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NEW DIPHOSPHINE-SUBSTITUTED CARBONYL COMPLEXES OF MANGANESE

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SUMMARY

Treatment of $Mn_2(CO)_{10}$ with the diphosphines $Ph_2P(CH_2)_2PPh_2$ (DPE) and $Ph_2PCH_2PPh_2$ (DPM) has given, in addition to the known products $Mn(CO)_3(DPE)$ and $Mn(CO)(DPE)_2$, a dimeric species containing a single diphosphine bridge and complexes of stoichiometry $[Mn(CO)_3L_2]_2$, (L_2 = DPE or DPM). Evidence has been obtained for the possible existence of a second conformer of $Mn(CO)(DPE)_2$. With $Mn(CO)_5Br$, up to four carbonyl groups have been replaced to give the unusually highly substituted compounds $Mn(CO)(L_2)_2Br$, (L_2 = DPE or DPM). These results are interpreted in terms of the steric and chelating properties of the diphosphine ligands.

INTRODUCTION

Few reactions of $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$ with the chelating diphosphine $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$, (DPE), have been reported. Hieber and Freyer[1] treated $Mn_2(CO)_{10}$ with an excess of DPE in refluxing xylene to give $Mn_2(CO)_8(DPE)$, which was characterised only from analytical data, and no structural information was given. In a more thorough survey, Sacco[2] obtained a number of products by treating $Mn_2(CO)_{10}$ with DPE under varying reaction conditions. For example, a paramagnetic monomer $Mn(CO)(DPE)_2$ was formed with $Mn_2(CO)_{10}$ and an excess of DPE after extended refluxing in dioxane, whereas the disproportionation product $[Mn(CO)_2(DPE)_2][Mn(CO)_5]$ was obtained with dimethoxyethane as solvent. Using this solvent, a second paramagnetic monomer $Mn(CO)_3(DPE)$ was isolated with a DPE/Mn ratio of 1/1.

The direct reaction of $Mn(CO)_5Br$ with DPE at 150° was reported[3] to give the complex $Mn(CO)_3(DPE)Br$. When this reaction was performed in refluxing methanol the cation $[Mn(CO)_2(DPE)_2]^+$ was formed[4]. A highly substituted, related compound formulated as $(CF_3CO_2)Mn(CO)[(CH_3)_2P(CH_2)_2P(CH_3)_2]_2$ was obtained by reacting $(CF_3CO_2)Mn(CO)_5$ with $(CH_3)_2P(CH_2)_2P(CH_3)_2$ in hexane under UV irradiation[5]. By contrast, the corresponding rhenium carbonyl and rhenium car-

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bonyl bromide complexes react with DPE to form, in addition to the analogous manganese compounds already mentioned, the further substituted products *cis*-$[Re(CO)_3(DPE)]_2$, $Re(CO)_2(DPE)_2$ and $Re(CO)(DPE)_2Br$[6,7].

We have reinvestigated the reactions of $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$ with DPE together with the related diphosphine $(C_6H_5)_2PCH_2P(C_6H_5)_2$, (DPM), and the results of this study are reported here.

RESULTS AND DISCUSSION

Reactions of $Mn_2(CO)_{10}$

The reactions of $Mn_2(CO)_{10}$ have given both monomeric and dimeric products although monomeric products could be isolated only for DPE. Both thermal and UV methods of preparation were used with UV irradiation proving to be the less successful and resulting in a large percentage of decomposition products. Whereas heating has given both monomeric and dimeric species, UV irradiation has produced only monomeric complexes. This is in contrast to the reactions of $Mn_2(CO)_{10}$ with $P(C_6H_5)_3$ which were reported to give monomeric products under thermal excitation[8] and dimeric products with UV irradiation[9].

The known compound $Mn(CO)_3(DPE)$[2], has been obtained from $Mn_2(CO)_{10}$ with a stoichiometric amount of ligand in benzene solution, using both thermal or UV excitation and has been confirmed by infrared spectroscopy (see Table 1).

TABLE 1

IR DATA

Compound	*Carbonyl stretching frequencies* $(cm^{-1})^a$
$Mn(CO)_3(DPE)$	1998 s, 1918 s(br)
$Mn(CO)(DPE)_2$ (yellow)	1818 (br), [1820^b]
$Mn(CO)(DPE)_2$ (red)	1822 (br), [1800^b]
$Mn_2(CO)_8(DPM)$	2057 s, 1999 vs, 1977 vs, 1966 (sh), 1954 (sh), 1924 s
$Mn_2(CO)_8(DPM)Br_2$	2094 s, 2021 (sh), 2012 vs, 1970 s^c
$[Mn(CO)_3(DPM)]_2$	1994 w, 1918 s, 1870 m^c
$[Mn(CO)_3(DPE)]_2$	1992 w, 1899 s, 1859 m^c
fac-$Mn(CO)_3(DPM)Br$	2025 s, 1955 m, 1920 s
fac-$Mn(CO)_3(DPE)Br$	2023 s, 1956 m, 1917 m
$Mn(CO)(DPM)_2Br$	1842 (br)
$Mn(CO)(DPE)_2Br$	1821 (br)

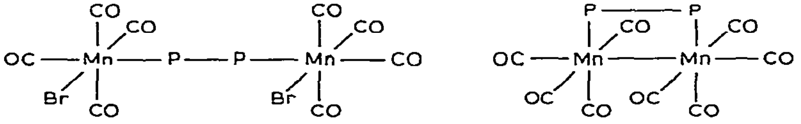
[a] In benzene solution unless otherwise stated.
[b] In nujol.
[c] In dichloromethane solution.

Treatment of $Mn_2(CO)_{10}$ with an excess of DPE in benzene using UV irradiation gave a yellow compound with a carbonyl stretching frequency of 1820 cm^{-1} in nujol and which melted at 178–180°. This compound thus closely resembles the complex of the same stoichiometry first reported by Sacco[2] [m.p. 173–174°; $\nu(CO)$ (nujol) 1800 cm^{-1}]. When the reaction of $Mn_2(CO)_{10}$ with an excess of DPE was performed in refluxing xylene however, a monomeric compound of identical stoichiometry to

Sacco's complex was obtained but which was red in colour and melted at 217–220°. This second complex exhibited a single carbonyl stretching frequency at 1800 cm^{-1} in nujol. However, in benzene solution, both red and yellow forms of $Mn(CO)(DPE)_2$ gave a similar broad $\nu(CO)$ band (1822 and 1818 cm^{-1}, respectively). Because of the similarity of the solution infrared spectra of these two forms of $Mn(CO)(DPE)_2$ and in the absence of spectroscopic evidence of a hydride, we have discounted the red form as being $HMn(CO)(DPE)_2$. It is possible that the red complex represents another conformer of $Mn(CO)(DPE)_2$ or that these variations are due to differences in crystal packing. Effects of crystal packing have recently been proposed to account for the two crystalline forms of the complex $\{Ir(CO)_2[P(CH_3)_2(C_6H_5)]_3\}ClO_4$[10].

Reaction of $Mn_2(CO)_{10}$ with one mole of DPM per dimer in refluxing benzene gave a compound of stoichiometry $Mn_2(CO)_8(DPM)$. Treatment of this complex with one mole of bromine in carbon tetrachloride solution at 0° gave a single bromination product identified by analytical and molecular weight data as the dimeric complex $Mn_2(CO)_8(DPM)Br_2$. Bromination of manganese dimers with stoichiometric amounts of bromine has been shown to occur with fission of the metal–metal bond to give monomeric products containing one bromide ligand per manganese atom. This bromination of $Mn_2(CO)_8(DPM)$ to give $Mn_2(CO)_8(DPM)Br_2$ indicates that in both complexes the diphosphine ligand bridges the two metal atoms. A number of complexes containing diphosphine ligands bridging two metal atoms have been reported previously[11].

The infrared spectrum of $Mn_2(CO)_8(DPM)Br_2$ contains four carbonyl stretching frequencies, consistent with C_s symmetry $(3A'+A'')$, indicating that no isomerisation has occurred on bromination and that the product has a stereochemistry similar to the *cis*-$[Mn(CO)_4LBr]$ species [see (I) in Fig. 1]. The proposed structure of $Mn_2(CO)_8(DPM)$ [see (II) in Fig. 1] possesses C_{2v} symmetry for which seven infrared active modes of vibration $(3A_1+B_1+3B_2)$ are predicted. Six of these expected bands are observed with the seventh probably being obscured.



(I) (II)

Fig. 1. Proposed structures for $Mn_2(CO)_8(DPM)Br_2$ and $Mn_2(CO)_8(DPM)$ (P–P represents DPM).

Treatment of $Mn_2(CO)_{10}$ with an excess of DPE or DPM, (L_2), in refluxing benzene for extended periods has given the yellow complexes $[Mn(CO)_3L_2]_2$, analogous to the known compounds $[Mn(CO)_3(Diars)]_2$[18] [Diars = *o*-phenylenebis(dimethylarsine)] and $[Re(CO)_3(DPE)]_2$. The infrared spectra of $[Mn(CO)_3(DPE)]_2$ and $[Mn(CO)_3(DPM)]_2$ are identical in the carbonyl region, both containing three bands. This spectral pattern is consistent with three possible structures for the $[Mn(CO)_3L_2]_2$ species [see (I)–(III), Fig. 2], of either C_{2h} or D_{2h} symmetry.

Bromination of $[Mn(CO)_3L_2]_2$ at 0° gave exclusively the monomeric compounds *fac*-$Mn(CO)_3L_2Br$, identical with those described later as prepared from $Mn(CO)_5Br$ and L_2. This implies a symmetrical substitution pattern for $[Mn(CO)_3L_2]_2$ with one diphosphine ligand bonded to each metal atom, *i.e.* (I) and (II) in Fig. 2.

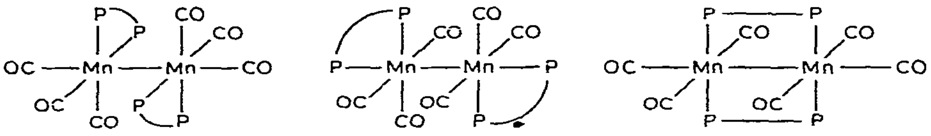

(I) (C_{2h}) (II) (C_{2h}) (III) (D_{2h})

Fig. 2. Possible structures and symmetries of $[Mn(CO)_3L_2]_2$, (P–P = L_2 = DPE or DPM).

We have discounted (III) (Fig. 2) as a possibility as brominations under the conditions used above have not caused fission of the diphosphine bridge in the related $Mn_2(CO)_8$-(DPM) complex, indicating that this bridge is not easily ruptured.

Reactions of $[Mn(CO)_5Br]$

These reactions were performed most conveniently in benzene solution using UV irradiation with varying amounts of the diphosphine ligands DPE and DPM (L_2).

The known compounds $Mn(CO)_3L_2Br$ were prepared with stoichiometric amounts of L_2 and shown to be of identical stereochemistry by infrared spectroscopy. Spectra of $Mn(CO)_3L_2Br$ exhibit three strong carbonyl bands which correspond to C_s symmetry ($2A'+A''$) implying that the *fac*-isomer is formed [see (I) in Fig. 3]. Our solution spectrum of $Mn(CO)_3(DPE)Br$ [ν(CO) 2023 s, 1956 m, 1917 m cm^{-1}] does not agree with the solution spectrum reported previously for this compound [ν(CO) reported 2030 s, 1968 s, 1958 s, 1920 s cm^{-1}][3], although they appear to be very similar in all other respects.

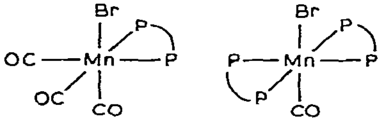

(I) (II)

Fig. 3. Proposed structures for *fac*-$Mn(CO)_3L_2Br$ and $Mn(CO)(L_2)_2Br$, (P–P = L_2 = DPE or DPM).

$Mn(CO)_5Br$ reacts with an excess of L_2 to give the monocarbonyl complexes $Mn(CO)(L_2)_2Br$ in high yield. Substitution of four carbonyl groups in $Mn(CO)_5Br$ has previously been reported only for the monodentate phosphite ligand $P(OCH_3)_3$[12] although four CO's have been replaced in $Mn(CO)_5CN$[13] and $(CF_3CO_2)Mn(CO)_5$ [5] with the quadridentate tris[*o*-(diphenylphosphino)phenyl]phosphine and the bidentate $(CH_3)_2P(CH_2)_2P(CH_3)_2$ ligands respectively.

Models of $Mn(CO)(L_2)_2Br$, (L_2 = DPE or DPM), show that the least restricted structure for these complexes is one with a *trans*-configuration of the L_2 ligands [see (II) in Fig. 3]. Such a structure is supported by the extreme resistance to substitution shown by the carbonyl group *trans* to the bromide ligand in $Mn(CO)_5Br$. Recent molecular orbital calculations[14] on a series of compounds $Mn(CO)_5X$, (X = halogen or hydride), have further demonstrated quantitatively that a stronger metal–carbon π-bond exists for the CO *trans* to X than for the *cis* CO groups.

The inertness to substitution by manganese carbonyl compounds has been attributed to the decrease in lability of the remaining CO's on successive substitutions by weaker π-bonding ligands. Thus the formation of $Mn(CO)_2[P(OCH_3)_3]_3Br$ and $Mn(CO)[P(OCH_3)_3]_4Br$ was ascribed to the "carbonyl-like" π-acceptor properties of the $P(OCH_3)_3$ ligand[12]. However, this work with nucleophilic diphosphines, together with recent reactions with $P(CH_3)_2C_6H_5$[15] have shown that higher substitutions of $Mn(CO)_5Br$ readily occur under relatively mild conditions, although none of these ligands can be considered to be powerful π-acceptors.

Recently, Tolman[16] proposed that steric and chelation factors play a dominant role in phosphine substitutions of nickel carbonyl and nickel phosphine complexes. From his exchange reactions, Tolman found the subsitution properties of $(CH_3)_2P(CH_2)_2P(CH_3)_2$ close to those of $P(OCH_3)_3$ and attributed this to the chelation effect. It seems that the chelation effect is also responsible for the similarity in substitution properties of the more bulky ligands DPE and DPM with $P(OCH_3)_3$, since all three form the highly substituted monocarbonyl species $Mn(CO)(L_2)_2Br$. For these diphosphine ligands, the stability of this species can be attributed to a lowering of the steric requirements of the ligands by "meshing"[16] of the bonded phenyl rings.

EXPERIMENTAL

All reactions were carried out under nitrogen. $Mn_2(CO)_{10}$ and the diphosphines DPE and DPM were obtained commercially and were not further purified. $Mn(CO)_5Br$ was prepared by the method of Abel and Wilkinson[17]. Melting points were recorded on a Kofler hot stage melting point apparatus. Molecular weights were measured using a Mechrolab vapour pressure osmometer at 37°. Elemental analyses were performed by Mr. G. J. Roberts of this laboratory. Infrared spectra were recorded using a Perkin–Elmer Model 457 grating infrared spectrophotometer.

Mn(CO)₃(DPE)

A solution of $Mn_2(CO)_{10}$ (1.0 g, 2.56 mmoles) and DPE (1.0 g, 2.46 mmoles) in benzene (175 ml) was irradiated for 3 h. Evaporation of the solvent under vacuum gave a red oil which, on dissolving in a minimum quantity of benzene and precipitating with petroleum ether (b.p. 60–80°), gave the complex as yellow microcrystals. These were identified from the melting point and infrared spectrum. M.p. 136–139°, $\nu(CO)$ in benzene: 1998 s, 1918 s cm^{-1}. [Reported for $Mn(CO)_3(DPE)$: m.p. 127–128°, $\nu(CO)$ in chloroform: 2000, 1915 cm^{-1}.]

Mn(CO)(DPE)₂

(*a*). A solution of $Mn_2(CO)_{10}$ (2.0 g, 5.12 mmoles) and DPE (10.0 g, 25.12 mmoles) in benzene (175 ml) was irradiated for 2 h and the resultant crimson solution concentrated under vacuum to a red oil. Recrystallisation from petroleum ether (b.p. 80–100°) gave, after cooling for one week, the required compound as yellow microcrystalline clusters of analytical purity. M.p. 178–180°. Yield: 0.44 g, 10%. (Found: C, 72.20; H, 5.72. $C_{53}H_{48}OP_4Mn$ calcd.: C, 72. 36; H, 5.50%.)

(*b*). $Mn_2(CO)_{10}$ (2.0 g, 5.12 mmoles) and DPE (10.0 g, 25.12 mmoles) were refluxed in xylene (50 ml) for 24 h. The solution was filtered while hot, and concentrated under vacuum to a red oil. Petroleum ether (b.p. 40–60°) was added and after one week at 0°, red microcrystalline clusters were deposited from the solution. Recrystallisation resulted only in decomposition of the product formed. M.p. 217–220°. Yield: 0.07 g, 2%. (Found: C, 71.45; H, 5.26%; mol.wt. in chloroform, 855. $C_{53}H_{48}OP_4Mn$ calcd.: mol.wt., 880.) A large quantity of $Mn(CO)_3(DPE)$ was formed as the major portion of this preparation.

$Mn_2(CO)_8(DPM)$

$Mn_2(CO)_{10}$ (1.0 g, 2.57 mmoles) was refluxed in benzene (25 ml) with DPM (0.98 g, 2.56 mmoles) for 8 h. The resultant deep red solution was concentrated and kept at 0° for 2 days, yielding large yellow prisms which were of analytical purity. M.p. 196–198°. Yield 0.62 g, 33%. (Found: C, 55.23; H, 3.15; mol.wt. in chloroform, 734. $C_{33}H_{22}O_8P_2Mn_2$ calcd.: C, 55.15; H, 3.06%; mol.wt., 718.)

$Mn_2(CO)_8(DPM)Br_2$

$Mn_2(CO)_8(DPM)$ (1.3 g, 1.82 mmoles) was dissolved in carbon tetrachloride (50 ml) and cooled to 0°. A solution of bromine (0.44 g, 2.75 mmoles) in CCl_4 (5 ml) was then added dropwise with stirring. After standing at 0° for 1 h the mixture was evaporated to dryness under reduced pressure and the yellow solid obtained was recrystallised from dichloromethane/pentane to give light orange prisms of the required product. M.p. 133°. Yield: 1.35 g, 83%. (Found: C, 45.14; H, 2.50; Br, 18.50; mol.wt. in chloroform, 820. $C_{33}H_{22}Br_2O_8P_2Mn_2$ calcd.: C, 45.10; H, 2.51; Br, 18.22%; mol.-wt., 878.)

$[Mn(CO)_3(DPM)]_2$

$Mn_2(CO)_{10}$ (1.0 g, 2.56 mmoles) was refluxed in benzene (25 ml) with DPM (2.0 g, 5.20 mmoles) for 24 h. The resultant solution was concentrated and left to stand at 0° for 4 days. Large red crystals appeared which gave air-sensitive, yellow prisms of analytical purity on washing with petroleum ether (b.p. 40–60°). M.p. 216–218°. Yield: 0.48 g, 18%. (Found: C, 64.53; H, 4.29; mol.wt. in chloroform, 1078. $C_{56}H_{44}O_6P_4Mn_2$ calcd.: C, 64.24; H, 4.20%; mol.wt., 1046.)

$[Mn(CO)_3(DPE)]_2$

This compound was prepared similarly to $[Mn(CO)_3(DPM)]_2$ by treating $Mn_2(CO)_{10}$ (1.0 g, 2.57 mmoles) with DPE (2.0 g, 5.20 mmoles) in refluxing benzene (25 ml) for 5 h. Air-sensitive, yellow prisms crystallised out of the reaction mixture and were washed with petroleum ether (b.p. 40–60°). M.p. 183°. Yield: 0.83 g, 30%. (Found: C, 64.63; H, 4.61. $C_{58}H_{48}O_6P_4Mn_2$ calcd.: C, 64.80; H, 4.47%.)

fac-$Mn(CO)_3(DPM)Br$

$Mn(CO)_5Br$ (0.80 g, 2.91 mmoles) was completely dissolved in warm benzene (175 ml). DPM (1.0 g, 2.61 mmoles) was added before irradiating for 12 min. The resultant yellow solution was evaporated to dryness under vacuum and the residue recrystallised from warm methanol to give light yellow microcrystals. M.p. 174–177°. Yield: 1.35 g, 77%. (Found: C, 55.46; H, 3.73; Br, 13.01. $C_{28}H_{22}O_3P_2BrMn$ calcd.: C, 55.74; H, 3.67; Br, 13.24%.)

fac-$Mn(CO)_3(DPE)Br$

This compound was prepared by an analogous procedure to that for *fac*-$Mn(CO)_3(DPM)Br$, from $Mn(CO)_5Br$ (0.80 g, 2.91 mmoles) and DPE (1.04 g, 2.62 mmoles). Recrystallisation from methanol/water gave the product as yellow microcrystals. M.p. 183–185°. Yield: 1.51 g, 84%. (Found: C, 56.73; H, 3.90; Br, 12.95. $C_{29}H_{24}O_3P_2BrMn$ calcd.: C, 56.42; H, 3.92; Br, 12.94%.)

$Mn(CO)(DPM)_2Br$

$Mn(CO)_5Br$ (0.80 g, 2.91 mmoles) and DPM (2.68 g, 6.97 mmoles) were irradiated in benzene solution for 45 min. The deep red solution formed was evaporated to dryness under vacuum and the residue recrystallised from benzene/ethanol to give orange microcrystals. M.p. 150°. Yield: 1.71 g, 63%. (Found: C, 64.58; H, 4.84; Br, 8.77. $C_{51}H_{44}OP_4BrMn$ calcd.: C, 65.74; H, 4.76; Br, 8.57%.)

$Mn(CO)(DPE)_2Br$

This compound was prepared in a similar manner as the DPM analogue by irradiating $Mn(CO)_5Br$ (0.80 g, 2.91 mmoles) with DPE (2.78 g, 6.98 mmoles) in benzene solution for 30 min. Recrystallisation from benzene/ethanol gave orange microcrystals. M.p. 161–164°. Yield: 1.69 g, 61%. (Found: C, 65.42; H, 5.30; Br, 7.99. $C_{53}H_{48}OP_4BrMn$ calcd.: C, 66.33; H, 5.04; Br, 8.32%.)

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