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Synthesis and Structure of Some Cobalt(II) Complexes with the Tridentate Ligand 1,1,1-Tris(diphenylphospinomethyl)ethane

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The tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, p$_3$, forms five-coordinate complexes with cobalt(II) with the empirical formula CoX(p$_3$)B(C$_6$H$_5$)$_4$. When X is Cl, Br, or OH, i.e., is a monodentate ligand, the complexes are binuclear with bridging X. The ions [Co$_2$X$_2$(p$_3$)]$^{2+}$ show antiferromagnetic behavior. When X is acetate (ac), nitrate (NO$_3$), or acetylacetonate (acac), monomeric complexes are formed where magnetic susceptibility obeys the Curie–Weiss law. The hydroxide derivative [Co$_2$(OH)$_2$(p$_3$)$_2$][B(C$_6$H$_5$)$_4$]$_2$·x(CH$_3$)$_2$CO crystallizes in the triclinic system, space group P1, with unit cell dimensions $a = 16.905$ (3) Å, $b = 15.774$ (2) Å, $c = 13.850$ (2) Å, $\alpha = 111.67$ (3)°, $\beta = 91.07$ (3)°, and $\gamma = 115.06$ (4)°. Each cobalt atom is five-coordinated by three phosphorus atoms from a p$_3$ ligand and two oxygen atoms from the bridging hydroxide groups. The acetate derivative [Co(ac)(p$_3$)][B(C$_6$H$_5$)$_4$]·x(CH$_3$)$_2$CO crystallizes in the monoclinic space group P2$_1$/n with unit cell dimensions $a = 19.995$ (3) Å, $b = 19.201$ (3) Å, $c = 17.211$ (2) Å, and $\beta = 110.44$ (3)°. The acetate ligand is bidentate and thus the cobalt atom is five-coordinate.

Introduction

The coordinating behavior of the eponymous ligand CH$_3$C(CH$_2$P(C$_6$H$_5$)$_2$)$_3$, p$_3$, toward cobalt ions has been studied in recent years. The reactions fall into three categories.

In the presence of the reducing agent NaBH$_4$, cobalt(II) chloride and bromide are reduced to the tetrahedral cobalt(I) complexes [CoX(p$_3$)] (X = Cl, Br);[1] the iodide is spontaneously reduced without added reducing agent.[1] Other cobalt(II) salts yield, in the presence of NaB(C$_6$H$_5$)$_4$, the triply bridged dimeric cobalt(II) compound [Co$_2$H$_3$(p$_3$)$_2$][B(C$_6$H$_5$)$_4$].[2]

When no reducing agent is present, the results are often ambiguous. It has been claimed that the only well-characterized complex to be formed is the thiocyanate [Co(NCS)$_2$(p$_3$)].[3] The recently prepared complexes [CoX$_2$(p$_3$)] (X = Cl, Br)[4] have some physical properties suggestive of the presence of phosphine oxide, while the agreement between observed and calculated analytical figures is based on erroneously calculated values.

In order to clarify the situation we have conducted similar experiments with p$_3$ and cobalt(II) salts, *with rigorous exclusion of air*; under these conditions well-defined cobalt(II) complexes are obtained. The X-ray crystal structures of the hydroxo and acetato derivatives have helped to clarify the stereochemistry in these systems.

Experimental Section

Reagents. The cobalt salts, sodium tetraphenylborate, ethanol, 1-butanol, acetone, tetrahydrofuran, methylene chloride, and petroleum ether were reagent grade and were used without further purification. The preparation of the ligand has already been described.[5]

Preparation of the Complexes. All operations were performed under dry nitrogen. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen.

Di-μ-chloro-bis[1,1,1-tris(diphenylphosphinomethyl)ethane]dicobalt(II) Tetraphenylborate, [Co$_2$Cl$_2$(p$_3$)$_2$][B(C$_6$H$_5$)$_4$]$_2$·x(solvent),[6] and Di-μ-bromo-bis[1,1,1-tris(diphenylphosphinomethyl)ethane]dicobalt(II) Tetraphenylborate, [Co$_2$Br$_2$(p$_3$)$_2$][B(C$_6$H$_5$)$_4$]$_2$·x(solvent) (Solvent = Acetone, Methylene Chloride). Anhydrous cobalt(II) halide (1 mmol) in 20 ml of 1-butanol was added, after filtration, to 1 mmol of p$_3$ and 1 mmol of NaB(C$_6$H$_5$)$_4$ in 30 ml of solvent. Red-brown crystals were obtained by evaporation of the dark brown solution. The crystals were washed with butanol and petroleum ether.

Di-μ-hydroxo-bis[1,1,1-tris(diphenylphosphinomethyl)ethane]dicobalt(II) Tetraphenylborate, [Co$_2$(OH)$_2$(p$_3$)][B(C$_6$H$_5$)$_4$]$_2$·x(solvent) (Solvent = Acetone, THF). Co(H$_2$O)$_6$(BF$_4$)$_2$ or Co(H$_2$O)$_6$(ClO$_4$)$_2$ (1 mmol) in 20 ml of 1-butanol was added to a solution of p$_3$ (1 mmol) and NaB(C$_6$H$_5$)$_4$ (1 mmol) in 15 ml of acetone (or THF). A rapid stream of nitrogen was passed through the mixture to stir it and the color changed slowly to deep brown. After ca. 0.3 hr the red-brown crystals began to separate. They were treated as above.

Acetato[1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(II) Tetraphenylborate, [Co(ac)(p$_3$)][B(C$_6$H$_5$)$_4$]·x(CH$_3$)$_2$CO, Acetylacetonato[1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(II) Tetraphenylborate, [Co(acac)(p$_3$)][B(C$_6$H$_5$)$_4$], and Nitrato[1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(II) Tetraphenylborate, [Co(NO$_3$)(p$_3$)][B(C$_6$H$_5$)$_4$]·x(CH$_3$)$_2$CO. These compounds which appear as orange-brown crystals were prepared from cobalt(II) acetate, acetylacetonate, and nitrate, respectively, in the same manner as the halide complexes.

Physical Measurements. The methods used for the magnetic and molar conductance measurements and the recordings of infrared and

Table I. Final Least-Squares Parameters of $[Co_2(OH)_2(p_3)_2][B(C_6H_5)_4]_2$ Nongroup Atoms

Atom	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co1	0.2500	0.2500	0.2500	0.029 (3)[b]	0.053 (4)	0.051 (4)	0.026 (3)	0.020 (3)	0.031 (3)
Co2	0.4379 (3)	0.2681 (4)	0.2669 (4)	0.018 (3)	0.031 (3)	0.039 (3)	0.010 (3)	0.001 (2)	0.009 (3)
P1	0.2129 (6)	0.3528 (8)	0.3864 (8)	0.028 (6)	0.057 (7)	0.040 (7)	0.027 (6)	0.015 (5)	0.018 (6)
P2	0.1783 (7)	0.2797 (8)	0.1387 (8)	0.041 (7)	0.038 (7)	0.048 (7)	0.019 (6)	0.006 (6)	0.023 (6)
P3	0.1237 (7)	0.1082 (8)	0.2202 (8)	0.041 (7)	0.045 (7)	0.051 (8)	0.015 (6)	0.007 (6)	0.031 (6)
P4	0.5661 (6)	0.4097 (8)	0.3677 (8)	0.034 (6)	0.044 (7)	0.042 (7)	0.014 (5)	0.005 (5)	0.026 (6)
P5	0.4779 (7)	0.1714 (8)	0.3202 (9)	0.032 (6)	0.044 (7)	0.062 (8)	0.022 (5)	−0.004 (5)	0.022 (6)
P6	0.5088 (7)	0.2419 (8)	0.1279 (8)	0.051 (7)	0.057 (7)	0.037 (7)	0.034 (6)	0.021 (5)	0.020 (6)

Atom	x	y	z	U, Å^2	Atom	x	y	z	U, Å^2
B1	0.6766 (27)	0.8781 (32)	0.0590 (34)	0.042 (12)	C127	0.5966 (31)	0.1941 (35)	0.3263 (37)	0.092 (16)
B2	0.0105 (26)	0.6623 (30)	0.5134 (32)	0.038 (12)	C128	0.6218 (25)	0.2495 (29)	0.1677 (31)	0.068 (12)
C121	0.0971 (21)	0.3312 (24)	0.3524 (26)	0.042 (10)	C129	0.6570 (28)	0.2836 (32)	0.2822 (34)	0.069 (13)
C122	0.0618 (22)	0.2485 (26)	0.1542 (27)	0.048 (10)	C130	0.7504 (25)	0.2892 (28)	0.2962 (29)	0.052 (12)
C123	0.0230 (22)	0.1326 (26)	0.2469 (27)	0.046 (10)	O1[c]	0.3706 (25)	0.3220 (28)	0.2306 (29)	0.043 (18)
C124	0.0356 (23)	0.2377 (26)	0.2525 (27)	0.040 (10)	O11[d]	0.3672 (38)	0.3045 (49)	0.3425 (45)	0.105 (18)
C125	−0.0587 (23)	0.2269 (25)	0.2512 (27)	0.046 (10)	O2[e]	0.3117 (37)	0.1687 (43)	0.2296 (54)	0.080 (16)
C126	0.6684 (30)	0.3921 (35)	0.3557 (36)	0.090 (14)	O22[f]	0.3243 (36)	0.2110 (48)	0.3103 (49)	0.077 (16)

[a] The thermal parameters are of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. [b] The numbers in parentheses are the estimated standard deviations from the last cycle of least-squares refinement. [c] Population parameter 0.568 (36). [d] Population parameter 0.515 (50). [e] Population parameter 0.472 (52). [f] Population parameter 0.478 (52).

Table II. Final Least-squares Parameters of $[Co_2(OH)_2(p_3)_2][B(C_6H_5)_4]_2$ Groups

Group	x_c[a]	y_c	z_c	ϑ,[b] deg	φ, deg	ψ, deg	U, Å^2
P1–Ph1	0.3236 (10)	0.5962 (12)	0.4658 (12)	38.47 (83)	−105.42 (91)	118.80 (62)	0.062 (4)
P1–Ph2	0.2348 (13)	0.3350 (13)	0.6061 (15)	144.27 (91)	8.63 (1.48)	145.32 (1.52)	0.081 (5)
P2–Ph3	0.2803 (10)	0.5071 (12)	0.1553 (12)	149.74 (95)	61.54 (89)	−70.91 (80)	0.060 (5)
P2–Ph4	0.1529 (10)	0.1419 (12)	−0.1092 (12)	84.45 (91)	118.61 (89)	−155.63 (1.13)	0.065 (5)
P3–Ph5	0.0666 (11)	−0.0784 (13)	−0.0077 (15)	112.25 (96)	−118.99 (1.09)	26.61 (1.32)	0.077 (5)
P3–Ph6	0.1214 (11)	−0.0098 (13)	0.3691 (14)	118.76 (1.07)	−31.33 (1.16)	100.18 (1.13)	0.079 (5)
P4–Ph7	0.5704 (10)	0.5020 (12)	0.6169 (14)	102.81 (1.01)	44.74 (96)	−138.18 (98)	0.070 (5)
P4–Ph8	0.6253 (10)	0.6122 (12)	0.3311 (12)	142.88 (85)	−30.93 (1.38)	98.06 (1.10)	0.057 (4)
P5–Ph9	0.3598 (11)	−0.0714 (13)	0.1729 (13)	37.08 (83)	−1.30 (1.41)	133.57 (1.42)	0.065 (5)
P5–Ph10	0.4601 (10)	0.1716 (11)	0.5511 (14)	111.30 (86)	153.41 (91)	−143.12 (93)	0.065 (5)
P6–Ph11	0.5415 (13)	0.3979 (14)	0.0199 (14)	144.52 (1.01)	−8.94 (1.93)	110.31 (1.78)	0.076 (6)
P6–Ph12	0.4188 (13)	0.0361 (14)	−0.0784 (15)	64.84 (87)	−113.01 (1.22)	134.72 (1.30)	0.077 (6)
B1–Ph13	0.6510 (11)	−0.0359 (13)	0.2860 (14)	42.59 (98)	6.73 (1.24)	123.39 (1.40)	0.057 (5)
B1–Ph14	0.7761 (10)	0.7577 (12)	0.0469 (14)	86.70 (1.16)	84.18 (1.02)	−148.33 (1.10)	0.068 (5)
B1–Ph15	0.4859 (13)	0.7268 (15)	0.9019 (16)	113.04 (1.20)	74.33 (1.05)	105.67 (85)	0.083 (6)
B1–Ph16	0.7804 (11)	0.0496 (13)	−0.0131 (13)	149.84 (89)	76.19 (1.16)	−100.74 (90)	0.073 (5)
B2–Ph17	0.8843 (12)	0.7338 (12)	0.6244 (12)	149.98 (81)	0.82 (1.68)	−98.37 (1.69)	0.066 (5)
B2–Ph18	0.0323 (10)	0.5143 (12)	0.6022 (13)	48.46 (94)	−107.99 (99)	−95.01 (73)	0.066 (5)
B2–Ph19	0.1968 (11)	0.8196 (13)	0.5198 (14)	63.67 (99)	−110.78 (99)	136.48 (76)	0.075 (5)
B2–Ph20	0.9153 (10)	0.5342 (12)	0.2655 (14)	80.89 (86)	131.19 (87)	−151.80 (99)	0.068 (5)
Acet1	0.6234 (37)	0.9302 (44)	0.6697 (41)	88.63 (5.23)	68.67 (3.13)	−140.25 (4.00)	0.207 (19)
Acet2	0.7390 (44)	0.2927 (58)	0.7383 (53)	149.16 (4.90)	43.89 (4.87)	−104.66 (7.32)	0.235 (25)
Acet3	0.9195 (30)	0.1048 (41)	0.5396 (40)	43.13 (5.28)	132.18 (2.81)	−127.06 (5.01)	0.252 (17)
Acet4	0.0710 (36)	0.4630 (40)	0.9434 (35)	162.67 (3.33)	26.38 (2.51)	−111.27 (3.04)	0.140 (16)

[a] x_c, y_c, and z_c are the coordinates of the baricenter of the group. [b] The Goldstein definition is used for Euler angles; H. Goldstein, "Classical Mechanics" Addison-Wesley, Reading, Mass., 1959.

uv–visible spectra have been described previously.[7]

Collection and Reduction of the X-Ray Intensity Data. Both compounds crystallize as irregular prisms. They were mounted in random orientation on a glass fiber and protected from the air by a coating of paraffin.

A Philips PW 1100 automated diffractometer was used. Cell constants were determined and refined, after the "peak hunting" procedure[8] had found the setting angles of 20 reflections for each compound. The hydroxo complex is triclinic and crystallizes in a unit cell of dimensions $a = 16.905$ (3) Å, $b = 15.774$ (2) Å, $c = 13.850$ (2) Å, $\alpha = 111.67$ (3)°, $\beta = 91.07$ (3)°, and $\gamma = 115.06$ (4)°. These parameters refer to the Delaunay reduced cell in direct space. The unit cell of the acetato complex is monoclinic with space group $P2_1/n$ and has dimensions $a = 19.995$ (3) Å, $b = 19.201$ (3) Å, $c = 17.211$ (2) Å, and $\beta = 110.44$ (3)°.

The calculated density of the hydroxo compound, assuming two formula units of $Co(OH)(p_3)B(C_6H_5)_4 \cdot 2(CH_3)_2CO$ present in the cell, is 1.24 g/cm³. A value of 1.20 g/cm³ was determined by flotation in a mixture of carbon tetrachloride and cyclohexane. For four formula units of $Co(ac)(p_3)B(C_6H_5)_4 \cdot (CH_3)_2CO$ in the cell, the calculated density of 1.19 g/cm³ is close to the value of 1.16 g/cm³ measured by flotation in the same mixture as above. The hydroxo compound crystal had dimensions 0.1 × 0.2 × 0.3 mm. The acetato crystal had dimensions 0.1 × 0.2 × 0.2 mm.

Mo Kα radiation was used for the collection of each data set employing a θ–2θ scan technique; symmetric scan ranges in 2θ of 1.6 and 2.0° were used for the hydroxo compound and for the acetato compound, respectively; the scan rate was 0.16°/sec in both cases.

Intensity data collection included hkl planes out to $\theta = 20°$. Totals of 5565 and 6336 reflections were measured for the two compounds. During the course of collection of each data set, the intensities of three standard reflections were regularly monitored. The PW 1100's software provides an automatic reorientation of the crystal if the azimuths of the standard reflections reveal a little misalignment. The hydroxo derivative standard reflections showed a regular decrease in intensity up to a maximum of 18% with respect to the initial values. This was attributed to decomposition of the crystal. On the contrary the acetate derivative's standard reflections were fairly stable, with a maximum decrease in intensity of 4%. Corrections were applied for this effect.

The intensity σ's[9] were calculated according to the formula

$$\sigma(I) = [S + ST/BT)^2(B_1 + B_2) + (RT)^2]^{1/2}$$

where S is the scan count, B_1 and B_2 are the background counts, ST and BT are scan time and time for one background measurement,

Table III. Derived Group Atom Positional Parameters for [Co$_2$(OH)$_2$(p$_3$)$_2$][B(C$_6$H$_5$)$_4$]$_2$

Atom	x	y	z	Atom	x	y	z
Ph1–C1	0.2771 (16)	0.4898 (18)	0.4301 (16)	Ph6–C69	0.3336 (19)	−0.0409 (19)	−0.0903 (22)
Ph1–C2	0.3560 (15)	0.5343 (18)	0.3977 (18)	Ph6–C70	0.3814 (19)	−0.0551 (17)	−0.1703 (19)
Ph1–C3	0.4026 (13)	0.6408 (21)	0.4333 (18)	Ph6–C71	0.4665 (17)	0.0218 (22)	−0.1585 (19)
Ph1–C4	0.3702 (16)	0.7027 (18)	0.5015 (16)	Ph6–C72	0.5039 (19)	0.1130 (19)	−0.0666 (23)
Ph1–C5	0.2913 (15)	0.6583 (18)	0.5339 (18)	B1–C73	0.6562 (16)	−0.0739 (20)	0.1795 (20)
Ph1–C6	0.2447 (13)	0.5518 (21)	0.4981 (16)	B1–C74	0.7240 (17)	0.0202 (22)	0.2517 (20)
Ph1–C7	0.2249 (19)	0.3427 (22)	0.5103 (17)	B1–C75	0.7189 (19)	0.0582 (22)	0.3582 (22)
Ph1–C8	0.3095 (15)	0.3908 (20)	0.5739 (21)	B1–C76	0.6459 (16)	0.0021 (20)	0.3925 (20)
Ph1–C9	0.3194 (14)	0.3829 (19)	0.6697 (21)	B1–C77	0.5780 (17)	−0.0920 (22)	0.3202 (20)
Ph1–C10	0.2447 (19)	0.3269 (21)	0.7020 (17)	B1–C78	0.5832 (19)	−0.1300 (22)	0.2137 (22)
Ph1–C11	0.1602 (15)	0.2789 (19)	0.6383 (21)	B1–C79	0.7300 (16)	0.8100 (18)	0.0495 (24)
Ph1–C12	0.1503 (14)	0.2868 (19)	0.5425 (21)	B1–C80	0.7761 (14)	0.8254 (18)	0.1438 (17)
Ph2–C13	0.2297 (17)	0.4058 (17)	0.1421 (15)	B1–C81	0.8254 (13)	0.7731 (18)	0.1411 (17)
Ph2–C14	0.3072 (15)	0.4331 (17)	0.1018 (19)	B1–C82	0.8286 (16)	0.7054 (17)	0.0442 (24)
Ph2–C15	0.3576 (13)	0.5344 (22)	0.1149 (18)	B1–C83	0.7824 (14)	0.6899 (18)	−0.0500 (17)
Ph2–C16	0.3308 (17)	0.6083 (17)	0.1684 (15)	B1–C84	0.7332 (13)	0.7423 (18)	−0.0474 (18)
Ph2–C17	0.2534 (15)	0.5810 (17)	0.2088 (19)	B1–C85	0.5547 (20)	0.8011 (22)	0.9894 (20)
Ph2–C18	0.2028 (13)	0.4798 (22)	0.1957 (19)	B1–C86	0.4959 (22)	0.7076 (25)	0.9905 (19)
Ph2–C19	0.1649 (14)	0.2025 (17)	−0.0020 (14)	B1–C87	0.4271 (20)	0.6333 (21)	0.9031 (27)
Ph2–C20	0.2138 (14)	0.1485 (19)	−0.0343 (18)	B1–C88	0.4172 (20)	0.6524 (21)	0.8144 (20)
Ph2–C21	0.2018 (17)	0.0879 (16)	−0.1416 (21)	B1–C89	0.4760 (23)	0.7459 (24)	0.8133 (19)
Ph2–C22	0.1408 (14)	0.0813 (17)	−0.2164 (14)	B1–C90	0.5447 (20)	0.8202 (21)	0.9007 (28)
Ph2–C23	0.0919 (14)	0.1352 (19)	−0.1843 (18)	B1–C91	0.7276 (15)	−0.0298 (20)	0.0147 (17)
Ph2–C24	0.1039 (17)	0.1958 (16)	−0.0770 (21)	B1–C92	0.7139 (11)	0.0564 (20)	0.0425 (20)
Ph3–C25	0.0928 (18)	0.0056 (17)	0.0899 (17)	B1–C93	0.7667 (17)	0.1359 (18)	0.0146 (17)
Ph3–C26	0.1377 (14)	−0.0535 (20)	0.0675 (21)	B1–C94	0.8331 (16)	0.1291 (20)	−0.0409 (18)
Ph3–C27	0.1115 (19)	−0.1375 (18)	−0.0300 (24)	B1–C95	0.8468 (11)	0.0428 (21)	−0.0686 (20)
Ph3–C28	0.0403 (18)	−0.1625 (17)	−0.1053 (17)	B1–C96	0.7940 (17)	−0.0367 (19)	−0.0407 (17)
Ph3–C29	−0.0046 (14)	−0.1033 (20)	−0.0829 (22)	B2–C97	−0.0594 (14)	0.6981 (19)	0.5712 (18)
Ph3–C30	0.0216 (19)	−0.0293 (18)	0.0147 (24)	B2–C98	−0.1246 (16)	0.6379 (14)	0.6107 (19)
Ph3–C31	0.1246 (18)	0.0401 (20)	0.3037 (20)	B2–C99	−0.1819 (14)	0.6736 (17)	0.6640 (19)
Ph3–C32	0.1873 (15)	0.0909 (14)	0.3984 (24)	B2–C100	−0.1719 (14)	0.7694 (18)	0.6777 (18)
Ph3–C33	0.1841 (13)	0.0410 (23)	0.4638 (18)	B2–C101	−0.1067 (16)	0.8296 (14)	0.6382 (19)
Ph3–C34	0.1183 (18)	−0.0598 (20)	0.4345 (20)	B2–C102	−0.0504 (14)	0.7940 (17)	0.5849 (19)
Ph3–C35	0.0555 (15)	−0.1106 (14)	0.3399 (24)	B2–C103	0.0179 (17)	0.5727 (20)	0.5560 (19)
Ph3–C36	0.0587 (13)	−0.0606 (23)	0.2745 (18)	B2–C104	−0.0409 (15)	0.4682 (19)	0.5197 (18)
Ph4–C37	0.5748 (13)	0.4664 (20)	0.5100 (15)	B2–C105	−0.0264 (15)	0.4098 (13)	0.5659 (19)
Ph4–C38	0.6032 (16)	0.4315 (19)	0.5757 (22)	B2–C106	0.0467 (17)	0.4559 (20)	0.6483 (19)
Ph4–C39	0.5989 (16)	0.4672 (18)	0.6825 (20)	B2–C107	0.1055 (15)	0.5602 (19)	0.6846 (18)
Ph4–C40	0.5660 (13)	0.5376 (20)	0.7238 (15)	B2–C108	0.0911 (15)	0.6187 (13)	0.6385 (19)
Ph4–C41	0.5375 (16)	0.5725 (19)	0.6582 (22)	B2–C109	0.1107 (16)	0.7469 (21)	0.5124 (22)
Ph4–C42	0.5419 (16)	0.5368 (18)	0.5513 (20)	B2–C110	0.1519 (18)	0.8403 (20)	0.6016 (19)
Ph4–C43	0.5966 (15)	0.5234 (13)	0.3488 (20)	B2–C111	0.2379 (17)	0.9131 (18)	0.6090 (16)
Ph4–C44	0.5391 (11)	0.5323 (16)	0.2842 (18)	B2–C112	0.2829 (17)	0.8923 (20)	0.5273 (22)
Ph4–C45	0.5679 (13)	0.6211 (20)	0.2666 (18)	B2–C113	0.2419 (17)	0.7988 (19)	0.4380 (19)
Ph4–C46	0.6540 (15)	0.7009 (13)	0.3135 (19)	B2–C114	0.1557 (18)	0.7261 (18)	0.4306 (16)
Ph4–C47	0.7115 (11)	0.6921 (16)	0.3780 (18)	B2–C115	−0.0441 (13)	0.5818 (18)	0.3726 (15)
Ph4–C48	0.6827 (13)	0.6033 (20)	0.3957 (18)	B2–C116	−0.0234 (15)	0.5092 (18)	0.3007 (21)
Ph5–C49	0.4127 (16)	0.0329 (14)	0.2364 (18)	B2–C117	−0.0639 (17)	0.4617 (15)	0.1935 (19)
Ph5–C50	0.4435 (13)	−0.0189 (19)	0.1339 (20)	B2–C118	−0.1252 (13)	0.4867 (18)	0.1584 (15)
Ph5–C51	0.3906 (17)	−0.1233 (19)	0.0904 (17)	B2–C119	−0.1460 (15)	0.5592 (18)	0.2303 (21)
Ph5–C52	0.3069 (16)	−0.1758 (14)	0.1095 (18)	B2–C120	−0.1054 (17)	0.6068 (15)	0.3375 (19)
Ph5–C53	0.2762 (13)	−0.1239 (16)	0.1920 (20)	Acet1–O1	0.6469 (75)	0.8646 (103)	0.6316 (96)
Ph5–C54	0.3291 (17)	−0.0195 (19)	0.2554 (17)	Acet1–C1	0.6229 (57)	0.9314 (73)	0.6704 (76)
Ph5–C55	0.4630 (16)	0.1698 (19)	0.4501 (16)	Acet1–C2	0.6415 (73)	0.9902 (120)	0.7919 (80)
Ph5–C56	0.4233 (16)	0.2225 (18)	0.5176 (21)	Acet1–C3	0.5746 (100)	0.9563 (113)	0.5976 (133)
Ph5–C57	0.4205 (16)	0.2244 (16)	0.6187 (19)	Acet2–O2	0.7098 (82)	0.3534 (111)	0.7918 (104)
Ph5–C58	0.4573 (16)	0.1734 (19)	0.6523 (16)	Acet2–C4	0.7395 (66)	0.2915 (88)	0.7576 (80)
Ph5–C59	0.4969 (16)	0.1206 (18)	0.5846 (21)	Acet2–C5	0.7007 (149)	0.1924 (151)	0.7760 (117)
Ph5–C60	0.4997 (16)	0.1187 (16)	0.4835 (19)	Acet2–C6	0.8157 (74)	0.3135 (155)	0.6967 (169)
Ph6–C61	0.5276 (20)	0.3260 (18)	0.0616 (24)	Acet3–O3	0.8850 (58)	0.1522 (66)	0.5220 (64)
Ph6–C62	0.4577 (14)	0.3137 (18)	−0.0058 (24)	Acet3–C7	0.9202 (45)	0.1039 (55)	0.5399 (55)
Ph6–C63	0.4715 (16)	0.3856 (23)	−0.0474 (21)	Acet3–C8	1.0099 (49)	0.1617 (91)	0.6196 (110)
Ph6–C64	0.5554 (20)	0.4697 (18)	−0.0217 (24)	Acet3–C9	0.8744 (84)	−0.0145 (58)	0.4828 (76)
Ph6–C65	0.6254 (14)	0.4821 (18)	0.0456 (24)	Acet4–O4	0.0408 (61)	0.5226 (71)	0.9575 (63)
Ph6–C66	0.6116 (16)	0.4102 (23)	0.0873 (20)	Acet4–C10	0.0716 (51)	0.4619 (62)	0.9431 (54)
Ph6–C67	0.4562 (20)	0.1273 (17)	0.0136 (19)	Acet4–C11	0.0207 (101)	0.3638 (85)	0.9615 (77)
Ph6–C68	0.3710 (17)	0.0503 (22)	0.0018 (19)	Acet4–C12	0.1609 (61)	0.4839 (112)	0.9067 (121)

T is the total number of counts, and *R* is an instability factor determined by a least-squares analysis of the intensities of the standard reflections. *R* was found to be 0.01 for the acetato compound and 0.2 for the hydroxo compound. The numbers of observed reflections at $I \geq 3\sigma(I)$ were 1384 and 2588 for the acetate and hydroxo compounds, respectively.

The intensities were corrected for Lorentz–polarization effects. The calculated absorption coefficients, μ, are 4.18 and 4.10 cm^{-1} for the hydroxo and acetato derivatives, respectively. After rotating the crystal about the reciprocal lattice vector by small angles, the maximum change in intensity of any reflection was ±5%, so no absorption correction was applied.

An anomalous dispersion correction was included in the structure factor calculation with the acetato derivative; the imaginary part was not introduced for the hydroxo derivative because of the poor quality of data. The data did not allow us to discern the absolute configuration

Table V. Final Least-Squares Parameters of $[Co(ac)(p_3)][B(C_6H_5)_4]$ Nongroup Atoms

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.1173 (2)	−0.0319 (2)	0.2117 (2)	0.042 (3)	0.051 (3)	0.045 (3)	0.007 (3)	0.013 (2)	0.005 (3)
P1	0.1134 (4)	−0.0226 (4)	0.3275 (4)	0.053 (6)	0.056 (7)	0.039 (6)	0.005 (6)	0.020 (5)	0.002 (6)
P2	0.1505 (4)	−0.0659 (4)	0.1677 (4)	0.060 (6)	0.055 (7)	0.036 (6)	0.006 (6)	0.019 (5)	0.004 (6)
P3	0.2309 (4)	0.0615 (4)	0.2749 (5)	0.043 (6)	0.052 (7)	0.051 (7)	0.008 (5)	0.012 (5)	0.015 (6)
O1	0.0769 (9)	0.1284 (10)	0.1975 (12)	0.059 (14)	0.079 (18)	0.136 (20)	0.019 (14)	0.026 (14)	−0.013 (16)
O2	0.0126 (9)	0.0380 (9)	0.1403 (11)	0.075 (17)	0.033 (15)	0.119 (19)	0.005 (14)	0.010 (14)	0.015 (15)

Atom	x	y	z	U, Å^2	Atom	x	y	z	U, Å^2
B1	0.6691 (15)	0.0504 (16)	0.2630 (18)	0.044 (11)	C64	0.2507 (12)	−0.0797 (13)	0.3363 (15)	0.032 (8)
C61	0.1974 (13)	−0.0683 (14)	0.3843 (15)	0.060 (10)	C65	0.3097 (13)	−0.1281 (14)	0.3934 (15)	0.060 (9)
C62	0.2132 (12)	−0.1189 (13)	0.2502 (15)	0.043 (9)	C66	0.0169 (13)	0.1019 (14)	0.1561 (15)	0.055 (9)
C63	0.2891 (11)	−0.0102 (12)	0.3236 (14)	0.036 (8)	C67	−0.0503 (15)	0.1416 (15)	0.1265 (18)	0.089 (11)

Table VI. Final Least-Squares Parameters of $[Co(ac)(p_3)][B(C_6H_5)_4]$ Groups

Group	x_c	y_c	z_c	ϑ, deg	φ, deg	ψ, deg	U, Å^2
P1–Ph1	0.0814 (4)	0.0310 (6)	0.4666 (7)	114.25 (75)	37.56 (87)	−105.65 (74)	0.065 (4)
P1–Ph2	0.5151 (6)	0.3650 (6)	0.2165 (5)	21.60 (52)	7.12 (1.64)	−97.17 (1.46)	0.056 (4)
P2–Ph3	0.4679 (6)	0.3192 (6)	0.4289 (6)	149.83 (64)	−109.49 (96)	135.26 (58)	0.069 (4)
P2–Ph4	0.2860 (6)	0.4702 (5)	0.4776 (7)	65.02 (70)	−138.21 (94)	168.37 (93)	0.081 (4)
P3–Ph5	0.3042 (6)	0.1327 (5)	0.1537 (7)	121.87 (84)	62.03 (1.06)	180.81 (1.55)	0.080 (5)
P3–Ph6	0.2432 (5)	0.1778 (7)	0.4131 (8)	86.60 (98)	35.78 (98)	−108.99 (88)	0.080 (5)
B–Ph7	0.7930 (5)	0.4005 (6)	0.2660 (7)	114.15 (49)	−6.37 (90)	106.63 (60)	0.066 (4)
B–Ph8	0.5683 (5)	0.0515 (6)	0.3678 (6)	142.12 (53)	48.29 (1.10)	−126.20 (82)	0.081 (4)
B–Ph9	0.5838 (6)	0.1313 (6)	0.1009 (7)	120.84 (68)	94.66 (1.02)	137.01 (51)	0.086 (5)
B–Ph10	0.8071 (6)	0.1336 (5)	0.3616 (7)	48.97 (61)	−26.07 (96)	173.07 (80)	0.068 (4)
Acet^a	0.0451 (12)	0.3663 (11)	0.2666 (12)	22.51 (1.44)	−114.85 (1.50)	126.10 (1.34)	0.134 (10)

^{a} Multiplicity factor for acetone group is $\alpha - 0.70$ (3).

of the model on the basis of the anomalous dispersion correction. The error that would have resulted from arbitrarily choosing positive or negative values for $\Delta f''$ would have been greater, had we made the wrong choice, than that incurred by neglecting the correction itself.[10]

Solution and Refinement of the Structures. The structures were solved and refined using the XRY72 crystallographic system kindly supplied by J. M. Stewart, adapted for the University of Florence CII 10070 computer.

Di-μ-hydroxo-bis[1,1,1-tris(diphenylphosphinomethyl)ethane]dicobalt(II) Tetraphenylborate. The main problem in solving the structure of the hydroxo complex was to determine whether or not the structure is centrosymmetric. Examination of the statistical distribution of E's did not help, the experimental values being just halfway between the theoretical values expected for centrosymmetric and noncentrosymmetric structures.

The Patterson map clearly showed a peak corresponding to the Co–Co vector, whose length of 3.1 Å suggested the presence of a dimeric molecule. Three other diffuse peaks were assigned to the Co–P vectors on the basis of their length of about 2.2 Å. By setting a center of symmetry halfway between the two cobalt atoms, we attempted to develop the remaining part of the structure. All attempts to refine this model led to divergence. Assigning arbitrary coordinates to one cobalt atom (0.25, 0.25, 0.25) and working in noncentrosymmetric space group $P1$ with an initial model that contained a second cobalt atom and three phosphorus atoms, the structure was found to be acentric. The dimer is formed by two Co(p3) moieties, in a nearly eclipsed configuration. Because of the acentric space group there are 142 unique nonhydrogen atoms in the unit cell, rising to 158 if the acetone molecules are also considered. A series of four Fourier maps enabled us to detect all the nonhydrogen atoms except for some of the acetone atoms. At this stage we decided to begin the refinement of the structure. The number of parameters to be refined is very high (greater than 600 also if we consider a simple isotropic refinement) and the structure refinement was performed by blocking the least-squares matrix and imposing some constraints on parameters (for example rigid-body refinement). The residual R_1 and R_2 are defined as $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$. Prior to the first cycle of refinement R_1 was 0.255 and one isotropic cycle reduced it to 0.155. In this cycle the 20 phenyl groups were constrained to have D_{6h} symmetry, with a C–C distance of 1.392 Å and temperature factors that only contributed to the overall temperature factor. Two more cycles, using weights from counting statistics reduced R_1 and R_2 to 0.141 and 0.132, respectively. The isotropic temperature factors of the bridging oxygen atoms rose to unusually high values ($U = 0.2$). A subsequent difference Fourier

map showed disorder in the region of the hydroxide bridges and also in the region where the solvent molecules were expected. Very rough models for the acetone molecules were constructed and refined in a subsequent cycle which reduced R_1 but which raised the temperature factors of these atoms to excessively high values. This can be due to the nonstoichiometry with respect to solvate molecules, which merely fill up the cavities between the bulky cations and anions in the cell. The four molecules were then assigned C_{2v} geometry with a C–C distance of 1.54 Å and C–O distance of 1.23 Å and were treated as rigid groups with population parameters fixed at 0.5.

Two more cycles, in which the atoms coordinated to the metals were refined anisotropically, gave $R_1 = 0.125$ and $R_2 = 0.115$. The ellipsoids of the two bridging oxygen atoms were particularly long in a direction perpendicular to the Co–Co axis. A difference Fourier map made without the contribution of the bridging oxygen atoms showed that the electron density is extensively spread around a circle normal to the metal–metal axis and centered on it. We were able to assign two different locations to each oxygen atom (see below for the description of the structures) and refine in the two final least-squares cycles thermal, positional, and population parameters of these atoms, whose final values all seem to be normal; no peculiar trend was observed among their correlation coefficients.

Prior to the execution of the two final cycles, hydrogen atoms were introduced at calculated positions with isotropic temperature factors of 6.0 Å^2 and a new weighting function $w = 1$ if $F_o \leq 60$ and $w = 60/F_o$ if $F_o > 60$. This was preferred to the statistical weighting function because the presence of systematic errors due to the decomposition of the crystal greatly affected the refinement of the structure and the values of the standard deviations of the parameters. Although much effort has been done to give a definite solution to the solvent's problem, its disorder has prevented us from obtaining highly precise results. Nevertheless the present model can be considered satisfactory in order to derive the desired chemical information. Therefore it has been decided to waste no more computing time in the attempt of getting a better crystallographic agreement. The final atomic positional and thermal parameters along with their standard deviations as estimated from the inverse matrix are given in Table I. Table II lists the positional parameters of the 20 phenyl rings and the four molecules of acetone. Table III lists the carbon atom positions derived from the data of Table II together with the corresponding isotropic thermal parameters. The final values of $10|F_o|$ and $10|F_c|$ are given in Table IV;[11] only the reflections which were used in the refinement are listed in this table.

Acetato[1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(II) Tetraphenylborate. The structure of the acetate derivative was solved

**Table VII.** Derived Group Atom Positional Parameters for [Co(ac)(p$_3$)][B(C$_6$H$_5$)$_4$]

Atom	x	y	z
Ph1–C1	0.0968 (6)	0.0310 (11)	0.4078 (11)
Ph1–C2	0.0990 (7)	0.0015 (7)	0.4826 (14)
Ph1–C3	0.0836 (6)	0.0418 (12)	0.5413 (9)
Ph1–C4	0.0660 (6)	0.1117 (12)	0.5254 (11)
Ph1–C5	0.0638 (7)	0.1414 (8)	0.4508 (14)
Ph1–C6	0.0791 (6)	0.1010 (12)	0.3920 (9)
Ph1–C7	0.0420 (9)	−0.0886 (10)	0.3054 (10)
Ph1–C8	−0.0277 (12)	−0.0636 (6)	0.2744 (10)
Ph1–C9	−0.0847 (7)	−0.1101 (11)	0.2527 (9)
Ph1–C10	−0.0721 (7)	−0.1815 (10)	0.2618 (10)
Ph1–C11	−0.0024 (12)	−0.2064 (6)	0.2926 (10)
Ph1–C12	0.0547 (7)	−0.1600 (11)	0.3143 (9)
Ph2–C13	0.0823 (11)	−0.1313 (9)	0.1138 (10)
Ph2–C14	0.0008 (13)	−0.1164 (9)	0.0902 (9)
Ph2–C15	−0.0404 (7)	−0.1660 (13)	0.0477 (10)
Ph2–C16	−0.0181 (11)	−0.2302 (10)	0.0284 (10)
Ph2–C17	0.0443 (13)	−0.2451 (8)	0.0518 (9)
Ph2–C18	0.1046 (7)	−0.1957 (13)	0.0945 (10)
Ph2–C19	0.1899 (12)	−0.0462 (10)	0.0870 (10)
Ph2–C20	0.1447 (8)	−0.0128 (8)	0.0162 (15)
Ph2–C21	0.1688 (11)	0.0036 (7)	−0.0481 (10)
Ph2–C22	0.2381 (12)	−0.0133 (9)	−0.0421 (10)
Ph2–C23	0.2834 (8)	−0.0467 (8)	0.0286 (14)
Ph2–C24	0.2592 (11)	−0.0631 (8)	0.0930 (10)
Ph3–C25	0.2737 (13)	0.1039 (8)	0.2077 (11)
Ph3–C26	0.3469 (13)	0.0991 (8)	0.2255 (11)
Ph3–C27	0.3774 (6)	0.1278 (8)	0.1715 (15)
Ph3–C28	0.3347 (13)	0.1615 (8)	0.0997 (12)
Ph3–C29	0.2614 (13)	0.1665 (9)	0.0820 (11)
Ph3–C30	0.2309 (6)	0.1377 (8)	0.1359 (15)
Ph3–C31	0.2396 (9)	0.1265 (11)	0.3546 (13)
Ph3–C32	0.2736 (9)	0.1128 (10)	0.4385 (16)
Ph3–C33	0.2772 (7)	0.1641 (14)	0.4972 (9)
Ph3–C34	0.2468 (9)	0.2292 (11)	0.4717 (13)
Ph3–C35	0.2127 (9)	0.2429 (10)	0.3876 (16)
Ph3–C36	0.2091 (7)	0.1916 (13)	0.3291 (9)
B–C37	0.8078 (10)	0.4697 (6)	0.2549 (14)
B–C38	0.8407 (7)	0.4377 (11)	0.3313 (10)
B–C39	0.8259 (9)	0.3685 (11)	0.3425 (9)
B–C40	0.7782 (10)	0.3311 (6)	0.2770 (14)
B–C41	0.7453 (7)	0.3632 (10)	0.2006 (10)
B–C42	0.7601 (9)	0.4326 (11)	0.1896 (9)
B–C43	0.6132 (6)	0.0523 (12)	0.3215 (10)
B–C44	0.6097 (8)	−0.0066 (9)	0.3671 (12)
B–C45	0.5648 (10)	−0.0074 (8)	0.4133 (9)
B–C46	0.5233 (6)	0.0506 (12)	0.4140 (10)
B–C47	0.5268 (8)	0.1096 (9)	0.3684 (12)
B–C48	0.5717 (10)	0.1104 (8)	0.3222 (9)
B–C49	0.6226 (12)	0.0973 (10)	0.1742 (9)
B–C50	0.6527 (8)	0.1532 (11)	0.1468 (14)
B–C51	0.6138 (13)	0.1874 (8)	0.0734 (14)
B–C52	0.5450 (12)	0.1654 (10)	0.0275 (9)
B–C53	0.5150 (8)	0.1093 (11)	0.0550 (14)
B–C54	0.5538 (13)	0.0753 (8)	0.1283 (14)
B–C55	0.7448 (8)	0.0972 (9)	0.3193 (11)
B–C56	0.7478 (9)	0.1396 (9)	0.3858 (13)
B–C57	0.8101 (12)	0.1760 (8)	0.4282 (9)
B–C58	0.8694 (8)	0.1701 (9)	0.4041 (11)
B–C59	0.8665 (9)	0.1275 (9)	0.3375 (13)
B–C60	0.8042 (12)	0.0911 (8)	0.2949 (9)
Acet–O3	0.0943 (12)	0.3614 (14)	0.2417 (18)
Acet–C68	0.0442 (12)	0.3664 (11)	0.2671 (12)
Acet–C69	0.0273 (19)	0.4370 (26)	0.2985 (25)
Acet–C70	−0.0017 (17)	0.3021 (23)	0.2985 (25)

by Patterson and Fourier methods. Group refinement was used for phenyl groups and for the acetone molecule present in the asymmetric unit, whose population parameters were also refined. The weighting function used throughout the refinement was $w = 1/\sigma(F_o)$. At the end of the totally isotropic cycles, when R_1 and R_2 were 0.099 and 0.087, respectively, hydrogen atoms were introduced at calculated positions (C–H = 0.95 Å) and were allotted isotropic temperature factors of 5.0 Å^2 but were not refined. In the last few cycles of refinement the polyhedron's atoms were allowed to vibrate anisotropically. Final R factors are $R_1 = 0.079$ and $R_2 = 0.070$. A final difference Fourier map shows no major feature but some disorder

around the solvent molecules, whose refined population parameter has a value of 0.70. Tables V, VI, VII, and VIII[11] are the equivalent of Tables I, II, III, and IV for what concerns the acetate derivative final parameters.

Results and Discussion

Cobalt(II) chloride and bromide react with p$_3$ and NaB(C$_6$H$_5$)$_4$ in a solution of 1-butanol–acetone, alcohol–methylene chloride, or alcohol–THF at room temperature and under nitrogen to give garnet-brown crystals with the empirical formula CoX(p$_3$)B(C$_6$H$_5$)$_4$·x(solvent) (I). Cobalt(II) iodide undergoes spontaneous reduction in the presence of the phosphine, to give the cobalt(I) complex [CoI(p$_3$)].[1] Salts of cobalt(II) hexahydrate whose anions are weakly coordinating (e.g., ClO$_4^-$, BF$_4^-$) react with the same reagents to give garnet-brown crystals with the empirical formula Co(OH)-(p$_3$)B(C$_6$H$_5$)$_4$·x(solvent). The infrared spectrum of each product contains an O–H stretching band at ca. 3.620 kK. This reaction takes place slowly and is finished only in tens of minutes. Evidently the phosphine acts as a base, removing a proton from a hydrate molecule and thus increasing the concentration of the hydroxide ion. The presence of the hydrate molecules is necessary for the reaction to occur since solutions of the anhydrous salts in 1-butanol do not react with p$_3$ and NaB(C$_6$H$_5$)$_4$. Thus the compounds are probably formed according to

$$Co(H_2O)_n{}^{2+} + 2p_3 + B(C_6H_5)_4{}^- \rightarrow Co(OH)(p_3)B(C_6H_5)_4 +$$
$$(p_3H)^+ + (n-1)H_2O$$
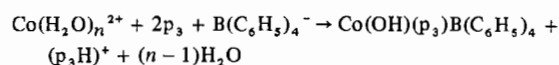
If the anion can behave as a bidentate ligand, brown-ocher compounds are obtained with the empirical formula CoY-(p$_3$)B(C$_6$H$_5$)$_4$·x(solvent) (Y = NO$_3$, ac, acac) (III).

The analytical data of the complexes are given in Table IX.

The halide derivatives decompose rapidly in air and the hydroxo complexes are slightly more stable. Compounds III are stable for many days in air. The latter compounds are soluble in methylene chloride, 1,2-dichloroethane, etc., and the conductivity data are consistent with the presence of 1:1 electrolytes (Table IX). Complexes I and II are sparingly soluble in chlorinated hydrocarbons and are decomposed rapidly in solvents such as nitroethane and nitromethane, as shown by the absorption spectra. For this reason compounds I and II have not been studied in solution.

The diffuse-reflectance spectra of all the compounds are similar and show one band between 9.5 and 11.8 kK with shoulders at 14.3–16 and 20–23.25 kK (Table X). These spectra are fully comparable to the spectra of the low-spin, distorted trigonal-bipyramidal complex [CoCl(QP)][B-(C$_6$H$_5$)$_4$][12] where QP is to tris(o-diphenylphosphinophenyl)phosphine (Figure 1). The solution spectra of class III compounds are essentially identical with the reflectance spectra.

Description of the Structures. Hydroxo Derivative. The structure consists of [B(C$_6$H$_5$)$_4$]$^-$ anions and [(p$_3$)Co-(OH)$_2$Co(p$_3$)]$^{2+}$ cations in which there are two hydroxide bridges joining the cobalt atoms. The inner coordination geometry of the cation is shown in Figure 2, and a stereoscopic view of the cation is shown in Figure 3. Selected interatomic distances and angles are presented in Tables XI and XII. The five coordinating atoms around each cobalt consist of two oxygen atoms from these hydroxo groups and three phosphorus atoms furnished by the p$_3$ ligand. The two Co(p$_3$) units have a configuration intermediate between staggered ($\tau = 60°$) and eclipsed ($\tau = 0°$) with a dihedral angle $\tau = 28.2°$. The Co–P distances are similar to other 3d metal–p$_3$ interatomic distances. The P–Co–P angles vary from 87.9 to 93.6°, which may be compared to the angle of 90° found in octahedral iron compound[13] and 94° found in tetrahedral nickel compounds.[14] Each oxygen atom is distributed over two preferred sites. The

Table IX. Analytical and Some Physical Data for the Complexes

	% calcd				% found				Λ_M,[c] ohm^{-1} mol^{-1} cm^2	μ_{eff}, BM (293 K)
Compd	C	H	Co	P	C	H	Co	P		
$[Co_2(OH)_2(p_3)_2][B(C_6H_5)_4]_2 \cdot 4C_3H_6O$	75.04	6.39	5.19	8.19	74.83	6.71	5.14	8.00		1.90
$[Co_2Cl_2(p_3)_2][B(C_6H_5)_4]_2 \cdot 4CH_2Cl_2$[a]	66.61	5.26	4.88	7.70	66.12	5.35	4.96	7.60		1.70
$[Co_2Br_2(p_3)_2][B(C_6H_5)_4]_2 \cdot 4CH_2Cl_2$	64.26	5.07	4.70		63.52	5.15	4.65			1.48
$[Co(ac)(p_3)][B(C_6H_5)_4] \cdot C_3H_6O$	75.13	6.12	5.26	8.30	74.96	5.98	5.37	8.36	25, 45	2.08
$[Co(acac)(p_3)][B(C_6H_5)_4]$	76.22	6.13	5.35	8.43	76.71	5.97	5.05	8.60	26, 47	2.04
$[Co(NO_3)(p_3)][B(C_6H_5)_4] \cdot 2C_3H_6O$[b]	72.19	6.06	4.99		72.15	5.85	5.21		22, 50	2.01

[a] Calcd: Cl, 14.65. Found: Cl, 13.48. [b] Calcd: N, 1.18. Found: N, 1.22. [c] Molar conductance values for 10^{-3} M 1,2-dichloroethane and nitroethane solutions, respectively.
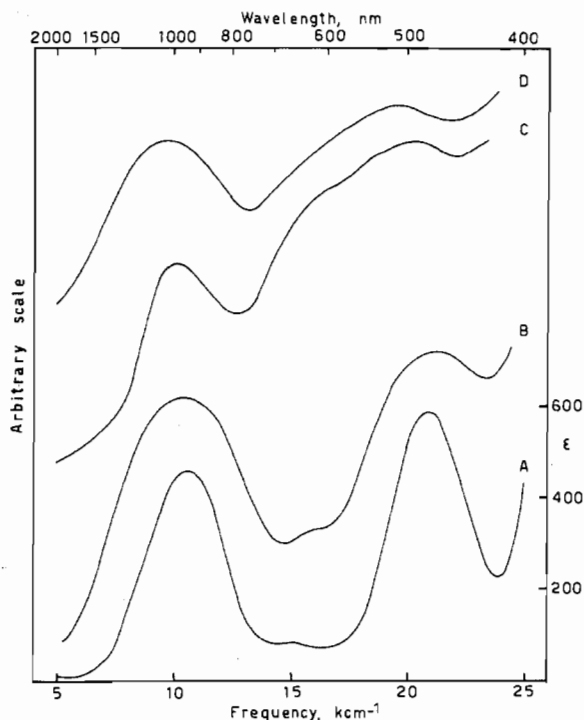
Figure 1. Absorption spectrum of $[Co(ac)(p_3)][B(C_6H_5)_4] \cdot C_3H_6O$ in 1,2-dichloroethane (curve A). Solid-state spectra (arbitrary scale) of $[Co(ac)(p_3)][B(C_6H_5)_4] \cdot C_3H_6O$ (curve B), $[CoCl(QP)][B(C_6H_5)_4]$ (curve C), and $[Co_2(OH)_2(p_3)_2][B(C_6H_5)_4]_2 \cdot 4C_3H_6O$ (curve D).
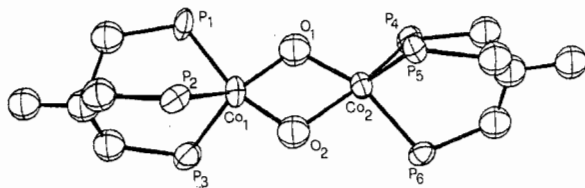
Figure 2. Perspective view of the inner coordination sphere of the $[Co_2(OH)_2(p_3)_2]^{2+}$ dimer cation (ORTEP diagram).
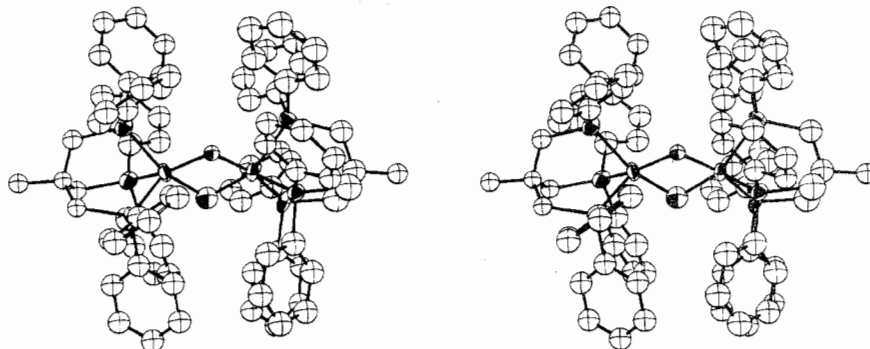
Table X. Absorption Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

| Compd	Absorption max,[a] kK (ϵ_M for soln)
$[Co_2(OH)_2(p_3)_2[B(C_6H_5)_4] \cdot 4C_3H_6O$	A: 8.0 sh, 9.5, 16.7 sh, 19.8
$[Co_2Cl_2(p_3)_2][B(C_6H_5)_4]_2 \cdot 4CH_2Cl_2$	A: 10, 15.4 sh, 20
$[Co_2Br_2(p_3)_2][B(C_6H_5)_4]_2 \cdot 4CH_2Cl_2$	A: 8.7 sh, 9.7, 16 sh, 20
$[Co(ac)(p_3)][B(C_6H_5)_4] \cdot C_3H_6O$	A: 10.5, 16 (sh), 21.1
	B: 10.6 (464), 15.3 (73), 21.1 (596)
$[Co(acac)(p_3)][B(C_6H_5)_4]$	A: 10 sh, 11.8, 14.3 sh, 23.25 sh
	C: 11.05 (450), 15.5 sh, 20 sh
$[Co(NO_3)(p_3)][B(C_6H_5)_4] \cdot 2C_3H_6O$	A: 8.7 sh, 10.2, 16.7 sh, 22.2
	C: 10.4 (420), 15.5 (93), 22.2 (1074)

[a] Key: A, solid; B, 1,2-dichloroethane solution; C, nitroethane solution.

crystallographic analysis gives only an average picture of the dimers as they exist in the crystal. Clearly there is no unique orientation of the oxygen atoms within the dimer. Since there are four possible locations for the two oxygen atoms of each dimer, there are six possible combinations of these sites. Three of these combinations can be dismissed because they lead to a physically unreasonable situation (maximum contact distance 1.67 Å). The remaining three combinations represent possible configurations for the two oxygen atoms relative to the remainder of the dimer. Contacts inside two of these couples (2.18, 2.28 Å) are of the same order of magnitude found in the acetate complex, where the rigidity of the acetate anion imposes a contact of 2.18 Å. Only the couple O2–O11 has a shorter contact of 1.92 Å, which is to be attributed to the degree of uncertainty still present in the model. The geometry around each metal atom in these three configurations varies between square-pyramidal and trigonal-bipyramidal limits. Because of the strain in the O–Co–O system [this angle varies from 58.8 (2.6) to 73.7 (2.9)°] the limiting geometries cannot be attained.

The bridge M–O–M angles are from 104.6 to 110.1° similar

Figure 3. Stereoscopic view of the $[Co_2(OH)_2(p_3)_2]^{2+}$ cation.

Table XI. Selected Intramolecular Bond Distances (Å) for
[Co$_2$(OH)$_2$(p$_3$)$_2$][B(C$_6$H$_5$)$_4$]$_2$

Co1–Co2	3.063 (6)	P4–C37	1.812 (22)
Co1–P1	2.287 (11)	P4–C43	1.766 (28)
Co1–P2	2.238 (14)	P5–C127	1.877 (55)
Co1–P3	2.230 (9)	P5–C49	1.837 (18)
Co2–P4	2.263 (9)	P5–C55	1.828 (27)
Co2–P5	2.240 (17)	P6–C128	1.921 (49)
Co2–P6	2.286 (13)	P6–C61	1.804 (38)
Co1–O1	1.950 (38)	P6–C67	1.743 (21)
Co1–O2	1.921 (77)	C121–C124	1.520 (37)
Co1–O11	1.989 (62)	C122–C124	1.485 (57)
Co1–O22	1.910 (83)	C123–C124	1.551 (63)
Co2–O1	1.839 (53)	C124–C125	1.530 (59)
Co2–O2	1.951 (50)	C126–C129	1.558 (67)
Co2–O11	1.743 (69)	C127–C129	1.688 (74)
Co2–O22	1.959 (60)	C128–C129	1.489 (62)
P1–C121	1.859 (40)	C129–C130	1.549 (69)
P1–C1	1.799 (26)	B1–C73	1.669 (52)
P1–C7	1.797 (32)	B1–C79	1.645 (67)
P2–C122	1.854 (39)	B1–C85	1.896 (48)
P2–C13	1.783 (28)	B1–C91	1.687 (59)
P2–C19	1.825 (20)	B2–C97	1.620 (55)
P3–C123	1.912 (45)	B2–C103	1.768 (66)
P3–C25	1.800 (21)	B2–C109	1.659 (45)
P3–C31	1.851 (39)	B2–C115	1.838 (40)
P4–C126	1.865 (59)		
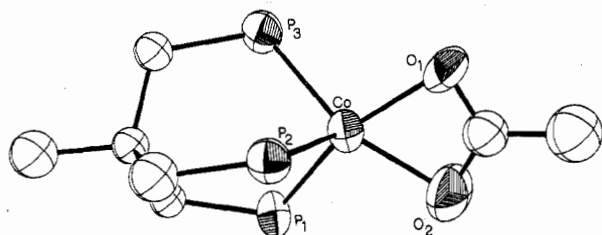
Figure 4. Perspective view of the inner coordination sphere of the [Co(ac)(p$_3$)]$^+$ cation (ORTEP diagram).

to the range 99–104.4° found in the hydroxo-bridged, antiferromagnetic copper complexes.[15]

The Co–O bond lengths are subject to large uncertainties so we shall not compare them to analogous cases. The Co–Co distance of 3.067 (6) Å is close to the intermetallic distance in copper and chromium hydroxo-bridged antiferromagnetic complexes.[16-19]

Acetato Derivative. In the cation [Co(ac)(p$_3$)]$^+$ the cobalt atom is surrounded by three phosphorus atoms and two oxygen atoms belonging to an acetate group. The geometry of the coordinating polyhedron (Figures 4 and 5) is a distorted square pyramid with P1 in the apical position. The donor atoms are 0.08–0.13 Å away from the mean basal plane while the cobalt atom is 0.32 Å above it. In Tables XIII and XIV selected intramolecular distances and angles are presented. The
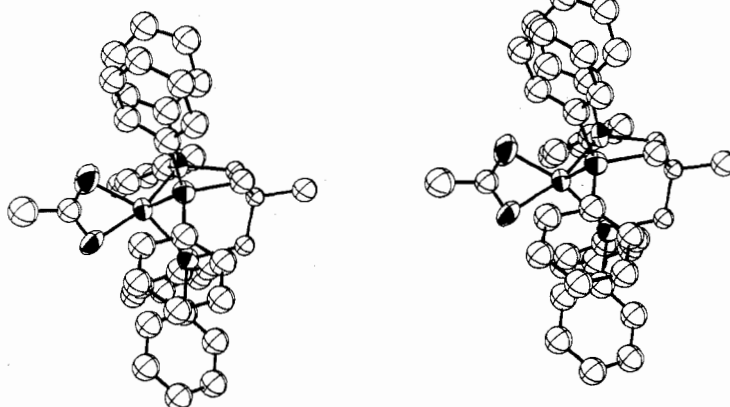
Table XII. Selected Intramolecular Bond Angles (deg) for
[Co$_2$(OH)$_2$(p$_3$)$_2$][B(C$_6$H$_5$)$_4$]$_2$

P1–Co1–P2	87.9 (4)	P4–Co2–P5	90.2 (5)
P1–Co1–P3	93.6 (4)	P4–Co2–P6	89.1 (4)
P2–Co1–P3	87.9 (4)	P5–Co2–P6	90.6 (5)
P1–Co1–O1	113.1 (1.1)	P4–Co2–O1	103.2 (1.0)
P2–Co1–O1	97.9 (1.5)	P5–Co2–O1	161.6 (1.3)
P3–Co1–O1	152.8 (1.2)	P6–Co2–O1	102.1 (1.4)
P1–Co1–O2	138.7 (2.2)	P4–Co2–O2	157.6 (2.0)
P2–Co1–O2	133.4 (2.2)	P5–Co2–O2	92.5 (2.5)
P3–Co1–O2	87.9 (1.6)	P6–Co2–O2	113.1 (2.0)
P1–Co1–O11	87.8 (1.9)	P4–Co2–O11	96.0 (1.5)
P2–Co1–O11	143.4 (2.2)	P5–Co2–O11	111.2 (2.8)
P3–Co1–O11	128.7 (2.3)	P6–Co2–O11	157.6 (2.7)
P1–Co1–O22	107.8 (1.9)	P4–Co2–O22	127.5 (1.6)
P2–Co1–O22	163.7 (2.0)	P5–Co2–O22	88.2 (2.6)
P3–Co1–O22	95.1 (1.7)	P6–Co2–O22	143.4 (1.5)
O1–Co1–O2	68.7 (2.3)	O1–Co2–O2	70.3 (2.7)
O1–Co1–O22	72.4 (2.4)	O1–Co2–O22	73.7 (2.9)
O2–Co1–O11	58.8 (2.6)	O2–Co2–O11	62.3 (2.5)
Co1–O1–Co2	104.6 (2.8)	Co1–O11–Co2	110.1 (2.7)
Co1–O2–Co2	107.8 (2.3)	Co1–O22–Co2	104.6 (3.8)
Co1–P1–C121	112.4 (1.0)	Co2–P4–C126	114.6 (1.3)
Co1–P1–C1	117.4 (1.0)	Co2–P4–C37	118.2 (8)
Co1–P1–C7	115.5 (1.4)	Co2–P4–C43	118.6 (1.0)
C121–P1–C1	102.3 (1.6)	C126–P4–C37	103.1 (1.7)
C121–P1–C7	107.4 (1.7)	C126–P4–C43	102.7 (1.9)
C1–P1–C7	100.1 (1.2)	C37–P4–C43	96.9 (1.3)
Co1–P2–C122	112.6 (1.5)	Co2–P5–C127	118.2 (2.0)
Co1–P2–C13	116.9 (1.0)	Co2–P5–C49	113.1 (1.1)
Co1–P2–C19	114.9 (1.2)	Co2–P5–C55	119.9 (1.2)
C122–P2–C13	107.5 (1.8)	C127–P5–C49	103.4 (1.8)
C122–P2–C19	103.0 (1.3)	C127–P5–C55	100.2 (2.0)
C13–P2–C19	100.4 (1.2)	C49–P5–C55	99.0 (1.2)
Co1–P3–C123	113.8 (1.2)	Co2–P6–C128	112.5 (1.4)
Co1–P3–C25	115.2 (1.0)	Co2–P6–C61	116.2 (1.3)
Co1–P3–C31	115.5 (9)	Co2–P6–C67	119.6 (1.1)
C123–P3–C25	107.9 (1.4)	C128–P6–C61	107.2 (1.9)
C123–P3–C31	102.5 (1.7)	C128–P6–C67	103.4 (1.7)
C25–P3–C31	100.4 (1.3)	C61–P6–C67	96.0 (1.4)
C124–C121–P1	118.0 (2.9)	C129–C126–P4	118.0 (2.7)
C124–C122–P2	118.8 (3.0)	C129–C127–P5	112.4 (4.1)
C124–C123–P3	114.5 (2.4)	C129–C128–P6	118.5 (3.3)
C121–C124–C125	108.2 (3.0)	C126–C129–C130	106.5 (3.0)
C122–C124–C125	107.6 (3.5)	C127–C129–C130	102.6 (4.3)
C123–C124–C125	102.9 (2.8)	C128–C129–C130	109.6 (3.7)
C73–B1–C79	114.1 (3.7)	C97–B2–C103	108.4 (3.0)
C73–B1–C85	94.7 (2.6)	C97–B2–C109	121.8 (2.9)
C73–B1–C91	111.7 (2.8)	C97–B2–C115	106.6 (2.6)
C79–B1–C85	115.3 (2.5)	C103–B2–C109	111.1 (3.2)
C79–B1–C91	111.7 (3.0)	C103–B2–C115	102.2 (2.3)
C85–B1–C91	108.3 (3.2)	C109–B2–C115	104.9 (2.7)

P–Co–P angles between 90.4 (3) and 91.8 (3)° fall in the same range as those for the dimeric complex described above. The acetate group is almost planar and the dihedral angle between this plane and the pyramidal basal plane is only 8°. The

Figure 5. Stereoscopic view of the [Co(ac)(p$_3$)]$^+$ cation.

Table XIII. Selected Intramolecular Bond Distances (A) for [Co(ac)(p₃)][B(C₆H₅)₄]

Co–P1	2.278 (9)	P3–C31	1.818 (24)
Co–P2	2.211 (9)	O1–C66	1.268 (28)
Co–P3	2.222 (8)	O2–C66	1.252 (31)
Co–O1	2.001 (19)	C66–C67	1.473 (38)
Co–O2	2.027 (15)	C61–C64	1.575 (41)
P1–C61	1.844 (25)	C62–C64	1.597 (32)
P1–C1	1.845 (22)	C63–C64	1.593 (36)
P1–C7	1.846 (20)	C64–C65	1.553 (32)
P2–C62	1.840 (23)	B–C37	1.673 (34)
P2–C13	1.848 (19)	B–C43	1.746 (39)
P2–C19	1.859 (25)	B–C49	1.739 (31)
P3–C63	1.809 (23)	B–C55	1.736 (30)
P3–C25	1.851 (26)		

Table XIV. Selected Intramolecular Bond Angles (deg) for [Co(ac)(p₃)][B(C₆H₅)₄]

P1–Co–P2	90.9 (3)	Co–P3–C25	115.0 (7)
P1–Co–P3	91.8 (3)	Co–P3–C31	110.9 (7)
P2–Co–P3	90.4 (3)	C63–P3–C25	105.1 (1.1)
O1–Co–O2	65.5 (7)	C63–P3–C31	107.3 (1.0)
P1–Co–O1	113.4 (7)	C25–P3–C31	103.1 (1.0)
P1–Co–O2	102.3 (6)	Co–O1–C66	87.7 (1.5)
P2–Co–O1	154.2 (6)	Co–O2–C66	87.0 (1.3)
P2–Co–O2	102.2 (6)	O1–C66–O2	119.6 (2.2)
P3–Co–O1	97.1 (5)	O1–C66–C67	123.9 (2.4)
P3–Co–O2	160.8 (6)	O2–C66–C67	116.5 (2.1)
Co–P1–C61	112.3 (1.0)	C64–C61–P1	116.5 (1.7)
Co–P1–C1	118.0 (8)	C64–C62–P2	115.3 (1.7)
Co–P1–C7	113.3 (6)	C64–C63–P3	116.0 (1.5)
C61–P1–C1	103.8 (1.0)	C61–C64–C65	104.8 (2.0)
C61–P1–C7	106.2 (1.1)	C62–C64–C65	108.2 (2.0)
C1–P1–C7	102.1 (9)	C63–C64–C65	106.9 (1.8)
Co–P2–C62	114.3 (9)	C37–B–C43	113.6 (2.1)
Co–P2–C13	119.5 (8)	C37–B–C49	114.5 (1.9)
Co–P2–C19	109.9 (7)	C37–B–C55	109.8 (1.7)
C62–P2–C13	101.2 (1.0)	C43–B–C49	104.0 (1.8)
C62–P2–C19	109.6 (1.1)	C43–B–C55	106.0 (1.8)
C13–P2–C19	101.1 (9)	C49–B–C55	108.4 (1.9)
Co–P3–C63	114.5 (8)		

O–Co–O angle of 65.5 (7)° allows the O–Co–O angle of the acetate group to remain close to 120°. The Co–P distances, 2.211 (9)–2.278 (8) Å, are like the Co–P distances in the hydroxo derivative.

The chloro and bromo derivatives have chemical characteristics similar to, reflectance spectra identical with, and magnetic behavior similar to those of the hydroxo derivative. Therefore a similar doubly bridged structure is assigned to these compounds, with two halide bridges between a pair of cobalt atoms. The nitrato and acetylacetonato derivatives have chemical, spectral, and magnetic properties similar to those of the acetato derivative. These compounds are therefore assigned a five-coordinate mononuclear structure in which the anion is bound as a bidentate ligand. For the nitrato derivative such a conclusion is corroborated by the infrared spectrum which shows a band centered about 1.55 kK which can be attributed to a bidentate nitrate group.

Magnetic Measurements. At room temperature the magnetic moments lie between 1.48 and 2.08 BM. The higher values indicate a low-spin d^7 configuration with the usual orbital contribution raising the value above 1.73 BM. These values are found for the monomeric acetato derivative and for the nitrato and acetylacetonato derivatives whose spectra and conductivity data are indicative of a monomeric structure. The acetato and nitrato complexes follow the Curie–Weiss law between 84 and 294 K, with $\theta \approx 0°$.

At room temperature the hydroxo complex has a moment of 1.90 BM, the chloro complex a moment of 1.70 BM, and the bromo complex a moment of 1.48 BM. The moments of these three complexes decrease with temperature. The magnetic susceptibility of each complex initially increases with decreasing temperature and after reaching a maximum value
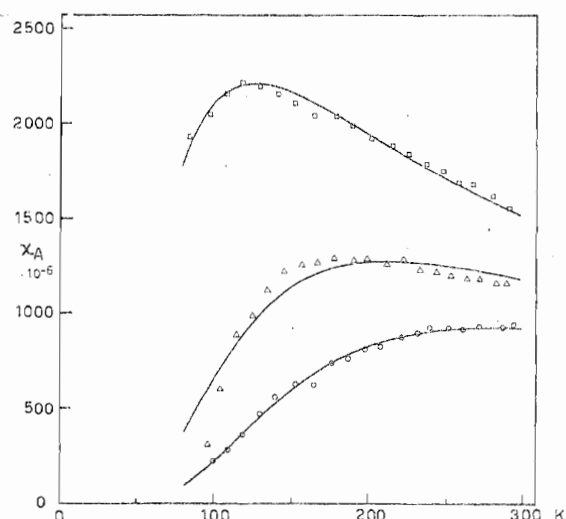
Figure 6. Experimental values of magnetic susceptibilities of [Co₂(OH)₂(p₃)₂][B(C₆H₅)₄]₂·4C₃H₆O (□), [Co₂(Cl)₂(p₃)₂][B(C₆H₅)₄]₂·4CH₂Cl₂ (△), and [Co₂(Br)₂(p₃)₂][B(C₆H₅)₄]₂·4CH₂Cl₂ (○). Continuous lines are calculated curves.

decreases as the temperature decreases toward 90 K (Figure 6). This behavior is characteristic of antiferromagnetism, and this is the first time that antiferromagnetic behavior has been observed in low-spin cobalt(II) complexes. Magnetic exchange between ions with a single unpaired electron has been observed in oxygen- and halogen-bridged complexes of copper(II), titanium(III), and oxovanadium(IV).[20-23]

The Co–Co distance of 3.067 (6) Å is markedly longer than the sum of covalent radii of the two metal atoms. This renders improbable any direct Co–Co interaction, though it cannot be excluded. It is more likely that a spin singlet state is generated via superexchange across the diamagnetic bridging atoms. The effects of orbital degeneracy can be ignored as an orbital singlet is the likely ground state of an isolated cobalt ion in an environment of such low symmetry. Thus, the decrease in observed magnetic moment can be related to a single exchange term in the Hamiltonian of the form $-2JS_1S_2$. Since $S_1 = S_2 = 1/2$, the susceptibility of the paired system is given by the Bleaney–Bowers equation[24]

$$\chi_A = 3K/T[1/(3 + x^2)] + N\alpha$$
$$K = Ng^2\beta^2/3k \quad ex = \exp(-J/kT)$$

This expression was fitted to the experimental data, assuming zero temperature-independent paramagnetism. The best pair of values of g and J/k was determined using a direct method to minimize the error-square sum ($\sum(\chi_{obsd} - \chi_{calcd})^2$) over the observed susceptibilities. The best fits are found for the following values of J and g: [Co₂(OH)₂(p₃)₂][B(C₆H₅)₄]₂·4C₃H₆O, $g = 2.45$, $J = -72$ cm⁻¹; [Co₂Cl₂(p₃)₂][B(C₆H₅)₄]₂·4CH₂Cl₂, $g = 2.38$, $J = -117$ cm⁻¹; [Co₂Br₂(p₃)₂][B(C₆H₅)₄]₂·4CH₂Cl₂, $g = 2.33$, $J = -157$ cm⁻¹.

The calculated J values indicate the presence of a strong antiferromagnetic exchange interaction, as indeed is the case in many other complexes which contain

$$M\!\!\diagdown\!\!\overset{X}{\underset{X}{}}\!\!\diagup\!\!M$$

units.[20-23] The strength of the interaction increases as the electronegativity of the bridge anion decreases, namely, $|J_{OH}| < |J_{Cl}| < |J_{Br}|$. This is the trend usually observed[25] and is explained by considering the effective charge on the metal atoms. As the charge decreases, the metal orbitals can expand and the possibility of the exchange is increased. However, the model is highly approximate and too much significance should not be read into the results of these calculations.

Registry No. [Co2(OH)2(p3)2][B(C6H5)4]2·xC3H6O, 56172-83-9; [Co2Cl2(p3)2][B(C6H5)4]2, 56172-85-1; [Co2Br2(p3)2][B(C6H5)4]2, 56172-87-3; [Co(ac)(p3)][B(C6H5)4]·xC3H6O, 56172-90-8; [Co-(acac)(p3)][B(C6H5)4], 56172-92-0; [Co(NO3)(p3)][B(C6H5)4], 56172-94-2.

Supplementary Material Available. Tables IV and VIII, listings of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40810Y-10-75.

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(6) Here and elsewhere in the paper, unless otherwise specified, the amount of solvent in the formulas is left undetermined, because it varies depending on many factors such as the nature of the solvent itself, the conditions of preparation, etc. Moreover not always a good agreement has been found between the results of elementary analysis and the density measurements of crystals coming from the same source. Moreover the LS refined population parameter of the acetone molecule present in the asymmetric unit of the acetate derivative is not particularly significant, the X-ray analysis being conducted on a single specimen. The ranges of x values, as derived from all of the above cited sources, are 2–4 for the hydroxo derivative and 0.7–1 for the acetato derivative. When the use of a well-defined molecular weight of a certain compound was necessary (e.g., during a physical measurement), the number of molecules of solvent was fixed as the integer closest to the analytical data.
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Reactions of (RC≡CR')Co2(CO)6 Complexes with Mono- and Bidentate Group 5 Ligands

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Various (RC≡CR')Co2(CO)6 derivatives (R, R' = H, CH2OH, or C6H5) undergo replacement of one or both axial CO groups on heating with monodentate phosphines, phosphites, and arsines. Bulky ligands such as (o-CH3C6H4)3P do not react, but (CH3O)3P may displace up to four carbonyl ligands in a series of reversible reactions. Bidentate fluorocarbon- and hydrocarbon-bridged ligands react similarly but tend to occupy equatorial coordination positions about the metal atoms either by bridging two cobalt atoms in the same molecule or by chelating to one of them. They may displace two or four CO groups. Infrared and NMR spectra are reported.

The products of formula (RC≡CR')Co2(CO)6, obtained from the reactions of alkynes with dicobalt octacarbonyl, are well-known and have the structure indicated in I.[2] Only a

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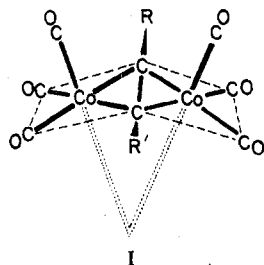
limited number of studies on the reactions of these compounds with group 5 ligands have been made.[2b-5]

The present work has been carried out to investigate the carbonyl substitution reactions of these compounds with a wide range of monodentate phosphines, phosphites, and arsines, and, of particular interest, with fluorocarbon-bridged di(tertiary ligands). It is an extension of earlier studies on these[5] and the closely related [μ-RSFe(CO)3]2 compounds.[6]

Experimental Section

Infrared spectra (Tables I and II) were run on Perkin-Elmer Model 337 or 457 spectrometers. NMR spectra (Tables III and IV) were recorded on Varian T-60 and HA-100 or Perkin-Elmer R 12 spectrometers. Chemical shifts are reported in ppm downfield from internal TMS (^{1}H) and upfield from internal CFCl3 (^{19}F). Molecular weights were determined in benzene solution using a Mechrolab vapor pressure osmometer. Elemental analyses (Tables I and II) were carried out by Mr. P. Borda (University of British Columbia) or Mrs. E. Carey (University College, Dublin).

Ligands and starting materials were prepared as described in the literature. All reactions were carried out in sealed tubes or under an atmosphere of nitrogen using purified solvents.

1. Reaction of (RC≡CR')Co2(CO)6 with Monodentate Ligands.