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Synthesis of some manganese and rhenium trifluoroacetoxymethyl and iodomethyl complexes. X-ray structures of *cis*-$Re(CO)_4(PPh_3)CH_2OC(O)CF_3$, *fac*-$Re(CO)_3(dppp)CH_2OC(O)CF_3$ and *cis*-$Re(CO)_4(PPh_3)CH_2I$

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Abstract

The manganese and rhenium trifluoroacetoxymethyl complexes, *cis*-$Re(CO)_4(PPh_3)CH_2OC(O)CF_3$ (**1**), *fac*-$Mn(CO)_3(dppe)CH_2OC(O)CF_3$ (**2**), *fac*-$Mn(CO)_3(dppp)CH_2OC(O)CF_3$ (**3**), *fac*-$Re(CO)_3(dppe)CH_2OC(O)CF_3$ (**4**), *fac*-$Re(CO)_3(dppp)CH_2OC(O)CF_3$ (**5**) and the manganese iodomethyl complex *fac*-$Mn(CO)_3(dppp)CH_2I$ (**6**), have been prepared by treating the corresponding methoxymethyl complexes with CF_3COOH and $(CH_3)_3SiI$, respectively. Structural characterizations of **1**, **5** and *cis*-$Re(CO)_4(PPh_3)CH_2I$ (**7**) show rhenium–carbon (Re–CH_2) bond lengths of 2.267(8), 2.242(3) and 2.38(8) Å, respectively. The Re–C^{CH2}–I bond angle of 118.8(3)° in **7** indicates that the methylene carbon is severely distorted from tetrahedral geometry.

Keywords: Synthesis; Manganese; Rhenium; Trifluoroacetoxymethyl; Iodomethyl; X-ray structures

1. Introduction

The chemistry of functional groups bonded to a transition metal can be vastly different from the chemistry of the same functional groups observed in traditional organic chemistry. Consider the ester grouping, –C(O)OR. Although ionization to $–C(O)^+OR^-$ is rare in organic chemistry, the Mn complex, $(dppe)(CO)_3Mn–C(O)OCH_3$ ionizes in CH_2Cl_2 solution almost completely leading to a series of remarkable interconversions at room temperature and the isolation of the corresponding bridging carbonato complex, $[(dppe)(CO)_3Mn]_2(\mu-O_2C)$ [1]. In a particularly interesting reaction, transition metal complexes of the type $L_4Fe–CH_2Z$ where Z = Cl, Br, or I can act as methylene transfer agents resulting in the cyclopropanation of β-methylstyrene [2] and cyclohexene [3]. As a preliminary to a study of the possibility of $L_5MCH_2–Z$ (M = Mn, Re and the particularly good leaving groups Z = $OC(O)CF_3$, I) undergoing similar interesting reactions we report herein the synthesis of *cis*-$Re(CO)_4(PPh_3)CH_2OC(O)CF_3$ (**1**), *fac*-$Mn(CO)_3(dppe)CH_2OC(O)CF_3$ (**2**), *fac*-$Mn(CO)_3(dppp)CH_2OC(O)CF_3$ (**3**), *fac*-$Re(CO)_3(dppe)CH_2OC(O)CF_3$ (**4**), *fac*-$Re(CO)_3(dppp)CH_2OC(O)CF_3$ (**5**) and *fac*-$Mn(CO)_3(dppp)CH_2I$ (**6**) and the X-ray crystal structures of **1**, **5** and *cis*-$Re(CO)_4(PPh_3)CH_2I$ (**7**).

2. Results and discussion

2.1. Synthesis of manganese and rhenium trifluoroacetoxymethyl complexes, 1–5

Complexes **1**–**5** were prepared by allowing the corresponding methoxymethyl complexes [4] to react with

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trifluoroacetic acid in nonpolar solvents. For example, *fac*-$Mn(CO)_3(dppp)CH_2OC(O)CF_3$ (**3**) was prepared from the reaction of the methoxymethyl complex, *fac*-$Mn(CO)_3(dppp)CH_2OCH_3$ with trifluoroacetic acid in a 9:1 mixture of hexane and benzene, Eq. (1):

$$fac\text{-}Mn(CO)_3(dppp)CH_2OCH_3 + CF_3COOH \rightarrow \mathbf{3} + CH_3OH \quad (1)$$

Complex **3** was isolated by evaporating the solvents. A small amount of the corresponding tetracarbonyl trifluoroacetate salts, $[M(CO)_4\{Ph_2P(CH_2)_nPPh_2\}]$-$[CF_3CO_2]$, where, M = Mn, Re and $n = 2, 3$, were also produced during the preparations of **2**–**5**. Fractional crystallizations in methylene chloride–hexane led to the isolation of pure **2**–**5**.

2.2. Synthesis of the iodomethyl complexes, *fac*-$Mn(CO)_3(dppp)CH_2I$ (**6**) and *cis*-$Re(CO)_4(PPh_3)CH_2I$ (**7**)

Complex **6** was prepared from the reaction of the corresponding methoxymethyl complex, *fac*-$Mn(CO)_3$-$(dppp)CH_2OCH_3$ with $(CH_3)_3SiI$ [5,6] Eq. (2):

$$fac\text{-}Mn(CO)_3(dppp)CH_2OCH_3 + (CH_3)_3SiI \rightarrow \mathbf{6} + (CH_3)_3SiOCH_3 \quad (2)$$

The solvent and the volatile $(CH_3)_3SiOCH_3$ were evaporated to obtain an impure solid residue of **6**. Crystallization of **6** from CH_2Cl_2–hexane at −35°C yielded light-yellow crystalline **6**. The synthesis and spectral characterization of **7** were reported previously [5].

2.3. Spectral studies

The IR spectral data for the complexes **1**–**6** are given in Section 3. The IR spectrum of **1** shows four strong stretching frequencies ($\nu(C{\equiv}O)$s) expected for *cis* geometry and each of compounds **2**–**5** shows three strong $\nu(C{\equiv}O)$s expected for facial geometry of the terminal carbonyls. Compounds **1**–**5** exhibit a medium intensity $\nu(C{=}O)$ in the 1770–1760 cm^{-1} region for the C=O of the $-OC(O)CF_3$ group. The ^1H- and ^{13}C-NMR spectral data are listed in Table 1. As expected, the ^1H- and ^{13}C-NMR spectral data of **1** exhibit one doublet in each case for the methylene protons and methylene carbon coupled to phosphorus. Similarly, the ^1H- and ^{13}C-NMR spectral data of **2**–**5** show one triplet in each case associated with the methylene protons and methylene carbons. The ^{13}C-NMR spectra of **1**–**5** exhibit a quartet with $^1J(CF) \approx 285$ Hz for the CF_3 carbon and a quartet with $^2J(CF) \approx 40$ Hz for the OC(O) carbon. The ^{13}C-NMR spectrum of **1** exhibits three doublets for the terminal carbonyls as observed for the analogous *cis* disubstituted manganese and rhenium tetracarbonyl complexes [5] and both rhenium complexes **4** and **5** show a doublet of doublets and a triplet for the two sets of terminal carbonyls. However, the ^{13}C-NMR spectra of the manganese complexes **2** and **3** show broad resonances for the terminal carbonyls. As expected, the ^1H- and ^{13}C-NMR spectra of **6** exhibit one triplet for the methylene protons and methylene carbon of CH_2I group.

2.4. X-ray structures of **1**, **5** and **7**

The conformations and atomic numbering schemes for **1**, **5** and **7** are shown in Figs. 1–3, respectively. Crystal data for **1**, **5** and **7** were obtained under the conditions summarized in Table 2.

Selected bond lengths and angles for **1** are compiled in Table 3. The Re atom in **1** is octahedrally coordinated to four carbonyls, triphenylphosphine and the trifluoroacetoxymethyl group. The rhenium–carbon (Re–C(5)) bond length of 2.267 (8) Å for the trifluoroacetoxymethyl ligand in **1** is similar to the bond length observed for related rhenium methyl complexes [7]. The $Re{-}C^{CH^2}{-}O$ bond angle of 113.6(4)° is slightly larger than the Re(1)–C(9)–O(20) bond angle of 111.0 (2)° in $[\{LRe(NO)(CO)\}_2(\mu\text{-}CH_2OCH_2)]I_2$ (where, L = 1,4,7-triazacyclononane) [8]. Thus, the methylene carbon in **1** is slightly distorted from tetrahedral geometry.

Selected bond lengths and angles for **5** are compiled in Table 4. The Re atom in **5** is octahedrally coordinated to three carbonyls, dppp [1,3-bis(diphenylphosphino)propane] and the trifluoroacetoxymethyl group. The rhenium–carbon (Re(1)–C(4)) bond length of 2.242(3) Å for the trifluoroacetoxymethyl ligand in **5** is very similar to the bond lengths of 2.267 (8) Å observed in **1** (vide supra), 2.214(15) Å in $[NEt_4]_2[Re_3(\mu\text{-}H)_3$-$(\mu_3\text{-}\eta^2\text{-}CH_2O)(CO)_9]$ [9], 2.225(7) Å in $[NEt_4][fac\text{-}(CO_3)ReP(C_6H_5)_2(o\text{-}C_6H_4C(H)OC{=}O)]$ [10] and 2.24–2.55 Å in related rhenium methyl complexes [7]. The $Re{-}C_{CH_2}{-}O$ bond angle of 108.3(2)° in **5** is only slightly larger than the Re(2)–C(19)–O(20) bond angle of 107.0(2)° in $[\{LRe(NO)(CO)\}_2(\mu\text{-}CH_2OCH_2)]I_2$ [8] and the Re(1)–C–O bond angle of 106.0(8)° in $[NEt_4]_2$-$[Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}CH_2O)(CO)_9]$ [9] and appreciably smaller than the $Re{-}C_{CH_2}{-}O$ bond angle of 113.6(4)° in **1**.

Selected bond lengths and angles for **7** are compiled in Table 5. The Re atom in **7** is octahedrally coordinated to four carbonyls, triphenylphosphine and the iodomethyl group. The $Re{-}C_{CH_2}$ bond length of 2.38(8) Å is longer than the corresponding bond length of 2.267(8) Å in **1**, 2.214(15) Å in $[NEt_4]_2[Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}CH_2O)(CO)_9]$ [9] and 2.225(7) Å in $[NEt_4][fac\text{-}(CO_3)ReP(C_6H_5)_2(o\text{-}C_6H_4C(H)OC{=}O)]$ [10]. However, larger rhenium–carbon bond lengths of 2.55 Å have been observed in some rhenium methyl complexes (vide supra). It has been suggested for analogous manganese

Table 1
^{1}H- and ^{13}C-NMR data for *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$OC(O)CF$_3$ (**1**), *fac*-Mn(CO)$_3$(dppe)CH$_2$OC(O)CF$_3$ (**2**), *fac*-Mn(CO)$_3$(dppp)CH$_2$OC(O)CF$_3$ (**3**), *fac*-Re(CO)$_3$(dppe)CH$_2$OC(O)CF$_3$ (**4**), *fac*-Re(CO)$_3$(dppp)CH$_2$OC(O)CF$_3$ (**5**) and *fac*-Mn(CO)$_3$(dppp)CH$_2$I (**6**)

Complex	^{1}H-NMR (δ)		^{13}C-NMR (δ)			
	Phenyl	Methylene	Carbonyl	Phenyl	Methylene	CF$_3$
1 [a]	7.55(m, 15H)	4.71(d, J(PH) = 5 Hz, 2H)	189.34(d, J(PC) = 9 Hz, 2C$\equiv$O), 187.78 (d, J(PC) = 9 Hz, C$\equiv$O), 186.95(d, J(PC) = 48 Hz, C$\equiv$O), 158.85(q, J(CF) = 40 Hz, C=O)	133.56(d, J(PC) = 12 Hz), 132.45(d, J(PC) = 49 Hz), 131.47(s), 129.32(d, J(PC) = 9 Hz)	54.62(d, J(PC) = 5 Hz)	115.48(q, J(CF) = 285 Hz)
2 [b]	7.35(m, 20H)	4.10(t, J(PH) = 6 Hz, 2H) [d], 2.77(m, 4H) [e]	220.87(m, C$\equiv$O), 159.75(q, J(CF) = 40 Hz, C=O)	135.96–128.35(m)	73.17(t, J(PC) = 11 Hz) [d], 28.10(t, J(PC) = 12 Hz) [e]	115.10(q, J(CF) = 284 Hz)
3 [b]	7.09(m,20H)	5.10(t, J(PH) = 8 Hz, 2H) [d], 1.71(m, 4H) [e], 1.35(m, 2H) [e]	220.95(m, C$\equiv$O), 159.50(q, J(CF) = 40 Hz, C=O)	136.25–128.90(m)	73.81(t, J(PC) = 12 Hz) [d], 25.64(t, J(PC) = 13 Hz) [e], 18.89(s) [e]	115.15 (q, J(CF) = 285 Hz)
4 [c]	7.35(m,20H)	3.98(t, J(PH) = 6 Hz, 2H) [d], 2.69(m, 4H) [e]	194.51(dd, J(PC) = 55 Hz, 10 Hz, 2C$\equiv$O), 191.80(t, J(PC) = 8 Hz C$\equiv$O), 158.95(q, J(CF) = 40 Hz, C=O)	135.10–128.77(m)	56.37(t, J(PC) = 8 Hz) [d], 27.57(m) [e]	114.72(q, J(CF) = 287 Hz)
5 [c]	7.34(m,20H)	4.88(t, J(PH) = 6 Hz, 2H) [d], 2.45(m, 4H) [e], 2.16 (m, 2H) [e]	193.14(dd, J(PC) = 61 Hz, 9 Hz, 2C$\equiv$O), 191.30 (t, J(PC) = 5 Hz, C$\equiv$O), 158.87(q, J(CF) = 40 Hz, C=O	135.55/134.15(t, J(PC) = 18/24 Hz, *ipso*, C$_6$H$_5$), 133.15/ 132.77(t, J(PC) = 5/6 Hz, *o*, C$_6$H$_5$), 131.68(t, J(PC) = 5 Hz, *m*, C$_6$H$_5$), 130.41/130.20(s, C^{6}H^5), 128.56(t, J(PC) = 5Hz, *m*, C$_6$H$_5$)	58.47(t, J(PC) = 10 Hz) [d], 25.87(t, J(PC) = 16 Hz) [e], 19.71(s) [e]	119.43 (q, J(CF) = 285 Hz)
6 [c]	7.30(m, 2H) [e]	2.41(t, J(PH) = 10 Hz, 2H) [d], 2.11(m, 4H) [e], 1.59(m, 2H) [e]	221.48(br, m)	136.19–128.31(m)	25.15(t, J(PC) = 13 Hz) [e], 18.91(s) [e], 5.20(t, J(PC) = 15 Hz)[d]	

[a] In CD$_2$Cl$_2$.
[b] In C$_6$D$_6$.
[c] In CDCl$_3$.
[d] Resonances due to methylene bonded to Mn or Re.
[e] Resonances due to methylenes of the diphosphine ligands.

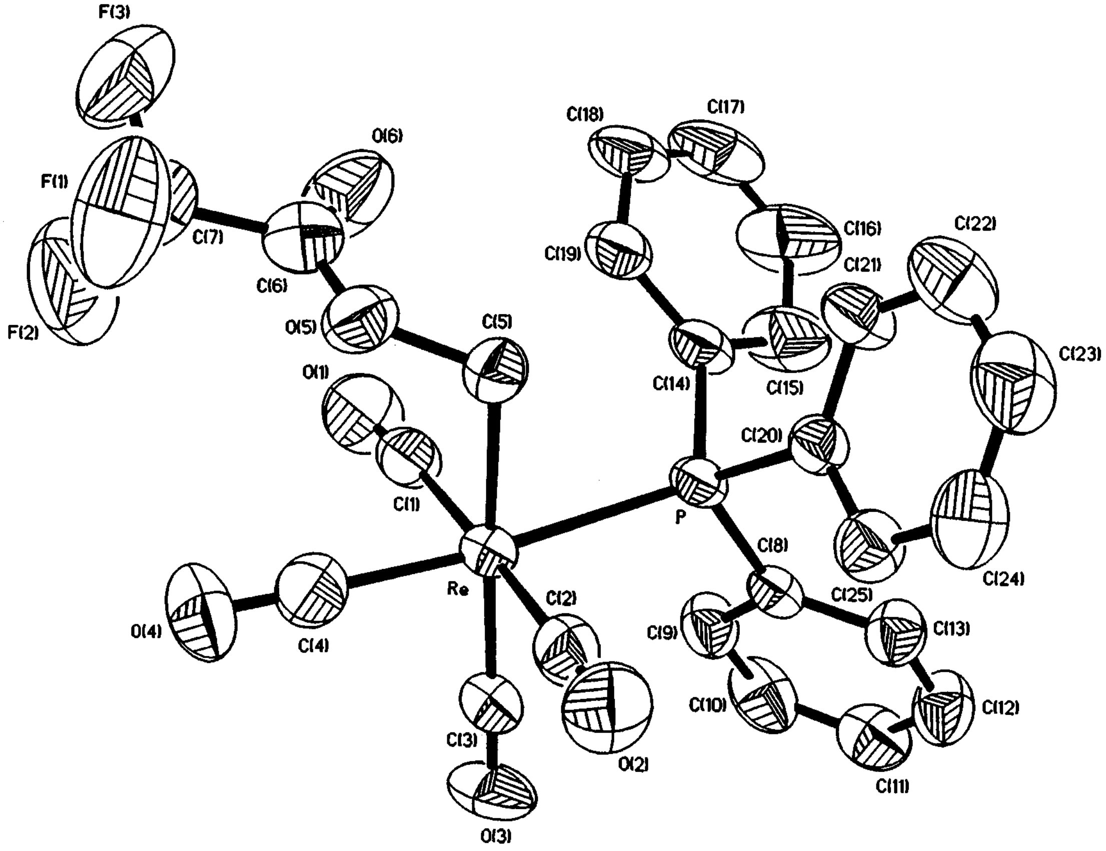

Fig. 1. A perspective drawing of molecule **1**.

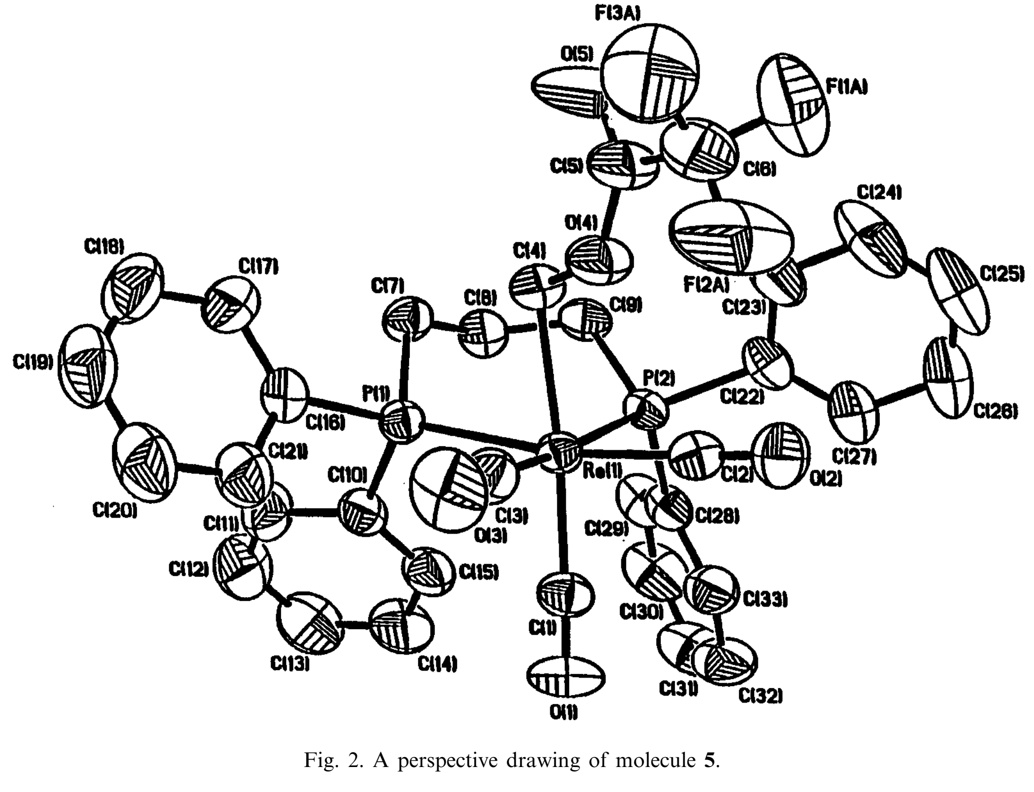

Fig. 2. A perspective drawing of molecule **5**.

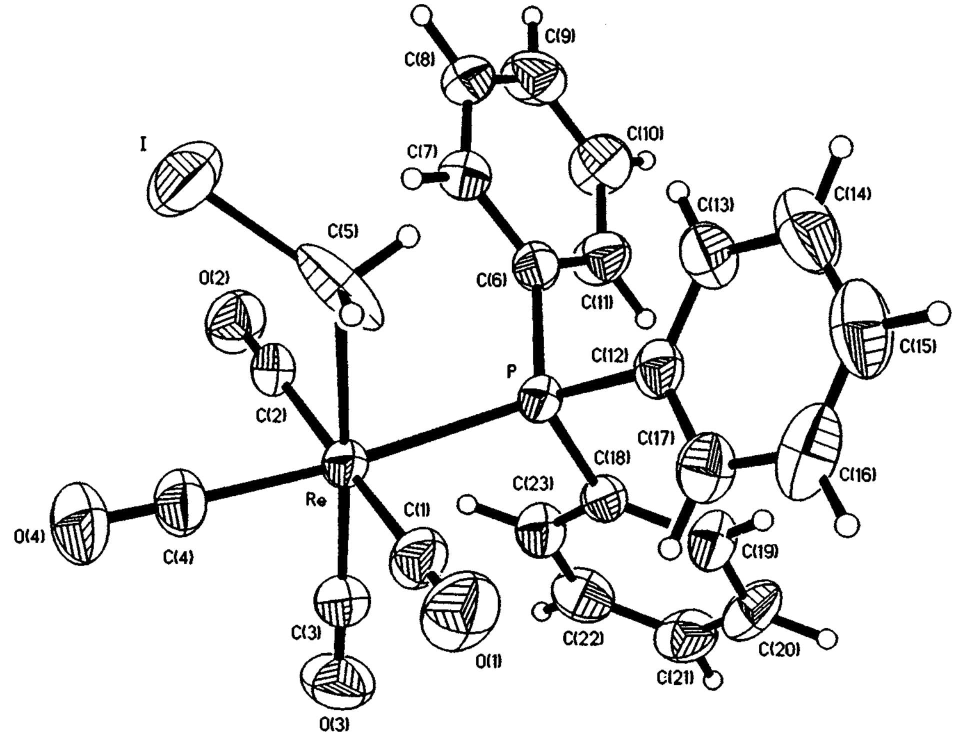

Fig. 3. A perspective drawing of molecule **7**.

Table 2
Summary of crystal data for *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$OC(O)CF$_3$ (**1**), *fac*-Re(CO)$_3$(dppp)-CH$_2$OC(O)CF$_3$ (**5**) and *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$I (**7**)

	1	**5**	**7**
Color and habit	Colorless prisms	Colorless prisms	Orange prisms
Crystal size, mm	0.12 × 0.35 × 0.38	0.18 × 0.08 × 0.08	0.25 × 0.28 × 0.35
Chemical formula	$C_{25}H_{17}F_3O_6$Pre	$C_{33}H_{28}F_3O_5P_2$Re	$C_{23}H_{17}IO_4$PRe
a (Å)	11.101(1)	11.1401(1)	10.5947(9)
b (Å)	11.352(1)	18.3169(2)	10.8709(10)
c (Å)	12.018(1)	16.1414(2)	11.3868(11)
α (°)	108.565(8)	90	91.422(8)
β (°)	116.572(8)	98.4024(5)	103.389(7)
γ (°)	90.829(8)	90	114.633(7)
V (Å^3)	1261.9(2)	3258.33(6)	1148.7(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P2(1)/c$	$P\bar{1}$ (No. 2)
Z	2	4	2
Diffractometer	Siemens R3m/V	Nonius KappaCCD	Siemens R3m/V
μ (Mo–K$_\alpha$), (cm^{-1})	49.98	38.83	67.84
Scan mode	$3° \leq 2\theta \leq 55.0°$	$1.69° \leq \theta \leq 27.48°$	$3° \leq 2\theta \leq 55.0°$
Limiting indices	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $0 \leq l \leq 15$	$-14 \leq h \leq 14$, $0 \leq k \leq 23$, $0 \leq l \leq 20$	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $0 \leq l \leq 14$
Absorption correction	Semi-empirical (XEMP)	XPREP ellipsoidal	Semi-empirical (XEMP)
Reflections collected	5678	59878	5577
Reflections merged (Rm)	5421(0.0116)	7463(0.0693)	5307(0.0086)
Reflections observed	4648; $F \geq 6\sigma(F)$	6484; $F \geq 4\sigma(F)$	4427; $F \geq 6\sigma(F)$
No. of variables	326	426	289
[a] R	0.0441	0.0242	0.0329
[b] R_w	0.0545	0.0550	0.0408
Goodness of fit	2.07	1.081	1.85
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F	Full-matrix least-squares on F

[a] $R = \Sigma(|F_o| - |F_o|)/\Sigma|F_o|$.

[b] $R_w = [\Sigma\, w_i(|F_o| - |F_o|)^2/\Sigma\, w_i|F_o|^2]^{1/2}$.

Table 3
Selected bond lengths (Å) and angles (°) for *cis*-$Re(CO)_4(PPh_3)CH_2OC(O)CF_3$ (**1**)

Bond lengths			
Re–P	2.485(2)	F(2)–C(7)	1.290(11)
Re–C(1)	1.995(10)	F(3)–C(7)	1.328(19)
Re–C(2)	2.005(10)	O(1)–C(1)	1.131(13)
Re–C(3)	1.957(9)	O(2)–C(2)	1.121(12)
Re–C(4)	1.950(8)	O(3)–C(3)	1.148(11)
Re–C(5)	2.267(8)	O(4)–C(4)	1.153(10)
P–C(8)	1.824(8)	O(5)–C(5)	1.452(12)
P–C(14)	1.835(8)	O(5)–C(6)	1.281(14)
P–C(20)	1.832(6)	O(6)–C(6)	1.185(12)
F(1)–C(7)	1.331(15)	C(6)–C(7)	1.507(16)
Bond angles			
P–Re–C(1)	90.8(1)	C(5)–O(5)–C(6)	119.4(7)
P–Re–C(2)	92.2(2)	Re–C(1)–O(1)	176.4(6)
C(1)–Re–C(2)	175.9(4)	Re–C(2)–O(2)	175.3(9)
P–Re–C(3)	94.2(2)	Re–C(3)–O(3)	178.2(7)
C(1)–Re–C(3)	91.4(4)	Re–C(4)–O(4)	178.1(10)
C(2)–Re–C(3)	91.1(4)	Re–C(5)–O(5)	113.6(4)
P–Re–C(4)	174.3(3)	O(5)–C(6)–O(6)	128.9(11)
C(1)–Re–C(4)	88.1(4)	O(5)–C(6)–C(7)	112.7(8)
C(2)–Re–C(4)	88.6(4)	O(6)–C(6)–C(7)	118.3(12)
C(3)–Re–C(4)	91.4(4)	F(1)–C(7)–F(2)	105.5(8)
P–Re–C(5)	85.5(2)	F(1)–C(7)–F(3)	105.7(11)
C(1)–Re–C(5)	93.9(4)	F(2)–C(7)–F(3)	107.6(12)
C(2)–Re–C(5)	83.6(4)	F(1)–C(7)–C(6)	113.2(11)
C(3)–Re–C(5)	174.7(4)	F(2)–C(7)–C(6)	113.0(10)
C(4)–Re–C(5)	89.0(3)	F(3)–C(7)–C(6)	111.4(8)
Re–P–C(8)	115.8(2)	P–C(8)–C(9)	116.8(7)
Re–P–C(14)	118.3(3)	P–C(8)–C(13)	124.2(5)
C(8)–P–C(14)	100.7(4)	P–C(14)–C(15)	120.2(9)
Re–P–C(20)	111.8(2)	P–C(14)–C(19)	120.8(5)
C(8)–P–C(20)	105.4(4)	P–C(20)–C(21)	121.1(7)
C(14)–P–C(20)	103.2(3)	P–C(20)–C(25)	119.9(5)

Table 4
Selected bond lengths (Å) and angles (°) for *fac*-$Re(CO)_3(dppp)CH_2OC(O)CF_3$ (**5**)

Bond lengths			
Re(1)–C(1)	1.938(3)	C(6)–F(2A)	1.278(7)
Re(1)–C(2)	1.944(3)	C(6)–F(3B)	1.280(9)
Re(1)–C(3)	1.925(3)	C(6)–F(3A)	1.306(6)
Re(1)–C(4)	2.242(3)	C(6)–F(1A)	1.329(6)
Re(1)–P(1)	2.4429(8)	C(6)–F(1B)	1.341(10)
Re(1)–P(2)	2.4623(7)	P(1)–C(16)	1.828(3)
C(1)–O(1)	1.145(4)	P(1)–C(7)	1.831(3)
C(2)–O(2)	1.141(4)	P(1)–C(10)	1.836(3)
C(3)–O(3)	1.146(4)	C(7)–C(8)	1.536(5)
C(4)–O(4)	1.497(4)	C(8)–C(9)	1.526(5)
C(4)–O(5)	1.277(4)	C(9)–P(2)	1.830(3)
C(5)–O(5)	1.180(5)	P(2)–C(28)	1.822(3)
C(5)–C(6)	1.514(6)	P(2)–C(22)	1.827(3)
C(6)–F(2B)	1.265(9)		
Bond angles			
C(3)–Re(1)–C(1)	90.54(14)	F(2A)–C(6)–F(1A)	107.6(7)
C(3)–Re(1)–C(2)	89.13(14)	F(3A)–C(6)–F(1A)	104.2(5)
C(1)–Re(1)–C(2)	94.91(13)	F(2B)–C(6)–F(1B)	99.5(14)
C(3)–Re(1)–C(4)	85.01(13)	F(3B)–C(6)–F(1B)	97.3(13)
C(1)–Re(1)–C(4)	174.27(13)	F(2B)–C(6)–C(5)	117.1(11)
C(2)–Re(1)–C(4)	88.64(12)	F(2A)–C(6)–C(5)	117.1(4)
C(3)–Re(1)–P(1)	93.81(10)	F(3B)–C(6)–C(5)	112.1(8)
C(1)–Re(1)–P(1)	93.61(10)	F(3A)–C(6)–C(5)	108.8(5)
C(2)–Re(1)–P(1)	170.96(9)	F(1A)–C(6)–C(5)	109.0(5)
C(4)–Re(1)–P(1)	83.11(8)	F(1B)–C(6)–C(5)	108.8(7)
C(3)–Re(1)–P(2)	173.66(11)	C(16)–P(1)–C(7)	104.0(2)
C(1)–Re(1)–P(2)	95.20(10)	C(16)–P(1)–C(10)	102.3(2)
C(2)–Re(1)–P(2)	87.70(9)	C(7)–P(1)–C(10)	101.2(2)
C(4)–Re(1)–P(2)	89.43(8)	C(16)–P(1)–Re(1)	114.20(11)
P(1)–Re(1)–P(2)	88.53(3)	C(7)–P(1)–Re(1)	112.66(11)
O(1)–C(1)–Re(1)	176.8(3)	C(10)–P(1)–Re(1)	120.48(11)
O(2)–C(2)–Re(1)	178.5(3)	C(8)–C(7)–P(1)	113.5(2)
O(3)–C(3)–Re(1)	177.0(3)	C(9)–C(8)–C(7)	115.3(2)
O(4)–C(4)–Re(1)	108.3(2)	C(8)–C(9)–P(2)	116.2(2)
C(5)–O(4)–C(4)	119.5(3)	C(28)–P(2)–C(22)	103.9(2)
O(5)–C(5)–O(4)	128.0(4)	C(28)–P(2)–C(9)	105.5(2)
O(5)–C(5)–C(6)	120.3(4)	C(22)–P(2)–C(9)	102.4(2)
O(4)–C(5)–C(6)	111.8(3)	C(28)–P(2)–Re(1)	115.37(10)
F(2B)–C(6)–F(3B)	118.5(13)	C(22)–P(2)–Re(1)	112.82(10)
F(2A)–C(6)–F(3A)	109.4(8)	C(9)–P(2)–Re(1)	115.36(11)

iodomethyl complexes that a hyperconjugative effect operates [6]:

$$MnCH_2I \leftrightarrow Mn = CH_2^+ I^-$$

Apparently a similar hyperconjugative effect is not operating in **7**. The rhenium–phosphorus bond length of 2.487(1) Å is very close to the rhenium–phosphorus bond lengths in **1** and **5**. The Re–C^{CH_2}–I bond angle of 118.8(3)° is almost equal to the corresponding bond angle of 118.5(2)° in the manganese analog. Thus, the methylene carbon is severely distorted from tetrahedral geometry.

3. Experimental

All manipulations were carried out under an argon atmosphere and the solvents were dried prior to use. Reagent grade chemicals were used without further purification. Trifluoroacetic acid and trimethylsilyl iodide were obtained from Aldrich Chemical. The starting materials *cis*-$Re(CO)_4(PPh_3)CH_2OCH_3$, *fac*-$Mn(CO)_3(dppe)CH_2OCH_3$, *fac*-$Mn(CO)_3(dppp)CH_2OCH_3$, *fac*-$Re(CO)_3(dppe)CH_2OCH_3$ and *fac*-$Re(CO)_3(dppp)CH_2OCH_3$ were synthesized according to literature procedures [4,5].

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; 62.896 MHz, ^{13}C) spectrometer. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Microanalyses were conducted by Galbraith Laboratories.

Table 5
Selected bond lengths (Å) and angles (°) for *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$I (**7**)

Bond lengths			
Re–C(1)	1.984(7)	C(2)–O(2)	1.136(9)
Re–C(2)	1.993(7)	C(3)–O(3)	1.156(10)
Re–C(3)	1.945(8)	C(4)–O(4)	1.138(7)
Re–C(4)	1.946(5)	C(5)–I	1.992(10)
Re–C(5)	2.380(8)	P–C(6)	1.842(7)
Re–P	2.487(1)	P–C(12)	1.838(6)
C(1)–O(1)	1.123(10)	P–C(18)	1.823(7)
Bond angles			
C(1)–Re–C(2)	176.4(3)	Re–C(5)–I	118.8(3)
C(1)–Re–C(3)	92.3(3)	Re–P–C(6)	115.9(2)
C(2)–Re–C(3)	90.9(3)	Re–P–C(12)	114.4(2)
C(1)–Re–C(4)	88.9(3)	C(6)–P–C(12)	103.0(3)
C(2)–Re–C(4)	89.3(3)	Re–P–C(18)	115.2(2)
C(3)–Re–C(4)	90.1(3)	C(6)–P–C(18)	102.3(3)
C(1)–Re–C(5)	86.0(3)	C(12)–P–C(18)	104.3(3)
C(2)–Re–C(5)	90.7(3)	P–C(6)–C(7)	120.1(4)
C(3)–Re–C(5)	176.3(2)	P–C(6)–C(11)	120.7(6)
C(4)–Re–C(5)	86.6(3)	P–C(12)–C(13)	122.6(6)
C(1)–Re–P	92.6(2)	P–C(12)–C(17)	118.9(5)
C(2)–Re–P	88.9(1)	P–C(18)–C(19)	123.5(5)
C(3)–Re–P	94.3(2)	P–C(18)–C(23)	118.4(5)
C(4)–Re–P	175.2(3)	Re–C(5)–H(5a)	107.1(1)
C(5)–Re–P	89.0(2)	Re–C(5)–H(5b)	107.1(2)
Re–C(1)–O(1)	175.8(7)	H(5a)–C(5)–H(5b)	109.5(1)
Re–C(2)–O(2)	178.5(6)	H(5a)–C(5)–I	107.1(2)
Re–C(3)–O(3)	176.9(5)	H(5b)–C(5)–I	107.1(2)
Re–C(4)–O(4)	178.4(8)		

3.1. Synthesis of *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$OC(O)CF$_3$ (1)

A solution of *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$OCH$_3$ (0.50 g, 0.82 mmol) in hexane (100 cm^3) was stirred with trifluoroacetic acid (0.13 cm^3, 1.69 mmol) at room temperature (r.t.) for 4 h. The solvent and excess trifluoroacetic acid were removed on a rotary evaporator to give a white residue. The residue was dissolved in a minimum quantity of CH$_2$Cl$_2$–hexane and cooled to -5°C. White crystalline **1** (0.36 g, 0.52 mmol, 63%), m.p. 120–122°C was collected by filtration. IR (cm^{-1}, C$_6$H$_6$): ν(C≡O) 2090s, 2001s, 1983vs, 1950s and ν(C=O) 1770 m, br. Anal. Found: C, 44.0; H, 2.6. C$_{25}$H$_{17}$O$_6$F$_3$PRe Calc.: C, 43.7; H, 2.5.

3.2. Synthesis of *fac*-M(CO)$_3${Ph$_2$P(CH$_2$)$_n$PPh$_2$}CH$_2$OC(O)CF$_3$ (2, M = Mn, n = 2; 3, M = Mn, n = 3; 4, M = Re, n = 2; 5, M = Re, n = 3)

To 0.69–0.86 mmol of *fac*-M(CO)$_3${Ph$_2$P(CH$_2$)$_n$ PPh$_2$}CH$_2$OCH$_3$ (M = Mn, Re; n = 2,3) dissolved in about 100 cm^3 of a 9:1 mixture of hexane–benzene was added trifluoroacetic acid (0.11–0.13 cm^3, 1.38–1.72 mmol) and the solution was stirred for 4 h. The solvents and excess trifluoroacetic acid were removed by rotary evaporation to give pale-yellow to white residues. The residues were crystallized from CH$_2$Cl$_2$–hexane at -5°C. Pure crystalline trifluoroacetoxymethyl complexes **2**–**5** were collected by filtration. Data for **2**: yield, 57%. M.p. 152–154°C. IR (cm^{-1}, CH$_2$Cl$_2$): ν(C≡O) 2006vs, 1933s, 1909s and ν(C=O) 1761m, br. Anal. Found: C, 57.7; H, 3.8. C$_{32}$H$_{26}$O$_5$F$_3$MnP$_2$ Calc.: C, 57.8; H, 3.9. Data for **3**: yield: 62%. M.p. 169–171°C (dec.). IR (cm^{-1}, CH$_2$Cl$_2$): ν(C≡O) 2010vs, 1940s, 1903s and ν(C=O) 1762m, br. Anal. Found: C, 58.4; H, 4.2. C$_{33}$H$_{28}$O$_5$F$_3$MnP$_2$ Calc.: C, 58.4; H, 4.2. Data for **4**: yield, 69%. M.p.160–163°C. IR (cm^{-1}, CH$_2$Cl$_2$): ν(C≡O) 2018vs, 1936s, 1910s and ν(C=O) 1759m, br. Anal. Found: C, 48.6; H, 3.4. C$_{32}$H$_{26}$O$_5$F$_3$P$_2$Re Calc.: C, 48.3; H, 3.3. Data for **5**. M.p. 182–184°C. IR (cm^{-1}, CH$_2$Cl$_2$): ν(C≡O) 2021vs, 1941s, 1905s and ν(C=O) 1761m, br. Anal. Found: C, 48.9; H, 3.5. C$_{33}$H$_{28}$O$_5$F$_3$P$_2$Re Calc.: C, 48.9; H, 3.5.

The IR spectra of the filtrates indicated the presence of tetracarbonyl cationic complexes, [M(CO)$_4${Ph$_2$P(CH$_2$)$_n$PPh$_2$}][CF$_3$CO$_2$] [11].

3.3. Synthesis of *fac*-Mn(CO)$_3$(dppp)CH$_2$I (6)

To a solution of *fac*-Mn(CO)$_3$(dppp)CH$_2$OCH$_3$ (1.0 g, 1.68 mmol) in CH$_2$Cl$_2$ (40 cm^3) was added (CH$_3$)$_3$SiI (0.25 cm^3, 1.76 mmol) at -78°C. The reaction mixture was stirred for 15 min and allowed to warm to r.t. When the solvent was removed on a rotary evaporator, a pale-yellow residue was obtained. The residue was recrystallized in CH$_2$Cl$_2$–hexane at 35°C. Light-brown crystals of **6** (1.02 g, 1.47 mmol, 88%, m.p. 172–174°C (dec.)) were collected by filtration. IR (cm^{-1}, CH$_2$Cl$_2$): ν(C≡O) 2008vs, 1938s and 1904s. Anal. Found: C, 53.7; H, 4.1. C$_{31}$H$_{28}$O$_3$IMnP$_2$ Calc.: C, 53.7; H, 4.1.

3.4. X-ray crystal structure of *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$OC(O)CF$_3$ (1)

Crystals of **1** were grown from CH$_2$Cl$_2$–hexane at -5°C. Data were collected on a Siemens R3m/V diffractometer and corrected for Lorentz-polarization and absorption effects. The structure was solved by heavy-atom methods and refined by full-matrix least-squares on F using SHELXTL PLUS (version 3.43). The non-hydrogen atoms were refined anisotropically and the hydrogens were allowed to ride on their respective carbons. The hydrogens were assigned fixed isotropic displacement coefficients U(H) = 0.08 and an extinction parameter was included in the refinements. Convergence gave $R = 0.0441$ for 4648 reflections with $F \geq 6\sigma(F)$. Additional crystallographic data and results are summarized in Table 2.

3.5. X-ray crystal structure of *fac*-Re(CO)$_3$(dppp)CH$_2$OC(O)CF$_3$ (**5**)

Crystals of **5** were grown from CH_2Cl_2–hexane at −5°C. Data were collected on a Nonius KappaCCD diffractometer and corrected for Lorentz-polarization and absorption effects. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL (version 5). The non-hydrogen atoms were refined anisotropically and the hydrogens were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ and allowed to ride on their respective carbons. The trifluoromethyl group was treated with a two-site rotational disorder model with distance and similarity restraints and with site occupancy factors of 0.72(2) and 0.28(2), respectively. Convergence gave $R = 0.0242$ for 6484 reflections with $F \geq 4\sigma(F)$. Additional crystallographic data and results are summarized in Table 2.

3.6. X-ray crystal structure of *cis*-Re(CO)$_4$(PPh$_3$)CH$_2$I (7)

Crystals of **7** were grown from CH_2Cl_2–hexane at −35°C. Data were collected on a Siemens R3m/V diffractometer and corrected for Lorentz-polarization and absorption effects. The structure was solved by heavy-atom methods and refined by full-matrix least-squares on F using SHELXTL PLUS (version 3.43). The non-hydrogen atoms were refined anisotropically and the hydrogens were allowed to ride on their respective carbons. The hydrogen isotropic displacement coefficients were also allowed to vary and an extinction parameter was included in the refinements. Convergence gave $R = 0.0329$ for 4427 reflections with $F \geq 6\sigma(F)$. Additional crystallographic data and results rre summarized in Table 2.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 121959 for compound **1**, CCDC no. 121960 for compound **5** and CCDC no. 121961 for compound **7**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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