Chemistry of Methinyl Tricobalt Enneacarbonyls. Part 13.[†] Preparation and Structure of Phosphite Derivatives, and the Crystal and Molecular Structure of $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$ [‡]

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Mono-, di-, and tri-substituted tertiary phosphite derivatives of methinyl tricobalt enneacarbonyls have been prepared. These invariably adopt carbonyl non-bridged structures and are inert to ligand dissociation in solution, in contrast to the previously characterised phosphine derivatives. The crystal and molecular structure of the tri-substituted complex $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$ has been determined from X-ray diffractometer data by direct methods. Crystals are monoclinic, space group $P2_1/c$ with a = 1 618.7(3), b = 1 470.3(3), c = 1 269.5(3) pm, β = 101.86(1)°, and Z = 4. The structure was refined by full-matrix least squares to R = 0.073 for 2 614 observed reflections. The monomeric structure closely resembles that of the parent compound with the three phosphite ligands occupying equatorial positions on the Co_3 triangle. The carbonyl groups are all terminal.

REPLACEMENT of carbon monoxide by Group 5A ligands in the methinyl tricobalt enneacarbonyl cluster series has led to the identification of two classes of substitution product.[1-4] In the first, all the remaining carbonyl ligands are terminal, while the second has carbonyl ligands bridging the Co–Co bonds in the Co_3 triangle. Carbonyl-bridged derivatives are found to be favoured when the apical substituent Y to the $YCCo_3$ cluster unit is an electron donor, or when more than one carbonyl group is replaced by a Group 5A ligand.[3] This latter observation is in contrast to the behaviour of isocyanide derivatives, $[Co_3(CY)(CO)_{9-n}(CNR)_n]$, which are found to be non-bridged for n = 1—4.[5]

In the course of work on the redox properties of tricobalt carbon cluster compounds,[6-8] it became necessary to prepare complexes of the phosphite ligands, $P(OR)_3$ (R = Me, Ph). This paper reports the synthesis and characterisation of a number of complexes $[Co_3(CY)(CO)_{9-n}\{P(OR)_3\}_n]$ (Y = Me, F; n = 1—3), together with the X-ray structural determination of the derivative $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$.

EXPERIMENTAL

The methinyl tricobalt enneacarbonyls were prepared according to published methods [9,10] and purified by vacuum sublimation; $P(OMe)_3$ and $P(OPh)_3$ (Aldrich) were used without further purification. The products were sufficiently stable to oxidation, both as solids or in solution, to be handled in air. Analytical data are given in Table 1. The i.r. spectra were recorded on a Perkin-Elmer 225 spectrometer to an accuracy of ±0.5 cm^{-1}, ^{13}C n.m.r. spectra at 15.04 MHz on a JEOL FX-60 FT spectrometer, and mass spectra on a Varian CH-7 mass spectrometer using a direct-insertion probe.

Preparation of Fluoromethinyloctacarbonyltriphenyl phosphitetricobalt.—Triphenyl phosphite (0.25 g, 0.81 mmol) and $[Co_3(CF)(CO)_9]$ (0.25 g, 0.54 mmol) were dissolved in deoxygenated hexane (30 cm^3) and the solution was stirred at reflux for 30 min. During this time the solution was seen to darken in colour. The reaction time is crucial, with more conversion of starting material, but increased decomposition and production of more highly substituted derivatives, when the reaction is prolonged.

The solution was filtered, the residue washed with dichloromethane, and the solvents removed *in vacuo* to leave a purple-black oil. This was dissolved in CH_2Cl_2 (5 cm^3) and absorbed on silica gel (PF_{254}) preparative t.l.c. plates (20 × 20 cm × 1.25 mm); the plates were developed in hexane. Three major bands developed: (1) purple (unchanged $[Co_3(CF)(CO)_9]$), (2) black-purple, and (3) black (bis- and tris-substituted products). The dominant band (2) was eluted with CH_2Cl_2; the solvent was removed *in vacuo* and the residue recrystallised from pentane at 263 K. Fluoromethinyloctacarbonyltriphenyl phosphitetricobalt (0.08 g) was obtained as small black crystals. The compound was air-stable and soluble in all organic solvents; no evidence for decomposition or ligand dissociation was observed in solutions of the complex over a period of hours.

Preparation of Other Phosphite-substituted Derivatives.—Other monosubstituted derivatives were prepared using the procedure outlined above; all the products were black. A significant amount of the more highly substituted derivatives, particularly the bis-product, could be recovered from these reactions. Higher yields of the bis- and tris-substituted compounds were obtained by similar experimental procedures but increasing the ligand : cluster ratio and the reaction time. A $P(OR)_3 : [Co_3(CY)(CO)_9]$ ratio of 2.5 : 1 and a reaction time of 45 min gave predominantly the bis-

TABLE 1

Analytical data for phosphite derivatives of $[Co_3(CY)(CO)_9]$

	Calculated (%)		Found (%)	
	C	H	C	H
$[Co_3(CF)(CO)_8L]$				
L = $P(OPh)_3$	43.7	2.05	43.9	2.10
L = $P(OMe)_3$	25.9	1.65	26.1	1.65
$[Co_3(CMe)(CO)_8\{P(OMe)_3\}]$ [a]	28.3	2.20	31.1	2.70
$[Co_3(CF)(CO)_7L_2]$				
L = $P(OPh)_3$	51.6	2.95	52.25	3.60
L = $P(OMe)_3$	25.8	2.80	26.2	3.00
$[Co_3(CMe)(CO)_7L_2]$				
L = $P(OPh)_3$	52.95	3.25	53.55	3.85
L = $P(OMe)_3$	27.8	3.25	28.35	3.80
$[Co_3(CF)(CO)_6L_3]$				
L = $P(OPh)_3$	56.05	3.45	55.75	3.85
L = $P(OMe)_3$	25.7	3.65	25.9	3.60
$[Co_3(CMe)(CO)_6L_3]$				
L = $P(OPh)_3$	57.15	3.70	57.2	3.60
L = $P(OMe)_3$ [b]	27.45	4.05	28.05	4.50

[a] Oil, contaminated with $P(OMe)_3$. [b] Co: calc., 23.75; found 23.55%.

[†] Part 12, A. Cartner, R. G. Cunninghame, and B. H. Robinson, *J. Organometallic Chem.*, 1975, **92**, 42.

[‡] Hexacarbonyl-μ_3-ethylidyne-tris(trimethyl phosphite)-*triangulo*-tricobalt.

product whereas a 4.5 : 1 reactant ratio, refluxed for 1 h, gave almost entirely the tris-substituted compound. It was often necessary to repeat the t.l.c. separation of these polysubstituted derivatives in order to achieve products of high purity. The R_F values for the tris-derivatives were always lower than those of the bis-products.

The solubility of the phosphite-substituted complexes in hydrocarbon solvents decreases as the degree of substitution increases. Crystallisation of the bis- and tris-phosphite derivatives from pentane or hexane is nonetheless possible, the solutions affording black crystals within a few hours at 263 K.

Preparation of ^{13}*CO-Enriched Samples.*—A mixture of $[Co_3(CMe)(CO)_7\{P(OMe)_3\}_2]$ and $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$ in CH_2Cl_2 was stirred for 24 h in an atmosphere of ^{13}C-enriched carbon monoxide (Prochem 91.8%); the ^{13}CO was replenished with fresh material after 9 h. The enriched compounds were subsequently separated by t.l.c. and purified as described above.

Crystal Structure Determinations.—A sample of $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$ prepared as outlined previously was recrystallised from pentane at 263 K. Diffraction data were collected from a black rectangular crystal with dimensions 0.38 × 0.33 × 0.18 mm.

Crystal data. $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$ ($C_{17}H_{30}Co_3O_{15}P_3$), $M = 744.1$ g mol^{-1}, Monoclinic, $P2_1/c$, $a = 1\,618.7(3)$, $b = 1\,470.3(3)$, $c = 1\,269.5(3)$ pm, $\beta = 101.86°$, $U = 2.957\,0 \times 10^9$ pm^3, $D_m = 1.67(3)$ g cm^{-3}, $Z = 4$, $D_c = 1.67$ g cm^{-3}, μ(Mo-K_α) = 19.55 cm^{-1}.

The space group was uniquely determinined as $P2_1/c$ from the systematic absences. Accurate lattice and orientation parameters were obtained from a least-squares refinement [11] of the setting angles of twelve strong, high-angle reflections centred in a 5-mm diameter, circular receiving aperture set 23 cm from the crystal on a Hilger and Watts, four-circle, computer-controlled diffractometer. The mosaicity of the crystal was examined by means of open counter ω-scans at a take-off angle of 3°; the widths at half height for typical intense, low-angle reflections ranged from 0.15 to 0.20°.

Zirconium-filtered Mo-K_α radiation, and the θ—2θ scan technique, were used to collect the intensities of 4 333 independent reflections in the positive *h*, positive *k* quadrant of reciprocal space for $0 < 2\theta < 24°$. A symmetric scan range of 1.20° in 2θ, centred on the calculated peak position, was composed of 60 steps of 1 s duration. Stationary-crystal–stationary-counter background counts of 15 s were measured at each end of the scan range. Where necessary, to bring reflections within the linear response range of the scintillation counter, attenuators were automatically inserted in the primary beam. Throughout the data collection, three standard reflections were regularly monitored and a drop of only 3—4% from their original values was recorded at the end. These observations were used to scale the data to compensate for the apparent decomposition of the crystal.

An initial correction for background was made and the standard deviation $\sigma(I)$ of the corrected intensity (I) was estimated as previously described. For the initial refinement, p [12] was given the value 0.05 and is the factor included to avoid overweighting the more intense reflections. The intensities were corrected for Lorentz and polarisation effects.

Of the 4 333 reflections collected, 2 614 had values of $|F_o|^2$ that were greater than three times their estimated standard deviations and it was these that were used in the final refinement of structure parameters.

Solution and refinement of the structure. In the full-matrix least-squares refinements the function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes respectively, and where the weight w is $4F_o/\sigma^2(F_o^2)$. The agreement factors R and R' have their usual definitions. Atomic scattering factors for all atoms were from Cromer and Waber.[13] The effects of anomalous dispersion of the cobalt and phosphorus atoms were included as detailed by Cromer.[14]

The normalised structure factors were calculated and an E map computed using direct methods, which revealed the positions of the three cobalt and three phosphorus atoms. Refinement of these co-ordinates together with isotropic temperature factors gave values of 0.288 and 0.378 for R and R', respectively. A number of difference-Fourier syntheses revealed the co-ordinates of the remaining non-hydrogen atoms and the structure converged to $R = 0.092$ and $R' = 0.113$. However, high and increasing values for the isotropic temperature factors of the three oxygen atoms of one phosphite group suggested that their positions were unsatisfactory. Inspection of a difference-Fourier map in this region indicated that the electron density attributable to these atoms was smeared out, effectively giving two positions for each of the atoms. The three oxygen atoms were therefore each assigned two sets of co-ordinates and each position given an occupancy factor of 0.5. The disorder is believed to be crystallographic rather than chemical, as neither of the other phosphite groups in the molecule behaved in this way. The refinement was continued, with anisotropic temperature factors for the oxygens of the carbonyl groups, until convergence, with the final values of R and R' being 0.073 and 0.088 respectively.

A final difference-Fourier synthesis showed no anomalously high peaks. The relative weighting scheme appeared satisfactory, since the minimised function showed only slight dependence on $|F_o|$ and $\sin\theta/\lambda$.

The positional and vibrational parameters obtained from the last cycle of refinement are listed in Table 2. Root-mean-square amplitudes of vibration for the atoms refined anisotropically, and final observed and calculated structure factors, are listed in Supplementary Publication No. SUP 22600 (10 pp.).*

All calculations were carried out using a Burroughs 6712 computer. The data-processing program HILGOUT is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens). The structure was solved by direct methods using the MULTAN 74 suite of programs (P. Main, M. M. Woolfson, and G. Germain). Programs used in the structure refinement and for production of structure diagrams have been described previously.[15]

RESULTS AND DISCUSSION

Preparations.—The direct reaction between $[Co_3(CY)(CO)_9]$ (Y = Me or F) and tertiary phosphites $P(OR)_3$ (R = Me or Ph) in refluxing hexane gave a series of mono-, di-, and tri-substituted products. The relative amounts of the various substituted derivatives were determined by the ratio of ligand to parent cluster. The reactions invariably gave mixtures of the substituted species and reaction times and ligand : cluster ratios were set accord-

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 2

Positional and isotropic thermal parameters for $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$

Atom	x	y	z	$10^4\beta$ (pm^2) [a]
Co(1)	0.786 0(1)	0.904 4(1)	0.755 2(1)	2.99(4)
Co(2)	0.663 0(1)	1.006 4(1)	0.692 1(1)	2.84(4)
Co(3)	0.782 2(1)	1.002 9(1)	0.596 2(1)	3.08(4)
P(1)	0.906 1(2)	0.845 5(2)	0.749 4(2)	3.43(7)
P(2)	0.607 6(2)	0.498 6(2)	0.332 5(3)	3.75(7)
P(3)	0.747 3(2)	1.115 6(2)	0.491 1(3)	3.83(7)
C(ap)	−0.221 4(8)	0.034 0(8)	−0.259 3(9)	3.0(2)
C(111)	0.196 6(9)	0.095 4(9)	0.103(1)	4.4(3)
C(112)	0.275 1(9)	0.191(1)	0.298(1)	4.2(3)
C(221)	0.409 6(9)	0.063 9(9)	0.401(1)	4.1(3)
C(222)	−0.370 5(8)	0.119 0(9)	−0.338(1)	3.7(3)
C(331)	0.254 4(9)	0.087(1)	0.494(1)	4.3(3)
C(332)	−0.111(1)	0.021(1)	−0.400(1)	4.8(3)
O(111)	0.180 8(7)	0.093 9(8)	0.011 4(7)	
O(112)	0.315 2(7)	0.252 9(7)	0.330 0(9)	
O(221)	0.453 9(6)	0.106 5(7)	−0.537 2(8)	
O(222)	−0.395 3(6)	0.191 4(6)	−0.354 8(8)	
O(331)	0.282 2(7)	0.144 7(7)	−0.445 9(8)	
O(332)	−0.041 7(7)	0.037 6(9)	−0.400(1)	
C(Me)	−0.180 5(8)	0.108 5(9)	−0.186(1)	4.2(3)
O(11)	0.062 8(6)	0.234 9(6)	0.166 8(7)	4.9(2)
O(12)	0.087 2(6)	0.194 7(6)	0.364 1(7)	4.5(2)
O(13)	0.007 5(6)	0.098 0(6)	0.222 6(7)	4.4(2)
C(11)	−0.118(1)	0.187(1)	−0.338(1)	7.1(4)
C(12)	0.009(1)	0.241(1)	0.382(1)	6.8(4)
C(13)	−0.014(1)	0.046(1)	0.125(1)	5.3(3)
O(31)	−0.347 7(6)	0.116 0(6)	0.428 5(7)	4.8(2)
O(32)	−0.244 5(6)	0.218 0(7)	−0.461 9(7)	5.5(2)
O(33)	−0.197 0(6)	0.131 1(7)	0.397 9(8)	5.4(2)
C(31)	−0.382(1)	0.189(1)	0.353(1)	7.0(4)
C(32)	−0.161(1)	0.256(1)	−0.418(1)	6.2(4)
C(33)	−0.186(1)	0.057(1)	0.329(1)	6.3(4)
O(21) [b]	−0.332(1)	0.031(1)	−0.061(2)	4.9(5)
O(21A)	−0.352(1)	0.075(1)	−0.081(1)	4.2(4)
O(22) [b]	0.491(1)	−0.005(1)	0.182(1)	4.4(4)
O(22A)	−0.470(1)	0.078(1)	−0.172(1)	4.2(4)
O(23) [b]	0.442(1)	0.080(1)	0.138(1)	4.8(4)
O(23A)	0.380(1)	0.086(1)	0.086(2)	5.6(5)
C(21)	−0.368(1)	0.066(1)	0.035(2)	9.0(5)
C(22)	0.455(1)	0.067(1)	−0.255(1)	6.2(4)
C(23)	0.411(1)	0.170(1)	0.110(1)	7.1(4)

[a] The isotropic temperature factor expression is $T = \exp\{-(\beta\sin^2\theta/\lambda^2)\}$. [b] These are the pairs of positions, each assigned an occupancy factor of 0.5, given to the three phosphite oxygens for which no satisfactory single positions could be obtained.

ing to the desired product(s). In contrast to the reactions of alkyl and aryl phosphines and arsines,[1] polysubstitution by the phosphite ligands occurs reasonably readily.

$$[Co_3(CY)(CO)_9] + nP(OR)_3 \longrightarrow [Co_3(CY)(CO)_{9-n}\{P(OR)_3\}_n] + nCO \quad (n = 1\text{—}3)$$

The phosphite derivatives were obtained as purple to black crystalline solids, which were stable in air and could be kept indefinitely at 273 K. They are soluble in most common organic solvents and, unlike the phosphine analogues,[1] show no tendency to revert to less substituted species in solution.

The Structure of $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$.—The crystal consists of well separated monomeric molecules, with the closest intermolecular contact (not involving hydrogen atoms) being 310 pm. The atom numbering scheme shown in Figure 1, which views the molecule normal to the tricobalt triangle, is retained throughout this discussion. Unique positions could not be assigned to the oxygen atoms on the P(2) phosphite group. These were therefore assigned two different and half-populated positions (see Experimental section). Figure 1 shows the molecule with only one of these two sets of oxygen positions. Figure 2 shows the molecule viewed parallel to the Co_3 plane, with the methoxy-groups of the trimethyl phosphite ligands omitted for clarity. The bond lengths and angles within the molecule are listed in Tables 3 and 4, and selected non-bonded distances are given in Table 5.

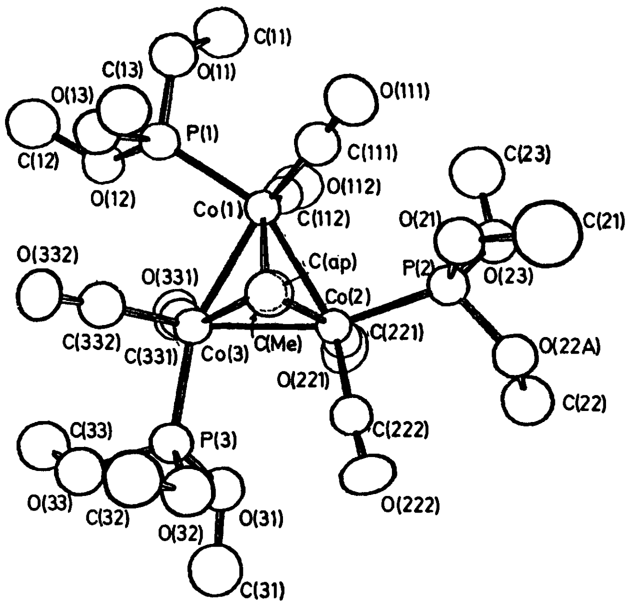


FIGURE 1 The molecule $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$ viewed approximately normal to the Co_3 triangle

The structure of the molecule is based on the pyramidal Co_3C unit [16,17] with the phosphite ligands co-ordinated in an equatorial position, one on each of the three cobalt atoms. The carbonyl groups on each cobalt atom are terminal and are arranged, one equatorially and one axially, such that the cobalt atoms have a distorted

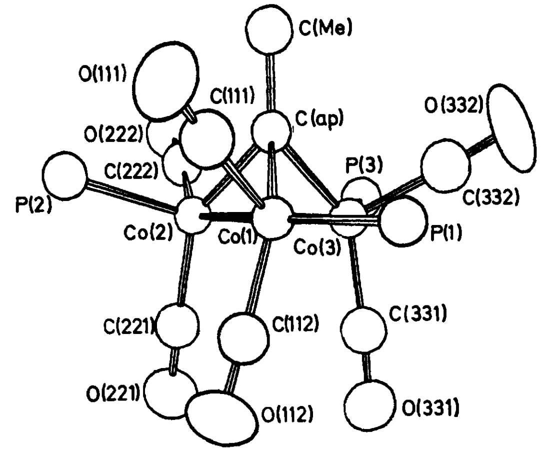


FIGURE 2 The molecule $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$ viewed parallel to the Co_3 triangle

TABLE 3

Bond distances (pm) in $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$

Co(1)–Co(2)	249.1(2)	C(111)–O(111)	114(1)
Co(1)–Co(3)	247.5(2)	C(112)–O(112)	114(1)
Co(2)–Co(3)	248.5(2)	C(221)–O(221)	114(1)
		C(222)–O(222)	114(1)
Co(1)–P(1)	214.3(4)	C(331)–O(331)	117(1)
Co(2)–P(2)	215.6(4)	C(332)–O(332)	115(2)
Co(3)–P(3)	213.0(4)		
		P(1)–O(11)	160(1)
Co(1)–C(111)	177(1)	P(1)–O(12)	158.1(9)
Co(1)–C(112)	177(1)	P(1)–O(13)	160.3(9)
Co(2)–C(221)	181(1)		
Co(2)–C(222)	176(1)	P(3)–O(31)	158(1)
Co(3)–C(331)	177(1)	P(3)–O(32)	162(1)
Co(3)–C(332)	174(2)	P(3)–O(33)	164(1)
Co(1)–C(ap)	192(1)	P(2)–O(21)	157(2)
Co(2)–C(ap)	189(1)	P(2)–O(21A)	158(2)
Co(3)–C(ap)	190(1)	P(2)–O(22)	157(2)
		P(2)–O(22A)	168(2)
C(ap)–C(Me)	150(2)	P(2)–O(23)	153(2)
O(11)–C(11)	147(2)	P(2)–O(23A)	163(2)
O(12)–C(12)	149(2)	O(21)–C(21)	153(3)
O(13)–C(13)	144(2)	O(21A)–C(21)	154(3)
		O(22)–C(22)	147(2)
O(31)–C(31)	147(2)	O(22A)–C(22)	145(2)
O(32)–C(32)	146(2)	O(23)–C(23)	143(2)
O(33)–C(33)	143(2)	O(23A)–C(23)	135(2)

octahedral environment. The alternative carbonyl-bridged structure [3] is not adopted.

The average Co–Co bond length of 248.4(8) pm is slightly longer than that for the unsubstituted molecule, $[Co_3(CMe)(CO)_9]$.[16] This may be rationalised in terms of an increase in electron density on the cobalt atoms as carbonyl groups are replaced by poorer π-acceptor phosphite ligands. A similar effect has been reported for a series of substituted iron carbonyls.[18]

The average Co–P bond length is 214.3(4) pm. This is significantly shorter than the corresponding lengths observed in $[Co_3(CMe)(CO)_8(PPh_3)]$ and $[Co_3(CMe)(CO)_8\{P(C_6H_{11})_3\}]$,[3] which reflects the increased π-acceptor ability of the phosphite over the phosphine ligands. The Co–CO bond lengths at 177(2) pm show the anticipated decrease that accompanies CO substitution. The corresponding increase in the C–O bond length is observed, the average value being 115 pm.

In the equatorially substituted PPh_3 derivative,[2] the apical methyl group is bent away from the phosphine ligand. However in the symmetrical tris-phosphite species there is no such distortion, and the average Co–C(ap)–C(Me) angle is identical to that in $[Co_3(CMe)(CO)_9]$ [16] and the Co–C(ap) and C(ap)–C(Me) bond lengths are close to the average values observed for tricobalt carbon clusters.[17] The bond parameters in the phosphite ligands are unexceptional although the closest intramolecular non-bonded contacts in the structure occur within these groups.

It would appear that on substitution the cluster has adopted a structure to minimise phosphite–apical group and carbonyl–carbonyl steric interactions. Hence the Co–P bonds are bent significantly away from the apical group to give an average C(ap)–Co–P angle of 111°. The equatorial CO groups are bent closer to the apical carbon atom and further away from the Co_3 plane, the average C(ap)–Co–CO(eq) angle being 97°. The steric requirement of the phosphite ligand is in fact difficult to compare with that of a carbonyl group. The cone angle for $(MeO)_3P$ is 107°,[19] making it one of the smallest phosphorus ligands, but the steric effects not only depend on the groups on the phosphorus atom but, because of the longer Co–P bond distance, there is actually some relief in steric crowding at the carbonyl carbon level. Hence the angles P–Co–CO(ax) and P–Co–CO(eq) have decreased from the corresponding angles in $[Co_3(CMe)(CO)_9]$ while the OC(eq)–Co–CO(ax) angle shows a significant increase. Effectively, these distortions result from a small rotation of each CoL_3 unit upon replacement of a carbonyl by a trimethyl phosphite ligand.

I.r. Spectra (2 200—1 700 cm^{-1}).—The carbonyl stretching frequencies from solution spectra of all the

TABLE 4

Bond angles (°) for $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$

Co(2)–Co(1)–Co(3)	60.06(6)	C(ap)–Co(1)–P(1)	115.9(4)
Co(1)–Co(2)–Co(3)	59.65(6)	C(ap)–Co(2)–P(2)	106.8(4)
Co(2)–Co(3)–Co(1)	60.29(6)	C(ap)–Co(3)–P(3)	111.1(4)
Co(1)–C(ap)–Co(2)	81.7(5)	C(ap)–Co(1)–C(111)	95.1(6)
Co(1)–C(ap)–Co(3)	80.8(5)	C(ap)–Co(2)–C(222)	96.3(6)
Co(2)–C(ap)–Co(3)	81.8(5)	C(ap)–Co(3)–C(332)	99.5(6)
C(ap)–Co(1)–Co(2)	48.7(4)	C(ap)–Co(1)–C(112)	137.2(6)
C(ap)–Co(2)–Co(1)	49.6(4)	C(ap)–Co(2)–C(221)	143.3(6)
C(ap)–Co(2)–Co(3)	49.3(3)	C(ap)–Co(3)–C(331)	137.1(6)
C(ap)–Co(3)–Co(2)	48.9(4)		
C(ap)–Co(3)–Co(1)	49.8(4)	Co(2)–Co(1)–P(1)	154.6(1)
C(ap)–Co(1)–Co(3)	49.4(3)	Co(1)–Co(3)–P(3)	157.7(1)
		Co(3)–Co(2)–P(2)	154.3(1)
C(Me)–C(ap)–Co(1)	131.0(9)		
C(Me)–C(ap)–Co(2)	129.8(9)	Co(3)–Co(1)–P(1)	94.5(1)
C(Me)–C(ap)–Co(3)	132.5(9)	Co(1)–Co(2)–P(2)	98.9(1)
		Co(2)–Co(3)–P(3)	99.1(1)
Co(3)–Co(1)–C(111)	143.4(5)	P(1)–Co(1)–C(111)	94.6(5)
Co(1)–Co(2)–C(222)	145.8(4)	P(2)–Co(2)–C(222)	93.0(4)
Co(2)–Co(3)–C(332)	148.4(5)	P(3)–Co(3)–C(332)	91.9(5)
Co(2)–Co(1)–C(111)	106.1(5)	P(1)–Co(1)–C(112)	96.1(5)
Co(1)–Co(3)–C(332)	102.1(5)	P(2)–Co(2)–C(221)	101.3(4)
Co(3)–Co(2)–C(222)	98.5(4)	P(3)–Co(3)–C(331)	99.4(4)
Co(3)–Co(1)–C(112)	103.5(4)	C(111)–Co(1)–C(112)	110.6(6)
Co(1)–Co(2)–C(221)	103.6(4)	C(222)–Co(2)–C(221)	105.4(6)
Co(2)–Co(3)–C(331)	98.2(5)	C(332)–Co(3)–C(331)	109.2(7)
Co(2)–Co(1)–C(112)	90.5(4)	Co(1)–C(111)–O(111)	176.1(1.3)
Co(1)–Co(3)–C(331)	92.4(4)	Co(2)–C(222)–O(222)	176.4(1.2)
Co(3)–Co(2)–C(221)	97.6(4)	Co(3)–C(332)–O(332)	176.0(1.3)
		Co(1)–C(112)–O(112)	178.1(1.3)
Co(1)–P(1)–O(11)	116.1(4)	Co(2)–C(221)–O(221)	177.3(1.3)
Co(1)–P(1)–O(12)	114.6(4)	Co(3)–C(331)–O(331)	176.9(1.3)
Co(1)–P(1)–O(13)	122.7(4)	O(31)–P(3)–O(32)	100.4(5)
Co(2)–P(2)–O(21)	114.3(8)	O(31)–P(3)–O(33)	105.0(5)
Co(2)–P(2)–O(21A)	111.8(7)	O(32)–P(3)–O(33)	97.0(5)
Co(2)–P(2)–O(22)	119.3(6)	O–P(2)–O	98(1) *
Co(2)–P(2)–O(22A)	112.5(6)		
Co(2)–P(2)–O(23)	123.6(7)	P(1)–O(11)–C(11)	120.0(9)
Co(2)–P(2)–O(23A)	122.2(7)	P(1)–O(12)–C(12)	121.8(9)
		P(1)–O(13)–C(13)	120.6(9)
Co(3)–P(3)–O(31)	115.1(4)		
Co(3)–P(3)–O(32)	120.2(4)	P(3)–O(31)–C(31)	122.2(9)
Co(3)–P(3)–O(33)	116.4(4)	P(3)–O(32)–C(32)	120.0(9)
		P(3)–O(33)–C(33)	119.3(9)
O(11)–P(1)–O(12)	104.9(5)		
O(11)–P(1)–O(13)	95.4(5)	P(2)–O(21)–C(21)	120.1(1.6)
O(12)–P(1)–O(13)	100.1(5)	P(2)–O(21A)–C(21)	118.9(1.5)
		P(2)–O(22)–C(22)	123.6(1.4)
		P(2)–O(22A)–C(22)	117.2(1.3)
		P(2)–O(23)–C(23)	128.0(1.6)
		P(2)–O(23A)–C(23)	126.0(1.6)

* Average value for all such angles, excluding those between the peaks representing the same atoms.

TABLE 5

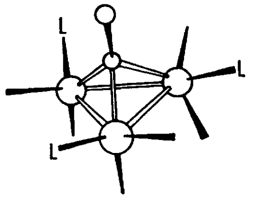
Selected intramolecular non-bonded distances (pm)

Co(1) · · · C(31)	310	C(111) · · · C(112)	291
Co(2) · · · C(12)	307	C(222) · · · C(221)	284
		C(331) · · · C(332)	286
Co(1) · · · C(Me)	311		
Co(2) · · · C(Me)	308	C(331) · · · C(112)	300
Co(3) · · · C(Me)	312	C(331) · · · C(221)	300
		C(112) · · · C(221)	296
Co(1) · · · O(12)	315		
Co(3) · · · O(31)	314	C(Me) · · · C(111)	321
C(ap) · · · C(22)	272	C(222) · · · O(31)	306
C(ap) · · · C(11)	272	C(332) · · · O(13)	307
C(ap) · · · C(32)	278		
		O(222) · · · O(32)	305
C(ap) · · · P(1)	344	O(332) · · · O(13)	298
C(ap) · · · P(2)	325		
C(ap) · · · P(3)	333	C(111) · · · O(11)	321
		C(332) · · · O(33)	311
P(1) · · · C(111)	289	O(11) · · · O(12)	252
P(2) · · · C(222)	285	O(31) · · · O(33)	256
P(3) · · · C(332)	279		
		O(33) · · · C(31)	306
P(1) · · · C(112)	292	O(32) · · · C(31)	292
P(2) · · · C(221)	308	O(33) · · · C(32)	294
P(3) · · · C(331)		O(11) · · · C(12)	303
P(1) · · · C(332)	318	O(13) · · · C(12)	291
P(2) · · · C(111)	342	O(11) · · · C(13)	304
P(3) · · · C(222)	317		

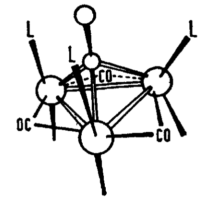
Shortest intermolecular non-bonded distance
O(222) · · · C(31) 314

phosphite derivatives are listed in Table 6; some possible structures for $[Co_3(CY)(CO)_{9-n}L_n]$ ($n = 1$—3) are depicted as (A)—(F). No bands attributable to bridging carbonyl groups were observed in the solid-phase spectra of any of these derivatives. Thus, unlike the phosphine-substituted compounds,[1] there is no reorganisation to a bridged-carbonyl configuration, regardless of the degree of substitution or the nature of the apical substituent Y.

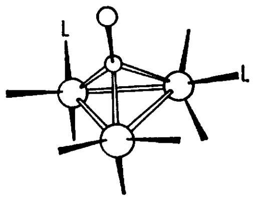
The small number of bands observed in the terminal ν(CO) region of the solution spectra of the species $[Co_3(CY)(CO)_6\{P(OR)_3\}_3]$ indicates that the symmetrical C_3 structure (A), found in the crystallographic determination of $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$, is retained in solution. However, for two compounds (Y = Me and R = Me or Ph) the solution spectra did exhibit weak bands due to bridging carbonyl groups. It would therefore seem that in solutions of these compounds a small concentration of a carbonyl-bridged isomer (B) is in equilibrium with the non-bridged form. This type of structural isomerism in solution has been observed previously for the complex $[Co_3(CPh)(CO)_8\{P(cyclohexyl)_3\}]$ [1] but occurs in the opposite sense of the well documented isomerism displayed by $[Co_2(CO)_8]$.[20]



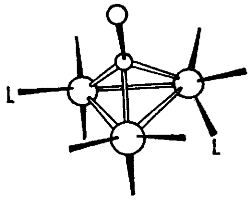
(A)



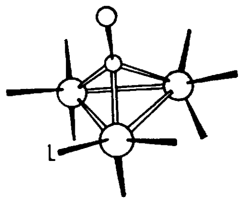
(B)



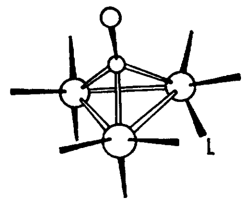
(C)



(D)



(E)



(F)

The solution spectra of the bis-substituted phosphite compounds show that all the CO groups are terminal. Several molecular configurations are possible, all of low symmetry (C_1 or C_s), so that i.r. data cannot be used to distinguish between them. Structure (C) is considered the most likely by analogy with the known structure of the tris-substituted species. In this structure, both carbonyl–carbonyl and phosphite–phosphite steric interactions are minimised. An alternative configuration (D) with one phosphite ligand equatorial and the other axial would also minimise steric interactions and is

TABLE 6

Carbonyl stretching frequencies for $[Co_3(CY)(CO)_{9-n}L_n]$ complexes (cm^{-1}) *

	Y	L	ν(CO)						
$n = 1$	F	$P(OPh)_3$	2 091s	2 047vs	2 036vs	2 026vs	2 010vw	2 004w	1 995vw
	F	$P(OMe)_3$	2 089s	2 045vs	2 033vs	2 023vs	2 009vw	2 002vw	1 984w
	Me	$P(OPh)_3$	2 083s	2 038vs	2 026vs	2 017vs			1 977m
	Me	$P(OMe)_3$	2 081s	2 036vs	2 023vs	2 014vs	1 999vw	1 991vw	1 974m
$n = 2$	F	$P(OPh)_3$	2 071s	2 031vs	2 027vs	2 018vs	2 011vs	1 985vw	
	F	$P(OMe)_3$	2 067s	2 020vs		2 010vs	2 003vs	1 977w	
	Me	$P(OPh)_3$	2 064s	2 017vs		2 009s	1 999s	1 977w	
	Me	$P(OMe)_3$	2 057s	2 009vs	2 008vs	2 000vs	1 991vs	1 965m	
$n = 3$	F	$P(OPh)_3$	2 050s	2 003vs	1 989vs	1 975vw			
	F	$P(OMe)_3$	2 039s	1 995 (sh)— 1 990vs	1 978vs	1 965sh	1 953vw		
	Me	$P(OPh)_3$	2 043s	1 995vs	1 977vs	1 965vw		1 845w	
	Me	$P(OMe)_3$	2 028s	1 979vs	1 966vs	1 950vw		1 829m	

* Recorded in cyclohexane, accuracy ±0.5 cm^{-1}.

similar to that postulated for phosphine-disubstituted tricobalt clusters.[1]

In view of the observed structures of $[Co_3(CMe)(CO)_8(PPh_3)]$ [2] and $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$, the $[Co_3(CY)(CO)_8\{P(OR)_3\}]$ species presumably also adopt a structure with the phosphite equatorial (E). However, from the i.r. data this configuration cannot be distinguished from a structure with the ligand in an axial orientation (F).

The high-frequency totally-symmetric carbonyl stretching mode has been shown to be very sensitive to changes in electron density on the Co_3C core.[1,17] The data from Table 6 show that there is a steady shift to lower energy as the degree of phosphite substitution increases. Similarly, within an identically substituted pair of derivatives, changing the apical substituent from fluorine to methyl causes a decrease in the frequency of this mode.[21] This effect has been explained by considering the Co_3C core to be an electron sink, which facilitates the transmission of changes in electron density to the cobalt atom and then onto the CO groups.

I.r. Spectra (1 700—400 cm^{-1}).—Exceptionally high values for the C–X (X = F or Cl) stretching vibrations are notable features of the spectra of tricobalt carbon clusters with a halogen substituent on the apical carbon.[1,22] There are numerous indications that the Co_3C core can participate in ' push–pull ' electronic interactions [17] with either the apical substituent or the carbonyl ligands. In the case of a fluorine substituent, it is suggested that a mesomeric effect using the filled *p*-orbitals of the fluorine atom compensates for the electron-withdrawing ability of the halogen substituent, with a concomitant increase in the strength of the C–X bond.[6]

The ν(C–F) frequencies for the phosphite-substituted fluorine clusters, detailed in Table 7, show that the strength of the C–F bond decreases with increased phosphite substitution. This could be caused by a distortion of the C–F bond due to steric interactions with the equatorial ligands. Alternatively, increasing the charge on the cluster due to the donor substituents would, to some extent, reduce the electron-withdrawing ability of the Co_3C core with respect to the apical group, thus weakening the C–F bond. The fact that the more bulky but better π-acceptor ligand $P(OPh)_3$ causes a greater decrease in ν(C–F) than $P(OMe)_3$ suggests that the steric factor may predominate in this case.

TABLE 7

Carbon–fluorine stretching frequencies [a]

	ν(C–F) (cm^{-1})
$[Co_3(CF)(CO)_9]$	1 164
$[Co_3(CF)(CO)_8\{P(OMe)_3\}]$	1 138
$[Co_3(CF)(CO)_7\{P(OMe)_3\}_2]$	1 095
$[Co_3(CF)(CO)_6\{P(OMe)_3\}_3]$	1 076
$[Co_3(CF)(CO)_8\{P(OPh)_3\}]$	1 127
$[Co_3(CF)(CO)_8\{P(C_6H_{11})_3\}]$	1 104 [b]
$[Co_3(CF)(CO)_8(PPh_3)]$	1 090 [b]
$[Co_3(CF)(CO)_7(PPh_3)_2]$	1 085 [b]

[a] Nujol mull. [b] Taken from ref. 1.

TABLE 8

^{13}C N.m.r. spectra

	T/K	CO resonance (δ) [a]
$[Co_3(CMe)(CO)_7\{P(OMe)_3\}_2]$	311	−206.5
	234	−206.2
$[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$	308	−211.4
	223	−211.5
$[Co_3(CMe)(CO)_8(PPh_3)]$ [b]	313	−203.9
	193	−206.7

[a] Recorded in CD_2Cl_2 at 15.04 MHz; values in p.p.m. relative to $SiMe_4$. [b] Taken from reference 4.

TABLE 9

Mass spectrum of $[Co_3(CF)(CO)_8\{P(OMe)_3\}]$ [a,b]

	m/e	Ion	A [c]
	566	$[Co_3(CF)(CO)_8L]^+$ [d]	19
	528	$[Co_3(CF)(CO)_7L]^+$	12
	500	$[Co_3(CF)(CO)_6L]^+$	30
	472	$[Co_3(CF)(CO)_5L]^+$	31
	444	$[Co_3(CF)(CO)_4L]^+$	64
	416	$[Co_3(CF)(CO)_3L]^+$	100
	388	$[Co_3(CF)(CO)_2L]^+$	65
	360	$[Co_3(CF)(CO)L]^+$	80
(*i*)	332	$[Co_3(CF)L]^+$	54
(*ii*)	302	$[Co_3(CF)\{HP(OMe)_2\}]^+$	14
	301	$[Co_3(CF)\{P(OMe)_2\}]^+$	8
	272	$[Co_3(CF)\{H_2POMe\}]^+$	10
	270	$[Co_3(CF)\{POMe\}]^+$	16
	264	$[Co_3(CF)(CO)_2]^+$	3
	258		42
	240		14
	239	$[Co_3(CF)P]^+$	10
	236	$[Co_3(CF)(CO)]^+$	5
	228		12
	209		12
	208	$[Co_3(CF)]^+$	20
	196		8
	190		9
	189	$[Co_3C]^+$	8
	183		8
	180		8
	177	$[Co_3]^+$	5
	149	$[Co_2(CF)]^+$	11
	137	$[Co_2F]^+$	5
	130	$[Co_2C]^+$	11
	118	$[Co_2]^+$	8
	115	$[Co(CO)_2]^+$	7
	93		9
	87	$[Co(CO)]^+$	7
	74		11
	59	Co^+	22

[a] Metastables were observed for all the carbonyl fragmentation steps and for the process (*i*)→(*ii*). [b] Major metal containing peaks only. [c] Relative abundance. [d] L = $P(OMe)_3$.

^{13}C *N.M.R. Spectra.*—A single, sharp ^{13}CO resonance was observed for both compounds studied (Table 8) at temperatures down to 233 K. The chemical shifts of these averaged signals indicate that the non-bridged configuration is retained in solution over this temperature range.[4] The position of the ^{13}CO resonance is known to be dependent on the donor ability of the substituting ligand; the greater the σ-donor effect of the non-carbonyl ligand the more the ^{13}CO resonance is deshielded.[23] This is reflected in a comparison of the ^{13}C resonances of the phosphite derivatives with those of a non-bridged phosphine compound (Table 8) and also in the downfield shift of the resonance for the phosphite trisubstituted species. The observed equivalence of all the carbonyl groups indicates that a facile carbonyl 'scrambling' process is operating in solution. The two mechanisms, involving non-bridged–bridged interconversions and local axial–equatorial interconversions, proposed [4] for the scrambling process in the phosphine-substituted tricobalt clusters could also be applicable to the phosphite derivatives.

Mass Spectra.—The mass spectra of the mono-, bis-, and tris-phosphite substituted species were readily obtained with parent molecular ions being observed in high abundance. This is in sharp contrast to the phosphine derivatives, which generally produced only a spectrum of the free ligand and the corresponding parent cluster.[1]

Table 9 lists the spectrum of a typical phosphite derivative, $[Co_3(CF)(CO)_8\{P(OMe)_3\}]$. Fragmentation involves the normal stepwise loss of all the carbonyl groups from the parent molecular ion, followed by a complicated secondary breakdown of the co-ordinated phosphite. A minor decay scheme involves the loss of the phosphite ligand followed by successive loss of the remaining carbonyls. The lower mass range of the spectrum is very similar to that of $[Co_3(CF)(CO)_9]$,[24] with cleavage of Co–Co bonds and expulsion of cobalt rather than the apical carbon predominating.

We thank the University of Canterbury for making their diffractometer facilities available to us, Professor B. R. Penfold for helpful advice, and the New Zealand Universities Grants Committee for financial support and the award of a Postgraduate Scholarship (to P. A. D.).

[8/2112 *Received, 7th December,* 1978]

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