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Preliminary communication

Reaction of $Os_3H_2(CO)_9(C_6H_4)$ with diphenylacetylene: the formation and structural characterisation of $Os_3(CO)_7(C_6H_4)[PhCC(H)Ph]_2$

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Abstract

The reaction of the 'benzyne' cluster $Os_3H_2(CO)_9(C_6H_4)$ with diphenylacetylene affords the new compound $Os_3(CO)_7(C_6H_4)[PhCC(H)Ph]_2$; a single crystal X-ray analysis of this product shows that two PhCC(H)Ph units and the benzyne moiety are bonded to the Os_3 core as separate ligands, and that under these conditions there is no ligand condensation.

Recent studies of the reactions of alkynes with dodecacarbonyltriosmium have shown that the formation of complexes is often accompanied by cyclic trimerisation of alkynes to produce benzene derivatives [1]. This carbonyl has also been shown to be a catalyst for the conversion of diphenylacetylene into hexaphenylbenzene [2]. These reports led us to consider the possibility of the cyclic co-trimerisation of coordinated benzyne and alkynes. In this communication we report the results of an investigation into the reaction of the preformed benzyne derivative $Os_3H_2(CO)_9(C_6H_4)$ (1) with diphenylacetylene, and the separation and full characterisation of the compound $Os_3(CO)_7(C_6H_4)[PhCC(H)Ph]_2$ (2), which is a key intermediate in our proposed cyclic co-trimerisation.

The reaction of $Os_3H_2(CO)_9(C_6H_4)$ (1) in MeCN with Me_3NO yielded the activated cluster $Os_3H_2(CO)_7(MeCN)_2(C_6H_4)$ (3), which has not been fully characterised. After filtration through silica and removal of solvent under vacuum, cluster 3 was redissolved in dichloromethane and the solution treated with an excess of Ph_2C_2 at room temperature. After 0.5 h a red-brown solution was obtained. The solvent was removed under vacuum and after TLC on silica (eluent 20% CH_2Cl_2/hexane), three compounds were isolated. The first, green-violet compound which was obtained in ca. 15% yield, was identified initially on the basis of its spectroscopic data (MS(FAB) $m/e = 1206$; IR (cm^{-1}, hexane): 2064m, 2029ms, 2016s, 2000mw, 1982w, 1952vw; ^1H NMR (CD_2Cl_2, δ ppm): 6.00–7.71m, 5.23s, and 4.50s) as $[Os_3(CO)_7(C_6H_4)[PhCC(H)Ph]_2$ (2); this was later confirmed by a single crystal

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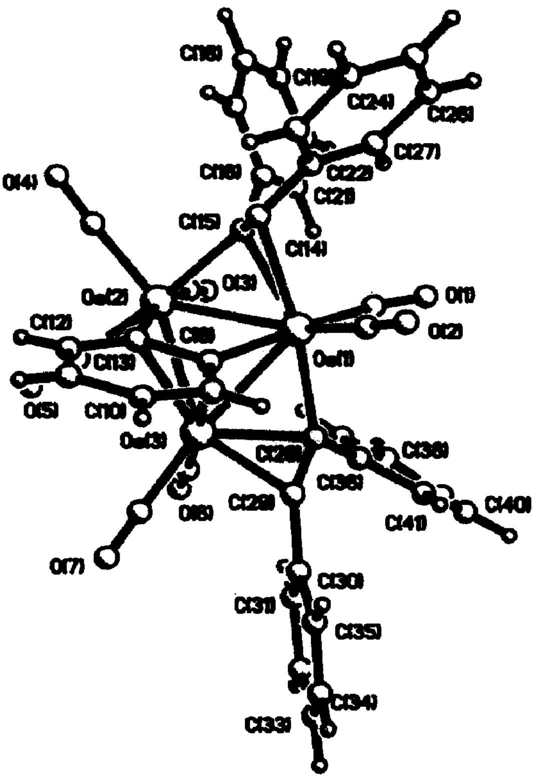

Fig. 1. The molecular structure of $Os_3(CO)_7(C_6H_4)[PhCC(H)Ph]_2$ showing the atom labelling. Bond lengths: Os(1)–Os(2), 2.885(1); Os(1)–Os(3), 2.714(1); Os(2)–Os(3), 2.717(2); Os(1)–C(8), 2.713(16); Os(2)–C(13), 2.138(18); Os(3)–C(8), 2.312(23). Os(3)–C(13), 2.427(24); Os(1)–C(14), 2.376(26); Os(1)–C(15), 2.208(23); Os(2)–C(15), 2.182(19); Os(1)–C(28), 2.141(25); Os(3)–C(28), 2.146(16); Os(3)–C(29), 2.239(19); C(8)–C(13), 1.49(3); C(14)–C(15), 1.44(3); C(28)–C(29), 1.41(3) Å. Bond angles: Os(2)–Os(1)–Os(3), 58.0(1); Os(1)–Os(2)–Os(3), 57.9(1); Os(1)–Os(3)–Os(2), 64.2(1); Os(1)–C(8)–C(13), 107.9(12); Os(2)–C(13)–C(8), 109.5(11); Os(1)–C(14)–C(15), 65.5(13); Os(1)–C(14)–C(22), 121.7(14); C(15)–C(14)–C(22), 127.8(16); Os(1)–C(15)–Os(2), 82.8(8); Os(1)–C(15)–C(14), 78.2(13); Os(2)–C(15)–C(14), 122.1(12); Os(1)–C(15)–C(16), 131.2(14); Os(2)–C(15)–C(16), 116.7(12); Os(1)–C(28)–Os(3), 78.5(8); Os(1)–C(28)–C(29), 120.9(16); Os(3)–C(28)–C(29), 74.9(10); Os(1)–C(28)–C(26), 122.7(14); Os(3)–C(28)–C(36), 125.8(13); C(29)–C(28)–C(26), 115.7(22); Os(3)–C(29)–C(28), 67.7(11); Os(3)–C(29)–C(30), 119.2(12); C(28)–C(29)–C(30), 126.6(19)°.

X-ray study. On the basis of its spectroscopic data (MS(FAB) $m/e = 1026$; IR (cm^{-1}, hexane): 2091m, 2055s, 2032m, 2019vs,sh, 1961w), the second yellow compound is considered to be $Os_3(CO)_7(C_6H_4)(Ph_2C_2)$ (4), but it is highly unstable, decomposing rapidly on silica to give an intractable material, and so has not been fully identified. The third orange compound has the same molecular weight as **2**, but has also not been fully characterised.

Dark red, prismatic crystals of compound **2** suitable for the X-ray study were obtained by slow evaporation from hexane solution at room temperature. The analysis was undertaken and the molecular structure of $Os_3(CO)_7(C_6H_4)[PhCC(H)Ph]_2$ (**2**) together with selected bond parameters, is shown in Fig. 1 *. The Os atoms define an isosceles triangle, the two shorter edges of which are bridged by the PhCC(H)Ph ligands, while the C_6H_4 group caps the triangle, being π-bound to

Os(3) and σ-bound to Os(1) and Os(2). The osmium atom Os(2) is coordinated to three terminal carbonyl ligands, two in equatorial sites and one in an axial site. The two atoms Os(1) and Os(2) are both coordinated to two terminal carbonyls. One of the PhCC(H)Ph groups is π-bound to Os(1) and σ-bound to Os(2), while the second is σ-bound to Os(1) and π-bound to Os(3). In terms of electron counting, each metal atom obeys the 18-electron rule, with the C_6H_4 ligand acting as a 4-electron donor and each of the PhCC(H)Ph groups acting as a 3-electron donor.

The metal–metal distances within the Os_3 triangle reflect the nature of the interaction between the metals and the ligands. The Os(2)–Os(3) distance (2.717(2) Å) is similar to the unbridged Os–Os edge length of 2.751(2) Å in $Os_3H_2(CO)_9(C_6H_4)$ [3], in which the benzyne ligand also caps the triangle. These distances are significantly shorter than the average Os–Os distance of 2.877(3) Å in $Os_3(CO)_{12}$ [4], which is consistent with the capping benzyne exerting an edge shortening influence on the metal triangle. This influence is also illustrated by the short Os(1)–Os(3) distance (2.714(1) Å), which is significantly below the range of Os–Os distances (2.814–2.834 Å) found for a number of other triosmium clusters in which an Os–Os edge is bridged both by an μ-η^2-alkenyl ligand and a hydride [5–7]. However, for the latter complexes the hydride exerts an edge lengthening influence. The Os(1)–Os(2) edge (2.885(1) Å), which is bridged both by the benzyne and an alkenyl ligand, is shorter than the equivalent edge in $Os_3H_2(CO)_9(C_6H_4)$ [3] (3.026(2) Å), in which the edge is bridged by the benzyne and a hydride ligand, and much shorter than the edges of 3.929(5) and 3.791(1) Å, in $Os_3H(C_6H_4)(CO)_9(AsMe_2)$ [8] and $Os_3H(C_6H_4)(CO)_9(SMe)$ [9], respectively, in which the edge is bridged by the benzyne and the arsenic or sulphur donor ligand. These donor groups exert an edge lengthening effect because of their bulk, and because they donate three electrons to the clusters, making them 50 electron systems. It appears that in the case of **2** both the benzyne and the alkenyl ligands exert an edge shortening influence on the metal triangle.

In respect of a reaction pathway to the product $Os_3(CO)_7(C_6H_4)[PhCC(H)Ph]_2$ (**2**), the activated complex $Os_3H_2(CO)_7(MeCN)_2(C_6H_4)$ (**3**) could readily lose the two acetonitrile ligands, which may then be replaced by the two alkyne ligands. These two alkyne ligands are potentially four-electron donors but, consistent with the retention of 48-electron count for the complexes, the two hydrides in **3** migrate to the alkyne ligands to form three-electron donor alkenyl units. A similar hydrogen shift has previously been observed for $Os_6(CO)_{16}[C{=}C(H)Ph]$ [10].

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* (2) $C_{41}H_{26}O_7Os_3$, $M = 1201.22$, trigonal, space group $R\bar{3}$ (No. 148), a 31.251(6), c 24.065(4) Å, V 20354 Å^3, $Z = 18$, D_c 1.76 g cm^{-3}, $F(000) = 10008$, μ(Mo-K_α) 84.6 cm^{-1}. 10054 reflections measured as a Nicolet R3mV diffractometer with graphite-monochromated Mo-K_α radiation (λ 0.71073 Å), and $2\theta_{max}$ 45°, give 5934 unique absorption corrected data ($R_{int} = 0.032$), and 4106 observed with $F > 5\sigma(F)$. Structure solved by direct methods (Os atoms) and Fourier difference techniques, and refined by full-matrix least squares (all non-hydrogen atoms anisotropic) to $R = 0.058$, w$R = 0.075$; hydrogen atoms in fixed positions riding on relevant C atom. Details of atomic coordinates, thermal parameters, bond parameters and structure factors may be obtained from the authors.

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