Amine-oxide-mediated reactions of Re$_2$(CO)$_{10}$ with phenol and aliphatic alcohols: The formation of Re$_3$(CO)$_{14}$(μ-H) and a hydroxo-methoxo trirhenium aggregate [Me$_3$NH]$^+$[Re$_3$(CO)$_9$(μ-OH)$_2$(μ-OMe)(μ_3-OMe)]$^-$

Chenghua Jiang [a], Yuh-Sheng Wen [c], Ling-Kang Liu [c,*], T.S. Andy Hor [a,1], Yaw Kai Yan [b,1]

[a] *Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge 119260, Singapore*
[b] *Division of Chemistry, National Institute of Education, Nanyang Technological University, 469 Bukit Timah Road, Nanyang 259756, Singapore*
[c] *Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan*

Abstract

Oxidative decarbonylation of Re$_2$(CO)$_{10}$ by Me$_3$NO in a mixture of THF and phenol resulted in Re$_3$(CO)$_{14}$(μ-H), **1**, and [Me$_3$NH]$^+$[Re$_2$(CO)$_6$(μ-OPh)$_3$]$^-$, **2**, in 30 and 17% yields respectively. In the analogous reaction in THF–MeOH mixture, a trinuclear complex, [Me$_3$NH]$^+$[Re$_3$(CO)$_9$(μ-OH)$_2$(μ-OMe)(μ_3-OMe)]$^-$, **3**, was isolated instead. The structure of **3** was determined by single-crystal X-ray diffraction analysis: orthorhombic, space group *Ama2*, $a = 14.022(2)$, $b = 18.003(5)$, $c = 9.601(2)$ Å, final $R = 0.031$ for 958 reflections. The anion contains a Re$_3$ triangle edge-bridged by one methoxy and two hydroxy ligands and capped by a methoxy group. No formal Re–Re bond (Re $\cdots$ Re 3.423 and 3.439 Å) is envisaged. Possible mechanisms for the formation of **1**, **2** and **3** are proposed. © 1997 Elsevier Science S.A.

Keywords: Dirhenium decacarbonyl; Trimethylamine *N*-oxide; Hydride; Carbonyl-hydroxo-alkoxo-complex; Decarbonylation; Protolysis

1. Introduction

Much interest is currently focused on transition-metal carbonyl alkoxides [1–4] because they are likely intermediates in the carboalkoxylation of olefins [5,6] and in metal-catalyzed hydrogenation of CO [7]. We recently reported the facile methoxylation of the Re–Re bond in Re$_2$(CO)$_{10}$ by methanol [8]. A series of dimethoxo-bridged complexes Re$_2$(CO)$_6$(μ-OMe)$_2$(μ-PP) [PP = dppf (1,1'-bis(diphenylphosphino)ferrocene); Ph$_2$P(CH$_2$)$_n$PPh$_2$, $n = 1$–4], **4**, were synthesized by the addition of diphosphines to the 'activated mixture' obtained from the reaction of Re$_2$(CO)$_{10}$ with Me$_3$NO in THF–MeOH (2:1) [8,9]. In order to investigate the mechanism for the formation of these rhenium carbonyl-methoxo complexes and to study the general reactivities of Re$_2$(CO)$_{10}$ with other alcohols, we set out to

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* Corresponding author.
1 Also corresponding author.

isolate the rhenium complexes from the reaction mixtures derived from phenol, methanol, ethanol, and 2-chloro-ethanol.

1

2

3

4

$\overset{\frown}{P\ P}$ = diphosphine
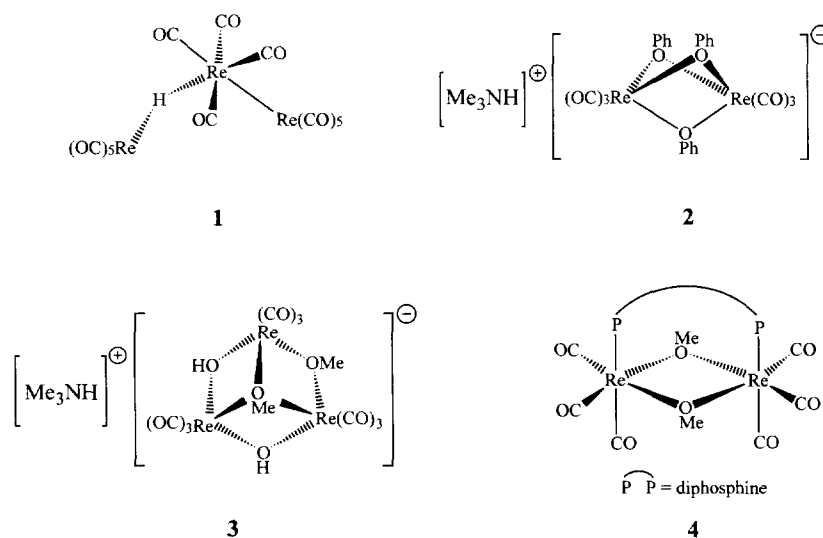
The results of these studies are reported in this paper together with a discussion of a possible mechanism for the reaction of $Re_2(CO)_{10}$ with phenol or methanol and Me_3NO. In this context we also report the crystal structure of the product of the reaction involving methanol.

2. Results and discussion

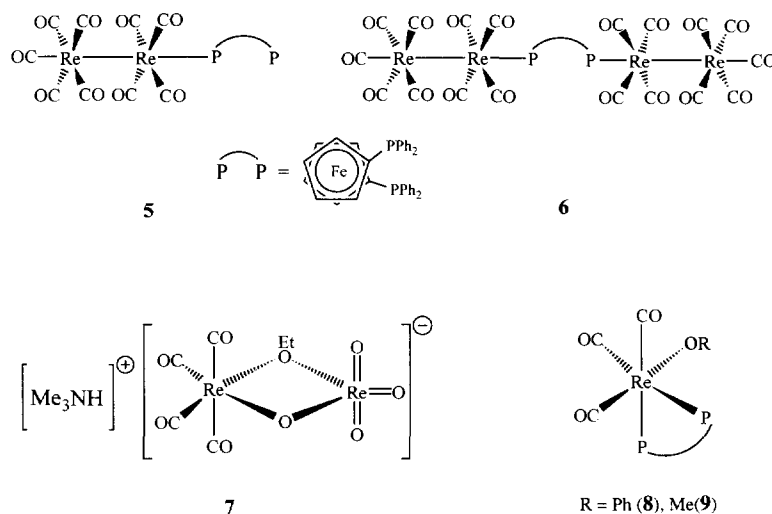### 2.1. Reaction of $Re_2(CO)_{10}$ with phenol and Me_3NO

In THF at r.t., the Me_3NO-assisted decarbonylation of $Re_2(CO)_{10}$ in the presence of phenol led to the formation of $[Me_3NH]^+[Re_2(CO)_6(\mu\text{-}OPh)_3]^-$, 2, in 17% yield (based on Re) and a significant quantity (30% based on Re) of an unexpected product $Re_3(CO)_{14}(\mu\text{-}H)$, 1. Formation of 1, especially in such amount, is surprising since the medium contains Me_3NO, which is an oxidizing agent, and that 1 is known to be prone to oxidation [10]. Complex 1 is usually synthesized under reductive conditions by the acidification of a mixture of the reaction of $Re_2(CO)_{10}$ with an excess of $NaBH_4$ [10]. The acidity of phenol is a likely key factor responsible for the formation of 1 in our synthetic procedure. Besides providing the proton for the formation of the hydride, phenol also consumes the NMe_3 generated from Me_3NO, thus preventing it from further reaction with the hydride.

Complex 2 belongs to a family of $[Re_2(CO)_6(\mu\text{-}X)_3]^-$ anions, where X is either an alkoxide (X = OMe, OEt, OPr^i, OPh) [11–14] or a halide (X = Cl, Br) [15]. The anion $[Re_2(CO)_6(\mu\text{-}OPh)_3]^-$, which was the most recently-reported one in this series, was produced from the degradation of the cluster $[Re_3(CO)_{10}(\mu\text{-}H)_4]^-$ with an excess of phenol under refluxing conditions (in acetone) [14]. The present use of $Re_2(CO)_{10}$ at r.t. is therefore comparatively straightforward and convenient. Attempts to synthesize similar complexes from $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$ led to products which are presently unidentified.

2.2. Reaction of dppf [1,1'-bis(diphenylphosphino)ferrocene] with $Re_2(CO)_{10}$, Me_3NO and phenol

The reaction mixture obtained from $Re_2(CO)_{10}$, Me_3NO and phenol in THF reacts with dppf to give two dppf-containing products, viz., $Re_2(CO)_9(\eta^1\text{-}dppf)$, 5, and $Re_4(CO)_{18}(\mu\text{-}dppf)$, 6, which are reasonable secondary

products of **1** with dppf. There is no evidence of **1** or other phenoxo-dppf complex in the resultant mixture. This is a sharp contrast to the oxidative methanolysis reported earlier [8,9].

When dppf reacts with $Re_2(CO)_{10}$, phenol and Me_3NO in a one-pot reaction, the complex $Re(\eta^1\text{-}OPh)(CO)_3(\eta^2\text{-}dppf)$, **8**, was isolated. Evidence for the formation of the hydride complexes $ReH(CO)_3(\eta^2\text{-}dppf)$ and $ReH(CO)_4(\eta^1\text{-}dppf)$ (in minute quantities) is obtained from the ^1H-NMR analysis of the reaction mixture (in C_6D_6 after removal of THF). The spectrum shows a weak triplet at -3.54 ppm (J_{H-Re-P} 29 Hz) and a weak doublet at -4.23 ppm (J_{H-Re-P} 27 Hz). Both the shift and coupling constants of the triplet are similar to those reported for the complex $ReH(CO)_3(\eta^2\text{-}dppm)$ [δ_H (C_6D_6) -3.23 ppm, J_{H-Re-P} 26 Hz] [16].

2.3. Mechanism for the formation of complexes 1 and 2

A possible mechanism for the formation of **1** and **2** is shown in Scheme 1. The acidity of phenol is probably an important factor for the formation of $Re_3(CO)_{14}(\mu\text{-}H)$, since this hydride was not observed in the analogous reactions with aliphatic alcohols (see below). A crucial step involves an intramolecular oxidative addition of O–H (of the coordinated PhOH) across the Re–Re bond. Cleavage of the latter as a result leads to the formation of $ReH(CO)_5$ and $Re(OPh)(CO)_4$. Addition of $ReH(CO)_5$ to $Re_2(CO)_9L$ would yield **1** whereas dimerization of $Re(OPh)(CO)_4$ followed by nucleophilic attack by the excess OPh^- would explain the formation of **2**. Complex **1** has been synthesized by Gard and Brown in the similar reaction of $eq\text{-}Re_2(CO)_9(OH_2)$ with $ReH(CO)_5$ in THF at 25°C [17]. The presence of the $Re(OPh)(CO)_4$ intermediate is supported by the formation of $Re(\eta^1\text{-}OPh)(CO)_3(\eta^2\text{-}dppf)$, **8**, in the one-pot reaction with dppf. Complex **8** presumably results from the trapping of $Re(OPh)(CO)_4$ by dppf chelation. The hydride complexes detected are probable products of the reaction between dppf and $ReH(CO)_5$. Their presence in only trace amounts can be attributed to the instability of the terminal hydride ligand in the acidic environment provided by phenol [18].
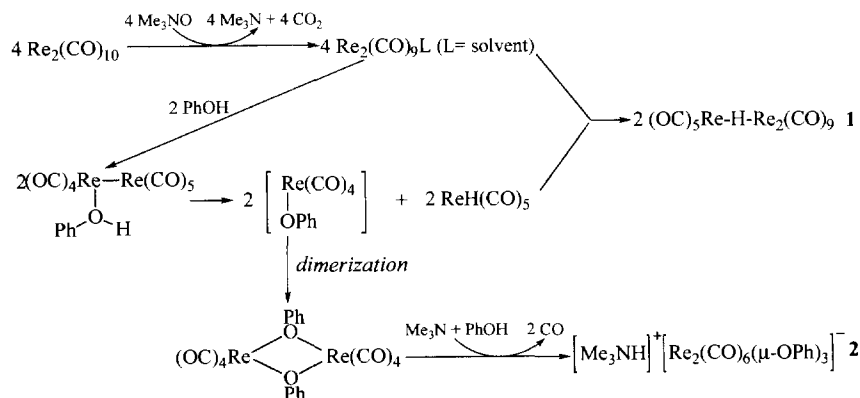
Scheme 1. Proposed mechanism for the formation of $Re_3(CO)_{14}(\mu\text{-}H)$, **1**, and $[Me_3NH]^+[Re_2(CO)_6(\mu\text{-}OPh)_3]^-$, **2**.
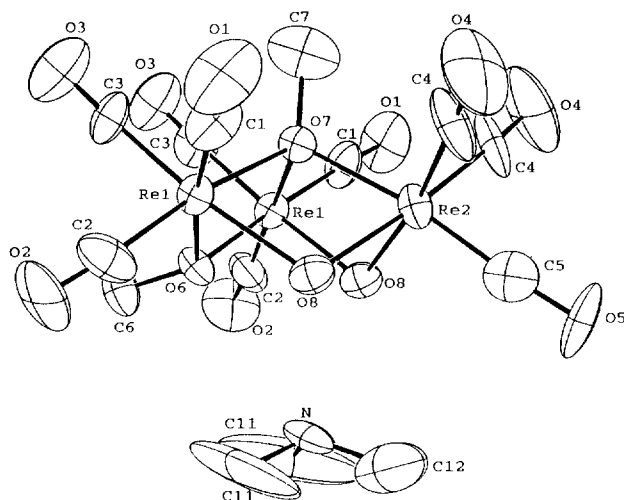
Fig. 1. Crystal structure of $[Me_3NH]^+[Re_3(CO)_9(\mu\text{-OH})_2(\mu\text{-OMe})(\mu_3\text{-OMe})]^-$, **3**.

2.4. Reaction of $Re_2(CO)_{10}$ with Me_3NO and methanol

The reaction of $Re_2(CO)_{10}$ with Me_3NO and MeOH resulted in a pale yellow solution from which $[Me_3NH]^+[Re_3(CO)_9(\mu\text{-OH})_2(\mu\text{-OMe})(\mu_3\text{-OMe})]^-$, **3**, was isolated. There was no evidence for the formation of **1** or the methoxy analogue of **2**, viz., $[Re_2(CO)_6(\mu\text{-OMe})_3]^-$.

The structure of **3** (Fig. 1) was determined by single-crystal X-ray crystallography (see below). The anion $[Re_3(CO)_9(\mu\text{-OH})_2(\mu\text{-OMe})(\mu_3\text{-OMe})]^-$ is unusual in that it contains both hydroxy and methoxy groups and two bridging forms (μ_2 and μ_3) of the latter. To our knowledge, this is the first of such example in Group 7 carbonyl complexes. Ample examples are documented for homo-alkoxo-bridged complexes, e.g., $Mn_3(CO)_9(\mu\text{-OR})(\mu_3\text{-OR})_2$ (R = Me, Et, Pr^i, Bu^n, C_6H_{11}, $CH_2CH=CH_2$ or CH_2Ph), $Mn_3(CO)_8(\mu\text{-OEt})(\mu_3\text{-OEt})_2(PMe_2Ph)$ [19–21], $[Re_3(CO)_9(\mu\text{-OH})_3(\mu_3\text{-OH})]^-$ [22], $[Tc_3(CO)_9(\mu\text{-OMe})_3(\mu_3\text{-OMe})]^-$ [23], $[Re(CO)_3(\mu_3\text{-OH})]_4$ [17,24–26], and $[Mn(CO)_3(\mu_3\text{-OH})]_4$ [27,28].

It ought to be pointed out that **3** was isolated instead of $Re_2(CO)_8(\mu\text{-OMe})_2$ or $Re_2(CO)_8(\mu\text{-H})(\mu\text{-OMe})$, which has been proposed as intermediates in the reaction of $Re_2(CO)_{10}$ with Me_3NO and methanol [29,30]. There is IR evidence that **3** is a secondary product derived from the unstable primary intermediates generated by the action of Me_3NO and methanol on $Re_2(CO)_{10}$. It however does not react with dppf to form $Re_2(CO)_6(\mu\text{-OMe})_2(\mu\text{-dppf})$ and hence is not responsible for the formation of the latter.

2.4.1. Crystal structure of $[Me_3NH]^+[Re_3(CO)_9(\mu\text{-OH})_2(\mu\text{-OMe})(\mu_3\text{-OMe})]^-$, 3

The crystal structure of **3** consists of discrete $[Me_3NH]^+$ cations and $[Re_3(CO)_9(\mu\text{-OH})_2(\mu\text{-OMe})(\mu_3\text{-OMe})]^-$ anions in the orthorhombic space group *Ama2*. With $Z = 4$, the ions are required to possess rigid mirror symmetry so that one half of the formula is crystallographically independent. Located on the crystallographic mirror plane are one of the Re atoms, one of the CO ligands, and both of the OMe ligands of the anion, and one of the Me groups and the N and H atoms of the cation.

The $[Re_3(CO)_9(\mu\text{-OH})_2(\mu\text{-OMe})(\mu_3\text{-OMe})]^-$ anion consists of a Re_3 triangle held together by a methoxy and two hydroxy bridges and face-capped by a methoxy group, with no Re–Re bonds. It can alternatively be viewed as a cubane-like skeleton (Re_4O_4) with one of the Re vertices missing. Each Re(I) centre is octahedrally coordinated to three carbonyl and three alkoxy (or hydroxy) groups. The inner angles of the incomplete cubane average 75.3(2.5)° around Re and 104.9(2.9)° around O. The Re–(μ_3-O) distances [average 2.200(16) Å] are not significantly longer than the lengths of the Re–(μ_2-O) bonds [average 2.126(15) Å]. The length of the Re–C(CO) bonds *trans* to the Re–(μ_3-O) bonds [average 1.84(3) Å] are also similar to those of the other Re–C(CO) bonds [average 1.90(3) Å]. These geometric parameters do not differ significantly from those observed in the closely analogous complex $[Re_3(CO)_9(\mu\text{-OH})_3(\mu_3\text{-OH})]^-$ [22]. To our knowledge, no other $[Re_3(CO)_9(\mu\text{-OR})_3(\mu_3\text{-OR})]^-$ complexes have been structurally characterized.

With a 54-electron core consisting of three Re(I) atoms, no direct Re–Re bond is envisaged. The Re(1) $\cdots$ Re(1') and Re(1) $\cdots$ Re(2) distances [3.439 and 3.423 Å respectively] are similar to the Re $\cdots$ Re non-bonding distances in $Re_2(CO)_6(\mu\text{-OMe})_2(\mu\text{-dppf})$ [3.4042(6) Å] [8] and $Re_2(CO)_6(\mu\text{-OMe})_2(\mu\text{-dppm})$ [3.3916(7) Å] [9] despite the
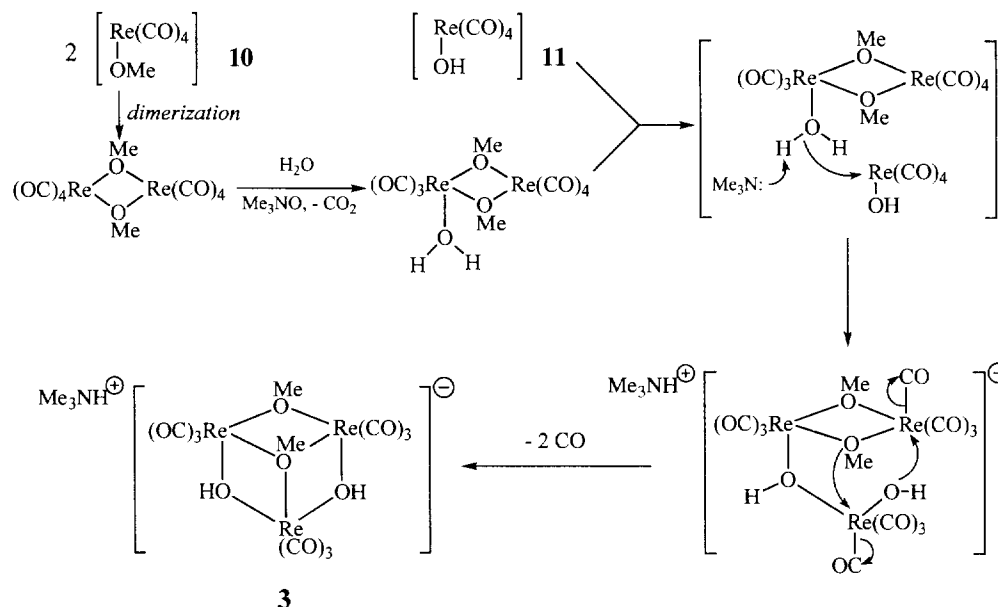
Scheme 2. Proposed mechanism for the formation of $[Me_3NH]^+[Re_3(CO)_9(\mu\text{-OH})_2(\mu\text{-OMe})(\mu_3\text{-OMe})]^-$, 3.

absence of the sterically-demanding diphosphine ligands. These distances are significantly longer than the non-bonding Re $\cdots$ Re distances in the dinuclear tri-alkoxo-bridged complexes $[Re_2(CO)_6(\mu\text{-OMe})_3]^-$ [3.086(3) Å] [31] and $[Re_2(CO)_6(\mu\text{-OPh})_3]^-$ [3.154(1) Å] [14]. The ionic complex is further stabilized by hydrogen-bonding interaction between the cation and anion pair [N $\cdots$ O(8) 2.90 Å, H(N) $\cdots$ O(8) 2.19 Å, $\angle$N–H(N) $\cdots$ O(8) 141.9°]. As a result, the $[Me_3NH]^+$ cation is located on the side of the Re_3 triangle opposite to the μ_3-OMe ligand and in proximity to the missing vertex of the cubane.

2.4.2. Mechanism for the formation of complex 3

A possible mechanism for the formation of 3 is proposed in Scheme 2. The intermediates $Re(OMe)(CO)_4$, 10, and $Re(OH)(CO)_4$, 11, probably arise via a pathway analogous to that for $Re(OPh)(CO)_4$ in Scheme 1. Carbonyl displacement by the basic hydroxy or methoxy ligands would facilitate the formation of the observed product. The involvement of the $Re(OMe)(CO)_4$ intermediate is supported by the formation of $Re(\eta^1\text{-OMe})(CO)_3(\eta^2\text{-dppf})$, 9, in the one-pot reaction of $Re_2(CO)_{10}$ with MeOH, Me_3NO and dppf (see Section 3).

The role of amine oxide is threefold: (1) to activate $Re_2(CO)_{10}$ through oxidative decarbonylation [32–37], (2) to provide a ready source of amine (NMe_3) which promotes protolysis of the coordinated H_2O or MeOH, and (3) to stabilize the anionic complex as a source of $[Me_3NH]^+$. The hydride complex $ReH(CO)_5$ is unlikely to survive in the presence of NMe_3 and hence is not observed in the reaction mixture.

In this mechanism H_2O plays an important role. The most probable source of H_2O is $Me_3NO \cdot 2H_2O$. In the presence of excess H_2O (THF/H_2O = 2:1, v/v) at r.t., however, the decarbonylation of $Re_2(CO)_{10}$ by Me_3NO appears to stop at the $Re_2(CO)_9L$ stage [28]. Gard and Brown also reported that $Re_2(CO)_{10}$ only undergoes substitution of one CO to form eq-$Re_2(CO)_9L$ when it is treated with 2 equivalents of $Me_3NO \cdot 2H_2O$ in wet THF (3% H_2O by volume) at 25°C [17]. It is thus probable that the $Re(OH)(CO)_4$ intermediate (11) is formed via an exchange reaction between $Re(OMe)(CO)_4$ (10) and H_2O, and not directly from $Re_2(CO)_9(OH_2)$.

2.5. Me_3NO-mediated reactions of $Re_2(CO)_{10}$ with ethanol and 2-chloroethanol

The reaction of $Re_2(CO)_{10}$ with EtOH and Me_3NO yielded a colourless compound, tentatively assigned as $[Me_3NH]^+[(OC)_4Re(\mu\text{-O})(\mu\text{-OEt})ReO_3]^-$, 7, based on its ^{1}H-NMR and elemental analyses. That the products obtained from reactions in MeOH and EtOH are so dissimilar may be attributed to the different steric demands of the ethoxy and methoxy ligands. Thus, $Re(OEt)(CO)_4$ may not dimerize like $Re(OMe)(CO)_4$ in Scheme 2 but preferentially couples with $[ReO_4]^-$ instead. The formation of the $[ReO_4]^-$ anion in the reaction of $Re_2(CO)_{10}$ with Me_3NO has been documented [38].

Attempts to obtain single crystals of 7 for X-ray diffraction study were unsuccessful. Compound 7 does not react with dppf. Attempted reaction of $Re_2(CO)_{10}$ with $ClCH_2CH_2OH$ and Me_3NO only yielded an uncharacterizable product.

There is no evidence for the formation of **1** and the tri-alkoxo-bridged complexes $[Re_2(CO)_6(\mu\text{-}OR)_3]^-$ (OR = ethoxo, 2-chloroethoxo) in the above reactions. The nature of the mixture of decarbonylated species in the 'activated mixtures' derived from PhOH, MeOH, EtOH, and $ClCH_2CH_2OH$ is complex and could be solvent-dependent. This may account for the difficulties we experienced in the syntheses of the phenoxo, ethoxo and 2-chloroethoxo analogues of $Re_2(CO)_6(\mu\text{-}OMe)_2(\mu\text{-}dppf)$ under similar conditions [29,30].

3. Experimental section

3.1. General methods

All reactions were performed under pure dry argon using standard Schlenk techniquies. All reagents were AR grade and obtained from commercial sources. Solvents used were reagent grade and freshly distilled under N_2 before use. Precoated silica plates of layer thickness 0.25 mm were obtained from Merck. Infrared spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrometer or a Bio-Rad FT-IR Spectrometer. ^1H − (300.0 MHz) and ^{31}P-NMR (121.5 MHz) spectra were obtained on a Bruker ARX-300 Superconducting FT-NMR Spectrometer. ^1H − and ^{31}P-chemical shifts are quoted in ppm downfield of tetramethylsilane and 80% H_3PO_4 respectively. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry of the National University of Singapore.

3.2. Reaction of $Re_2(CO)_{10}$ with PhOH and Me_3NO

A solution of $Re_2(CO)_{10}$ (0.151 g, 0.23 mmol) in THF (10 cm^3) was transferred into a stirred suspension of $Me_3NO \cdot 2H_2O$ (0.062 g, 0.56 mmol) in a solution of PhOH (0.113 g, 1.20 mmol) in THF (10 cm^3). The resultant mixture was stirred under partial vacuum at r.t. for 4 h. The solvent was removed under reduced pressure and the residue extracted with 10 cm^3 of CH_2Cl_2 giving a greenish yellow solution **A** and an off-white solid residue **B**.

The solvent was removed from solution **A** under reduced pressure and the yellow residue was extracted with MeOH (20 cm^3). Most of the unreacted $Re_2(CO)_{10}$ remained undissolved. The filtered yellow solution was evaporated under reduced pressure and the resultant residue redissolved in Et_2O (~ 3 cm^3) and the solvent was removed under reduced pressure. This process was repeated two to three times to remove MeOH completely. The resultant residue was redissolved in Et_2O (10 cm^3) and the clear greenish yellow solution was kept at − 10°C. Bright yellow, air-stable, prismatic crystals of $Re_3(CO)_{14}(\mu\text{-}H)$, **1**, were formed after 1–2 weeks. Yield 0.044 g (0.046 mmol, 30% based on Re) (found: C, 17.64; H, 0.0%. $C_{14}HO_{14}Re_3$ requires C, 17.65; H, 0.1%). $v_{max}(CO)$ 2146w, 2102w, 2047vs, 2017m, 1990s, 1965m(sh), 1922m cm^{-1} (CH_2Cl_2); 2147w, 2101w, 2046vs, 2016m, 1991s, 1948w, 1924m cm^{-1} (benzene); 2145vw, 2101w, 2047vs, 2018m, 2013m, 1993m(br), 1976m, 1966w, 1956w, 1931m cm^{-1} (cyclohexane). δ_H − 15.4 (CD_2Cl_2) ppm; − 15.2 ($CDCl_3$) ppm; − 15.4 (C_6D_6) ppm; lit. [10] − 16.25 ppm (unknown solvent).

The off-white solid **B** (pre-washed by THF twice) was redissolved in THF (10 cm^3). The filtered solution was crystallized by THF/hexane diffusion. Colourless, prismatic crystals (complex **2**, $[Me_3NH]^+[Re_2(CO)_6(\mu\text{-}OPh)_3]^-$) were obtained in 1 week, yield 0.034 g (0.039 mmol, 17% based on Re). Found: C, 36.35; H, 2.7; N, 1.6; Re, 41.5%. $C_{27}H_{25}NO_9Re_2$ requires C, 36.84; H, 2.8; N, 1.6; Re, 42.1%. $v_{max}(CO)$ 2010s, 1896vs cm^{-1} (THF); 2011s, 1899vs cm^{-1} (acetone); lit. [14] 2015s, 1897vs cm^{-1} (acetone). δ_H (d_6-acetone) 7.28 ~ 7.19 (m, 12H, μ-OPh); 6.81 ~ 6.76 (tt, 3H, μ-OPh); 3.20 (s, 9H, Me_3NH^+) ppm.

3.3. Reaction of dppf with $Re_2(CO)_{10}$, PhOH and Me_3NO

3.3.1. Two-step reaction–addition of dppf to the 'activated mixture' of $Re_2(CO)_{10}$, PhOH, and Me_3NO

The 'activated mixture' was prepared as described in Section 3.2. 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 [8,9]. The solvent was removed and the residue was redissolved in minimum of CH_2Cl_2 and chromatographed on silica TLC plates (CH_2Cl_2/hexane 2:3). Complexes $Re_2(CO)_9(\eta^1\text{-}dppf)$, **5**, and $Re_4(CO)_{18}(\mu\text{-}dppf)$, **6**, were isolated from the main bands, which were identified by IR, ^1H and ^{31}P NMR spectra. These complexes were previously reported [39].

3.3.2. One-pot reaction of $Re_2(CO)_{10}$ with PhOH, Me_3NO, and dppf

A solution of $Re_2(CO)_{10}$ (0.151 g, 0.23 mmol) and PhOH (0.113 g, 1.20 mmol) in THF (20 cm^3) was transferred into a stirred suspension of $Me_3NO \cdot 2H_2O$ (0.062 g, 0.56 mmol) and dppf (0.128 g, 0.23 mmol) in THF (20 cm^3).

The resultant mixture was stirred under partial vacuum at r.t. for 4 h. The solvent was removed under reduced pressure and the residue was redissolved in minimum THF and chromatographed on silica TLC plates (benzene/hexane 1:4). The complex $Re(\eta^1\text{-OPh})(CO)_3(\eta^2\text{-dppf})$, **8**, was isolated from the main band ($R_f = 0.21$). Yellow solid of **8** was obtained from the cooling of its benzene/hexane solution. Yield 0.021 g (0.023 mmol, 5%). $v_{max}(CO)$ 2024vs, 1933m, 1894s cm^{-1} (C_6H_6); 2019vs, 1929s, 1893s cm^{-1} (acetone). δ_H (C_6D_6) 7.93–6.95 (m, 25H, C_6H_5 and OC_6H_5), 5.17 (s, 2H, CpH), 4.44 (s, 2H, CpH), 3.92 (s, 2H, CpH), 3.87 (s, 2H, CpH) ppm; δ_P (C_6D_6) 3.35 (s) ppm. Complexes **5** and **6** were also isolated and identified by IR, ^1H – and ^{31}P-NMR spectra.

3.4. Analogous reactions of $Re_2(CO)_{10}$ with other alcohols

3.4.1. Reaction of $Re_2(CO)_{10}$ with MeOH

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 $Re_2(CO)_{10}$ (0.151 g, 0.23 mmol) in THF (10 cm^3) at r.t. This solution was stirred in vacuo for 4 h at r.t. The resultant mixture was evaporated to dryness and the residue was crystallized in CH_2Cl_2/hexane. In 2–3 days an off-white precipitate was formed. The precipitate was redissolved in CH_2Cl_2–MeOH (10:1) mixture. The solution was filtered and hexane was added to allow for diffusion to give colourless, air-stable crystalline needles in 1–2 weeks, together with some white powder. The crystals (complex **3**, $[Me_3NH]^+[Re_3(CO)_9(\mu\text{-OH})_2(\mu\text{-OMe})(\mu_3\text{-OMe})]^-$) were manually separated from the powder. Yield 0.032 g (0.033 mmol, 22% based on Re). Found: C, 17.9; H, 2.0; N, 1.46; Re, 57.9%. $C_{14}H_{18}NO_{13}Re_3$ requires C, 17.4; H, 1.9; N, 1.45; Re, 57.8%. δ_H (CD_2Cl_2) 4.59(s, 3H, $\mu_3\text{-OMe}$); 4.42(s, 3H, $\mu\text{-OMe}$); 2.92(s, 9H, NMe_3). $v_{max}(CO)$:

Table 1
Crystal and refinement data for $[Me_3NH]^+[Re_3(CO)_9(\mu\text{-OH})_2(\mu\text{-OMe})(\mu_3\text{-OMe})]^-$, **3**

(a) Crystal data	
Chemical formula	$C_{14}H_{18}NO_{13}Re_3$
FW	966.9
Crystal system	orthorhombic
Space group	Ama2
Unit cell dimensions: a (Å)	14.0221(19)
b (Å)	18.003(5)
c (Å)	9.6006(19)
V (Å³)	2423.5(9)
Z	4
D_{calcd} (g cm⁻³)	2.650
$F(000)$	1738
Colour, habit	colourless needles
Crystal size (mm)	$0.38 \times 0.09 \times 0.09$
μ (cm⁻¹)	152.122 (Mo-K_α)
(b) Data collection and processing	
Diffractometer	Nonius
X-radiation [λ(Å)]	Mo-K_α(0.71069)
Scan type	$\theta/2\theta$
Scan width (°)	$2(1.87 + 0.67\tan\theta)$
2θ (max) (°)	50.0
No. of reflections:	
Total	2324
Unique (R_{int})	1186 (0.022)
Observed [$I > 2.0\ \sigma(I)$]	958
Absorption correction	ψ-scan
Min, max transmission	0.882, 1.000
(c) Structure analysis and refinement	
No. of parameters	154
Weighting scheme	$w^{-1} = \sigma^2(F_o) + 0.000150F_o^2$
R_f (observed data) (%)	0.031
R_w (observed data) (%)	0.032
Min, max residual electron density (eÅ⁻³)	$-1.180, 1.270$ [a]

[a] Highest peaks are 0.89–1.00 Å from Re(1).

2033w, 2015m, 1900s, 1886(sh) cm^{-1} (CH$_2$Cl$_2$); v_{max}(CO): 2028w, 2009m, 1898vs, 1884s(sh) cm^{-1} (acetone); v_{max}(OH, NH): 3670m, 3631m, 3590m cm^{-1} (KBr). Conductivity: 94.1 S cm^2 mol^{-1} in nitromethane (consistent with complex 3 being a 1:1 salt).

3.4.2. One-pot reaction of Re$_2$(CO)$_{10}$ with MeOH, Me$_3$NO, and dppf

A similiar procedure was carried out as described in Section 3.3.2 except that PhOH was replaced by MeOH (10 cm^3). The resultant chrome-yellow mixture was treated similarly as described in Section 3.3.2 by TLC (benzene/hexane 1:4). Complexes 4 (diphosphine = dppf), 5, 6 were isolated and identified by IR, ^{1}H and ^{31}P-NMR spectra. The complexes retained on the baseline of the plates were extracted by acetone and re-chromatographed on TLC (acetone/hexane 1:4). The complex Re(η^1-OMe)(CO)$_3$(η^2-dppf), 9, was isolated from the main band (R_f = 0.23). Yellow solid of 9 was obtained from the cooling of its benzene/hexane solution. Yield 0.016 g (0.019 mmol, 4%). v_{max}(CO) 2037vs, 1948m, 1899s cm^{-1} (C$_6$H$_6$); 2033vs, 1951s, 1900s cm^{-1} (acetone). δ_H (C$_6$D$_6$) 7.94–7.82(m), 7.17–7.02 (m) (20H, C$_6$H$_5$), 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$_3$) ppm (addition of MeOH to NMR sample showed signal of free MeOH at 3.11 ppm in C$_6$D$_6$); δ_P (C$_6$D$_6$) 7.23 (s) ppm.

3.4.3. Reaction of Re$_2$(CO)$_{10}$ with ethanol and 2-choloroethanol

Reactions with ethanol and 2-chloroethanol were carried out in a similar manner to that described above.

For the reaction with ethanol, a white powder was obtained from CH$_2$Cl$_2$/hexane crystallization. v_{max}(CO) 2022w, 2003s, 1885vs cm^{-1} (CH$_2$Cl$_2$); v(NH) 3610s cm^{-1} (KBr). δ_H (d$_6$-acetone) 4.37 (q, 2H, μ-OEt), 3.19 (s, 9H, NMe$_3$), 1.40 (t, 3H, μ-OEt). Proposed formula: [Me$_3$NH]$^+$[(OC)$_4$Re(μ-O)(μ-OEt)ReO$_3$]$^-$, 7. Found C, 16.2; H, 2.2; N, 2.1; Re, 58.2%; C$_9$H$_{15}$NO$_9$Re$_2$ requires C, 16.5; H, 2.3; N, 2.1; Re, 57.0%.

For the reaction with 2-chloroethanol, only an oily residue was obtained. Freshly dried residue: v_{max}(CO) 2006m, 1890vs (CH$_2$Cl$_2$); oily residue from crystallization by CH$_2$Cl$_2$/hexane: v_{max}(CO) 2015m, 1887vs (CH$_2$Cl$_2$).

Table 2
Final fractional coordinates for [Me$_3$NH]$^+$[Re$_3$(CO)$_9$(μ-OH)$_2$(μ-OMe) (μ_3-OMe)]$^-$, 3

Atom	x	y	z	Biso
Re(1)	0.62742(5)	0.86494(4)	0.48354	2.54(3)
Re(2)	0.75000	0.81207(8)	0.77550(20)	3.10(5)
N	0.7500	0.6443(13)	0.4960(40)	4.5(14)
O(1)	0.4576(11)	0.9176(11)	0.6586(27)	7.0(10)
O(2)	0.4805(12)	0.8031(11)	0.2862(35)	7.3(11)
O(3)	0.6142(11)	1.0077(10)	0.3171(25)	6.9(10)
O(4)	0.6005(16)	0.8817(14)	0.9652(42)	10.4(16)
O(5)	0.7500	0.6778(15)	0.9717(33)	8.9(18)
O(6)	0.7500	0.8206(11)	0.3865(24)	2.8(9)
O(7)	0.7500	0.8976(10)	0.6138(23)	2.7(8)
O(8)	0.6565(9)	0.7727(7)	0.6176(20)	3.3(6)
C(1)	0.5257(16)	0.8996(13)	0.5940(30)	4.4(11)
C(2)	0.5371(18)	0.8244(15)	0.3655(28)	5.1(13)
C(3)	0.6199(14)	0.9523(13)	0.3783(28)	4.2(10)
C(4)	0.6534(18)	0.8552(17)	0.8981(27)	5.6(15)
C(5)	0.7500	0.7300(21)	0.8884(48)	5.9(21)
C(6)	0.7500	0.8204(24)	0.2410(36)	4.4(19)
C(7)	0.7500	0.9744(22)	0.6671(52)	6.3(21)
C(11)	0.6715(32)	0.6310(21)	0.4157(70)	19.3(41)
C(12)	0.7500	0.6006(28)	0.6162(69)	14.8(59)
H(N)	0.750	0.688	0.525	5.7
H(O)	0.608	0.758	0.652	4.1
H(6)-(1)	0.750	0.873	0.207	5.2
H(6)-(2)	0.689	0.798	0.207	5.2
H(7)-(1)	0.750	1.012	0.590	5.2
H(7)-(2)	0.693	0.984	0.726	7.0
H(11)-(1)	0.668	1.078	0.883	7.0
H(11)-(2)	0.614	0.638	0.475	20.2
H(11)-(3)	0.664	0.666	0.336	20.0
H(12)-(1)	0.750	0.547	0.591	15.3
H(12)-(2)	0.808	0.610	0.674	15.3

Table 3
Selected bond length (Å) and angles (°) for [Me$_3$NH]$^+$[Re$_3$(CO)$_9$(μ-OH)$_2$ (μ-OMe)(μ_3-OMe)]$^-$, 3

Re(1)–O(6)	2.112(12)	Re(1)–C(3)	1.872(23)
Re(1)–O(7)	2.206(13)	Re(2)–O(7)	2.187(21)
Re(1)–O(8)	2.141(15)	Re(2)–O(8)	2.126(17)
Re(1)–C(1)	1.884(24)	Re(2)–C(4)	1.95(3)
Re(1)–C(2)	1.85(3)	Re(2)–C(5)	1.83(4)
O(6)–Re(1)–O(7)	73.5(6)	Re(1)–O(6)–Re(1')	109.0(9)
O(6)–Re(1)–O(8)	79.4(7)	Re(1)–O(7)–Re(1')	102.4(9)
O(7)–Re(1)–O(8)	73.6(6)	Re(1)–O(7)–Re(2)	102.4(6)
O(7)–Re(2)–O(8)	74.3(6)	Re(1)–O(8)–Re(2)	106.7(6)
O(8)–Re(2)–O(8')	76.1(6)	Re(1')–O(7)–Re(2)	102.4(6)
C(1)–Re(1)–C(2)	87.6(11)	C(4)–Re(2)–C(4')	87.7(11)
C(1)–Re(1)–C(3)	89.0(10)	C(4)–Re(2)–C(5)	87.9(13)
C(2)–Re(1)–C(3)	87.8(11)		

3.5. X-ray crystallography

The crystal data and refinement parameters of compound 3 are summarised in Table 1. Fractional atomic coordinates are given in Table 2 and selected bond length and angles in Table 3.

The structure was solved by direct methods (MULTAN [40]). All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. At the anisotropic convergence, hydrogen atoms were introduced in calculated positions (C–H 1.00 Å, N–H 0.84 Å, O–H 0.80 Å) and then held fixed in later cycles of the refinement. Calculations were performed on a Microvax 3600 computer with the NRCVAX system [41]. The large thermal parameters of C(11) and C(12) suggest a disorder between the Me$_3$NH cation reported and its symmetry related one by a rotation around the N–H axis by 180°. An attempted refinement based on the disordered model varying occupancies of the above two cation positions did not give better R-values. The final difference map calculated based on the reported atomic coordinates exhibits more than 10 large ripples at positions near Re atom positions at distances about 1.1–1.3 Å.

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