126. *Photochemically Produced Tertiary-phosphine Derivatives of Decacarbonyldimanganese.*

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The reactions of decacarbonyldimanganese with various tertiary phosphines have been investigated, in particular their photochemical initiation. The complexes $[Mn(CO)_4PR_3]_2$, (R = Ph, OPh, p-C_6H_4F, and Et) have been isolated and their physical properties determined. Infrared measurements in the C–O stretching region are consistent with a point-group symmetry approximating to D_{4d} for these complexes.

Monodentate ligands have been reported to react with decacarbonyldimanganese in one or more of four ways: (i) substitution with retention of the metal–metal bond, *e.g.*, $[Mn(CO)_4P(OPh)_3]_2$;[1] (ii) substitution with fission of the metal–metal bond, *e.g.*, $Mn(CO)_4PPh_3$;[1] (iii) disproportionation of the carbonyl, *e.g.*, $[Mn(py)_6][Mn(CO)_5]_2$;[2] and (iv) formation of a product containing covalently bound bridging ligands, *e.g.*, $[Mn(CO)_4AsPh_2]_2$.[3] This Paper concerns the preparation and structure of complexes of type (i). Previous work by Hieber and Freyer[1] has indicated that reactions of the phosphorus-containing ligands $P(OPh)_3$ and $P(cyclohexyl)_3$ lead to compounds of this type, whereas other tertiary phosphines produce complexes of type (ii). It appeared, however, desirable to look more closely into these reactions, since it is feasible that, in experimental conditions other than those investigated by Hieber and Freyer, different products might be formed.

Most of the complexes now described were prepared by photochemically initiated reactions. Although this technique has been applied to other carbonyl systems,[4] the reactions of decacarbonyldimanganese under ultraviolet irradiation have not been investigated previously. Such reactions proceed very readily in cyclohexane to produce the compounds listed in Table 1. The physical properties of the complexes containing triphenyl- and triethyl-phosphines and triphenyl phosphite are consistent with their formulation as dimeric species in which the metal–metal bond of the parent carbonyl is retained. Complexes containing the ligands $(p\text{-}F\cdot C_6H_4)_3P$ and $AsPh_3$ (which were analytically pure) are, however, weakly paramagnetic. The former complex is not sufficiently soluble for its molecular weight to be determined, but the apparent molecular weight of the latter appears to indicate the presence of the monomer $Mn(CO)_4AsPh_3$. Attempts to obtain a homogeneous species were unsuccessful. It is of interest that, in contrast to the solution reactions of Hieber and Freyer,[1] the photochemical technique

Table 1.

Carbonylmanganese complexes.

			Conductance in $Ph\cdot NO_2$		C–O stretching freq. (cm.$^{-1}$, in $CHCl_3$)	*M* (osmometric in C_6H_6)	
Compound *	Colour	M. p.	Λ_M(Ω^{-1} cm.^{2})	Concn. (10^{-3}M)		Found	Calc.
$[Mn(CO)_4PPh_3]_2$	Dark orange	189—190°	0·038	1·04	1980sh, 1956vs	820	858
$[Mn(CO)_4PEt_3]_2$	Yellow	153—154	0·030	1·05	1978sh, 1956vs §	550	570
$[Mn(CO)_4P(OPh)_3]_2$	Lemon yellow	140	0·014	1·34	2000sh, 1982vs	922	954
$[Mn(CO)_4P(p\text{-}F\cdot C_6H_4)_3]_2$ †	Dark orange	210(d)	¶	—	1975sh, 1956vs	¶	—
$[Mn(CO)_4AsPh_3]_2$ ‡	Dark orange	155	0·12	1·00	1975sh, 1956vs	840	946

* All diamagnetic in the solid state except where indicated. † $\mu_{eff.}$ = 0·72 B.M. ‡ $\mu_{eff.}$ = 0·38 B.M. § In cyclohexane. ¶ Insufficiently soluble.

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[1] Hieber and Freyer, *Chem. Ber.*, 1959, **92**, 1765.

[2] Hieber and Schropp, *Z. Naturforsch.*, 1960, **15**b, 271.

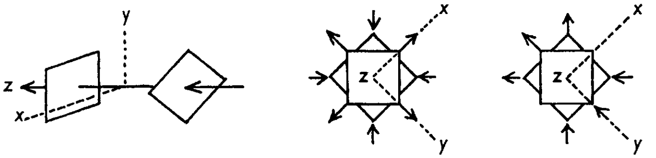
[3] Lambert, *Chem. and Ind.*, 1961, 830.

[4] Strohmeier *et al.*, *Z. Naturforsch*, 1962, **17**b, 502, and earlier papers; Lewis, Nyholm, Osborne, Sandhu, and Stiddard, *Chem. and Ind.*, 1963, 1398; Nyholm, Sandhu, and Stiddard, *J.*, 1963, 5916.

leads predominantly to dimeric, diamagnetic products which further emphasise its usefulness in producing substituted carbonyls of unusual structure.

Direct reactions of triphenyl-phosphine and -arsine with the carbonyl in sealed tubes have also been investigated. At 120—130° the phosphine produces the same diamagnetic compound. The arsine at 120° gives a bridged arsenic complex, $[Mn(CO)_4AsPh_2]_2$, produced previously by a solution reaction.[3]

The main matter remaining for discussion is the structure of the dimeric compounds, $[Mn(CO)_4L]_2$. Spectrophotometric titrations [5] have shown that two equivalents of bromine are used in oxidation of the compound $[Mn(CO)_4PPh_3]_2$ and, on a preparative scale, a good yield of the known product,[6] $Mn(CO)_4(PPh_3)Br$, has been obtained. The symmetrical nature of this product being thus established, it remains to differentiate between various possible structures. Since the infrared spectra of all our compounds are very similar, it seems reasonable to suggest that they have identical structures. Their spectra are very simple, and simple group theory [7] implies that only structures with symmetries D_{4d} and D_{4h} need be considered. In both cases two infrared C–O stretching frequencies are to be expected, so that simple spectroscopic measurements alone cannot differentiate between them. However, in view of the known staggered structure of the parent carbonyl,[8] the D_{4d} structure is favoured. Now, application of simple group theory to the carbonyl $Mn_2(CO)_{10}$ predicts three infrared-active C–O stretching modes ($2B_2 + E_1$) (see Figure). For simplicity, the motions of the carbon and oxygen atoms are replaced by a single "oscillating dipole."[9] Without further coupling, two intense bands [E_1 and $B_2(a)$] and one very weak band [$B_2(b)$] are thus expected. However, the two B_2 modes can mix to produce two bands of more comparable intensities. This is in accord with the observed spectrum. If the D_{4d} symmetry of the substituted complexes is accepted, modes analogous to those of the parent carbonyl are expected except that, of course, the $B_2(a)$ mode must be absent. Observations are consistent with this. The very strong band observed is that designated E_1, and the B_2 band is much weaker since it can no longer increase its intensity by coupling with the other B_2 mode.



$B_2(a)$ $B_2(b)$ E_1

Infrared-active C–O stretching vibrations in decacarbonyldimanganese.

In the spectra of compounds thought to contain monomers as impurities, no evidence of the latter could be found. It is certain that amounts of monomers present are quite small, but recent observations [10] indicate that compounds of the type $Mn(CO)_4L$ and $[Mn(CO)_4L]_2$ have virtually identical infrared spectra in the C–O stretching region. Evidently, the A_1 and E vibrations of the C_{4v} monomer coincide approximately with the B_2 and E_1 vibrations of the dimer.

There are differences in the infrared spectra observed by Hieber and Freyer [1] and by us. Some of their bands in the 1960—2100 cm.$^{-1}$ region can be accounted for only by the presence of oxidised manganese(I) species and we have observed [10] that the monomer $Mn(CO)_4PPh_3$ in chlorinated solvents produces the compound $Mn(CO)_4(PPh_3)Cl$. On the

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[5] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1806.

[6] Angelici and Basolo, *J. Amer. Chem. Soc.*, 1962, **84**, 2495; Hieber, Faulhaber, and Theubert, *Z. anorg. Chem.*, 1962, **314**, 125.

[7] El-Sayed and Kaesz, *Inorg. Chem.*, 1963, **2**, 158.

[8] Dahl and Rundle, *Acta Cryst.*, 1963, **16**, 419.

[9] El-Sayed and Kaesz, *J. Mol. Spectroscopy*, 1962, **9**, 310.

[10] Kasenally, Nyholm, and Stiddard, unpublished work.

other hand, we find no evidence for similar reactions of the dimeric species at room temperature, and conclude that the dimers reported by Hieber and Freyer[1] contained some monomer impurities and/or several isomers. Experiments are in progress to clarify these points.

EXPERIMENTAL

Photochemical Reactions.—Decacarbonyldimanganese (*ca.* 0·3 g.) and the ligand (*ca.* 2·5 equiv.) were dissolved in the minimum quantity of dry cyclohexane (*ca.* 20 ml.), sealed in an evacuated Pyrex tube, and irradiated with ultraviolet light (80 w Osram) for the times indicated in Table 2. The product was isolated by filtration if it had separated during reaction, or by removal of solvent. Crystallisation from benzene–pentane gave the pure *product*, which was dried *in vacuo*. Yields and analyses are also given in Table 2.

TABLE 2.

Photochemical reactions.

Compound	Reaction time (hr.)	Yield (%)	Found (%)				Required (%)			
			C	H	P	Mn	C	H	P	Mn
$[Mn(CO)_4PPh_3]_2$	12	68	61·7	3·95	7·3	12·6	61·55	3·5	7·2	12·8
$[Mn(CO)_4PEt_3]_2$	18	69	42·1	5·2	11·2	19·0	42·1	5·3	10·9	19·3
$[Mn(CO)_4P(OPh)_3]_2$	20	58	55·5	3·5	6·8	11·3	55·4	3·2	6·5	11·5
$[Mn(CO)_4P(p\text{-}F{\cdot}C_6H_4)_3]_2$ ...	14	67	54·1	2·7	6·8	—	54·5	2·2	6·4	—
$[Mn(CO)_4AsPh_3]_2$	22	30	55·85	3·7	—	11·4	55·8	3·2	—	11·6

Octacarbonylbistriphenylphosphinedimanganese(0). Decacarbonyldimanganese (0·3 g.) and triphenylphosphine (0·4 g.) were heated in an evacuated tube at 120—130° for 4 hr. The *product* (0·4 g.) was crystallised from benzene–light petroleum and dried *in vacuo* (Found: C, 61·6; H, 3·6; Mn, 12·6; P, 7·2%; *M*, 826. $C_{44}H_{30}Mn_2O_8P_2$ requires C, 61·55; H, 3·5; Mn, 12·8; P, 7·2%; *M*, 858). Other physical properties were identical with those of the same compound prepared by the photochemical method.

Di-μ-diphenylarsino-octacarbonyldimanganese(I). Decacarbonyldimanganese (0·3 g.) and triphenylarsine (0·48 g.) were treated as above at 140° for 5 hr. The *product* (0·1 g.) was washed with benzene (2 × 5 ml.) and light petroleum (10 ml.) and dried *in vacuo* (Found: C, 48·4; H, 2·6; As, 18·1. $C_{32}H_{20}As_2Mn_2O_8$ requires C, 48·5; H, 2·5; As, 18·9%), $\nu_{max.}$ (in CCl_4) 2020, 1990, and 1960 cm.$^{-1}$ (cf. ref. 3).

Bromotetracarbonyltriphenylphosphinemanganese(I). To a suspension of the complex $[Mn(CO)_4PPh_3]_2$ (0·2 g.) in carbon tetrachloride (25 ml.) was added dropwise bromine (0·04 g.) in the same solvent (10 ml.). After gentle shaking, the red solution was filtered and concentrated to 20 ml. Addition of light petroleum (10 ml.) precipitated the orange *product* (0·14 g.) which was washed with light petroleum (10 ml.) and dried *in vacuo* (Found: C, 51·9; H, 3·1; P, 6·1%; *M*, 490. $C_{22}H_{15}BrMnO_4$ requires C, 51·9; H, 2·95; P, 6·1%; *M*, 509), $\nu_{max.}$ (in $CHCl_3$) 2090, 2040, and 1965 cm.$^{-1}$ (cf. Angelici *et al.*[6]).

Infrared Spectra.—These were kindly determined by Dr. G. W. Gray and Miss J. Sales (University of Hull), using a Unicam S.P. 100 spectrometer.

Molecular Weights.—These were determined in benzene in a Meckrolab vapour-pressure osmometer, model 301A.

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