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Ligand Substitution Processes in Tetranuclear Carbonyl Clusters. 3. Molecular Structures of $Co_4(CO)_8(\mu\text{-}CO)_3[P(C_6H_5)_3]$ and $Co_4(CO)_7(\mu\text{-}CO)_3[P(OCH_3)_3]_2$[1,2]

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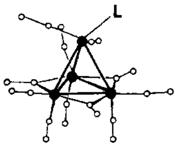
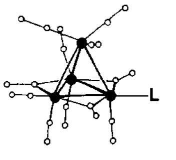
The structures of $Co_4(CO)_{11}[P(C_6H_5)_3]$ (**1**) and $Co_4(CO)_{10}[P(OCH_3)_3]_2$ (**2**) have been determined by single-crystal X-ray investigations. These are derived from the C_{3v} structures of the parent $Co_4(CO)_{12}$ species where one and two of the axial carbonyl ligands are replaced by $P(C_6H_5)_3$ and $P(OCH_3)_3$, respectively. Complex **1** crystallizes in the monoclinic space group $P2_1/n$ with a = 11.841 (4) Å, b = 17.045 (5) Å, c = 15.482 (4) Å, β = 100.55 (2)°, V = 3072 (1) Å^3, Z = 4, and ρ(calcd) = 1.74 g cm^{-3}. Diffraction data (2θ out to 55°) were collected with a four-circle autodiffractometer using Mo K$\bar{\alpha}$ radiation. The structure was refined by using the full-matrix least-squares procedure, and the resulting discrepancy indices were R_1 = 0.035 and R_2 = 0.039 for 4610 independent reflections. Complex **2** also crystallizes in the monoclinic space group $P2_1/n$ with a = 14.865 (3) Å, b = 11.904 (3) Å, c = 15.583 (3) Å, β = 90.94 (2)°, V = 2757 (1) Å^3, Z = 4, and ρ(calcd) = 1.84 g cm^{-3}. The discrepancy indices were R_1 = 0.045 and R_2 = 0.059 for 4156 independent reflections. Important bond distance parameters for complexes **1** and **2**, respectively, are as follows: Co–Co (basal-apical) = 2.530 and 2.528 Å, Co–Co (basal-basal) = 2.482 and 2.454 Å, Co–C(br)$_{av}$ = 1.937 and 1.929 Å, and Co–C(term)$_{av}$ = 1.797 and 1.784 Å. Two of the bridging CO ligands are asymmetrical in both complexes, with slightly shorter Co–C bond distances to the phosphine- or phosphite-substituted cobalt centers.

Introduction

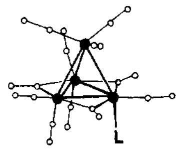
Successive carbon monoxide substitutional processes in the tetranuclear cobalt carbonyl cluster compounds $Co_4(CO)_9(\mu\text{-}CO)_3$ offer the possibility for formation of a large array of different isomeric species. For instance, substitution of one carbon monoxide group with a phosphine or phosphite ligand can lead to three different monosubstituted derivatives, at apical (I), equatorial (II), or axial (III) carbonyl sites. Further substitution of CO by L can afford up to seven disubstituted isomers. Fortunately the ^{13}C NMR spectrum of $Co_4(CO)_{11}[P(OCH_3)_3]$ at −82 °C indicates the presence of only one major species which is derived from the parent C_{3v} structure of $Co_4(CO)_9(\mu\text{-}CO)_3$ with the trimethyl phosphite ligand occupying either an axial or equatorial position in the basal plane.[3] The solution infrared spectrum in the ν(CO) region at ambient temperature is also consistent with substitution in the basal plane. Similarly, infrared analysis of ν(CO) vibrational modes in the disubstituted species $Co_4(CO)_7(\mu\text{-}CO)_3[P(OCH_3)_3]_2$ strongly suggests the presence of only one dominant isomeric form involving substitution in the basal cobalt triangle.[2]



I



II



III

The structures of $Ir_4(CO)_{10}[P(C_6H_5)_3]_2$ and $Ir_4(CO)_9[P(C_6H_5)_3]_3$ in the solid state have been determined with the configurations of carbonyl and phosphorus atoms around the Ir_4 cluster being as depicted in Figure 1.[4] These stereochemistries persist in solution for the analogous $Ir_4(CO)_{10}[P(C_6H_5)_2CH_3]_2$ and $Ir_4(CO)_9[P(C_6H_5)_2CH_3]_3$ derivatives as revealed by ^{13}C NMR investigations.[5] In contrast both X-ray and neutron diffraction studies on $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ show all three $P(OCH_3)_3$ ligands to be axially substituted about the plane of cobalt atoms.[6,7] Steric effects could nevertheless account for the difference in arrangements of phosphorus atoms in $Ir_4(CO)_9[P(C_6H_5)_3]_3$ and $HFeCo_3(CO)_9[P(OCH_3)_3]_3$.[8] In addition, the more highly substituted derivative of $Rh_4(CO)_{12}$, $[(C_6H_5)_2PCH_2P(C_6H_5)_2]_2Rh_4(CO)_8$, has been investigated by single-crystal X-ray methods and demonstrated to be derived from the C_{3v} structure of the parent dodecacarbonyl where one terminal carbonyl ligand on each rhodium is replaced by a phosphorus atom.[9]

In earlier papers in this series[2] we have embarked on reactivity studies in tetranuclear metal carbonyl clusters initially aimed at observing the kinetic parameters for progressive CO substitutional processes.[10] Our results for the relative rates of *dissociative* carbon monoxide loss with successive trimethyl phosphite substitution in the $Co_4(CO)_{12}$ species are provided in eq 1. These observations are in stark contrast to the

$$Co_4(CO)_{12} \xrightarrow{1} Co_4(CO)_{11}[P(OCH_3)_3] \xrightarrow{1.7} Co_4(CO)_{10}[P(OCH_3)_3]_2 \xrightarrow{3.9} Co_4(CO)_9[P(OCH_3)_3]_3 \quad (1)$$

$Ir_4(CO)_{12}$ system (eq 2), where substantial rate enhancement

$$Ir_4(CO)_{12} \xrightarrow{1} Ir_4(CO)_{11}[PPh_3] \xrightarrow{1320} Ir_4(CO)_{10}[PPh_3]_2 \xrightarrow{41\,800} Ir_4(CO)_9[PPh_3]_3 \quad (2)$$

for CO dissociation was noted with progressive triphenylphosphine substitution.[11] This enormous difference in behavior is likely in part to be due to steric effects, for indeed steric interactions are often responsible for large variances in ligand dissociation reactivities in mononuclear metal carbonyl phosphine and phosphite derivatives.[12]

So that the stereochemistry of products of the types afforded in eq 1 could be unequivocally established, the complexes $Co_4(CO)_{11}[P(C_6H_5)_3]$ and $Co_4(CO)_{10}[P(OCH_3)_3]_2$ have been fully characterized via single-crystal X-ray diffraction studies. Structural investigations of simple Lewis base derivatives of

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(1) Dedicated to the memory of Professor Paolo Chini.

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Table I. Atomic Coordinates for Nonhydrogen Atoms in Crystalline $Co_4(CO)_{11}[P(C_6H_5)_3]$[a]

atom type[b]	fractional coordinates			atom type[b]	fractional coordinates		
	x/a	y/b	z/c		x/a	y/b	z/c
Co(1)	0.140 64 (5)	0.106 06 (3)	0.164 03 (4)	C(8)	−0.002 46 (37)	0.063 55 (26)	0.102 03 (29)
Co(2)	0.156 45 (4)	0.248 43 (3)	0.131 81 (3)	C(9)	−0.064 54 (43)	0.291 29 (31)	0.230 48 (30)
Co(3)	−0.021 28 (4)	0.174 34 (3)	0.071 13 (3)	C(10)	0.122 82 (43)	0.220 49 (30)	0.336 88 (31)
Co(4)	0.023 91 (5)	0.203 13 (3)	0.233 87 (3)	C(11)	−0.072 63 (39)	0.128 56 (29)	0.265 02 (29)
P	0.272 44 (8)	0.277 78 (6)	0.036 68 (6)	C(12)	0.330 46 (34)	0.193 06 (23)	−0.013 44 (25)
O(1)	0.168 39 (38)	0.024 78 (24)	0.332 20 (25)	C(13)	0.257 27 (35)	0.137 72 (26)	−0.060 27 (29)
O(2)	0.281 34 (45)	−0.006 15 (27)	0.089 04 (31)	C(14)	0.299 51 (42)	0.073 14 (28)	−0.098 35 (30)
O(3)	0.354 06 (31)	0.180 23 (26)	0.247 49 (33)	C(15)	0.416 08 (45)	0.061 66 (29)	−0.087 43 (32)
O(4)	0.191 63 (38)	0.391 94 (24)	0.233 55 (28)	C(16)	0.489 63 (41)	0.114 63 (32)	−0.039 62 (38)
O(5)	−0.031 30 (28)	0.341 54 (19)	0.032 26 (26)	C(17)	0.447 98 (37)	0.179 90 (27)	−0.003 41 (32)
O(6)	−0.261 77 (29)	0.188 57 (29)	0.086 60 (26)	C(18)	0.402 23 (33)	0.334 57 (22)	0.077 87 (26)
O(7)	−0.068 28 (35)	0.155 92 (26)	−0.118 98 (23)	C(19)	0.458 43 (40)	0.373 59 (29)	0.018 78 (30)
O(8)	−0.051 97 (32)	0.005 41 (20)	0.090 26 (26)	C(20)	0.562 57 (44)	0.410 28 (30)	0.046 58 (37)
O(9)	−0.119 83 (39)	0.345 30 (26)	0.226 96 (29)	C(21)	0.611 47 (39)	0.408 95 (29)	0.134 14 (38)
O(10)	0.184 85 (38)	0.231 80 (30)	0.399 88 (26)	C(22)	0.557 54 (43)	0.372 50 (34)	0.193 57 (34)
O(11)	−0.130 90 (33)	0.081 41 (24)	0.281 75 (28)	C(23)	0.452 95 (39)	0.334 67 (29)	0.165 79 (29)
C(1)	0.156 94 (39)	0.056 13 (27)	0.266 41 (31)	C(24)	0.202 31 (35)	0.339 28 (24)	−0.053 69 (26)
C(2)	0.226 98 (46)	0.039 09 (31)	0.114 63 (35)	C(25)	0.171 44 (37)	0.313 97 (29)	−0.140 12 (29)
C(3)	0.265 57 (38)	0.182 23 (28)	0.200 17 (33)	C(26)	0.112 39 (45)	0.364 27 (40)	−0.203 60 (34)
C(4)	0.181 28 (41)	0.335 57 (29)	0.193 05 (31)	C(27)	0.085 69 (47)	0.438 58 (42)	−0.181 59 (41)
C(5)	0.017 23 (34)	0.286 51 (24)	0.062 57 (28)	C(28)	0.115 51 (51)	0.463 98 (34)	−0.098 36 (44)
C(6)	−0.167 77 (38)	0.183 95 (29)	0.080 84 (28)	C(29)	0.174 19 (45)	0.415 27 (29)	−0.033 64 (34)
C(7)	−0.047 25 (38)	0.161 29 (28)	−0.045 49 (29)				

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

Table II. Anisotropic Thermal Parameters for Nonhydrogen Atoms in Crystalline $Co_4(CO)_{11}[P(C_6H_5)_3]$[a,b]

atom type[c]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	2.56 (2)	2.41 (2)	3.10 (2)	0.47 (2)	0.82 (2)	0.38 (2)
Co(2)	2.24 (2)	2.28 (2)	2.63 (2)	−0.10 (2)	0.46 (2)	0.05 (2)
Co(3)	2.27 (2)	2.84 (2)	2.43 (2)	−0.00 (2)	0.28 (2)	−0.14 (2)
Co(4)	2.77 (2)	3.21 (2)	2.46 (2)	0.17 (2)	0.80 (2)	−0.20 (2)
P	2.41 (4)	2.48 (4)	2.47 (4)	−0.25 (3)	0.41 (3)	−0.04 (3)
O(1)	8.29 (25)	5.38 (20)	4.64 (18)	1.84 (18)	1.99 (17)	2.02 (16)
O(2)	10.52 (32)	7.06 (25)	8.14 (27)	5.60 (24)	5.66 (25)	2.37 (21)
O(3)	3.27 (16)	6.75 (24)	10.54 (31)	−1.03 (16)	−2.27 (18)	3.74 (22)
O(4)	8.02 (25)	4.93 (20)	6.90 (23)	−2.31 (18)	2.62 (20)	−3.12 (18)
O(5)	3.80 (15)	3.47 (16)	7.43 (22)	0.86 (12)	0.32 (14)	1.51 (15)
O(6)	2.68 (15)	10.98 (32)	5.35 (19)	0.11 (17)	0.84 (13)	0.23 (20)
O(7)	6.88 (22)	8.24 (26)	2.78 (14)	1.47 (19)	0.20 (14)	−0.54 (16)
O(8)	5.25 (18)	3.31 (15)	6.78 (21)	−1.54 (13)	0.98 (16)	−0.45 (14)
O(9)	7.73 (25)	6.27 (23)	6.52 (23)	3.88 (21)	0.78 (19)	−1.07 (18)
O(10)	6.43 (23)	9.74 (31)	4.17 (18)	−0.47 (21)	−0.92 (17)	−1.36 (19)
O(11)	5.05 (19)	5.68 (20)	7.36 (23)	−0.83 (16)	3.18 (17)	1.06 (17)
C(1)	3.94 (20)	3.15 (19)	4.16 (21)	0.45 (16)	1.23 (17)	0.62 (16)
C(2)	4.97 (24)	4.51 (24)	4.89 (24)	1.70 (20)	2.18 (20)	1.38 (20)
C(3)	2.87 (18)	4.03 (22)	5.00 (23)	−0.07 (16)	0.24 (17)	1.35 (18)
C(4)	4.14 (21)	3.83 (22)	3.84 (20)	−0.72 (17)	1.00 (17)	−0.50 (17)
C(5)	2.67 (16)	2.72 (18)	3.91 (19)	0.25 (14)	0.69 (14)	0.08 (15)
C(6)	3.16 (19)	4.92 (24)	2.93 (18)	0.05 (17)	0.29 (14)	−0.18 (16)
C(7)	3.60 (19)	4.29 (22)	2.95 (19)	0.52 (16)	0.23 (15)	−0.21 (16)
C(8)	3.42 (18)	3.12 (19)	3.71 (19)	−0.20 (15)	0.94 (15)	−0.45 (15)
C(9)	4.58 (23)	4.42 (23)	3.41 (19)	0.75 (19)	0.69 (17)	−0.65 (17)
C(10)	4.37 (22)	4.75 (24)	3.21 (19)	−0.07 (19)	0.47 (17)	−0.57 (17)
C(11)	3.64 (20)	4.51 (23)	3.20 (18)	0.92 (18)	1.45 (15)	0.42 (16)
C(12)	3.00 (16)	2.66 (17)	2.65 (15)	−0.27 (13)	0.61 (13)	−0.03 (13)
C(13)	2.95 (17)	3.47 (19)	3.84 (19)	−0.46 (15)	1.11 (14)	−0.54 (15)
C(14)	4.49 (22)	3.46 (20)	3.72 (20)	−0.66 (17)	1.21 (17)	−0.91 (16)
C(15)	5.07 (24)	3.58 (21)	4.00 (21)	0.88 (18)	1.34 (18)	−0.31 (17)
C(16)	3.02 (19)	4.74 (25)	6.32 (28)	1.11 (18)	0.68 (19)	−0.59 (22)
C(17)	2.93 (17)	3.60 (20)	4.69 (22)	0.14 (16)	0.34 (16)	−0.79 (17)
C(18)	2.60 (15)	2.43 (16)	3.31 (17)	−0.34 (12)	0.42 (13)	−0.22 (13)
C(19)	3.78 (20)	4.54 (23)	3.64 (20)	−1.10 (18)	0.80 (16)	0.49 (17)
C(20)	4.16 (22)	4.44 (24)	5.41 (26)	−1.38 (19)	1.65 (20)	0.25 (20)
C(21)	2.85 (19)	3.70 (22)	6.65 (30)	−0.95 (16)	0.62 (19)	−0.39 (20)
C(22)	3.96 (22)	5.87 (29)	4.31 (23)	−1.59 (21)	−0.34 (18)	−0.44 (21)
C(23)	3.67 (19)	4.35 (23)	3.42 (19)	−1.43 (17)	0.36 (15)	0.19 (16)
C(24)	2.96 (17)	3.21 (18)	3.05 (17)	−0.18 (14)	0.70 (13)	0.52 (14)
C(25)	3.23 (19)	4.68 (23)	3.34 (18)	−0.61 (16)	0.38 (15)	0.33 (17)
C(26)	3.99 (23)	7.25 (35)	3.94 (23)	−0.72 (24)	−0.40 (18)	1.50 (23)
C(27)	4.33 (25)	7.38 (37)	5.49 (31)	0.90 (25)	0.25 (22)	3.63 (28)
C(28)	5.42 (28)	4.75 (27)	6.76 (34)	0.99 (22)	1.36 (25)	2.24 (25)
C(29)	4.95 (24)	3.60 (21)	4.67 (23)	0.44 (18)	1.21 (19)	0.60 (18)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] The form of the anisotropic thermal parameter is given in ref 18. [c] Atoms are labeled in agreement with Figure 1.

Table III. Atomic Coordinates for Nonhydrogen Atoms in Crystalline $Co_4(CO)_{10}[P(OCH_3)_3]_2$[a]

atom type[b]	fractional coordinates		
	x/a	y/b	z/c
Co(1)	0.021 28 (5)	0.190 30 (5)	0.173 45 (4)
Co(2)	0.018 89 (5)	0.215 47 (6)	0.330 34 (4)
Co(3)	−0.105 27 (5)	0.286 35 (6)	0.240 64 (5)
Co(4)	−0.089 29 (5)	0.077 27 (6)	0.259 82 (5)
P(1)	0.107 96 (11)	0.309 40 (12)	0.111 32 (9)
P(2)	0.104 36 (12)	0.352 95 (14)	0.370 70 (10)
O(1)	0.063 99 (43)	−0.004 20 (44)	0.070 55 (36)
O(2)	0.173 88 (29)	0.092 25 (39)	0.266 05 (30)
O(3)	0.067 74 (51)	0.077 73 (66)	0.476 15 (46)
O(4)	−0.130 14 (35)	0.310 02 (50)	0.425 89 (32)
O(5)	−0.300 87 (34)	0.269 53 (48)	0.232 39 (41)
O(6)	−0.092 90 (40)	0.530 08 (40)	0.222 21 (41)
O(7)	−0.119 85 (32)	0.262 92 (47)	0.053 77 (29)
O(8)	−0.217 21 (42)	0.040 28 (58)	0.398 01 (38)
O(9)	0.017 16 (39)	−0.127 56 (47)	0.282 35 (51)
O(10)	−0.204 84 (40)	0.005 37 (52)	0.115 30 (40)
O(11)	0.096 55 (37)	0.329 44 (43)	0.011 37 (29)
O(12)	0.095 08 (39)	0.434 02 (37)	0.141 82 (35)
O(13)	0.210 91 (31)	0.280 36 (42)	0.126 66 (34)
O(14)	0.067 06 (39)	0.471 45 (40)	0.343 60 (37)
O(15)	0.127 35 (73)	0.364 82 (68)	0.467 54 (40)
O(16)	0.202 17 (39)	0.358 47 (59)	0.330 32 (45)
C(1)	0.045 78 (44)	0.074 97 (51)	0.108 66 (40)
C(2)	0.107 58 (39)	0.142 91 (47)	0.259 95 (37)
C(3)	0.045 85 (51)	0.132 72 (65)	0.420 04 (47)
C(4)	−0.088 53 (44)	0.282 66 (54)	0.366 12 (41)
C(5)	−0.224 32 (48)	0.275 84 (53)	0.235 26 (46)
C(6)	−0.096 07 (46)	0.435 34 (51)	0.229 60 (46)
C(7)	−0.083 11 (38)	0.250 11 (49)	0.119 31 (38)
C(8)	−0.167 73 (49)	0.057 68 (59)	0.346 73 (49)
C(9)	−0.022 03 (45)	−0.046 98 (58)	0.274 22 (54)
C(10)	−0.160 81 (46)	0.034 43 (53)	0.169 93 (47)
C(11)	0.105 61 (74)	0.244 18 (78)	−0.051 34 (51)
C(12)	0.108 70 (78)	0.534 95 (66)	0.092 37 (76)
C(13)	0.284 95 (50)	0.351 01 (73)	0.102 86 (62)
C(14)	0.119 30 (71)	0.575 63 (68)	0.349 58 (75)
C(15)	0.089 10 (94)	0.369 36 (145)	0.539 87 (67)
C(16)	0.280 66 (69)	0.313 29 (131)	0.358 45 (93)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 2.

Table IV. Anisotropic Thermal Parameters for Nonhydrogen Atoms in Crystalline $Co_4(CO)_{10}[P(OCH_3)_3]_2$[a,b]

atom type[c]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	3.52 (3)	3.00 (3)	3.82 (3)	0.00 (2)	−0.15 (2)	0.03 (2)
Co(2)	3.66 (3)	3.52 (3)	3.75 (3)	−0.41 (2)	−0.28 (2)	0.35 (2)
Co(3)	3.60 (3)	3.30 (3)	4.69 (3)	0.39 (2)	−0.19 (2)	0.08 (2)
Co(4)	3.69 (4)	3.20 (3)	5.50 (4)	−0.58 (2)	−0.18 (3)	0.36 (3)
P(1)	4.35 (7)	3.54 (6)	4.17 (6)	−0.17 (5)	0.31 (5)	0.24 (5)
P(2)	5.13 (8)	4.71 (7)	4.38 (7)	−0.86 (6)	−0.73 (6)	−0.54 (6)
O(1)	10.65 (39)	5.12 (24)	7.60 (30)	1.76 (25)	−1.36 (27)	−2.24 (22)
O(2)	4.20 (21)	5.66 (22)	6.58 (24)	1.27 (17)	−0.52 (17)	0.57 (19)
O(3)	11.73 (48)	12.20 (52)	9.88 (42)	−2.80 (40)	−3.57 (37)	7.15 (40)
O(4)	6.25 (27)	9.40 (35)	5.38 (23)	0.45 (24)	1.41 (20)	−1.31 (23)
O(5)	3.77 (25)	7.27 (30)	11.13 (40)	0.57 (21)	−0.15 (23)	0.18 (27)
O(6)	8.99 (35)	3.73 (21)	10.70 (40)	0.72 (22)	−0.63 (29)	0.73 (23)
O(7)	5.96 (25)	7.68 (28)	5.00 (21)	0.35 (21)	−1.73 (18)	0.48 (20)
O(8)	7.68 (33)	10.23 (41)	6.94 (30)	−2.11 (30)	2.23 (26)	0.07 (28)
O(9)	6.70 (32)	5.14 (26)	15.93 (59)	1.05 (23)	−1.27 (33)	2.08 (31)
O(10)	7.75 (33)	7.96 (33)	8.60 (34)	−1.72 (27)	−2.59 (27)	−1.61 (28)
O(11)	8.33 (31)	6.44 (26)	4.70 (21)	−1.35 (23)	0.36 (20)	0.51 (19)
O(12)	9.39 (34)	3.81 (20)	7.64 (29)	0.14 (20)	2.88 (25)	0.10 (19)
O(13)	4.58 (22)	6.11 (24)	7.90 (28)	−0.76 (18)	0.15 (19)	1.90 (21)
O(14)	8.72 (33)	4.18 (21)	8.44 (31)	−1.58 (21)	−1.51 (25)	−0.12 (21)
O(15)	23.97 (92)	10.63 (49)	4.69 (28)	−5.08 (55)	−3.04 (42)	−0.63 (30)
O(16)	6.13 (32)	9.78 (40)	10.78 (43)	−1.99 (29)	−0.27 (29)	−2.19 (33)
C(1)	5.36 (32)	4.01 (25)	4.96 (28)	0.22 (22)	−1.08 (23)	−0.29 (22)
C(2)	3.73 (27)	3.76 (22)	4.84 (25)	−0.20 (20)	−0.32 (19)	0.17 (19)
C(3)	6.25 (38)	6.39 (37)	5.51 (33)	−1.21 (30)	−0.52 (28)	1.78 (29)
C(4)	4.66 (30)	4.95 (28)	5.06 (28)	−0.40 (23)	0.32 (23)	−0.14 (23)
C(5)	4.47 (35)	4.29 (27)	6.86 (36)	0.70 (23)	−0.18 (25)	−0.28 (25)
C(6)	5.60 (35)	3.56 (25)	6.65 (35)	0.66 (23)	−0.68 (27)	0.20 (23)
C(7)	3.88 (27)	4.08 (23)	4.89 (27)	0.15 (20)	−0.36 (20)	0.38 (20)
C(8)	5.29 (36)	5.27 (32)	6.27 (36)	−0.77 (26)	−0.02 (28)	0.30 (27)
C(9)	4.29 (32)	4.38 (29)	9.42 (49)	−0.65 (24)	−0.43 (30)	0.98 (30)
C(10)	5.15 (33)	4.09 (26)	6.80 (36)	−0.87 (24)	−0.49 (27)	−0.15 (25)
C(11)	13.44 (74)	6.56 (42)	5.15 (35)	−1.58 (46)	1.81 (41)	−1.38 (32)
C(12)	12.67 (74)	3.75 (32)	12.83 (75)	0.06 (39)	2.41 (59)	2.17 (40)
C(13)	4.50 (36)	7.36 (44)	10.24 (56)	−1.35 (32)	0.28 (34)	0.80 (41)
C(14)	10.41 (64)	4.39 (35)	13.54 (80)	−2.25 (39)	0.90 (57)	−1.21 (41)
C(15)	13.76 (94)	20.51 (139)	5.33 (46)	1.05 (92)	1.55 (53)	−2.31 (66)
C(16)	5.22 (51)	18.50 (130)	14.24 (96)	2.37 (63)	−1.40 (54)	2.25 (86)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] The form of the anisotropic thermal parameter is given in ref 18. [c] Atoms are labeled in agreement with Figure 2.

$Co_4(CO)_{12}$ are moreover of importance because of inherent inaccuracies in the molecular dimensions in the parent species due to disorder.[9,13-15]

Experimental Section

Crystallographic Studies. All crystallographic analyses were carried out by Dr. Cynthia S. Day at Crystalytics Co. (Lincoln, NE) on crystals obtained by methods described in our previous publications on this subject.[2]

$Co_4(CO)_{11}[P(C_6H_5)_3]$. A parallelepiped-shaped crystal with dimensions of 0.50 × 0.50 × 0.63 mm was glued to the inside of a thin glass capillary under nitrogen. This crystal was then accurately centered optically on a computer-controlled four-circle Nicolet au-

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(13) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 1812.

(14) Wei, C. H.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 4792.

(15) Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384.

Table V. Bond Distances (Å) in $Co_4(CO)_{11}[P(C_6H_5)_3]$

atom 1	atom 2	dist[a]	atom 1	atom 2	dist[a]	atom 1	atom 2	dist[a]	atom 1	atom 2	dist[a]
Co(1)	Co(2)	2.491 (1)	Co(2)	P	2.246 (1)	Co(4)	C(9)	1.827 (5)	C(4)	O(4)	1.142 (6)
Co(1)	Co(3)	2.468 (1)	Co(2)	C(3)	1.887 (5)	Co(4)	C(10)	1.822 (5)	C(5)	O(5)	1.154 (5)
Co(1)	Co(4)	2.523 (1)	Co(2)	C(4)	1.758 (5)	Co(4)	C(11)	1.832 (5)	C(6)	O(6)	1.136 (6)
Co(1)	C(1)	1.778 (5)	Co(2)	C(5)	1.908 (4)	P	C(12)	1.832 (4)	C(7)	O(7)	1.123 (6)
Co(1)	C(2)	1.794 (5)	Co(3)	Co(4)	2.526 (1)	P	C(18)	1.829 (4)	C(8)	O(8)	1.149 (6)
Co(1)	C(3)	1.971 (5)	Co(3)	C(5)	1.976 (4)	P	C(24)	1.822 (4)	C(9)	O(9)	1.125 (7)
Co(1)	C(8)	1.929 (4)	Co(3)	C(6)	1.776 (5)	C(1)	O(1)	1.136 (6)	C(10)	O(10)	1.125 (6)
Co(2)	Co(3)	2.487 (3)	Co(3)	C(7)	1.789 (4)	C(2)	O(2)	1.122 (7)	C(11)	O(11)	1.120 (6)
Co(2)	Co(4)	2.542 (1)	Co(3)	C(8)	1.951 (4)	C(3)	O(3)	1.164 (6)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Bond Angles (Deg) for $Co_4(CO)_{11}[P(C_6H_5)_3]$

atom 1	atom 2	atom 3	angle[a]	atom 1	atom 2	atom 3	angle[a]
Co(2)	Co(1)	Co(3)	60.19 (2)	Co(2)	Co(3)	C(7)	114.94 (15)
Co(2)	Co(1)	Co(4)	60.93 (2)	Co(2)	Co(3)	C(8)	110.38 (13)
Co(2)	Co(1)	C(1)	130.15 (15)	Co(4)	Co(3)	C(5)	82.51 (12)
Co(2)	Co(1)	C(2)	117.70 (17)	Co(4)	Co(3)	C(6)	85.96 (15)
Co(2)	Co(1)	C(3)	48.33 (14)	Co(4)	Co(3)	C(7)	175.27 (15)
Co(2)	Co(1)	C(8)	110.95 (13)	Co(4)	Co(3)	C(8)	87.11 (13)
Co(3)	Co(1)	Co(4)	60.81 (2)	C(5)	Co(3)	C(6)	99.06 (19)
Co(3)	Co(1)	C(1)	133.73 (15)	C(5)	Co(3)	C(7)	92.96 (19)
Co(3)	Co(1)	C(2)	119.61 (17)	C(5)	Co(3)	C(8)	159.37 (18)
Co(3)	Co(1)	C(3)	108.52 (14)	C(6)	Co(3)	C(7)	96.13 (21)
Co(3)	Co(1)	C(8)	50.89 (13)	C(6)	Co(3)	C(8)	97.94 (20)
Co(4)	Co(1)	C(1)	84.86 (15)	C(7)	Co(3)	C(8)	96.78 (20)
Co(4)	Co(1)	C(2)	178.33 (17)	Co(1)	Co(4)	Co(2)	58.92 (2)
Co(4)	Co(1)	C(3)	83.57 (14)	Co(1)	Co(4)	Co(3)	58.52 (2)
Co(4)	Co(1)	C(8)	87.67 (13)	Co(1)	Co(4)	C(9)	152.04 (16)
C(1)	Co(1)	C(2)	95.63 (23)	Co(1)	Co(4)	C(10)	99.60 (16)
C(1)	Co(1)	C(3)	96.25 (21)	Co(1)	Co(4)	C(11)	94.31 (15)
C(1)	Co(1)	C(8)	101.88 (20)	Co(2)	Co(4)	Co(3)	58.76 (2)
C(2)	Co(1)	C(3)	94.79 (22)	Co(2)	Co(4)	C(9)	98.52 (16)
C(2)	Co(1)	C(8)	93.79 (22)	Co(2)	Co(4)	C(10)	97.10 (16)
C(3)	Co(1)	C(8)	159.06 (19)	Co(2)	Co(4)	C(11)	149.34 (15)
Co(1)	Co(2)	Co(3)	59.44 (2)	Co(3)	Co(4)	C(9)	96.63 (16)
Co(1)	Co(2)	Co(4)	60.14 (2)	Co(3)	Co(4)	C(10)	152.81 (16)
Co(1)	Co(2)	P	115.19 (3)	Co(3)	Co(4)	C(11)	95.70 (15)
Co(1)	Co(2)	C(3)	51.26 (15)	C(9)	Co(4)	C(10)	99.49 (22)
Co(1)	Co(2)	C(4)	136.58 (16)	C(9)	Co(4)	C(11)	101.31 (22)
Co(1)	Co(2)	C(5)	110.79 (13)	C(10)	Co(4)	C(11)	102.38 (22)
Co(3)	Co(2)	Co(4)	60.30 (2)	Co(2)	P	C(12)	115.08 (13)
Co(3)	Co(2)	P	116.24 (3)	Co(2)	P	C(18)	117.70 (13)
Co(3)	Co(2)	C(3)	110.70 (15)	Co(2)	P	C(24)	112.59 (14)
Co(3)	Co(2)	C(4)	132.80 (16)	C(12)	P	C(18)	102.03 (18)
Co(3)	Co(2)	C(5)	51.40 (13)	C(12)	P	C(24)	106.37 (18)
Co(4)	Co(2)	P	174.98 (4)	C(18)	P	C(24)	101.47 (18)
Co(4)	Co(2)	C(3)	84.67 (15)	Co(1)	C(1)	O(1)	179.21 (44)
Co(4)	Co(2)	C(4)	89.01 (16)	Co(1)	C(2)	O(2)	174.91 (51)
Co(4)	Co(2)	C(5)	83.36 (13)	Co(1)	C(3)	Co(2)	80.41 (19)
P	Co(2)	C(3)	93.60 (15)	Co(1)	C(3)	O(3)	134.57 (41)
P	Co(2)	C(4)	95.94 (16)	Co(2)	C(3)	O(3)	144.64 (43)
P	Co(2)	C(5)	97.17 (13)	Co(2)	C(4)	O(4)	176.42 (46)
C(3)	Co(2)	C(4)	99.96 (22)	Co(2)	C(5)	Co(3)	79.59 (16)
C(3)	Co(2)	C(5)	161.94 (20)	Co(2)	C(5)	O(5)	145.05 (37)
C(4)	Co(2)	C(5)	93.30 (20)	Co(3)	C(5)	O(5)	135.25 (36)
Co(1)	Co(3)	Co(2)	60.38 (2)	Co(3)	C(6)	O(6)	178.64 (44)
Co(1)	Co(3)	Co(4)	60.67 (2)	Co(3)	C(7)	O(7)	176.26 (43)
Co(1)	Co(3)	C(5)	109.34 (12)	Co(1)	C(8)	Co(3)	78.98 (17)
Co(1)	Co(3)	C(6)	131.37 (15)	Co(1)	C(8)	O(8)	141.18 (38)
Co(1)	Co(3)	C(7)	120.08 (15)	Co(3)	C(8)	O(8)	139.82 (38)
Co(1)	Co(3)	C(8)	50.12 (13)	Co(4)	C(9)	O(9)	178.83 (47)
Co(2)	Co(3)	Co(4)	60.95 (2)	Co(4)	C(10)	O(10)	179.04 (47)
Co(2)	Co(3)	C(5)	49.01 (12)	Co(4)	C(11)	O(11)	177.60 (44)
Co(2)	Co(3)	C(6)	133.90 (15)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

todiffractometer, and a total of 15 high-angle ($2\theta_{\mathrm{Mo}\,K\bar{\alpha}} > 30°$) reflections were used to align the crystal and calculate angular settings for each reflection. A least-squares refinement of the diffraction geometry for these 15 reflections recorded at ambient laboratory temperature of 20 ± 1 °C with graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.71073 Å) showed the crystal to belong to the monoclinic system with lattice constants a = 11.841 (4) Å, b = 17.045 (5) Å, c = 15.482 (4) Å, and β = 100.55 (2)°. Systematic absences indicated the space group to be $P2_1/n$ (a special setting of $P2_1/c$–C_{2h}^5, No. 14).[16] A unit cell of four $Co_4(CO)_{11}[P(C_6H_5)_3]$ molecules per 3072 (1) Å^3 afforded a calculated density of 1.74 g cm^{-3}. The linear absorption coefficient of the crystal for Mo K$\bar{\alpha}$ radiation is 23.2 cm^{-1}.[17a]

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(16) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I.

(17) "International Tables for X-Ray Crystallography"; Vol. IV, Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 55–66; (b) pp 149–150.

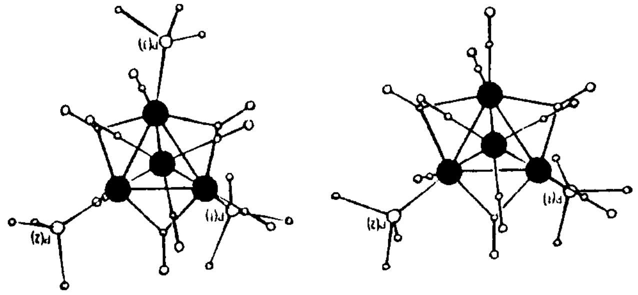

Figure 1. Projection of the $Ir_4(CO)_{10}[PPh_3]_2$ and $Ir_4(CO)_9[PPh_3]_3$ molecules on the basal iridium plane (taken from ref 4; reprinted with permission of The Chemical Society).

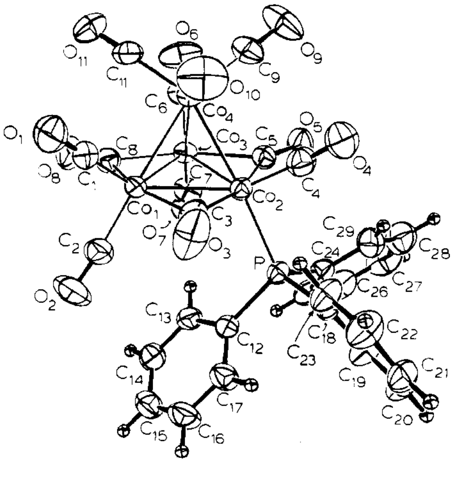

Figure 2. Perspective ORTEP drawing of the $Co_4(CO)_{11}[P(C_6H_5)_3]$ molecule. All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

Intensity measurements utilized graphite-monochromated Mo $K\bar{\alpha}$ radiation and the ω scanning technique with a 4° takeoff angle and a normal-focus X-ray tube. A total of 7044 independent reflections having $2\theta \leq 55°$ were measured in two shells. A scanning rate of 4°/min was employed for the scan between ω settings 0.50° respectively above and below the calculated $K\bar{\alpha}$ doublet value for those reflections having $3° < 2\theta_{Mo\,K\bar{\alpha}} \leq 43°$, and a scanning rate of 3°/min was used for reflections having $43° < 2\theta_{Mo\,K\bar{\alpha}} \leq 55°$. Each of these 0.90° scans was divided into 19 equal time intervals, and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for one-fourth the total time used for the net scan, were measured at ω settings 0.9° above and below the calculated value for each reflection. The six standard reflections, measured every 300 reflections as a monitor for possible disalignment and/or deterioration of the crystal, gave no indication of either. The intensities were reduced without absorption corrections to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 7044 reflections examined, 2434 were eventually rejected as unobserved by applying the rejection criterion $I < 3.0\ \sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity computed from $\sigma^2(I) = (C_t + k^2B)$, where C_t is the total scan count, k is the ratio of scan time to background time, and B is the total background count.

The four cobalt atoms were located by using direct methods; the 41 remaining nonhydrogen atoms appeared in a single difference Fourier synthesis based on refined parameters for the Co atoms [$R_1 = 0.336$ and 2752 independent reflections having $2\theta_{Mo\,K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$]. Isotropic unit-weighted full-matrix least-squares refinement for the 45 nonhydrogen atoms gave R_1 (unweighted, based on F) = 0.064 and R_2 (weighted) = 0.067, where

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| \qquad R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2\}^{1/2}$$

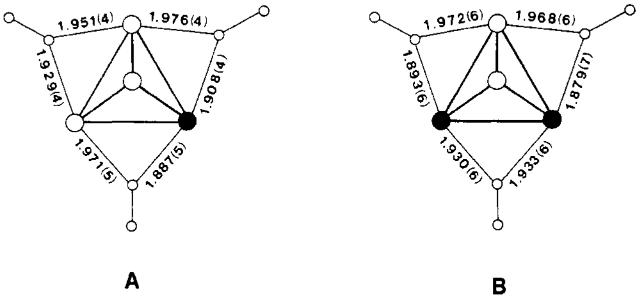

Figure 3. Cobalt–carbon bond distances of the bridging CO groups in (A) $Co_4(CO)_{11}[P(C_6H_5)_3]$ and (B) $Co_4(CO)_{10}[P(OCH_3)_3]_2$. The phosphorus donor ligands are attached to the cobalt atoms represented by closed circles.

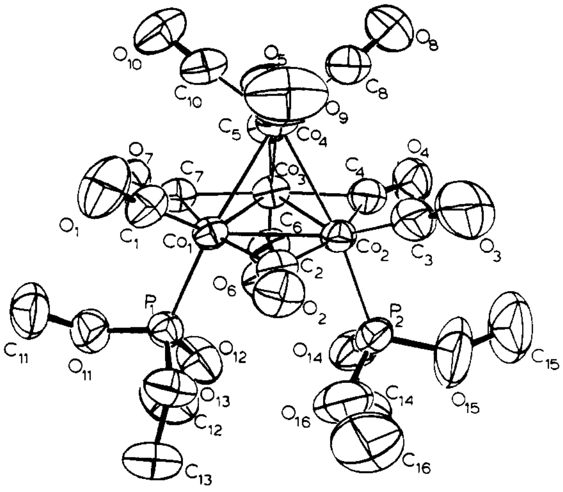

Figure 4. Perspective ORTEP drawing of the $Co_4(CO)_{10}[P(OCH_3)_3]_2$ molecule. All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Atom C_9 is partially hidden from view.

Anisotropic refinement converged to $R_1 = 0.035$ and $R_2 = 0.041$ for 2752 reflections having $2\theta_{Mo\,K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$.[18] These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann[19] and an anomalous dispersion correction to the scattering factors of the cobalt and phosphorus atoms.[17b]

Atomic positions were then calculated for all hydrogen atoms with assumption of idealized sp^2 geometry and a C–H bond length of 0.95 Å. The final cycles of empirically weighted[20,21a] full-matrix least-squares refinement, in which the structural parameters for all nonhydrogen atoms were varied but those for isotropic (B = 5.00 Å) hydrogen atoms were not, converged to $R_1 = 0.035$, $R_2 = 0.039$, and GOF = 1.329[22] for 4610 independent reflections having $2\theta_{Mo\,K\bar{\alpha}} \leq 55.0°$ and $I > 3\sigma(I)$. During the final cycle of refinement, no parameter shifted by more than $0.02\sigma_p$ with the average shift being $0.00\sigma_p$ where σ_p is the estimated standard deviation of the parameter. A final difference Fourier synthesis revealed no peaks present above the noise level.

$Co_4(CO)_{10}[P(OCH_3)_3]_2$. Data collection was carried out in a totally

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(18) The anisotropic thermal parameter is of the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

(19) Cromer, D. T.; Mann, J. L. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(20) The weighting scheme used in the least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ is defined as $w = 1/\sigma_F^2$.

(21) For empirical weights $\sigma_F = \sum_0^3 a_n|F_o|^n = a_0 + a_1|F_o| + a_2|F_o|^2 + a_3|F_o|^3$ with the a_n being coefficients from the least-squares fitting of the curve $||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$: (a) for $Co_4(CO)_{11}[P(C_6H_5)_3]$ $a_0 = 1.97$, $a_1 = -3.59 \times 10^{-2}$, $a_2 = 4.36 \times 10^{-4}$, $a_3 = -1.00 \times 10^{-6}$; (b) for $Co_4(CO)_{10}[P(OCH_3)_3]_2$: $a_0 = 1.42$, $a_1 = -1.63 \times 10^{-2}$, $a_2 = 4.00 \times 10^{-4}$, $a_3 = -1.09 \times 10^{-6}$.

(22) GOF = $\{\sum w(|F_o| - |F_c|)^2/(NO - NV)\}^{1/2}$, where NO is the number of observations and NV is the number of variables.

Table VII. Bond Distances (Å) in $Co_4(CO)_{10}[P(OCH_3)_3]_2$

atom 1	atom 2	dist[a]	atom 1	atom 2	dist[a]	atom 1	atom 2	dist[a]	atom 1	atom 2	dist[a]
Co(1)	Co(2)	2.464 (1)	Co(2)	C(3)	1.751 (7)	P(1)	O(12)	1.570 (5)	C(7)	O(7)	1.160 (8)
Co(1)	Co(3)	2.451 (1)	Co(2)	C(4)	1.879 (7)	P(1)	O(13)	1.583 (5)	C(8)	O(8)	1.114 (10)
Co(1)	Co(4)	2.529 (1)	Co(3)	Co(4)	2.518 (1)	P(2)	O(14)	1.571 (5)	C(9)	O(9)	1.128 (9)
Co(1)	P(1)	2.156 (2)	Co(3)	C(5)	1.775 (7)	P(2)	O(15)	1.548 (7)	C(10)	O(10)	1.120 (9)
Co(1)	C(1)	1.746 (6)	Co(3)	C(6)	1.787 (6)	P(2)	O(16)	1.595 (6)	C(11)	O(11)	1.417 (10)
Co(1)	C(2)	1.930 (6)	Co(3)	C(4)	1.968 (6)	C(1)	O(1)	1.149 (8)	C(12)	O(12)	1.443 (10)
Co(1)	C(7)	1.893 (6)	Co(3)	C(7)	1.972 (6)	C(2)	O(2)	1.158 (7)	C(13)	O(13)	1.439 (9)
Co(2)	Co(3)	2.447 (1)	Co(4)	C(8)	1.817 (7)	C(3)	O(3)	1.136 (11)	C(14)	O(14)	1.465 (10)
Co(2)	Co(4)	2.538 (1)	Co(4)	C(9)	1.797 (7)	C(4)	O(4)	1.173 (8)	C(15)	O(15)	1.272 (14)
Co(2)	P(2)	2.159 (2)	Co(4)	C(10)	1.817 (7)	C(5)	O(5)	1.141 (9)	C(16)	O(16)	1.351 (13)
Co(2)	C(2)	1.933 (6)	P(1)	O(11)	1.582 (5)	C(6)	O(6)	1.135 (8)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VIII. Bond Angles (Deg) for $Co_4(CO)_{10}[P(OCH_3)_3]_2$

atom 1	atom 2	atom 3	angle[a]	atom 1	atom 2	atom 3	angle[a]
Co(2)	Co(1)	Co(3)	59.72 (3)	Co(4)	Co(3)	C(7)	83.14 (17)
Co(2)	Co(1)	Co(4)	61.09 (3)	C(4)	Co(3)	C(5)	98.92 (29)
Co(2)	Co(1)	P(1)	112.59 (5)	C(4)	Co(3)	C(6)	96.27 (29)
Co(2)	Co(1)	C(1)	132.52 (21)	C(4)	Co(3)	C(7)	158.04 (26)
Co(2)	Co(1)	C(2)	50.41 (17)	C(5)	Co(3)	C(6)	98.23 (31)
Co(2)	Co(1)	C(7)	111.80 (18)	C(5)	Co(3)	C(7)	96.98 (28)
Co(3)	Co(1)	Co(4)	60.71 (3)	C(6)	Co(3)	C(7)	96.35 (28)
Co(3)	Co(1)	P(1)	110.71 (5)	Co(1)	Co(4)	Co(2)	58.19 (3)
Co(3)	Co(1)	C(1)	141.51 (21)	Co(1)	Co(4)	Co(3)	58.11 (3)
Co(3)	Co(1)	C(2)	110.13 (17)	Co(1)	Co(4)	C(8)	153.60 (23)
Co(3)	Co(1)	C(7)	52.09 (18)	Co(1)	Co(4)	C(9)	98.00 (24)
Co(4)	Co(1)	P(1)	170.84 (5)	Co(1)	Co(4)	C(10)	96.67 (22)
Co(4)	Co(1)	C(1)	91.89 (21)	Co(2)	Co(4)	Co(3)	57.89 (3)
Co(4)	Co(1)	C(2)	84.44 (17)	Co(2)	Co(4)	C(8)	99.80 (23)
Co(4)	Co(1)	C(7)	84.38 (18)	Co(2)	Co(4)	C(9)	97.59 (24)
P(1)	Co(1)	C(1)	97.21 (21)	Co(2)	Co(4)	C(10)	150.92 (22)
P(1)	Co(1)	C(2)	96.34 (18)	Co(3)	Co(4)	C(8)	98.91 (23)
P(1)	Co(1)	C(7)	92.53 (18)	Co(3)	Co(4)	C(9)	151.59 (24)
C(1)	Co(1)	C(2)	91.80 (27)	Co(3)	Co(4)	C(10)	97.65 (22)
C(1)	Co(1)	C(7)	102.43 (27)	C(8)	Co(4)	C(9)	99.43 (33)
C(2)	Co(1)	C(7)	162.16 (25)	C(8)	Co(4)	C(10)	99.44 (32)
Co(1)	Co(2)	Co(3)	59.88 (3)	C(9)	Co(4)	C(10)	100.51 (32)
Co(1)	Co(2)	Co(4)	60.72 (3)	Co(1)	P(1)	O(11)	119.08 (20)
Co(1)	Co(2)	P(2)	111.30 (6)	Co(1)	P(1)	O(12)	114.11 (21)
Co(1)	Co(2)	C(2)	50.31 (17)	Co(1)	P(1)	O(13)	111.84 (20)
Co(1)	Co(2)	C(3)	135.79 (25)	O(11)	P(1)	O(12)	98.27 (28)
Co(1)	Co(2)	C(4)	111.87 (20)	O(11)	P(1)	O(13)	105.62 (27)
Co(3)	Co(2)	Co(4)	60.64 (3)	O(12)	P(1)	O(13)	106.44 (27)
Co(3)	Co(2)	P(2)	109.86 (6)	Co(2)	P(2)	O(14)	113.51 (22)
Co(3)	Co(2)	C(2)	110.18 (17)	Co(2)	P(2)	O(15)	118.20 (33)
Co(3)	Co(2)	C(3)	144.15 (25)	Co(2)	P(2)	O(16)	116.88 (26)
Co(3)	Co(2)	C(4)	52.12 (20)	O(14)	P(2)	O(15)	104.56 (39)
Co(4)	Co(2)	P(2)	169.43 (6)	O(14)	P(2)	O(16)	100.18 (32)
Co(4)	Co(2)	C(2)	84.13 (17)	O(15)	P(2)	O(16)	101.11 (41)
Co(4)	Co(2)	C(3)	96.66 (25)	P(1)	O(11)	C(11)	124.13 (52)
Co(4)	Co(2)	C(4)	82.47 (20)	P(1)	O(12)	C(12)	127.29 (55)
P(2)	Co(2)	C(2)	95.77 (18)	P(1)	O(13)	C(13)	125.10 (48)
P(2)	Co(2)	C(3)	93.90 (25)	P(2)	O(14)	C(14)	123.96 (54)
P(2)	Co(2)	C(4)	95.15 (20)	P(2)	O(15)	C(15)	140.61 (93)
C(2)	Co(2)	C(3)	93.00 (30)	P(2)	O(16)	C(16)	130.04 (75)
C(2)	Co(2)	C(4)	161.76 (26)	Co(1)	C(1)	O(1)	175.72 (59)
C(3)	Co(2)	C(4)	100.78 (32)	Co(1)	C(2)	Co(2)	79.28 (22)
Co(1)	Co(3)	Co(2)	60.41 (3)	Co(1)	C(2)	O(2)	139.88 (48)
Co(1)	Co(3)	Co(4)	61.18 (3)	Co(2)	C(2)	O(2)	140.69 (49)
Co(1)	Co(3)	C(4)	109.19 (19)	Co(2)	C(3)	O(3)	176.21 (73)
Co(1)	Co(3)	C(5)	135.95 (23)	Co(2)	C(4)	Co(3)	78.97 (25)
Co(1)	Co(3)	C(6)	111.19 (22)	Co(2)	C(4)	O(4)	144.68 (56)
Co(1)	Co(3)	C(7)	49.23 (17)	Co(3)	C(4)	O(4)	136.34 (54)
Co(2)	Co(3)	Co(4)	61.48 (3)	Co(3)	C(5)	O(5)	179.47 (64)
Co(2)	Co(3)	C(4)	48.91 (19)	Co(3)	C(6)	O(6)	177.98 (62)
Co(2)	Co(3)	C(5)	138.14 (23)	Co(1)	C(7)	Co(3)	78.68 (22)
Co(2)	Co(3)	C(6)	109.82 (22)	Co(1)	C(7)	O(7)	144.32 (51)
Co(2)	Co(3)	C(7)	109.62 (17)	Co(3)	C(7)	O(7)	137.00 (50)
Co(4)	Co(3)	C(4)	81.36 (19)	Co(4)	C(8)	O(8)	176.19 (69)
Co(4)	Co(3)	C(5)	91.60 (22)	Co(4)	C(9)	O(9)	177.14 (70)
Co(4)	Co(3)	C(6)	170.14 (22)	Co(4)	C(10)	O(10)	178.27 (65)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

analogous manner to that described for the triphenylphosphine derivative. The crystal was found to belong to the monoclinic system with lattice constants a = 14.865 (3) Å, b = 11.904 (3) Å, c = 15.583 (3) Å, and β = 90.94 (2)°. Systematic absences indicated the space

Table IX. Comparative Pertinent Bond Distances (Å) in $Co_4(CO)_{12-n}L_n$ (n = 0–2) Derivatives

	$Co_4(CO)_{12}$[a]		$Co_4(CO)_{11}[P(C_6H_5)_3]$		$Co_4(CO)_{10}[P(OCH_3)_3]_2$	
bond type	av	range	av	range	av	range
Co–Co						
basal–apical	2.492	2.457–2.527	2.530	2.523–2.542	2.528	2.518–2.538
basal–basal			2.482	2.468–2.491	2.454	2.447–2.464
Co–C(br)	2.043	1.958–2.191	1.937	1.887–1.976	1.929	1.879–1.972
Co–C(term)						
apical	1.834	1.610–2.032	1.827	1.822–1.832	1.810	1.797–1.817
equatorial			1.771	1.758–1.778	1.757	1.746–1.775
axial			1.792	1.789–1.794	1.787	1.787
			(1.797)[b]	(1.758–1.832)	(1.784)[b]	(1.746–1.817)

[a] Data were taken from ref 9. [b] The value in parentheses corresponds to the average terminal Co–C distance.

group to be $P2_1/n$ (a special setting of $P2_1/c$–C^5_{2h}, No. 14). A unit cell of four $Co_4(CO)_{10}[P(OCH_3)_3]_2$ molecules per 2757 (1) Å^3 afforded a calculated density of 1.84 g cm^{-3}. The linear absorption coefficient of the crystal for Mo K$\bar{\alpha}$ radiation is 26.4 cm^{-1}. A total of 6801 independent reflections having $2\theta_{\text{Mo K}\bar{\alpha}} \leq 58.7°$ were measured in three concentric shells of increasing 2θ, with 4156 of these having $I > 3\sigma(I)$.

The four cobalts were located by using direct methods; the 34 remaining nonhydrogen atoms appeared in a single difference Fourier synthesis based on refined parameters for the Co atoms [R_1 = 0.364 for 2536 independent reflections having $2\theta_{\text{Mo K}\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$]. Isotropic unit-weighted full-matrix least-squares refinement for the 38 nonhydrogen atoms gave R_1 = 0.086 and R_2 = 0.086; anisotropic refinement converged to R_1 = 0.040 and R_2 = 0.044 for 2536 reflections. The final cycle of empirically weighted full-matrix least-squares refinement,[21b] in which the structural parameters for all nonhydrogen atoms were varied, converged to R_1 = 0.045, R_2 = 0.059, and GOF = 1.36 for 4156 independent reflections having $2\theta_{\text{Mo K}\bar{\alpha}} \leq 58.7°$ and $I > 3\sigma(I)$. During the final cycle of refinement, no parameter shifted by more than $0.21\sigma_p$ with the average shift being $0.01\sigma_p$. There were no peaks present in the final difference Fourier above the noise level other than those anticipated for some of the hydrogen atoms.

All calculations were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a parallel floating-point processor for 32- and 64-bit arithmetic and a Data General disk with 10 million 16-bit words using versions of the Nicolet (Syntex) E-XTL or SHELXTL interactive crystallographic software package as modified at Crystalytics Co.

Results

$Co(CO)_{11}[P(C_6H_5)_3]$. The final atomic coordinates and anisotropic thermal parameters for all nonhydrogen atoms are provided in Tables I and II, respectively. The calculated atomic coordinates for the hydrogen atoms in crystalline $Co_4(CO)_{11}[P(C_6H_5)_3]$ are available as supplementary material. Figure 2 presents a perspective view of the structure and defines the atomic numbering scheme employed. In Tables III and IV are given bond distances and angles for all atoms in $Co_4(CO)_{11}[P(C_6H_5)_3]$, except those involving the phenyl rings which are available as supplementary material.

The molecule contains a central tetrahedron of cobalt atoms bridged on three edges by CO groups with the $P(C_6H_5)_3$ ligand occupying an axial site (as in III) in the coordinate sphere of Co(2). Two of the CO bridges are asymmetrical with a slightly shorter Co–CO bond distance to the Co(2) atom which bears the triphenylphosphine ligand (see skeletal drawing in Figure 3A).

$Co_4(CO)_{10}[P(OCH_3)_3]_2$. The final positional and anisotropic thermal parameters for all nonhydrogen atoms are listed in Tables V and VI, respectively. Bond lengths and bond angles are presented in Tables VII and VIII. Figure 4 depicts a perspective view of the structure and defines the atomic numbering scheme used.

The solid-state structure of $Co_4(CO)_{10}[P(OCH_3)_3]_2$ is derived from the C_{3v} structure of the parent species, $Co_4(CO)_{12}$, where the three bridging CO groups along one triangular set of edges are retained with however two of the axial CO ligands being replaced by trimethyl phosphite groups. As seen in the $Co_4(CO)_{11}[P(C_6H_5)_3]$ structure two of the bridging CO ligands are slightly asymmetrical, being displaced toward the cobalt atoms bearing the phosphite ligand (Figure 3B).

Discussion

The basal–basal cobalt–cobalt bonding distances have little scatter, varying from 2.468 to 2.491 and from 2.447 to 2.464 Å in the $Co_4(CO)_{11}[P(C_6H_5)_3]$ and $Co_4(CO)_{10}[P(OCH_3)_3]_2$ derivatives, respectively. Similarly, the apical–basal cobalt–cobalt bonds vary over narrow ranges of 2.523–2.542 and 2.518–2.538 Å in $Co_4(CO)_{11}[P(C_6H_5)_3]$ and $Co_4(CO)_{10}[P(OCH_3)_3]_2$ and are significantly longer (0.048 and 0.074 Å) than the corresponding basal–basal cobalt–cobalt bonds. The individual esd's on the above-mentioned Co–Co bond distances are 0.001 Å. As can be seen from Table IX, the average cobalt–cobalt bond distance (2.506 and 2.491 Å) in these derivatives is in close agreement with that determined in the parent $Co_4(CO)_{12}$ species (2.492 Å).[9,13-15]

On the other hand Co–C bond distances in $Co_4(CO)_{12}$ are known much less precisely and display wide variations which are attributed to crystallographic disorder. Nevertheless, the average values reported for these distances, particularly for the Co–C(term) groups, do not greatly differ from those more accurately determined in $Co_4(CO)_{11}[P(C_6H_5)_3]$ and $Co_4(CO)_{10}[P(OCH_3)_3]_2$ (see Table IX). Although the Co–C bond distances for the metal centers bearing the phosphorus donor ligands lie to the short end of the Co–C bond ranges, these are not significantly different than the Co–C bonds on cobalt centers which are unsubstituted. The most significant effect of CO replacement by a phosphorus donor ligand is the asymmetric Co–C(br) bonds where the shorter bond is with the phosphorus-substituted cobalt center (vide supra). C–O bond distances, including both terminal and bridging carbonyls, range from 1.123 to 1.164 and from 1.114 to 1.173 Å in $Co_4(CO)_{11}P(C_6H_5)_3$ and $Co_4(CO)_{10}[P(OCH_3)_3]_2$, respectively.

The Co–P bond distance in $Co_4(CO)_{11}[P(C_6H_5)_3]$ (2.246 (1) Å) is significantly longer, by 0.088 Å, than the average Co–P bond distance in $Co_4(CO)_{10}[P(OCH_3)_3]_2$ (2.158 (2) Å). This difference in metal–phosphorus bond lengths is consistent with what is known about relative metal–phosphorus bond strengths in mononuclear low-valent metal complexes[12,23] and with the greater ease with which $Co_4(CO)_{11}[P(C_6H_5)_3]$ undergoes ligand substitution with CO (eq 3) to reform $Co_4(CO)_{12}$ as compared with its trimethyl phosphite analogue.[2,24]

$$Co_4(CO)_{11}P(C_6H_5)_3 + CO \rightleftharpoons Co_4(CO)_{12} + P(C_6H_5)_3 \quad (3)$$

The infrared band patterns in the ν(CO) region of Co$_4$(C-

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$O)_{11}L$ ($L = P(C_6H_5)_3$ and $P(OCH_3)_3$) are very similar with respect to number of peaks and their relative intensities,[25] thus these complexes are assumed to be isostructural. Additionally, the three trimethyl phosphite ligands in $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ all occupy axial positions, and it is likely that the $Co_4(CO)_9[P(OCH_3)_3]_3$ derivative has an analogous structure. Hence, the stereochemistries of the products afforded by progressive replacement of CO groups in $Co_4(CO)_{12}$ with $P(OCH_3)_3$ (eq 1) can be viewed as successive substitution of an axial CO ligand with the $P(OCH_3)_3$ ligand. However, questions regarding the site of CO loss in metal carbonyl clusters remain a perplexing challenge.

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Supplementary Material Available: Lists of the structure factor amplitudes, calculated atomic coordinates for hydrogen atoms, and bond angles and lengths of the phenyl groups in $Co_4(CO)_{11}P(C_6H_5)_3$ (43 pages). Ordering information is given on any current masthead page.

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(25) Axial and equatorial monocarbonyl substitution in $Co_4(CO)_{12}$ would not however be expected to differ greatly in their ν(CO) infrared spectra. In this connection we are currently performing more quantitative studies (including normal coordinate analyses) on a large variety of monosubstituted and more highly substituted derivatives of group 8 tetranuclear clusters in order to definitively assess solution stereochemistries by means of ν(CO) infrared spectroscopy.

Notes

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Studies Using $(n\text{-}Bu)_3P{=}O$ as a Carbon Monoxide Labilizing Ligand in the Synthesis of Metal Carbonyl Complexes Highly Enriched in ^{13}CO

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The requisite utilization of metal carbonyls enriched in carbon-13 has been demonstrated in many investigations. An enumeration of some of these studies would include the following: (1) the determination of intra- and intermolecular CO exchange processes in metal carbonyl mononuclear and cluster species,[1–8] (2) the specification of the site of ligand dissociation and the nature of the resultant intermediate in ligand displacement reactions in solution,[9–12] (3) the identification of metal carbonyl fragments isolated in low-temperature matrices by means of vibrational spectroscopy,[13–15] and (4) the confirmation of the origin of products afforded by catalytic reduction of CO.[16,17]

In all of the processes described above, with the exception of (2) where stereoselective labeling is necessary, the availability of highly ^{13}C-enriched metal carbonyl complexes is generally desirable. Although a few metal carbonyls undergo exchange reactions with free ^{13}CO under mild conditions (e.g., $Ni(CO)_4$ and $Rh_4(CO)_{12}$), most undergo this ligand exchange process reluctantly. Hence straightforward synthetic techniques for the preparation of a large variety of parent metal carbonyl complexes highly enriched in ^{13}CO are imperative. We have briefly reported the preparation of iron pentacarbonyl and the group 6B hexacarbonyls extensively enriched in carbon-13, taking advantage of the CO-labilizing ability of $(n\text{-}Bu)_3P{=}O$.[18] As part of an ongoing program to develop the methodology for the syntheses of ^{13}C-labeled metal carbonyl complexes and their derivatives, the scope of the use of $(n\text{-}Bu)_3P{=}O$ as a CO-labilizer has been extended, and the results of this investigation are reported herein.

Experimental Section

Materials. $(n\text{-}Bu)_3P{=}O$, $Me_3P{=}O$, and $Me_3NO{\cdot}2H_2O$ were used as obtained from Apache Chemical Co., Strem Chemical Co., and Aldrich Chemical Co., respectively. Except for $Fe(CO)_5$ (Alfa-Ventron, distilled under N_2 prior to use), all binary metal carbonyls as well as (butadiene)$Fe(CO)_3$ were purchased from Strem Chemical Co. and used without further purification. The substituted metal carbonyl complexes $Cr(CO)_3(NH_3)_3$,[19] $Mo(CO)_4[P(OMe)_3][NHC_5H_{10}]$,[20] $pyFe(CO)_4$,[21] $(pip)_2W(CO)_4$,[22] $(CHT)Cr(CO)_3$,[23] and $K^+(\mu\text{-}H)[Cr(CO)_5]_2^-$[24] were prepared in these laboratories by the literature procedures. Carbon-13-enriched CO (93.3% ^{13}CO) was obtained from Prochem., B.O.C., Ltd., Longon, England. The hexane solvent commonly used in the ^{13}CO-exchange reactions was purified by stirring over H_2SO_4/HNO_3, was then washed with water, and finally was distilled from $LiAlH_4$ under N_2. Benzene was distilled under N_2 from sodium wire. Reagent grade octane was not further purified.

Reactions. Schlenk flasks were charged with $(n\text{-}Bu)_3P{=}O$ in an argon-filled glovebox. Other manipulations were done under nitrogen by using standard Schlenk techniques.

Reaction of $(H_3N)_3Cr(CO)_3$ with ^{13}CO. The reactions of amine-substituted group 6B metal carbonyl derivatives, $M(CO)_{6-n}(\text{amine})_n$ (n = 1–3, and amine = ammonia, piperidine (pip), or pyridine (py)), and ^{13}CO in the presence of excess $(n\text{-}Bu)_3P{=}O$ were all performed in a similar manner. In a typical reaction triamminechromium tricarbonyl (0.272 g, 1.45 mmol, solubility limit) was placed in a 500-mL

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