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Cluster chemistry

LXXXVII *. Some homo- and hetero-nuclear complexes derived from $C_2(PPh_2)_2$: Crystal structures of $Re_3(\mu\text{-H})_3(\mu\text{-dppa})(CO)_{10}$ {dppa = $C_2(PPh_2)_2$}, $Re_3(\mu\text{-H})_3(CO)_{11}\{PPh_2[\mu\text{-}C_2Ru_2(\mu\text{-}PPh_2)(CO)_6]\}$ and $Os_3Ru_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$

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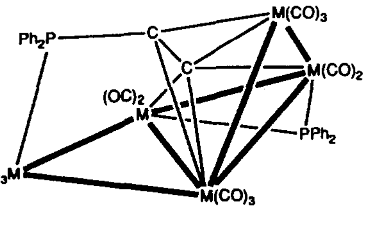
Abstract

Reaction of two equivalents of $Re_3(\mu\text{-H})_3(CO)_{11}(NCMe)$ with dppa produces the complex $\{Re_3(\mu\text{-H})_3(CO)_{11}\}_2(\mu\text{-dppa})$ (2). When an excess of dppa is used, mono-substituted $Re_3(\mu\text{-H})_3(CO)_{11}(dppa)$ (3) and $Re_3(\mu\text{-H})_3(\mu\text{-dppa})(CO)_{10}$ (4) were produced. When 3 is treated with $Ru_3(CO)_{12}$, the complex $\{Re_3(\mu\text{-H})_3(CO)_{11}\}(\mu\text{-dppa})\{Ru_3(CO)_{11}\}$ (5) is produced in high yield. When 5 is heated, the complex $Re_3(\mu\text{-H})_3(CO)_{11}\{PPh_2[\mu\text{-}C_2Ru_2(\mu\text{-}PPh_2)(CO)_6]\}$ (6) is produced. Using the same methodology, $\{Os_3(CO)_{11}\}(\mu\text{-dppa})\{Ru_3(CO)_{11}\}$ (8) and $\{Os_3(CO)_{11}\}(\mu\text{-dppa})\{Re_3(\mu\text{-H})_3(CO)_{11}\}$ (11) were prepared. When 8 is heated, the heteronuclear M_5 cluster $Os_3Ru_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (10) is produced. Complexes 4, 6 and 10 were identified by single crystal X-ray studies.

1. Introduction

The linear bis-tertiary phosphine $C_2(PPh_2)_2$(dppa) readily coordinates to two metal centres in an exo-bidentate fashion. Several groups have used this property to attach both mononuclear groups [2] and metal clusters [3–6] to each phosphorus atom. In two cases, thermal condensation of the two clusters have been reported, with the formation of pentanuclear clusters by interaction of the C≡C triple bond with the metal atoms and further alteration of the ligand [5,6]. Thus, with $M_3(CO)_{12}$ (M = Ru, Os), one of the C(sp)–P bonds in $\{M_3(CO)_{11}\}_2(\mu\text{-dppa})$ is cleaved by oxidative addition across one of the M–M bonds to give $M_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1, M = Ru, Os).



(1, M = Ru, Os)

We have begun an examination of other clusters that might be coordinated to dppa and undergo related condensation reactions. This paper reports on some products obtained during an investigation of derivatives obtained from a trinuclear rhenium cluster, when both homo and hetero-nuclear derivatives were pre-

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pared, together with a study of the pyrolysis of the mixed complex $\{Os_3(CO)_{11}\}(\mu\text{-dppa})\{Ru_3(CO)_{11}\}$.

2. Results and discussion

A reaction between two equivalents of $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ and dppa at room temperature afforded a moderate yield of the bis-Re_3 complex, $\{Re_3(\mu\text{-}H)_3(CO)_{11}\}_2(\mu\text{-dppa})$ (**2**) as a pale yellow powder. This complex was characterized analytically and from its mass spectrum, which contained a parent ion at m/z 2134 and showed loss of up to 22 CO groups. There is a limited amount of information about monosubstituted derivatives of $Re_3(\mu\text{-}H)_3(CO)_{12}$, but the IR spectrum of **2** is similar to that of the PPh_3 derivative [7]. If excess dppa was used in a reaction carried out in benzene at 50°C, a good yield of the mono-Re_3 complex $Re_3(\mu\text{-}H)_3(CO)_{11}(dppa)$ (**3**) was obtained, together with another trinuclear decacarbonyl complex (**4**); only a small amount of **2** was separated from the reaction mixture. Complex **3** was identified readily by analysis and from its mass spectrum; its IR $\nu(CO)$ spectrum was very similar to that of **2**.

Complex **4** was not readily identified. The crystal structure determination revealed the presence of $(Ph_2P)C{\equiv}C(PPh_2)$ (dppa) bring bridging an Re–Re bond in the parent trinuclear cluster. The analytical data for the bulk sample were consistent with the solid state structure, with a molecular ion at m/z 1236. The $\nu(CO)$ region of the IR spectrum differs slightly from that observed for $Re_3(\mu\text{-}H)_3(dppm)(CO)_{10}$ [8].

2.1. Molecular structure of $Re_3(\mu\text{-}H)_3(\mu\text{-dppa})(CO)_{10}$ (4)

Figure 1 shows a plot of a molecule of **4** and Table 1 gives selected bond parameters. A $(Ph_2P)C{\equiv}C(PPh_2)$ (dppa) ligand bridges one Re–Re bond [3.303(1) Å] of an isosceles triangular Re_3 core [Re(1)–Re(3), Re(2)–Re(3) both 3.290(1) Å] and is bound to axial sites. The ten CO groups are distributed four to Re(3) and three each to Re(1) and Re(2). The major point of interest is the distortion about the short C≡C triple bond [C(1)–C(2) 1.24(2) Å] in the dppa ligand, angles P–C–C at C(1) and C(2) being 152(2) and 150(2)°, respectively, while the Re–P–C angles are normal at 106.2(6) and 107.8(5)°. This distortion is probably a result of the spanning of the long Re–Re bond: the bending associated with bonding of the C≡C in dppa to W has allowed the preparation of the chelate complexes $W(CO)(S_2CNEt_2)\{(\mu\text{-dppa})Mo(CO)_4\}$ and $W(CO)(S_2CNEt_2)\{(\mu\text{-dppa})Co_2(\mu\text{-}CO)_2(CO)_4\}$ [9]. The cluster-bound hydrogen atoms were not located. The ^1H NMR spectrum contained two resonances, in a ratio of 2 : 1, in the metal hydride region. The hydrides bridging

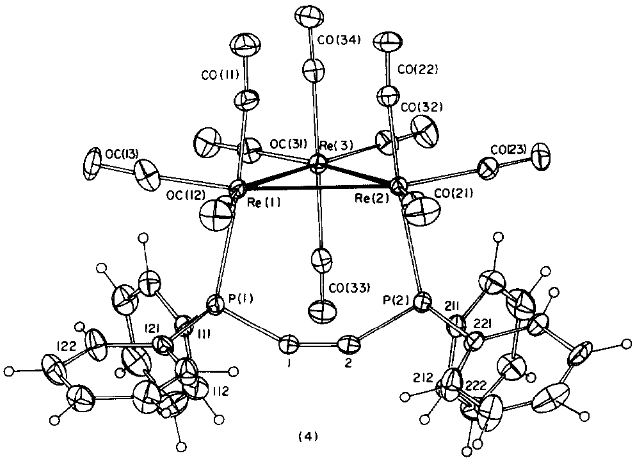


Fig. 1. Molecular plot of a molecule of $Re_3(\mu\text{-}H)_3(\mu\text{-dppa})(CO)_{10}$ (4), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

TABLE 1. Selected bond lengths (Å) and angles (°) for $Re_3(\mu\text{-}H)_3(\mu\text{-dppa})(CO)_{10}$ (4) and $Re_3(\mu\text{-}H)_3(CO)_{11}\{\mu\text{-}PPh_2C_2[Ru_2(\mu\text{-}PPh_2)(CO)_6]\}$ (6)

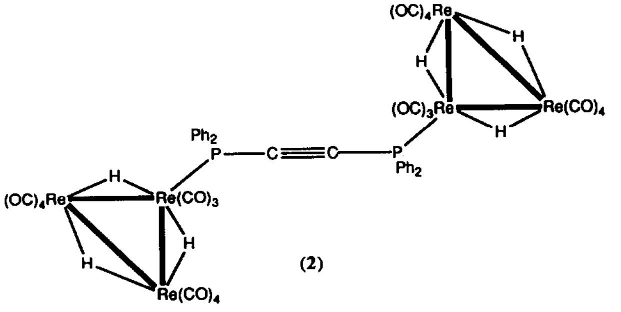
Bonds	4	6
Re(1)–Re(2)	3.303(1)	3.229(1)
Re(1)–Re(3)	3.290(1)	3.254(1)
Re(2)–Re(3)	3.290(1)	3.243(1)
Ru(4)–Ru(5)	–	2.770(2)
Re(1)–P(1)	2.456(5)	2.376(3)
Re(2)–P(2)	2.457(5)	–
Ru(4)–P(2)	–	2.364(3)
Ru(5)–P(2)	–	2.339(4)
Ru(4)–C(1)	–	2.36(1)
Ru(4)–C(2)	–	2.27(1)
P(1)–C(1)	1.72(2)	1.78(1)
P(2)–C(2)	1.75(2)	–
C(1)–C(2)	1.24(2)	1.23(1)
For 4:		
Re–CO	Range 1.90–2.05(2), av. 1.95	
C–O	Range 1.10–1.17(2), av. 1.13	
P–C(Ph)	Range 1.79–1.83(2), av. 1.81	
For 6:		
Re–CO	Range 1.82–2.04(1), av. 1.94	
Ru–CO	Range 1.89–1.96(2), av. 1.93	
C–O (Re)	Range 1.09–1.29(2), av. 1.16	
C–O (Ru)	Range 1.10–1.14(2), av. 1.12	
P–C(Ph)	Range 1.81–1.83(1), av. 1.82	
Angles		
Re(2)–Re(1)–P(1)	102.0(1)	162.76(7)
Re(3)–Re(1)–P(1)	93.5(1)	102.73(8)
Re(1)–P(1)–C(1)	106.2(6)	114.2(4)
Re(2)–P(2)–C(2)	107.8(5)	–
Ru(5)–C(2)–C(1)	–	158.1(9)
P(1)–C(1)–C(2)	152(2)	154(1)
P(2)–C(2)–C(1)	150(2)	–

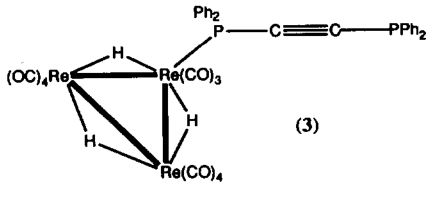
$$\begin{array}{c}\mathrm{Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)}\\ +\\ \text{dppa (excess)}\end{array} \longrightarrow \begin{array}{c}\mathrm{Re_3(\mu\text{-}H)_3(CO)_{11}(dppa)}\\ (\mathbf{3};\ 68\%)\end{array} \xrightarrow{\mathrm{Ru_3(CO)_{12}}} \begin{array}{c}\{\mathrm{Ru_3(CO)_{11}}\}(\mu\text{-dppa})\{\mathrm{Re_3(\mu\text{-}H)_3(CO)_{11}}\}\\ (\mathbf{5};\ 95\%)\end{array}$$

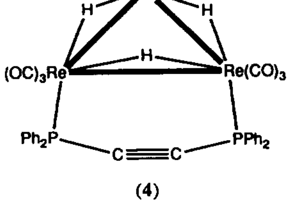
Scheme 1

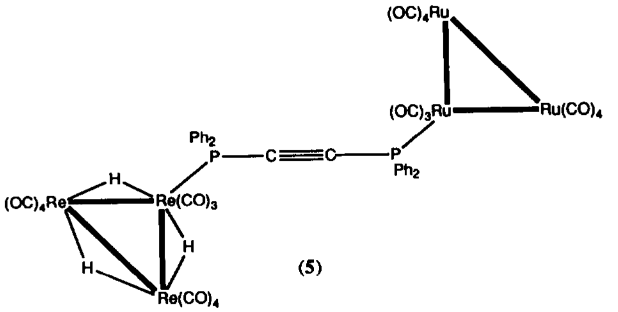
the Re(1)–Re(3) and Re(2)–Re(3) bonds were observed at δ −17.52 (d, J(HP) = 13.7 Hz), while that bridging the Re(1)–Re(2) bond was located at δ −11.95 (t, J(HP) = 11.4 Hz).

Complex **3** contains a free P-donor site and it was used in a reaction with $Ru_3(CO)_{12}$, carried out in the presence of sodium diphenylketyl (a method to introduce tertairy phosphines on the Ru_3 cluster under mild conditions [10]), to prepare the mixed Re–Ru derivative, $\{Re_3(\mu\text{-}H)_3(CO)_{11}\}(\mu\text{-dppa})\{Ru_3(CO)_{11}\}$ (**5**) (Scheme 1). This compound formed red needles; the analytically pure material gave a mass spectrum with a molecular ion at m/z 1876.

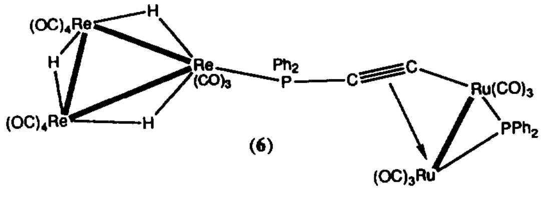

(**2**)


(**3**)


(**4**)

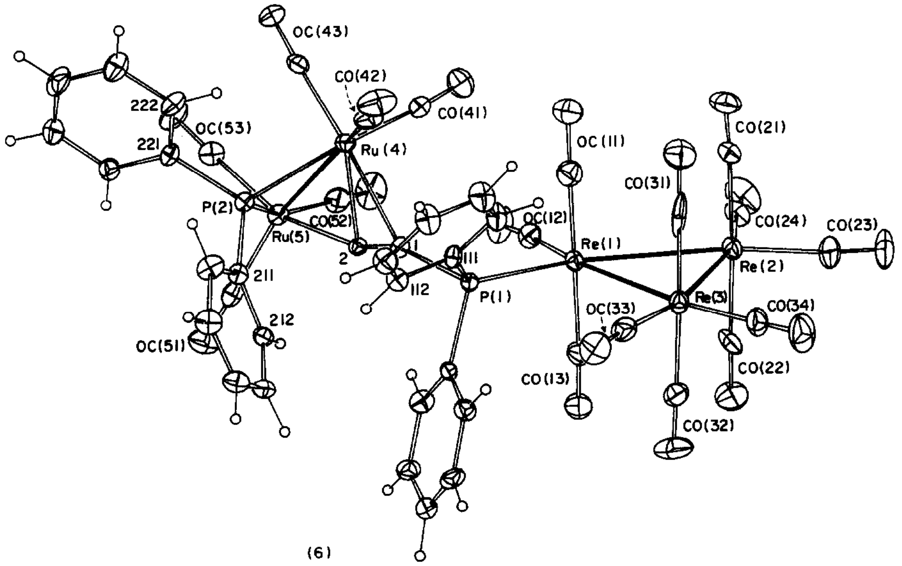

(**5**)

Complex **5** was heated in toluene at reflux point for a short time while the solution was purged with nitrogen. The major product was light yellow $\{Re_3(\mu\text{-}H)_3(CO)_{11}\}\{\mu\text{-}PPh_2C_2[Ru_2(\mu\text{-}PPh_2)(CO)_6]\}$ (**6**) which was isolated in high yield. The complex was characterized by single crystal X-ray studies, since the mass spectrum did not provide a definitive identification, the highest ion being subsequently identified as $[M-2CO]^+$.


(**6**)

2.2. Molecular structure of $Re_3(\mu\text{-}H)_3(CO)_{11}\{\mu\text{-}PPh_2C_2\text{-}[Ru_2(\mu\text{-}PPh_2)(CO)_6]\}$ (6)

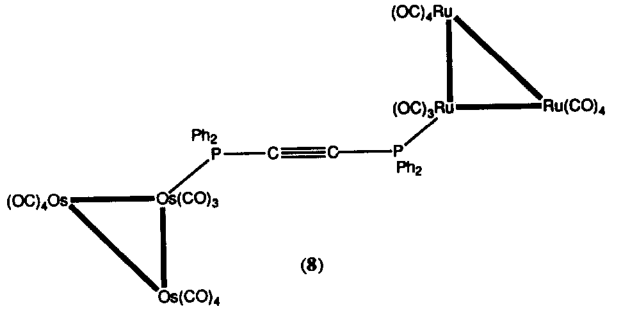
A molecule of **6** is shown in Fig. 2 and selected bond parameters are listed in Table 1, from which it can be seen that the molecule is a mono-substituted derivative of $Re_3(\mu\text{-}H)_3(CO)_{12}$, containing an Re_3 triangle [Re–Re 3.229–3.254(1), av. 3.242 Å]. The geometry of the Re_3 cluster is similar to that in $Re_3(\mu\text{-}H)_3(CO)_{11}(PPh_3)$ [7] or in **3**. To Re(1) is attached the P atom of a diphenylphosphino-acetylide ligand [Re(1)–P(1) 2.376 (3) Å] which also bridges the Ru–Ru bond [2.770(2) Å] of an $Ru_2(\mu\text{-}PPh_2)(CO)_6$ unit. The $\mu\text{-}PPh_2$ group nearly symmetrically bridges the Ru(4)–Ru(5) vector [Ru(4)–P(2) 2.364, Ru(5)–P(2) 2.339(4) Å], while the acetylide is attached in the familiar σ,η^2 fashion



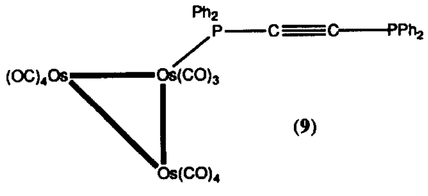
(6)

Fig. 2. Molecular plot of a molecule of $Re_3(\mu\text{-}H)_3(CO)_{11}\{\mu\text{-}PPh_2C_2[Ru_2(\mu\text{-}PPh_2)(CO)_6]\}$ (6), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

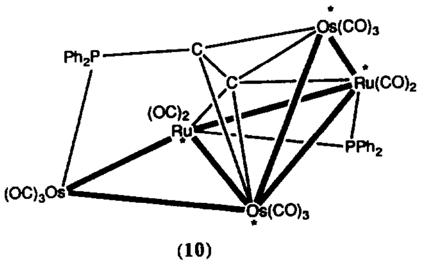
[Ru(4)–C(1) 2.36(1), Ru(4)–C(2) 2.27(1), Ru(5)–C(2) 2.03(1) Å]. This part of the molecule resembles that found in, for example, $Ru_2(\mu\text{-}PPh_2)(\mu\text{-}C_2^tBu)(CO)_6$ (7) [11], which has Ru–Ru 2.752(1), Ru–P 2.340(1), 2.341(1), C–C 1.218(4) Å and Ru–C interactions of 2.044(3) Å (σ) and 2.285(3), 2.417(3) Å (η^2).



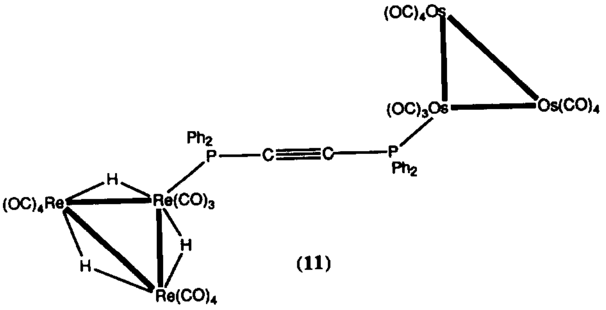
(8)



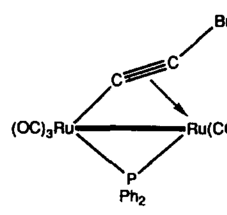
(9)



(10)



(11)



(7)

Our successful synthesis of complexes containing dppa attached to only one cluster unit encouraged us to look again at the condensation of the complexes $\{M_3(CO)_{11}\}_2(\mu\text{-dppa})$ to the pentanuclear clusters $M_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**, M = Ru, Os). We made the mixed complex $\{Os_3(CO)_{11}\}(\mu\text{-dppa})\{Ru_3(CO)_{11}\}$ (**8**) by a similar method to that used to prepare **5**; $Os_3(CO)_{11}(dppa)$ (**9**) was reacted with $Ru_3(CO)_{12}$ in the presence of sodium diphenylketyl to produce **8** as red needles. Complex **9** was prepared from $Os_3(CO)_{11}(NCMe)$ and excess dppa, in a similar fashion to **3**. This reaction sequence is summarized in Scheme 2. Pyrolysis of **8** in refluxing toluene for 5 h afforded the black mixed Os–Ru cluster $Os_3Ru_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**10**) in nearly 60% yield. The physical properties of **10** closely resembled those of the homometallic Os_5 and Ru_5 analogues. We were interested to see which locations were occupied by the two types of metal, or indeed, whether scrambling had occurred among the five metal atoms, so a single crystal X-ray structural study was carried out.

2.3. *Molecular structure of $Os_3Ru_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (10)*

Figure 3 shows a plot of the molecular structure of **10** and significant bond parameters are listed in Table 2. The overall geometry, as expected, is very similar to that of the Ru and Os analogues. A comparison of bond lengths (Table 2) emphasizes this similarity. However, only four of the metal atoms show evidence of partial occupancies by the two metals, namely M(2) (Os/Ru = 88.2/11.8), M(3) (91.7/8.3), M(4) (24.2/75.8) and M(5) (9.7/90.3); M(1) is 100% Os.

The structure of **10**, together with our findings on the course of pyrolysis of the mixed Re–Ru complex **5**,

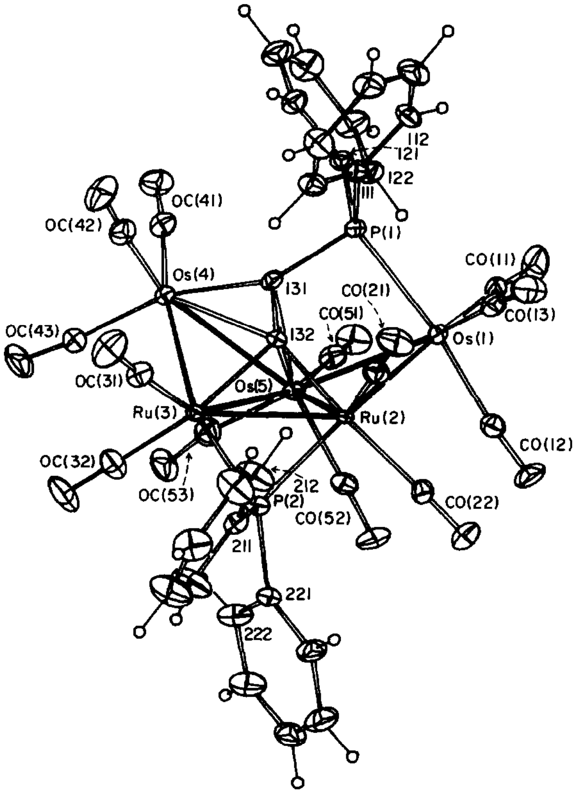
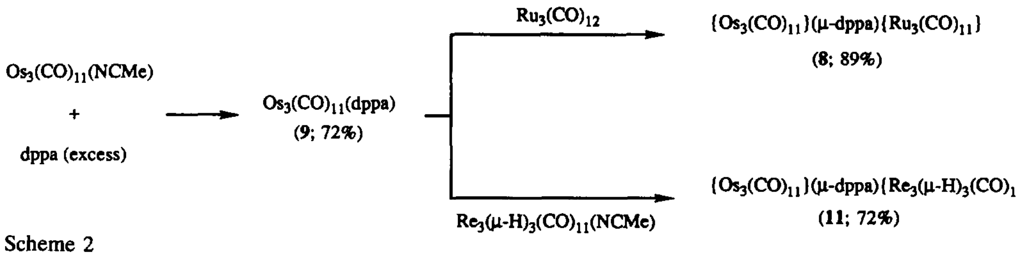


Fig. 3. Molecular plot of a molecule of $Os_3Ru_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**10**), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

and of $\{Ru_4(\mu\text{-}H)_4(CO)_{11}\}_2(\mu\text{-dppa})$ [12], led us to suggest the mechanism shown in Scheme 3 for the formation of **10**, and by implication, the homometallic clusters as well. The first step involves loss of a "$Ru(CO)_n$" fragment, recovered as $Ru_3(CO)_{12}$, to produce **8a**. This intermediate has essentially the same structure as **6**. Attack by the $Ru_2(\mu\text{-}PPh_2)(CO)_6(\sigma,\eta^2\text{-}C_2)$ end of **8a** on either face of the $Os_3(CO)_{11}$ triangle leads to the formation of **10**, in which scrambling of Ru(4), Ru(5), Os(2) and Os(3) results. The $Os_3(CO)_{11}$ triangle is free to rotate about the Os(1)–P bond. The lack of any



Scheme 2

scrambling of Os(1) is consistent with the $Ph_2POs(1)$ fragment acting as a "pivot" in the reaction.

Complex **9** was also treated with $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ to yield the yellow $\{Os_3(CO)_{11}\}(\mu\text{-dppa})\{Re_3(\mu\text{-}H)_3(CO)_{11}\}$ (**11**) (Scheme 2). Complex **11** was identified readily by microanalysis and from its mass spectrum which contained a molecular ion at m/z 2143.

3. Conclusions

Formation of the mono-substituted dppa complexes **3** and **9** has allowed the preparation of the heteronuclear complexes **5**, **8** and **11**. In the preparation of **3**, a complex containing a dppa-bridged Re–Re bond (**4**) was also isolated. The homonuclear complex **2** was prepared in good yield when a 2:1 ratio of $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$/dppa was used.

Pyrolysis of heteronuclear **5** produced **6** in high yield. Complex **6** is formed by cleavage of a P–C bond in **5** with concomitant formation of a σ,η^2-acetylide and loss of an Ru atom. In the case of pyrolysis of heteronuclear **8** further condensation occurs resulting in the formation of **10**. Complex **10** has an analogous structure to those previously reported [5,6] for **1** (M=Ru, Os). In the case of **10**, however, there is some scrambling of four (two Ru and two Os) of the metal atoms. This scrambling is consistent with competing pathways in the reaction mechanism.

4. Experimental details

4.1. General conditions

All reactions were carried out under dry, high-purity nitrogen by use of standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. Preparative TLC was carried out on glass plates (20×20 cm^2) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

4.2. Starting materials

$Ru_3(CO)_{12}$ [13], $Ru_3(CO)_{11}(NCMe)$ [14], $Os_3(CO)_{12}$ [15], $Os_3(CO)_{11}(NCMe)$ [14, 16], $Re_3(\mu\text{-}H)_3(CO)_{12}$ [17] and $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ [18] were prepared by the cited procedures. $Re_2(CO)_{10}$ (Strem) was used as received. Dppa was prepared by treating PPh_2Cl with the di-Grignard reagent BrMgC≡CMgBr [19].

4.3. Instrumentation

IR: Perkin–Elmer 1700X FT IR; 683 double beam, NaCl optics. NMR: Bruker ACP300 (^{1}H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz). FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7kV).

TABLE 2. Comparison of selected bond lengths (Å) for $M_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ ($M_5 = Os_3Ru_2$ (**10**), Ru_5 and Os_5)

Bond	**10** [a]	Ru_5	Os_5
M(1)–M(2)	2.915(3) (OsRu)	2.932(2)	2.9128(7)
M(1)–M(5)	2.916(3) (OsOs)	2.912(2)	2.9252(7)
M(2)–M(3)	2.732(4) (RuRu)	2.731(2)	2.7420(7)
M(2)–M(5)	2.918(4) (RuOs)	2.890(1)	2.9217(7)
M(3)–M(4)	2.883(2) (RuOs)	2.854(2)	2.8775(7)
M(3)–M(5)	2.915(3) (RuOs)	2.909(1)	2.9344(7)
M(4)–M(5)	2.897(3) (OsOs)	2.848(1)	2.8952(7)
M(1)–P(1)	2.408(2) (Os)	2.373(2)	2.389(3)
M(2)–P(2)	2.349(4) (Ru)	2.353(2)	2.358(3)
M(3)–P(2)	2.302(3) (Ru)	2.279(2)	2.286(3)
M(2)–C(132)	2.01(1) (Ru)	2.016(5)	2.01(2)
M(3)–C(132)	2.02(1) (Ru)	2.024(5)	2.04(1)
M(4)–C(131)	2.042(8) (Os)	2.055(5)	2.05(1)
M(5)–C(131)	2.27(1) (Os)	2.279(4)	2.27(1)
M(5)–C(132)	2.18(1) (Os)	2.154(4)	2.19(1)
P(1)–C(131)	1.77(1)	1.762(5)	1.78(1)
C(131)–C(132)·	1.40(1)	1.383(6)	1.38(2)
Dihedrals:	Os(1)–M(2)–M(3)/M(2)–M(3)–M(5) 154.3(2)° (152.4° (Ru_5); 153.2° (Os_5)) M(2)–M(3)–M(5)/M(3)–M(4)–M(5) 134.7° (134.3° (Ru_5); 134.9° (Os_5))		

[a] Major components only; distances between metal components are: Os(2) ··· Ru(2) 0.028(8) Å; Os(3) ··· Ru(3) 0.012(14) Å; Os(4) ··· Ru(4) 0.24(4) Å; Os(5) ··· Ru(5) 0.18(3) Å.

TABLE 3. Non-hydrogen atomic coordinates and isotropic thermal parameters for $Re_3(\mu\text{-}H)_3(\mu\text{-dppa})(CO)_{10}$ (4)

Atom	x	y	z	U_{eq} (Å^2)
Re(1)	0.62531(4)	0.20705(4)	0.73624(3)	0.0366(3)
Re(2)	0.81594(4)	0.33516(4)	0.73499(3)	0.0346(3)
Re(3)	0.83615(4)	0.13353(4)	0.79898(3)	0.0361(3)
C(11)	0.655(1)	0.170(1)	0.6553(9)	0.06(1)
O(11)	0.664(1)	0.144(1)	0.6041(7)	0.09(1)
C(12)	0.530(1)	0.290(1)	0.6937(9)	0.06(1)
O(12)	0.475(1)	0.336(1)	0.6687(7)	0.09(1)
C(13)	0.534(1)	0.111(1)	0.734(1)	0.07(1)
O(13)	0.4786(9)	0.0530(9)	0.7283(8)	0.09(1)
C(21)	0.756(1)	0.440(1)	0.6919(8)	0.05(1)
O(21)	0.721(1)	0.5005(9)	0.6673(7)	0.09(1)
C(22)	0.824(1)	0.282(1)	0.6535(8)	0.05(1)
O(22)	0.837(1)	0.253(1)	0.6055(7)	0.08(1)
C(23)	0.942(1)	0.382(1)	0.7317(9)	0.05(1)
O(23)	1.0178(9)	0.4079(9)	0.7296(7)	0.076(9)
C(31)	0.811(1)	0.013(1)	0.8271(9)	0.06(1)
O(31)	0.792(1)	−0.0581(8)	0.8419(7)	0.08(1)
C(32)	0.976(1)	0.119(1)	0.8215(9)	0.05(1)
O(32)	1.0534(8)	0.109(1)	0.8348(7)	0.09(1)
C(33)	0.824(1)	0.179(1)	0.8895(9)	0.05(1)
O(33)	0.8212(9)	0.1962(9)	0.9405(6)	0.068(8)
C(34)	0.849(1)	0.086(1)	0.7125(8)	0.046(9)
O(34)	0.8573(9)	0.0549(9)	0.6644(6)	0.075(9)
P(1)	0.5751(3)	0.2432(3)	0.8406(2)	0.041(2)
C(111)	0.591(1)	0.162(1)	0.9040(8)	0.05(1)
C(112)	0.601(1)	0.191(1)	0.9680(9)	0.06(1)
C(113)	0.614(2)	0.130(1)	1.017(1)	0.08(1)
C(114)	0.615(2)	0.040(2)	1.003(1)	0.09(2)
C(115)	0.607(1)	0.011(1)	0.942(1)	0.08(1)
C(116)	0.594(1)	0.074(1)	0.8926(9)	0.06(1)
C(121)	0.453(1)	0.278(1)	0.8380(8)	0.05(1)
C(122)	0.382(1)	0.214(1)	0.843(1)	0.07(1)
C(123)	0.287(1)	0.238(2)	0.835(1)	0.08(2)
C(124)	0.263(1)	0.328(2)	0.824(1)	0.07(1)
C(125)	0.333(1)	0.391(2)	0.816(1)	0.10(2)
C(126)	0.427(1)	0.364(1)	0.825(1)	0.07(1)
C(1)	0.643(1)	0.333(1)	0.8696(8)	0.044(9)
C(2)	0.713(1)	0.383(1)	0.8697(8)	0.043(9)
P(2)	0.8175(3)	0.4128(3)	0.8379(2)	0.041(2)
C(211)	0.817(1)	0.535(1)	0.8237(8)	0.044(9)
C(212)	0.739(1)	0.585(1)	0.840(1)	0.08(1)
C(213)	0.739(1)	0.675(1)	0.835(1)	0.10(2)
C(214)	0.818(2)	0.713(1)	0.825(1)	0.09(2)
C(215)	0.903(2)	0.670(1)	0.817(1)	0.08(1)
C(216)	0.901(1)	0.575(1)	0.821(1)	0.06(1)
C(221)	0.909(1)	0.388(1)	0.9028(8)	0.045(9)
C(222)	0.892(1)	0.404(1)	0.9655(9)	0.06(1)
C(223)	0.962(1)	0.387(1)	1.0167(9)	0.07(1)
C(224)	1.050(1)	0.358(2)	1.0053(9)	0.07(1)
C(225)	1.067(1)	0.343(2)	0.943(1)	0.09(2)
C(226)	0.995(1)	0.358(1)	0.8901(9)	0.06(1)
C(01)	0.923(3)	−0.049(3)	1.002(2)	0.09(2)
C(02)	0.934(3)	0.030(3)	1.030(2)	0.08(1)
C(03)	1.004(3)	0.079(3)	1.027(2)	0.08(1)
C(0)	0.872(7)	−0.082(7)	1.005(5)	0.09(3)

4.4. Reactions between $Re_3(\mu\text{-}H)_3(CO)_{12}$ and dppa

A mixture of $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ (150 mg, 0.165 mmol) and dppa (32 mg, 0.080 mmol) in CH_2Cl_2 (15 ml) was stirred for 6 days at room temperature. After the solvent was removed, the residue was purified by preparative TLC (light petroleum/CH_2Cl_2 5:1). The major band was recrystallized (CH_2Cl_2/MeOH) yielding **2** (80 mg, 45%) as a pale yellow powder, m.p. 178–180°C. Anal. Found: C, 26.99; H, 1.30: M^+, 2134 (mass spectrometry). $C_{48}H_{26}O_{22}P_2Re_6$ calc.: C, 27.02; H, 1.23%; M, 2134. IR (cyclohexane): ν(CO) 2104w, 2090m, 2054w, 2021vs, 2011m, 2001m, 1974s, 1946w cm^{-1}. FAB MS: 2134, M^+; 2106, 1826–1518 $[M-nCO]^+$ ($n = 1$, 11–22).

(ii) A solution of $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ (150 mg, 0.16 mmol) in benzene (40 ml) was added dropwise to a solution of dppa (133 mg, 0.34 mmol) in benzene (40 ml) at 50°C over *ca.* 18 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3) to yield four major bands. The first band (R_f 0.6) was dppa (50 mg, 38%). The major band (R_f 0.5) yielded **3** (137 mg, 68%). Anal. Found: C, 33.82; H, 1.82; M^+, 1264 (mass spectrometry). $C_{37}H_{23}O_{11}P_2Re_3 \cdot CH_2Cl_2$ calc.: C, 33.83; H, 1.87%; M, 1264. IR (cyclohexane): ν(CO) 2113w, 2090m, 2052m, 2035m, 2019vs, 2008m, 2000s, 1992s, 1988w 1967(sh), 1948m, 1942m cm^{-1}. FAB MS: 1264, M^+; 1236–956, $[M-nCO]^+$ ($n = 1$–11). The third band (R_f 0.4) was **2** (16 mg, 9%). The final band (R_f 0.3) yielded **4** (49 mg, 25%), m.p. 148–150°C (decomp.) Anal. Found: C, 38.37; H, 2.54; M^+, 1236 (mass spectrometry). $C_{36}H_{23}O_{10}P_2Re_3$ calc.: C, 34.98; H, 1.88%; M, 1236. ^1H NMR ($CDCl_3$): δ −17.52 (2H, d, J(HP) = 13.7 Hz, Re–H); −11.95 (1H, t, J(HP) = 11.4 Hz, Re–H); 7.43–7.94 (20H, m, Ph). IR (cyclohexane): ν(CO) 2104 m, 2046 vs, 2023m, 2008s, 1997s, 1969m, 1962s, 1938s cm^{-1}. FAB MS: 1236, M^+; 1208–956, $[M-nCO]^+$ ($n = 1$–10).

4.5. Preparation of 5

Sodium diphenylketyl in tetrahydrofuran was added to a solution of $Ru_3(CO)_{12}$ (77 mg, 0.12 mmol) and **3** (136 mg, 0.108 mmol) in tetrahydrofuran (50 ml) until a colour change was observed (13–15 drops). After 20 min the solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3) to yield several bands. The major band (R_f 0.4) was recrystallized from CH_2Cl_2/MeOH to yield red needles of **5** (192 mg, 95%), m.p. 132–136°C (decomp.) Anal. Found: C, 30.51; H, 1.28; M^+, 1877 (mass spectrometry). $C_{48}H_{23}O_{22}P_2Re_3Ru_3$ calc.: C, 30.69; H, 1.40%; M, 1877. IR (cyclohexane): ν(CO) 2113w, 2098w, 2090m, 2061w, 2048m, 2032(sh), 2029(sh), 2018vs, 2001m, 1972m, 1952(sh), 1945m cm^{-1}. ^1H NMR ($CDCl_3$): δ −17.22 (1H, s (br), Re–H); −16.77 (1H, s (br), Re–H); −16.16 (1H, d (br)); 7.46–7.70 (20H, m, Ph). Two minor signals (*ca.* 0.1H each, br) were also

TABLE 4. Non-hydrogen atomic coordinates and isotropic thermal parameters for $Re_3(\mu\text{-}H)_3(CO)_{11}\{\mu\text{-}PPh_2C_2[Ru_2(\mu\text{-}PPh_2)(CO)_6]\}$ (**6**)

Atom	x	y	z	U_{eq} (Å^2)
Re(1)	0.68492(4)	0.15860(1)	0.01562(5)	0.0366(2)
Re(2)	0.46809(4)	0.20408(1)	−0.03565(5)	0.0448(3)
Re(3)	0.58139(4)	0.19065(1)	−0.26692(5)	0.0445(3)
Ru(4)	1.07852(8)	0.14139(2)	0.27783(9)	0.0384(5)
Ru(5)	1.06165(8)	0.07861(3)	0.38903(8)	0.0369(5)
C(11) [a]	0.769(1)	0.1957(4)	0.071(1)	0.067(4)
O(11)	0.8247(9)	0.2223(3)	0.116(1)	0.082(7)
C(12)	0.717(1)	0.1430(4)	0.189(1)	0.054(8)
O(12)	0.7369(8)	0.1312(3)	0.2918(9)	0.083(7)
C(13)	0.593(1)	0.1179(3)	−0.032(1)	0.059(8)
O(13)	0.5423(8)	0.0934(3)	−0.052(1)	0.090(7)
C(21)	0.561(1)	0.2467(3)	0.013(1)	0.057(8)
O(21)	0.6137(9)	0.2686(3)	0.040(1)	0.089(7)
C(22)	0.384(1)	0.1615(3)	−0.082(2)	0.065(9)
O(22)	0.3333(9)	0.1375(3)	−0.112(1)	0.112(9)
C(23)	0.337(1)	0.2307(4)	−0.111(2)	0.07(1)
O(23)	0.2654(8)	0.2469(3)	−0.141(1)	0.105(9)
C(24)	0.434(1)	0.2046(4)	0.131(1)	0.064(9)
O(24)	0.410(1)	0.2048(3)	0.225(1)	0.105(9)
C(31)	0.659(1)	0.2293(5)	−0.217(1)	0.11(1)
O(31)	0.716(1)	0.2571(3)	−0.189(1)	0.095(8)
C(32)	0.498(1)	0.1474(4)	−0.306(1)	0.063(8)
O(32)	0.451(1)	0.1221(3)	−0.329(1)	0.107(9)
C(33)	0.677(1)	0.1759(4)	−0.368(1)	0.066(9)
O(33)	0.7278(9)	0.1678(3)	−0.437(1)	0.091(8)
C(34)	0.491(1)	0.2131(4)	−0.414(1)	0.068(9)
O(34)	0.411(1)	0.2264(3)	−0.502(1)	0.12(1)
C(41)	0.977(1)	0.1686(3)	0.342(1)	0.057(8)
O(41)	0.9232(9)	0.1846(3)	0.386(1)	0.094(8)
C(42)	1.117(1)	0.1720(3)	0.154(1)	0.061(8)
O(42)	1.146(1)	0.1890(3)	0.089(1)	0.095(8)
C(43)	1.188(1)	0.1563(3)	0.420(1)	0.053(7)
O(43)	1.2526(8)	0.1662(3)	0.502(1)	0.084(7)
O(51)	1.0441(9)	0.0007(3)	0.3711(9)	0.079(7)
C(51)	1.0499(9)	0.0298(3)	0.379(1)	0.048(7)
C(52)	0.950(1)	0.0889(4)	0.477(1)	0.061(8)
O(52)	0.8871(9)	0.0953(3)	0.529(1)	0.095(8)
C(53)	1.177(1)	0.0790(3)	0.543(1)	0.050(7)
O(53)	1.2454(8)	0.0806(3)	0.6315(8)	0.076(7)
C(1)	0.9303(8)	0.1158(3)	0.132(1)	0.034(6)
C(2)	0.9618(8)	0.0970(3)	0.226(1)	0.032(5)
P(1)	0.8380(2)	0.12860(7)	−0.0129(3)	0.032(1)
C(111)	0.9264(9)	0.1476(3)	−0.102(1)	0.037(6)
C(112)	1.003(1)	0.1281(3)	−0.137(1)	0.044(7)
C(113)	1.068(1)	0.1422(4)	−0.206(1)	0.060(8)
C(114)	1.061(1)	0.1759(4)	−0.240(1)	0.062(9)
C(115)	0.987(1)	0.1950(4)	−0.205(1)	0.068(9)
C(116)	0.916(1)	0.1809(3)	−0.140(1)	0.057(8)
C(121)	0.8022(8)	0.0880(3)	−0.092(1)	0.033(5)
C(122)	0.784(1)	0.0861(3)	−0.226(1)	0.047(7)
C(123)	0.749(1)	0.0548(4)	−0.285(1)	0.054(8)
C(124)	0.731(1)	0.0266(3)	−0.215(1)	0.063(8)
C(125)	0.752(1)	0.0283(3)	−0.085(1)	0.054(7)
C(126)	0.785(1)	0.0594(3)	−0.026(1)	0.050(7)
P(2)	1.1784(2)	0.09161(8)	0.2614(3)	0.035(1)
C(211)	1.1660(9)	0.0702(3)	0.110(1)	0.037(6)
C(212)	1.077(1)	0.0500(3)	0.055(1)	0.041(6)
C(213)	1.065(1)	0.0367(3)	−0.067(1)	0.045(7)
C(214)	1.142(1)	0.0416(3)	−0.133(1)	0.052(7)
C(215)	1.231(1)	0.0601(3)	−0.079(1)	0.053(8)
C(216)	1.244(1)	0.0751(4)	0.041(1)	0.054(8)
C(221)	1.3233(9)	0.0925(3)	0.330(1)	0.042(6)
C(222)	1.383(1)	0.1214(4)	0.311(1)	0.055(8)
C(223)	1.496(1)	0.1224(4)	0.359(1)	0.068(9)
C(224)	1.546(1)	0.0959(4)	0.424(2)	0.08(1)
C(225)	1.489(1)	0.0669(4)	0.446(1)	0.068(9)
C(226)	1.376(1)	0.0649(3)	0.397(1)	0.048(7)
Cl(1)	1.2724(7)	−0.0236(3)	−0.327(1)	0.25(1)
Cl(2)	1.4515(9)	0.0092(3)	−0.222(1)	0.32(1)
C(0)	1.402(3)	−0.0252(7)	−0.184(3)	0.21(3)

[a] Atom refined with isotropic thermal parameter.

seen at −17.75, −16.08 (J(HP) = 18.5 Hz, Re–H). FAB MS: 1877, M^+; 1765–1261, $[M - nCO]^+$ (n = 4–22).

4.6. *Pyrolysis of 5*

Nitrogen was bubbled through a solution of **5** (50 mg, 0.027 mmol) in toluene (20 ml) at reflux for 15 min. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3). The major light yellow band (R_f 0.6) was recrystallized from CH_2Cl_2/MeOH to yield **6** (38 mg, 87%), m.p. 148–152°C. Anal. Found: C, 30.62; H, 1.48; $[M - 2CO]^+$, 1580 (mass spectrometry). $C_{43}H_{23}O_{17}P_2Re_3Ru_2 \cdot CH_2Cl_2$ calc.: C, 30.74; H, 1.47%; M − 2CO, 1580. IR (cyclohexane): ν(CO) 2113w, 2090m, 2062m, 2051w, 2028m, 2018vs, 2010(sh), 1999m, 1971s, 1954w, 1944m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −17.20 (1H, s (br), Re–H); −16.90 (1H, s (br), Re–H); −15.76 (1H, d (br), J(HP) = 17.4 Hz, Re–H); −17.83 (< 0.1H, s); 7.03–7.57 (20H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 88.12 (d, J(CP) = 9.0 Hz); 88.91 (d, J(CP) = 8.9 Hz) (C_2); 127.93–134.42 (m, Ph); 135.66–144.66 (m, *ipso* C); 179.81 (s); 180.09 (s); 180.83(s); 180.99 (s); 182.17 (s); 182.66 (s); 186.37 (d, J(CP) = 7.6 Hz); 188.08 (m, br); 192.52 (d, J(CP) = 5.7 Hz); 196.68 (d, J(CP) = 12 Hz) (CO). FAB MS: 1580–1160, $[M - nCO]^+$ (n = 2–17).

4.7. *Preparation of 9*

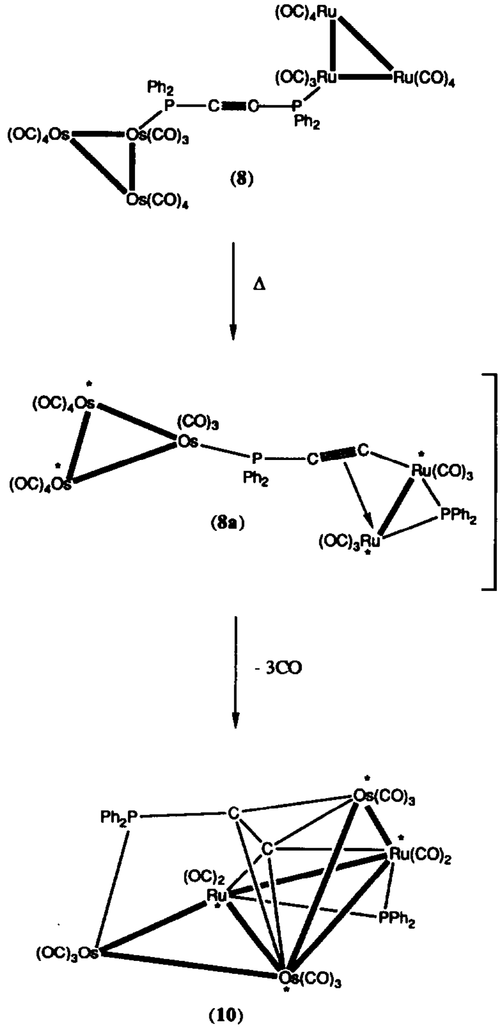
A solution of $Os_3(CO)_{11}(NCMe)$ (180 mg, 0.196 mmol) in CH_2Cl_2 (80 ml) was added dropwise to a solution of dppa (118 mg, 0.30 mmol) in CH_2Cl_2 (80 ml) over *ca.* 18 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3) to yield three major bands. The fastest moving band (R_f 0.5) was dppa (56 mg, 47%). The second band (R_f 0.4) yielded **9** (179 mg, 72%). Anal Found: C, 34.93; H, 1.61; M^+, 1274 (mass spectrometry). $C_{37}H_{20}O_{11}P_2Os_3$ calc.: C, 34.91; H, 1.58%; M, 1274. IR (cyclohexane): ν(CO) 2108m, 2056m, 2036m, 2020vs, 2002m, 1991m, 1980m, 1972(sh),

TABLE 5. Non-hydrogen atomic coordinates and isotropic thermal parameters for $Os_3Ru_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**10**)

Atom	x	y	z	U_{eq} (Å^2)
Os(1)	0.96611(2)	0.16855(2)	0.07647(3)	0.0331(1)
Ru(2) [a]	0.9163(2)	0.2372(2)	0.2507(2)	0.0190(5)
Os(2) [a]	0.9170(4)	0.2358(4)	0.2512(5)	0.051(2)
Ru(3) [a]	0.7583(1)	0.2395(1)	0.2785(1)	0.0239(4)
Os(3) [a]	0.7586(8)	0.2389(8)	0.2781(9)	0.075(4)
Os(4) [a]	0.67859(3)	0.20671(5)	0.10164(4)	0.0325(2)
Ru(4) [a]	0.675(2)	0.194(2)	0.106(2)	0.14(3)
Os(5) [a]	0.8187(2)	0.1206(1)	0.1562(2)	0.0300(3)
Ru(5) [a]	0.816(2)	0.111(1)	0.152(2)	0.024(3)
C(11)	0.9962(6)	0.1134(7)	−0.0307(7)	0.052(4)
O(11)	1.0198(5)	0.0808(7)	−0.0925(6)	0.096(4)
C(12)	1.0342(6)	0.1018(6)	0.1530(7)	0.048(4)
O(12)	1.0778(5)	0.0627(5)	0.1922(5)	0.074(3)
C(13)	1.0403(6)	0.2483(7)	0.0707(7)	0.052(4)
O(13)	1.0870(5)	0.2940(5)	0.0692(6)	0.083(4)
C(21)	0.9640(6)	0.3316(6)	0.2386(7)	0.048(4)
O(21)	0.9921(5)	0.3915(4)	0.2273(6)	0.076(3)
C(22)	1.0095(5)	0.1952(6)	0.3148(7)	0.045(3)
O(22)	1.0638(4)	0.1736(4)	0.3552(5)	0.064(3)
C(31)	0.7174(6)	0.3370(6)	0.2933(7)	0.050(4)
O(31)	0.6956(5)	0.3989(5)	0.3013(7)	0.093(4)
C(32)	0.6753(7)	0.1976(8)	0.3431(8)	0.065(5)
O(32)	0.6237(5)	0.1708(6)	0.3793(6)	0.096(4)
C(41)	0.6415(6)	0.1681(6)	−0.0186(7)	0.047(4)
O(41)	0.6143(5)	0.1477(5)	−0.0877(5)	0.070(3)
C(42)	0.6437(6)	0.3070(7)	0.0823(8)	0.054(4)
O(42)	0.6275(5)	0.3704(5)	0.0702(7)	0.089(4)
C(43)	0.5850(6)	0.1713(8)	0.1631(8)	0.066(5)
O(43)	0.5283(5)	0.1538(7)	0.1937(7)	0.110(5)
C(51)	0.8255(6)	0.0457(5)	0.0577(7)	0.047(3)
O(51)	0.8270(5)	−0.0014(4)	0.0017(5)	0.069(3)
C(52)	0.8842(6)	0.0614(6)	0.2414(7)	0.047(4)
O(52)	0.9206(4)	0.0233(4)	0.2898(5)	0.064(3)
C(53)	0.7273(7)	0.0739(7)	0.2050(8)	0.060(4)
O(53)	0.6801(5)	0.0348(5)	0.2376(6)	0.077(4)
P(1)	0.8664(1)	0.2385(1)	−0.0119(2)	0.0330(7)
C(111)	0.8812(5)	0.3415(5)	−0.0319(7)	0.038(3)
C(112)	0.9238(6)	0.3635(6)	−0.1073(7)	0.053(4)
C(113)	0.9383(7)	0.4407(7)	−0.1239(9)	0.070(5)
C(114)	0.9128(7)	0.4955(6)	−0.0641(9)	0.066(5)
C(115)	0.8726(7)	0.4726(6)	0.0141(9)	0.066(5)
C(116)	0.8554(6)	0.3956(6)	0.0280(7)	0.051(4)
C(121)	0.8197(5)	0.2061(5)	−0.1238(6)	0.038(3)
C(122)	0.8308(6)	0.1324(6)	−0.1559(7)	0.051(4)
C(123)	0.7886(8)	0.1070(7)	−0.2352(8)	0.069(5)
C(124)	0.7359(8)	0.1540(8)	−0.2800(8)	0.072(5)
C(125)	0.7238(7)	0.2271(7)	−0.2472(8)	0.068(5)
C(126)	0.7651(6)	0.2531(6)	−0.1690(7)	0.051(4)
C(131)	0.7929(5)	0.2285(5)	0.0717(6)	0.034(3)
C(132)	0.8222(5)	0.2456(5)	0.1625(6)	0.032(3)
P(2)	0.8550(1)	0.2404(1)	0.3953(2)	0.0377(8)
C(211)	0.8636(5)	0.3236(5)	0.4727(7)	0.040(3)
C(212)	0.8902(8)	0.3931(7)	0.4437(9)	0.076(5)
C(213)	0.8920(9)	0.4565(8)	0.501(10	0.087(6)
C(214)	0.8651(9)	0.4532(8)	0.589(1)	0.082(6)
C(215)	0.836(1)	0.3840(9)	0.6173(9)	0.101(7)
C(216)	0.8351(9)	0.3185(8)	0.5653(9)	0.088(6)
C(221)	0.8714(6)	0.1589(6)	0.4727(6)	0.045(3)
C(222)	0.8224(7)	0.0949(6)	0.4677(8)	0.060(4)
C(223)	0.8386(8)	0.0322(7)	0.5237(9)	0.076(5)
C(224)	0.8999(9)	0.0317(8)	0.585(1)	0.082(6)
C(225)	0.9470(8)	0.094(1)	0.594(1)	0.103(7)
C(226)	0.9340(7)	0.1588(7)	0.5383(9)	0.074(5)

[a] Populations of Ru, Os (2–5): Ru(2) 0.740(4), Os (2) 0.260(4); Ru(3) 0.871(4), Os(3) 0.129(4); Ru(4) 0.088(6), Os(4) 0.912(6); Ru(5) 0.157(3), Os(5) 0.843(3).

1966(sh) cm^{-1}. FAB MS: 1274, M$^+$; 1245–965, [M − nCO]$^+$ (n = 1–11). The final band (R_f 0.25) was $\{Os_3(CO)_{11}\}_2(\mu\text{-dppa})$ (38 mg, 18%). This complex was identified by its mass spectrum and comparison of its IR ν(CO) spectrum with that previously reported [6].



Scheme 3

TABLE 6. Crystal data and refinement details for **4**, **6** and **10** [a]

Compound	4	6	10
Formula	$C_{36}H_{20}O_{10}P_2Re_3 \cdot 0.25C_7H_8$	$C_{43}H_{20}O_{17}P_2Re_3Ru_2 \cdot CH_2Cl_2$	$C_{39}H_{20}O_{13}Os_3P_2Ru_2$
M	1253.1	1716.3	1651.2
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	14.124(3)	12.832(4)	17.025(5)
b (Å)	14.894(6)	39.164(15)	17.358(7)
c (Å)	21.094(8)	10.814(5)	14.294(7)
β (°)	97.23(2)	104.91(3)	92.07(4)
U (Å^3)	4402	5250	4220
Z	4	4	4
D_c (g cm^{-3})	1.89	2.17	2.60
F(000)	2334	3196	2816
Crystal size (mm)	0.28 × 0.25 × 0.18	0.50 × 0.45 × 0.65	0.08 × 0.70 × 0.36
A^* (min, max)	3.28, 6.2	8.7, 19.6	3.00, 16.6
μ (cm^{-1})	78.2	73.6	95.4
2θ limit (°)	50	55	65
No data collected	7728	11914	14675
No data used	5930	8646	8487
R	0.045	0.057	0.046
R_w	0.069	0.061	0.043

[a] Abnormal features/variations in procedure: **4**: After consideration of behaviour during refinement, toluene carbon atoms were set at a population of 0.5 and refined with isotropic thermal parameters. The molecule is disordered through an inversion centre, the methyl carbon population being set at 0.25. **6**: C(11) was refined with an isotropic thermal parameter, the anisotropic "ellipsoid" being non-positive definite; possibly a consequence of minor reflection overlap, an extended counter arm being used in data collection, because of the long axis. **10**: Osmium and ruthenium components were refined independently at each site with total population constrained to unity and the minor component being assigned an isotropic thermal parameter. The compound is isomorphous with, and given in the same setting as, its Ru_5 analogue [5].

4.8. *Preparation of 8*

To a solution of $Ru_3(CO)_{12}$ (109 mg, 0.17 mmol) and **9** (179 mg, 0.141 mmol) in tetrahydrofuran (50 ml) was added sodium diphenylketyl in tetrahydrofuran, until a colour change was observed (2–3 drops). After 20 min the solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3) to yield several bands. The major band (R_f 0.4) was recrystallized from CH_2Cl_2/MeOH to yield red needles of **8** (238 mg, 89%), m.p. 142–148°C (decomp.) Anal. Found: C, 30.95; H, 1.28; M^+, 1886 (mass spectrometry). $C_{48}H_{20}O_{22}Os_3P_2Ru_3$ calc.: C, 30.59; H, 1.07%; M, 1886. IR (cyclohexane): ν(CO) 2108w, 2099w, 2090w, 2056m, 2049(sh), 2035(sh), 2029(sh), 2020vs, 1992m, 1981m, 1964w cm^{-1}. FAB MS: 1886, M^+; 1858–1270, $[M - nCO]^+$ (n = 1–22).

4.9. *Pyrolysis of 8*

Nitrogen was bubbled through a solution of **8** (82 mg, 0.044 mmol) in toluene (25 ml) at reflux for 5 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 4:1). The major band (R_f 0.4) was recrystallized from CH_2Cl_2/MeOH to yield black crystals of **10** (38 mg, 57%), m.p. 203–204°C. Anal. Found: C, 30.45; H, 1.39; M^+ 1532 (mass spectrometry). $C_{39}H_{20}O_{13}Os_3P_2Ru_2$ calc.: C, 30.59; H, 1.32%; M, 1532. IR (cyclohexane): ν(CO) 2079w, 2059vs, 2018s, 2002m, 1982m, 1970w, 1943vw cm^{-1}. FAB MS: 1532, M^+; 1504–1168, $[M - nCO]^+$ (n = 1–13).

4.10. *Preparation of 11*

A mixture of $Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)$ (109 mg, 0.12 mmol) and **9** (147 mg, 0.115 mmol) in benzene (40 ml) was heated (70°C) for 8 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 4:1) to yield three bands. The major yellow band (R_f 0.5) was recrystallized from CH_2Cl_2/MeOH to yield **11** (177 mg, 72%) as a yellow powder, m.p. 180–182°C (decomp.) Anal. Found: C, 26.95; H, 1.20; M^+, 2141 (mass spectrometry). $C_{48}H_{23}O_{22}Os_3P_2Re_3$ calc.: C, 26.90; H, 1.08%; M, 2141. IR (cyclohexane): ν(CO) 2110w, 2090w, 2057m, 2037m, 2021vs, 2001(sh), 1994m, 1983(sh), 1974m, 1950w cm^{-1}. FAB MS: m/z 2141, M^+. A colourless band (R_f 0.4; 15 mg) and a yellow band (R_f 0.3; 54 mg) have not been identified.

4.11. Crystallography

Unique data sets were measured at *ca.* 295 K within the specified $2\theta_{max}$ limits using an Enraf–Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo Kα radiation, λ 0.7107$_3$ Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system [20] implemented by S.R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables. Tables of hydrogen atom coordinates, thermal parameters, full non-hydrogen geometries and structure factor amplitudes are available from the authors.

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