The Crystal Structures of Bis(tricarbonyltributylphosphinecobalt) and Bis(tricarbonyltriethylphosphinecobalt)mercury

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WE report the crystal structures, obtained by X-ray diffraction methods, of two cobalt carbonyls containing unbridged metal–metal bonds.

Bis(tricarbonyltributylphosphinecobalt) crystallises from methanol as thin red-brown plates.† The space group is $P2_1/c$, $a = 11{\cdot}23$, $b = 13{\cdot}14$, $c = 15{\cdot}89$ Å, $\beta = 125°50'$, $Z = 2$. The molecules have a centre of symmetry imposed by crystallographic requirement. Measurement of 820 independent reflections significantly above background was performed with a single crystal mounted so as to rotate about a^* on a Hilger Watts linear diffractometer. Mo-K_α radiation was used with balanced filters.

Bis(tricarbonyltriethylphosphinecobalt)mercury gives brown prisms from benzene–hexane; $a = 7{\cdot}32$, $b = 14{\cdot}24$, $c = 14{\cdot}94$ Å, $\beta = 123°\ 10'$, $P2_1/c$, and $Z = 2$ with molecular centrosymmetry again implied. Measurement of 1030 reflections was performed as before from a crystal set to rotate about b^*.

Both structures were solved by the heavy-atom method and refined by Fourier, difference Fourier, and block-diagonal least-squares methods to final values of R of 0·11 and 0·07 respectively. Anisotropic thermal parameters were used for the metal and phosphorus atoms and absorption corrections were applied in the case of the mercury compound.

Bis(tricarbonyltributylphosphinecobalt) has the four atoms P–Co–Co–P in an almost linear array, Co–Co–P = 178°, and contains an unbridged Co–Co bond of length 2·67(1) Å. Other geometrical parameters of interest are: Co–P 2·19(1) mean Co–C 1·77, mean C–O 1·12, and mean P–C 1·87 Å. The average Co–Co–C angle is 86°, acute as in all similar molecules, while the average Co–P–C angle is 112°. Two of the butyl side chains are in a disordered state and no unique positions can be ascribed to six of the carbon atoms.

The unbridged Co–Co distance may be compared with the values of 2·913(6) Å and 2·92(1) Å found for the Mn–Mn separation in $[\mathrm{Mn(CO)_4PEt_3}]_2$[1] and in decacarbonyldimanganese[2] respectively. Since the substitution of a *trans*-triethylphosphine group for a carbonyl group in the manganese system clearly has no significant effect upon the metal–metal distance and since the replacement of carbonyl by triethylphosphine in the cobalt–mercury compound described has no measurable effect upon the metal–metal distance, it is likely that the value of 2·67 Å is close to that expected for the unbridged $[\mathrm{Co(CO)_4}]_2$ present in solution equilibrium.

In the mercury-containing compound the Co–Hg distance is 2·499(5) Å. This is much shorter than the values of 2·56(1) Å found in $(\pi\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2HgCo(CO)_4}$,[3] and 2·58(1) Å in $(\pi\text{-}\mathrm{C_5H_5})\mathrm{Co(CO)_2}$-$\mathrm{HgCl_2}$.[4] It is, however, identical with those found in $\mathrm{Hg[Co(CO)_4]_2}$,[5] 2·499(6) and 2·496(6) Å, showing that the substitution of a trialkylphosphine moiety for a *trans*-carbonyl group has no measurable effect upon the M–M separations in these homologous symmetrical carbonyls. This is in marked contrast to the situation in heterogeneous systems such as Sn–Mn compounds where such a substitution significantly diminishes the metal–metal bond distance.[6] Other distances of interest in this molecule are in agreement with those found in octacarbonyldicobaltmercury, Co–P 2·19(1), mean Co–C 1·73, and mean C–O 1·19 Å. The mean Hg–Co–C angle is 86° as compared to 82° in that compound.

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† Professor James Ibers informs us that he has determined the crystal structure of $[\mathrm{Co(CO)_3PBu^n_3}]_2$ in a cubic modification crystallised from iso-octane. He found the Co–Co distance = 2·66(1) Å with other geometrical parameters in agreement with our results. However, his molecule possesses D_{3d} symmetry whereas in our case the symmetry is $\bar{1}$. This difference in crystal morphology is no doubt due to the disorder of the butyl groups in our own case as opposed to the other where they are ordered. We thank Professor Ibers for permission to quote his results in advance of publication (*J. Organometallic Chem.*, 1968, in the press).

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