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Amine-oxide-mediated oxidative methanolysis of metal–metal bonds in $[MM'(CO)_{10}]$ (M = Mn, Re; M′ = Re) and $[Os_3(CO)_{12}]$: crystal structure of *fac*-$[Re\{OC(O)OMe\}(CO)_3(\eta^2\text{-dppf})]$

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Abstract

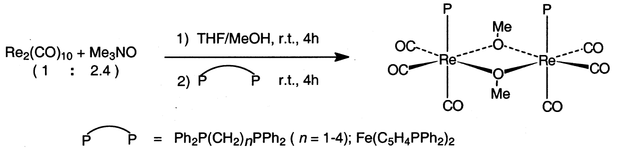
The reaction of 1,1′-bis(diphenylphosphino)ferrocene (dppf) with a mixture of $[MnRe(CO)_{10}]$, MeOH and Me_3NO afforded the complexes *fac*-$[MnH(CO)_3(\eta^2\text{-dppf})]$ and $[Re_2(\mu\text{-OMe})_2(\mu\text{-dppf})(CO)_6]$. In the one-pot reaction of $[Re_2(CO)_{10}]$ with Me_3NO, MeOH and dppf, the major mononuclear Re species isolated was the CO_2-inserted complex *fac*-$[Re\{OC(O)OMe\}(CO)_3(\eta^2\text{-dppf})]$, the crystal structure of which was determined. The coordination sphere of the rhenium atom is roughly octahedral, consisting of an oxygen atom from the methyl carbonate ligand, two phosphorus atoms from a chelating dppf ligand, and three carbon atoms from a facial arrangement of three terminally bonded carbonyls. Analogous Me_3NO-mediated methoxylation reactions involving $[Os_3(CO)_{12}]$ were also investigated. With a $[Me_3NO]:[Os_3(CO)_{12}]$ ratio of 2:1, the major product is $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OMe})]$. With three molar equivalents of Me_3NO, significant quantities of $[Os_3(CO)_{10}(\mu\text{-OMe})_2]$ are also obtained.

Keywords: Amine oxide; Methanolysis; Rhenium; Osmium; Carbonyl; Methylcarbonate

1. Introduction

Transition-metal carbonyl hydroxides and alkoxides have been proposed as intermediates in a number of important reactions, such as metal-catalysed hydrogenation of CO [1], the water-gas shift reaction [2], and carboalkoxylation of olefins [3]. They are also molecular models of silica-anchored $M(CO)_n$ species, the only structural difference between alkoxy and surfaced anchored complexes being that the –OR group is replaced by an –OSi≡ group [4].

We have reported the facile synthesis of a series of dimethoxo-bridged complexes $[Re_2(\mu\text{-OMe})_2(\mu\text{-PP})(CO)_6]$ (PP = dppf (1,1′-bis(diphenylphosphino)ferrocene) or $Ph_2P(CH_2)_nPPh_2$, $n = 1$–4) by the addition of diphosphines to a mixture obtained from the reaction of $[Re_2(CO)_{10}]$ with Me_3NO in THF–MeOH mixture at room temperature (Scheme 1) [5,6]. The facile rupture of the Re–Re bond under such mild conditions is in sharp contrast to the general observation that metal–metal bonds are quite resistant to thermal cleavage [7,8] and that Re–Re bond alcoholysis requires rather drastic conditions, such as refluxing in methanolic KOH [9].



Scheme 1.

At first, a mechanism for the Me_3NO-aided oxidative methoxylation reaction in which the originally bonded Re atoms in $[Re_2(CO)_{10}]$ remain paired in the same molecule of the product $[Re_2(\mu\text{-OMe})_2(\mu\text{-PP})(CO)_6]$ (Scheme 2) seemed plausible [10]. We then extended our investigations to the reaction of $[Re_2(CO)_{10}]$ with Me_3NO and phenol, which yielded the complexes $[Re_3(\mu\text{-H})(CO)_{14}]$ and $[Re_2(\mu\text{-OPh})_3(CO)_6]^-$ [11]. This suggested a mechanism involving the separation of the Re atoms of $[Re_2(CO)_{10}]$ into mononuclear hydrido and phenoxo species, followed by dimerisation of the phenoxo species to form the bis(phenoxo)-bridged intermediate $[Re_2(\mu\text{-OPh})_2(CO)_8]$ [11]. It seemed probable that the oxidative methoxylation reaction also follows a similar pathway involving Re–Re

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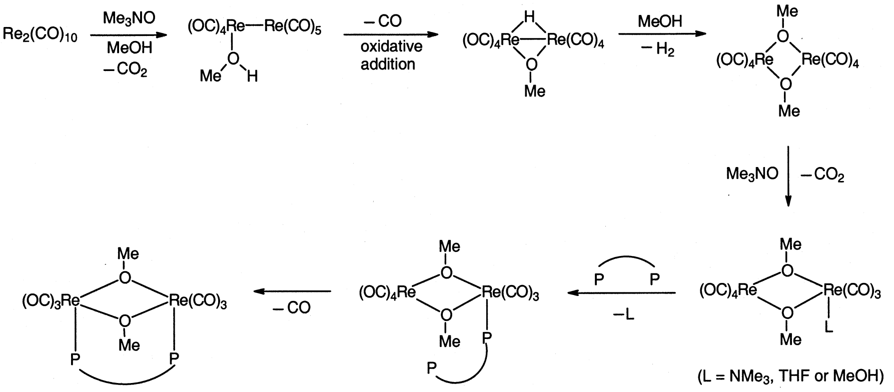
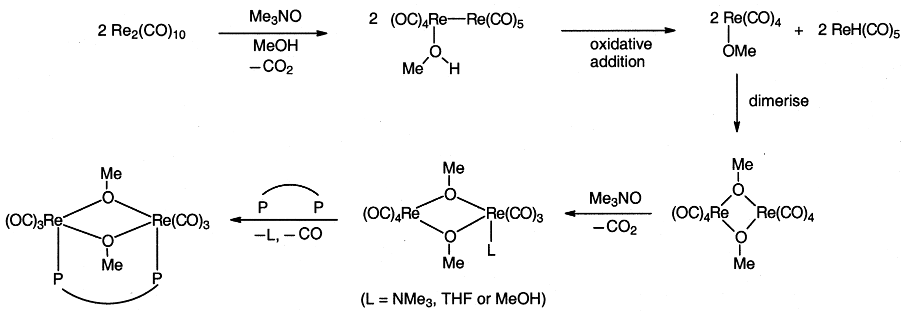


Scheme 2.



Scheme 3.

bond heterolysis, but we have not been able to observe any rhenium hydrido species in this reaction. The reaction of $[Re_2(CO)_{10}]$ with Me_3NO and methanol (without diphosphine) yields $[Me_3NH]^+[Re_3(\mu_3\text{-}OMe)(\mu\text{-}OMe)(\mu\text{-}OH)_2(CO)_9]^-$ as the only isolable product [11].

In an effort to throw more light onto the mechanism of Me_3NO-aided oxidative methoxylation, we studied the reaction of dppf with the mixture of $[MnRe(CO)_{10}]$, MeOH and Me_3NO. The products of this reaction should indicate whether the Re and Mn atoms are separated during the reaction. Formation of the homometallic complexes $[Re_2(\mu\text{-}OMe)_2(\mu\text{-dppf})(CO)_6]$ and/or $[Mn_2(\mu\text{-}OMe)_2(\mu\text{-dppf})(CO)_6]$ would support the M–M bond heterolysis mechanism. The results of this study are reported in this paper. We also report a similar amine-oxide mediated methoxylation of Os–Os bonds in the cluster $[Os_3(CO)_{12}]$ to form $[Os_3(\mu\text{-}H)(\mu\text{-}OMe)(CO)_{10}]$ and $[Os_3(\mu\text{-}OMe)_2(CO)_{10}]$. These methoxo clusters were first reported in 1968 [12], but to date no convenient one-pot synthesis giving high yields of these clusters from $[Os_3(CO)_{12}]$ has been reported [4,13–16].

2. Results and discussion

2.1. Reaction of dppf with $MnRe(CO)_{10}$, MeOH and Me_3NO

The reaction of dppf with the mixture of $[MnRe(CO)_{10}]$, MeOH and Me_3NO afforded the complexes *fac*-$[MnH(CO)_3(\eta^2\text{-dppf})]$ (8%), $[Re_2(\mu\text{-}OMe)_2(\mu\text{-dppf})(CO)_6]$ (26%) and a trace amount of *fac*-$[ReCl(CO)_3(\eta^2\text{-dppf})]$. These results confirm the occurrence of metal–metal bond cleavage and the formation of metal hydride intermediates in the reaction. The mechanism for the formation of $[Re_2(\mu\text{-}OMe)_2(\mu\text{-dppf})(CO)_6]$ from the reaction of dppf with $[Re_2(CO)_{10}]$, MeOH and Me_3NO is therefore proposed as shown in Scheme 3.

Interestingly, the complexes $[Mn_2(\mu\text{-}OMe)_2(\mu\text{-dppf})(CO)_6]$ and $[ReH(CO)_3(\eta^2\text{-dppf})]$ are not observed as products of the reaction, probably because these complexes are unstable under the conditions of the reaction and isolation of products. The complex $[ReCl(CO)_3(\eta^2\text{-dppf})]$ is likely to be produced from the reaction of initially formed $[ReH(CO)_3(\eta^2\text{-dppf})]$ with CH_2Cl_2 used during the isolation of products by TLC [17]. We have also not been able to synthesise $[Mn_2(\mu\text{-}OMe)_2(\mu\text{-dppf})(CO)_6]$ via the reaction of dppf with the mixture of $[Mn_2(CO)_{10}]$, Me_3NO and MeOH.

2.2. One-pot reaction of $[Re_2(CO)_{10}]$ with Me_3NO, MeOH and dppf

In an attempt to trap the $[Re(OMe)(CO)_4]$ intermediate in the reaction of $[Re_2(CO)_{10}]$ with Me_3NO and MeOH, the one-pot reaction of $[Re_2(CO)_{10}]$ with Me_3NO, MeOH and dppf has been carried out [11]. The major mononuclear Re complex formed in this reaction (**1**) was mistakenly identified as the terminal methoxo complex *fac*-$[Re(OMe)(CO)_3(\eta^2\text{-dppf})]$ in Ref. [11]. We have subsequently determined the crystal structure of **1** (see below), and identified it as the methyl carbonate complex *fac*-[Re{OC(O)OMe}$(CO)_3$(η^2-dppf)].

Complex **1** is most probably formed by the insertion of CO_2 into the intermediate complex *fac*-[Re(OMe)$(CO)_3$(η^2-dppf)] resulting from the reaction of dppf with [Re(OMe)$(CO)_4$]. The CO_2 needed for the insertion reaction is probably produced by the decarbonylation of [$Re_2(CO)_{10}$] by Me_3NO. The facile CO_2-insertion reactions of the complexes *fac*-[Re(OR)$(CO)_3$(η^2-PP)] (R = Me, Et, CF_3CH_2; PP = 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane) with atmospheric CO_2 has been reported [18].

2.3. Crystal structure of fac-[Re{OC(O)OMe}-$(CO)_3$(η^2-dppf)] (**1**)

The crystal structure of **1** (Fig. 1) is similar to that of *fac*-[Mn{OC(O)OMe}$(CO)_3$(η^2-dppe)] [18]. The coordination sphere of the rhenium atom is roughly octahedral, consisting of an oxygen atom from the methyl carbonate ligand (taken to occupy an axial position), two phosphorus atoms from a chelating dppf ligand, and three carbon atoms from a facial arrangement of three terminally bound carbonyls. The P–Re–P angle in **1** (Table 1) is larger than the P–Mn–P angle in *fac*-[Mn{OC(O)OMe}$(CO)_3$(η^2-dppe)] (84.1(1)°), probably owing to the greater steric demand of dppf compared to dppe. The Re–CO(eq) distances (average 1.943(7) Å) are longer than the Re–CO(ax) distance (1.890(7) Å). Correspondingly, the C–O bond length of the axial carbonyl (1.154(8) Å) is longer than the lengths of 1.131(7) and 1.138(7) Å observed for the equatorial carbonyls. This can be attributed to the greater extent of M → CO backbonding experienced by the axial carbonyl, which is *trans* to the π-donating methyl carbonate ligand. The Re–O(1) bond to the methyl carbonate ligand has a length of 2.150(4) Å, which is comparable to the Re–O bond lengths of 2.150(4) Å in *fac*-[Re(OPh)$(CO)_3$(η^2-dppe)] [19], 2.162(6) Å (average) in [$Re_2(\mu\text{-}OMe)_2(\mu$-dppf)$(CO)_6$] [5], and 2.143(8) Å (average) in [$Re_2(\mu\text{-}OMe)_2(\mu$-dppm)$(CO)_6$] [6].

2.4. Reactions of [$Os_3(CO)_{12}$] with Me_3NO and MeOH

Reaction of [$Os_3(CO)_{12}$] with Me_3NO (1.2 molar equivalents) in refluxing THF–methanol (7:1) mixture for 4 h gave the complex [$Os_3(\mu\text{-}H)(\mu\text{-}OMe)(CO)_{10}$] (**2**) in 71% yield. Increasing the amount of amine oxide (2.4 molar equivalents) and methanol (THF:MeOH 4:1) did not significantly increase the yield of **2** (73%). The same cluster has been prepared in 10% yield by direct reaction of [$Os_3(CO)_{12}$] with methanol at 170°C for 38 h in vacuo in a steel-lined autoclave [13]. It can also be prepared via multi-step processes involving [$Os_3(CO)_{10}$(cyclohexa-1,3-diene)] [14], [$Os_3(CO)_{10}$(cyclooctene)$_2$] [15], [$Os_3(CO)_{10}(CH_3CN)_2$] [15], or [$Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}$] [16] as intermediates. However, since three or four steps are required starting from [$Os_3(CO)_{12}$], overall yields are never more than 50%. More recently, the reaction of methanol with the silica-anchored cluster [$Os_3(\mu\text{-}H)(\mu\text{-}OSi\equiv)(CO)_{10}$] (prepared by refluxing an *n*-octane solution of [$Os_3(CO)_{12}$] with silica for 10 h) was reported to give complex **2** in 52% yield (starting from [$Os_3(CO)_{12}$]) [4]. An alternative route involving the reaction of methanol with [$Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}$] (prepared by heating a suspension of [$Os_3(\mu\text{-}H)(\mu\text{-}OSi\equiv)(CO)_{10}$] in a water–toluene mixture at 95°C for 5 h) gives complex **2** in 82% overall yield from [$Os_3(CO)_{12}$] [4]. Compared with the reported syntheses of **2**, the present method is much more attractive since it is a high-yield one-pot synthesis over 4 h, starting directly from [$Os_3(CO)_{12}$], under relatively mild conditions.

When the molar ratio of Me_3NO to [$Os_3(CO)_{12}$] is increased to 3.3:1, the bis(methoxo) cluster [$Os_3(\mu\text{-}OMe)_2(CO)_{10}$] (**3**) is obtained in 11% yield, while complex **2** is obtained in 33% yield. The yield of **3** is increased to 17% when 4.3 molar equivalents of amine oxide are used, while the yield of **2** remains essentially unchanged. As far as we are aware, the highest-yield synthesis for **3** reported thus far involves direct reaction of [$Os_3(CO)_{12}$] with methanol at 170°C for 38 h in vacuo in a steel-lined autoclave, which

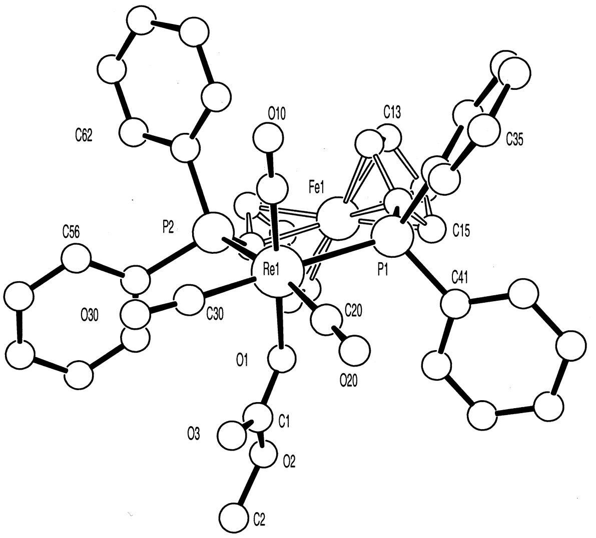


Fig. 1. Crystal structure of *fac*-[Re{OC(O)OMe}$(CO)_3$(η^2-dppf)] (**1**). Hydrogen atoms are omitted for clarity.

Table 1
Bond lengths (Å) and angles (°) for *fac*-[Re{OC(O)OMe}$(CO)_3$(η^2-dppf)] (**1**)

Re(1)–P(1)	2.508(2)	C(20)–O(20)	1.131(7)
Re(1)–P(2)	2.505(2)	C(30)–O(30)	1.138(7)
Re(1)–O(1)	2.150(4)	C(1)–O(1)	1.300(7)
Re(1)–C(10)	1.890(7)	C(1)–O(2)	1.244(8)
Re(1)–C(20)	1.946(7)	C(1)–O(3)	1.224(7)
Re(1)–C(30)	1.940(7)	O(2)–C(2)	1.438(8)
C(10)–O(10)	1.154(8)		
P(1)–Re(1)–P(2)	96.18(5)	O(1)–C(1)–O(3)	124.1(7)
Re(1)–O(1)–C(1)	125.6(4)	C(1)–O(2)–C(2)	118.1(6)
O(1)–C(1)–O(2)	112.3(5)	O(2)–C(1)–O(3)	123.6(7)

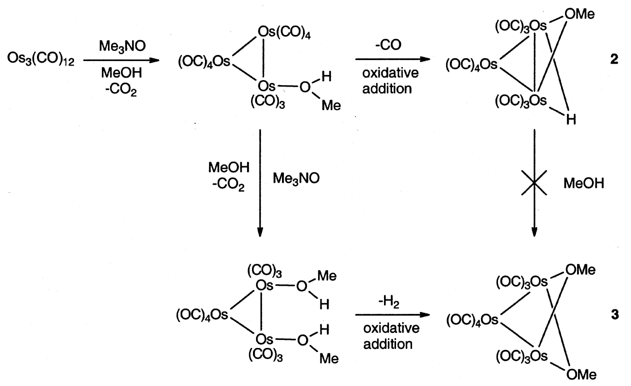
gives **3** in 13% yield and **2** in 10% yield (see above) [13]. The present one-pot synthesis for **3** is comparatively more convenient and gives a similar yield of the cluster.

*2.5. Proposed mechanism for the formation of clusters **2** and **3***

A plausible mechanism for the formation of clusters **2** and **3** is given in Scheme 4. As in the proposed mechanism for the formation of $[Re_2(\mu\text{-}OMe)_2(\mu\text{-dppf})(CO)_6]$ from $[Re_2(CO)_{10}]$, the first step involves Me_3NO-assisted substitution of a CO ligand by methanol. Oxidative addition of MeO–H across the M–M bond does not, however, result in the formation of two separate mononuclear species $[OsH(CO)_3]$ and $[Os(OMe)(CO)_3]$, since the two $[Os(CO)_3]$ fragments are still bonded to the third osmium atom, which keeps them in close proximity. The oxidative addition reaction therefore results preferentially in the hydrido- and methoxo-bridged cluster $[Os_3(\mu\text{-}H)(\mu\text{-}OMe)(CO)_{10}]$ (**2**), with three Os–Os bonds. The loss of the second CO ligand which accompanies the oxidative addition presumably does not require Me_3NO, since there is no significant difference in the yield of **2** whether 1.2 or 2.4 molar equivalents of amine oxide is used.

The cluster $[Os_3(\mu\text{-}OMe)_2(CO)_{10}]$ (**3**) is probably formed by the oxidative addition of methanol and elimination of H_2 from the disubstituted intermediate $[Os_3(CO)_{10}(MeOH)_2]$. The formation of $[Os_3(CO)_{10}(MeOH)_2]$ from $[Os_3(CO)_{11}(MeOH)]$ probably requires Me_3NO and is slow compared to the conversion of $[Os_3(CO)_{11}(MeOH)]$ to $[Os_3(\mu\text{-}H)(\mu\text{-}OMe)(CO)_{10}]$. Hence cluster **3** is only formed in significant quantities when excess amine oxide is used. The higher concentration of Me_3NO probably increases the rate of formation of $[Os_3(CO)_{10}(MeOH)_2]$, enabling this process to compete more effectively against the formation of $[Os_3(\mu\text{-}H)(\mu\text{-}OMe)(CO)_{10}]$. Cluster **3** is unlikely to be formed from the secondary reaction of **2** with excess methanol since **2** remains unchanged when refluxed in methanol for 4 h.

Interestingly, Deeming et al. reported that $[Ru_3(CO)_{12}]$ reacts with $Me_3NO \cdot 2H_2O$ (5.8 molar equivalents) in the presence of (*R*)-BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) to give an 80% yield of the dihydroxo complex $[Ru_3(\mu\text{-}OH)_2(CO)_8\{\mu\text{-}(R)\text{-BINAP}\}]$ [20]. Although the authors identified $Me_3NO \cdot 2H_2O$ as the probable source of the hydroxo ligands, they did not propose any mechanism for the formation of $[Ru_3(\mu\text{-}OH)_2(CO)_8\{\mu\text{-}(R)\text{-BINAP}\}]$. We believe that the mechanism is similar to that proposed above for the formation of $[Os_3(\mu\text{-}OMe)_2(CO)_{10}]$. The complex $[Ru_3(\mu\text{-}OH)_2(CO)_{10}]$ is probably formed, and is further decarbonylated by the excess Me_3NO present to give an unsaturated intermediate which reacts with BINAP to form $[Ru_3(\mu\text{-}OH)_2(CO)_8\{\mu\text{-}(R)\text{-BINAP}\}]$. It is noteworthy that when dppm (bis(diphenylphosphino)methane) was added to the mixture resulting from the reaction of $[Os_3(CO)_{12}]$ with 4.3 molar equivalents of Me_3NO in THF–MeOH, a product tentatively identified as $[Os_3(\mu\text{-}H)(\mu\text{-}OMe)(\mu\text{-dppm})(CO)_8]$ could be isolated.



Scheme 4.

So far, we have not observed products where two or more Os–Os bonds have been methoxylated.

3. Summary and conclusions

The reaction of dppf with the mixture of $MnRe(CO)_{10}$, MeOH and Me_3NO gives the complexes *fac*-$[MnH(CO)_3(\eta^2\text{-dppf})]$ and $[Re_2(\mu\text{-}OMe)_2(\mu\text{-dppf})(CO)_6]$, confirming that mononuclear alkoxo and hydrido intermediates are formed during the reaction. Reaction of $[Os_3(CO)_{12}]$ with Me_3NO (1–2 molar equivalents) and methanol gives $[Os_3(\mu\text{-}H)(\mu\text{-}OMe)(CO)_{10}]$ in good yield. With 3 molar equivalents of Me_3NO, significant quantities of $[Os_3(\mu\text{-}OMe)_2(CO)_{10}]$ are also obtained. No further methoxylation of Os–Os bonds occurs when the $[Me_3NO]$:$[Os_3(CO)_{12}]$ ratio is increased to 4:1.

4. Experimental

All reactions were performed under pure dry argon using standard Schlenk techniques. Solvents used were of reagent grade and were dried by published procedures and freshly distilled under argon before use. Unless otherwise stated, all reagents and starting materials used were of AR grade and were obtained from commercial sources and used as supplied. Precoated silica plates of layer thickness 0.25 mm were obtained from Merck. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at ca. 300 K on a Bruker ACF 300 MHz spectrometer. ^1H and ^{31}P chemical shifts are quoted in ppm downfield of tetramethylsilane and external 80% H_3PO_4, respectively. Infrared spectra were recorded on either a Perkin Elmer 1600 or a Bio-Rad FTS165 FT-IR spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, National University of Singapore.

4.1. Preparation of $[MnRe(CO)_{10}]$

The reported method [21,22] for the preparation of $[MnRe(CO)_{10}]$ was used with slight modification. A degassed solution of [$Mn_2(CO)_{10}$] (0.235 g, 0.60 mmol) in freshly dried THF (10 cm^3) was transferred into a Schlenk flask (cooled in an ice bath) containing sodium amalgam (3% Na by weight) ($\sim$1 g). The resultant suspension was stirred under argon at 0°C for 1 h, then at room temperature for another 1 h. The solution was then filtered under argon into a flask containing a stirred solution of [$ReBr(CO)_5$] (0.406 g, 1.0 mmol) in THF (10 cm^3). Reaction was continued at room temperature under argon for 4 h. Solvent was removed under reduced pressure and the resultant residue was exposed in air for 1 week to oxidise any unreacted [$Mn_2(CO)_{10}$]. The orange solid obtained was then sublimed at 55°C, 0.3 mmHg. The compound [$MnRe(CO)_{10}$] was obtained as an orange solid with a yield of 0.40 g (77% based on Re).

The purity of the [$MnRe(CO)_{10}$] obtained was ascertained by IR spectroscopy and elemental analysis. ν_{max}(CO): 2054s, 2017 vs,1978s cm^{-1} (cyclohexane) (none of the IR absorption peaks of [$Mn_2(CO)_{10}$] and [$Re_2(CO)_{10}$] were detected). *Anal.* $C_{10}MnO_{10}Re$ requires: C, 23.0. Found: C, 23.4%.

4.2. Reaction of dppf with [MnRe(CO)$_{10}$], MeOH and TMNO

The solution of $Me_3NO \cdot 2H_2O$ (0.062 g, 0.56 mmol) in THF–MeOH (1:1, 20 cm^3) was transferred into a Schlenk flask containing a stirred solution of [$MnRe(CO)_{10}$] (0.120 g, 0.23 mmol) in THF (10 cm^3) at room temperature. This solution was stirred in vacuo for 4 h at room temperature. Solid dppf (0.128 g, 0.23 mmol) was added and the orange solution so formed was stirred in vacuo for 1 h. It was then evaporated to half its volume and stirred for 3 h. The solvent was then removed and the residue was redissolved in a minimum amount of CH_2Cl_2 and chromatographed on silica TLC plates (CH_2Cl_2:hexane 2:3). From the main bands the complexes *fac*-[$MnH(CO)_3(\eta^2$-dppf)] ($R_f = 0.57$) and [$Re_2(\mu$-OMe$)_2(\mu$-dppf$)(CO)_6$] ($R_f = 0.47$) were isolated with yields of 0.012 g (8%) and 0.035 g (26%), respectively. A trace amount of *fac*-[$ReCl(CO)_3(\eta^2$-dppf)] ($R_f = 0.13$) was also isolated.

The complex *fac*-[$MnH(CO)_3(\eta^2$-dppf)] was recrystallised from CH_2Cl_2–MeOH mixture at 0°C. *Anal.* Found: C, 63.5; H, 4.3; P, 8.8. $C_{37}H_{29}O_3P_2FeMn$ (FW 694) requires: C, 64.0; H, 4.2; P, 8.9%. ν_{max}(CO): 1998s, 1920m(sh), 1903m ($CHCl_3$); 1996s, 1917m(sh), 1903m (CH_2Cl_2); 1997s, 1922m(sh), 1906m cm^{-1} (THF). δ_H ($CDCl_3$) 7.7–7.4 (m) (20H, Ph), 4.38 (s, 2H, CpH), 4.29 (s, 2H, CpH), 4.18 (s, 2H, CpH), 4.08 (s, 2H, CpH), -6.18 (t, 1H, hydride), $J_{(P\text{–}Mn\text{–}H)}$ 50 Hz; δ_p ($CDCl_3$) 64.8. The complexes [$Re_2(\mu$-OMe$)_2(\mu$-dppf$)(CO)_6$] and *fac*-[$ReCl(CO)_3(\eta^2$-dppf)] were identified by IR, ^{1}H and ^{31}P NMR spectroscopy [5,23].

4.3. Preparation of fac-[Re{OC(O)OMe}(CO)$_3$(η^2-dppf)] (**1**)

A solution of $Re_2(CO)_{10}$ (0.151 g, 0.23 mmol) in THF (20 cm^3) was transferred into a stirred solution of $Me_3NO \cdot 2H_2O$ (0.062 g, 0.56 mmol) and dppf (0.128 g, 0.23 mmol) in a mixture of MeOH (10 cm^3) and THF (20 cm^3). The resultant solution was stirred under partial vacuum at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was redissolved in a minimum amount of THF and chromatographed on silica TLC plates (acetone:hexane 1:4). The complex *fac*-[Re{OC(O)OMe}$(CO)_3(\eta^2$-dppf)] (**1**) was isolated from the chrome-yellow band at $R_f = 0.23$. Air-stable orange prismatic crystals of **1** were obtained by cooling a solution of **1** in benzene–hexane–MeOH mixture to -10°C. Yield 0.016 g (4%). The crystals have the composition [Re{OC(O)-OMe}$(CO)_3(\eta^2$-dppf)]$(C_6H_6)_{0.5}$. *Anal.* $C_{42}H_{34}FeO_6P_2Re$ (FW 938.7) requires: C, 53.7; H, 3.6; P, 6.5. Found: C, 53.8; H, 3.7; P, 6.4%. ν_{max}(CO) 2037vs, 1948m, 1899s (C_6H_6); 2033vs, 1951s, 1900s (acetone); 2029s, 1947s, 1895s cm^{-1} (KBr); ν(C=O methyl carbonate ligand) 1678m cm^{-1} (KBr). δ_H (C_6D_6) 7.94–7.82 (m), 7.17–7.02 (m) (20H, C_6H_5), 5.06 (s, 2H, CpH), 4.32 (s, 2H, CpH), 3.90 (s, 2H, CpH), 3.81 (s, 2H, CpH), 3.59 (s, 3H, OCH_3); δ_P (C_6D_6) 7.23 (s).

4.4. Reaction of [Os$_3$(CO)$_{12}$] with MeOH and one molar equivalent of Me$_3$NO

Tetrahydrofuran (60 cm^3) and [$Os_3(CO)_{12}$] (0.0365 g, 0.040 mmol) were placed in a 250 ml three-neck round-bottom flask fitted with a reflux condenser, an argon inlet, and a 100 ml pressure-equalising dropping funnel. The reaction mixture was stirred and heated to reflux (oil bath temperature maintained at 80°C). A solution of $Me_3NO \cdot 2H_2O$ (0.0052 g, 0.047 mmol) in THF–methanol (1:1) mixture (20 cm^3) was then added dropwise over an hour. The resultant solution was refluxed for a further 3 h. The yellow solution obtained was then cooled to room temperature and filtered through silica. The silica was washed with THF until the washings were colourless. The combined filtrate and washings was rotary evaporated to obtain an oily residue. The residue was redissolved in a minimum amount of CH_2Cl_2 and chromatographed on silica TLC plates, eluting with CH_2Cl_2–hexane (5:95) mixture. A major yellow band ($R_f = 0.72$) was obtained and extracted with CH_2Cl_2 to give [$Os_3(\mu$-H$)(\mu$-OMe$)(CO)_{10}$] (**2**). Yield 0.0251 g (71%). The identity of this compound was confirmed by IR and ^{1}H NMR spectroscopy [12].

4.5. Reaction of [Os$_3$(CO)$_{12}$] with MeOH and two molar equivalents of Me$_3$NO

The procedure adopted was similar to that for the reaction with one molar equivalent of Me_3NO except for the relative amounts of reagents used: [$Os_3(CO)_{12}$] 0.0352 g, 0.039 mmol; $Me_3NO\cdot 2H_2O$ 0.0103 g, 0.093 mmol; dissolved in THF–methanol (1:1) mixture (40 cm^3). Yield of **2** was 0.0249 g (73%).

4.6. Reaction of [$Os_3(CO)_{12}$] with MeOH and three molar equivalents of Me_3NO

The amounts of reagents used were as follows: [$Os_3(CO)_{12}$] 0.0356 g, 0.039 mmol; $Me_3NO\cdot 2H_2O$ 0.0143 g, 0.129 mmol; dissolved in THF–methanol (1:1) mixture (60 cm^3). TLC on silica plates (CH_2Cl_2:hexane 1:9) gave two main yellow bands: **2** ($R_f = 0.87$, 0.0173 g, 49%) and **3** [$Os_3(\mu\text{-}OMe)_2(CO)_{10}$] ($R_f = 0.71$, 0.0039 g, 11%). The identity of compound **3** was confirmed by IR and ^{1}H NMR spectroscopy [12].

4.7. Reaction of [$Os_3(CO)_{12}$] with MeOH and four molar equivalents of Me_3NO

The amounts of reagents used were as follows: [$Os_3(CO)_{12}$] 0.0335 g, 0.037 mmol; $Me_3NO\cdot 2H_2O$ 0.0178 g, 0.160 mmol; dissolved in THF–methanol (1:1) mixture (80 cm^3). Yields: **2** (0.0103 g, 32%); **3** (0.0056 g, 17%).

4.8. Reaction of [$Os_3(CO)_{12}$] with MeOH, four molar equivalents of Me_3NO, and one equivalent of bis(diphenylphosphino)methane (dppm)

The compounds [$Os_3(CO)_{12}$] (0.0556 g, 0.061 mmol), $Me_3NO\cdot 2H_2O$ (0.0294 g, 0.265 mmol, dissolved in THF–methanol (1:1) mixture (80 cm^3)) were allowed to react as above. After 4 h, dppm (0.0243 g, 0.093 mmol) was added. The solution was stirred for another 30 min, during which the colour of the solution darkened somewhat. The solution was filtered through silica and the filtrate was rotary evaporated to obtain an oily residue. The residue was dissolved in CH_2Cl_2 and loaded onto a silica column. Elution with CH_2Cl_2–hexane mixture (1:4) yielded a major yellow band which gave IR and ^{1}H NMR spectra consistent with the formulation [$Os_3(\mu\text{-}H)(\mu\text{-}OMe)(\mu\text{-}dppm)(CO)_8$]. ν_{max}(CO) 2086vw, 2074m, 2048w, 2038vw, 2003vs, 1990sh, 1941m cm^{-1} (hexane). δ_H ($CDCl_3$) 7.3–7.5 (m) (20H, Ph), 3.4 (s) (3H, OCH_3), 3.1 (dt) (1H, CH_2), 2.9 (dt) (1H, CH_2), −11.2 (t) (1H, hydride), $J_{(H–P)}$ 12 Hz; δ_P ($CDCl_3$) −8.4 (s).

4.9. X-ray crystallography of fac-[Re{OC(O)OMe}-$(CO)_3(\eta^2\text{-dppf})$] (**1**)

Data were collected on a crystal of dimensions 0.17×0.30×0.40 mm using a Siemens P4 diffractometer in the θ–2θ mode, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data: $C_{39}H_{31}FeO_6P_2Re\cdot 0.5(C_6H_6)$, monoclinic, $P2_1/n$, $a = 9.670(2)$, $b = 18.983(4)$, $c = 20.823(5)$ Å, $\beta = 92.58(1)°$, $V = 3819(2)$ Å^3, $Z = 4$. Data were collected at 297 K to a maximum 2θ value of 55.0°. A total of 9993 reflections were measured, of which 8004 were unique ($R_{int} = 0.034$). The number of data used for structure solution and refinement was 5303 ($I > 2.0\sigma(I)$). Empirical ψ corrections were made; the minimum and maximum transmission factors were 0.7130 and 0.9560 respectively. The structure was solved by direct methods. All non-hydrogen atoms (except those of the disordered solvate molecule) were refined anisotropically by the full-matrix least-squares method (on F^2). Hydrogen atoms were introduced in calculated positions and refined isotropically (riding model) in the final cycles of least-squares refinement. The disordered benzene solvate is located about a crystallographic inversion centre. The unique half of the benzene molecule was modelled isotropically in terms of two overlapping C_3 fragments of half occupancy each (C(100)–C(300)) and (C(101)–C(301)), with the constraint C–C = 1.390 ± 0.002 Å. The C(100)···C(300) and C(101)···C(301) distances were constrained to be 2.400 ± 0.002 Å to fix the C–C–C angles at 120°. The last least-squares cycle was calculated with 466 parameters and 7950 reflections (all of the unique reflections except very negative ones), and converged with $R_1 = 0.040$ and $wR_2 = 0.080$ (for reflections with $I > 2.0\sigma(I)$) ($R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$). The weighting function used was $w^{-1} = \sigma^2(F_o^2) + (0.0400P)^2$, where $P = (F_o^2 + 2F_c^2)/3$. In the last difference map the deepest hole was −0.605 e Å^{-3}, and the highest peak was 0.677 e Å^{-3}. Computations were carried out on a Pentium PC using the SHELXTL PLUS software package [24].

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), CCDC no. 135934.

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