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The synthesis and rearrangement of *cis*-$M(CO)_4(PPh_3)CH_2I$ (M = Mn, Re)

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Abstract

Manganese and rhenium iodomethyl complexes, *cis*-$M(CO)_4(PPh_3)CH_2I$ (**1a**, M = Mn; **1b**, M = Re) have been prepared by treating the corresponding methoxymethyl complexes, *cis*-$M(CO)_4(PPh_3)CH_2OCH_3$ (**2a**, M = Mn; **2b**, M = Re) with $(CH_3)_3SiI$. The attempted alternate synthesis of **1a** involving the reaction of *cis*-$Mn(CO)_4(PPh_3)CHO$ with aqueous HI in toluene unexpectedly gave $[(CO)_4(PPh_3)MnCH_2]_2O$, **3**. The manganese complex **1a** undergoes spontaneous ligand rearrangement in solution at room temperature to *cis*-$Mn(CO)_4I(CH_2PPh_3)$, **4**, whereas the rhenium analog **1b**, is stable in solution.

Introduction

The interest in the synthesis and chemistry of homo- and heterobimetallic methylene-bridged complexes stems from the demonstrated or proposed involvement of these and related species in carbon monoxide reduction chemistry [1], olefin metathesis reactions [2], alkyne polymerizations [2], and methylene transfer reactions [3]. We are attempting to synthesize heterobimetallic methylene-bridged complexes having the structural nucleus $(CO)_xMCH_2M'(CO)_y$ in an effort to determine whether such compounds undergo the migratory insertion reaction and if so to ascertain the influence of the nature of the metal on the reaction. An obvious route to such hetero bimetallic complexes is the nucleophilic displacement reaction, eq. 1:

$$(CO)_xMCH_2I + [M'(CO)_y]^- \longrightarrow (CO)_xMCH_2M'(CO)_y \qquad (1)$$

We report herein the synthesis of manganese and rhenium iodomethyl complexes **1a** and **1b**, the inadvertent synthesis of a manganese complex containing the novel bridging group 2-oxapropane-1,3-diide, **3**, the spontaneous rearrangement of **1a** to **4** in solution and the X-ray crystal structures of **1a**, **3**, and **4**. Scheme 1 summarizes the reactions and products investigated in this work.

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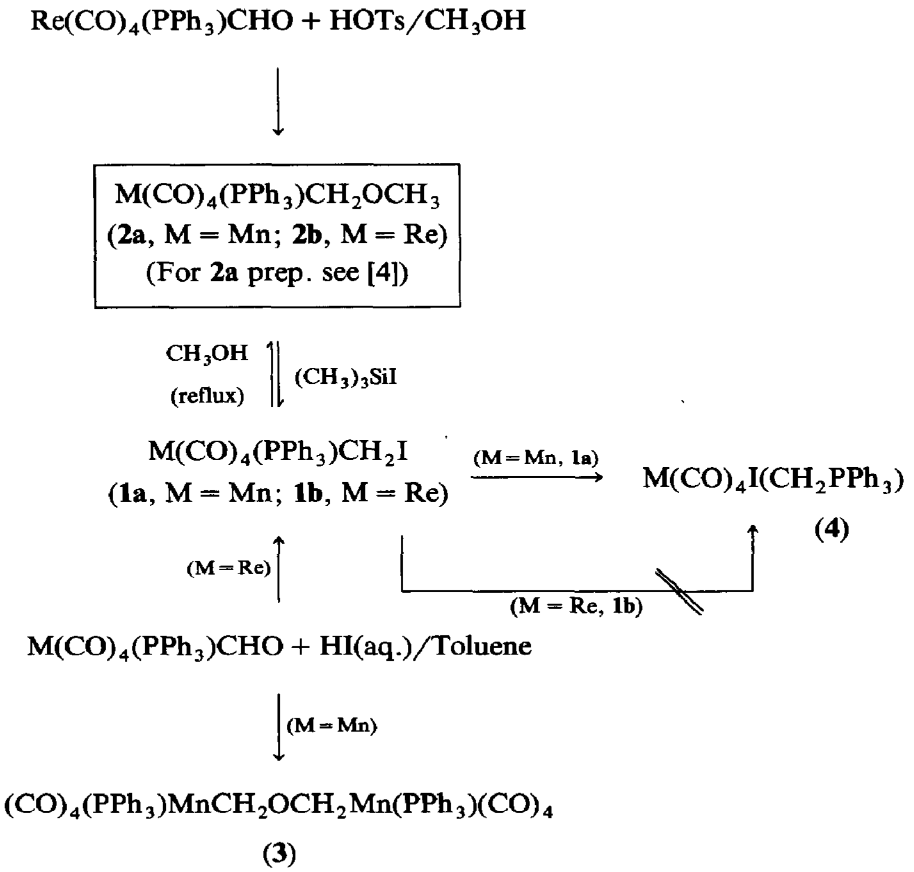

Scheme 1. Summary of reactions.

Results and discussion

Synthesis of cis-*$M(CO)_4(PPh_3)CH_2OCH_3$ (**2a**, M = Mn; **2b**, M = Re)*

The synthesis of **2a** was carried out according to the published procedures [4]. **2b** was synthesized from its known [5] formyl precursor according to eq. 2:

$$Re(CO)_4(PPh_3)CHO \xrightarrow[-78^\circ C]{HOTs,\ MeOH} \mathbf{2b} + [Re(CO)_5PPh_3]^+OTs^- + H_2O \qquad (2)$$

From the reaction mixture, **2b** was isolated from the cationic complex by extracting with hexane. A small amount of the metallacycle, $(CO)_4\overline{\mathrm{ReP(C_6H_5)_2(}o\mathrm{\text{-}C_6H_4C}}\mathrm{H_2)}$ was detected in the hexane extract but fractional crystallization led to the isolation of pure **2b**. The rhenium metallacycle has been previously synthesized by a different route [6].

Synthesis of cis-*$M(CO)_4(PPh_3)CH_2I$ (**1a**, M = Mn; **1b**, M = Re) and $[(CO)_4(PPh_3)MnCH_2]_2O$, **3**.*

1a and **1b** were prepared by reacting the methoxymethyl complexes **2a** and **2b** with $(CH_3)_3SiI$, eq. 3:

$$M(CO)_4(PPh_3)CH_2OCH_3 + (CH_3)_3SiI \longrightarrow M(CO)_4(PPh_3)CH_2I + (CH_3)_3SiOCH_3 \qquad (3)$$

The residue after vacuum evaporation of the solvent and the volatile $(CH_3)_3SiOCH_3$ (b.p. 57–58 °C) consisted of the iodomethyl complex. Subsequent crystallization in CH_2Cl_2/hexane at −35 °C afforded light yellow crystalline **1a** suitable for X-ray structure determination. Crystallization of **1b** was optimum at −5 °C and white crystals also suitable for X-ray structure determination were obtained. $Mn(CO)_5CH_2I$ has been synthesized previously [7] from the reaction of the corresponding methoxymethyl complex with $(CH_3)_3SiI$. The mechanism suggested in the previous work involves the initial formation of the intermediate silylated oxonium ion, $(CO)_4(PPh_3)MCH_2\overset{+}{O}CH_3[Si(CH_3)_3]I^-$ and subsequent rapid dissociation of $CH_3OSi(CH_3)_3$ to yield the cationic methylidene $[(CO)_4(PPh_3)M{=}CH_2]^+I^-$, followed by internal return of I^-. **1a** has been synthesized very recently [8] by an alternate route involving the reaction of its formyl precursor with aqueous HI in CH_2Cl_2 to give the desired **1a** and $[Mn(CO)_5PPh_3]^+I^-$. In our hands this preparation sometimes led to some decomposition of **1a** during work up. A change of solvent from CH_2Cl_2 to toluene unexpectedly afforded the toluene soluble compound, $(CO)_4(PPh_3)MnCH_2OCH_2Mn(PPh_3)(CO)_4$, **3** along with the insoluble expected salt, $[Mn(CO)_5PPh_3]^+I^-$; no trace of **1a** was found. Filtration and vacuum evaporation of the toluene yielded **3** as a light yellow solid in about 23% yield. Crystallization from toluene/hexane at −5 °C produced light yellow crystals suitable for X-ray crystallography. $Rh(OEP)CH_2OH$ has been reported elsewhere [9] to undergo an intermolecular self-condensation reaction to form an equilibrium mixture with $(OEP)RhCH_2OCH_2Rh(OEP)$ where, OEP is octaethylporphin. Similarly, $[(CO)_4RePPh_2(o\text{-}C_6H_4CH)]_2O$ was obtained from the treatment of $[(CO)_4RePPh_2(o\text{-}C_6H_4CHOH)$ with 0.06 equivalent of CF_3SO_3H in acetone/water [6]. Acid promoted conversion of $(\eta^5\text{-}C_5H_5)Re(NO)(CO)CH_2OCH_3$ to the ether dimer $[(\eta^5\text{-}C_5H_5)(CO)(NO)ReCH_2]_2O$ has been previously observed [10]. An analogous compound of rhenium has been reported [11] as arising from the hydrolysis of a rhenium iodomethyl cationic complex, eq. 4:

$$[L(NO)(CO)ReCH_2I]^+ \xrightarrow{H_2O} [L(NO)(CO)ReCH_2OCH_2Re(CO)(NO)L]^{2+}$$
$$(L = 1,4,7\text{-triazacyclononane}) \qquad (4)$$

It was suggested that in this reaction a hydroxymethyl intermediate, $[L(NO)(CO)ReCH_2OH]^+$ is formed initially; we believe that a similar hydroxymethyl complex, $[(CO)_4(PPh_3)MnCH_2OH]$ is formed in our reaction as an intermediate to **3**:

$$\begin{tikzcd}
\underset{(5)}{(CO)_4(PPh_3)MnCHO} \arrow[r, "H^+"] & {[(CO)_4(PPh_3)Mn{=}CHOH]^+} \arrow[d, "{5, -[(CO)_5(PPh_3)Mn]^+}"] \\
 & \underset{(6)}{(CO)_4(PPh_3)MnCH_2OH} \arrow[d, "{H^+, -H_2O}"] \\
3 & {[(CO)_4(PPh_3)Mn{=}CH_2]^+} \arrow[l, "6"', "-H^+"]
\end{tikzcd}$$

A solvent effect on a related reaction has also been observed previously [12] in which reduction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ with $NaBH_3CN$ in alcohol was reported to give $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2OR$ but in toluene a transient thermally unstable hydroxymethyl complex, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2OH$ was formed.

We were unable to prepare the Re analog of **3**. When the solution in which the formyl precursor was generated was treated with HI in toluene the iodomethyl, **1b**, and the expected iodide salt $[Re(CO)_5PPh_3]^+I^-$ were obtained.

Isomerization of cis-*$Mn(CO)_4(PPh_3)CH_2I$, 1a*

A benzene, methylene chloride, or acetone solution of **1a** at room temperature is slowly converted to the rearranged isomer, **4** in about a day:

$$\underset{\textbf{(1a)}}{cis\text{-}Mn(CO)_4(PPh_3)CH_2I} \longrightarrow \underset{\textbf{(4)}}{cis\text{-}Mn(CO)_4I(CH_2PPh_3)} \qquad (5)$$

Solvent removal and subsequent crystallization from CH_2Cl_2/hexane yielded **4** as a red crystalline product suitable for X-ray crystallography. Analogous ligand rearrangement of a cationic rhodium complex, $[(\eta^5\text{-}C_5H_5)Rh(PR_3)_2CH_2I]^+$ to $[\eta^5\text{-}C_5H_5)Rh(PR_3)I(CH_2PR_3)]^+$ was observed earlier [13]. However, for the octahedral situation only one related example appears in the literature [14] and involves the isomerization of presumed intermediates *mer,trans*-$Rh(PMe_3)_3Cl_2(CH_2Cl)$ to *mer,trans*-$Rh(PMe_3)_2Cl_3(CH_2PMe_3)$ and *fac*-$[Rh(PMe_3)_4Cl(CH_2Cl)]^+$ to *fac*-$[Rh(PMe_3)_3Cl_2(CH_2PMe_3)]^+$. In both cases these isomerizations were assumed to be promoted by the PMe_3 ligands *trans* to the chloromethyl group. The spontaneous rearrangement of our manganese iodomethyl complex, **1a** which possess the π-acceptor CO ligand *trans* to the iodomethyl group in a neutral species appears unusual. The rhenium analogue **1b** failed for unknown reason to undergo such isomerization even after six months in benzene at room temperature.

Alcoholysis of cis-*$M(CO)_4(PPh_3)CH_2I$ (1a, M = Mn; 1b, M = Re)*

When **1a** or **1b** was refluxed in methanol, the corresponding methoxymethyl complex, *cis*-$M(CO)_4(PPh_3)CH_2OCH_3$ (**2a**, M = Mn; **2b**, M = Re) was obtained in almost quantitative yield. Similar solvolysis reactions have been observed in the chloromethyl complexes of osmium [15].

Spectral studies

1a has been previously characterized and we found similar spectral properties. The IR, ^{31}P NMR data for the complexes, **1b**, **2b**, **3** and **4** as well as the (m/e) spectra of complex **1b** are given in the Experimental Section. The ^1H and ^{13}C NMR spectral data of complexes **1b**, **2b**, **3** and **4** are listed in Table 1. As expected the ^1H and ^{13}C NMR spectra of **1b**, **2b**, **3** and **4** exhibit one doublet in each case associated with the methylene protons and methylene carbons coupled to phosphorus. The off-resonance ^{13}C NMR spectra of **3** exhibits a triplet of doublets (^1J(CH) 145 Hz, ^2J(PC) 12 Hz) as expected for the methylene carbons coupled to phosphorus and hydrogen. The ^1H NMR spectra of **4** shows the two-bond coupling constant $^2J(PH) = 14$ Hz as compared to the three-bond coupling constants $^3J(PH) = 7$ to 8 Hz in **1b**, **2b** and **3**; again the ^{13}C NMR spectra of **4** shows the one-bond coupling constant $^1J(PC) = 26$ Hz which is significantly higher than the two-bond coupling

Table 1

^{1}H and ^{13}C NMR data for *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$I (**1b**), *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$OCH$_3$ (**2b**), (CO)$_4$(PPh$_3$)MnCH$_2$OCH$_2$Mn(PPh$_3$)(CO)$_4$ (**3**) [a] and *cis*-Mn(CO)$_4$I(CH$_2$PPh$_3$) (**4**)

Complex	^{1}H NMR (δ) [b]			^{13}C NMR (δ) [b]			Other
	phenyl	methylene	other	CO	phenyl	methylene	
1b	7.25 (m, 15H)	2.33 (d, J(PH) = 8 Hz, 2H)		191.12 (d, J(PC) = 11 Hz), 189.57 (d, J(PC) = 53 Hz), 187.09 (d, J(PC) = 8 Hz)	133.70 (d, J(PC) = 11 Hz), 132.81 (d, J(PC) = 44 Hz), 131.42 (s), 129.41 (d, J(PC) = 8 Hz)	−31.25 (d, J(PC) = 7 Hz)	
2b	7.35 (m, 15H)	4.00 (d, J(PH) = 7 Hz, 2H)	3.09 (s, 3H, CH$_3$)	191.59 (d, J(PC) = 10 Hz), 189.37 (d, J(PC) = 21 Hz), 188.90 (d, J(PC) = 22 Hz)	133.91 (d, J(PC) = 11 Hz), 132.74 (d, J(PC) = 45 Hz), 130.90 (s), 129.06 (d, J(PC) = 10 Hz)	57.14 (d, J(PC) = 8 Hz)	65.47 (s, CH$_3$)
3	7.84 (m, 15H)	3.98 (d, J(PH) = 8 Hz 4H)	[c]	219.05 (d, J(PC) = 12 Hz), 218.12 (d, J(PC) = 22 Hz), 216.02 (d, J(PC) = 16 Hz)	134.37 (d, J(PC) = 40 Hz), 133.45 (d, J(PC) = 12 Hz), 130.27 (s), 128.72 (d, J(PC) = 9 Hz)	75.00 (d, J(PC) = 12 Hz)	[c]
4 [d]	7.75 (m, 15H)	3.15 (d, J(PH) = 14 Hz, 2H)		223.33 (br), 215.27 (br), 214.85 (br)	133.51 (d, J(PC) = 3 Hz), 133.12 (d, J(PC) = 9 Hz), 129.67 (d, J(PC) = 11 Hz), 125.68 (d, J(PC) = 83 Hz)	−12.33 (d, J(PC) = 26 Hz)	

[a] At 250 MHz, ambient probe temperature, and referenced to (CH$_3$)$_4$Si. [b] In C$_6$D$_6$ unless noted. [c] Resonances due to hexane, [d] In CD$_3$COCD$_3$ for ^{1}H NMR and CD$_2$Cl$_2$ for ^{13}C NMR.

constant ^{2}J(PC) of **1b**, **2b** and **3**. The chemical shifts of methylene carbons of **1b** and **4** are highly shielded as has been noted in Mn(CO)$_5$CH$_2$I [7], Mn(CO)$_4$(PPh$_3$)CH$_2$I [8], Fe(CO)$_4$CH$_2$PPh$_3$ [16], [(η^5-C$_5$H$_5$)Fe(CO)$_2$CH$_2$PPh$_3$]$^+$BF$_4^-$ [17] and [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)CH$_2$PPh$_3$]$^+$PF$_6^-$ [18]. The ^{13}C NMR spectra of **4** shows a doublet with J(PC) = 83 Hz for the P-bound phenyl carbon (*ipso*). A similar large coupling constant for the *ipso* carbon was also observed for [(η^5-C$_5$H$_5$)Fe(CO)$_2$CH$_2$PPh$_3$]$^+$BF$_4^-$ [17]. ^{13}C NMR spectra of each of **1b**, **2b** and **3** exhibits three doublets for the terminal carbonyls as expected for *cis* disubstituted manganese and rhenium tetracarbonyl complexes; however, three broad resonances are observed for the terminal carbonyls of **4**. The ^{1}H NMR spectrum of **3** shows resonances at δ 1.23 and 0.88 as multiplets due to hexane. The integration ratio shows that in this sample about 0.14 mol of hexane is associated with 1 mol of **3**. The ^{13}C NMR spectra of **3** also shows resonances at δ 31.88, 22.97 and 14.28 due to hexane [19]. The position of the ^{31}P NMR chemical shifts of **1b** and **2b** (12.53 and 11.34 ppm, respectively) indicate considerable shielding compared to the corresponding chemical shift positions for analogous **1a** and **2a** (59.8 and 60.9 ppm, respectively) [20]. The literature reports on other *cis*-disubstituted Mn compounds [6,21] indicate the generality of this difference.

X-ray structures of 1a, 3 and 4

The conformations and atomic numbering schemes for **1a**, **3** and **4** are shown in Fig. 1, 2 and 3 respectively. Crystal data for **1a**, **3** and **4** were obtained under the conditions summarized in Table 2.

The atomic coordinates and equivalent isotropic displacement parameters for **1a** are given in Table 3, and selected bond lengths and angles for **1a** are compiled in Table 4. The Mn atom in **1a** is octahedrally coordinated to four carbonyls, triphenyl phosphine, and the iodomethyl group. The Mn–C_{CH_2} bond length of 2.146(4) Å is approximately equal to the sum of the covalent radii of zero oxidation Mn (1.39 Å) [22] and sp^3 C (0.772 Å) but appreciably shorter than Mn–C_{CH_2} bond length of $CH_3COCH_2Mn(CO)_4P(C_6H_5)_3$ (2.210(5) Å) [23] and Mn–C_{CH_3} bond length of $CH_3Mn(CO)_4P(C_6H_5)_3$ (2.30(6) Å) [24]. It is possible therefore that as has been suggested previously [25] a hyperconjugative effect is operating:

$$MnCH_2I \longleftrightarrow Mn{=}CH_2{}^{+}I^{-}$$

The Mn–P bond length of 2.362(1) Å is shorter than the "σ-only" value of 2.48 Å

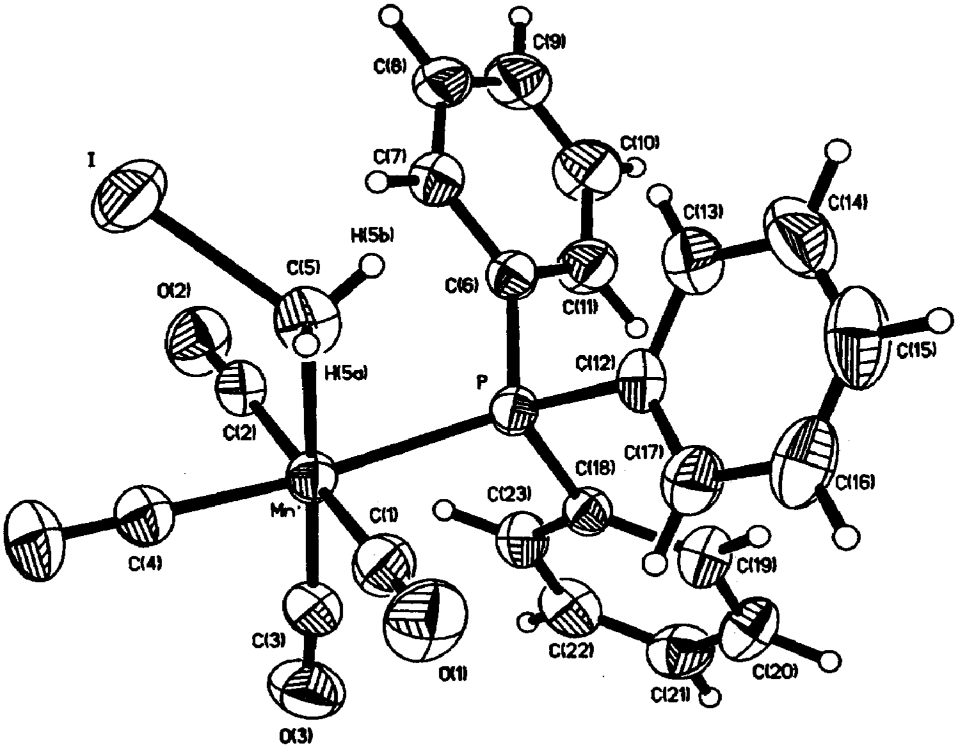

Fig. 1. A perspective drawing of molecule **1a**.

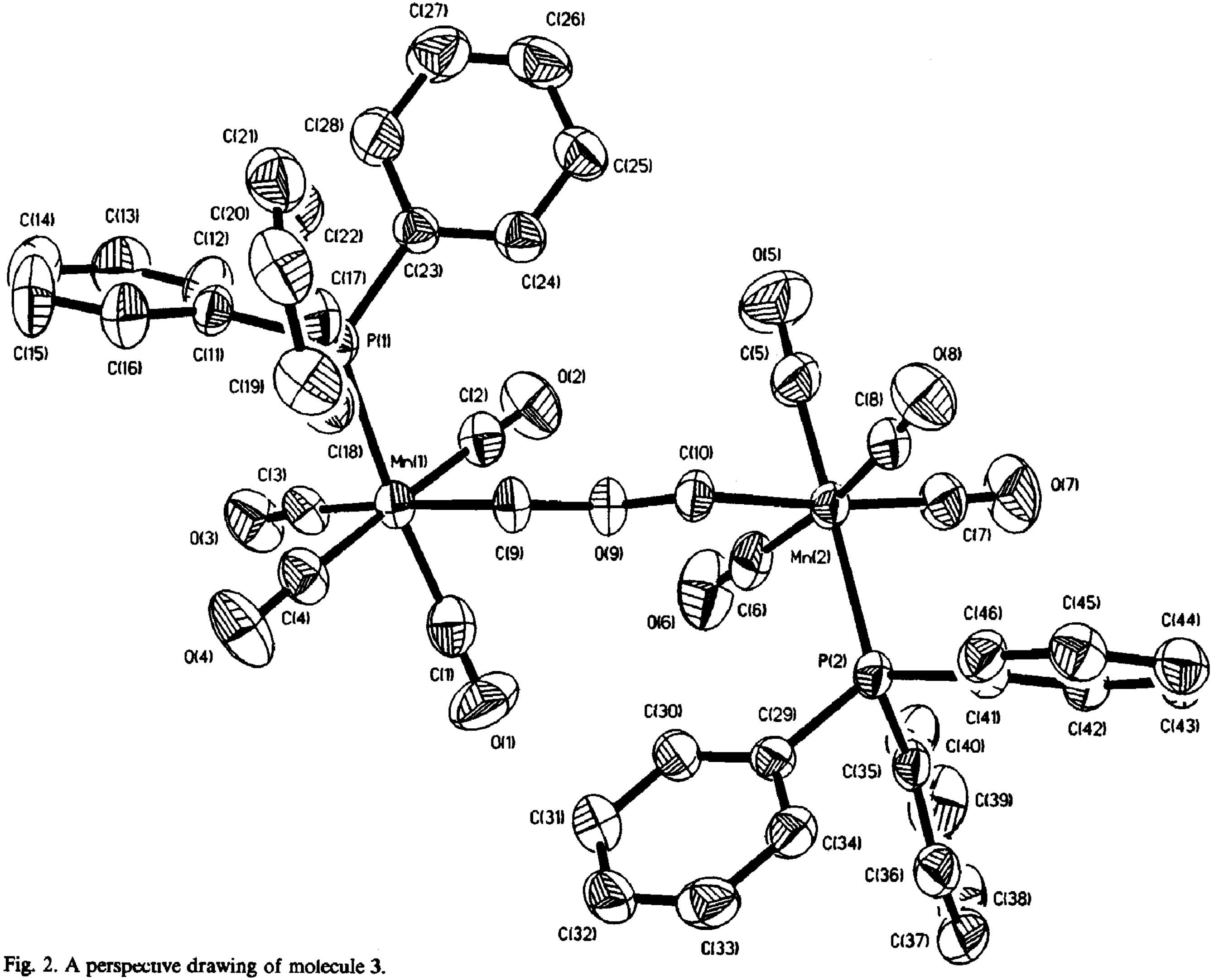

Fig. 2. A perspective drawing of molecule 3.

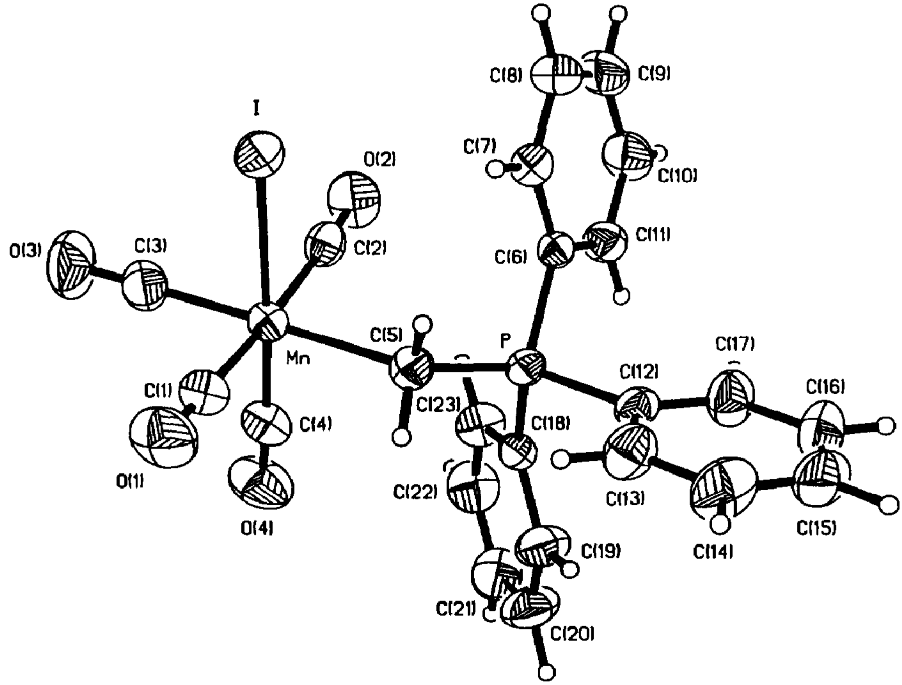

Fig. 3. A perspective drawing of molecule 4.

[26]; however, similar bond lengths were observed in $CH_3COCH_2Mn(CO)_4P(C_6H_5)_3$ (2.343(1) Å) [23] and $CH_3Mn(CO)_4P(C_6H_5)_3$ (2.311(18) Å) [24]. Structures of three iodomethyl complexes have been reported to date [25,27,28] and may be used for comparison, The $Mn-C_{CH_2}-I$ bond angle of 118.5(2)° in **1a** is larger than the corresponding bond angle of 110.5(9) and 115.0(7)° in *cis*-$PtI(PPh_3)_2CH_2I$ [27] and $[\{Ir(\mu\text{-}C_5H_4NS)(CO)_2\}_2(CH_2I)I]$ [28] respectively but smaller than the corresponding bond angle of 120(1)° in *trans*-$Fe(CO)_2[P(O\text{-}{}^iPr)_3]_2(I)CH_2I$ [25]; however, almost the same bond angle of 118.8(3)° has been observed in **1b** [29*]. Thus the methylene carbons in **1a** and **1b** are severely distorted from tetrahedral geometry.

The atomic coordinates and equivalent isotropic displacement parameters for **3** are given in Table 5, and selected bond lengths and angles for **3** are compiled in Table 6. Both Mn(1) and Mn(2) in **3** are octahedrally coordinated to four terminal carbonyls, one triphenylphosphine and one bridging 2-oxapropane-1,3-diide. The average $Mn-C_{CH_2}$ bond length of 2.152(4) Å is within the usual range for a Mn–C single bond; the average $C_{CH_2}-O$ bond length of 1.436 Å is virtually identical to the C–O "σ-only" value of 1.43 Å. A similar average C_{CH_2}-bond length of 1.44 Å was observed in $[L(NO)(CO)ReCH_2OCH_2Re(CO)(NO)L)I_2$ [11].

The atomic coordinates and equivalent isotropic displacement parameters for **4** are given in Table 7, and selected bond lengths and angles for **4** are given in Table 8. The central manganese atom in **4** is also octahedrally coordinated to four carbonyls, one iodine and the ylid ligand, (CH_2PPh_3). $C_{CH_2}-P$ bond lengths of 1.761(3) Å in **4** is shorter than the 1.806 Å bond length for the average $P-C_{Ph}$ bond. Thus, the

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* Reference number with asterisk indicates a note in the list of references.

Table 2

Summary of crystal data for *cis*-$Mn(CO)_4(PPh_3)CH_2I$ (**1a**), $[(CO)_4(PPh_3)MnCH_2]_2O \cdot 1/2C_6H_{14}$ (**3**) [a] and *cis*-$Mn(CO)_4I(CH_2PPh_3)$ (**4**)

	1a	**3**	**4**
Formula	$C_{23}H_{17}IMnO_4P$	$C_{49}H_{41}Mn_2O_9P_2$	$C_{23}H_{17}IMnO_4P$
M	570.2	945.7	570.2
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$
a (Å)	10.469(1)	9.780(2)	15.519(2)
b (Å)	10.758(1)	12.238(2)	9.525(1)
c (Å)	11.384(1)	20.508(3)	17.031(2)
α (°)	91.699(7)	106.56(1)	
β (°)	102.949(6)	91.69(1)	115.699(8)
γ (°)	115.349(6)	101.02(1)	
V (Å^3)	1117.7(2)	2300.1(6)	2268.4(4)
Z	2	2	4
d(calcd.), $g \cdot cm^{-3}$	1.69	1.37	1.67
μ ($M_0 - K_\alpha$), cm^{-1}	20.3	6.47	20.0
crystal size, mm.	0.32×0.32×0.42	0.05×0.12×0.45	0.28×0.50×0.50
F(000)	560	974	1120
Reflections collected	5421	10899	5745
Reflections merged (Rm)	5158(0.0093)	10606(0.0243)	5242(0.0140)
Reflections observed, $F \geqslant 6\sigma(F)$	3858	4662	3819
No. of variables	295	559	289
R	0.0296	0.0462	0.0295
R_w	0.0380	0.0484	0.0317
Goodness of fit	1.55	1.32	1.60

[a] Details of measurement: Diffractometer: Nicolet R3m for **1a** and **4** and Siemens R3m/V for **3**, radiation: Mo-K_α ($\lambda = 0.71073$), monochrometer: highly oriented graphite crystal, temperature: 294 K, scan type: $2\theta - \theta$, 2θ range: 3–55°, scan speed: 2–8°/min for **1a** and **4** and 4–8°/min for **3**, scan range (°): 0.8 on either side of $K_{\alpha_{12}}$, R: $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, R_w: $[\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i|F_o|^2]^{1/2}$ where, $w = [\sigma^2(F) + |g|F^2]^{-1}$ and $g = 0.000254$ for **1a**, $g = 0.000321$ for **3** and $g = 0.000113$ for **4**.

C_{CH_2}–P bond length is slightly shorter than expected for a single bond but longer than expected for a double bond (1.67 Å). Similar C_{CH_2}–P bond lengths of 1.787(7), 1.791(5), 1.755(13), 1.77(3), 1.748(7) and 1.80(2) Å were observed in $Mn_2(CO)_6(S_2CPCy_3)$ [30], $[(\eta^5\text{-}C_5H_5)(CO)_2Mn\{\mu\text{-}C(PMe_3)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]BF_4$ [31], $Me_3AuCH_2PPh_3$ [32], *trans*-$[Pt(CH_2PEt_3)(PEt_3)_2I]I$ [33], $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3][CF_3SO_3]$ [34] and *cis*-$[Pt(CH_2PPh_3)(PPh_3)_2Cl]I$ [35] respectively. In CH_2PPh_3 [36] the C_{CH_2}–P bond length of 1.661(8) Å clearly indicates the sp^2 hybridization of the methylene carbon. Thus the increased C_{CH_2}–P bond length in **4** and the ylid complexes noted above indicates that these methylene carbons are best described as sp^3 hybridized. The Mn–C_{CH_2}–P angle of 123.6(2)° in **4** is appreciably larger than the tetrahedral geometry; these severe distortions were also observed in the ylid complexes noted above and in $[(\eta^5\text{-}C_5Me_5)W(CO)_3CH_2PPh_3]I$ [37]. As noted previously [37] compounds with the longest C_{CH_2}–P bond length tend to have the largest M–C_{CH_2}–P angles; also, the M–C_{CH_2}–P angle appears to be dependent on the metal and its ligands.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *cis*-$Mn(CO)_4(PPh_3)CH_2I$ (**1a**)

Atom	x	y	z	U_{eq} [a]
Mn	3519(1)	1264(1)	1726(1)	33(1)
C(1)	4062(3)	−7(3)	2453(3)	45(1)
O(1)	4319(3)	−815(3)	2932(3)	68(1)
C(2)	2916(3)	2550(3)	1089(3)	39(1)
O(2)	2519(3)	3292(3)	658(2)	57(1)
C(3)	3685(3)	742(3)	250(3)	44(1)
O(3)	3704(3)	352(3)	−686(2)	61(1)
C(4)	1621(3)	−42(3)	1354(3)	46(1)
O(4)	430(3)	−855(3)	1123(3)	71(1)
C(5)	3271(4)	1682(4)	3495(3)	44(1)
I	1396(1)	2001(1)	3610(1)	63(1)
P	5935(1)	3069(1)	2355(1)	31(1)
C(6)	6135(3)	4846(3)	2557(3)	34(1)
C(7)	5180(3)	5145(3)	3065(3)	41(1)
C(8)	5392(4)	6498(3)	3275(3)	45(1)
C(9)	6518(4)	7557(4)	2985(3)	52(2)
C(10)	7459(4)	7292(3)	2469(4)	58(2)
C(11)	7277(4)	5947(3)	2260(3)	48(1)
C(12)	7037(3)	2971(3)	3816(3)	36(1)
C(13)	7551(4)	3988(4)	4819(3)	50(2)
C(14)	8389(4)	3872(5)	5907(4)	68(2)
C(15)	8727(4)	2771(5)	5996(4)	69(2)
C(16)	8240(4)	1769(4)	5020(4)	58(2)
C(17)	7369(3)	1854(3)	3925(3)	45(1)
C(18)	7049(3)	3184(3)	1295(3)	32(1)
C(19)	8375(3)	3126(3)	1621(3)	43(1)
C(20)	9154(4)	3201(4)	760(3)	53(2)
C(21)	8643(4)	3369(3)	−404(3)	51(2)
C(22)	7344(4)	3462(4)	−737(3)	50(2)
C(23)	6543(3)	3359(3)	106(3)	42(1)
				U_{iso}
H(5a)	3136(35)	988(36)	3900(31)	42(9)
H(5b)	3968(36)	2408(34)	3981(30)	37(9)
H(7)	4374	4405	3269	40(9)
H(8)	4736	6693	3630	53(10)
H(9)	6657	8494	3141	65(11)
H(10)	8244	8042	2252	74(13)
H(11)	7945	5770	1908	58(10)
H(13)	7329	4766	4760	43(9)
H(14)	8735	4568	6602	63(11)
H(15)	9310	2706	6752	101(16)
H(16)	8493	1010	5083	74(13)
H(17)	6999	1135	3245	58(11)
H(19)	8760	3034	2444	43(9)
H(20)	10060	3134	990	68(12)
H(21)	9189	3423	−991	68(12)
H(22)	6991	3598	−1554	62(11)
H(23)	5629	3411	−136	42(9)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4

Selected bond length (Å) and bond angles (°) for *cis*-$Mn(CO)_4(PPh_3)CH_2I$ (**1a**)

Mn–C(1)	1.844(4)	C(3)–O(3)	1.140(5)
Mn–C(2)	1.855(4)	C(4)–O(4)	1.138(4)
Mn–C(3)	1.825(4)	C(5)–I	2.164(5)
Mn–C(4)	1.816(3)	P–C(6)	1.833(3)
Mn–C(5)	2.146(4)	P–C(12)	1.834(3)
Mn–P	2.362(1)	P–C(18)	1.830(4)
C(1)–O(1)	1.135(5)	C(5)–H(5a)	0.866(38)
C(2)–O(2)	1.125(5)	C(5)–H(5b)	0.868(26)
C(1)–Mn–C(2)	175.8(2)	Mn–C(2)–O(2)	177.1(3)
C(1)–Mn–C(3)	92.7(2)	Mn–C(3)–O(3)	175.8(2)
C(2)–Mn–C(3)	91.3(2)	Mn–C(4)–O(4)	179.7(5)
C(1)–Mn–C(4)	89.0(2)	Mn–C(5)–I	118.5(2)
C(2)–Mn–C(4)	89.7(2)	Mn–P–C(6)	116.7(1)
C(3)–Mn–C(4)	90.5(2)	Mn–P–C(12)	115.1(1)
C(1)–Mn–C(5)	82.7(2)	C(6)–P–C(12)	102.8(1)
C(2)–Mn–C(5)	93.3(2)	Mn–P–C(18)	114.4(1)
C(3)–Mn–C(5)	174.6(2)	C(6)–P–C(18)	102.0(1)
C(4)–Mn–C(5)	86.8(2)	C(12)–P–C(18)	104.0(1)
C(1)–Mn–P	92.6(1)	Mn–C(5)–H(5a)	112.3(27)
C(2)–Mn–P	88.4(1)	Mn–C(5)–H(5b)	117.9(25)
C(3)–Mn–P	94.7(1)	H(5a)–C(5)–H(5b)	106.0(31)
C(4)–Mn–P	174.5(1)	H(5a)–C(5)–I	99.8(28)
C(5)–Mn–P	88.2(1)	H(5b)–C(5)–I	100.1(30)
Mn–C(1)–O(1)	175.5(4)		

Experimental

All reactions and preparations were carried out under a nitrogen atmosphere and with solvents dried prior to use. Reagent grade chemicals were used without further purification. The following compounds were obtained commercially: $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (Pressure Chemical Co.); HI (57% solution in water), *p*-toluenesulfonic acid monohydrate and $(CH_3)_3SiI$ (Aldrich Chemical Company, Inc.). Starting material **2a** [4], *cis*-$Mn(CO)_4(PPh_3)CHO$ [38] and *cis*-$Re(CO)_4(PPh_3)CHO$ [5] were synthesized by literature procedures.

IR spectra were recorded on a Perkin Elmer 1600 series FT-IR instrument. NMR spectra were recorded on a Bruker AC 250 (250.133 MHz, ^1H; 101.256 MHz, ^{31}P; 62.896, MHz, ^{13}C) spectrometer. Mass spectra were obtained on a Kratos MS 80 for high resolution and HP 5995C for low resolution. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Microanalyses were conducted by Galbraith Laboratories, Inc.

Synthesis of cis-*$Re(CO)_4(PPh_3)CH_2OCH_3$* (*2b*)

A solution of $[Re(CO)_5PPh_3]^+BF_4^-$ [39*] (2.5 g, 3.70 mmol) in CH_2Cl_2 (35 ml) at −78°C was treated with 3.7 ml (3.70 mmol) of 1.0 *M* $Li(C_2H_5)_3BH$ in THF. The reaction mixture was warmed and at −23°C [5] *p*-toluenesulfonic acid monohydrate (0.75 g, 3.94 mmol) in methanol (200 ml) was added and the solution was stirred vigorously. When the solution came to room temperature, the solvents

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[(CO)_4(PPh_3)MnCH_2]_2O \cdot 1/2C_6H_{14}$ (3)

Atom	x	y	z	U_{eq} [a]
Mn(1)	2895(1)	201(1)	3978(1)	36(1)
Mn(2)	7946(1)	2366(1)	2078(1)	37(1)
P(1)	3359(1)	−1522(1)	3222(1)	36(1)
P(2)	7098(1)	2973(1)	1190(1)	33(1)
O(1)	2522(5)	2300(4)	2699(3)	86(2)
O(2)	5412(4)	1649(3)	4012(2)	70(2)
O(3)	1103(4)	703(4)	4222(2)	68(2)
O(4)	234(4)	−1022(4)	2224(2)	78(2)
O(5)	8983(5)	1621(5)	3211(3)	99(3)
O(6)	6133(5)	3616(4)	3036(2)	82(2)
O(7)	10452(4)	4264(4)	2356(3)	90(2)
O(8)	9307(4)	659(4)	1137(2)	70(2)
O(9)	5324(3)	979(3)	2377(2)	41(1)
C(1)	2679(6)	1503(5)	2846(3)	52(3)
C(2)	4489(6)	1073(5)	3652(3)	47(2)
C(3)	1811(5)	473(5)	3792(3)	43(2)
C(4)	1295(6)	−597(5)	2535(3)	47(2)
C(5)	8574(6)	1904(5)	2770(3)	55(3)
C(6)	6805(6)	3142(5)	2662(3)	50(2)
C(7)	9459(6)	3556(5)	2249(3)	53(3)
C(8)	8795(5)	1355(5)	1491(3)	43(2)
C(9)	4172(5)	−13(4)	2230(2)	38(2)
C(10)	6296(5)	841(4)	1867(3)	39(2)
C(11)	2166(5)	−2098(4)	3776(3)	40(2)
C(12)	2297(6)	−1525(5)	4474(3)	54(2)
C(13)	1379(7)	−1936(6)	4890(3)	66(3)
C(14)	311(7)	−2895(6)	4617(4)	74(3)
C(15)	148(6)	−3437(6)	3927(4)	75(3)
C(16)	1088(6)	−3040(5)	3508(3)	55(2)
C(17)	3249(5)	−2798(4)	2467(3)	37(2)
C(18)	2705(5)	−2835(5)	1828(3)	47(2)
C(19)	2605(6)	−3835(5)	1278(3)	55(3)
C(20)	3036(6)	−4793(5)	1371(3)	59(3)
C(21)	3583(6)	−4762(5)	1998(3)	58(3)
C(22)	3687(5)	−3777(5)	2542(3)	50(2)
C(23)	5111(5)	−1425(4)	3609(3)	37(2)
C(24)	6266(5)	−843(4)	3372(3)	46(2)
C(25)	7613(6)	−801(5)	3617(3)	52(2)
C(26)	7838(6)	−1329(5)	4104(3)	65(3)
C(27)	6715(7)	−1904(5)	4350(3)	73(3)
C(28)	5358(6)	−1958(5)	4099(3)	60(3)
C(29)	5293(5)	2315(4)	807(3)	36(2)
C(30)	4278(5)	2219(4)	1256(3)	43(2)
C(31)	2874(5)	1823(5)	1019(3)	55(3)
C(32)	2482(6)	1488(5)	331(3)	55(3)
C(33)	3478(6)	1582(5)	−118(3)	54(2)
C(34)	4887(5)	1995(4)	115(3)	46(2)
C(35)	7066(5)	4528(4)	1374(3)	37(2)
C(36)	6497(6)	4917(5)	857(3)	48(2)
C(37)	6497(6)	6087(6)	981(4)	65(3)
C(38)	6925(7)	6868(5)	1617(4)	70(3)

Table 5 (continued)

Atom	x	y	z	U_{eq} [a]
C(39)	7427(7)	6491(6)	2127(4)	76(3)
C(40)	7493(6)	5330(5)	2008(3)	56(3)
C(41)	8197(8)	2750(4)	480(2)	34(2)
C(42)	8301(5)	3637(4)	451(3)	40(2)
C(43)	10176(5)	3433(5)	−66(3)	45(2)
C(44)	9968(6)	2381(5)	−563(3)	49(2)
C(45)	8889(5)	1491(5)	−533(3)	47(2)
C(46)	8023(5)	1662(4)	−15(3)	40(2)
C(1S)	5358(50)	4883(34)	5248(23)	332(30)
C(2S)	6815(41)	5292(26)	5220(17)	386(27)
C(3S)	7610(32)	5406(21)	5788(10)	287(19)
				U_{iso}
H(9a)	3623	−64	1823	80
H(9b)	4525	−713	2166	80
H(10a)	6693	179	1860	80
H(10b)	5813	716	1429	80
H(12)	3023	−846	4666	80
H(13)	1484	−1552	5373	80
H(14)	−316	−3183	4910	80
H(15)	−613	−4088	3733	80
H(16)	982	−3429	3025	80
H(18)	2396	−2171	1764	80
H(19)	2235	−3858	835	80
H(20)	2951	−5485	992	80
H(21)	3894	−5427	2059	80
H(22)	4069	−3763	2982	80
H(24)	6123	−465	3032	80
H(25)	8394	−399	3445	80
H(26)	8774	−1299	4273	80
H(27)	6868	−2269	4695	80
H(28)	4582	−2371	4269	80
H(30)	4548	2427	1737	80
H(31)	2176	1784	1336	80
H(32)	1515	1190	165	80
H(33)	3201	1360	−598	80
H(34)	5575	2057	−204	80
H(36)	6237	4375	414	80
H(37)	6158	6351	620	80
H(38)	6872	7671	1704	80
H(39)	7736	7035	2569	80
H(40)	7840	5079	2372	80
H(42)	9452	4385	789	80
H(43)	10948	4042	−77	80
H(44)	10567	2265	−929	80
H(45)	8744	749	−876	80
H(46)	7293	1030	9	80

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

were removed on a rotary evaporator. Extraction of the residue with hexane separated **2b** from the cation, $[Re(CO)_5PPh_3]^+OTs^-$. The hexane solution was extracted with water in order to remove any dissolved *p*-toluenesulfonic acid.

Table 6

Selected bond length (Å) and bond angles (°) for $[(CO)_4(PPh_3)MnCH_2]_2O \cdot 1/2C_6H_{14}$ (3)

Mn(1)–P(1)	2.336(2)	Mn(2)–C(10)	2.150(4)
Mn(1)–C(1)	1.834(7)	O(1)–C(1)	1.136(9)
Mn(1)–C(2)	1.869(5)	O(2)–C(2)	1.131(6)
Mn(1)–C(3)	1.824(5)	O(3)–C(3)	1.143(7)
Mn(1)–C(4)	1.826(5)	O(4)–C(4)	1.148(6)
Mn(1)–C(9)	2.155(5)	O(5)–C(5)	1.142(9)
Mn(2)–P(2)	2.340(2)	O(6)–C(6)	1.131(7)
Mn(2)–C(5)	1.803(7)	O(7)–C(7)	1.140(6)
Mn(2)–C(6)	1.849(6)	O(8)–C(8)	1.155(7)
Mn(2)–C(7)	1.813(5)	O(9)–C(9)	1.443(5)
Mn(2)–C(8)	1.809(5)	O(9)–C(10)	1.430(6)
P(1)–Mn(1)–C(1)	171.1(2)	P(2)–Mn(2)–C(8)	91.3(2)
P(1)–Mn(1)–C(2)	90.9(2)	C(5)–Mn(2)–C(8)	89.5(3)
C(1)–Mn(1)–C(1)	89.7(3)	C(6)–Mn(2)–C(8)	168.7(2)
P(1)–Mn(1)–C(3)	94.9(2)	C(7)–Mn(2)–C(8)	93.7(2)
C(1)–Mn(1)–C(3)	94.0(3)	P(2)–Mn(2)–C(10)	93.4(2)
C(2)–Mn(1)–C(3)	90.7(2)	C(5)–Mn(2)–C(10)	86.3(2)
P(1)–Mn(1)–C(4)	91.1(2)	C(6)–Mn(2)–C(10)	87.1(2)
C(1)–Mn(1)–C(4)	88.6(3)	C(7)–Mn(2)–C(10)	174.3(2)
C(2)–Mn(1)–C(4)	177.4(3)	C(8)–Mn(2)–C(10)	81.7(2)
C(3)–Mn(1)–C(4)	87.5(2)	C(9)–O(9)–C(10)	111.9(3)
P(1)–Mn(1)–C(9)	88.6(2)	Mn(1)–C(1)–O(1)	178,8)
C(1)–Mn(1)–C(9)	82.5(2)	Mn–(1)–C(2)–O(2)	176.0(5)
C(2)–Mn(1)–C(9)	88.6(2)	Mn(1)–C(3)–O(3)	175.1(6)
C(3)–Mn(1)–C(9)	176.5(2)	Mn(1)–C(4)–O(4)	174.0(5)
C(4)–Mn(1)–C(9)	93.1(2)	Mn(2)–C(5)–O(5)	179.3(5)
P(2)–Mn(2)–C(5)	179.0(2)	Mn(2)–C(6)–O(6)	177.8(6)
P(2)–Mn(2)–C(6)	90.4(2)	Mn(2)–C(8)–O(8)	175,7(6)
C(5)–Mn(2)–C(6)	88.7(3)	Mn(2)–C(8)–O(8)	175.7(6)
P(2)–Mn(2)–C(7)	89.9(2)	Mn(1)–C(9)–O(9)	108.8(3)
C(5)–Mn(2)–C(7)	90.5(3)	Mn(2)–C(10)–O(9)	110.8(3)
C(6)–Mn(2)–C(7)	97.5(2)		

Drying the hexane solution with anhydrous $MgSO_4$ and removal of hexane on a rotary evaporator gave a white residue which contained **2b** and a trace of $(CO)_4ReP(C_6H_5)_2(o\text{-}C_6H_4CH_2)$. Crystallization of the crude mixture in hexane afforded white crystalline **2b** (0.87 g, 1.44 mmol, 39%), m.p. 80–81°C. IR (cm^{-1}, hexane): $\nu_{(C\equiv O)}$ 2071.2m, 1999.5s, 1982.3vs, 1947.0s. $^{31}P\{^1H\}$ NMR(δ, C_6D_6): 11.35(s). Anal. Found: C, 47.3; H, 3.2. $C_{24}H_{20}O_5PRe$ calcd.: C, 47.6; H, 3.3%.

The hexane insoluble product was dissolved in CH_2Cl_2 (30 ml) and extracted with water. The CH_2Cl_2 solution obtained after drying with anhydrous $MgSO_4$ was evaporated to dryness to give $[Re(CO)_5PPh_3]^+OTs^-$ (1.21 g, 1.59 mmol, 43%) as a white solid.

Synthesis of cis-*Mn(CO)$_4$(PPh$_3$)CH$_2$I (1a)*

To a solution of **2a** (1.5 g, 3.16 mmol) in CH_2Cl_2 (75 ml) was added $(CH_3)_3SiI$ (0.65 ml, 4.74 mmol) at −78°C. The solution was allowed to warm to room temperature and the solvent was removed under vacuum. The residue was dissolved in a minimum quantity of CH_2Cl_2/hexane and cooled to −35°C. Light yellow

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *cis*-$Mn(CO)_4I(CH_2PPh_3)$ (4)

Atom	x	y	z	$U_{eq.}$ [a]
Mn	1248(1)	1771(1)	−914(1)	33(1)
I	2606(1)	604(1)	559(1)	46(1)
C(1)	1730(3)	636(4)	−1517(2)	45(1)
O(1)	2028(2)	−43(3)	−1862(2)	69(1)
C(2)	869(2)	2818(3)	−198(2)	39(1)
O(2)	601(2)	3405(3)	231(2)	59(1)
C(3)	458(3)	357(4)	−914(2)	48(2)
O(3)	−44(2)	−498(3)	−926(2)	81(2)
C(4)	318(3)	2467(4)	−1890(2)	45(2)
O(4)	−309(2)	2846(3)	−2506(2)	70(1)
P	2263(1)	5082(1)	−735(1)	28(1)
C(5)	2307(2)	3270(3)	−919(2)	34(1)
C(6)	2289(2)	5460(3)	312(2)	30(1)
C(7)	2801(2)	4577(3)	1011(2)	39(1)
C(8)	2864(3)	4865(4)	1826(2)	53(2)
C(9)	2408(3)	6028(5)	1950(2)	59(2)
C(10)	1913(3)	6928(4)	1270(2)	53(2)
C(11)	1854(2)	6653(3)	451(2)	40(1)
C(12)	3275(2)	6013(3)	−748(2)	34(1)
C(13)	3891(2)	5364(4)	−1024(2)	49(2)
C(14)	4640(3)	6107(5)	−1059(3)	64(2)
C(15)	4772(3)	7484(5)	−820(3)	66(2)
C(16)	4169(3)	8128(5)	−541(3)	67(2)
C(17)	3414(3)	7395(4)	−507(3)	51(2)
C(18)	1221(2)	5858(3)	−1592(2)	31(1)
C(19)	1277(3)	6311(4)	−2340(2)	52(2)
C(20)	466(3)	6826(5)	−3036(3)	67(2)
C(21)	−388(3)	6922(4)	−2972(3)	59(2)
C(22)	−446(3)	6474(4)	−2239(3)	56(2)
C(23)	346(2)	5926(4)	−1553(2)	44(1)
				U_{iso}
H(5a)	2302	3189	−1483	53(10)
H(5b)	2911	2950	−481	46(10)
H(7)	3113	3761	924	33(8)
H(8)	3225	4257	2308	58(11)
H(9)	2436	6212	2515	65(11)
H(10)	1609	7747	1364	88(15)
H(11)	1513	7284	−22	38(9)
H(13)	3799	4393	−1192	52(11)
H(14)	5067	5651	−1251	86(15)
H(15)	5289	8001	−848	72(13)
H(16)	4268	9096	−368	65(12)
H(17)	2989	7856	−314	67(12)
H(19)	1875	6269	−2380	64(12)
H(20)	501	7115	−3561	77(13)
H(21)	−942	7306	−3446	68(12)
H(22)	−1042	6539	−2198	104(17)
H(23)	292	5590	−1045	46(10)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8

Selected bond length (Å) and bond angles (°) for *cis*-$Mn(CO)_4I(CH_2PPh_3)$ (4)

Mn–I	2.717(1)	C(2)–O(2)	1.133(5)
Mn–C(1)	1.858(4)	C(3)–O(3)	1.121(5)
Mn–C(2)	1.856(4)	C(4)–O(4)	1.137(4)
Mn–C(3)	1.821(4)	P–C(5)	1.761(3)
Mn–C(4)	1.790(3)	P–C(6)	1.802(4)
Mn–C(5)	2.181(3)	P–C(12)	1.813(4)
C(1)–O(1)	1.103(6)	P–C(18)	1.802(3)
I–Mn–C(1)	86.3(1)	C(3)–Mn–C(5)	173.2(2)
I–Mn–C(2)	87.3(1)	C(4)–Mn–C(5)	93.4(1)
C(1)–Mn–C(2)	173.6(1)	Mn–C(1)–O(1)	178.9(3)
I–Mn–C(3)	87.2(1)	Mn–C(2)–O(2)	176.3(3)
C(1)–Mn–C(3)	90.1(2)	Mn–C(3)–O(3)	178.6(3)
C(2)–Mn–C(3)	89.6(2)	Mn–C(4)–O(4)	175.7(4)
I–Mn–C(4)	177.3(1)	C(5)–P–C(6)	112.7(2)
C(1)–Mn–C(4)	93.3(2)	C(5)–P–C(12)	112.1(2)
C(2)–Mn–C(4)	93.1(2)	C(6)–P–C(12)	105.5(1)
C(3)–Mn–C(4)	90.2(2)	C(5)–P–C(18)	110.4(1)
I–Mn–C(5)	89.3(1)	C(6)–P–C(18)	110.3(2)
C(1)–Mn–C(5)	83.9(2)	C(12)–P–C(18)	105.5(1)
C(2)–Mn–C(5)	96.0(1)	Mn–C(5)–P	123.6(2)

crystals of **1a** (1.5 g, 2.63 mmol, 83%) were collected by filtration. The spectral characteristics of **1a** were reported previously [8].

Synthesis of cis-*$Re(CO)_4(PPh_3)CH_2I$ (1b)*

To a solution of **2b** (1.5 g, 2.14 mmol) in CH_2Cl_2 (75 ml) was added $(CH_3)_3SiI$ (0.45 ml, 3.16 mmol) at −78 °C. The solution was allowed to warm to room temperature and the solvent was removed under vacuum. The residue was dissolved in a minimum amount of CH_2Cl_2/hexane and cooled to −5 °C. White crystalline **2a** (1.35 g, 1.92 mmol, 90%), m.p. 110–111 °C was collected by filtration. IR(cm^{-1}, C_6H_6): $\nu_{(C\equiv O)}$ 2087.3m, 1988.7s, 1981.3vs, 1944.0s. $^{31}P\{^1H\}$ NMR(δ, C_6D_6): 12.44(s). Mass spectrum *m/e* (re. abund, comment): 701.9497 (75, M^+); 575 (33, $M^+ - I$); 646 (14, $M^+ - 2CO$); 618 (13, $M^+ - 3CO$); 590(48, $M^+ - 4CO$); 561 (100, $M^+ - CH_2I$); 533 (400, $M^+ - CH_2I - CO$); 505 (400, $M^+ - CH_2I - 2CO$); 449 (700, $M^+ - CH_2I - 4CO$); 262 (1000, PPh_3). Anal. Found: C, 39.7; H, 2.4. $C_{23}H_{17}IO_4PRe$ calcd.: C, 39.4; H, 2.4%.

Synthesis of $(CO)_4(PPh_4)MnCH_2OCH_2Mn(CO)_4(PPh_3)$ (3)

To a solution of *cis*-$Mn(CO)_4(PPh_3)CHO$ (1.5 g, 3.27 mmol) in toluene (50 ml) at −78 °C was added HI (57% in water, 0.75 ml, 3.34 mmol) with stirring. After 5 min the reaction mixture was allowed to warm up to room temperature. The mixture was filtered through a pad of Celite and the filtrate was evaporated to dryness under vacuum. The solid residue was then crystallized from a mixture of toluene and hexane at −5 °C. Light brown crystals of **3** (0.68, 0.75 mmol, 23%) were separated by filtration, m.p. 159–160 °C, IR (cm^{-1}, C_6H_6): $\nu_{(C\equiv O)}$ 2065.4m, 2056.2m, 1991.8s, 1967.9vs, 1962.2vs, 2065.4m, 1934.3vs. $^{31}P\{^1H\}$ NMR(δ, C_6D_6): 62.0(s). Anal. Found: C, 61.9; H, 4.2. $C_{46}H_{34}Mn_2O_9P_2 \cdot 0.35C_6H_{14}$ calcd.: C, 61.9; H, 4.2%.

Failed synthesis of the rhenium analog of 3

A solution of $[Re(CO)_5PPh_3]^+BF_4^-$ [39] (2.5 g, 3.70 mmol) in CH_2Cl_2 (30 ml) at −78°C was treated with 3.7 ml (3.70 mmol) of 1.0 *M* $Li(C_2H_5)_3BH$ in THF. The reaction mixture was warmed, at −23°C [5] toluene (200 ml) (previously cooled to −30°C) was added and the mixture was cooled to −78°C. HI (57% in water, 0.85 ml, 3.79 mmol) was added and stirred for 5 min. The mixture was warmed to room temperature and the solvents were removed under vacuum. The residue was extracted with benzene (150 ml) and the benzene solution was evaporated to dryness giving **1b** (1.11 g, 1.58 mmol, 43%) as a white solid.

The benzene insoluble product was dissolved in CH_2Cl_2 (30 ml) and extracted with water. The CH_2Cl_2 solution after drying with anhydrous $MgSO_4$ was evaporated to dryness to give $[Re(CO)_5PPh_3]^+I^-$ (1.17 g, 1.63 mmol, 44%) as an almost white powder.

Rearrangement of cis-*Mn(CO)₄(PPh₃)CH₂I (1a) to* cis-*Mn(CO)₄I(CH₂PPh₃) (4)*

A solution of **1a** (1.5 g, 2.63 mmol) in benzene (70 ml) was kept at room temperature for a day. After evaporation of the solvent under vacuum, the residue was crystallized from CH_2Cl_2/hexane at −5°C. Red crystals of **4** (1.37 g, 2.400 mmol, 91%) were obtained after filtration, m.p. 142–144°C. IR(cm^{-1}, C_6H_6): $\nu_{(C\equiv O)}$ 2066.0m, 1987.1vs, 1974.4s, 1929.8m, 1916.5m. $^{31}P\{^1H\}$ NMR(δ, CD_2Cl_2): 39.1(s). Anal. Found: C, 48.4; H, 3.0. $C_{23}H_{17}IMnO_4P$ calcd.: C, 48.4; H, 3.0%.

Attempted isomerization of cis-*Re(CO)₄(PPh₃)CH₂I (1b)*

A solution of **1b** (0.020 g, 0.029 mmol) in C_6D_6 (0.35 ml) was placed into a capped 5mm NMR tube and kept at room temperature. Periodic check of the disappearance of **1b** was performed by recording ^1H NMR spectrum. Even after 6 months practically no change was observed.

Methanolysis of 1a

1a (0.5 g, 0.88 mmol) was dissolved in methanol (100 ml) and refluxed for about an hour. The solvent was then removed under vacuum leaving a pale yellow solid **2a** (0.37 g, 0.78 mmol, 89%).

Methanolysis of 1b

1b (0.5 g, 0.71 mmol) was dissolved in methanol (150 ml) and refluxed for three hours. The solvent was removed under vacuum giving a white solid **2b** (0.41 g, 0.68 mmol, 96%).

X-ray crystal structure of cis-*Mn(CO)₄(PPh₃)CH₂I (1a)*

Suitable single crystals of **1a** were grown by crystallization from CH_2Cl_2/hexane at −35°C. Data were collected on a Nicolet R3m four-circle diffractometer as outlined in Table 2. Of 5158 reflections with $3 \leqslant 2\theta \leqslant 55°$ collected, 3858 with $F \geqslant 6\sigma(F)$ were used in the final refinement. The structure was solved by the Patterson method and refined by full-matrix least-squares. The non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were allowed to ride on their respective carbons (C–H = 0.96 Å) and the positional parameters for the methylene H atoms were free to vary. A final *R* index of 0.0296 with $R_w = 0.0380$ was obtained.

X-ray crystal structure of $(CO)_4(PPh_3)MnCH_2OCH_2Mn(PPh_3)(CO)_4$ *(3)*

Suitable crystals of **3** were grown by crystallization from toluene/hexane at −5 °C. Data were collected on a Siemens R3m/V diffractometer as outlined in Table 2. Of 10606 reflections with $3 \leqslant 2\theta \leqslant 55°$ collected, 4662 with $F \geqslant 6\sigma(F)$ were used in the final refinement. The structure was solved by direct method and refined by full-matrix least-squares. The non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were allowed to ride on their respective carbons (C–H = 0.96 Å). A hexane solvent molecule with inversion symmetry was located, and attempts were made to refine the site occupancy factors of its carbon atoms. Occupancies near 1.0 were obtained corresponding to a 2:1 mole ratio of complex : hexane. The H-atoms for the highly anisotropic hexane solvent molecule could not be seen in difference-Fourier maps, and were not included in any of the refinements. A final R index of 0.0462 with $R_w = 0.0484$ was obtained.

X-ray crystal structure of cis-$Mn(CO)_4I(CH_2PPh_3)$ *(4)*

Suitable single crystals of **4** were grown by crystallization from CH_2Cl_2/hexane at −5 °C. Data were collected on a Nicolet R3m four-circle diffractometer as outlined in Table 2. Of 5242 reflections with $3 \leqslant 2\theta \leqslant 55°$ collected, 3819 with $F \geqslant 6\sigma(F)$ were used in the final refinement. The structure was solved by the Patterson method and refined by full-matrix least-squares. The non-hydrogen atoms were refined with anisotropic temperature parameters and the hydrogen atoms were allowed to ride on their respective carbons (C–H = 0.96 Å). A final R index of 0.0295 with $R_w = 0.0317$ was obtained.

Details of structure factors and anisotropic temperature parameters of **1a**, **3** and **4** are available from the authors.

References and notes

1 (a) C. Masters, Adv. Organomet. Chem., 17 (1979) 61; (b) For recent references see A.R. Cutler, P.K. Hanna, J.C. Vites, Chem. Rev., 88 (1988) 1363.

2 (a) F. Garnier, P. Krausz, J. Mol. Catal., 8 (1980) 91; (b) H. Rudler, F. Rose, M. Rudler, C. Alvarez, ibid., 15 (1982) 81; (c) U. Klabunde, F.N. Tebbe, G.W. Parshall, R.L. Harlow, ibid., 8 (1980) 37; (d) H. Rudler, ibid., 8 (1980) 53; (e) T.R. Howard; J.B. Lee, R.H. Grubbs, J. Am. Chem. Soc., 102 (1980) 6876; (f) K.C. Ott, R.H. Grubbs, ibid., 103 (1981) 5922; (g) J. Levisalles, F. Rose-Munch, H. Rudler, J.C. Daran, Y. Dromzee, Y. Jeannin, J. Chem. Soc., Chem. Commun., (1981) 152; (h) A.F. Dyke, S.A.R. Knox, P.J. Naish, G.E. Traylor, ibid., (1980) 803.

3 (a) S.H. Pine, R. Zahler, D.A. Evans, R.H. Grubbs, J. Am. Chem. Soc., 102 (1980) 3270; (b) F.W. Hartner, Jr., J. Schwartz, ibid., 103 (1981) 4979.

4 (a) J.N. Cawse, R.A. Fiato, R.L. Pruett, J. Organomet. Chem., 172 (1979) 405; (b) S. Pelling, C. Botha, J.R. Moss, J. Chem. Soc., Dalton Trans., (1983) 1495.

5 W. Tam, G.-Y. Lin, J.A. Gladysz, Organometallics, 1 (1982) 525.

6 (a) G.D. Vaughn, J.A. Gladysz, J. Am. Chem. Soc., 103 (1981) 5608; (b) G.D. Vaughn, C.E. Strouse, J.A. Gladysz, J. Am. Chem. Soc., 108 (1986) 1462.

7 K.C. Brinkman, G.D. Vaughn, J.A. Gladysz, Organometallics, 1 (1982) 1056.

8 D.H. Gibson, S.K. Mandal, K. Owens, W.E. Sattich, J.O. Franco, Organometallics, 8 (1989) 1114.

9 S.L. Van Voorhees, B.B. Wayland, Organometallics, 4 (1985) 1887.

10 (a) C.P. Casey, S.M. Neumann, M.A. Andrews, D.R. McAlister, Pure Appl. Chem., 52 (1980) 624; (b) C.P. Casey, Mark A. Andrews, D.R. McAlister, J.E. Rinz, J. Am. Chem. Soc., 102 (1980) 1927.

11 (a) C. Pomp, H. Duddeck, K. Wieghardt, B. Nuber, J. Weiss, Angew. Chem., Int. Ed. Engl., 26 (1987) 924; (b) C. Pomp, K. Wieghardt, Inorg. Chem., 227 (1988) 3796.

12 T. Bodnar, E. Coman, K. Menard, A. Cutler, Inorg. Chem., 21 (1982) 1275.

13 H. Werner, L. Hofmann, R. Feser, W. Paul, J. Organomet. Chem., 281 (1985) 317.

14 T.B. Marder, W.C. Fultz, J.C. Calabrese, R.L. Harlow, D. Milstein, J. Chem. Soc., Chem. Commun., (1987) 1543.

15 (a) K.L. Borwn, G.R. Clark, C.E.L. Headford, K. Marsden, W.R. Roper, J. Am. Chem. Soc., 101 (1979) 503; (b) A.F. Hill, W.R. Roper, J.M. Waters, A.H. Wright, ibid., 105 (1983) 5939.

16 H. des Abbayes, J.-C. Clement, P. Laurent, J.-J. Yaouanc, G. Tanguy, B. Weinberger, J. Organomet. Chem., 359 (1989) 205.

17 D.L. Reger, E.C. Culbertson, J. Organomet. Chem., 131 (1977) 297.

18 W. Tam, G.-Y. Lin, W.-K. Wong, W.A. Kiel, V.K. Wong, J.A. Gladysz, J. Am. Chem. Soc., 104 (1982) 141.

19 R.M. Silverstein, G.C. Bassler, T.C. Morril, Spectrometric Identification of Organic Compounds, John Wiley & Sons, Inc., New York, 1981, p. 297.

20 S.K. Mandal, Ph.D. Thesis, University of Louisville, 1988.

21 G.D. Vaughn, J.A. Gladysz, J. Am. Chem. Soc., 108 (1986) 1473.

22 F.A. Cotton, D.C. Richardson, Inorg. Chem., 5 (1966) 1851.

23 J. Engelbrecht, T. Greiser, E. Weiss, J. Organomet. Chem., 204 (1981) 79.

24 A. Mawby, G.E. Pringle, J. Inorg. Nucl. Chem., 34 (1972) 877.

25 H. Berke, R. Birk, G. Huttner, L. Zsolnai, Z. Naturforsch. B, 39 (1984) 1380.

26 (a) M.J. Bennett, R. Mason, Nature, 205 (1965) 760; (b) M.R. Churchill, in: J.D. Dunitz, J.A. Ibers (Eds.), Perspectives in Structural Chemistry, John Wiley & Sons, New York, 1970, Vol. III, p. 126.

27 N.J. Kermode, M.F. Lappert, B.W. Skelton, A.H. White, J. Chem. Soc., Chem. Commun., (1981) 698.

28 M.A. Ciriano, F. Biguri, L.A. Oro, A. Tiripichhio, M. Tripichhio-Camellini, Angew. Chem., Int. Ed. Engl., 26 (1987) 444.

29 Details of the X-ray structure parameters of **1b** will be published shortly.

30 D. Miguel, V. Riera, J.A. Miguel, X. Solans, M. Font-Altaba, J. Chem. Soc., Chem. Commun., (1987) 472.

31 J.C. Jeffery, R. Navarro, H. Razay, F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1981) 2471.

32 J. Stein, J.P. Fackler, Jr., C. Paparizos, H.-W. Chem, J. Am. Chem. Soc., 103 (1981) 2192.

33 N.J. Kermode, M.F. Lappert, B.W. Skelton, A.H. White, J. Holton, J. Organomet. Chem., 228 (1982) C71.

34 M.R. Churchill, H.J. Wasserman, Inorg. Chem., 21 (1982) 3913.

35 C. Engelter, J.R. Moss, M.L. Niven, L.R. Nasimbeni, G. Reid, J.C. Spiers, J. Organomet. Chem., 315 (1986) 255.

36 J.C.J. Bart, J. Chem. Soc. B, (1969) 350.

37 J.R. Moss, M.L. Niven, P.M. Stretch, Inorg. Chim. Acta, 119 (1986) 177.

38 D.H. Gibson, K. Owens, S.K. Mandal, W.E. Sattich, J.O. Franco, Organometallics, 8 (1989) 498.

39 See D. Drew, D.J. Darensbourg, M.Y. Darensbourg, Inorg. Chem., 14 (1975) 1579; the method is similar to the $PPhMe_2$-substituted cation using $NO^+BF_4^-$ instead of $NO^+PF_6^-$.