

ideal packing and are displaced towards the Al atoms. This displacement probably arises from the larger electrostatic interaction of the ions Al³⁺ and F⁻ in comparison with the interactions between Sr²⁺ and F⁻ and Li⁺ and F⁻; each F⁻ anion is 3-coordinate, binding to Sr²⁺, Li⁺, and Al³⁺. From inspection of Fig. 1, it is seen that the displacements will occur in an opposite sense relative to the trigonal axis for adjacent F layers, affording the observed distortions of the AlF₆ units. Because the potential well for the Sr–F interaction is probably wider and softer than that of the Ca–F interaction it is not surprising that a larger displacement toward the Al³⁺ ion and a more distorted AlF₆ group in the Sr derivative are observed.

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Reaction of PhCCo₃(CO)₉ with Bis(dimethylphosphino)ethane and Structure of PhCCo₃(CO)₅(dmpe)₂·(toluene). Observation of Phosphine Bridging and Chelation

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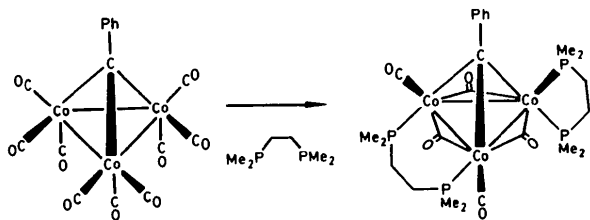
Abstract. Tri- μ -carbonyl-dicarbonyl-mono-(μ_3 -benzylidene)-1,2-ethanediylbis(dimethylphosphino)-tricobalt(1)(3Co–Co) toluene solvate, [PhCCo₃(CO)₅(dmpe)₂].toluene (where dmpe = Me₂PCH₂CH₂PMe₂), C₂₄H₃₇Co₃O₅P₄·C₇H₈, *M_r* = 798.39, monoclinic, *P*2₁/*c*, *a* = 9.861 (2), *b* = 11.172 (2), *c* = 32.935 (5) Å, β = 82.91 (1)°, *V* = 3600.5 (10) Å³, *Z* = 4, *D_x* = 1.473 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 15.74 cm⁻¹, *F*(000) = 1648, *T* = 295 K, *R* = 0.0758 for 3810 independent reflections. The cobalt atoms are in a triangular array with a capping μ_3 -benzylidene ligand completing the *nido* polyhedral core. One dmpe ligand bridges a pair of cobalt atoms while the second dmpe ligand chelates

the unique cobalt atom. Three μ_2 -carbonyl groups are observed due to the high degree of phosphine substitution.

Introduction. Olefin hydroformylation using PhCCo₃(CO)₉ has been extensively studied because it was believed that the capping μ_3 -benzylidene ligand might stabilize the triangular array of cobalt atoms against fragmentation and, thus, promote metal cluster catalysis (Pittman & Ryan, 1978; Ryan, Pittman & O'Connor, 1977). However, other studies suggest that clusters based on RCCo₃(CO)₉ (where *R* = Ph or Me) readily decompose under reducing conditions to give mononuclear cobalt species which are responsible for the observed catalytic activity (Murata & Matsuda, 1980; Withers & Seyferth, 1983). Stabili-

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zation of polynuclear clusters through the use of bidentate phosphines is widely accepted (Richmond & Kochi, 1987a) and has been demonstrated in phosphine-substituted clusters derived from $\text{RCCo}_3(\text{CO})_9$ using the bidentate phosphines $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), $\text{Ph}_2\text{PCH}_2\text{PMe}_2$, and $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (dppe) (Aime, Botta, Gobetto & Osella, 1987; Balavoine, Collin, Bonnet & Lavigne, 1985; Collin, Jossart & Balavoine, 1986; Downard, Robinson & Simpson, 1986). Such phosphine ligand systems effectively shield the reactive metal centers during hydroformylation and reduce the amount of cluster fragmentation; however, improved cluster stability is accompanied by a dramatic rate retardation. In order to take full advantage of the tethering nature of the bidentate phosphine while at the same time minimizing the steric hindrance of the aryl groups, we have studied the reaction between $\text{PhCCo}_3(\text{CO})_9$ and bis(dimethylphosphino)ethane (dmpe). Our interest in the dmpe ligand derives from the presence of the smaller methyl groups which should lead to phosphine-substituted clusters with altered physical and catalytic properties in addition to the fact that dmpe substitution chemistry in metal clusters remains relatively unexplored (Schulman, Richmond, Watson & Nagl, 1989). Herein we report the single-crystal X-ray determination of $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$, the product from $\text{PhCCo}_3(\text{CO})_9$ and dmpe (2 equiv.), which establishes the bridging and chelating nature of the two dmpe ligands.



Experimental. The title cluster was prepared from the reaction of 0.20 g of $\text{PhCCo}_3(\text{CO})_9$ (0.39 mmol) and 0.12 g of dmpe (0.79 mmol) in 50 ml of THF. The reaction was stirred overnight at room temperature and then examined by TLC analysis which indicated that no starting material remained. The solvent was removed under vacuum and the residue was extracted with benzene, followed by filtration through filter paper. All work-up procedures were conducted in a Vacuum Atmospheres Dri-lab since solutions of the dmpe-substituted cluster are air sensitive. The IR spectrum (CH_2Cl_2) revealed the presence of five $\nu(\text{CO})$ bands [1957 (s), 1931 (vs), 1820 (m), 1778 (s), and 1769 (s) cm^{-1}] which are much lower in frequency than those observed in other tricobalt clusters with one bidentate phosphine

ligand. Accordingly, we sought to characterize unequivocally the nature of this cluster by X-ray diffraction analysis. Black crystals suitable for X-ray analysis were obtained from a toluene/heptane (1/1) solution (0.10 g isolated; 40% yield). Crystal dimensions of $0.12 \times 0.23 \times 0.33$ mm; Nicolet $R3m/\mu$ update of $P2_1$ diffractometer; data collected in the ω -scan mode ($3 \leq 2\theta \leq 50^\circ$), scan rate 4 to $29.3^\circ \text{min}^{-1}$, graphite-monochromated $\text{Mo K}\alpha$ radiation, lattice parameters from a least-squares refinement of 25 reflections ($22.00 \leq 2\theta \leq 25.54^\circ$), angles measured by a centering routine; Laue symmetry and statistics consistent with space group $P2_1/c$; monitored reflections (221 and $\bar{2}00$) showed no changes in intensities; 8875 reflections measured ($-11 \leq h \leq 11$, $0 \leq k \leq 13$, $0 \leq l \leq 39$), $R_{\text{int}} = 0.009$, $3810 \geq 3\sigma(I)$; Lorentz-polarization corrections and a ψ -scan absorption correction (transmission factors 0.916 to 0.709) applied; structure solved by direct methods, block-cascade least-squares refinement; the phenyl group and the toluene solvate were subjected to group refinement; H atoms were located in the difference maps but were allowed to ride at fixed distances from the attached atoms; the methyl H atoms, the ethane H atoms and the phenyl and toluene H-atom isotropic thermal parameters were refined as individual entities; final $R = 0.0758$, $wR = 0.0523$ for 365 parameters and 3810 reflections ($R = 0.1284$, $wR = 0.0564$ for all data), $S = 1.503$, $(\Delta/\sigma)_{\text{max}} = 0.017$, $(\Delta/\sigma)_{\text{av}} = 0.004$; largest peaks in final difference map $+0.69$ and $-0.70 \text{ e } \text{\AA}^{-3}$; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0.00008 F_c^{21}]^{-1}$; extinction correction $F^* = F_c/[1.0 + 6(2) \times 10^{-8} F_c^2/\sin(2\theta)]^{0.25}$ applied. All computer programs supplied by Nicolet (Nicolet Instrument Corporation, 1986) for Desktop 30 Microclipse and Nova 4/c configuration; atomic scattering factors and anomalous-dispersion corrections taken from the *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1 lists atomic positional parameters for $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$ while Table 2 gives bond distances and valence angles.* Fig. 1 is a drawing of the dmpe-substituted cluster while the cross-sectional view through the tricobalt plane in Fig. 2 illustrates the disparate bridging Co—CO bond lengths.

Discussion. The structure of $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$ consists of three Co atoms in a triangular array with one dmpe ligand chelating the unique cobalt atom [Co(1)]; the remaining dmpe ligand serves to bridge Co(2) and Co(3) through axial coordination. The

* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53253 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

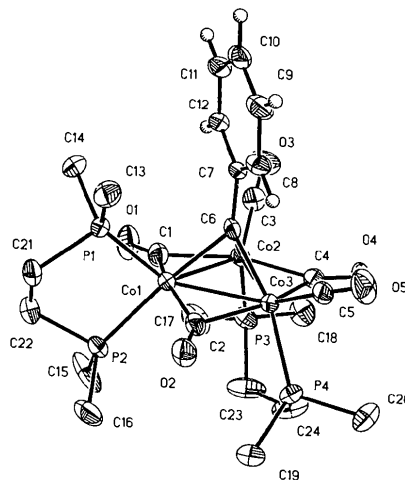
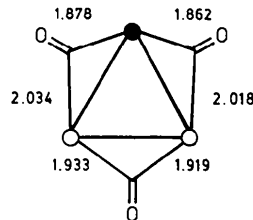
	x	y	z	U
Co(1)	3919 (1)	3362 (1)	982 (1)	35 (1)
Co(2)	5428 (1)	3374 (1)	1528 (1)	39 (1)
Co(3)	5641 (1)	4957 (1)	1021 (1)	36 (1)
P(1)	3605 (2)	2038 (2)	522 (1)	44 (1)
P(2)	1637 (2)	3626 (2)	1077 (1)	49 (1)
P(3)	4383 (2)	4165 (2)	2103 (1)	51 (1)
P(4)	4734 (2)	6615 (2)	1312 (1)	49 (1)
C(1)	3798 (8)	2361 (8)	1437 (2)	55 (3)
O(1)	3206 (7)	1567 (6)	1615 (2)	81 (3)
C(2)	4163 (7)	4728 (7)	649 (2)	41 (3)
O(2)	3794 (6)	5269 (5)	382 (2)	61 (2)
C(3)	6427 (9)	2291 (8)	1718 (2)	55 (3)
O(3)	7102 (7)	1589 (6)	1852 (2)	93 (3)
C(4)	6643 (8)	4723 (7)	1484 (2)	44 (3)
O(4)	7541 (6)	5162 (6)	1637 (2)	65 (2)
C(5)	6923 (8)	5620 (7)	695 (2)	45 (3)
O(5)	7811 (7)	6102 (6)	499 (2)	82 (3)
C(6)	5905 (7)	3263 (7)	946 (2)	40 (3)
C(8)	7486 (5)	3047 (4)	303 (2)	46 (3)
C(9)	8325	2352	24	61 (4)
C(10)	8572	1156	112	61 (4)
C(11)	7979	655	480	62 (4)
C(12)	7140	1350	759	50 (3)
C(7)	6894	2546	671	37 (3)
C(13)	4501 (8)	2097 (8)	8 (2)	63 (4)
C(14)	3764 (9)	468 (7)	656 (3)	70 (4)
C(15)	640 (8)	3556 (13)	1570 (3)	118 (6)
C(16)	838 (9)	4862 (9)	848 (4)	110 (5)
C(17)	3077 (9)	3295 (10)	2412 (2)	88 (5)
C(18)	5504 (9)	4534 (9)	2489 (2)	75 (4)
C(19)	3287 (9)	7301 (8)	1121 (3)	81 (4)
C(20)	5894 (10)	7882 (8)	1292 (3)	84 (5)
C(21)	1809 (8)	2115 (9)	426 (3)	69 (4)
C(22)	940 (9)	2360 (8)	821 (3)	73 (4)
C(23)	3459 (11)	5544 (9)	2047 (3)	88 (5)
C(24)	4206 (12)	6552 (9)	1869 (3)	86 (5)
C(26)	9661 (7)	-2593 (11)	1764 (3)	94 (6)
C(27)	9957	-3114	2128	129 (7)
C(28)	10666	-2464	2396	175 (12)
C(29)	11078	-1293	2300	204 (12)
C(30)	10783	-772	1936	204 (14)
C(25)	10074	-1422	1668	126 (7)
C(31)	9768 (16)	-920 (16)	1307 (5)	293 (14)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Co(1)—Co(2)	2.472 (1)	Co(1)—Co(3)	2.476 (1)
Co(1)—P(1)	2.166 (2)	Co(1)—P(2)	2.253 (2)
Co(1)—C(1)	1.862 (8)	Co(2)—C(2)	1.878 (8)
Co(1)—C(6)	1.950 (7)	Co(2)—Co(3)	2.424 (1)
Co(2)—P(3)	2.222 (2)	Co(2)—C(1)	2.018 (9)
Co(2)—C(3)	1.726 (9)	Co(2)—C(4)	1.919 (8)
Co(2)—C(6)	1.923 (7)	Co(3)—P(4)	2.222 (2)
Co(3)—C(2)	2.034 (8)	Co(3)—C(4)	1.933 (8)
Co(3)—C(5)	1.723 (8)	Co(3)—C(6)	1.923 (8)
C(1)—O(1)	1.178 (10)	C(2)—O(2)	1.161 (10)
C(3)—O(3)	1.151 (11)	C(4)—O(4)	1.179 (10)
C(5)—O(5)	1.155 (10)	C(6)—C(7)	1.481 (8)
Co(2)—Co(1)—Co(3)	58.7 (1)	Co(2)—Co(1)—P(1)	131.5 (1)
Co(2)—Co(1)—P(2)	125.4 (1)	P(1)—Co(1)—P(2)	87.7 (1)
Co(2)—Co(1)—C(1)	53.3 (3)	Co(3)—Co(1)—C(1)	111.5 (3)
Co(2)—Co(1)—C(2)	112.1 (2)	Co(3)—Co(1)—C(2)	53.6 (2)
C(1)—Co(1)—C(2)	161.7 (4)	Co(2)—Co(1)—C(6)	49.8 (2)
Co(3)—Co(1)—C(6)	49.8 (2)	C(2)—Co(1)—C(6)	87.4 (3)
Co(1)—Co(2)—Co(3)	60.7 (1)	Co(1)—Co(2)—P(3)	111.4 (1)
Co(1)—Co(2)—C(1)	47.7 (2)	Co(3)—Co(2)—C(1)	108.0 (2)
Co(1)—Co(2)—C(3)	133.0 (3)	Co(3)—Co(2)—C(3)	139.1 (3)
C(1)—Co(2)—C(3)	99.3 (4)	Co(1)—Co(2)—C(4)	112.0 (2)
Co(3)—Co(2)—C(4)	51.3 (2)	C(1)—Co(2)—C(4)	158.4 (3)
C(2)—Co(3)—C(4)	158.8 (3)	C(4)—Co(3)—C(5)	98.2 (4)
Co(1)—C(1)—O(1)	146.3 (7)	Co(2)—C(1)—O(1)	134.7 (7)
Co(1)—C(2)—Co(3)	78.4 (3)	Co(1)—C(2)—O(2)	146.7 (7)
Co(3)—C(2)—O(2)	134.9 (6)	Co(2)—C(3)—O(3)	178.4 (8)
Co(3)—C(4)—O(4)	139.9 (6)	Co(3)—C(5)—O(5)	175.3 (8)
Co(1)—C(6)—Co(2)	79.3 (2)	Co(1)—C(6)—Co(3)	79.5 (3)
Co(2)—C(6)—C(7)	134.9 (5)	Co(2)—C(6)—Co(3)	78.2 (3)

observed 0.05 \AA shortening in the dmpe-bridged Co(2)—Co(3) bond [2.424 (1) \AA] relative to the two other non-dmpe-bridged Co—Co bonds [2.474 (1) \AA av.] is expected based on the tethering effect of the bridging phosphine. A μ_3 -benzylidyne group caps one triangular face of the cluster to give the *nido* polyhedral core commonly observed in this genre of cluster. The PhCCo₃(CO)₅(dmpe)₂ molecules form two-dimensional layers approximately perpendicular to the z axis with toluene molecules filling in the voids between the layers. The shortest contacts between the inorganic complex and the calculated hydrogen atom positions of the toluene are H...H = 2.31 and 2.46 \AA and H...O = 2.57 \AA .

The two dmpe ligands associated with the cluster serve to increase the electron density at each Co center relative to the parent cluster which, in turn, causes three of the five carbonyl groups to bridge adjacent Co centers. The adoption of bridging μ_2 -CO groups facilitates removal of excess electron density from the Co atoms through more effective $d\pi \rightarrow \pi^*$ (μ_2 -CO) backbonding (Penfold & Robinson, 1973). As a result of uneven electron density

Fig. 1. ORTEP diagram of PhCCo₃(CO)₅(dmpe)₂ with the thermal ellipsoids drawn at the 30% probability level. Methyl and ethane H atoms omitted for clarity.Fig. 2. Cross-sectional view of the tricobalt plane illustrating the bridging Co—CO bond lengths (\AA). The closed circle represents the dmpe-chelated cobalt atom.

distribution within the cluster, disparate μ_2 -bridging Co—CO bond lengths are observed. The bridging carbonyl distances range from 1.862 (8) to 2.034 (8) Å and follow the trend observed in other phosphine-substituted clusters (Richmond & Kochi, 1986, 1987*b*). The cross section in Fig. 2 shows the asymmetric bridging carbonyls. It is readily seen that the shorter bridging Co—CO bonds are associated with the more highly substituted Co(1) atom consistent with the $d\pi \rightarrow \pi^*$ backbonding electronic effect. The terminal Co—CO, Co—P, C—C, and P—C distances and angles are unexceptional and deserve no further comment.

At this point we cannot say with certainty whether the initial dmpe ligand coordinates in a bridging or chelating fashion. Assuming a stepwise substitution process is operative, the intermediate monosubstituted phosphine cluster $\text{PhCCO}_3(\text{CO})_8(\eta^1\text{-dmpe})$ with a free, dangling phosphine group is expected to react in an associative manifold to furnish either the bridged or the chelated cluster $\text{PhCCO}_3(\text{CO})_7(\text{dmpe})$. The subtle entropic balance between these two pathways undoubtedly controls which cluster is initially produced. Infrared studies are planned in order to address the coordination mode of the first dmpe ligand.

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Structure of $[\text{HTMPP}]_3\text{W}_2\text{Cl}_9$ [HTMPP = Tris(2,4,6-trimethoxyphenyl)-phosphonium]

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Abstract. Tris(2,4,6-trimethoxyphenyl)phosphonium nonachloroditungstate(III)-pyridine-tetrahydrofuran (1/2/1), $3\text{C}_{27}\text{H}_{34}\text{O}_9\text{P}^+ \cdot \text{W}_2\text{Cl}_9^{3-} \cdot 2\text{C}_5\text{H}_5\text{N} \cdot \text{C}_4\text{H}_4\text{O}$ (1), $M_r = 2513.7$, triclinic, $P\bar{1}$, $a = 16.993$ (5), $b = 24.746$ (9), $c = 14.094$ (4) Å, $\alpha = 95.170$ (2), $\beta = 111.690$ (2), $\gamma = 87.630$ (3)°, $V = 5484$ (3) Å³, $Z = 2$, $D_x = 1.522$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 24.7$ cm⁻¹, $F(000) = 2540$, $T = 295$ K, $R = 0.057$ for 9260 unique reflections total with $F_o^2 > 3\sigma(F_o^2)$. The asymmetric unit is composed of one triply bonded confacial bioctahedral $[\text{W}_2\text{Cl}_9]^{3-}$ dimer with three

crystallographically independent protonated phosphine counterions, HTMPP^+ , and three interstitial solvent molecules (two pyridines and one tetrahydrofuran). The W—W distance is 2.4329 (6) Å, the average W—Cl bridging distance is 2.490 (6) Å, and the average W—Cl terminal distance is 2.414 (6) Å.

Introduction. One of the current interests in our laboratory is the reactivity of a new triphenylphosphine derivative, TMPP [TMPP = tris(2,4,6-trimethoxyphenyl)phosphine]. This unusually bulky and basic functionalized phosphine has already exhibited a diverse range of coordination modes from

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