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Reactions of dirhenium heptoxide with manganese(I) and rhenium(I) hydrido, alkoxo, methylcarbonato, carbonato-bridged, and methoxymethyl complexes. The X-ray structures of *fac*-$(CO)_3(dppp)MnOReO_3$ and *fac*-$(CO)_3(dppp)ReOReO_3$

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Abstract

Treatment of Re_2O_7 with manganese(I) and rhenium(I) hydrido {*fac*-$(CO)_3$(P–P)MH}, alkoxo {*fac*-$(CO)_3$(P–P)MOR}, methylcarbonato {*fac*-$(CO)_3$(P–P)MOC(O)OCH_3}, carbonato-bridged [$(CO)_3$(P–P)M]$_2${μ-OC(O)O} and methoxymethyl {*fac*-$(CO)_3$(P–P)MCH_2OCH_3} complexes, where, R is CH_3 or CH_2CH_3, P–P is dppe {1,2-bis(diphenylphosphino)ethane} or dppp {1,3-bis(diphenylphosphino)propane}, yielded the corresponding perrhenato complexes, *fac*-$(CO)_3$(P–P)$MOReO_3$ (**1**, M = Mn, P–P = dppe; **2**, M = Mn, P–P = dppp; **3**, M = Re, P–P = dppe; **4**, M = Re, P–P = dppp), in moderate to excellent yield. The perrhenato complexes have been characterized spectroscopically and the molecular structures of *fac*-$(CO)_3(dppp)MnOReO_3$, **2** and *fac*-$(CO)_3(dppp)ReOReO_3$, **4** have been established through X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Manganese; Rhenium; Rhenium heptoxide; Perrhenato complexes; X-ray

1. Introduction

Dirhenium heptoxide was used extensively for the synthesis of numerous alkyl and arylrhenium oxides and related complexes [1]. Treatments of silanols with Re_2O_7 were reported to yield the corresponding siloxane perrhenates [2]. We have observed that Re_2O_7 reacts with a variety of metal carbonyl complexes to afford the corresponding metal carbonyl perrhenato complexes [3]. However, analogous perrhenato complexes were synthesized previously from the reaction of the corresponding metal carbonyl halides with $AgReO_4$. For example, $(CO)_5ReOReO_3$ was synthesized from the reaction of $(CO)_5ReCl$ with $AgReO_4$ [4]. Here we present the reactions of Re_2O_7 with manganese(I) and rhenium(I) hydrido {*fac*-$(CO)_3$(P–P)MH}, alkoxo {*fac*-$(CO)_3$(P–P)MOR}, methylcarbonato {*fac*-$(CO)_3$(P–P)MOC(O)OCH_3}, carbonato-bridged [$(CO)_3$(P–P)M]$_2${μ-OC(O)O}, and methoxymethyl {*fac*-$(CO)_3$(P–P)MCH_2OCH_3} complexes, where, R is CH_3 or CH_2CH_3 and P–P is 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane (dppp) and the X-ray structures of *fac*-$(CO)_3(dppp)MnOReO_3$, **2** and *fac*-$(CO)_3(dppp)ReOReO_3$, **4**.

2. Results and discussion

2.1. Reactions of hydrido manganese(I) and rhenium(I) complexes, *fac*-$(CO)_3$(P–P)MH with Re_2O_7

The reaction of *fac*-$(CO)_3$(P–P)MH with Re_2O_7 (2:1 mol ratio) in moist dichloromethane yielded the corresponding perrhenato complexes, *fac*-$(CO)_3$(P–P)$MOReO_3$, **1**–**4**, in high yield (Eq. (1)):

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$$2fac(CO)_3(P\text{–}P)MH + Re_2O_7 + H_2O \rightarrow 2fac(CO)_3(P\text{–}P)MOReO_3,\ \mathbf{1}\text{–}\mathbf{4} + 2H_2 \quad (1)$$

Similar synthesis of the platinum perrhenato complex, $[Pt_4(\mu\text{-}CO)_2(PPh_3)_4(ReO_4)_2]$, from the reaction of the platinum hydrido complex, $[Pt_4H(CO)(\mu\text{-}CO)_3(PPh_3)_4]ReO_4$, with Re_2O_7 in moist dichloromethane was reported previously [5]. The perrhenato complexes, **1**–**4**, were characterized spectroscopically. The IR spectrum of each exhibits three strong $\nu(C\equiv O)$'s characteristic of facial geometry. Two medium intensity bands in the region 955–900 cm^{-1} are attributed to the ReO vibrations of the perrhenates. Similar bands were also observed in related perrhenato complexes [4]. The ^1H-NMR spectra are not helpful to identify these complexes because there are no diagnostic groups present in these complexes. The ^{13}C-NMR spectra of the manganese perrhenato complexes, **1** and **2**, did not show any well-resolved resonances due to the terminal carbonyls ($C\equiv O$)'s. However, the rhenium complexes, **3** and **4**, showed well-resolved carbonyl carbon resonances. For example, the *cis* carbonyl carbon in **4** is observed at δ 193.5 as a triplet coupled to the two *cis* phosphorus atoms of the dppp ligand with a coupling constant of 6 Hz; the carbonyls *trans* to the corresponding phosphorus atoms are observed at δ 191.5 and 191.0 as triplets coupled to two phosphorus atoms with a coupling constant of 23 Hz each.

2.2. Reactions of alkoxo manganese(I) and rhenium(I) complexes, *fac*-$(CO)_3(P\text{–}P)MOR$ with Re_2O_7, where, R is CH_3 or CH_2CH_3

When a mixture of the alkoxo complexes and Re_2O_7 (1:1 mol ratio) in dichloromethane was stirred, the corresponding perrhenato complexes, **1**–**4** were obtained in high yield. The reaction might proceed according to Eq. (2):

$$fac(CO)_3(P\text{–}P)MOR + Re_2O_7 \rightarrow fac(CO)_3(P\text{–}P)MOReO_3 + ROReO_3 \quad (2)$$

The alkyl perrhenates, $ROReO_3$, thus formed are unstable [6]. The final products are black precipitates presumed to be lower oxides of rhenium. The black precipitates are not soluble in water or common organic solvents. Similar black precipitates were also observed during the preparation of $Ta_2(OMe)_8(ReO_4)_2$ from the reaction of $Ta_2(OMe)_{10}$ with Re_2O_7 and confirmed by SEM-EDS to be a rhenium-containing compound [7].

2.3. Reactions of methylcarbonato complexes, *fac*-$(CO)_3(P\text{–}P)MOC(O)OCH_3$ with Re_2O_7

When an equimolar mixture of a methylcarbonato complex and Re_2O_7 in dichloromethane was stirred, the corresponding perrhenato complex was obtained in high yield (Eq. (3)):

$$(CO)_3(P\text{–}P)MOC(O)OCH_3 + Re_2O_7 \rightarrow fac(CO)_3(P\text{–}P)MOReO_3 + CH_3OReO_3 + CO_2 \quad (3)$$

The black precipitates are presumed to be lower oxides of rhenium.

2.4. Reactions of carbonato-bridged complexes, $[(CO)_3(P\text{–}P)M]_2\{\mu\text{-}OC(O)O\}$ with Re_2O_7

When an equimolar mixture of $[(CO)_3(P\text{–}P)M]_2\{\mu\text{-}OC(O)O\}$ and Re_2O_7 in dichloromethane was stirred, the corresponding perrhenato complexes were obtained in high yield (Eq. (4)):

$$[(CO)_3(P\text{–}P)M]_2\{\mu OC(O)O\} + Re_2O_7 \rightarrow 2fac(CO)_3(P\text{–}P)MOReO_3 + CO_2 \quad (4)$$

We believe that first Re_2O_7 is converted to $HReO_4$ by adventitious water [5]. Then $HReO_4$ reacts with $[(CO)_3(P\text{–}P)M]_2\{\mu\text{-}OC(O)O\}$ to yield the corresponding perrhenato complexes (Eq. (5)):

$$[(CO)_3(P\text{–}P)M]_2\{\mu OC(O)O\} + 2HReO_4 \rightarrow 2fac(CO)_3(P\text{–}P)MOReO_3 + CO_2 + H_2O \quad (5)$$

In a separate experiment we observed that a dichloromethane solution of $[(CO)_3(P\text{–}P)M]_2\{\mu\text{-}OC(O)O\}$ reacted rapidly with two equivalents of $HReO_4$ to yield the perrhenato complexes almost quantitatively.

2.5. Reactions of methoxymethyl complexes, *fac*-$(CO)_3(P\text{–}P)MCH_2OCH_3$ with Re_2O_7

When an equimolar mixture of a methoxymethyl complex, *fac*-$(CO)_3(P\text{–}P)MCH_2OCH_3$ and Re_2O_7 in dichloromethane was stirred, the corresponding perrhenato complexes were obtained in moderate to high yield. During the course of the reaction the color of the solution changed from pale-yellow to red with simultaneous precipitation of some lower oxides of rhenium. We did not attempt to study the mechanism of this reaction. It is believed that Re_2O_7 ionizes in polar solvents as $ReO_3^+ReO_4^-$. Therefore, it is possible that an intermediate carbene complex, $[fac\text{-}(CO)_3(P\text{–}P)M{=}CH_2]^+[ReO_4]^-$ is generated in the initial stage of the reaction (Eq. (6)):

$$fac(CO)_3(P\text{–}P)MCH_2OCH_3 + Re_2O_7 \rightarrow [fac(CO)_3(P\text{–}P)M{=}CH_2]^+[ReO_4]^- + CH_3OReO_3 \quad (6)$$

Alternatively, the carbene complexes may be formed from *O*-protonation reaction of the methoxymethyl complexes, *fac*-$(CO)_3(P\text{–}P)MCH_2OCH_3$ with $HReO_4$ formed in situ from the reaction of Re_2O_7 with adventitious water (Eq. (7)):

$$fac(CO)_3(P\text{–}P)MCH_2OCH_3 + HReO_4 \rightarrow [fac(CO)_3(P\text{–}P)M{=}CH_2]^+[ReO_4]^- + CH_3OH \quad (7)$$

Similar *O*-protonation of methoxymethyl complexes with acids are known. For example, the reaction of $(C_5Me_5)(dppe)FeCH_2OMe$ with HBF_4 was reported to yield the carbene complex, $[(C_5Me_5)(dppe)Fe{=}CH_2]^+[BF_4]^-$ [8]. It is possible that the carbene complexes decompose rapidly to afford the corresponding perrhenato complexes (Eq. (8)):

$$2[fac(CO)_3(P\text{–}P)M{=}CH_2]^+[ReO_4]^- \rightarrow 2[fac(CO)_3(P\text{–}P)MOReO_3 + C_2H_4(?) \quad (8)$$

Similar decomposition of $(CO)_5ReCH_2I$ was also reported to yield C_2H_4 [9]. Among the starting materials, the hydrido complexes are readily available [10]. Also the reactions of Re_2O_7 with the hydrido complexes afforded reasonably good yields of the perrhenato complexes. Therefore, the reaction noted in Eq. 1 is the preferred method of synthesis of perrhenato complexes.

Table 1
Summary of crystal data for *fac*-$(CO)_3(dppp)MnOReO_3$ (**2**) and *fac*-$(CO)_3(dppp)ReOReO_3$ (**4**)

	2	**4**
Color and habit	Orange prisms	Colorless prisms
Crystal size (mm)	$0.18 \times 0.32 \times 0.38$	$0.15 \times 0.15 \times 0.08$
Chemical formula	$C_{30}H_{26}MnO_7P_2Re$	$C_{30}H_{26}O_7P_2Re_2$
a (Å)	9.7779(2)	9.7675(2)
b (Å)	11.8671(2)	11.9913(2)
c (Å)	13.6100(2)	13.6469(2)
α (°)	95.912(1)	96.773(1)
β (°)	90.387(1)	90.723(1)
γ (°)	107.105(1)	107.168(1)
V (Å^3)	1500.22(5)	1514.62(5)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
Diffractometer	Nonius KappaCCD	Nonius KappaCCD
μ (Mo–K$_\alpha$) (mm^{-1})	4.603	8.135
Scan mode	ω, 1° × 800	ω, 1° × 800
θ Range (°)	1.51–27.47	1.50 × 30.02
Limiting indices	$-12 \le h \le 12$, $-15 \le k \le 15$, $0 \le l \le 17$	$13 \le h \le 13$, $-16 \le k \le 16$, $0 \le l \le 19$
Absorption correction	Gaussian	Gaussian
Reflections collected	30 513	34 122
Reflections/R_{int}	6866 (0.0611)	8801 (0.0556)
Reflections observed	6339; $I > 2\sigma(I)$	7507; $I > 2\sigma(I)$
Number of variables	371	371
R	0.0290 (0.0644) [a]	0.0306 (0.0726) [a]
R_w	0.0330 (0.0695) [a]	0.0397 (0.0923) [a]
Goodness-of-fit on F^2	1.082	1.051
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

[a] Definitions of R and R_w; $R = \Sigma(||F_0| - |F_c||)/\Sigma(|F_0|$, $R_w = [\Sigma(w(F_0^2 - F_c^2)^2/\Sigma\, w(F_0^2)^2]^{1/2}$.

2.6. X-ray crystal structures of *fac*-$(CO)_3(dppp)MnOReO_3$ (2) and *fac*-$(CO)_3(dppp)ReOReO_3$ (4)

Crystal data for **2** and **4** were determined under the conditions summarized in Table 1. The molecular plots for **2** and **4** are provided in Fig. 1. Selected distances and angles for **2** and **4** are provided in Table 2. As expected, the central metal atom of **2** or **4** are octahedrally coordinated to three terminal carbonyl ligands in a facial arrangement, a bidentate dppp, and a monodentate perrhenate anion. The Mn–$OReO_3$ bond in **2** is 2.066(2) Å which is slightly longer than the corresponding distances of 2.020–2.043(2) Å reported for manganese carboxylato complexes [11]. To the best of our knowledge, no manganese(I) perrhenato complex was characterized previously by X-ray diffraction. The Re–$OReO_3$ bond distance of 2.175(3) Å in **4** is comparable to the corresponding distances of 2.152(4) [12] and 2.207(3) Å [13] reported for analogous rhenium–perrhenato complexes. Similarly, the ReO–ReO_3 bond distance of 1.744(3) Å in **4** is comparable to the corresponding distances of 1.739(4) [12] and 1.754(3) Å [13] reported for rhenium–perrhenato complexes noted above. The Re–O–Re angle of 153.1(2)° observed in **4** is comparable to the corresponding angles of 135–164° reported for related rhenium–perrhenato complexes [14]. The Mn–CO (*trans*) distance of 1.782(3) Å and Re–CO (*trans*) distance of 1.894(4) Å are shorter than their corresponding M–CO (*cis*) distances. Also the MnC–O (*trans*) distance of 1.143(4) Å and the ReC–O (*trans*) distance of 1.151(5) Å are longer than the corresponding M–CO (*cis*) distances. Similar M–CO (*trans*) bond shortening and MC–O (*trans*) bond lengthening were observed in analogous rhenium–perrhenato complexes [12,13]. This is attributed to low trans directing effect of the ReO_4 ligand.

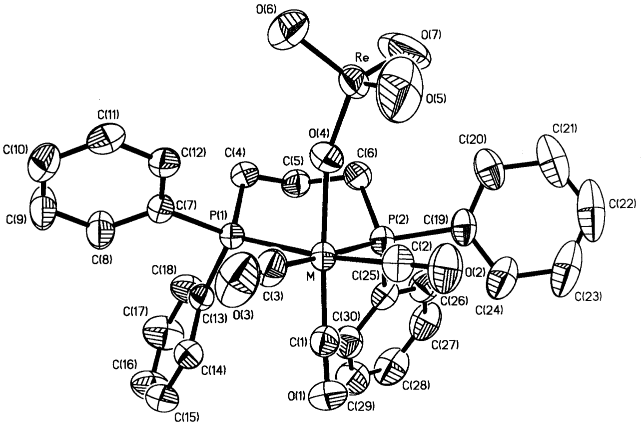

Fig. 1. The X-ray crystal structure of **2** or **4**.

Table 2
Selected bond lengths (Å) and bond angles (°) for *fac*-(CO)$_3$(dppp)MnOReO$_3$ (**2**) and *fac*-(CO)$_3$(dppp)ReOReO$_3$ (**4**)

2		**4**	
Bond lengths			
Mn–C(1)	1.782(3)	Re(1)–C(1)	1.894(4)
Mn–C(2)	1.832(4)	Re(1)–C(2)	1.956(4)
Mn–C(3)	1.823(4)	Re(1)–C(3)	1.963(5)
Mn–O(4)	2.066(2)	Re(1)–O(4)	2.175(3)
Mn–P(1)	2.3712(9)	Re(1)–P(1)	2.4873(9)
Mn–P(2)	2.3499(9)	Re(1)–P(2)	2.4653(10)
C(1)–O(1)	1.143(4)	C(1)–O(1)	1.151(5)
C(2)–O(2)	1.134(4)	C(2)–O(2)	1.138(5)
C(3)–O(3)	1.134(5)	C(3)–O(3)	1.122(6)
Re–O(4)	1.739(2)	Re(2)–O(4)	1.744(3)
Re–O(5)	1.683(4)	Re(2)–O(5)	1.677(6)
Re–O(6)	1.686(3)	Re(2)–O(6)	1.683(4)
Re–O(7)	1.694(4)	Re(2)–O(7)	1.699(5)
P(1)–C(4)	1.829(3)	P(1)–C(4)	1.829(4)
P(1)–C(7)	1.827(3)	P(1)–C(7)	1.831(4)
P(1)–C(13)	1.817(3)	P(1)–C(13)	1.819(4)
P(2)–C(6)	1.830(3)	P(2)–C(6)	1.833(4)
P(2)–C(19)	1.820(3)	P(2)–C(19)	1.819(4)
P(2)–C(25)	1.833(3)	P(2)–C(25)	1.828(4)
Bond angles			
C(1)–Mn–C(2)	88.6(2)	C(1)–Re(1)–C(2)	89.1(2)
C(1)–Mn–C(3)	88.8(2)	C(1)–Re(1)–C(3)	89.5(2)
C(2)–Mn–C(3)	89.4(2)	C(2)–Re(1)–C(3)	89.7(2)
C(1)–Mn–O(4)	176.92(13)	C(1)–Re(1)–O(4)	178.3(2)
C(2)–Mn–O(4)	89.26(14)	C(2)–Re(1)–O(4)	90.5(2)
C(3)–Mn–O(4)	93.4(2)	C(3)–Re(1)–O(4)	92.1(2)
C(1)–Mn–P(2)	92.66(11)	C(1)–Re(1)–P(2)	93.91(13)
C(2)–Mn–P(2)	91.59(12)	C(2)–Re(1)–P(2)	91.71(14)
C(3)–Mn–P(2)	178.26(12)	C(3)–Re(1)–P(2)	176.32(14)
O(4)–Mn–P(2)	85.15(8)	O(4)–Re(1)–P(2)	84.45(9)
C(1)–Mn–P(1)	98.00(11)	C(1)–Re(1)–P(1)	97.69(13)
C(2)–Mn–P(1)	173.21(12)	C(2)–Re(1)–P(1)	173.26(14)
C(3)–Mn–P(1)	89.40(12)	C(3)–Re(1)–P(1)	90.43(14)
O(4)–Mn–P(1)	84.15(7)	O(4)–Re(1)–P(1)	82.74(9)
P(2)–Mn–P(1)	89.47(3)	P(2)–Re(1)–P(1)	87.78(3)
O(1)–C(1)–Mn	176.0(3)	O(1)–C(1)–Re(1)	178.3(4)
O(2)–C(2)–Mn	176.6(4)	O(2)–C(2)–Re(1)	178.4(4)
O(3)–C(3)–Mn	175.4(4)	O(3)–C(3)–Re(1)	177.0(5)
O(5)–Re–O(6)	109.9(2)	O(5)–Re(2)–O(6)	110.7(3)
O(5)–Re–O(7)	107.6(3)	O(5)–Re(2)–O(7)	106.9(4)
O(6)–Re–O(7)	110.5(2)	O(6)–Re(2)–O(7)	110.1(3)
O(5)–Re–O(4)	110.1(2)	O(5)–Re(2)–O(4)	109.8(3)
O(6)–Re–O(4)	110.2(2)	O(6)–Re(2)–O(4)	110.4(2)
O(7)–Re–O(4)	108.6(2)	O(7)–Re(2)–O(4)	108.8(2)
Re–O(4)–Mn	154.5(2)	Re(2)–O(4)–Re(1)	153.1(2)
C(13)–P(1)–C(7)	101.79(14)	C(13)–P(1)–C(7)	102.2(2)
C(13)–P(1)–C(4)	105.8(2)	C(13)–P(1)–C(4)	106.1(2)
C(7)–P(1)–C(4)	101.4(2)	C(7)–P(1)–C(4)	102.1(2)
C(13)–P(1)–Mn	118.39(10)	C(13)–P(1)–Re(1)	117.57(12)
C(7)–P(1)–Mn	114.71(11)	C(7)–P(1)–Re(1)	114.75(13)
C(4)–P(1)–Mn	112.82(11)	C(4)–P(1)–Re(1)	112.45(13)
C(5)–C(4)–P(1)	115.9(2)	C(5)–C(4)–P(1)	116.2(3)
C(6)–C(5)–C(4)	114.3(3)	C(6)–C(5)–C(4)	114.5(4)
C(5)–C(6)–P(2)	112.2(2)	C(5)–C(6)–P(2)	112.6(3)
C(19)–P(2)–C(6)	104.7(2)	C(19)–P(2)–C(6)	105.2(2)
C(19)–P(2)–C(25)	100.9(2)	C(19)–P(2)–C(25)	101.5(2)
C(6)–P(2)–C(25)	101.1(2)	C(6)–P(2)–C(25)	101.4(2)
C(19)–P(2)–Mn	113.10(12)	C(19)–P(2)–Re(1)	113.71(13)
C(6)–P(2)–Mn	112.79(11)	C(6)–P(2)–Re(1)	112.29(13)
C(25)–P(2)–Mn	122.15(12)	C(25)–P(2)–Re(1)	120.92(14)
C(12)–C(7)–P(1)	120.0(2)	C(12)–C(7)–P(1)	119.7(3)
C(8)–C(7)–P(1)	121.6(3)	C(8)–C(7)–P(1)	121.7(3)
C(18)–C(13)–P(1)	122.7(2)	C(18)–C(13)–P(1)	122.9(3)
C(14)–C(13)–P(1)	118.7(2)	C(14)–C(13)–P(1)	117.9(3)
C(24)–C(19)–P(2)	118.4(3)	C(24)–C(19)–P(2)	118.5(4)
C(20)–C(19)–P(2)	122.1(3)	C(20)–C(19)–P(2)	122.4(3)
C(30)–C(25)–P(2)	123.0(3)	C(30)–C(25)–P(2)	122.5(3)
C(26)–C(25)–P(2)	118.3(3)	C(26)–C(25)–P(2)	118.9(3)

3. Conclusion

Transtion-metal (carbonyl) perrhenato complexes can be easily synthesized from the reaction of Re_2O_7 with the corresponding transition-metal (carbonyl) hydrido, alkoxo, alkylcarbonato, carbonato-bridged, or alkoxymethyl complexes in CH_2Cl_2.

4. Experimental

All manipulations were carried out under a nitrogen atmosphere and the solvents were dried prior to use. Reagent grade chemicals were used without further purification. $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, Re_2O_7, $HReO_4$, dppe, and dppp were obtained from commercial sources. The starting materials, *fac*-(CO)$_3$(P–P)MH [10], *fac*-(CO)$_3$(P–P)MOR 11c[15], *fac*-(CO)$_3$(P–P)MOC(O)OR 11c, [(CO)$_3$(P–P)M]$_2${μ-OC(O)O} [16], and *fac*-(CO)$_3$(P–P)MCH$_2$OCH$_3$ [17] were synthesized according to literature procedures.

IR spectra were recorded on a Perkin–Elmer 1600 series FTIR instrument. NMR spectra were recorded on a Bruker AC 250 (250.133 MHz, ^{1}H; 62.896 MHz, ^{13}C) spectrometer. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Microanalyses were conducted by Quantitative Technologies Inc.

4.1. Reactions of hydrido manganese(I) and rhenium(I) complexes, *fac*-(CO)$_3$(P–P)MH with Re_2O_7

In a typical experiment a mixture of about 5 mmol of *fac*-(CO)$_3$(P–P)MH and 2.5 mmol of Re_2O_7 in 20 ml of moist CH_2Cl_2 was allowed to stir for 30 min at ambient temperature. The progress of the reaction was monitored with IR. The solvent was removed on a rotary evaporator. The residue was recrystallized in CH_2Cl_2–hexane at −5 °C. Filtration afforded colorless to pale-yellow crystals of perrhenato complexes, *fac*-(CO)$_3$(P–P)MOReO$_3$ (**1**, M = Mn, P–P = dppe; **2**, M = Mn, P–P = dppp; **3**, M = Re, P–P = dppe; **4**, M = Re, P–P = dppp). Data for **1**: yield, 72%; m.p. 195–197 °C with decomposition. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2034s, 1966s, 1930s; ν(ReO) 931m, 900m. ^{1}H-NMR (δ,

CD_2Cl_2): 7.68–7.18 (m, 20H), 3.0–2.68 (m, 4H). ^{13}C-NMR (δ, CD_2Cl_2): 214.8 (s, br, CO), 134.0–129.7 (m, C_6H_5), 25.8(t, J 18 Hz, $-PCH_2$) Anal. Calc. for $C_{29}H_{24}MnO_7P_2Re$: C, 44.2; H, 3.1. Found: C, 44.4; H, 3.2%. Data for **2**: yield, 76%; m.p. 185–186 °C with decomposition. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2038 s, 1972 s, 1925 s; ν(ReO) 928 m, 910 m. ^1H-NMR (δ, CD_2Cl_2): 7.56–7.34 (m, 20H), 2.52–1.54 (m, 6H). ^{13}C-NMR (δ, CD_2Cl_2): 215.2 (s, br, CO), 135.6–129.4 (m, C_6H_5), 25.1(t, J 12 Hz, $-PCH_2$), 18.9 (s, $H_2CCH_2CH_2$). Anal. Calc. for $C_{30}H_{26}MnO_7P_2Re$: C, 44.9; H, 3.3. Found: C, 44.6; H, 3.3%. Data for **3**: yield, 87%; m.p. 190–193 °C with decomposition. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2038s, 1962s, 1920s; ν(ReO) 933m, 910m. ^1H-NMR (δ, CD_2Cl_2): 7.79–7.24 (m, 20H), 3.08–2.62 (m, 4H). ^{13}C-NMR (δ, CD_2Cl_2): 193.0 (dd, 9Hz, 60 Hz, 2CO),191.2(t, 8 Hz, CO), 132.7–128.1(m, C_6H_5), 26.6(m,$-PCH_2$). Anal. Calc. for $C_{29}H_{24}O_7P_2Re_2$: C, 37.9; H, 2.6. Found: C, 37.9; H, 2.6%. Data for **4**: yield, 88%; m.p. 250–252 °C with decomposition. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2041s, 1965s, 1915s; ν(ReO) 955m, 935m. ^1H-NMR (δ, CD_2Cl_2): 7.55–7.35 (m, 20H), 2.70–1.74 (m, 6H). ^{13}C-NMR (δ, CD_2Cl_2): 193.5 (t, 6 Hz, CO), 191.5 (t, 23 Hz, CO), 191.0 (t, 23 Hz, CO), 134.9–129.6 (m, C_6H_5), 25.2(t, J 13 Hz, $-PCH_2$), 19.6 (s, $H_2CCH_2CH_2$). Anal. Calc. for $C_{30}H_{26}O_7P_2Re_2$: C, 38.6; H, 2.8. Found: C, 38.6; H, 2.8%.

4.2. Reactions of alkoxo manganese(I) and rhenium(I) complexes, *fac*-$(CO)_3(P-P)MOR$ with Re_2O_7, where, R is CH_3 or CH_2CH_3

In a typical experiment a mixture of about 2 mmol of *fac*-$(CO)_3(P-P)MOCH_3$ and 2 mmol of Re_2O_7 in 10 ml of CH_2Cl_2 was allowed to stir for 30 min at ambient temperature. The progress of the reaction was monitored with IR. During this period the color of the solution changed from yellow (alkoxo manganese complexes) or colorless (alkoxo rhenium complexes) to dark red and black precipitates were observed. The solvent was removed on a rotary evaporator and the residue was extracted with 20 ml of CH_2Cl_2. The solution was evaporated to dryness and the residue was recrystallized in CH_2Cl_2–hexane at −5 °C. Filtration afforded colorless to pale-yellow crystals of the perrhenato complexes, *fac*-$(CO)_3(P-P)MOReO_3$, **1**–**4**, in 81–85% yield.

4.3. Reactions of methylcarbonato complexes, *fac*-$(CO)_3(P-P)MOC(O)OCH_3$ with Re_2O_7

In a typical experiment a mixture of about 2 mmol of *fac*-$(CO)_3(P-P)MOC(O)OCH_3$ and 2 mmol of Re_2O_7 in 10 ml of CH_2Cl_2 was allowed to stir at 0 °C for 30 min. The progress of the reaction was monitored with IR. During the course of the reaction the color of the solution changed from yellow or colorless to red and black precipitates were observed. The solvent was removed on a rotary evaporator. The residue was recrystallized in CH_2Cl_2–hexane at −5 °C. Filtration afforded colorless to pale-yellow crystals of the perrhenato complexes, *fac*-$(CO)_3(P-P)MOReO_3$, **1**–**4**, in 78–83% yield.

4.4. Reactions of carbonato-bridged complexes, $[(CO)_3(P-P)M]_2\{\mu\text{-}OC(O)O\}$ with Re_2O_7

In a typical experiment an equimolar mixture of Re_2O_7 and $[(CO)_3(dppe)Mn]_2\{\mu\text{-}OC(O)O\}$, $[(CO)_3(dppp)Mn]_2\{\mu\text{-}OC(O)O\}$, or $[(CO)_3(dppe)Re]_2\{\mu\text{-}OC(O)O\}$ in 10 ml of moist CH_2Cl_2 was allowed to stir at ambient temperature for 30 min. The progress of the reaction was monitored with IR. The solvent was removed on a rotary evaporator. The residue was recrystallized in CH_2Cl_2–hexane at −5 °C. Filtration afforded colorless to pale-yellow crystals of the perrhenato complexes, *fac*-$(CO)_3(P-P)MOReO_3$, **1**–**3**, in 80–85% yield.

4.5. Reactions of methoxymethyl complexes, *fac*-$(CO)_3(P-P)MCH_2OCH_3$ with Re_2O_7

In a typical experiment a mixture of about 2 mmol of *fac*-$(CO)_3(P-P)MCH_2OCH_3$ and 2 mmol of Re_2O_7 in 10 ml of CH_2Cl_2 was allowed to stir at 0 °C for 30 min. The progress of the reaction was monitored with IR. A black precipitate was also observed in this reaction. The solvent was removed on a rotary evaporator. The residue was recrystallized in CH_2Cl_2–hexane at −5 °C. Filtration afforded colorless to pale-yellow crystals of the perrhenato complexes, *fac*-$(CO)_3(P-P)MOReO_3$, **1**–**4**, in 69–76% yield.

4.6. X-ray crystal structure of *fac*-$(CO)_3(dppp)MnOReO_3$ (**2**)

Crystals of **2** were grown from CH_2Cl_2–hexane on cooling at −5 °C. Data were collected on a Nonius KappaCCD diffractometer and corrected for Lorentz-polarization and absorption effects. The structure was direct methods and refined by full-matrix least-squares on F^2 using SHELXTL (version 5.04). The non-hydrogen atoms were refined anisotropically and the hydrogens were allowed to ride on their respective carbons. The hydrogens were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ and an extinction parameter was included in the refinements. Similar methods were used for **4**, which is isomorphous with **2**.

5. Supplementary material

The following crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 162600 for compound **2** and CCDC 162601 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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