butylphosphido-Bridged Dimers of Cobalt(I) Containing Cobalt–Cobalt Double Bonds. Crystal Structures of $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ and $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)L]_2$ (L = CO or N_2)

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Reaction of greater than 2.5 equiv of t-Bu_2PLi with $CoCl_2(PMe_3)_2$ in THF at −78 °C under dinitrogen yields $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)(N_2)]_2$ (1) in 40% yield. The dinitrogen ligands of 1 are replaced by CO (3 atm) to give $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)(CO)]_2$ (2) quantitatively. The tetracarbonyl complex $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (3) is produced in high yield from the reaction of $Co(CO)_4I$ (prepared in situ) with 1 equiv of Li-t-Bu_2P in THF at −78 °C. The structures of 1, 2, and 3 have been determined by single-crystal X-ray diffraction studies. In each case a short Co–Co interaction and the observed diamagnetism suggest a cobalt–cobalt double bond. The central Co_2P_2 core is planar in each case, and the terminal ligands give each cobalt(I) atom a distorted tetrahedral geometry. Crystal data: for 1, triclinic, $P\bar{1}$, $a = 8.994$ (5) Å, $b = 9.797$ (5) Å, $c = 10.946$ (6) Å, $\alpha = 69.82$ (3)°, $\beta = 67.01$ (3)°, $\gamma = 73.21$ (3)°, $U = 820.0$ Å^3, $D_{calcd} = 1.25$ g cm^{-3}, $Z = 1$ (dimer), $F(000) = 328$, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 12.61$ cm^{-1}, final $R = 0.028$, $R_w = 0.030$ from 1343 observed reflections (1454 measured); for 2, monoclinic, $P2_1/n$, $a = 10.702$ (5) Å, $b = 11.030$ (5) Å, $c = 14.266$ (6) Å, $\beta = 105.30$ (3)°, $U = 1624.3$ Å^3, $D_{calcd} = 1.26$ g cm^{-3}, $Z = 2$ (dimers), $F(000) = 656$, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 12.74$ cm^{-1}, final $R = 0.063$, $R_w = 0.074$ from 1111 observed reflections (4364 measured); for 3, monoclinic, $C2/m$, $a = 13.830$ (6) Å, $b = 11.908$ (5) Å, $c = 8.730$ (4) Å, $\beta = 118.39$ (4)°, $U = 1264.8$ Å^3, $D_{calcd} = 1.37$ g cm^{-3}, $Z = 2$ (dimers), $F(000) = 568$, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 15.09$ cm^{-1}, final $R = 0.051$, $R_w = 0.059$ from 814 observed reflections (1545 measured).

Introduction

The chemistry of transition-metal phosphido (R_2P^-) and phosphinidene (RP^{2-}) complexes is currently receiving considerable attention.[1] Our interests have been focused on the steric effects of the alkyl (or aryl) R groups of R_2P^- and RP^{2-}. We have initially investigated the use of the di-*tert*-butylphosphido (t-Bu_2P^-) ligand.[2,3] So far our results suggest that the substantial steric bulk of the *tert*-butyl groups of the t-Bu_2P unit tend to limit the coordination of other ligands to a metal center.[2,3] This may be partly the reason for the difference between other dialkylphosphido complexes such as those of Me_2P^- and Ph_2P^- and those of t-Bu_2P^-.

For cobalt, until recently only a few dinuclear phosphido-bridged complexes with μ-PPh_2 or μ-PMe_2 groups were known. These included complexes such as $[CpCo(\mu\text{-}PPh_2)]_2$,[4] $[Co(PPh_2)_2]_2$,[5] and $[Co(NO)_2(PPh_2)]_2$.[6] The oligomeric carbonyl $[Co(\mu\text{-}PPh_2)(CO)_3]_x$ was also reported sometime ago by Hayter.[7]

While this paper was in preparation, Geoffroy and coworkers reported their studies on related di- and trinuclear μ-PPh_2-bridged cobalt complexes[8,9] and have shown that the original Hayter system is quite complex. In particular they have made significant progress in the investigation of the interconversions of dimer, trimer, and oligomeric species. Of particular relevance to our work is the isolation and characterization of $[Co(\mu\text{-}PPh_2)(PEt_2Ph)CO]_2$[9] that has two pseudotetrahedral cobalt atoms linked by a formal Co–Co double bond (Co–Co = 2.343 (2) Å).

We report here details of several dinuclear Co(I) complexes employing t-Bu_2P^-. Although the bis(diphenylphosphido) complex $Co_2(PPh_2)_2(CO)_6$ containing no Co–Co bond is known,[8] we have not isolated any analogous complexes containing two μ-t-Bu_2P units with three two-electron donors at each end. It seems likely that this is due to the crowding of terminal sites by the sterically demanding μ-t-Bu_2P groups. The complexes that we have isolated all have planar central Co_2P_2 cores with each cobalt atom bearing two two-electron donor ligands. A Co–Co bond of order 2 would give each cobalt atom an 18-electron configuration, and this is supported by relatively short Co–Co distances (ca. 2.4 Å) in these diamagnetic complexes. Although they can be formally considered analogous to $[Co(\mu\text{-}PPh_2)(PEt_2Ph)CO]_2$,[9] their chemical behavior is notably different. For example, we have isolated the tetracarbonyl complex $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (3) and the bis(dinitrogen) species $[Co(\mu\text{-}t\text{-}Bu_2P)N_2(PMe_3)]_2$ (1) for which there appear to be no analogous PPh_2 com-

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 1, 2, and 3

	1	2	3
formula	$C_{22}H_{54}Co_2N_4P_4$	$C_{24}H_{54}Co_2O_2P_4$	$C_{20}H_{36}Co_2O_4P_2$
mol wt	616.54	616.52	520.36
space group	$P\bar{1}$	$P2_1/n$	$C2/m$
cell constants			
a, Å	8.994 (5)	10.702 (5)	13.830 (6)
b, Å	9.797 (5)	11.030 (5)	11.908 (5)
c, Å	10.946 (6)	14.266 (6)	8.730 (4)
α, deg	69.82 (3)		
β, deg	67.01 (3)	105.30 (3)	118.39 (4)
γ, deg	73.21 (3)		
cell vol, Å^3	820.0	1624.3	1264.8
molecules/unit cell	1 (dimer)	2 (dimers)	2 (dimers)
D_{calcd}, g cm^{-3}	1.25	1.26	1.37
μ(calcd), cm^{-1}	12.61	12.74	15.09
radiation, Å	Mo Kα 0.710 69	Mo Kα 0.710 69	Mo Kα 0.710 69
max cryst dimens, mm	0.15 × 0.20 × 0.35	0.10 × 0.20 × 0.35	0.15 × 0.20 × 0.30
std reflctns	300, 030, 003	400, 060, 004	200, 020, 002
variatn of stds	2%	2%	<2%
reflctns measd	1454	4364	1545
2θ range, deg	1-40	1-50	1-50
reflctns obsd ($I > 3\sigma(I)$)	1343	1111	814
no. of parameters varied	145	145	72
goodness of fit (GOF)	0.71	3.18	2.19
R	0.028	0.063	0.051
R_w	0.030	0.074	0.059

plexes so far reported. Unlike the PPh_2-bridged systems there also appears to be no facile interconversion of dimers and trimers. For example $[Co(\mu\text{-}t\text{-}Bu_2P)CO(PMe_3)]_2$ (2), which is most closely analogous to $[Co(\mu\text{-}PPh_2)CO(PEt_2Ph)]_2$, is formed from the bis(dinitrogen) complex 1 under CO; even at 50 atm and 50 °C the reaction does not proceed further with loss of phosphine and trimer formation as found for the μ-PPh_2 complex under far milder conditions.

Experimental Section

All reactions were performed under oxygen-free nitrogen or argon. Microanalyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Hexane and THF were dried over sodium and distilled from sodium/benzophenone under nitrogen before use. Instruments: IR, Perkin-Elmer 1330; NMR, Varian EM-390 (^{1}H, 90 MHz), FT-80 (^{31}P, 32.384 MHz). IR spectra were as Nujol mulls (KBr plates) or in solution (matched KBr cells). NMR spectra were recorded in C_6D_6 at ambient temperature and are referenced to Me_4Si (δ 0.0, ^{1}H) and 85% H_3PO_4(aq) (δ 0.0, ^{31}P).

$[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)N_2]_2$ (1). A solution of Li-t-Bu_2P[10] (20.0 mmol, 20.5 mL of a 0.971 M THF solution) was cooled to −96 °C and added slowly to a green suspension of $CoCl_2(PMe_3)_2$[11] (3.21 g, 10 mmol) in THF (70 mL) at −78 °C. The solution was allowed to warm slowly to room temperature over 2 h during which time the color changed from green to dark brown. Volatile materials were removed under vacuum, and the brown residue was extracted into hexane (4 × 25 mL) and the solution filtered. The volume was reduced to 20 mL and the solution cooled to −20 °C. The dark blue-brown crystals were collected and dried under vacuum: yield 1.23 g (40%); mp 90–95 °C dec; IR (hexane) 1910 (m) cm^{-1} (Nujol mull) 1900 (m), 1889 (vw), 1351 (m), 1257 (s), 1165 (w), 1010 (m), 925 (s), 791 (s), 700 (w), 653 (w) cm^{-1}; ^{1}H NMR δ 1.35 (m overlapping t-Bu_2P and Me_3P resonances); $^{31}P\{^1H\}$ NMR (in toluene-d_8) δ 214.95 br s, μ-t-Bu_2P, $\Delta\omega_{1/2}$ = 66 Hz), −18.26 (br s, PMe_3, $\Delta\omega_{1/2}$ = 62 Hz). Microanal. calcd for $C_{22}H_{54}Co_2N_4P_4$: C, 42.80; H, 8.76; N, 9.09; P, 20.10. Found: C, 43.25; H, 9.03; N, 8.92; P, 18.91.

$[Co(\mu\text{-}t\text{-}Bu_2P)(CO)(PMe_3)]_2$ (2). A solution of 1 (1.5 g, 0.96 mmol) in hexane (50 mL) was treated with CO (47 psi) in a Fischer-Porter bottle for 3 h. The pressure was released, the yellow-brown solution was evaporated to dryness under vacuum, and the residue was extracted into hexane (2 × 20 mL). The solution was filtered and evaporated to ca. 20 mL under vacuum. Cooling (−20 °C) yielded dark green crystals that were collected and dried under vacuum: yield 0.93 g (60%); mp 182–190 °C dec; IR (THF solution) 1895 (s) cm^{-1}, (Nujol mull) 1897 (s), 1429 (s), 1355 (s), 1300 (w), 1280 (s), 1260 (w), 1165 (s), 1012 (m), 930 (s), 838 (m), 805 (s), 705 (w), 660 (w), 575 (w), 530 (w), 491 (w) cm^{-1}; ^{1}H NMR δ 1.3 (m, overlapping t-Bu_2P and PMe_3 resonances); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 264.10 (br s, t-Bu_2P, $\Delta\omega_{1/2}$ = 30 Hz), −4.60 (br s, PMe_3, $\Delta\omega_{1/2}$ = 20 Hz). Microanal. Calcd for $C_{24}H_{54}Co_2O_2P_4$: C, 46.7; H, 8.76; P, 20.1. Found: C, 46.96; H, 8.67; P, 19.7. A similar reaction under CO (50 atm) at 50 °C yielded only 2 in high yield.

$[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (3). Iodine (0.5 g, 1.98 mmol) in THF (20 mL) was added to a solution of $Co_2(CO)_8$ (0.68 g, 1.98 mmol) in THF (30 mL) at −78 °C. The solution was stirred (2 h) while the color changed from brown to dark green. To the resulting solution was added 1 equiv of Li-t-Bu_2P (3.96 mmol, 2.82 mL of a 1.4 M THF solution). The reaction mixture was stirred (2 h) and allowed to come to room temperature. Volatile materials were removed under vacuum, and the residue was extracted into toluene (2 × 25 mL). The solution was filtered and the volume reduced to ca. 20 mL. Cooling (−20 °C) yielded dark green crystals of 3 which were collected and dried under vacuum: yield 0.72 g (70%); mp 215–218 °C dec; IR (toluene solution) 1997 (s), 1975 (s) cm^{-1}; ^{1}H NMR δ 1.15 (m, t-Bu_2P); $^{31}P\{^1H\}$ NMR δ 331.43 (s, $\Delta\omega_{1/2}$ = 33 Hz). Microanal. Calcd for $C_{20}H_{36}Co_2O_4P_2$: C, 46.1; H, 6.92; P, 11.9. Found: C, 45.9; H, 6.79; P, 11.7.

X-ray Crystallography

Suitable crystals of 1, 2, 3 were grown from hexane solutions at −20 °C and were sealed under vacuum in thin-walled glass capillaries (0.5 mm). Final lattice parameters were determined from 15 high angle reflections ($2\theta > 40°$) carefully centered on an Enraf-Nonius CAD-4 diffractometer. Data were collected by the $\omega/2\theta$ scan technique as previously described at 22 °C.[12] For 1 unit-cell dimensions and lack of systematic absences indicated a triclinic crystal system. $P\bar{1}$ was taken as the correct space group as evidenced by successful structure solution and refinement. For 2 the space group was uniquely defined by systematic absences to be $P2_1/n$. For 3 systematic absences indicated a C-centered monoclinic cell of Cm, $C2$, or $C2/m$ symmetry. Successful structure solution and refinement in the centrosymmetric space

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Table II. Selected Bond Lengths (Å) and Angles (deg) for $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)N_2]_2$ (1)

Bond Distances

Co(1)-Co(1)	2.414 (1)	C(1)-C(4)	1.532 (6)	P(2)-Me(2)	1.818 (5)
Co(1)-P(2)	2.238 (1)	C(5)-C(7)	1.520 (6)	N(1)-N(2)	1.092 (5)
P(1)-C(1)	1.900 (4)	Co(1)-P(1)	2.226 (1)	C(1)-C(3)	1.528 (6)
P(2)-Me(1)	1.815 (5)	Co(1)-N(1)	1.814 (4)	C(5)-C(6)	1.532 (6)
P(2)-Me(3)	1.807 (5)	P(1)-C(5)	1.902 (4)	C(5)-C(8)	1.531 (6)
C(1)-C(2)	1.534 (6)				

Bond Angles

P(1)-Co(1)-P(2)	117.03 (5)	C(2)-C(1)-C(4)	109.5 (4)	Me(1)-P(2)-Me(3)	100.7 (3)
P(2)-Co(1)-N(1)	87.9 (1)	P(1)-C(5)-C(6)	113.3 (3)	Co(1)-N(1)-N(2)	179.0 (4)
Co(1)-P(1)-C(1)	116.0 (1)	C(6)-C(5)-C(7)	108.1 (4)	P(1)-C(1)-C(3)	106.6 (3)
C(1)-P(1)-C(5)	108.4 (2)	C(6)-C(5)-C(8)	109.8 (4)	P(1)-C(1)-C(4)	111.9 (3)
Co(1)-P(2)-Me(2)	126.4 (2)	P(1)-Co(1)-N(1)	108.0 (1)	C(3)-C(1)-C(4)	107.3 (4)
Co(1)-P(2)-Me(3)	112.6 (2)	Co(1)-P(1)-Co(1)	65.61 (4)	P(1)-C(5)-C(7)	106.1 (3)
Me(2)-P(2)-Me(3)	100.4 (3)	Co(1)-P(1)-C(5)	123.0 (1)	P(1)-C(5)-C(8)	111.3 (3)
P(1)-C(1)-C(2)	113.5 (3)	Co(1)-P(2)-Me(1)	113.1 (2)	C(7)-C(5)-C(8)	108.0 (4)
C(2)-C(1)-C(3)	107.8 (4)	Me(1)-P(2)-Me(2)	100.0 (3)		

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)CO]_2$ (2)

Bond Distances

Co(1)-Co(1)	2.399 (4)	C(2)-C(5)	1.55 (2)	P(2)-Me(2)	1.87 (2)
Co(1)-P(2)	2.209 (5)	C(6)-C(8)	1.55 (2)	C(1)-O(1)	1.18 (2)
P(1)-C(2)	1.93 (1)	Co(1)-P(1)	2.216 (4)	C(2)-C(4)	1.52 (2)
P(2)-Me(1)	1.89 (2)	Co(1)-C(1)	1.70 (1)	C(6)-C(7)	1.55 (2)
P(2)-Me(3)	1.85 (2)	P(1)-C(6)	1.93 (1)	C(6)-C(9)	1.57 (2)
C(2)-C(3)	1.54 (2)				

Bond Angles

P(1)-Co(1)-P(2)	116.8 (2)	C(3)-C(2)-C(5)	108 (1)	Me(1)-P(2)-Me(3)	101.1 (9)
P(2)-Co(1)-C(1)	87.4 (6)	P(1)-C(6)-C(7)	111 (1)	Co(1)-C(1)-O(1)	179 (1)
Co(1)-P(1)-C(2)	117.7 (5)	C(7)-C(6)-C(8)	108 (1)	P(1)-C(2)-C(4)	112 (1)
C(2)-P(1)-C(6)	108.3 (7)	C(7)-C(6)-C(9)	108 (1)	P(1)-C(2)-C(5)	112 (1)
Co(1)-P(2)-Me(2)	114.5 (7)	P(1)-Co(1)-C(1)	108.9 (5)	C(4)-C(2)-C(5)	111 (1)
Co(1)-P(2)-Me(3)	114.1 (6)	Co(1)-P(1)-Co(1)	65.5 (1)	P(1)-C(6)-C(8)	105 (1)
Me(2)-P(2)-Me(3)	101.4 (9)	Co(1)-P(1)-C(6)	122.7 (5)	P(1)-C(6)-C(9)	114 (1)
P(1)-C(2)-C(3)	106 (1)	Co(1)-P(2)-Me(1)	123.8 (6)	C(8)-C(6)-C(9)	111 (1)
C(3)-C(2)-C(4)	109 (1)	Me(1)-P(2)-Me(2)	99 (1)		

Table IV. Selected Bond Lengths (Å) and Angles (deg) for $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (3)

Bond Distances

Co(1)-Co(1)	2.426 (2)	C(3)-C(5)	1.51 (1)	C(1)-C(1)	1.12 (1)
Co(1)-C(1)	1.79 (1)	Co(1)-P(1)	2.203 (2)	C(3)-C(4)	1.55 (1)
P(1)-C(3)	1.905 (7)	Co(1)-C(2)	1.77 (1)	C(3)-C(6)	1.51 (1)
C(2)-O(2)	1.16 (1)				

Bond Angles

P(1)-Co(1)-P(1)′	113.17 (8)	P(1)-C(3)-C(5)	108.2 (5)	C(3)-P(1)-C(3)′	110.0 (4)
P(1)-Co(1)-C(2)	112.6 (1)	P(1)-C(3)-C(6)	111.5 (5)	Co(1)-C(1)-O(1)	177 (1)
Co(1)-P(1)-Co(1)	66.83 (9)	C(5)-C(3)-C(6)	107.2 (7)	P(1)-C(3)-C(4)	110.2 (5)
Co(1)-P(1)-C(3)	119.5 (2)	P(1)-Co(1)-C(1)	109.7 (2)	C(4)-C(3)-C(5)	106.6 (6)
Co(1)-C(2)-O(2)	177.0 (9)	C(1)-Co(1)-C(2)	98.0 (5)	C(4)-C(3)-C(6)	112.9 (8)

group $C2/m$ showed this to be the correct choice of space group. Many crystals of **2** were examined but all diffracted poorly. Although data was collected up to $2\theta = 50°$ for the crystal finally chosen for measurement, the rapid falloff in intensity meant that many high angle data were unobserved. This inevitably resulted in a lower than preferred data/parameter ratio and a final structure of only moderate accuracy. Nevertheless, we feel that the analysis was justified in that the molecular structure is more than adequately determined.

A summary of the data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects but not for absorption. Corrections were applied for anomolous dispersion and scattering factors were taken from ref 13. Calculations were carried out with the SHELX system of computer programs.[14] The structures were solved by the application of the direct methods program MULTAN.[15] Least-squares refinement with anisotropic thermal parameters gave final values of $R = 0.028$ (**1**), 0.063 (**2**), and 0.051 (**3**). $R_w = \{\sum_w(|F_o| - |F_c|)^2/\sum_w(F_o)^2\}^{1/2} = 0.030$ (**1**), 0.074 (**2**), and 0.059 (**3**). Final difference Fourier maps showed no features greater than 0.3 e/Å^3 for each structure. Unit weights were used at all stages of each refinement. Selected bond lengths and angles for **1**, **2**, and **3**, are given in Tables II, III, and IV, respectively. The positional parameters for **1**, **2**, and **3** are collected in Tables V, VI, and VII, respectively. The thermal parameters and structure factors are available elsewhere.[16]

Results and Discussion

Under an atmosphere of either argon or dinitrogen the interaction of $CoCl_2(PMe_3)_2$ with exactly 2 equiv of Li-*t*-Bu_2P yielded the unusual paramagnetic Co(I)–Co(II) complex $Co_2(\mu\text{-}t\text{-}Bu_2P)_2(PMe_3)_2Cl$ in moderate yield.[2] If an excess of Li-*t*-Bu_2P (<2.5 equiv) is used, different products may be isolated depending on the inert atmo-

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[16] See paragraph at end of paper regarding supplementary material.

Table V. Positional Parameters for $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)N_2]_2$ (1)

atom	x/a	y/b	z/c	U(eqv), Å^2
Co(1)	0.93840 (6)	0.59756 (6)	0.05771 (5)	0.032
P(1)	1.0164 (1)	0.3648 (1)	0.1657 (1)	0.033
P(2)	0.7036 (1)	0.7219 (1)	0.1719 (1)	0.049
C(1)	1.1881 (5)	0.3316 (5)	0.2382 (4)	0.045
C(2)	1.2544 (6)	0.1674 (5)	0.2914 (5)	0.074
C(3)	1.3285 (5)	0.4005 (6)	0.1202 (4)	0.063
C(4)	1.1364 (6)	0.4094 (6)	0.3521 (5)	0.071
C(5)	0.8653 (5)	0.2374 (5)	0.2900 (4)	0.044
C(6)	0.8200 (6)	0.2365 (6)	0.4405 (4)	0.064
C(7)	0.7103 (5)	0.2967 (6)	0.2498 (5)	0.064
C(8)	0.9297 (6)	0.0793 (5)	0.2749 (5)	0.065
Me(1)	0.6950 (7)	0.7137 (7)	0.3427 (5)	0.088
Me(2)	0.4976 (6)	0.6935 (7)	0.2095 (6)	0.096
Me(3)	0.6811 (7)	0.9190 (6)	0.0947 (6)	0.088
N(1)	1.0463 (5)	0.7135 (4)	0.0793 (4)	0.056
N(2)	1.1114 (6)	0.7819 (5)	0.0940 (5)	0.093
H(1)	1.3500 (6)	0.1555 (5)	0.3115 (5)	(iso)
H(2)	1.1716 (6)	0.1131 (5)	0.3758 (5)	(iso)
H(3)	1.2781 (6)	0.1223 (5)	0.2150 (5)	(iso)
H(4)	1.4253 (5)	0.4041 (6)	0.1483 (4)	(iso)
H(5)	1.3225 (5)	0.5068 (6)	0.0697 (4)	(iso)
H(6)	1.3329 (5)	0.3349 (6)	0.0658 (4)	(iso)
H(7)	1.0500 (6)	0.3605 (6)	0.4387 (5)	(iso)
H(8)	1.0886 (6)	0.5152 (6)	0.3177 (5)	(iso)
H(9)	1.2347 (6)	0.4042 (6)	0.3761 (5)	(iso)
H(10)	0.7289 (6)	0.1783 (6)	0.4985 (4)	(iso)
H(11)	0.7720 (6)	0.3443 (6)	0.4543 (4)	(iso)
H(12)	0.9242 (6)	0.1921 (6)	0.4783 (4)	(iso)
H(13)	0.6267 (5)	0.2442 (6)	0.3087 (5)	(iso)
H(14)	0.6502 (5)	0.4109 (6)	0.2589 (5)	(iso)
H(15)	0.7305 (5)	0.2879 (6)	0.1590 (5)	(iso)
H(16)	0.8550 (6)	0.0022 (5)	0.3366 (5)	(iso)
H(17)	1.0374 (6)	0.0278 (5)	0.3009 (5)	(iso)
H(18)	0.9430 (6)	0.1010 (5)	0.1754 (5)	(iso)
H(19)	0.5972 (7)	0.7763 (7)	0.3881 (5)	(iso)
H(20)	0.7946 (7)	0.7467 (7)	0.3346 (5)	(iso)
H(21)	0.6949 (7)	0.6090 (7)	0.3999 (5)	(iso)
H(22)	0.4832 (6)	0.6044 (7)	0.2076 (6)	(iso)
H(23)	0.4517 (6)	0.7728 (7)	0.1403 (6)	(iso)
H(24)	0.4319 (6)	0.7066 (7)	0.3036 (6)	(iso)
H(25)	0.5981 (7)	0.9729 (6)	0.1416 (6)	(iso)
H(26)	0.6689 (7)	0.9382 (6)	0.0030 (6)	(iso)
H(27)	0.7838 (7)	0.9505 (6)	0.0818 (6)	(iso)

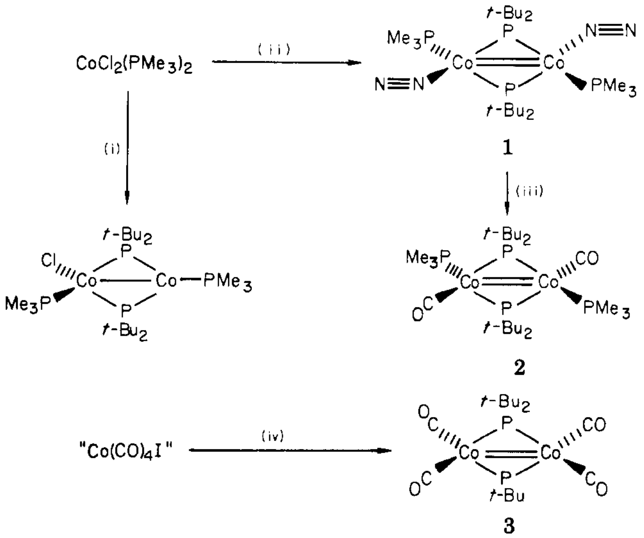
Table VI. Positional Parameters for $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)CO]_2$ (2)

atom	x/a	y/b	z/c	U(eqv), Å^2
Co(1)	0.5768 (2)	0.0777 (2)	0.0345 (1)	0.031
P(1)	0.3795 (3)	0.0709 (4)	0.0564 (2)	0.037
P(2)	0.6535 (4)	0.2589 (4)	0.0142 (3)	0.051
O(1)	0.765 (1)	0.070 (1)	0.2201 (8)	0.083
C(1)	0.687 (1)	0.073 (2)	0.145 (1)	0.049
C(2)	0.365 (2)	0.043 (1)	0.187 (1)	0.054
C(3)	0.458 (2)	−0.062 (2)	0.227 (1)	0.070
C(4)	0.229 (2)	0.005 (2)	0.187 (1)	0.088
C(5)	0.409 (2)	0.155 (2)	0.253 (1)	0.069
C(6)	0.244 (1)	0.180 (1)	−0.008 (1)	0.052
C(7)	0.113 (1)	0.112 (1)	−0.046 (1)	0.059
C(8)	0.285 (1)	0.229 (2)	−0.097 (1)	0.063
C(9)	0.220 (2)	0.288 (1)	0.058 (2)	0.083
Me(1)	0.610 (2)	0.344 (2)	−0.105 (1)	0.086
Me(2)	0.834 (2)	0.266 (2)	0.039 (2)	0.090
Me(3)	0.623 (2)	0.376 (1)	0.098 (1)	0.084

Table VII. Positional Parameters for $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (3)

atom	x/a	y/b	z/c
Co(1)	0.0956 (1)	0.0000	0.0324 (2)
F(1)	0.0000	0.1544 (2)	0.0000
C(1)	0.1467 (9)	0.0000	−0.119 (2)
O(1)	0.1863 (8)	0.0000	−0.207 (1)
C(2)	0.2224 (9)	0.0000	0.226 (1)
C(2)	0.3979 (6)	0.0000	0.349 (1)
C(3)	0.0329 (6)	0.2461 (7)	0.1976 (9)
C(4)	−0.0738 (8)	0.2987 (9)	0.182 (1)
C(5)	0.0790 (7)	0.1717 (8)	0.3570 (8)
C(6)	0.1198 (8)	0.3329 (9)	0.226 (1)
H(1)	−0.0559 (8)	0.3775 (9)	0.144 (1)
H(2)	−0.0769 (8)	0.3008 (9)	0.294 (1)
H(3)	−0.1415 (8)	0.2615 (9)	0.091 (1)
H(4)	0.1466 (7)	0.1167 (8)	0.3709 (8)
H(5)	0.0951 (7)	0.2125 (8)	0.4654 (8)
H(6)	0.0434 (7)	0.1009 (8)	0.3496 (8)
H(7)	0.1413 (8)	0.3555 (9)	0.318 (1)
H(8)	0.0747 (8)	0.3994 (9)	0.119 (1)
H(9)	0.1844 (8)	0.3030 (9)	0.216 (1)

Scheme I[a]



[a] (i) 2Li-*t*-Bu$_2$P, Ar or N$_2$, THF, −78 °C; (ii) ≥2.5 equiv. of Li-*t*-Bu$_2$P, N$_2$, THF, −78 °C; (iii) CO, 3 atm, hexane solution, (iv) Li-*t*-Bu$_2$P, THF, −78 °C.

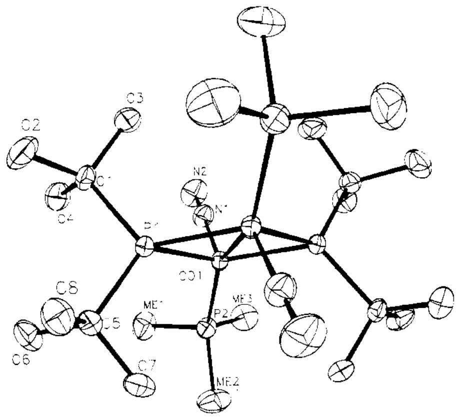


Figure 1. View of $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)N_2]_2$ (1). The ORTEP drawing of $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)(CO)]_2$ (2) is similar and is not shown here.

sphere employed. Under argon a mixture of $Co_2(\mu\text{-}t\text{-}Bu_2P)_2(PMe_3)_2Cl^2$ and $Co(PMe_3)_3Cl^{17}$ is obtained. Under dinitrogen however the main product is the bis(dinitrogen) complex $[Co(\mu\text{-}t\text{-}Bu_2P)(PMe_3)N_2]_2$ (1) which is obtained in good yield (see Scheme I).

The X-ray crystal structure of 1 (Figure 1) shows that the dimer has a geometry that is similar to the μ-PPh$_2$ dimer $[Co(\mu\text{-}PPh_2)(PEt_2Ph)(CO)]_2$ recently reported by Geoffroy and co-workers.[9] Thus the dinitrogen and PMe$_3$

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[17] Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 273.

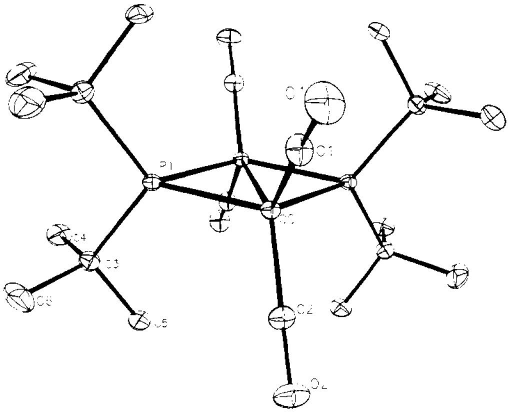

Figure 2. View of $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (**3**).

ligands lie in a plane perpendicular to the central $Co_2(t\text{-}Bu_2P)_2$ plane. Each cobalt atom has a distorted tetrahedral geometry with a short Co–Co distance of 2.414 Å, and each set of terminal ligands is trans with respect to the metal–metal bond. Both N_2 and PMe_3 ligands are bent away from the central Co_2P_2 core with the distortion from idealized tetrahedral geometry being greater for the larger PMe_3 group than for N_2 (P(2)–Co–Co′ = 145.7 (1)° and N(1)–Co–Co′ = 126.4 (1)°) (see Table II for the key structural parameters of **1**). The Co–Co distance in **1** is slightly longer than the Co═Co distances found for $[C_5Me_5Co(CO)]_2$ which should also have a cobalt–cobalt double bond (2.327 (2) and 2.338 (2) Å).[18] Cotton and Walton have noted that correlations between bond lengths and bond orders in Co–Co bonded complexes are complicated by changes in the nature of the bridging ligands.[19] For the complexes described here the Co–Co distances could be considered fairly long Co–Co double bonds; however since so few Co═Co bonded species have been described, further discussion of this point would be unduly speculative.

1 is unstable in hydrocarbon solutions at room temperature; a strong $\nu_{N\equiv N}$ stretch at 1910 cm^{-1} (solution) is rapidly replaced by several more peaks in the same region at 2070 (w), 2058 (w), 1900 (m), and 1892 (w) cm^{-1}, suggesting decomposition resulting in a mixture of species. We have been unable to isolate any new dinitrogen complexes from such solutions. Evaporation to dryness followed by recrystallization returns only **1** and small amounts of intractable pale brown materials that we have not characterized.

Carbonyl Complexes. The dinitrogen ligands of **1** are readily replaced by CO (3 atm) to give $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)(PMe_3)]_2$ (**2**). The structural parameters for **2** are very similar to those of **1** with the two terminal CO ligands occupying similar sites to those of the N_2 ligands in **1**. The bond lengths and angles of the central Co_2P_2 core of **2** are also similar to those of $[Co(\mu\text{-}Ph_2P)(CO)(PEt_2Ph)]_2$. Thus the Co–Co and Co–P(1) distances are 2.399 (4) and 2.216 (4) Å, respectively, in **2** vs. 2.343 (2) and 2.176 (2) Å in the diphenylphosphido-bridged complex. The Co–P(1)–Co and P–Co–P′ angles are also similar, 65.5 (1)° and 114.5 (5)°, respectively, for **2** vs. 65.23 (5) and 114.77 (5)°. Despite these similarities the chemical behavior of **2** is distinctly different from that of $[Co(\mu\text{-}Ph_2P)(CO)(PEt_2Ph)]_2$. Unlike $[Co(\mu\text{-}Ph_2P)CO(PEt_2Ph)]_2$ which readily reacts with CO (1 atm) at 25 °C to displace PEt_2Ph and quantitatively yields the trinuclear cluster $Co_3(\mu\text{-}PPh_2)_3(CO)_6$,[9] **2** does not react further with CO even at 50 atm and 50 °C.

The tetracarbonyl complex $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ (**3**) can be prepared in good yield by the straightforward reaction of "$Co(CO)_4I$" (generated in situ) with 1 equiv of Li-t-Bu_2P in THF. The structure has been determined by X-ray crystallography (Figure 2). It is similar to **1** and **2** in that two carbonyls occupy terminal sites on each "tetrahedral" cobalt with a planar Co_2P_2 core and a Co═Co distance of 2.426 (2) Å. So far, there appears to be no μ-Ph_2P analogue of **3** since $Co_2(\mu\text{-}PPh_2)_2(CO)_6$ with no metal–metal bond is light sensitive and readily loses CO to give the trinuclear complex $Co_3(\mu\text{-}PPh_2)_3(CO)_6$.[9]

NMR Data. The $^{31}P\{^1H\}$ NMR spectra of all three compounds show slightly broadened single resonances for the μ-t-Bu_2P groups; (**1**, δ 214.95, **2**, δ 264.10, **3**, δ 331.43). All are shifted well downfield and so are consistent with the phosphido bridging a short metal–metal distance. The downfield shifts in the ^{31}P NMR of Ph_2P groups bridging metal–metal bonds have already been noted by several groups of workers.[20]

For **1** and **2** single broad resonances to higher field (**1**, δ −18.26, **2**, δ −4.60) are assigned to the terminal PMe_3 groups. On cooling to −80 °C all spectra sharpen slightly; however no coupling between the phosphorus nuclei is observed in the spectra of either **1** and **2**. This is consistent with the distorted tetrahedral coordination about each Co with little s character in the metal ligand bonding orbitals. The broadening of the signals may also be due to quadrupolar coupling to the two ^{59}Co nuclei ($S = {}^7/_2$, 100%). Both these effects were observed by Geoffroy in the spectra of $[Co(\mu\text{-}Ph_2P)(PEt_2Ph)(CO)]_2$.[8,9] Futher studies on these and related systems are in progress.

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Registry No. 1, 86632-54-4; 2, 86632-55-5; 3, 86632-56-6; cobalt, 7440-48-4.

Supplementary Material Available: Tables of thermal parameters and structure factors for 1, 2, and 3 (23 pages). Ordering information is given on any current masthead page.

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(18) Bailey, W. I., Jr.; Collins, D. M.; Cotton, F. A.; Baldwin, J. C.; Kaska, W. C. *J. Organomet. Chem.* **1979**, *165*, 373. Ginsburg, R. E.; Cirjack, L. M.; Dahl, L. F. *J. Chem. Soc., Chem. Commun.* **1979**, 468.

(19) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; p 298 and references therein.

(20) See, for example Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163 and also reference 1.

(21) **Note Added in Proof**: See also: Hanson, B. E.; Fanurik, P. E.; Mancini, J. S. *Inorg. Chem.* **1982**, *21*, 3811 for a μ-PPh_2-bridged Co_2 complex.