Characterization of the Reported $[Mn(CO)(Ph_2PCH_2CH_2PPh_2)_2]$ (Red Isomer) as the Acylmanganese Complex $[Mn(CO)(COC_6H_4PhPCH_2CH_2PPh_2)(Ph_2PCH_2CH_2PPh_2)]$ by *X*-Ray Diffraction

By MICHAEL LAING* and PAUL M. TREICHEL
(*Department of Chemistry, University of Natal, Durban, South Africa* 4001)

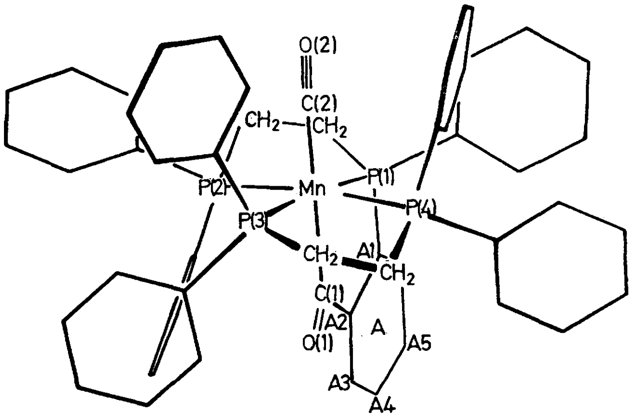
Summary One of the products of the reaction between $[Mn_2(CO)_{10}]$ and $Ph_2PCH_2CH_2PPh_2$, previously identified as a paramagnetic species $[Mn(CO)(Ph_2PCH_2CH_2PPh_2)_2]$, is in fact diamagnetic and contains an acyl carbonyl group linking the manganese to an *ortho* carbon of one phenyl ring and is correctly formulated as $[Mn(CO)(COC_6H_4PhPCH_2CH_2PPh_2)(Ph_2PCH_2CH_2PPh_2)]$.

FOUR products have been identified[1-3] from the reaction between $[Mn_2(CO)_{10}]$ and $Ph_2PCH_2CH_2PPh_2$ (dpe). A yellow diamagnetic compound, formulated as $[Mn(CO)_2(dpe)_2][Mn(CO)_5]$, is the major product which precipitates from solution when the reaction is carried out in benzene or toluene. The other complexes are said to be paramagnetic:[3] $[Mn(CO)_3(dpe)]$, and yellow and red isomers of $[Mn(CO)(dpe)_2]$. The last two are isolated in only small yields from reactions utilizing excess of dpe and forcing conditions. Believing all three of these species to be mischaracterized, we undertook a reinvestigation of this reaction.

The red compound '$[Mn(CO)(dpe)_2]$' is obtained in $< 3\%$ yield by reaction of $[Mn_2(CO)_{10}]$ and dpe in a molar ratio of 1 : 4 in refluxing xylene. It is isolated by chromatography on alumina and obtained as large red crystals from CH_2Cl_2–heptane, m.p. 217—220 °C; ν(CO), $CHCl_3$: 1818, KBr: 1810 s and 1595 w cm^{-1}. A better yield is obtained when a slurry of $[Mn(CO)_2(dpe)_2][Mn(CO)_5]$ is refluxed in xylene.

The crystals are triclinic, space group $P\bar{1}$, $a = 10{\cdot}60$, $b = 13{\cdot}37$, $c = 19{\cdot}62$ ($\pm 0{\cdot}01$) Å; $\alpha = 99{\cdot}1$, $\beta = 98{\cdot}1$, $\gamma = 112{\cdot}3$ ($\pm 0{\cdot}1$)°; $U = 2478$ Å^3, $D_m = 1{\cdot}4$ g cm^{-3}, $Z = 2$. Intensity data were collected on a Philips four-circle diffractometer with graphite-monochromated Mo-K_α radiation to $\theta = 20°$; the crystal was coated with varnish to prevent possible decomposition. Of 4700 measured intensities, 3800 were judged to be observed and used to calculate a three-dimensional Patterson map from which the positions of the manganese and phosphorus atoms were deduced. The remaining atoms were located in the subsequent Fourier map. In addition to the 61 atoms of the molecule, two molecules of the solvent CH_2Cl_2 were found. The 67 atom structure was refined by block-diagonal least-squares (Mn and four P atoms anisotropic) to $R = 0{\cdot}09$. A projection of the molecule down the *a* axis is shown in the Figure.

The co-ordination about the manganese atom is octahedral with the four P atoms in an approximate square plane. Bond lengths and angles are normal: mean Mn–P 2·28, mean P–C 1·85, Mn–C(2) 1·73, Mn–C(1) 2·05, C(2)–O(2) 1·20, C(1)–O(1) 1·25, C(A2)–C(1) 1·50 Å; Mn–C(1)–O(1) 126, Mn–C(1)–C(A2) 119, P(1)–C(A1)–C(A2) 113, P(1)–Mn–C(1) 83, P(1)–Mn–P(2) 82, P(3)–Mn–P(4) 83°.



FIGURE

The linking of phenyl ring A to the manganese atom *via* the acyl group imposes a greater rigidity on the ethylene chain linking P(1) to P(2). This results in a reduced torsion angle in this diphos–ethylene chain: 21° for P(1)–CH_2–CH_2–P(2) compared with 38° for P(3)–CH_2–CH_2–P(4). There are no short intramolecular non-bonded contacts: the molecule is remarkably strain free and is easily constructed from CPK or Leybold models.

It is possible that the compound is formed by the basic $[Mn(CO)_5]^-$ ion abstracting an *ortho* proton from one phenyl ring in $[Mn(CO)_2(dpe)_2]^+$ followed by a nucleophilic attack of the carbanion on the adjacent carbonyl group. This unusual reaction is favoured sterically and bears some resemblance to the formation of the well known internally metallated species. A reluctance of other complexes of chelating diphosphines to undergo internal metallation[4] is probably due to steric constraints.

We are grateful to the South African Council for Scientific and Industrial Research for support, and to Dr. Johan Coetzer of National Physical Research Laboratories, C.S.I.R., Pretoria, for collecting the intensity data.

(*Received, 7th July* 1975; *Com.* 778.)

---

[1] A. Sacco, *Gazzetta*, 1963, **93**, 698.
[2] A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 700.
[3] R. H. Reimann and E. Singleton, *J. Organometallic Chem.*, 1972, **38**, 113.
[4] M. G. Clerici, B. L. Shaw, and B. Weeks, *J.C.S. Chem. Comm.*, 1973, 516.