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Codimerisation of CO and a 1,3-diynyl–metal complex on an Ru_3 cluster

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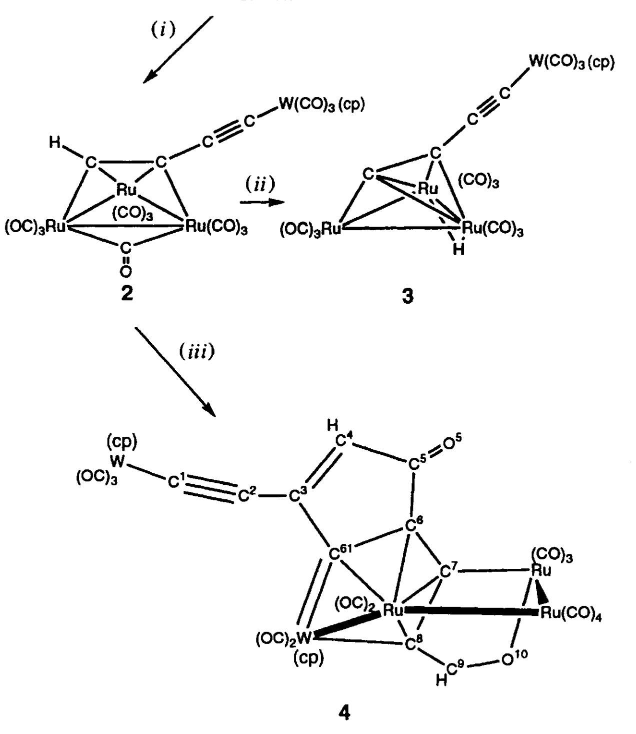
The reaction of $[W(C{\equiv}CC{\equiv}CH)(CO)_3(cp)]$ with $[Ru_3\{\mu_3\text{-}HC_2C{\equiv}C[W(CO)_3(cp)]\}(\mu\text{-}CO)(CO)_9]$ (cp = η-C_5H_5) afforded an unusual WRu_3 cluster bearing a ligand formed by dimerisation of the diynyl ligand with incorporation of two molecules of CO, as shown by a crystal-structure determination.

The synthesis and reactivity of long unsaturated carbon chains spanning two or more metal centres continues to excite interest.[1,2] We have recently prepared the air-stable molybdenum and tungsten complexes $[M(C{\equiv}CC{\equiv}CH)(CO)_3(cp)]$ (cp = η-C_5H_5) (M = Mo **1a** or M = W **1b**), and have been investigating their reactions in detail.[3] For example, that with $[Ru_3(CO)_{10}(NCMe)_2]$ gives complex **2** (Scheme 1), containing the diynyl–metal complex sitting on an Ru_3 cluster; the least hindered C≡C triple bond is co-ordinated to the cluster. As expected, thermolysis readily affords complex **3**, which is a new example of a complex containing the tetracarbon (C_4) ligand. These complexes will be described in detail later. However, if 2 equivalents of **1b** are used in the reaction with $[Ru_3(CO)_{10}(NCMe)_2]$ (thf, r.t., 30 min), a second product, the dark red complex **4**, is obtained which electrospray mass spectrometry (ESMS) showed to be formed by addition of two molecules of **1b** to the Ru_3 cluster with loss of the MeCN ligands.* Complex **4** can also be obtained as the major product (41% yield) from reactions between **1b** (0.07 mmol) and **2** (0.07 mmol) (thf, r.t., overnight). A single-crystal structure determination† revealed the unusual architecture depicted in Fig. 1 and Scheme 1.

The structure of complex **4** consists of a chain of three Ru atoms attached to an extended organic ligand made up of two molecules of **1b** and two molecules of CO. Cycloaddition of one molecule of **1b**, using the outer C≡C triple bond, together with one molecule of CO, to one of the C≡C triple bonds of the molecule of **1b** that is complexed to the Ru_3 cluster has occurred. It is not possible to determine which C≡C triple bond is involved, although the close interaction of C(7)–C(8) with the Ru atoms in complex **2** suggests that the outer one is again involved. At the same time, incorporation of a second molecule of CO [atoms C(9)–O(10)], probably by insertion into a C–Ru bond, results in the formation of new bonds C(8)–C(9) and O(10)–Ru(5). Migration of the H atom also present in **1b** to C(9) gives a formyl group, which bonds to Ru(5) *via* O(10). The cycloaddition results in bending of the C_4 chain, so that C(8) and C(61) now chelate W(2). The $C{\equiv}C[W(CO)_3(cp)]$ substituent on C(3) has the normal bond parameters found for this group, *e.g.* as found for $[W(C{\equiv}CC{\equiv}CSiMe_3)(CO)_3(cp)]$.[3]

Detailed consideration of the structure shows that there is an η^4 interaction between C(61)–C(6)–C(7)–C(8) and Ru(3), and that the W(2)–C(61) separation is short {2.096(9) Å, *cf.* 2.052(24) Å for W–C(carbene) in $[WI(CO)_2\{CPh(OEt)\}(cp)]$}.[5] The geometry of the Ru(3)–W(2)–C(61)–C(6) group strongly suggests that there is a tungsten–carbene interaction with Ru(3). An alternative explanation is that atoms W(2)–C(61)–C(6)–C(7)–C(8) form a tungstacyclopentadiene, which is attached to Ru(3) in the usual η^4 mode, with an Ru(3)→W(2) dative bond. Formation of the bicyclic system is novel, although the components have partial precedent in the



Scheme 1 (*i*) $[W(C{\equiv}CC{\equiv}CH)(CO)_3(cp)]$, CH_2Cl_2, 1.5 h, room temperature (r.t.); (*ii*) refluxing C_6H_6, 10 min; (*iii*) $[W(C{\equiv}CC{\equiv}CH)(CO)_3(cp)]$, tetrahydrofuran (thf), overnight, r.t.

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* Selected spectroscopic data for complex **4**. Infrared (cyclohexane): ν(C≡C) 2093m; ν(CO) 2058s, 2039m, 2025s, 2018vs, 2014vs, 2005m, 1990m, 1962s, 1947s, 1921w, 1918w cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.31 (s, 5 H, cp), 5.55 (s, 1 H, CH), 5.67 (s, 5 H, cp) and 8.98 (s, 1 H, CHO). ESMS: *m/z* 1347 (M^+). Satisfactory C, H analyses were obtained.

† Crystal data for complex **4**: $C_{34}H_{12}O_{16}Ru_3W_2$, $M = 1347.4$, monoclinic, space group $P2_1/c$, $a = 13.147(5)$, $b = 11.389(4)$, $c = 24.424(6)$ Å, $\beta = 93.86(2)°$, $U = 3648$ Å^3, $Z = 4$, $\mu = 76$ cm^{-1}, $T \approx 295$ K. Dark red crystal 0.30 × 0.18 × 0.09 mm, Mo-Kα radiation ($\lambda = 0.710\ 73$ Å), CAD4 diffractometer, 6410 absorption corrected intensities to $2\theta_{max} = 50°$, $A^*_{min,max}$ 1.93, 3.34. 4056 Unique data [$I > 3\sigma(I)$] were used for all calculations. Computation used the XTAL 3.0 program system implemented by Hall and Stewart,[4] neutral atom scattering factors were employed. Full-matrix least-squares refinement gave final $R = 0.032$, $R' = 0.034$, anisotropic thermal parameter refinement for non-hydrogen atoms. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/151.

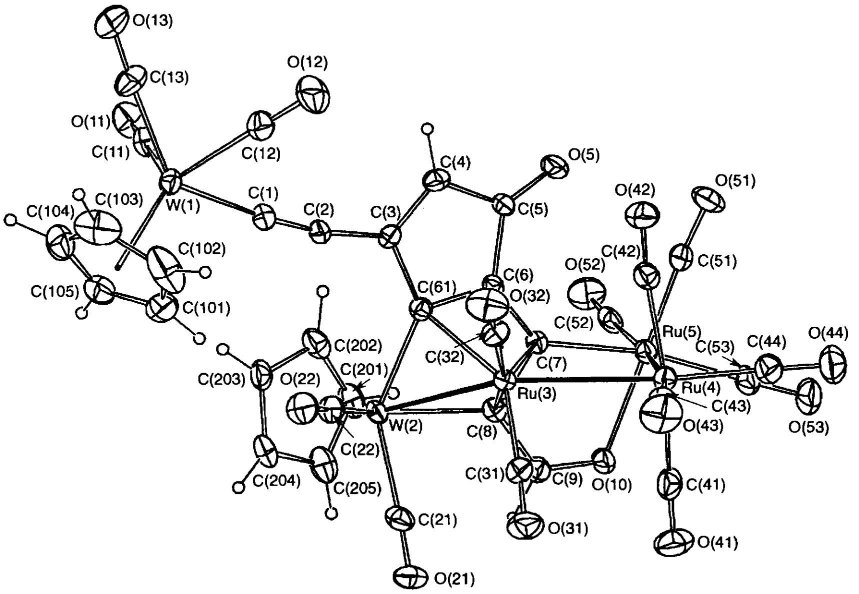

Fig. 1 Plot of a molecule of complex **4** showing atom numbering scheme. Important bond lengths: Ru(3)–Ru(4) 2.855(1), Ru(4)–Ru(5) 2.886(2), Ru(3)–W(2) 2.805(1), Ru(3)–C(6) 2.272(9), Ru(3)–C(7) 2.285(9), Ru(3)–C(8) 2.22(1), Ru(3)–C(61) 2.111(9), Ru(5)–C(7) 2.076(9), W(2)–C(61) 2.096(9), W(2)–C(8) 2.19(1), C(3)–C(4) 1.33(1), C(3)–C(61) 1.54(1), C(4)–C(5) 1.45(1), C(5)–C(6) 1.49(1), C(6)–C(7) 1.41(1), C(6)–C(61) 1.43(1), C(7)–C(8) 1.43(1), C(8)–C(9) 1.44(1) Å

formation of cyclopentadienone complexes from alkynes on iron carbonyls,[6] and the attack of CO on cluster-co-ordinated carbynes to give acyl complexes.[7] This latter reaction suggests that an electronic rearrangement of the diynyl group to a dicarbyne may be occurring during the course of the reaction described here.

The formation of complex **4** represents an unprecedented reaction of a metal-substituted diyne with a similar cluster-co-ordinated species and serves as a precursor for other chemistry of these systems, to be reported elsewhere.

Acknowledgements

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