Synthesis and *X*-Ray Crystal Structure of the Anion $[Co_6(CO)_{14}(\mu\text{-}CO)_2P]^-$; an Example of a 'Semi-interstitial Phosphide'

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Summary The anion $[Co_6(CO)_{16}P]^-$ has been obtained by reaction of PCl_3 with $Na[Co(CO)_4]$; the six metal atoms form four triangles linked in a chain surrounding a 'semi-interstitial' phosphide atom.

THE ability of phosphorous atoms to bridge triangular faces of clusters, *e.g.* in $[Co(\eta^5\text{-}C_5H_5)(\mu_3\text{-}P)]_4$[1] and $[Co_3(CO)_8(\mu_3\text{-}P)]_3$,[2,3] and of PR groups to bridge square faces, *e.g.* in $Ni_8(CO)_8(\mu_4\text{-}PPh)_6$[4] and $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$,[5] is well established. The available structural data[1,4,5] indicate that the phosphorus atoms in these compounds have an apparent radius smaller than that observed in binary phosphides of the transition metals, in which usually the phosphorus atom is found in a tricapped trigonal prismatic environment.[6] Since large carbonyl clusters can form cavities of suitable dimensions, and since phosphides would be expected to stabilise unusual geometries (similar to those observed for carbides),[7] we began a study of synthetic routes to this class of compounds. Preliminary results on the capped square antiprismatic dianion $[Rh_9(CO)_{21}P]^{2-}$, containing a central phosphorus atom, have been reported.[8]

The reaction of PCl_3 with $Na[Co(CO)_4]$ is known to give, *inter alia*, low yields of $Co_3(CO)_9P$, which quickly polymerizes to $[Co_3(CO)_8P]_3$.[2,3] When the reaction is carried out in tetrahydrofuran (THF) with a molar ratio Co : P of 6 : 1, this too results in a complicated mixture of compounds; extraction with water of the dried reaction product followed by saturation with solid KBr, precipitates $K[Co_6(CO)_{16}P]$. The corresponding $[NMe_4]^+$, $[NEt_4]^+$, $[NBu_4]^+$, and $[PPh_4]^+$ salts have been obtained in *ca.* 5—10% yield by metathesis in aqueous methanol. Attempts to improve the yield by using different Co : P ratios (2 : 1 and 4 : 1) or solvents (diethyl- and di-isopropyl-ether), or by using PCl_5 have been unsuccessful.

The compound $[PPh_4][Co_6(CO)_{16}P]$† was recrystallised from THF–heptane using the slow diffusion technique. In THF it shows i.r. carbonyl absorptions at 2070(w), 2020(s), 2010(sh), 1975(w), 1965(sh), and 1800(m) cm^{-1}. The ^{31}P n.m.r. spectrum‡ at −84 °C shows a broad resonance (as expected from the inequivalent Co atoms found in the solid state structure) at very low field (+486·2 p.p.m. from external H_3PO_4), in agreement with the range of values

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† Satisfactory analytical data for P were obtained only by neutron activation analysis: found 4·87 ± 0·2, calc. 5·29%. Satisfactory analysis was also obtained for Co.

‡ $[NBu_4][Co_6(CO)_{16}P]$ (141·6 mg) was dissolved in THF–$(CD_3)_2CO$ (5 : 1) (1·2 ml); at −35 °C the signal cannot be detected.

previously found for carbide resonances.[7] The structure of $[PPh_4][Co_6(CO)_{16}P]$ has been investigated by X-ray diffraction.

Crystal data: $C_{40}H_{20}Co_6O_{16}P_2$, M 1172·1, monoclinic, space group $P2_1/c$, $a = 10{\cdot}115(4)$, $b = 21{\cdot}233(9)$, $c = 20{\cdot}585(8)$ Å, $\beta = 91{\cdot}76(6)°$, $D_m = 1{\cdot}73$, $D_c = 1{\cdot}76$ g cm^{-3}, $Z = 4$. Intensities were collected on an automatic diffractometer with Mo-K_α radiation up to $2\theta \leqslant 50°$. The structure was solved by direct methods and refined by block-matrix least-squares, on the basis of 4698 independent observed reflections, to $R = 0{\cdot}075$.§

A view of the anion is shown in the Figure. It exhibits an overall idealized C_2 symmetry, the two-fold axis passing through the P atom and the middle of the Co(1)–Co(2) edge. The six metal atoms are disposed in an open array formed by four triangles linked in a chain wrapping the phosphide ligand. The metal atoms Co(5) and Co(6) bear three terminal carbonyl groups whereas each of the other metal atoms is connected to one edge-bridging and to two terminal CO groups (mean Co–C and C–O, 1·75 and 1·16 Å for terminal, and 1·89 and 1·20 Å for bridging carbonyl groups, respectively). Of the nine Co–Co bonds one, Co(1)–Co(2), is very long [2·935(2) Å], four, involving atoms Co(5) and Co(6), have a mean value of 2·655 Å, and the remaining four are shorter, with a mean value of 2·575 Å.

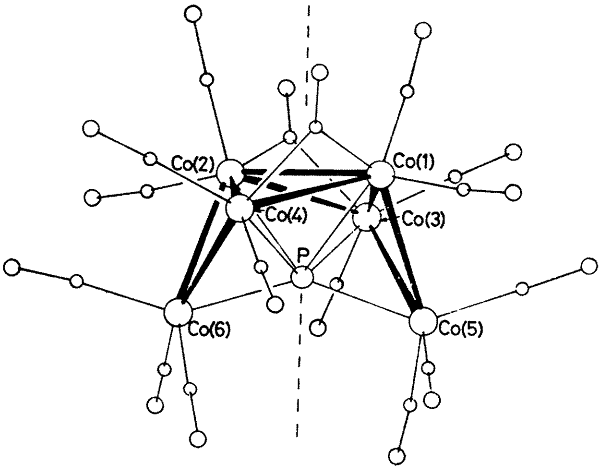

FIGURE. A view of the anion $[Co_6(CO)_{14}(\mu\text{-}CO)_2P]^-$; the dotted line indicates the direction of the ideal two-fold axis. The Co–Co bond lengths are: Co(1)–Co(2), 2·935; Co(1)–Co(3), 2·587; Co(1)–Co(4), 2·574; Co(1)–Co(5), 2·660; Co(2)–Co(3), 2·574; Co(2)–Co(4), 2·563; Co(2)–Co(6), 2·669; Co(3)–Co(5), 2·642; and Co(4)–Co(6), 2·650 Å (e.s.d.s 0·002 Å). The P atom shows distances from cobalt atoms Co(1)–Co(6) of 2·253, 2·265, 2·267, 2·269, 2·165, and 2·174 Å respectively (e.s.d.s 0·003 Å).

The phosphide ligand is bonded to all the metal atoms in such a way that, rather than a bridging ligand, it can be considered as a 'semi-interstitial' atom, the angle Co(5)–P–Co(6) being 142·2(1)°. Two Co–P bonds, with atoms Co(5) and Co(6), are significantly shorter (mean 2·170 Å) than the other four (mean 2·264 Å). The nature of this phosphide ligand is probably intermediate between that of an external bridging P atom (sharing three electrons) and that of an interstitial atom (sharing five electrons). This can also be inferred from the fact that the attainment of a closed shell configuration for each metal atom is achieved either with 92 total valency electrons and 8 metal–metal bonds, or with 90 valency electrons and 9 metal–metal bonds. Actually the Co(1)–Co(2) interaction is very weak so that the phosphorus atom seems to share more than three but less than five electrons, and some residual electron density must reside near to this atom on the open side of the cluster.

Finally the metal atom cluster geometry may be rationalized by considering the size of the phosphide atom which cannot occupy the cavity of an octahedron or a regular trigonal prism of cobalt atoms. The actual hexanuclear array may be derived either from an octahedron with three broken edges, or from a trigonal prism with one broken edge and distortion of the remaining square face. Alternatively it may be considered part of the surface of a larger polyhedron.

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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