Arsole Metal Complexes

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Summary The series of penta-, tetra-, and tri-carbonylmetal derivatives of tetraphenylarsole is reported for manganese and rhenium; an *X*-ray study of $Ph_4C_4AsMn(CO)_3$ shows it to have a novel π-arsole structure.

The tetraphenylarsolepentacarbonyls of manganese and rhenium show parent ions (*P*) corresponding to $Ph_4C_4As M(CO)_5^+$, and the stepwise loss of CO down to *P*—5CO.

The peaks corresponding to $Ph_4C_4AsM(CO)_3^+$ and $Ph_4C_4AsM^+$ were among the most intense in the spectra. To date no complexes of the type $R_2AsM(CO)_5$ have been isolated because of spontaneous formation of dimers.[1] Some cyclopentadienylmetal carbonyl arsine monomers such as (π-C_5H_5) $Mo(CO)_3AsR_2$ have been isolated,[2] however, where R is perfluoroalkyl or perfluoroaryl.

Whilst the compounds $Ph_4C_4AsM(CO)_5$ have an indefinite shelf life at ambient temperature, they can be made to lose carbon monoxide upon irradiation or heating. The initial loss of carbon monoxide involves dimerization to $[Ph_4C_4AsM(CO)_4]_2$.

Although the mass spectra of the products after a limited heating showed the peaks $[Ph_4C_4AsM(CO)_4]_2^+$, corresponding to the parent ions of the dimeric products, it is not yet possible to obtain the dimers perfectly pure. More prolonged heating or irradiation caused further loss of carbon monoxide and gave the monomeric compounds $Ph_4C_4As M(CO)_3$.

The monomeric pentacarbonylarsole and the dimeric tetracarbonylarsole could be assigned structures by analogy with known systems but the $Ph_4C_4AsM(CO)_3$ complexes were novel and an *X*-ray diffraction study was carried out on $Ph_4C_4AsMn(CO)_3$.

Crystal data: $C_{31}H_{20}O_3AsMn$, $M = 570{\cdot}4$; yellow monoclinic crystals, $a = 8{\cdot}83$, $b = 11{\cdot}12$, $c = 26{\cdot}72$ Å, $\beta = 98{\cdot}09°$ space group $P2_1/c$; $D_m = 1{\cdot}47$, $D_c = 1{\cdot}46$ for $Z = 4$. At the present stage of refinement $R = 0{\cdot}046$ for the 1336 independent reflexions having $1/\sigma(I) \geqslant 2$.

The structure (Figure) shows the presence of the arsole ring π-bonded to the tricarbonyl manganese group, with the plane containing the carbon atoms of the carbonyl groups effectively parallel to the arsole ring. The arsole ring is planar with the phenyl substituents twisted out of the plane by 40—60°.

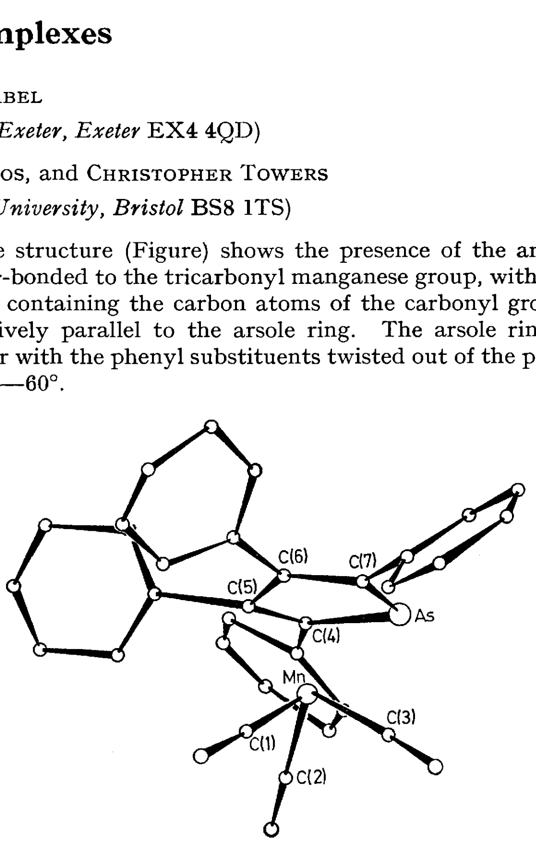

Figure. *Structure of* $Ph_4C_4AsMn(CO)_3$, *illustrating the π-arsolenyl bonding of the complex.*

The Mn–As bond length 2·492 (2) Å is shorter by some 0·1 Å than the sum of the covalent radii. The ring carbons are equidistant from the manganese to give a mean Mn–C (ring) distance of 2·193(5) Å, similar to values of 2·162(8) Å and 2·168(6) Å reported[3,4] in the π-cyclopentadienylmanganese complexes, $[C_5Ph_5SnPh]$ $Mn(CO)_3$ and $(C_5H_5)Mn$ $C_7H_8)(CO)_2$. Only small differences are observed in the three C–C distances of the ring, and the average value of 1·42(1) Å is close to the C–C distances found[3,4,5] in a number of π-cyclopentadienylmanganese complexes. The mean As–C (ring) distance of 1·90 (1) Å, is shorter than the sum of the covalent radii[6] (As–C_{sp2}, 1·95 Å), and also the

As–C distances found[7] in $(AsPh)_6$, mean 1·97(2) Å. All of this indicates delocalisation throughout the arsole ring. Incorporation of the arsenic into the delocalized system causes angular distortions within the planar ring, giving an average angle of 114° at the carbons and a C(4)–As–C(7) bond angle of 84·9(4)°.

We thank Philips (Eindhoven) for data collection on their PW1100 4-circle diffractometer.

(*Received*, 6*th December* 1972; *Com.* 2037.)

[1] R. G. Hayter, *J. Amer. Chem. Soc.*, 1964, **86**, 823.

[2] W. R. Cullen and R. G. Hayter, *J. Amer. Chem. Soc.*, 1964, **86**, 1030; M. Cooke, M. Green, and D. Kirkpatrick, *J. Chem. Soc.* (*A*), 1968, 1507.

[3] R. F. Bryan and H. P. Weber, *J. Chem. Soc.*, (*A*), 1967, 843.

[4] B. Granoff and R. A. Jacobson, *Inorg. Chem.*, 1968, **7**, 2328.

[5] A. F. Berndt and R. E. Marsh, *Acta Cryst.*, 1963, **16**, 118.

[6] L. Pauling, "The Nature of the Chemical Bond", 3rd Edn., Cornell Univ. Press, Ithaca, N.Y., 1960.

[7] K. Hedberg, E. W. Hughes, and J. Waser, *Acta Cryst* (*B*) 1961, **14**, 369.