Conversion of the Cluster Core Structure via CO Elimination and Activation of the Coordinated Hydrocarbon Ligand. Synthesis and Reactions of WO₃Cp(CO)₁₀(CMeCMeCCPh)

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Reaction of WCp(CO)₅C=CPh with Os₃(CO)₁₀(C₂Me₂) produced the butterfly cluster WO₃Cp(CO)₁₀(CMeCMeCCPh) 1 in moderate yield; treatment of 1 with Me₃NO followed by thermolysis in refluxing toluene yielded the spiked triangular cluster WO₃Cp(CO)₁₀[μ-H][CMeCMeCC(CH₂=CH₂)] 3 as a major product; on further thermolysis, complex 3 reconverted to a butterfly cluster WO₃Cp(CO)₁₀[CMeCMeCH(C[CH₃]C₂H₄)] and then to a tetrahedral cluster WO₃Cp(CO)₁₀[CMeCMeCC(CH₂=CH₂)] 6 via hydride migration followed by loss of CO; the structures of complexes 3, 5 and 6 have been determined by X-ray diffraction.

Systematically increasing the nuclearity of cluster compounds and transformation of the cluster core geometries continues to be a challenging and important task in the chemistry of transition metal cluster complexes. We have been exploring the use of group 6 mononuclear metal acetylide and hydride complexes in the stepwise synthesis of heterometallic cluster complexes; the preparation of the cluster core complex WO₃Cp(CO)₁₀[CMeCMeCCPh] 1 containing a multi-site bound C₄ hydrocarbon ligand has been achieved. Herein we report the activation of this C₄ hydrocarbon ligand via CO elimination and the sequential conversion of the cluster core from the spiked triangle to the tetrahedral arrangement.

Treatment of W(CO)₅C=CPH₄ and Os₃(CO)₁₀(C₂Me₂) in 1:1 molar ratio and in refluxing toluene (110 °C, 40 min) yielded two condensation products WO₃Cp(CO)₁₀[CMeCMeCCPh] 1 (41%) and WO₃Cp(CO)₁₀[CMeCMeCCPhCMeCMe] 2 (33%) (Scheme 1). Both complexes 1 and 2 were characterized by mass, IR and NMR spectroscopy. The exact molecular structures of these complexes were established by comparing their IR spectra with those of the structurally characterized cluster complexes WO₃Cp(CO)₁₀[C(C₂H₄)C(C₂H₄)Ph]₃ and WO₃Cp(CO)₁₀[CCPhC(C₂H₄)C(Tol)C(Tol)] respectively.

† For crystallographic enquiries.
‡ Spectral data for 1: MS (FAB, ³¹W, ¹⁸²Os), m/z 1260 (M⁺). IR (C_H) ν(CO) cm⁻¹ 2077vs, 2055s, 2048vs, 2027m, 2014s, 2010s, 1997m, 1975s, 1968s, 1952vw, 1939w, 1933w, 1920s, 1875s, 1860s, 1840m, 1825m, 1800m, 1770m, 1750m, 1730m, 1710m, 1690m, 1670m, 1650m, 1630m, 1610m, 1580m, 1560m, 1540w, 1520w, 1490w, 1470w, 1450w, 1430w, 1390w, 1370w, 1350w, 1330w, 1310w, 1290m, 1270m, 1250m, 1230w, 1210w, 1190w, 1170w, 1150m, 1130m, 1110m, 1090m, 1070m, 1050w, 1030w, 1010w, 990w, 970w, 950w, 930w, 910w, 890w, 870w, 850w, 830w, 810w, 790w, 770w, 750w, 730w, 710w, 690w, 670w, 650w, 630w, 610w, 590w, 570w, 550w, 530w, 510w, 490w, 470w, 450w, 430w, 410w, 390w, 370w, 350w, 330w, 310w, 290w, 270w, 250w, 230w, 210w, 190w, 170w, 150w, 130w, 110w, 90w, 70w, 50w, 30w, 10w, 0w.
to an orange cluster $\text{WO}_3\text{Cp}(\text{CO})_8[\text{MeCNMe}]_6$ $\text{C}_4\text{H}_8\text{O}_9\text{W}_3$ (18%).† Complex 3 was produced by the activation of the phenyl substituent of the $\text{C}_4\text{H}_8\text{O}_9$ hydrocarbon. Its $^1$H NMR spectrum exhibits four aromatic proton signals within the range $\delta$ 8.49–6.59 and a hydride signal at $\delta$ −14.26 with the characteristic tungsten–hydrogen coupling $J_{\text{W}-\text{H}}$ 73.8 Hz. In contrast, complex 4 was formed by C–C bond scission of the carbon chain. Its structure was unambiguously established by comparison of its solution IR v(CO) spectrum with that of the related derivative $\text{WO}_3\text{Cp}(\text{CO})_8[\text{MeCNMe}]_6[\text{CC(Tol)}\text{C(Tol)}]$ generated from the direct thermal reaction between $W\text{Cp}(\text{CO})_8\text{C}_2\text{C}_2\text{H}_2$ and $\text{OS}_3\text{C}(\text{C}_2\text{H}_5)$.$^7$

Complex 3 was examined by single-crystal X-ray diffraction.† The complex consists of two crystallographically distinct, but structurally similar molecules in the lattices; each displays a ‘spiked-triangular’ core arrangement with the tungsten atom located at the centre positions. An ORTEP diagram of one molecule is presented in Fig. 1. The osmium atom Os(3A) and the $\text{C}_4\text{H}_8\text{O}_9$ backbone are arranged like a metallacyclopentadentate fragment,$^8$ which coordinates to the tungsten atom via two alkenic π-interactions and a W–Os interaction and also links to a metal atom via the

Fig. 1 The molecular drawing of complex 3. Bond lengths (Å): Os(1A)–Os(2A) 2.745(1), Os(1A)–Os(3) 2.827(1), Os(1A)–W(1A) 2.987(2), Os(2A)–W(1A) 2.862(2), Os(3A)–W(1A) 2.865(2), Os(1A)–C(12A) 2.10(3), Os(1A)–C(19A) 2.06(3), Os(2A)–C(14A) 2.36(3), Os(2A)–C(19A) 2.21(3), Os(3A)–C(13A) 1.96(3), Os(3A)–C(12A) 2.15(3), W(1A)–C(10A) 2.38(3), W(1A)–C(11A) 2.23(3), W(1A)–C(12A) 2.19(3), W(1A)–C(13A) 2.35(3), C(11A)–C(12A) 1.45(3), C(12A)–C(13A) 1.38(4), C(13A)–C(14A) 1.51(4), C(14A)–C(19A) 1.41(4), C(14A)–C(15A) 1.42(4), C(15A)–C(16A) 1.40(4), C(16A)–C(17A) 1.45(4), C(17A)–C(18A) 1.37(4) and C(18A)–C(19A) 1.47(4).

Complex 3: $\text{C}_4\text{H}_8\text{O}_9\text{W}_3\text{Os}_3\text{Cp}(\text{CO})_8[\text{MeCNMe}]_6$ $\text{C}_4\text{H}_8\text{O}_9\text{W}_3\text{Os}_3\text{Cp}(\text{CO})_8[\text{MeCNMe}]_6$ $\text{C}_4\text{H}_8\text{O}_9\text{W}_3\text{Os}_3\text{Cp}(\text{CO})_8[\text{MeCNMe}]_6$. The phenyl substituent is now bound to the atom Os(1A) of the $\text{WO}_3\text{Cp}$ metal triangle and to the atom Os(2A) via π-coordination. This same bonding is seen in the pyrolysis products of triosmium and triruthenium phenylphosphine complexes.$^9$ Finally, the bridging hydride is proposed to be associated with the W(1A)–Os(1A) bond, because its bond length is the longest of the three W–Os bonds in the molecule.

Further pyrolysis of 3 in refluxing toluene as solvent for 2.34 h, inducing the hydride migration to the coordinated $\text{C}_4\text{H}_8\text{O}_9$ hydrocarbon, produced two cluster derivatives $\text{WO}_3\text{Cp}(\text{CO})_8[\text{MeCNMe}]_6[\text{C}_2\text{H}_5\text{O}_9\text{W}_3\text{Os}_3\text{Cp}(\text{CO})_8[\text{MeCNMe}]_6$ $\text{C}_4\text{H}_8\text{O}_9\text{W}_3\text{Os}_3\text{Cp}(\text{CO})_8[\text{MeCNMe}]_6$ $\text{C}_4\text{H}_8\text{O}_9\text{W}_3\text{Os}_3\text{Cp}(\text{CO})_8[\text{MeCNMe}]_6$. 26 and 31% yields.
respectively (Scheme 1). These complexes underwent reversible equilibration in refluxing toluene, because heating a solution of either complex 5 or 6 produced a mixture of both complexes within 30 min.** In addition, these complexes are stable at room temperature, which allows us to carry out the routine TLC separation and identification by elemental analysis, spectral methods** and X-ray diffraction.††

The structure of 5 adopts an Os₆W butterfly core geometry with the tungsten atom situated at one of the 'wingtip' positions (dihedral angle 177.32(2°)). As indicated by its molecular drawing (Fig. 2), the bridging hydride of 3 is moved to the third carbon atom C(13) of the C₄ hydrocarbon linkage, in which all four carbon atoms and the Os(3) atom take up a cyclic, planar disposition similar to complex 3. The phenyl substituent is linked to the C₆ linkage via the C(13)-C(14) bond and from the adjacent carbon atom C(15) which forms an asymmetric bridge over the Os(1)-Os(2) edge. The bonding between the phenyl group and the metal atoms is best described as the formation of Os(1)-C(15) α-bond and of a π-interaction with Os(2) from a delocalized molecular orbital of appropriate symmetry which is centred at C(15). Lewis and Johnson have utilized a similar description to account for the bonding of benzyl moieties in several trisomium complexes.10

Complex 6 crystallized in the P1 space group with two independent molecules in the unit cell. The ORTEP diagram of one molecule is shown in Fig. 3. As expected, the Os₆W cluster core consists of a tetrahedral geometry and the C₆ fragment adopts a similar type of bonding arrangement, except that the phenyl group has migrated from an Os-Os edge to an Os-W edge. It is possible that the transformation from butterfly to tetrahedral is initiated by the removal of CO from the tungsten atom and the formation of a new Os-W bond. The migration of phenyl substituent and fine adjustment of the C₆ chain plays the secondary role of balancing the number of formal electrons on each individual metal atom.

As our work has provided an interesting example of changing the cluster framework from a butterfly to a spiked triangle, then back to a butterfly and finally to a tetrahedral arrangement (Scheme 1). The coordinated hydrocarbon ligand serves as a reservoir to supply two pairs of electrons via ortho-metallation and complexation of the phenyl group via π-bonding to compensate the coordinative unsaturation generated during the formation of spiked triangular complex 3. The cluster conversion to butterfly conversion to tetrahedral via consecutive removal of two pairs of electrons as a result of hydride migration followed by loss of a second CO ligand. This sequence demonstrates some conceivable metal-metal and metal-substrate bonding interactions for chemisorbed hydrocarbons on catalytic surfaces.

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References


