

1126. Substituted Carbonylcyclopentadienylmanganese Complexes.

By R. S. NYHOLM, S. S. SANDHU, and M. H. B. STIDDARD.

The reactions of some tertiary phosphines and arsines with tricarbonylcyclopentadienylmanganese, $\text{CpMn}(\text{CO})_3$ and tricarbonyl(methylcyclopentadienyl)manganese, $(\text{MeCp})\text{Mn}(\text{CO})_3$ have been investigated by direct heating in an evacuated tube or under the influence of ultraviolet light. Reactions with the monodentate ligands PPh_3 and AsPh_3 lead to products of the type $\text{CpMn}(\text{CO})_2\text{L}$. Reactions with the bidentate ligands 1,2-bisdiphenylphosphinoethane (Diphos) and *o*-phenylenebisdimethylarsine (Diars) lead to two types of complexes: those in which the ligands act as bridging groups, *e.g.*, $[\text{CpMn}(\text{CO})_2]_2(\text{Diars})$ and those in which ligand atoms occupy normal chelate positions, *e.g.*, $\text{CpMn}(\text{CO})(\text{Diphos})$.

ALTHOUGH carbonyl replacements in decacarbonyldimanganese,¹ and its halogenocarbonyl derivatives² have attracted some attention, the corresponding reactions of carbonylmanganese complexes containing such ligands as the cyclopentadienyl group have been less studied. At the start of this investigation, the only reported compound of this type was the complex³ $\text{CpMn}(\text{CO})_2\text{py}$ (Cp = cyclopentadienyl). Subsequently, some similar derivatives containing triphenylphosphine⁴ and piperidine⁵ have been described, but without mention of their physical properties. We now report a series of substituted derivatives of tricarbonylcyclopentadienylmanganese and tricarbonyl(methylcyclopentadienyl)manganese, prepared by photochemical initiation or by direct heating.

The monodentate ligands triphenylphosphine and triphenylarsine react readily with the carbonylcyclopentadienyls in cyclohexane, on irradiation with ultraviolet light, to produce good yields of the complexes $\text{CpMn}(\text{CO})_2\text{L}$ and $(\text{MeCp})\text{Mn}(\text{CO})_2\text{L}$ (MeCp = methylcyclopentadienyl). They are stable in air and crystalline and their physical properties are given in the Table. Clearly, their formulations are consistent with their reported properties; the compounds are diamagnetic, non-electrolytes in nitrobenzene, and monomeric in benzene, and their infrared spectra show the expected two bands in the carbonyl stretching region. The triphenylphosphine compounds have also been obtained by direct reactions at 250°, but attempts to prepare the triphenylarsine analogues by the same method failed.

¹ Hieber and Freyer, *Chem. Ber.*, 1959, **92**, 1765; Nyholm and Ramana Rao, *Proc. Chem. Soc.*, 1959, 130; Osborne and Stiddard, *J.*, 1963, in the press.

² Abel and Wilkinson, *J.*, 1959, 1501; Hieber and Schropp, *Z. Naturforsch.*, 1959, **14b**, 460; Osborne and Stiddard, *J.*, 1962, 4715.

³ Strohmeier and Gerlach, *Z. Naturforsch.*, 1960, **15b**, 675.

⁴ Strohmeier and Barbeau, *Z. Naturforsch.*, 1962, **17b**, 848.

⁵ Strohmeier and Guttenberger, *Z. Naturforsch.*, 1963, **18b**, 80.

Carbonylcyclopentadienyl complexes.

Compound *	Colour	M. p.	Λ_M (Ω^{-1} cm. ²)	C—O stretch- ing freq. † (I.R., cm. ⁻¹) in CHCl ₃	Mol. wt., osmo- metric in C ₆ H ₆	
			10 ⁻³ M in PhNO ₂		Found	Calc.
CpMn(CO) ₂ PPh ₃	Golden yellow	210—212°	0.4	1934, 1862	429	438
(MeCp)Mn(CO) ₂ PPh ₃	Light yellow	119—120	0.3	1934, 1862	439	452
CpMn(CO) ₂ AsPh ₃	Yellow	165—166	0.1	1934, 1862	458	482
(MeCp)Mn(CO) ₂ AsPh ₃	Pale yellow	118—120	0.2	1934, 1862	479	496
[CpMn(CO) ₂] ₂ (Diphos) ...	Yellow	210—212	0.3	1934, 1862	747	750
[(MeCp)Mn(CO) ₂] ₂ (Diphos)	Pale yellow	181—183	0.2	1934, 1862	750	778
[CpMn(CO) ₂] ₂ (Diars)	Yellow	156—158	0.7	1934, 1862	‡	—
[(MeCp)Mn(CO) ₂] ₂ (Diars)	Yellow	138—140	0.2	1934, 1862	655	666
CpMn(CO)(Diphos)	Orange	160—161	0.3	1818	522	546
(MeCp)Mn(CO)(Diphos) ...	Red-brown	105—106	0.9	1818	555	560

* All are diamagnetic in the solid state at 20°. † All bands are very strong. ‡ Not sufficiently soluble.

The bidentate ligands 1,2-bisdiphenylphosphinoethane (Diphos) and *o*-phenylenebisdimethylarsine (Diars) have been found also to react with the carbonylcyclopentadienyls, to yield replacement products. On irradiation of cyclohexane solutions, the diphosphine reacts to give complexes in which the ligand behaves as a bridging group, with the phosphorus atoms co-ordinated independently to two manganese atoms. Such behaviour of ligands of this type has been reported previously by Chatt and Hart,⁶ and by Canziani and Zingales.⁷ On the other hand, prolonged irradiation of the reactants in benzene (in which the bridged complexes are soluble) produces the chelate complexes. Both the bridged and the chelate complexes are stable and crystalline. The Table shows their physical properties; particularly noteworthy are, of course, the observed molecular weights and the number of carbonyl stretching frequencies. Again the thermal has been less successful than the photochemical method, having failed to produce the compounds [CpMn(CO)₂]₂(Diphos) and (MeCp)Mn(CO)(Diphos). The diarsine reacts, under similar irradiation conditions in cyclohexane, to produce stable yellow crystals. The properties of these products again indicate that the ligand is acting as a bridging group. They are the first compounds to be described in which the diarsine, a powerful chelate, behaves in this way. At first sight, it might appear sterically unlikely that this type of bonding should occur. However, inspection of a model indicates that the co-ordination sites on the arsenic atoms, which in chelate compounds must be in positions *cis* to the plane of the benzene ring, can be twisted into *trans*-positions by rotation of the (phenylene) carbon-arsenic bonds. In these positions, it is suggested, the diarsine can behave as a bridging group. Attempts to prepare the chelate complexes of the diarsine were not wholly successful. Such complexes are certainly formed on ultraviolet irradiation in benzene, but are very unstable (particularly in solution) and difficult to purify. The compound CpMn(CO)diars has been obtained in a state of near analytical purity: it is diamagnetic and its infrared spectrum in the carbonyl stretching region is identical with those of the chelate diphosphine complexes. Thermal reactions of the diarsine failed to yield identifiable products.

EXPERIMENTAL

Dicarbonyl- π -cyclopentadienyltriphenylphosphinemanganese(I).—(a) A solution of the complex CpMn(CO)₃ (0.61 g.) and triphenylphosphine (0.53 g.) in cyclohexane (10 ml.) was sealed in an evacuated Pyrex tube and exposed to ultraviolet light (80 w, Osram) for 20 hr. The yellow crystalline *product* (0.68 g.), which separated during reaction, was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 68.9; H, 4.8; P, 6.7; Mn, 12.4. C₂₅H₂₀MnO₂P requires C, 68.5; H, 4.5; P, 7.1; Mn, 12.55%).

(b) The complex CpMn(CO)₃ (0.51 g.) and triphenylphosphine (1.02 g.) were heated in an evacuated tube for 8 hr. at 250°. After opening, re-evacuation, and resealing of the tube, the

⁶ Chatt and Hart, *J.*, 1960, 1378.

⁷ Canziani and Zingales, *Gazzetta*, 1962, 92, 343, 761.

heating was repeated; unchanged materials were removed by treatment with warm ethanol and vacuum-sublimation at 80°. The residual solid crystallised from light petroleum to produce the above product (0.41 g.) (Found: C, 68.8; H, 4.7; P, 6.7; Mn, 12.5%). This product, and those described subsequently, are all stable in air and crystalline, soluble in most non-polar solvents, but insoluble in ethanol. Solutions decompose on storage.

Dicarbonyl-(π -methylcyclopentadienyl)triphenylphosphinemanganese(I).—(a) A solution of the complex $(\text{MeCp})\text{Mn}(\text{CO})_3$ (2.6 ml.) and triphenylphosphine (0.61 g.) in cyclohexane (5 ml.) was exposed to ultraviolet light, as described above, for 20 hr. Ethanol (50 ml.) was added with shaking, and light yellow needles then separated on storage at room temperature. The product (0.38 g.) was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 69.2; H, 4.8; P, 7.0; Mn, 12.1. $\text{C}_{26}\text{H}_{22}\text{MnO}_2\text{P}$ requires C, 69.0; H, 4.9; P, 6.9; Mn, 12.2%).

(b) The complex $(\text{MeCp})\text{Mn}(\text{CO})_3$ (2.0 ml.) and triphenylphosphine (0.66 g.) were treated as above at 250° for 16 hr. After treatment with ethanol (50 ml.), yellow crystals separated on storage at room temperature. Crystallisation from light petroleum yielded the pure compound (0.63 g.) which was dried *in vacuo* (Found: C, 68.95; H, 5.0; P, 6.8; Mn, 12.4%).

Dicarbonyl- π -cyclopentadienyltriphenylarsinemanganese(I).—A solution of the complex $\text{CpMn}(\text{CO})_3$ (1.8 g.) and triphenylarsine (0.63 g.) in cyclohexane (12 ml.) was exposed to ultraviolet light for 20 hr. The bright yellow crystals of the complex (0.70 g.), which separated, were filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 62.4; H, 4.4; As, 15.3; Mn, 11.1. $\text{C}_{25}\text{H}_{20}\text{AsMnO}_2$ requires C, 62.3; H, 4.15; As, 15.6; Mn, 11.4%).

Dicarbonyl- π -(methylcyclopentadienyl)triphenylarsinemanganese(I).—Similar treatment of the complex $(\text{MeCp})\text{Mn}(\text{CO})_3$ (2.0 ml.) and triphenylarsine (0.64 g.) in cyclohexane (10 ml.) for 20 hr. gave the compound (0.47 g.) after addition of ethanol (50 ml.) (Found: C, 62.7; H, 4.5; As, 14.9; Mn, 10.6. $\text{C}_{28}\text{H}_{22}\text{AsMnO}_2$ requires C, 62.9; H, 4.4; As, 15.1; Mn, 11.0%).

$\mu\mu'$ -1,2-Bisdiphenylphosphinoethanetetracarbonyldi- π -cyclopentadienyl dimanganese(I).—A solution of the complex $\text{CpMn}(\text{CO})_3$ (0.63 g.) and the diphosphine (0.20 g.) in cyclohexane (10 ml.) was exposed to ultraviolet light for 12 hr. with occasional shaking. The crystals which separated were filtered off, and washed with cyclohexane. The pure product (0.43 g.) crystallised from a benzene-light petroleum and was dried *in vacuo* (Found: C, 64.2; H, 4.8; P, 8.0; Mn, 14.8. $\text{C}_{40}\text{H}_{34}\text{Mn}_2\text{O}_4\text{P}_2$ requires C, 64.0; H, 4.5; P, 8.3; Mn, 14.7%).

$\mu\mu'$ -1,2-Bisdiphenylphosphinoethanetetracarbonyldi- π -methylcyclopentadienyl dimanganese(I).—(a) Similar treatment of the complex $(\text{MeCp})\text{Mn}(\text{CO})_3$ (2.0 ml.) and the diphosphine (0.31 g.) in cyclohexane (11 ml.) for 12 hr. produced the yellow crystalline compound (0.32 g.) which was dried *in vacuo* (Found: C, 64.6; H, 4.7; P, 7.8; Mn, 14.35. $\text{C}_{42}\text{H}_{38}\text{O}_4\text{P}_2\text{Mn}_2$ requires C, 64.8; H, 4.9; P, 8.0; Mn, 14.1%).

(b) A mixture of the complex $(\text{MeCp})\text{Mn}(\text{CO})_3$ (2.0 ml.) and the diphosphine (0.51 g.) was heated in an evacuated tube at 250° for 16 hr., then treated with hot ethanol. Crystallisation from light petroleum yielded the compound (0.68 g.), which was dried *in vacuo* (Found: C, 64.6; H, 4.9; P, 8.1; Mn, 14.1%).

$\mu\mu'$ -o-Phenylenebisdimethylarsinetetracarbonyldi- π -cyclopentadienyl dimanganese(I).—A solution of the complex $\text{CpMn}(\text{CO})_3$ (1.11 g.) and the diarsine (1.0 ml.) in cyclohexane (5 ml.) was exposed to ultraviolet light for 60 hr. Orange crystals were formed, together with some decomposition products. The latter were carefully washed away with cyclohexane to leave the pure product (0.06 g.), which was crystallised from benzene and dried *in vacuo* (Found: C, 45.4; H, 4.1; As, 2.9. $\text{C}_{24}\text{H}_{26}\text{As}_2\text{Mn}_2\text{O}_4$ requires C, 45.1; H, 4.1; As, 23.5%).

$\mu\mu'$ -o-Phenylenebisdimethylarsinetetracarbonyldi- π -methylcyclopentadienyl dimanganese(I).—Similar treatment of a solution of the complex $(\text{MeCp})\text{Mn}(\text{CO})_3$ (2.2 ml.) and the diarsine (1.0 ml.) in cyclohexane (6 ml.) for 35 hr. produced the pure compound (0.68 g.) (Found: C, 46.9; H, 4.65; As, 22.1; Mn, 16.25. $\text{C}_{28}\text{H}_{30}\text{As}_2\text{Mn}_2\text{O}_4$ requires C, 46.85; H, 4.5; As, 22.5; Mn, 16.5%).

Monocarbonyl- π -cyclopentadienyl-1,2-bisdiphenylphosphinoethanemanganese(I).—(a) A solution of the complex $\text{CpMn}(\text{CO})_3$ (0.21 g.) and the diphosphine (0.41 g.) in benzene (25 ml.) was exposed to ultraviolet light for 50 hr. After filtration, the solution was concentrated to 5 ml. under a vacuum, and ethanol (50 ml.) was added. The solution was again concentrated, until the appearance of the product (0.47 g.), which was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 70.6; H, 5.4; P, 10.9; Mn, 10.6. $\text{C}_{32}\text{H}_{23}\text{MnOP}_2$ requires C, 70.4; H, 5.3; P, 11.4; Mn, 10.1%).

(b) The complex $\text{CpMn}(\text{CO})_3$ (0.66 g.) and the diphosphine (0.44 g.) were heated at 260° for 16 hr. After extraction of unused starting materials with hot ethanol, crystallisation from light

petroleum yielded the product (0.11 g.), which was dried *in vacuo* (Found: C, 70.6; H, 5.4; P, 10.9%).

Monocarbonyl- π -methylcyclopentadienyl-1,2-bisdiphenylphosphinoethanemanganese(I).—A solution of the complex $(\text{MeCp})\text{Mn}(\text{CO})_3$ (0.1 ml.) and the diphosphine (0.39 g.) in benzene (15 ml.) was exposed to ultraviolet light for 50 hr. The solution was filtered and concentrated to 4 ml. under a vacuum. Ethanol (40 ml.) was added and pumping continued until the *product* (0.31 g.) separated. It was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 70.5; H, 5.6; P, 10.7; Mn, 9.6. $\text{C}_{33}\text{H}_{31}\text{MnOP}_2$ requires C, 70.7; H, 5.5; P, 11.1; Mn, 9.8%).

Physical Measurements and Analyses.—Physical measurements were carried out as described previously,⁸ with the exception of molecular weights which were determined by using a Mechrolab vapour-pressure osmometer, model 301A. Manganese was estimated either gravimetrically as the pyrophosphate or volumetrically as permanganate.

We are indebted to the Commonwealth Scholarship Commission and the Dupont Company, U.S.A., for maintenance grants (to S. S. S.) and to the Ethyl Corporation for gifts of the carbonylcyclopentadienylmanganese compounds.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE,
GOWER STREET, LONDON W.C.1.

[Received, June 13th, 1963.]

⁸ Nigam, Nyholm, and Stiddard, *J.*, 1960, 1803, 1806.
