Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF METAL CARBONYL COMPLEXES

I*. HALODICARBONYL COMPLEXES OF MANGANESE(I)

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(Received March 17th, 1972)

SUMMARY

The halopentacarbonylmanganese(I) complexes, $Mn(CO)_5X$ (X = Cl, Br, I), react with trialkyl phosphites, L [X = Cl, L = $P(OMe)_3$; X = Br, L = $P(OMe)_3$, $P(OEt)_3$, $P(OCH_2CH_2Cl)_3$, $P(OCH_2CH{=}CH_2)_3$], $PPh(CH_2CH_2PPh_2)_2$ (Triphos), and PMe_2Ph to produce the halodicarbonyl complexes, $Mn(CO)_2L_3X$, $Mn(CO)_2$(Triphos)X, and $Mn(CO)_2(PMe_2Ph)_3Br$. The $Mn(CO)_2L_3X$ complexes react with $Ph_2PCH_2CH_2PPh_2$ (Diphos) and Triphos to give the mixed ligand complexes, $Mn(CO)_2$L(Diphos)X and $Mn(CO)_2$L(Triphos)X. The Triphos ligand is only coordinated to the manganese atom through two of its three phosphorus atoms in the Triphos complexes. Some of the Diphos complexes can also be prepared by the reaction of *fac*-$Mn(CO)_3$(Diphos)Br with L. The halotricarbonyl complexes, *mer*-{*trans*-$[P(OPh)_3]_2$}$Mn(CO)_3X$ (X = Cl, Br), react with a variety of bidentate ligands, A–A [X = Cl, A–A = Diphos; X = Br, A–A = Diphos, $Ph_2AsCH_2CH_2AsPh_2$ (Diarsine), etc.] to form the mixed ligand halodicarbonyl complexes, $Mn(CO)_2[P(OPh)_2]$(A–A)X, and small amounts of *fac*-$Mn(CO)_3$(A–A)X.

The structures proposed for the new complexes are discussed on the basis of their IR spectra and molar conductances.

INTRODUCTION

Extensive studies of the CO substitution reactions of the halopentacarbonylmanganese(I) complexes, $Mn(CO)_5X$ (X = Cl, Br, I), with a wide variety of ligands, L, have been carried out in recent years[1]. The results of these investigations can be summarized by the following stepwise reaction sequence:

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[*] Taken in part from the Ph.D. thesis of H.K.S., McGill University, 1970; presented in part at the 54th. National Meeting of the Chemical Institute of Canada, Halifax, Nova Scotia (Canada), May 1971.

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$$\mathrm{Mn(CO)_5X} \xrightarrow{\mathrm{L}} \textit{cis}\text{-}\mathrm{Mn(CO)_4LX} \xrightarrow{\mathrm{L}} \textit{fac}\text{- and/or } \textit{trans}\text{-}\mathrm{Mn(CO)_3L_2X}^{*}$$

Attempts to substitute more than two CO groups by ligands such as triphenylphosphine and pyridine have all failed, even at elevated temperatures. This has been explained on the basis of a π-bonding argument, *viz.*, the first two CO groups are replaced by ligands which are not as good π-acceptors as CO and this leads to a strengthening of the three remaining Mn–CO bonds such that no further substitution can take place[2]. This explanation is supported by the fact that phenyl isocyanide, a ligand which is considered to be a better π-acceptor than CO, replaces all five CO groups in $Mn(CO)_5Br$[3].

There is also some evidence which suggests that the substitution process is usually arrested at the $Mn(CO)_3L_2X$ stage because of the inability of the manganese atom to accommodate more than two bulky L groups in its coordination sphere. For instance, the *fac*-$Mn(CO)_3L_2Br$ [$L = P(OPh)_3$, $P(OBu)_3$, PBu_3, PCl_2Ph] complexes readily isomerize to the less sterically crowded *trans* isomers[4], while the presence of the larger rhenium atom in the analogous $Re(CO)_3L_2X$ complexes apparently obviates the need for isomerization as only the *fac* isomers (with the exception of $L = PPh_3$) are formed[5].

On the basis of infrared studies on substituted metal carbonyl complexes, tertiary phosphites are believed to be as good as if not better π-acceptors than CO[6]. Moreover, tertiary phosphites such as trimethylphosphite, $P(OMe)_3$, triethyl phosphite, $P(OEt)_3$, and triallyl phosphite, $P(OCH_2CH{=}CH_2)_3$, are not as bulky as any of the ligands whose reactions with $Mn(CO)_5X$ have been investigated to date. In view of this, we decided to undertake a study of reactions of this type of trialkyl phosphite with the $Mn(CO)_5X$ complexes to see whether or not more than two CO groups could be replaced by these ligands.

We report here the results of our investigation in which we found that trialkyl phosphite complexes of the general formula $Mn(CO)_2L_3X$ can be easily prepared**. These halodicarbonyl complexes and the related tricarbonyl complexes, *trans*-$Mn(CO)_3[P(OPh)_3]_2X$ ($X = Cl$, Br), react with bidentate chelating ligands, A–A, such as 1,2-bis(diphenylphosphino)ethane (Diphos) to produce the "mixed ligand" complexes, $Mn(CO)_2L(A{-}A)X$. The Diphos-containing mixed ligand complexes may also be prepared by reaction of *fac*-$Mn(CO)_3(Diphos)X$ with L. The new mixed-ligand halodicarbonyl complexes are of particular interest as they are the first ex-

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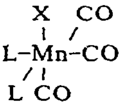
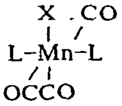
* The structures of these complexes according to this nomenclature system are:


facial


meridional *trans*-L_2

Throughout this paper, the *mer*-(*trans*-L_2)$Mn(CO)_3X$ complexes will be referred to as the *trans*-$Mn(CO)_3L_2X$ complexes.

** While this work was in progress, the preparation of $Mn(CO)_2[P(OMe)_3]_3Br$ from the reaction of $Mn(CO)_5Br$ with $P(OMe)_3$ in refluxing benzene was reported in a preliminary communication[7]. However, as full preparative details were not given and as we have made a somewhat more complete study of its physical properties, we have included our data for this complex in this paper.

amples of octahedral carbonyl complexes of a Group VIIB metal that contain three different non-carbonyl ligands. Prior to this study, such complexes were restricted to Group VIII metals such as iridium[8].

We have also studied the reactions of dimethylphenylphosphine, PMe_2Ph, and the potentially tridentate ligand bis[2-(diphenylphosphino)ethyl]phenylphosphine, $PPh(CH_2CH_2PPh_2)_2$, with the $Mn(CO)_5X$ complexes and some of their derivatives. Since these reactions also afford halodicarbonyl complexes, we have included the results of these studies here.

EXPERIMENTAL

Preparation and purification of materials

Chemicals were obtained from the following sources: dimanganese decacarbonyl (Alfa Inorganics, Inc.); trimethyl phosphite, triethyl phosphite, tris(1-chloroethyl) phosphite, triallyl phosphite, 1,2-bis(diphenylphosphino)ethane (Diphos), 1,2-bis(diphenylarsino)ethane (Diarsine), and *o*-phenylenebis(dimethylarsine) (Diars) (Aldrich Chemical Co.); bis[2-(diphenylphosphino)ethyl]phenylphosphine (Triphos) (Strem Chemical Co.); 2,2'-bipyridine (Bipy) (Fischer Chemical Co.).

The ligands were used without further purification. Reagent-grade solvents were dried over calcium hydride and were distilled under nitrogen before use.

The literature methods were used to prepare and purify $Mn(CO)_5X$ ($X=Cl$, Br[9]; $X=I$[10]), *trans*-$Mn(CO)_3[P(OPh)_3]_2X$ ($X=Cl$, Br)[11], and *fac*-$Mn(CO)_3$(Diphos)Br[12].

Physical measurements

The IR spectra were obtained with a Perkin–Elmer 337 grating spectrophotometer coupled to a Texas Instruments Servo/Riter model II expanded scale recorder. The spectra were calibrated against the 2143.2 cm^{-1} band of CO and the 1601.4 and 1583.1 cm^{-1} bands of polystyrene; the frequencies are precise to ± 1–$2\ cm^{-1}$.

Conductivity measurements were carried out on an Industrial Instruments RC 16B2 conductivity bridge for approximately 1×10^{-3} *M* nitromethane solutions at 22°.

The decomposition points were determined in capillaries on a Gallenkamp melting point apparatus and are uncorrected.

The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory Inc., Woodside, New York, U.S.A. The molecular weight determinations were carried out by vapour pressure osmometry in $CHCl_3$ solution by Mikronanalytisches Laboratorium Beller, Göttingen, Germany.

Preparation of the halodicarbonyl complexes

All the reactions described below were performed under an atmosphere of nitrogen. The reactions were monitored by following changes in the C–O stretching region of the IR spectra of the reaction mixtures and were terminated when no further changes could be detected. The reaction times, analytical data, and molar conductivities for some of halodicarbonyl complexes are given in Table 1. The C–O stretching frequencies for all the complexes are given in Table 2. All the complexes are readily soluble in polar solvents.

TABLE 1

HALODICARBONYL COMPLEXES OF MANGANESE(I)

Complex	*Prep. meth.*	*Reaction time (h)*	*Yield (%)*	*Colour*	*Decomp. (°C)*	*Analysis found (calcd.) (%)*				*Λ_m ($cm^{-1} \cdot \Omega^{-1} \cdot M^{-1}$)*
						C	*H*	*P*	*X*	
$Mn(CO)_2[P(OMe)_3]_3Cl$	I	8	69	Bright-yellow	143–145	25.6 (25.5)	4.9 (5.3)	15.9 (17.9)	7.6 (6.8)	
$Mn(CO)_2[P(OMe)_3]_3Br^a$	I	25	72	Orange	143–145	23.6 (23.5)	4.5 (4.8)	14.6 (16.5)	15.5 (14.2)	0.48
$Mn(CO)_2[P(OCH_2CH_2Cl)_3]_3Br^b$	I	23	70	Orange	Oil	25.1 (24.0)	3.6 (3.6)			3.9
$Mn(CO)_2[P(OCH_2CH{=}CH_2)_3]_3Br$	I	23	70	Orange	Oil	44.0 (43.7)	6.1 (5.7)	11.5 (11.7)	10.1 (10.0)	
$Mn(CO)_2(Triphos)Cl$	II	3	25	Lemon-yellow	226–228	62.9 (63.5)	5.0 (4.9)	11.9 (13.6)	7.6 (5.2)	0.37
$Mn(CO)_2(Triphos)Br^c$	II	1	50	Yellow	220–222	58.4 (59.6)	4.5 (4.6)	12.8 (12.5)		1.1
$Mn(CO)_2(Triphos)I$	II	5	40	Orange	224–226	55.4 (56.0)	4.2 (4.3)		15.8 (16.4)	5.6
$Mn(CO)_2[P(OMe)_3](Diphos)Cl \cdot CHCl_3$	IIIB	5	60	Yellow	180–182	49.0 (48.8)	4.4 (4.3)	11.8 (11.7)	17.4 (18.0)	1.1
$Mn(CO)_2[P(OMe)_3](Diphos)Br \cdot \frac{1}{2} CHCl_3{}^d$	IIIB	9	32	Orange	85–90	48.6 (48.9)	4.4 (4.3)	12.0 (10.6)		
$Mn(CO)_2[P(OMe)_3](Diphos)Br$	IIIC	4	32	Yellow	83–88	50.9 (52.2)	4.8 (4.7)			
$Mn(CO)_2[P(OMe)_3](Triphos)Br$	IIIB	6	40	Yellow	80–85	53.7 (55.1)	4.9 (5.0)	14.5 (14.6)		
$Mn(CO)_2[P(OEt)_3](Triphos)Br \cdot \frac{1}{2} CHCl_3$	IIIB	8	52	Yellow	52–56	53.9 (53.8)	5.6 (5.1)	13.1 (13.1)		

$Mn(CO)_2[P(OPh)_3](Diphos)Br^{e,f}$	IIIA	2	24	Yellow	153–157	61.4	4.7	9.9	9.1	3.9
						(61.4)	(4.4)	(10.3)	(8.9)	
$Mn(CO)_2[P(OPh)_3](Diars)Br^{g}$	IIIA	2	16	Yellow	158–162	46.1	4.0		10.9	1.4
						(45.8)	(4.0)		(10.2)	
$Mn(CO)_2[P(OCH_2CH_2Cl)_3](Triphos)Br$	IIIB	8	65	Yellow	58–63	51.7	4.6			
						(50.7)	(4.6)			
$Mn(CO)_2(PMe_2Ph)(Diphos)Br$	IIIC	24	30	Yellow	≈85	60.3	5.2	12.3		2.5
						(59.4)	(4.9)	(12.8)		

[a] The mass spectrum of this complex recorded on an A.E.I. MS902 mass spectrometer at 70 eV does not exhibit a peak corresponding to the parent molecular ion. The spectrum is complex and the majority of the peaks are associated with fragments of the $P(OMe)_3$ ligands attached to Mn, Mn(CO), or $Mn(CO)_2$, *e.g.*, $Mn[P(OMe)_3][P(OMe)OH]_2^+$ (*m/e* 337) and $Mn(CO)[P(OMe)_2H]_2^+$ (*m/e* 271). For further details on the mass spectrum of $P(OMe)_3$ see ref. 21. [b] The C and H analyses for these complexes were performed in our laboratory on a Hewlett-Packard Model 185 CHN analyser. [c] While this manuscript was in preparation, the preparation of this complex from $Mn(CO)_5Br$ and Triphos in refluxing benzene for 41 h and some of its physical properties were reported[13]. However, no structure was proposed for the complex. [d] Mol.wt.: Found (calcd.) 725 (713); λ_{max} ($CHCl_3$), 395 nm. [e] Mn (%): Found (calcd.) 6.5 (6.1); Mol.wt.: Found (calcd.) 917 (900). [f] This complex was also prepared by method (IIIC) and was identified by its IR spectrum in the C–O stretching region. [g] As (%): Found (calcd.) 18.8 (19.0); Mol.wt.: Found (calcd.) 778 (787).

TABLE 2

IR SPECTRA IN THE C–O STRETCHING REGION OF THE NEW HALODICARBONYLMANGANESE(I) COMPLEXES (CH_2Cl_2 SOLUTION)

Complex	*ν(CO) (cm^{-1})*[a]		
$Mn(CO)_2[P(OMe)_3]_3Cl$[b,c]	1979	1892	
$Mn(CO)_2[P(OMe)_3]_3Br$[d,e]	1977	1893	
$Mn(CO)_2[P(OEt)_3]_3Br$[f]	1966	1883	
$Mn(CO)_2[P(OCH_2CH_2Cl)_3]_3Br$[g]	1977	1901	
$Mn(CO)_2[P(OCH_2CH{=}CH_2)_3]_3Br$	1974	1892	
$Mn(CO)_2(PMe_2Ph)_3Br$[f,h]	1926	1848	
$Mn(CO)_2(Triphos)Cl$	1934	1861	
$Mn(CO)_2(Triphos)Br$[i,j]	1935	1865	
$Mn(CO)_2(Triphos)I$[k]	1936	1869	
$Mn(CO)_2[P(OMe)_3](Diphos)Cl$[l]	1947	1870	
$Mn(CO)_2[P(OMe)_3](Diphos)Br$[m]	1947	1874	
$Mn(CO)_2[P(OMe)_3](Triphos)Cl$[b,f]	1950	1872	
$Mn(CO)_2[P(OMe)_3](Triphos)Br$[n]	1945	1871	
$Mn(CO)_2[P(OEt)_3](Triphos)Br$[o]	1943	1869	
$Mn(CO)_2[P(OCH_2CH_2Cl)_3](Triphos)Br$[p]	1947	1874	
$Mn(CO)_2[P(OCH_2CH{=}CH_2)_3](Diphos)Br$[f]	1951	1877	
$Mn(CO)_2[P(OCH_2CH{=}CH_2)_3](Triphos)Br$[f]	1949	1875	
$Mn(CO)_2[P(OPh)_3](Diphos)Cl$[b,f]	1962	1883	
$Mn(CO)_2[P(OPh)_3](Diphos)Br$	1958	1885	
$Mn(CO)_2[P(OPh)_3](Diarsine)Br$[f,q]	1959	1885	
$Mn(CO)_2[P(OPh)_3](Diars)Br$	1957	1881	
$Mn(CO)_2[P(OPh)_3](Dipy)Br$[b,f]	1981	1913	
$Mn(CO)_2(PMe_2Ph)(Diphos)Br$[r]	1934	1860	
fac-$Mn(CO)_3(Diarsine)Br$[b,f]	2026	1957	1919
fac-$Mn(CO)_3(Dipy)Br$[b,f]	2033	1945	1924

[a] The bands are strong in every case.

[b] In $CHCl_3$ solution.

[c] ^1H NMR [$CDCl_3$ solution; TMS as internal standard (τ 10 ppm); Varian Associates A-60 spectrometer]: τ 6.24 ppm (complex multiplet).

[d] ^1H NMR: τ 6.13 ppm (~1/1/1 triplet-like).

[e] In $CHCl_3$ solution (ref. 7): ν(CO), 1980 s, 1898 s cm^{-1}; ^1H NMR, τ 6.19 ppm (triplet-like).

[f] These complexes were not isolated on a preparative scale. The similarity of their IR spectra to those of authentic halocarbonyl complexes was taken as sufficient proof of their identity.

[g] ^1H NMR: τ 5.48 (complex multiplet), 6.17 ppm (complex multiplet).

[h] In C_6H_6 solution (ref. 15): ν(CO), 1912 s, 1839 s cm^{-1}.

[i] Data from ref. 13: ν(CO), 1936 s, 1864 s cm^{-1}.

[j] ^1H NMR: τ 2.43, ~3.0 (doublet-like), 7.2 br ppm. In far-infrared spectrum (Nujol mull; Perkin–Elmer FIS 3 spectrometer): ν(Mn–Br), 209 cm^{-1}.

[k] In solid-state Raman spectrum [krypton laser (647.1 nm) excitation; Jarrell–Ash 25–300 spectrometer]: ν(Mn–I), 190 cm^{-1}.

[l] ^1H NMR: τ 2.4 (complex multiplet), 6.35 (doublet), ~8 br ppm.

[m] ^1H NMR: τ 2.6 (complex multiplet), 6.33 (doublet), ~8 br ppm.

[n] ^1H NMR: τ 2.5, 6.31 (complex multiplet), ~7.5 br ppm.

[o] ^1H NMR: τ 2.7, 6.0 (complex multiplet), ~8 br, 8.8 br ppm.

[p] ^1H NMR: τ 2.53, 5.8 (complex multiplet), 6.5 (complex multiplet), ~7.9 br, ~8.7 br ppm.

[q] In near-ultraviolet spectrum ($CHCl_3$ solution): λ_{max}, 402 nm,

[r] ^1H NMR: τ 2.62, 8.4 ppm (complex multiplet).

$Mn(CO)_2L_3X$ (Method I)

A mixture of the appropriate $Mn(CO)_5X$ complex (2 mmol) and trialkyl phosphite or PMe_2Ph (6–8 mmol) was dissolved in chloroform (50–100 ml) and the solution was maintained at reflux until no further reaction occurred. The solvent volume was then reduced on a rotary evaporator to about 5 ml, and n-hexane (50 ml) was added. This mixture was reduced in volume to about 5 ml. The precipitate which formed at this point was filtered off and was recrystallized from a chloroform/n-hexane mixture. In a few cases the reaction products were oils which could not be induced to crystallize. All the products, including those which were oils, were dried *in vacuo* (25°/0.001 mmHg) for 24 h.

$Mn(CO)_2(Triphos)X$ (Method II)

A xylene solution (20 ml) containing $Mn(CO)_5X$ (1 mmol) and triphos (1 mmol) was heated at 130° until the reaction was complete. The volume of the reaction mixture was then reduced at 25°/0.1 mmHg to about 5 ml, and n-hexane (50 ml) was added. The precipitate which formed was filtered off and was purified by column chromatography on silica using a 1/1 acetone/n-hexane mixture as eluant. The resulting product was recrystallized from a chloroform/n-hexane mixture.

The iodo-complex, $Mn(CO)_2(Triphos)I$, was also prepared in about 10% yield from the reaction of $Mn(CO)_5I$ with Triphos in refluxing dichloromethane for 17 days.

$Mn(CO)_2L(A\text{–}A)X$ (Method III)

Method A. A mixture of *trans*-$Mn(CO)_3[P(OPh)_3]_2X$ (1.5 mmol), bidentate ligand (A–A) (4 mmol), and $P(OPh)_3$ (8 mmol) was dissolved in chloroform (50 ml) and the solution was heated at reflux until no further reaction occurred. The solvent was then removed on a rotary evaporator. Chloroform (2 ml) was added to the resulting "oil" and the mixture was chromatographed on an alumina column. The eluants used were petroleum ether (30–60°), followed by a benzene/petroleum ether (30–60°) mixture (1/1 for A–A = Diphos, Diars; 1/3 for A–A = Diarsine). The required halodicarbonyl complex was eluted as the first coloured fraction. The solvent mixture was then removed under reduced pressure (25°/0.1 mmHg) and the product was recrystallized from n-hexane. A different chromatographic procedure was used for A–A = Bipy. The "oil" was chromatographed on an alumina column using, first benzene, followed by a 2/1 benzene/chloroform mixture as eluant. The desired product was the second species that developed on the column and was eluted with ethanol. Removal of solvent gave the product as a dark orange oil which failed to crystallize.

In all of the $Mn(CO)_2[P(OPh)_3](A\text{–}A)X$ preparations some *fac*-$Mn(CO)_3(A\text{–}A)X$ was also formed. These tricarbonyl complexes were not isolated from the reaction mixtures owing to the difficulty in effecting complete chromatographic separation of them from the dicarbonyl complexes. However, they were identified by the similarity of their IR spectra in the C–O stretching region to those of authentic samples of *fac*-$Mn(CO)_3(Diphos)Br$ and *fac*-$Mn(CO)_3(Bipy)Br$ [prepared from $Mn(CO)_5Br$ and excess Bipy] and those reported in the literature for *fac*-$Mn(CO)_3(Bipy)X$[9,14] and *fac*-$Mn(CO)_3(Diars)X$[12]. The C–O stretching frequencies for the previously unreported *fac*-$Mn(CO)_3(A\text{–}A)X$ complexes have been included in Table 2.

Method B. A chloroform solution (20 ml) containing $Mn(CO)_2L_3X$ (1 mmol) and Diphos or Triphos (1–2 mmol) was maintained at reflux until no further reaction took place. On cooling, n-hexane (50 ml) was added to the reaction mixture and the solvent volume was then reduced to about 5 ml. The precipitate which formed was filtered off. The Diphos-containing products were recrystallized from chloroform/n-hexane mixtures. The Triphos complexes were chromatographed on silica columns using 1/2 acetone/benzene mixtures as eluant. After removal of the solvent, the required products were obtained by recrystallization from chloroform/n-hexane mixtures.

Method C. A mixture of *fac*-$Mn(CO)_3$(Diphos)Br (0.5–1 mmol) and excess trialkyl phosphite or PMe_2Ph (2–4 mmol) in xylene (20 ml) was heated at 90–100° until no further reaction occurred. The solvent was removed under reduced pressure (25°/0.1 mmHg) and the resulting residue was recrystallized from a chloroform/n-hexane mixture to give the desired product.

In the case of the PMe_2Ph complexes, the residue was dissolved in a minimum of chloroform and then chromatographed on a silica column using a 3/5 acetone/n-hexane mixture as eluant. The products were then purified as above.

RESULTS AND DISCUSSION

The $Mn(CO)_5X$ complexes react with monodentate trialkyl phosphites and PMe_2Ph to produce, eventually, the halodicarbonyl complexes $Mn(CO)_2L_3X$*. With the potentially tridentate ligand Triphos the halodicarbonyl complexes $Mn(CO)_2$(Triphos)X are produced. The reactions with the monodentate ligands are best carried out in refluxing chloroform ($\approx$65°) and are usually complete in less than 24 h. Under the same conditions, the Triphos reactions are extremely slow and are still not complete after one month. However, in xylene solution at 130° these reactions are complete in less than 5 h.

The IR spectra of the reaction mixtures in the C–O stretching region indicate that, as expected, all the reactions proceed by the stepwise replacement of CO groups. In the case of the reactions with the monodentate ligands, they have all reached the disubstituted stage after 1 h. Slower reactions then transform the disubstituted complexes into the trisubstituted ones. (A qualitative comparison of the rates of formation of $Mn(CO)_2[P(OMe)_3]_3X$ (X = Cl, Br) indicates that the chloro-complex is formed significantly faster than the bromo-complex.) On the basis of the IR spectra there is no evidence of any further substitution occurring.

The Triphos reactions are slow enough for the intermediate complexes, $Mn(CO)_3$(Triphos)X, to be isolated and characterized. The Triphos ligand in these complexes is coordinated to the manganese atom through only two of its three phosphorus atoms. The complexes are similar to those of the potentially tetradentate ligand tris[*o*-(diphenylphosphino)phenyl]phosphine (QP), *fac*-$Mn(CO)_3$(QP)X, in which the QP ligand functions as a bidentate ligand[16]. The preparation and the physical and chemical properties of the "monodentate ligands", $Mn(CO)_3$(Triphos)X, will be the subject of a forthcoming publication.

The degree of CO substitution in the $Mn(CO)_5X$ complexes by PhNC is known

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* Another preparation of $Mn(CO)_2(PMe_2Ph)_3Br$ has been reported recently[15]. This preparation involves the reaction of $Mn(CO)_2(PMe_2Ph)_3NCO$ with dry HBr gas in carbon tetrachloride solution at 0°.

to be highly solvent-dependent[3]. For instance, the di-, tri-, and tetraisocyanide complexes are produced when $Mn(CO)_5Br$ is treated with PhNC in ethanol, diglyme, and tetrahydrofuran, respectively. Therefore, it seems that the more basic the solvent the higher the degree of CO substitution. Consequently, we hoped that similar reactions in our case would lead to tetra- or even penta-substitution. However, reaction of $Mn(CO)_2[P(OMe)_3]_3X$ with excess $P(OMe)_3$ in refluxing tetrahydrofuran affords no new products and reaction of $Mn(CO)_5Br$ with $P(OPh)_3$ in diglyme at 100° results only in complete decomposition of the carbonyl complex.

The halodicarbonyl complexes, $Mn(CO)_2[P(OMe)_3]_3X$, react with Diphos in refluxing chloroform to form the "mixed ligand" complexes, $Mn(CO)_2[P(OMe)_3]$(Diphos)X. The complexes tend to crystallize as chloroform solvates. Such solvation behaviour has been noted previously for Diphos-containing metal carbonyl complexes, *e.g.*, $[M(CO)_2(Diphos)_2]X_2$ (M = Mo, W; X = Cl, Br), which exhibit a great tendency to crystallize as dichloroethane solvates[17]. When the $Mn(CO)_2L_3X$ complexes undergo reaction with Triphos, instead of Diphos, the complexes $Mn(CO)_2L$(Triphos)X are produced. The Triphos ligand in these complexes is acting as a bidentate ligand.

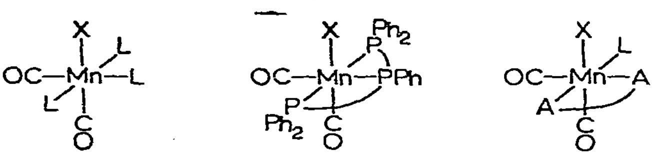
An alternative route to the mixed ligand type of halodicarbonyl complexes is through the reactions of *trans*-$Mn(CO)_3[P(OPh)_3]_2X$ in refluxing chloroform with bidentate ligands, A–A (for X = Cl, A–A = Diphos; for X = Br, A–A = Diphos, Diarsine, Diars, Bipy), in the presence of excess $P(OPh)_3$. Small amounts of *fac*-$Mn(CO)_3$(A–A)X are produced as by-products in these reactions. The excess $P(OPh)_3$ is added to the reaction mixtures because it minimizes the amount of undesired tricarbonyl complex formed. The rates of formation of the halodicarbonyl complexes are unaffected by the addition of $P(OPh)_3$.

The complex, $Mn(CO)_2[P(OPh)_3]$(Diphos)Br, is also produced in the reaction of *fac*-$Mn(CO)_3[P(OPh)_3]_2Br$ with Diphos but the proportion of the tricarbonyl derivative, *fac*-$Mn(CO)_3$(Diphos)Br, formed is greater than in the reaction with *trans*-$Mn(CO)_2[P(OPh)_3]_2Br$.

The mixed ligand complexes, $Mn(CO)_2L$(Diphos)Br [L = $P(OMe)_3$, $P(OPh)_3$, PMe_2Ph], may also be obtained by reaction of *fac*-$Mn(CO)_3$(Diphos)Br with L in xylene at 90–100°. In the case of PMe_2Ph some replacement of Diphos does take place because *trans*-$Mn(CO)_3(PMe_2Ph)_2Br$ is present in the crude reaction product. Presumably, two PMe_2Ph ligands displace the Diphos ligand to give initially *fac*-$Mn(CO)_3(PMe_2Ph)_2Br$ which, at the temperature of the reaction, readily isomerizes to the *trans* isomer[4]. This suggestion is supported by the fact that the reaction of $Mn(CO)_5Br$ with PMe_2Ph in xylene at 65° yields a complex whose IR spectrum in the C–O stretching region is typical of a *fac*-$Mn(CO)_3L_2X$ species. On raising the temperature to 95°, the spectrum becomes characteristic of a mixture of *trans*-$Mn(CO)_3L_2X$ and $Mn(CO)_2L_3X$.

All other attempts to obtain mixed ligand complexes of the type, $Mn(CO)_2L$(A–A)X, failed. For instance, the sole products of the reactions of *cis*-$Mn(CO)_4[P(OPh)_3]Br$ with A–A are *fac*-$Mn(CO)_3$(A–A)Br; there is no reaction between $Mn(CO)_2[P(OMe)_3]Br$ and Bipy in refluxing chloroform, even after 54 h, and reaction of *fac*-$Mn(CO)_3$(Bipy)Br with $P(OPh)_3$ only results in complete decomposition.

The non-ionic formulation of the new halodicarbonyl complexes, $Mn(CO)_2L_3X$, $Mn(CO)_2$(Triphos)X, and $Mn(CO)_2L$(A–A)X, is supported by the low molar conductances of representative examples of the complexes in nitromethane solutions (Table 1). All the complexes exhibit two strong IR active C–O stretching frequencies (Table 2). Because of this, the two CO groups in each complex are assigned *cis* rather than *trans* stereochemistry. [One weak band (symmetric C–O stretching mode) and one strong band (asymmetric C–O stretching mode) would be expected for a *trans* arrangement of the two CO groups.] We favour the structures shown in Fig. 1 for the three different types of halodicarbonyl complex because of the established geometry of $CH_3Mn(CO)_3[P(OMe)_3]_2$, $CH_3Mn(CO)[P(OMe)_3]_4$[7], and $CH_3COMn(CO)_3[P(OMe)_3]_2$[18] in which the $P(OMe)_3$ ligands are *cis* to the CH_3 and CH_3CO groups. Moreover, a $C^{18}O$ exchange study carried out in our laboratory on *trans*-$Mn(CO)_3[P(OPh)_3]_2Br$ indicates that the two *trans* CO groups are much more labile than the CO group *trans* to Br[19]. This suggests that the latter CO group is the least likely to undergo substitution. Structure (I) is the same structure that was preferred for $Mn(CO)_2[P(OMe)_3]_3Br$ in the preliminary report of its preparation[7]. Furthermore, it is identical to the structure proposed for the analogous $Re(CO)_2L_3Cl$ [$L = PPh_2H$, PPh_2Me, $P(OPh)_3$] complexes which are formed in the reaction of $[Re(CO)_6]ClO_4$ and the appropriate ligand, L[5].



(I) (II) (III)

Fig. 1. Probable structures of the halodicarbonylmanganese(I) complexes, $Mn(CO)_2L_3X$, $Mn(CO)_2$(Triphos)X, and $Mn(CO)_2L(A–A)X$. The methylene groups of the Triphos ligand have been omitted for the sake of clarity.

Although we did not carry out a detailed kinetic study of the rates of formation of the $Mn(CO)_2[P(OPh)_3](A–A)X$ complexes from *trans*-$Mn(CO)_3[P(OPh)_3]_2X$ and A–A in the presence of excess $P(OPh)_3$, we do feel that we can make a few observations concerning the possible mechanism of these reactions. In particular, that A–A replaces both a $P(OPh)_3$ and a CO ligand suggests that the halodicarbonyl complexes are formed by either A–A first replacing a $P(OPh)_3$ molecule and then a CO group or *vice versa*. The tricarbonyl complexes, *fac*-$Mn(CO)_3(A–A)X$, which are always present in the reaction mixtures are most probably produced by the sequential replacement of the two $P(OPh)_3$ ligands. All the CO and ligand substitution reactions of octahedral first-row transition metal carbonyl complexes that have been studied kinetically[1,14,20] appear to take place by S_N1 dissociative mechanisms. Therefore, it seems reasonable to assume that an S_N1 mechanism is operative in the reactions of *trans*-$Mn(CO)_3[P(OPh)_3]_2X$ with A–A. Consequently, the presence of excess $P(OPh)_3$ would be expected to retard the replacement of a coordinated $P(OPh)_3$ group and so decrease the amount of the tricarbonyl derivatives, *fac*-$Mn(CO)_3(A–A)X$, formed, as is observed experimentally. Moreover, since no appreciable change occurs in the rate of production of the halodicarbonyls when excess $P(OPh)_3$ is added to the reaction mixtures, this suggests that these complexes are formed mainly by a mechanism which initially involves CO replacement by A–A followed by chelate formation and expulsion of a $P(OPh)_3$ ligand.

CONCLUSIONS

The facile formation of the halodicarbonyl complexes, $Mn(CO)_2L_3X$, $Mn(CO)_2(Triphos)X$, and $Mn(CO)_2L(A\text{-}A)X$, indicates that such complexes are much more accessible than was previously realized. As expected, the nature of L plays an important role in the formation of the complexes. With the exception of the Triphos and PMe_2Ph complexes, all the new halodicarbonyl complexes contain at least one tertiary phosphite ligand. It appears that, as predicted, the strongly π-bonding tertiary phosphite ligands weaken the Mn–CO bonds in the tricarbonyl derivatives, $Mn(CO)_3L_2X$, sufficiently for one more CO substitution step to take place. Presumably, the formation of the mixed ligand complexes, $Mn(CO)_2L(A\text{-}A)X$, from *trans*-$Mn(CO)_3[P(OPh)_3]_2X$ and A–A and from *fac*-$Mn(CO)_3(Diphos)X$ and L depends on both the electronic and steric requirements of the entering ligand. The Triphos complexes are formed most probably because of the chelate effect of the tridentate ligand. Finally, the high basicity and small steric requirement of the PMe_2Ph ligand probably accounts for the formation of halodicarbonyl complexes containing this ligand.

ACKNOWLEDGEMENTS

This work was supported by a grant from the National Research Council of Canada. The award of scholarships by McGill University (N.J.C., Alexander McFee Scholarship, 1969–1970) and the National Research Council of Canada (N.J.C., 1970–1972; H.K.S., 1967–1970) is gratefully acknowledged.

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