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Preliminary communication

Fluxionality in mixed-metal osmium carbonyl clusters

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Abstract

The heteronuclear clusters $[Os_{10}C(CO)_{24}(MPR_3)_n]^{m-}$ ($n = 1$, $m = 1$; **2**: M = Au; **3**: M = Ag; **4**: M = Cu; **5**: $n = 2$, $m = 0$, M = Au; **6**: M = Ag) have been prepared. These clusters undergo molecular rearrangements in solution, and two isomeric forms of **2**, **3**, **4**, **5** and **6** have been identified. This interconversion is thought to involve a cap ⇄ edge bridge ⇄ cap pathway.

The mechanisms by which framework reorganisation in clusters occurs are currently under active consideration [1,2]. In order to obtain a clearer understanding of the various coordination/bonding modes of MPR_3 units (M = Cu, Ag or Au), we have synthesised a series of mixed metal custers of osmium containing either one or two MPR_3 units. The structures of these species have been established from spectroscopic data.

The reaction of the dianion $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (**1**) with one equivalent of $AuPR_3ClO_4$ (prepared from $AuPR_3Cl$ and $AgClO_4$) produces the known gold osmium cluster formulated as $[N(PPh_3)_2][Os_{10}C(CO)_{24}AuPR_3]$ (**2**), ($PR_3 = PMe_2Ph$ (**2a** + **2b**), PPh_3 (**2c**), and PEt_3 (**2d**)), see Scheme 1 [3]. In the monoanion **2c** the gold atom bridges the outer edge of a capping tetrahedron [3].

The ^1H NMR spectrum of **2a** ($PR_3 = PMe_2Ph$) in CD_2Cl_2 at room temperature shows a doublet at δ +1.90 for a freshly prepared solution, on standing for ca. 0.5 h a new doublet appears at δ +1.92. At equilibrium, ca. 1 h, the two peaks are in a ratio of 15/1 and at 280 K 12/1 with **2b** being the minor isomer [4*]. The $^{31}P\{^1H\}$ NMR spectrum of **2a** in CD_2Cl_2 at room temperature exhibits two broad resonances in the ratio of 10/1, which on cooling to 280 K changes to 9/1 [4*]. On further cooling to 273 K, the cluster precipitates from solution.

The spectroscopic data can be accounted for in terms of the existence in solution of two isomeric species that undergo rapid interconversion at room temperature, via an intramolecular rearrangement of the metal skeleton. One possible mechanism for the interconversion between the two isomers **2a** and **2b** is shown in Scheme 2. It is

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* This and other references marked with asterisks indicate notes occurring in the list of references.

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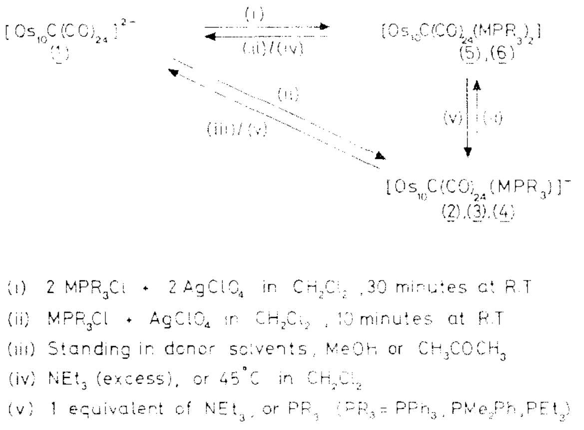
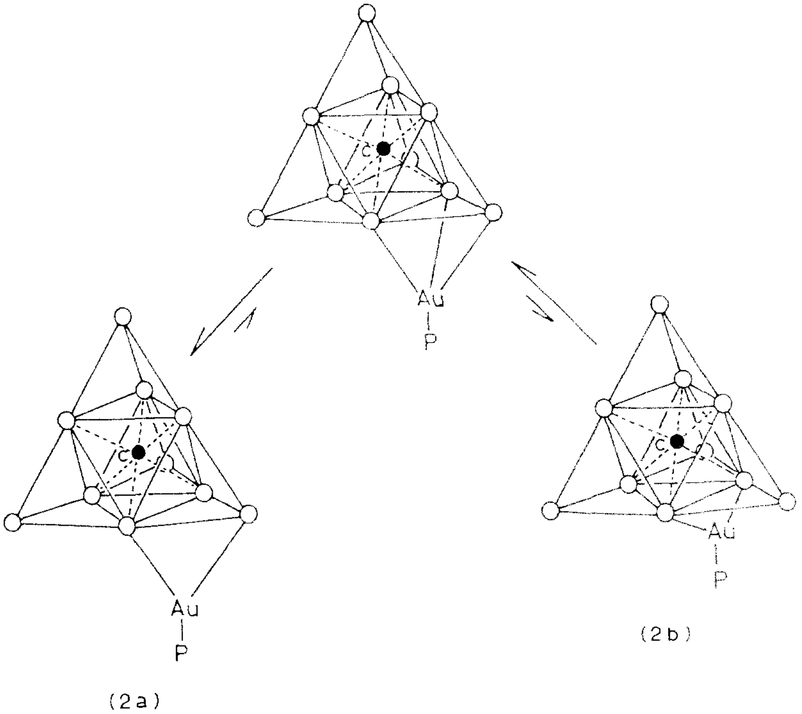


Scheme 1. The formation of mixed metal clusters of $[Os_{10}C(CO)_{24}]^{2-}$ (**2**: M = Au, **3**: M = Ag, **4**: M = Cu, **5**: M = M′ = Au, **6**: M = Ag).



Scheme 2. Proposed mechanism of interconversion of isomers of $[Os_{10}C(CO)_{24}(AuPR_3)]^-$ (**2**) (where **a**: PR_3 = PMe_2Ph; **c**: PR_3 = PPh_3 and **d**: PR_3 = PEt_3).

considered that the $[AuPPhMe_2]^+$ moiety moves across the surface of the cluster via a μ_3-intermediate. An alternative mechanism could involve interconversion between μ_2 and μ_3 isomers.

The monoanions $[Os_{10}C(CO)_{24}MPR_3]^-$ (**3**: M = Ag; **4**: M = Cu) can be obtained as crystalline solids as outlined for **2** in Scheme 1. The ^1H NMR spectra of **3** and **4** also show related behaviour. At room temperature the ^1H NMR spectrum of **3** ($PR_3 = PPh_3$) has a complex multiplet (δ +7.38–7.76) which becomes more complex on cooling [5*]. For **4** ($PR_3 = PMe_2Ph$) the ^1H NMR, spectrum displays two doublets in the ratio of 7/1 at 293 K, and on further cooling to 280 K the ratio of peaks changes to 5.5/1 [6*]. On cooling further (ca. 272 K) both compounds separate from the solution.

The $^{31}P\{^1H\}$ NMR spectrum of **3** in CD_2Cl_2 at room temperature exhibits two singlets in the ratio of 1/11 [5*]. The $^{31}P\{^1H\}$ NMR spectra of compounds containing $AgPPh_3$ fragments are broadened at room temperature by extra fluxional processes involving dissociation of PPh_3 groups and fluxionality of the metal framework [7–11]. On cooling a CD_2Cl_2/freon solution of **3** to 250 K, two pairs of doublets are observed in a 1/6 ratio, consistent with the presence of two interconverting isomers.

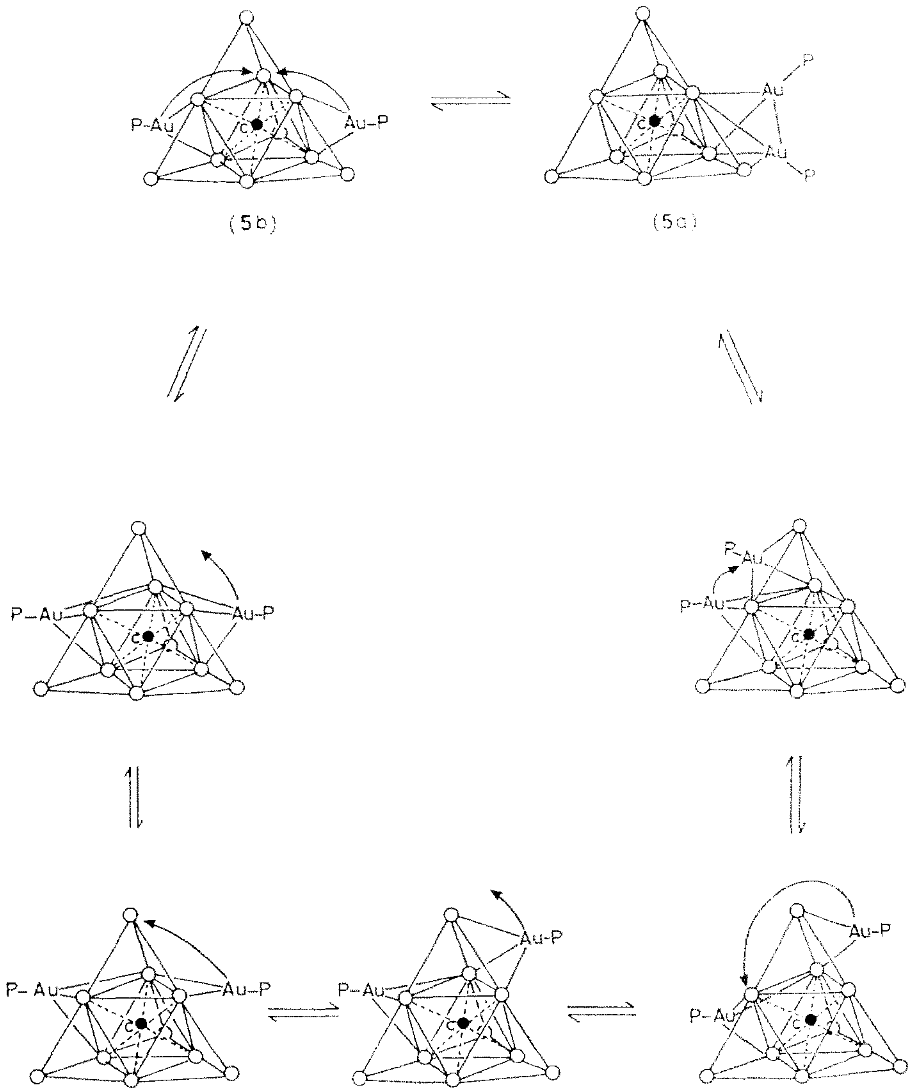
The $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2 at room temperature ($PR_3 = PMe_2Ph$) exhibits two broad resonances in a 7/1 ratio, that on cooling to 278 K changes to 6/1 [6]. On further cooling of a CD_2Cl_2 solution of **4** to 265 K the monoanion separates from the solution. Temperature-dependent line broadening has been observed previously for phosphorus atoms bonded directly to copper, and is attributed to quadrupolar effects arising from the copper [7,9,11].

The IR spectra of all three monoanions **2**, **3** and **4** are very similar, suggesting that they possibly contain similar metal frameworks with the $[M(PPh_3)]^+$ moieties (**2**: M = Au; **3**: M = Ag or **4**: M = Cu) in a μ_2-edge bridging position (Scheme 2).

Treatment of the monoanion $[Os_{10}C(CO)_{24}AuPR_3]^-$ (**2**) with one equivalent of $[AuPR_3]ClO_4$ gives a high yield of the neutral mixed-metal cluster $[Os_{10}C(CO)_{24}(AuPR_3)_2]$ (**5**) (**5a** + **5b**: $PR_3 = PMe_2Ph$; 5c: $PR_3 = PPh_3$; 5d: $PR_3 = PEt_3$) [12*].

The ^1H NMR spectrum of **5** ($PR_3 = PMe_2Ph$) in CD_2Cl_2 consists of a single doublet resonance at δ +1.91 (at room temperature), which is inconsistent with an unsymmetrical gold–gold bonded species [12*]. However in solution at ambient temperature, some heterometallic clusters with similar arrangements of $AuPR_3$ units as found in **5a** are known to undergo fluxional behaviour involving coinage metal site exchange, [7,9]. When a CD_2Cl_2/freon solution of **5a** is cooled to 230 K, the doublet splits into two doublets of equal intensity at δ +1.88 and δ +1.93. For **5b**, one doublet at δ +2.01 is observed, consistent with a symmetric gold arrangement. On gradual cooling of a CD_2Cl_2 solution of **5**, the peak intensities for the two isomers hardly change (see Scheme 3).

The $^{31}P\{^1H\}$ NMR spectrum of **5** in CD_2Cl_2 at room temperature exhibits two broad resonances in a 5/1 ratio [12*]. The singlet resonances observed for both **5a** and **5b** in the $^{31}P\{^1H\}$ spectra of these species implies extra fluxional processes occurring as outlined above. When a CD_2Cl_2/freon solution is cooled to 230 K, the peak ratio changes to 3/1 and a pair of singlets and a singlet resonance are observed. The resonances observed at 230 K may be assigned to two isomers of **5** that undergo slow interconversion at this temperature; this behaviour is similar to that recorded for $[Ru_5WC(CO)_{17}(AuPR_3)_2]$ [13]. The coalescence temperature for



Scheme 3. Proposed structures of the isomeric forms of [$Os_{10}C(CO)_{24}(AuPMe_2Ph)_2$] **5a** and **5b** and a possible mechanism for their interconversion.

the isomers could not be obtained, since above 318 K in toluene-d_8 the isomers **5a** and **5b** break down to give the monoanion [$Os_{10}C(CO)_{24}AuPMe_2Ph_3$]$^-$ (**2**).

We propose that in one isomer the gold moieties are arranged as shown in Scheme 3, **5a** with a gold–gold bond between the two gold atoms, whereas the other isomer, **5b**, may have a structure with no gold–gold bond. A process involving Os–Au polyhedral edge breaking/making is possible. Such a process is consistent with the observation that weak tangential gold–gold bonds in gold clusters allow facial skeletal rearrangements [14]. Simple exchange with PPh_3 does not occur, instead there is irreversible extrusion of [$AuPR_3$]$^+$ and generation of the monoanion

$[Os_{10}C(CO)_{24}(AuPR_3)]^-$ (**2**). The interconversion of isomers **5a** and **5b** is probably the result of an intramolecular rearrangement of gold metal atoms with $AuPR_3$ moieties moving across the surface of the cluster.

The neutral disilver cluster $[Os_{10}C(CO)_{24}(AgPPh_3)_2]$ (**6**) is prepared in an analogous manner to **5**. The IR spectrum of this cluster is identical in band pattern to that of **5a**–**5d** except that all the bands are 1–2 cm^{-1} lower in wave number [15*].

The $^{31}P\{^1H\}$ NMR spectrum of **6** in CD_2Cl_2 at room temperature exhibits two doublets in a 1/9.5 ratio [15*]. No ^{107}Ag–P or ^{109}Ag–P couplings are resolved at room temperature because of the dynamic behaviour involving exchange of PPh_3 groups as observed by Stone et al. [7,9,11]. The doublets observed for **6** in the $^{31}P\{^1H\}$ NMR spectra of these species imply extra fluxional processes occurring as explained previously [7–9]. When a CD_2Cl_2/freon solution of **6** is cooled to 230 K, the peak ratio changes to 1/6, and three pairs of doublet resonances with $^{107,109}Ag$–P couplings are observed. A process whereby a '$AgPR_3$' moiety moves across the surface of the cluster can be envisaged, as for the Au species **5a** and **5b**. We suggest that in one isomer there is a silver–silver bond and that the other isomer has a structure similar to **5b**, as in Scheme 3. A process involving Os–Ag polyhedral edge breaking/making may be invoked, such a process is consistent with the observation cited for **5a** and **5b**.

The mechanism by which large heterometallic carbonylosmium clusters undergo framework reorganisation appears to be a Cap ⇄ Edge bridge ⇄ Cap (CEC) pathway. Such a process minimizes the breaking of M–M contacts in coinage metal site exchange in dynamic fluxional processes.

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5 Spectroscopic data for **3**: IR (ν(CO), cm^{-1}) in CH_2Cl_2, 2082w, 2052vs, 2038m, 2000s; ^1H NMR in CD_2Cl_2, δ 2.32 (s, 3H), δ 7.83–7.44 (m,30H); $^{31}P\{^1H\}$ NMR in CD_2Cl_2 δ −37.62 (s, br), δ −48.51 (s, br) ratio of 1/11 at 293 K; δ −35.16 (2xd, $^1J(^{109}Ag$–P) 653, $^1J(^{107}Ag$–P) 576 Hz (**a**)), δ −52.33 (2xd, $^1J(^{109}Ag$–P) 521, $^1J(^{107}Ag$–P) 440 Hz (**b**)), ratio of **5a**/**5b** at 230 K is 1/6 in CD_2Cl_2/freon.

6 Spectroscopic data for **4**: IR (ν(CO), cm^{-1}) in CH_2Cl_2, 2082w, 2052vs, 2038m, 2000s; ^1H NMR in CD_2Cl_2, δ 1.89 (d, ^2J(PH) 10.5 Hz), δ 1.91 (d, ^2J(PH) 10 Hz), δ 7.76–7.37 (m, 35H); $^{31}P\{^1H\}$ NMR in CD_2Cl_2 δ −48.14 (s, br), δ −50.26 (s, br) ratio of 7/1 at 293 K.

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12 Spectroscopic data for **5a** and **5b**: IR (ν(CO), cm^{-1}) in CH_2Cl_2, 2092w, 2068vs, 2054m, 2016s, 2006msh, 1995w, 1940vw; ^{1}H NMR in CD_2Cl_2, 293 K, δ 1.91 (d, $^{2}J(PH)$ 10.9 Hz isomer **5a**), δ 1.88, 1.93 (2xd, $^{2}J(PH)$ 9.7, 11.6 Hz isomer **5a** at 230 K) CD_2Cl_2/freon; δ 2.01, (d, $^{2}J(PH)$ 8.1 Hz isomer **5b**) at 293 K, δ 7.88–7.40 (m, 10H); $^{31}P\{^{1}H\}$ NMR in CD_2Cl_2, δ −47.78 (s, br), δ −48.73 (s, br) ratio of 5/1 at 293 K, δ −46.06, δ −48.37 (2s, isomer **5a**), δ −50.47 (s, isomer **5b**) at 230 K, ratio **5a**/**5b** at 230 K is 3/1 in CD_2Cl_2/freon.

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15 Spectroscopic data for **6**: IR (ν(CO), cm^{-1}) in CH_2Cl_2, 2092w, 2067vs, 2053m, 2016s, 2008msh, 1995w, 1940vw; ^{1}H NMR in CD_2Cl_2, δ 7.82–7.39 (m, 30H); $^{31}P\{^{1}H\}$ NMR in CD_2Cl_2, δ −37.54 (d), δ −49.21 (d) ratio of 1/9.5 at 293 K, no ^{107}Ag or ^{109}Ag couplings seen at 293 K.; δ −34.62 (2xd, $^{1}J(^{109}Ag–P)$ 612, $^{1}J(^{107}Ag–P)$ 540 Hz) and δ −37.83 (2xd, $^{1}J(^{109}Ag–P)$ 640, $^{1}J(^{107}Ag–P)$ 579 Hz) isomer **6a**, δ −53.19 (2xd, $^{1}J(^{109}Ag–P)$ 512, $^{1}J(^{107}Ag–P)$ 443 Hz) isomer **6b**, ratio **6a**/**6b** at 240 K is 1/6 in CD_2Cl_2/freon.