

Chemistry of the Metal Carbonyls. Part 75.¹ Synthesis of Aquatetra-carbonyl(triphenylphosphine)manganese Tetrafluoroborate and Related Cationic Tetracarbonylmanganese Complexes

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The complex $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ reacts with $[\text{CPh}_3][\text{BF}_4]$ in wet dichloromethane to give the salt $cis\text{-}[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PPh}_3)][\text{BF}_4]$. The same aqua-cation is obtained on treating $[\text{MnR}(\text{CO})_4(\text{PPh}_3)]$ ($\text{R} = \text{H, Ph, or COMe}$)

with $[\text{CPh}_3][\text{BF}_4]$ under similar conditions, or by treating $[\text{MnR}(\text{CO})_4(\text{PPh}_3)]$ ($\text{R} = \text{Me or Br}$) or $[\text{Mn}\{\text{C}_6\text{H}_4(\text{PPh}_2)\}(\text{CO})_4]$ with $[\text{OMe}_3][\text{BF}_4]$ in dichloromethane. The related cations $cis\text{-}[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PR}_3)]^+$ [$\text{PR}_3 = \text{PEt}_3, \text{PMe}_2\text{Ph, PMePh}_2, \text{or PPh}(\text{OMe})_2$] are also reported. The complex $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ reacts with $[\text{CPh}_3][\text{BF}_4]$ in acetonitrile to give the salt $[\text{Mn}(\text{CO})_4(\text{NCMe})(\text{PPh}_3)][\text{BF}_4]$. The aqua-ligand in $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PPh}_3)]^+$ is readily replaced to give the species $[\text{Mn}(\text{CO})_4\text{L}(\text{PPh}_3)]^+$ ($\text{L} = \text{C}_5\text{H}_5\text{N, CNBu}^t, \text{CH}_2\text{:CHCN, SMEt}_2, \text{H}_2\text{S, PPh}_3, \text{or CO}$).

EARLIER we reported a variety of neutral and cationic carbene(carbonyl) complexes of manganese.²⁻⁴ These complexes involved hydroxy-, 2-oxacyclopentylidene-, and 2,5-dioxacyclopentylidene-carbene ligands. No mononuclear manganese complex containing a CH_2 ligand has been reported, although bridged methylene complexes $[\text{Mn}_2(\mu\text{-CH}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_4\text{R})]$ ($\text{R} = \text{H or Me}$) have been described.⁵ The methylene ligand co-ordinated to a single metal centre is now well established in the tantalum complex $[\text{TaMe}(\text{CH}_2)(\eta\text{-C}_5\text{H}_5)_2]$.⁶ With iron, evidence for the intermediacy of the species $[\text{Fe}(\text{CH}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^+$ has been obtained,^{7,8} and its phenyl-substituted derivative has recently been isolated as the salt $[\text{Fe}(\text{CHPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$.⁹ Since carbon-manganese σ bonds are often more robust than those in comparable iron complexes, it seemed possible that the cationic complex $[\text{Mn}(\text{CH}_2)(\text{CO})_5]^+$ could be isolable. A possible route to this and related species might involve treatment of $[\text{MnMe}(\text{CO})_4\text{L}]$ ($\text{L} = \text{CO or PR}_3$) with the hydride-abstracting reagent $[\text{CPh}_3][\text{BF}_4]$, a β -hydride abstraction from $[\text{MnEt}(\text{CO})_5]$ to afford $[\text{Mn}(\text{CO})_5(\text{C}_2\text{H}_4)]^+$ having been reported¹⁰ several years ago. However, reaction of $[\text{CPh}_3]^+$ with a MeMn group might follow a different reaction path. Lewis and his co-workers¹¹ have observed that electrophilic cleavage of allyl groups as tritylallyl occurs on treatment of certain allylruthenium complexes with $[\text{CPh}_3][\text{BF}_4]$. Hence this reagent might cleave methyl-manganese bonds rather than remove hydride from the methyl group. In order to investigate these possibilities the following studies were carried out.

RESULTS AND DISCUSSION

No reaction was observed in dichloromethane between pentacarbonylmethylmanganese and $[\text{CPh}_3][\text{BF}_4]$, but the latter reagent reacted at room temperature with $cis\text{-}[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ ¹² to give a yellow crystalline complex (1). The i.r. spectrum of (1), with $\nu_{\text{max}}(\text{CO})$ at 2111m, 2038(sh), 2024vs, and 1974m cm^{-1} , was characteristic of an octahedral cis -disubstituted tetracarbonylmanganese derivative. The relatively high frequency¹³ of the bands was in accord with the formation of a cationic species, and a band in the i.r. at 1050s, br cm^{-1} showed the presence of the anion $[\text{BF}_4]^-$. The ^1H n.m.r. spectrum showed resonances at τ 2.55 ($\text{C}_6\text{H}_5\text{P}$) and 6.39. The latter signal was not in the chemical-shift region associated with a proton attached to a carbon atom of a metal-carbene group. Thus in the cation $[\text{Fe}(\text{CHPh})(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^+$ the CH proton of the carbene group resonates at τ -7.43.⁹ Furthermore, examination of the full-range i.r. spectrum of (1) revealed a broad band at 3385 cm^{-1} characteristic of $\nu(\text{OH})$, and following this observation it was found that if the salt (1) was treated with D_2O and the ^1H n.m.r. spectrum re-examined the signal at τ 6.39 had disappeared while that due to the phenyl groups remained. Accordingly, (1) is formulated as the aqua-complex $cis\text{-}[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PPh}_3)][\text{BF}_4]$. Thus reaction of $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ with $[\text{CPh}_3][\text{BF}_4]$ results in electrophilic cleavage of the methyl group rather than abstraction of hydride. Characterisation of (1) led to the subsequent identification of CMePh_3 as the other product of reaction. Some precedent for the formation of (1)

¹ Part 74, J. C. Burt, S. A. R. Knox, R. J. McKinney, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1.

² J. R. Moss, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 975.

³ C. H. Game, M. Green, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 351.

⁴ D. H. Bowen, M. Green, D. M. Grove, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 1189.

⁵ W. A. Herrmann, B. Reiter, and H. Biersack, *J. Organometallic Chem.*, 1975, **97**, 245.

⁶ R. R. Schrock, *J. Amer. Chem. Soc.*, 1975, **97**, 6577; L. J. Guggenberger and R. R. Schrock, *ibid.*, p. 6778.

⁷ P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 5044.

⁸ M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc. (A)*, 1967, 1508.

⁹ M. Brookhart and G. O. Nelson, *J. Amer. Chem. Soc.*, 1977, **99**, 6099.

¹⁰ M. L. H. Green and P. L. I. Nagy, *J. Organometallic Chem.*, 1963, **1**, 58.

¹¹ R. R. Schrock, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 951.

¹² C. S. Kraihanzel and P. Maples, *J. Amer. Chem. Soc.*, 1965, **87**, 5267; *Inorg. Chem.*, 1968, **7**, 1806.

¹³ E. W. Abel and S. P. Tyfield, *Adv. Organometallic Chem.*, 1970, **8**, 117.

is found in the report¹⁴ that $[\text{FeMe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ and $[\text{CPh}_3][\text{ClO}_4]$ give $[\text{Fe}(\text{CO})_2(\text{OH}_2)(\eta\text{-C}_5\text{H}_5)]^+$ in small amounts after several hours in tetrahydrofuran.

The source of the aqua-ligand in (1) seemed likely to be derived from trace amounts of water in the dichloromethane solvent. Accordingly, reactions between

vacant co-ordination site which becomes occupied by a water molecule. It was observed that (1) could be similarly formed by treating $[\text{CPh}_3][\text{BF}_4]$ with $[\text{MnH}(\text{CO})_4(\text{PPh}_3)]$, or $[\text{Mn}(\text{COMe})(\text{CO})_4(\text{PPh}_3)]$.

Several other reactions were found to produce (1) in good yield, provided water was present. These included

TABLE I
Infrared and ^1H n.m.r. data for the new complexes

Complex	I.r. bands (cm^{-1}) ^a		N.m.r. chemical shift (τ) ^c
	$\nu(\text{CO})$	Other bands ^b	
(1) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PPh}_3)][\text{BF}_4]$	2 111m, 2 038 (sh), 2 024vs, 1 974s	3 385m, br (OH)	2.55 (15 H, m, Ph), 6.39 (2 H, m, OH)
(2) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{NCMe})(\text{PPh}_3)][\text{BF}_4]$	2 112m, 2 045 (sh), 2 029vs, 1 997s	2 328w, 2 296w (CN)	2.45 (15 H, m, Ph), 7.85 (3 H, s, Me)
(3) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PEt}_3)][\text{BF}_4]$	2 105m, 2 034 (sh), 2 017vs, 1 968s	3 380m, br (OH)	6.62 (2 H, m, OH), 7.95 (6 H, m, CH_2), 8.70 (9 H, m, Me)
(4) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PMe}_2\text{Ph})][\text{BF}_4]$	2 109m, 2 037 (sh), 2 021vs, 1 973s	3 380m, br (OH)	2.45 (5 H, m, Ph), 6.15 (2 H, m, OH), 8.02 (6 H, d, $J(\text{PH})$ 10 Hz)
(5) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PMePh}_2)][\text{BF}_4]$	2 109m, 2 073 (sh), 2 023vs, 1 977s	3 380m, br (OH)	2.40 (10 H, m, Ph), 6.15 (2 H, m, OH), 7.78 (3 H, d, $J(\text{PH})$ 10 Hz)
(6) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PPh}(\text{OMe})_2)][\text{BF}_4]$	2 113m, 2 053 (sh), 2 027vs, 1 978s	3 380m, br (OH)	2.45 (5 H, m, Ph), 6.30 (8 H, br m, OMe, OH)
(7) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)][\text{BF}_4]$	2 104s, 2 034s, 2 017vs, 1 990s		1.80 (2 H, m, $\text{C}_5\text{H}_5\text{N}$), 2.50 (18 H, br m, $\text{C}_5\text{H}_5\text{N}$, Ph)
(8) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{CNBu}^t)(\text{PPh}_3)][\text{BF}_4]$	2 106s, 2 049s, 2 029vs, 2 001 (sh)	2 197m (NC)	2.40 (15 H, m, Ph), 8.50 (9 H, s, Me)
(9) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{CH}_2\text{:CHCN})(\text{PPh}_3)][\text{BF}_4]$	2 115m, 2 043 (sh), 2 033s, 1 993s		2.35 (15 H, m, Ph), 4.0 (2 H, m, CH_2), 6.4 (1 H, CH)
(10) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{PPh}_3)(\text{SMe}_2)][\text{BF}_4]$	2 099m, 2 031s, 2 017vs, 2 001s		2.50 (15 H, m, Ph), 7.74 (6 H, br s)
(11) <i>cis</i> - $[\text{Mn}(\text{CO})_4(\text{PPh}_3)(\text{SH}_2)][\text{BF}_4]$	2 099m, 2 025s, 2 013 (sh), 1 981s	2 535vw (SH)	2.45 (15 H, m, Ph), 10.40 (2 H, m, SH)

^a Carbonyl bands recorded in CH_2Cl_2 , other bands in Nujol.

^b All the complexes show $\nu_{\text{max}}(\text{BF}_4)$ at 1 050m, br cm^{-1} .

^c In CDCl_3 solution.

$[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ and $[\text{CPh}_3][\text{BF}_4]$ were carried out in Schlenk tubes which had been strongly heated prior to use, and the dichloromethane solvent was distilled from P_4O_{10} . However, this procedure did not prevent the formation of (1), although the time required for complete consumption of the reactants increased to several hours. Addition of water to the anhydrous system resulted in very rapid formation of (1). Addition of D_2O correspondingly afforded $[\text{Mn}(\text{CO})_4(\text{OD}_2)(\text{PPh}_3)][\text{BF}_4]$, the i.r. spectrum of which was identical with that of (1) in the carbonyl-stretching region, but showed $\nu_{\text{max}}(\text{OD})$ at 2 540 cm^{-1} and no band at 3 385 cm^{-1} .

When P_4O_{10} -dried dichloromethane was used as solvent, examination of the reaction mixture by i.r. spectroscopy revealed initial formation of a transient species with $\nu_{\text{max}}(\text{CO})$ at 2 106m, 2 043(sh), 2 025vs, and 1 969s cm^{-1} . Exposure to air afforded (1) immediately. Although this intermediate was not identified, it is most unlikely to be $[\text{Mn}(\text{CH}_2)(\text{CO})_4(\text{PPh}_3)]^+$ in view of the isolation of CMePh_3 from the mixtures. The i.r. spectrum is clearly that of an octahedral *cis*-disubstituted cationic complex and this, taken with its great lability, leads to a tentative formulation as $[\text{Mn}(\text{CO})_4(\text{CH}_2\text{Cl}_2)(\text{PPh}_3)]^+$.

It is thus apparent that heterolytic cleavage of the Me-Mn bond in $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ by $[\text{CPh}_3]^+$ creates a

reaction of $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$, $[\text{Mn}\{\text{C}_6\text{H}_4(\text{PPh}_2)\}(\text{CO})_4]$, or $[\text{MnBr}(\text{CO})_4(\text{PPh}_3)]$ with $[\text{OMe}_3][\text{BF}_4]$ in dichloromethane. Evidently, the carbonium ion Me^+ readily removes Me^- and Br^- from the methyl- and bromo-manganese complexes, respectively, but in the

case of the orthometallated complex $[\text{Mn}\{\text{C}_6\text{H}_4(\text{PPh}_2)\}(\text{CO})_4]$ ¹⁵ it was necessary to heat the reactants under reflux to produce (1). Surprisingly, no incorporation of Me into the phenyl ring could be detected by n.m.r. spectroscopy. The aromatic ring evidently recovers hydrogen from the solvent to re-form triphenylphosphine, but overall the mode of formation of (1) by this route is obscure. Few aqua(carbonyl) complexes have been prepared previously but these include $[\text{MnX}(\text{CO})_3(\text{OH}_2)_2]$ ($\text{X} = \text{I}$ or OH) obtained by treating $[\text{MnI}(\text{CO})_3(\text{SPh}_2)_2]$ with water.¹⁶

As might be expected, treatment of $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ with $[\text{CPh}_3][\text{BF}_4]$ in the presence of acetonitrile affords the salt $[\text{Mn}(\text{CO})_4(\text{NCMe})(\text{PPh}_3)][\text{BF}_4]$ (2) in high yield. The i.r. spectrum in the carbonyl-stretching region (Table I) is in accord with a *cis* disposition of the acetonitrile and triphenylphosphine ligands. Complex (2) is also readily obtained by treating (1) with acetonitrile.

The formation of (1) from $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$, whereas $[\text{MnMe}(\text{CO})_5]$ did not appear to react with $[\text{CPh}_3][\text{BF}_4]$, led to an investigation of the effect of other tertiary phosphines on the course of the reaction. The complexes *cis*- $[\text{MnMe}(\text{CO})_4\text{L}]$ [$\text{L} = \text{PEt}_3$, PMe_2Ph , PMe -

¹⁴ M. L. H. Green and P. L. I. Nagy, *Proc. Chem. Soc.*, 1962, 74.

¹⁵ R. J. McKinney, R. Hoxmeier, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3059.

¹⁶ W. Hieber and F. Stanner, *Chem. Ber.*, 1969, **102**, 2930.

Ph_2 , $\text{PPh}(\text{OMe})_2$, $\text{P}(\text{OMe})_3$, or $\text{P}(\text{OPh})_3$] were synthesised^{12,15} and reactions with $[\text{CPh}_3][\text{BF}_4]$ in dichloromethane, to which a small amount of water was added, were studied. In this manner the cationic aqua-complexes (3)–(6) (Table 1) were obtained, but even over several days the species *cis*- $[\text{MnMe}(\text{CO})_4\text{L}]$ [$\text{L} = \text{P}(\text{OMe})_3$ or $\text{P}(\text{OPh})_3$] failed to produce aqua-cations; in the case of $\text{P}(\text{OMe})_3$ there was i.r. evidence of formation of trace amounts. Since trimethyl and triphenyl phosphite, like carbon monoxide, are strong π -acceptor ligands it appears necessary for the ligand L in *cis*- $[\text{MnMe}(\text{CO})_4\text{L}]$ to act predominantly as a σ donor in order to release Me^- in the reaction with $[\text{CPh}_3]^+$. Moreover, it was observed qualitatively that formation of complex (6) occurred much more slowly (*ca.* 3 h) than formation of (1) or (3)–(5), which was complete in a few minutes at room temperature.

The isolation in essentially quantitative yield of complex (1) and its ready conversion into the acetonitrile complex (2) suggested that (1) could be a useful precursor to a variety of *cis*-disubstituted species $[\text{Mn}(\text{CO})_4(\text{PPh}_3)_2]^+$. Tetracarbonyl cationic complexes are relatively rare whereas it has been possible to prepare¹⁷ from the complex $[\text{Mn}(\text{CO})_3(\text{NCMe})_3][\text{PF}_6]$ a variety of salts containing the tricarbonyl cations *fac*- $[\text{Mn}(\text{CO})_3\text{L}_2(\text{NCMe})]^+$ and *fac*- $[\text{Mn}(\text{CO})_3\text{L}(\text{NCMe})_2]^+$.

Reactions between (1) and pyridine, *t*-butyl isocyanide, acrylonitrile, dimethyl sulphide, and hydrogen sulphide have been found to afford the complexes (7)–(11) (Table 1), respectively, in yields of 70–90%. The *cis* stereochemistry of these complexes is established by the four-band pattern observed in the i.r. spectrum in the carbonyl-stretching region. These complexes are in general air-stable, except for $[\text{Mn}(\text{CO})_4(\text{PPh}_3)(\text{SH}_2)][\text{BF}_4]$ (11), which is exceedingly moisture-sensitive, readily re-forming complex (1). Complexes containing H_2S as a ligand are rare, the only other examples known at present of isolable complexes being $[\text{W}(\text{CO})_5(\text{SH}_2)]$,¹⁸ and $[\text{Ru}(\text{NH}_3)_5(\text{SH}_2)][\text{BF}_4]_2$ and $[\text{Ru}(\text{NH}_3)_4(\text{isn})(\text{SH}_2)][\text{BF}_4]_2$ (*isn* = isonicotinamide).¹⁹ A manganese complex $[\text{Mn}(\text{CO})_2(\text{SH}_2)(\eta\text{-C}_5\text{H}_5)]$ has been reported²⁰ but it is very unstable and was not fully characterised. In the i.r., complex (11) shows $\nu_{\text{max}}(\text{SH})$ at 2535 cm^{-1} , a very similar energy to that observed in the spectrum of the tungsten complex.

Complex (1) rapidly reacted with CO (10 atm)* to yield $[\text{Mn}(\text{CO})_5(\text{PPh}_3)][\text{BF}_4]$ quantitatively. The cation has been previously prepared²¹ by treating $[\text{MnCl}(\text{CO})_4(\text{PPh}_3)]$ with CO under high pressure in the presence of AlCl_3 , and by treating $[\text{Mn}(\text{CO})_5(\text{NCMe})]^+$ with PPh_3 .²² Complex (1) also reacted with PPh_3 to give the known^{10,21,23} cation $[\text{Mn}(\text{CO})_4(\text{PPh}_3)_2]^+$ quantitatively.

Reactions of (1) with NH_3 , NEt_3 , MeOH , $(\text{CH}_2)_4\text{O}$,

CS_2 , Me_2CO , $\text{C}_2(\text{CN})_4$, and $\text{P}(\text{OMe})_3$ led only to decomposition, while no reaction occurred between (1) and PhC_2Ph , $\text{Me}_3\text{SiC}_2\text{SiMe}_3$, or cyclo-octa-1,5-diene. Sodium tetrahydroborate reacted with complex (1) to give $[\text{MnH}(\text{CO})_4(\text{PPh}_3)]$.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on Varian Associates T60 and HA 100 spectrometers, i.r. spectra on a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained on an A.E.I. MS 902 mass spectrometer at 70 eV ionising potential. All the experiments were carried out under nitrogen. Dichloromethane was used as commercially supplied or dried over P_4O_{10} . The complexes *cis*- $[\text{MnMe}(\text{CO})_4(\text{PR}_3)]$ were prepared by published methods.^{12,15} Spectroscopic and analytical data for the new complexes are given in Tables 1 and 2.

TABLE 2

Analytical data for the cationic manganese complexes

Cation ^b	Analysis (%) ^a	
	C	H
$[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PPh}_3)]^+$	49.4 (49.4)	3.3 (3.2)
$[\text{Mn}(\text{CO})_4(^2\text{H}_5\text{O})(\text{PPh}_3)]^+$	49.2 (49.4)	3.4 (3.6)
$[\text{Mn}(\text{CO})_4(\text{NCMe})(\text{PPh}_3)]^+ \text{ } ^e$	51.0 (51.7)	3.4 (3.2)
$[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PEt}_3)]^+$	31.3 (30.8)	4.5 (4.4)
$[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PMePh}_2)]^+$	42.9 (43.2)	3.3 (3.2)
$[\text{Mn}(\text{CO})_4(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)]^+ \text{ } ^d$	54.8 (54.5)	3.7 (3.4)
$[\text{Mn}(\text{CO})_4(\text{CNBu}^t)(\text{PPh}_3)]^+ \text{ } ^e$	51.8 (54.0)	4.2 (4.0)
$[\text{Mn}(\text{CO})_4(\text{CH}_2\text{CHCN})(\text{PPh}_3)]^+$	51.5 (52.7)	3.6 (3.2)
$[\text{Mn}(\text{CO})_4(\text{PPh}_3)(\text{SMc}_2)]^+$	48.3 (48.2)	3.6 (3.6)
$[\text{Mn}(\text{CO})_4(\text{PPh}_3)(\text{SH}_2)]^+$	50.3 (48.2)	3.2 (3.1)

^a Calculated values are given in parentheses. ^b Analysed as $[\text{BF}_4]^-$ salts, all of which were yellow in colour. ^c N, 2.5 (2.5%). ^d N, 2.8 (2.4%). ^e N, 2.5 (2.5%). ^f N, 1.9 (2.5%).

Synthesis of the Salt $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PPh}_3)][\text{BF}_4]$ (1).—(a) The complex $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ (0.6 g, 1.35 mmol) and $[\text{CPh}_3][\text{BF}_4]$ (0.45 g, 1.35 mmol) were stirred in commercial dichloromethane (25 cm³) for 30 min at room temperature. The volume of solvent was reduced *in vacuo* to *ca.* 5 cm³ and diethyl ether (25 cm³) added. The precipitate obtained was washed with hexane to give, from dichloromethane-hexane, yellow crystals of (1) (0.62 g, 85%). The various solvent washings were combined and solvent removed *in vacuo* to give a residue. The latter was extracted with hexane and recrystallised to give CMePh_3 (0.2 g) (Found: C, 92.3; H, 7.2%, *M* 258. Calc. for $\text{C}_{20}\text{H}_{18}$: C, 93.0; H, 7.0%; *M* 258).

(b) Complex (1) (0.5 g, 94%) was similarly prepared from $[\text{MnH}(\text{CO})_4(\text{PPh}_3)]$ (0.45 g, 1.05 mmol) and $[\text{CPh}_3][\text{BF}_4]$ (0.34 g, 1.05 mmol) using commercial CH_2Cl_2 (25 cm³) as solvent. Similarly, $[\text{MnPh}(\text{CO})_4(\text{PPh}_3)]$ (0.60 g, 1.05 mmol) and $[\text{Mn}(\text{COMe})(\text{CO})_4(\text{PPh}_3)]$ (0.6 g, 1.3 mmol) gave (1) in 79 (0.43) and 68% (0.51 g) yield, respectively.

(c) The complex $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ (0.5 g, 1.12 mmol) and $[\text{OMe}_3][\text{BF}_4]$ (0.20 g, 1.36 mmol) were heated under reflux (1 h) in dichloromethane (25 cm³). The mixture was filtered, and the solvent removed *in vacuo* to give a

* Throughout this paper: 1 atm = 101 325 Pa; 1 eV $\approx 1.60 \times 10^{-19}$ J.

¹⁷ R. H. Reimann and E. Singleton, *J.C.S. Dalton*, 1974, 808.

¹⁸ M. Herberhold and G. Suss, *Angew. Chem. Internat. Edn.*, 1976, **15**, 366.

¹⁹ C. G. Kuehn and H. Taube, *J. Amer. Chem. Soc.*, 1976, **98**, 689.

²⁰ W. Strohmeier and J. F. Guttenberger, *Chem. Ber.*, 1964, **97**, 1871.

²¹ T. Kruck and M. Höfler, *Chem. Ber.*, 1963, **96**, 3035.

²² D. Drew, D. J. Darensbourg, and M. Y. Darensbourg, *Inorg. Chem.*, 1975, **14**, 1579.

²³ M. L. H. Green, A. G. Massey, J. T. Moelwyn-Hughes, and P. L. I. Nagy, *J. Organometallic Chem.*, 1967, **8**, 511.

yellow residue. The latter was recrystallised (dichloromethane–diethyl ether) affording the salt (1) (0.41 g, 72%).

Experiments using Anhydrous Dichloromethane.—The complex $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ (0.6 g, 1.35 mmol) and $[\text{CPh}_3][\text{BF}_4]$ (0.45 g, 1.35 mmol) were stirred in dichloromethane (25 cm³) which had been stored over P_4O_{10} for several days then distilled. Addition of D_2O (ca. 0.05 cm³) gave yellow crystals (0.6 g, 83%) of $[\text{Mn}(\text{CO})_4(\text{OD}_2)(\text{PPh}_3)]-[\text{BF}_4]$. The yellow crystalline complex $[\text{Mn}(\text{CO})_4(\text{NCMe})(\text{PPh}_3)][\text{BF}_4]$ (2) (0.68 g, 90%) was obtained by addition of MeCN (ca. 0.1 cm³) to a similarly prepared solution of $[\text{MnMe}(\text{CO})_4(\text{PPh}_3)]$ and $[\text{CPh}_3][\text{BF}_4]$ in dichloromethane.

Synthesis of the $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PR}_3)][\text{BF}_4]$ Salts.—The following preparation is representative of that for complexes (3)–(6). Complexes (4)–(6) were only identified spectroscopically (Table 1).

The complex $[\text{MnMe}(\text{CO})_4(\text{PEt}_3)]$ (0.65 g, 2.2 mmol) and $[\text{CPh}_3][\text{BF}_4]$ (0.7 g, 2.2 mmol) were mixed in commercial dichloromethane (25 cm³) for 30 min at room temperature. The volume of solvent was reduced *in vacuo* to ca. 5 cm³ and diethyl ether (25 cm³) added. Solvent was decanted from the solid residue which was washed with hexane and recrystallised from dichloromethane–hexane to afford

yellow crystals of $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PEt}_3)][\text{BF}_4]$ (3) (0.91 g, 84%).

Substitution Reactions of $[\text{Mn}(\text{CO})_4(\text{OH}_2)(\text{PPh}_3)][\text{BF}_4]$ (1).—The salt (1) (0.5 g, 0.98 mmol) was dissolved in pyridine (5 cm³) and the mixture stirred for 5 min at room temperature. Hexane (20 cm³) was added, precipitating the product. Solvent was removed *in vacuo* and the residue recrystallised from dichloromethane–hexane to give yellow microcrystals of $[\text{Mn}(\text{CO})_4(\text{C}_6\text{H}_5\text{N})(\text{PPh}_3)][\text{BF}_4]$ (7) (0.54 g, 90%). Complexes (8), (9), and (10) were similarly prepared in 64, 75, and 88% yield, respectively (Table 1). Complex (11) was prepared as follows.

Complex (1) (0.5 g, 0.98 mmol) was dissolved in dichloromethane (30 cm³, distilled from P_4O_{10}) and H_2S gas was bubbled through the solution for 20 min. Hexane (30 cm³) was added, precipitating the product which was recrystallised from dichloromethane–hexane to give very moisture-sensitive yellow crystals of (11) (0.3 g, 56%).

We thank the S.R.C. for the award of a research studentship (to P. J. H.).

[7/2129 Received, 5th December, 1977]