Reductive coupling of alkynes to give ruthenium and osmium clusters of the type [M₃(1,3-diene)(μ₃-X)(CO)₈] containing μ-η²,η²- or η⁴-1,3-diene

$$\text{Reductive coupling of alkynes to give ruthenium and osmium clusters of the type } [M_3(1,3\text{-diene})(\mu_3\text{-}X)(CO)_8] \text{ containing } \mu\text{-}\eta^2,\eta^2\text{- or } \eta^4\text{-}1,3\text{-diene}$$

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Replacement of a CO ligand by MeCN in the capped clusters [M₃(μ-H)₂(μ₃-X)(CO)₉] (M = Ru, X = NSO₂C₆H₄Me-4 or M = Os, X = S) allows reductive coupling of alkynes (RC≡CH, R = H or Ph) to give regioselectively the 1,3-diene clusters [M₃(C₄H₄R₂)(μ₃-X)(CO)₈], with the diene μ-η²,η²-coordinated for ruthenium and η⁴ for osmium.

Hydrido clusters usually react with alkynes to give μ-σ,η²-alkenyl containing clusters.[1–3] Dihydrido clusters either give hydrido–alkenyl compounds[1,2] or exceptionally dialkenyl compounds by double insertion.[3] Two organyl ligands formed by double insertion could couple to give new organic ligands. More commonly both hydride ligands are delivered to the same organic function leading to simple hydrogenation, for example alkyne to alkene. We now report 1,3-diene-containing clusters formed by double insertion of alkyne into M–H bonds, followed by alkenyl–alkenyl coupling. Reductive coupling of alkynes to give 1,3-dienes is not very common[4] and an alkenyl–alkenyl coupling mechanism has not been established previously, although alkenyl coupling with other organic ligands has been implicated in Fischer–Tropsch synthesis.[5] Our approach was to displace CO by more labile MeCN in strongly capped Os₃ and Ru₃ clusters with two basal hydrido bridges, thereby creating a reactive basal plane of metal atoms within a robust cluster.

The cluster [Ru₃(μ-H)₂(μ₃-NR)(CO)₉] (R = SO₂C₆H₄Me-4) **1**[6] was treated with Me₃NO·2H₂O and MeCN to form [Ru₃(μ-H)₂(μ₃-NR)(CO)₈(MeCN)] **2** with the MeCN ligand *cis* to the

2 M = Ru, X = NSOC₆H₄Me-4
6 M = Os, X = S

4 R = H
5 R = Ph
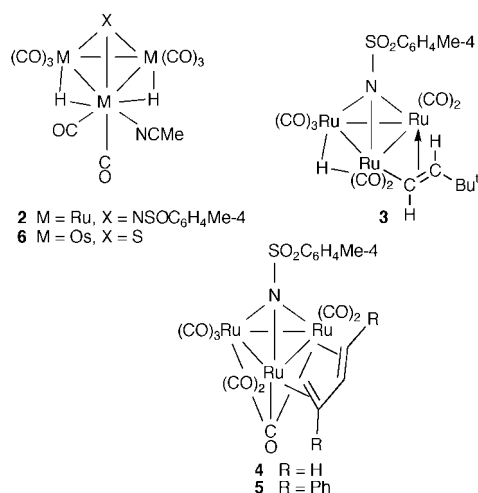
capping atom N; two sharp hydride ¹H NMR doublets observed at −25 °C are exchange-broadened at 20 °C. Treatment of **2** with BuᵗC≡CH gives the mono-insertion product [Ru₃(μ-H)(μ-*trans*-CH=CHBuᵗ)(μ₃-NR)(CO)₈] **3**† reversibly. Compound **3** liberates BuᵗCH=CH₂ and [Ru₃(μ₃-NR)(CO)₁₀] on treatment with CO at room temperature. In contrast, the less bulky alkynes RC≡CH (R = Ph or H) both react with **2** to give mixtures from which we could isolate two compounds, [Ru₃(μ-η²,η²-C₄H₄R₂)(μ₃-NR)(CO)₉] **4** (R = H) (7%) and **5** (R = Ph) (17%).

Spectra† show that **4** and **5** are very similar and ¹H NMR spectra for **5** confirm head-to-tail coupling of phenylacetylene to give the *trans*-1,3-diphenylbutadiene ligand. The single-crystal structure of **4** (Fig. 1)‡ shows the presence of μ₃-NR, μ₃-CO and μ-η²,η²-*s-cis*-butadiene. While μ-η²,η²-*s-cis*-1,3-diene is known in several cases,[7] μ-η²,η²-*s-trans*-butadiene,[8] μ-η¹,η³-*s-cis*-butadiene[9] and μ-η¹,η⁴-*s-cis*-1,3-diene[10] are also known. The cluster [Os₃(CO)₁₀(μ-C₄H₆)] contains μ-η²,η²-*s-trans*-butadiene.[11]

Intermediate alkenyl complexes were not observed in the formation of **4** and **5**, although the formation of **3** suggests that they are involved. The Os analogue of **2** only reacts with alkynes to give clusters related to **3**, without diene formation. However, the cluster [Os₃(μ-H)₂(μ₃-S)(CO)₈(MeCN)] **6**, formed as for **2**, was treated with PhC≡CH in refluxing THF for 24 h to give various insertion products: [Os₃(μ-H)(μ-PhC=CH₂)(μ₃-S)(CO)₈] **7** (23%), [Os₃(μ-H)(μ-CH=CHPh)(μ₃-S)(CO)₈] **8** (11%), [Os₃(μ-PhC₂H₂)₂(μ₃-S)(CO)₇] **9** (17%) and [Os₃(η⁴-PhCH=CHCPh=CH₂)(μ₃-S)(CO)₈] **10** (12%). The isomeric mono-insertion products **7** and **8** were shown by ¹H NMR to be non-interconverting regioisomers. The di-insertion product **9** exists as a mixture of isomers (¹H NMR evidence) with both CPh=CH₂ and CH=CHPh ligands present. The 1,3-diphenylbutadiene complex **10** from treatment of **6** with PhC≡CH is also formed by treating the dialkenyl cluster **9** with CO. ¹H NMR data for **10** confirm head-to-tail alkyne coupling but there are very different chemical shifts for the four vinylic hydrogen atoms in **10** compared with those for **5** (δ 1.55, 2.43, 3.58 and 6.79 for **10** *cf.* δ 2.98, 4.72, 5.53 and 5.82 for **5**).
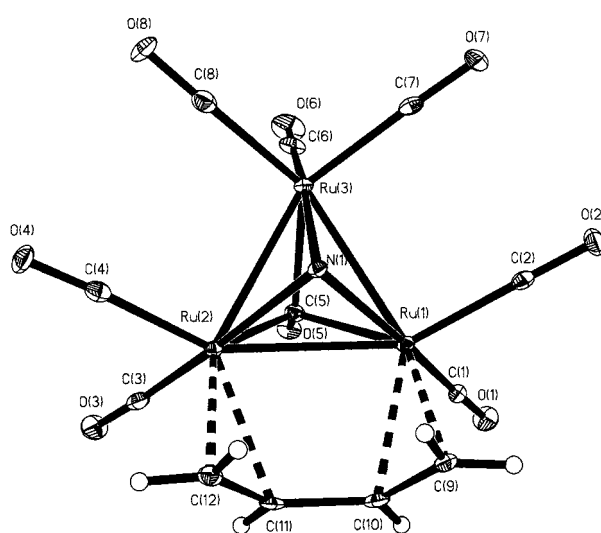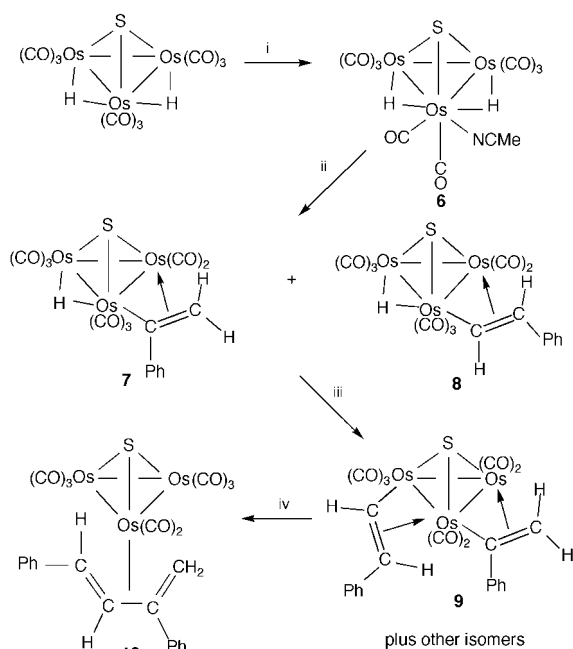

Fig. 1 Thermal ellipsoid drawing (30% probability) of [Ru₃(μ-η²,η²-C₄H₆)(μ₃-NSO₂C₆H₄Me-4)(CO)₈] **4** with the tosyl group omitted. Selected lengths (Å) and angles (°): Ru(1)–Ru(2) 2.7560(3), Ru(1)–Ru(3) 2.7416(4), Ru(2)–Ru(3) 2.7554(3), Ru(1)–C(9) 2.258(3), Ru(1)–C(10) 2.304(3), Ru(2)–C(11) 2.338(3), Ru(2)–C(12) 2.246(3), C(9)–C(10) 1.393(5), C(10)–C(11) 1.461(4), C(11)–C(12) 1.393(5); C(9)–C(10)–C(11) 127.5(3), C(10)–C(11)–C(12) 127.6(3).

Furthermore there is no IR evidence for μ_3-CO in **10**. A single-crystal structure determination (Fig. 2)‡ confirms that **10** has a different structure from that of **4** or **5**. Indeed there is no μ_3-CO in **10**, but instead the two CO ligands at Os(1) are semibridging to Os(2) and Os(3) respectively. More importantly the 1,3-diene is η^4-co-ordinated to Os(1) rather than bridging as in **4**.

The formation of 1,3-diene-containing clusters from simple alkynes is unique. The mono-insertion compounds $[M_3(\mu\text{-H})(\mu\text{-alkenyl})(\mu_3\text{-X})(CO)_8]$ appear to be more reactive towards further alkyne insertion into the second M–H bond than towards reductive elimination of alkene. This almost certainly results from the ligands being along separate M–M edges and indicates that hydrogenation reactions induced by clusters could be very different from those catalysed by mononuclear compounds. The formation of $\mu\text{-}\eta^2,\eta^2$-diene for Ru and η^4-diene for Os may reflect different alkenyl–alkenyl coupling mechanisms. We are attempting to establish the structures of the isomeric dialkenyl compounds and the geometric details of the alkenyl–alkenyl coupling.

Scheme 1 *Reagents and conditions*: i, Me₃NO·2H₂O, MeCN, CH₂Cl₂, 293 K, 30 min; ii, PhC₂H, THF, 293 K, 24 h; iii, PhC₂H; iv, CO.
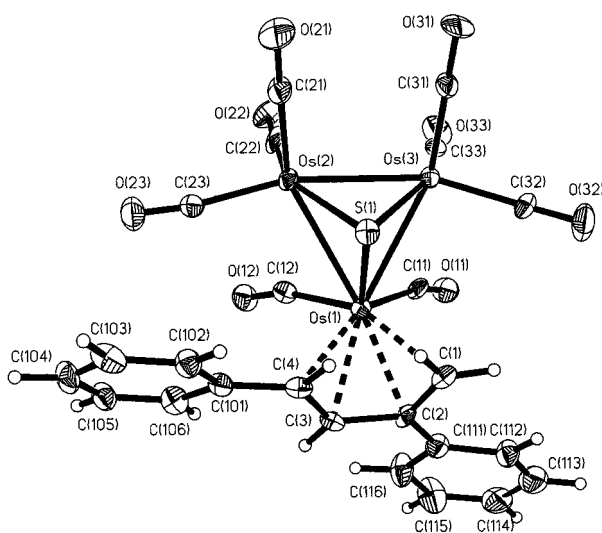
Fig. 2 Thermal ellipsoid drawing (30% probability) of $[Os_3(\eta^4\text{-PhCH=CHCPh=CH}_2)(\mu_3\text{-S})(CO)_8]$ **10**. Selected lengths (Å) and angles (°): Os(1)–Os(2) 2.8696(12), Os(1)–Os(3) 2.8524(10), Os(2)–Os(3) 2.7339(9), Os(1)–C(1) 2.214(13), Os(1)–C(2) 2.252(12), Os(1)–C(3) 2.252(12), Os(1)–C(4) 2.267(12), C(1)–C(2) 1.40(2), C(2)–C(3) 1.44(2), C(3)–C(4) 1.46(2); C(1)–C(2)–C(3) 116.9(12), C(2)–C(3)–C(4) 118.0(12).

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