

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

Shahbano Ali,^a Antony J. Deeming,^{*a} Graeme Hogarth,^{*a} Nikesh A. Mehta^a and Jonathan W. Steed^b

^a Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ.

E-mail: a.j.deeming@ucl.ac.uk and g.hogarth@ucl.ac.uk

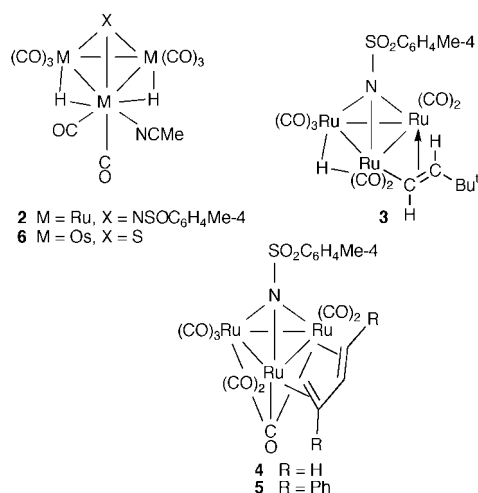
^b Department of Chemistry, King's College London, Strand, London, UK WC2R 2LS

Received (in Basel, Switzerland) 29th October 1999, Accepted 12th November 1999

Replacement of a CO ligand by MeCN in the capped clusters $[M_3(\mu\text{-}H)_2(\mu\text{-}X)(CO)_9]$ ($M = Ru, X = NSO_2C_6H_4Me\text{-}4$ or $M = Os, X = S$) allows reductive coupling of alkynes ($RC\equiv CH, R = H$ or Ph) to give regioselectively the 1,3-diene clusters $[M_3(C_4H_4R_2)(\mu\text{-}X)(CO)_8]$, with the diene $\mu\text{-}\eta^2, \eta^2\text{-}$ coordinated for ruthenium and η^4 for osmium.

Hydrido clusters usually react with alkynes to give $\mu\text{-}\sigma, \eta^2$ -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 $M\text{-}H$ bonds, followed by alkenyl-alkenyl coupling. Reductive coupling of alkynes to give 1,3-dienes is not very common⁴ 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 Os_3 and Ru_3 clusters with two basal hydrido bridges, thereby creating a reactive basal plane of metal atoms within a robust cluster.

The cluster $[Ru_3(\mu\text{-}H)_2(\mu\text{-}NR)(CO)_9]$ ($R = SO_2C_6H_4Me\text{-}4$) **1**⁶ was treated with $Me_3NO\cdot 2H_2O$ and MeCN to form $[Ru_3(\mu\text{-}H)_2(\mu\text{-}NR)(CO)_8(MeCN)]$ **2** with the MeCN ligand *cis* to the



capping atom N; two sharp hydride ¹H NMR doublets observed at $-25\text{ }^\circ\text{C}$ are exchange-broadened at $20\text{ }^\circ\text{C}$. Treatment of **2** with $Bu^tC\equiv CH$ gives the mono-insertion product $[Ru_3(\mu\text{-}H)(\mu\text{-}trans\text{-}CH=CHBu^t)(\mu\text{-}NR)(CO)_8]$ **3**[†] reversibly. Compound **3** liberates $Bu^tCH=CH_2$ and $[Ru_3(\mu\text{-}NR)(CO)_{10}]$ on treatment with CO at room temperature. In contrast, the less bulky alkynes $RC\equiv CH$ ($R = Ph$ or H) both react with **2** to give mixtures from which we could isolate two compounds, $[Ru_3(\mu\text{-}\eta^2, \eta^2\text{-}C_4H_4R_2)(\mu\text{-}NR)(CO)_9]$ **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 $\mu\text{-}3\text{-}NR, \mu\text{-}3\text{-}CO$ and $\mu\text{-}\eta^2, \eta^2\text{-}s\text{-}cis\text{-}butadiene$. While $\mu\text{-}\eta^2, \eta^2\text{-}s\text{-}cis\text{-}1,3\text{-diene}$ is known in several cases,⁷ $\mu\text{-}\eta^2, \eta^2\text{-}s\text{-}trans\text{-}butadiene$,⁸ $\mu\text{-}\eta^1, \eta^3\text{-}s\text{-}cis\text{-}butadiene$ ⁹ and $\mu\text{-}\eta^1, \eta^4\text{-}s\text{-}cis\text{-}1,3\text{-diene}$ ¹⁰ are also known. The cluster $[Os_3(CO)_{10}(\mu\text{-}C_4H_6)]$ contains $\mu\text{-}\eta^2, \eta^2\text{-}s\text{-}trans\text{-}butadiene$.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 $[Os_3(\mu\text{-}H)_2(\mu\text{-}S)(CO)_8(MeCN)]$ **6**, formed as for **2**, was treated with $PhC\equiv CH$ in refluxing THF for 24 h to give various insertion products: $[Os_3(\mu\text{-}H)(\mu\text{-}PhC=CH_2)(\mu\text{-}S)(CO)_8]$ **7** (23%), $[Os_3(\mu\text{-}H)(\mu\text{-}CH=CHPh)(\mu\text{-}S)(CO)_8]$ **8** (11%), $[Os_3(\mu\text{-}PhC_2H_2)_2(\mu\text{-}S)(CO)_7]$ **9** (17%) and $[Os_3(\eta^4\text{-}PhCH=CHCPh=CH_2)(\mu\text{-}S)(CO)_8]$ **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 $CPh=CH_2$ and $CH=CHPh$ ligands present. The 1,3-diphenylbutadiene complex **10** from treatment of **6** with $PhC\equiv CH$ 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**).

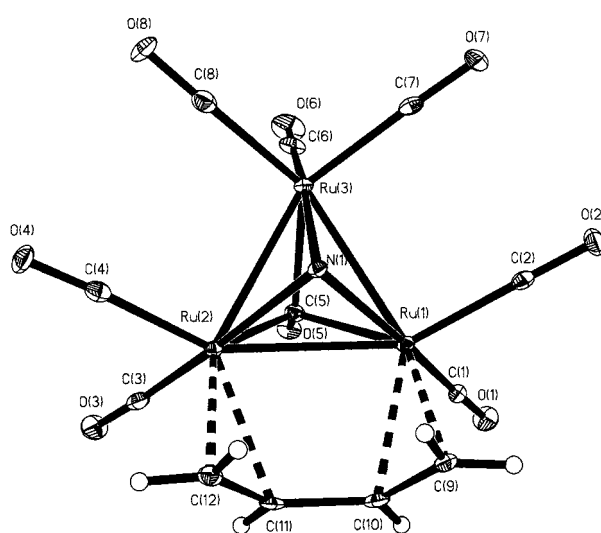
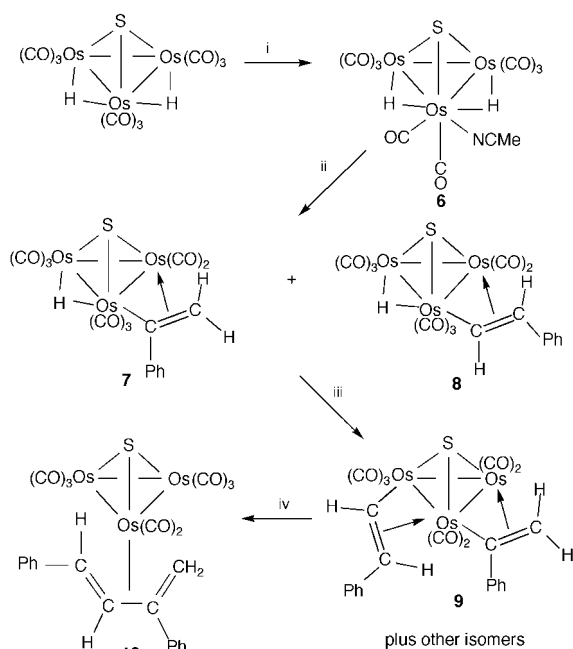


Fig. 1 Thermal ellipsoid drawing (30% probability) of $[Ru_3(\mu\text{-}\eta^2, \eta^2\text{-}C_4H_6)(\mu\text{-}3\text{-}NSO_2C_6H_4Me\text{-}4)(CO)_8]$ **4** with the tosyl group omitted. Selected lengths (\AA) and angles ($^\circ$): $Ru(1)\text{-}Ru(2)$ 2.7560(3), $Ru(1)\text{-}Ru(3)$ 2.7416(4), $Ru(2)\text{-}Ru(3)$ 2.7554(3), $Ru(1)\text{-}C(9)$ 2.258(3), $Ru(1)\text{-}C(10)$ 2.304(3), $Ru(2)\text{-}C(11)$ 2.338(3), $Ru(2)\text{-}C(12)$ 2.246(3), $C(9)\text{-}C(10)$ 1.393(5), $C(10)\text{-}C(11)$ 1.461(4), $C(11)\text{-}C(12)$ 1.393(5); $C(9)\text{-}C(10)\text{-}C(11)$ 127.5(3), $C(10)\text{-}C(11)\text{-}C(12)$ 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 semibringing 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 $[M_3(\mu-H)(\mu\text{-alkenyl})(\mu_3\text{-X})(CO)_8]$ 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 μ - η^2 , η^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



Scheme 1 Reagents and conditions: i, $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$, MeCN, CH_2Cl_2 , 293 K, 30 min; ii, PhC_2H , THF, 293 K, 24 h; iii, PhC_2H ; iv, CO.

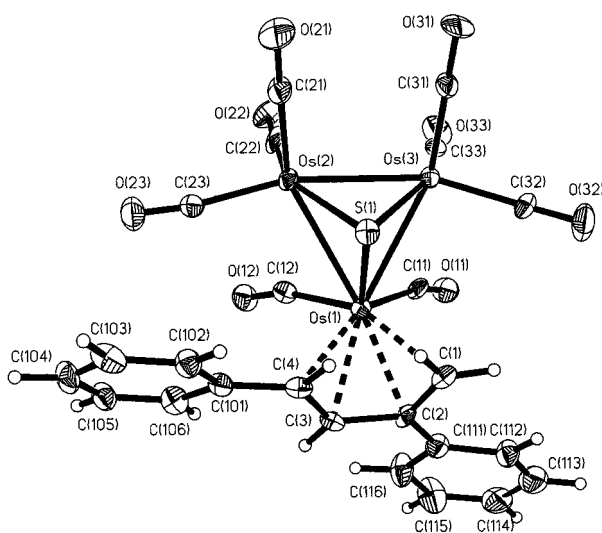


Fig. 2 Thermal ellipsoid drawing (30% probability) of $[\text{Os}_3(\eta^4\text{-PhCH=CHCPh=CH}_2)(\mu_3\text{-S})(\text{CO})_8]$ **10**. Selected lengths (Å) and angles ($^\circ$): Os(1)–Os(2) 2.8696(12), Os(1)–Os(3) 2.8524(10), Os(2)–Os(3) 2.7339(9), Os(1)–C(1) 2.214(13), Os(1)–C(2) 2.252(12), Os(1)–C(3) 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).

compounds and the geometric details of the alkenyl–alkenyl coupling.

Notes and references

[†] Selected spectroscopic data (IR for light petroleum solutions, ^1H NMR in CDCl_3 , 400 MHz, 25 $^\circ\text{C}$, unless stated otherwise; aryl and tosyl signals omitted). **2**: $\nu(\text{CO})/\text{cm}^{-1}$ (CH_2Cl_2) 2092m, 2065s, 2057s, 2013s, br; ^1H NMR (–25 $^\circ\text{C}$, 500 MHz): δ –22.37 (d, J 2.5 Hz), –16.63 (d, J 2.5 Hz), 2.32 (s, MeCN); **3**: $\nu(\text{CO})/\text{cm}^{-1}$ (CH_2Cl_2) 2105m, 2074s, 2040s, 1984m; ^1H NMR (300 MHz) δ –13.64 (s), 1.22 (s, Bu^t), 6.17 (d, J 12.2 Hz, CH=CHBu^t), 9.82 (d, J 12.2 Hz, CH=CHBu^t); **4**: $\nu(\text{CO})/\text{cm}^{-1}$ 2093s, 2054s, 2044s, 2029m, 2019m, 2006m, 1990w, 1758w, br; ^1H NMR (300 MHz) AA'BB'CC' spectrum for C_4H_6 : δ 2.91 (d, J 13.4 Hz), 3.98 (d, J 9.5 Hz), 4.58 (m); **5**: $\nu(\text{CO})/\text{cm}^{-1}$ 2090s, 2083m (sh), 2053s, 2043s, 2027m, 2018m, 2010m, 2004w, 1997w, 1990w, 1960w, 1948w 1752m, br; ^1H NMR (300 MHz) δ 2.98 (d, J 1.0 Hz), 4.72 (s), 5.53 (d, J 13.5 Hz), 5.82 (dd, J 1.5, 13.4 Hz); **6**: $\nu(\text{CO})/\text{cm}^{-1}$ (CH_2Cl_2) 2121w, 2085m, 2049s, 1996s, br; ^1H NMR δ –24.69 (s), –19.65 (d, J 1.2 Hz), 2.54 (s, MeCN); **7**: $\nu(\text{CO})/\text{cm}^{-1}$ 2097m, 2063s, 2037s, 2022m, 2013s, 2000m, 1990w, 1980m; ^1H NMR δ –13.52 (s), 4.29 (d, J 1.4 Hz), 4.59 (d, J 1.4 Hz); **8**: $\nu(\text{CO})/\text{cm}^{-1}$ 2099m, 2067s, 2035s, 2022m (sh), 2017s, 2004w, 1992w, 1978m; ^1H NMR δ –14.07 (s), 5.91 (d, J 11.6 Hz, CH=CHPh), 9.46 (d, J 11.6 Hz, CH=CHPh); **9**: $\nu(\text{CO})/\text{cm}^{-1}$ 2077m, 2044s, 2026, 2013s, 2009s, 1980ms, 1969w; **10**: $\nu(\text{CO})/\text{cm}^{-1}$ 2082m, 2049s, 2025m, 2006s, 1996m, 1979m, 1963w, 1918w; ^1H NMR δ 1.55 (d, J 3.5 Hz), 2.43 (d, J 3.4 Hz), 3.58, (d, J 9.1 Hz), 6.79 (d, J 9.0 Hz).

[‡] Crystal data: for **4**: $\text{C}_{19}\text{H}_{13}\text{NO}_{10}\text{Ru}_3\text{S}$, $M = 750.57$, orthorhombic, space group $Pbc2_1$, $a = 10.3720(2)$, $b = 13.5883(2)$, $c = 16.0282(3)$ Å, $V = 2258.98(7)$ Å³, $Z = 4$, $D_c = 2.207$ g cm^{–3}, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu = 2.129$ mm^{–1}, $F(000) = 1448$. 4203 independent reflections were measured in the θ range 3.80–26.00 $^\circ$ for a yellow crystal in an oil droplet solidified at $T = 100(2)$ K. 309 parameters were refined to give R (all data) = 0.0180 and $wR2$ (all data) = 0.0456. The Nonius 'Collect' program was used for indexing and data collection. The structure was solved by direct methods and refined (SHELXL-97) with all non-hydrogen atoms anisotropic and with hydrogen atoms included using a riding model.

For **10**: $\text{C}_{24}\text{H}_{14}\text{O}_8\text{Os}_3\text{S}$, $M = 1033.01$, triclinic, space group $P\bar{1}$, $a = 9.406(2)$, $b = 10.615(2)$, $c = 13.885(3)$ Å, $\alpha = 91.58(3)$, $\beta = 108.82(3)$, $\gamma = 104.51(3)$, $V = 1261.4(5)$ Å³, $Z = 2$, $D_c = 2.720$ g cm^{–3}, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu = 15.201$ mm^{–1}, $F(000) = 932$. 4421 independent reflections were measured at room temperature in the θ range 2.65–25.05 $^\circ$. 325 parameters were refined to give R (all data) = 0.0564 and $wR2$ (all data) = 0.1453. The structure was solved by direct methods and refined (SHELXL-97) with all non-hydrogen atoms anisotropic and with hydrogen atoms included using a riding model. CCDC 182/1484. See <http://www.rsc.org/suppdata/cc/1999/2541/> for crystallographic files in .cif format.

- A. J. Deeming, S. Hasso and M. Underhill, *J. Organomet. Chem.*, 1974, **80**, C53; *J. Chem. Soc., Dalton Trans.*, 1975, 1614.
- S. C. Brown and J. Evans, *J. Chem. Soc., Dalton Trans.*, 1982, 1049; D. H. Hamilton and J. R. Shapley, *Organometallics*, 1998, **17**, 3087; M. Koike, D. H. Hamilton, S. R. Wilson and J. R. Shapley, *Organometallics*, 1996, **15**, 4930.
- H. Chen, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Organomet. Chem.*, 1989, **376**, C7.
- N. Satyanarayana and M. Periasamy, *Tetrahedron Lett.*, 1986, **27**, 6253; S. A. Rao and M. Periasamy, *J. Chem. Soc., Chem. Commun.*, 1987, 495; I. Ryu, N. Kusumoto, A. Ogawa, N. Kambe and N. Sonoda, *Organometallics*, 1989, **8**, 2279; M. I. Bruce, G. A. Koutsantonis, E. R. T. Tiekink and B. K. Nicholson, *J. Organomet. Chem.*, 1991, **420**, 271; K. Tani, K. Ueda, K. Arimitsu, T. Yamagata and Y. Kataoka, *J. Organomet. Chem.*, 1998, **560**, 253.
- P. M. Maitlis, H. C. Long, R. Quyoum, M. L. Turner and Z.-Q. Wang, *Chem. Commun.*, 1996, 1.
- Prepared by reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with 4-MeC₆H₄SO₂NH₂.
- Y. Kaneko, T. Suzuki and K. Isobe, *Organometallics*, 1998, **17**, 996; J. A. King, Jr and K. P. C. Vollhardt, *Organometallics*, 1983, **2**, 684.
- V. C. Adams, J. A. J. Jarvis, B. T. Kilbourn and P. G. Owston, *Chem. Commun.*, 1971, 467; T. Murahashi, N. Kanehisa, Y. Kai, T. Otani and H. Kurosawa, *Chem. Commun.*, 1996, 825.
- A. Scholz, A. Smola, J. Scholz, J. Loebel, H. Schumann and K.-H. Thiele, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 435.
- J. T. Barry, J. C. Bollinger, M. H. Chisholm, K. C. Glasgow, J. C. Huffman, E. A. Lucas, E. B. Lubkovsky and W. E. Streib, *Organometallics*, 1999, **18**, 2300.
- M. Tachikawa, J. R. Shapley, R. C. Haltiwanger and C. G. Pierpont, *J. Am. Chem. Soc.*, 1976, **98**, 4651.

Communication 9/08706K