Electronic Control of the Co-ordination Mode of an Alkyne to a Trimetallic Cluster; X-ray Crystal Structure of $Os_3(CO)_7(\mu_3-\eta^2(\perp)-PhC=CPh)(Ph_2PCH_2PPh_2)$

Jennifer A. Clucas, P. Ann Dolby, Marjorie M. Harding, and Anthony K. Smith*

Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, U.K.

Treatment of the unsaturated triosmium cluster $Os_3(\mu-H)(CO)_8\{\mu-Ph_2PCH_2P(Ph)C_6H_4\}$ with diphenylacetylene leads to the formation of $Os_3(CO)_7(PhC\equiv CPh)(Ph_2PCH_2PPh_2)$, in which the alkyne ligand is bonded in a μ_3 - $\eta_2(\perp)$ mode, as shown by an X-ray crystal structure determination.

The co-ordination mode of an alkyne to a triangular metal cluster has been shown to be dependent on both the metal and the substituents on the alkyne. Thus, the μ_3 - $\eta^2(\bot)$ mode has been observed for Fe₃(CO)₉(RC₂R)¹ and Fe₂Ru(CO)₉-(RC₂R),² while the μ_3 - $\eta^2(\parallel)$ mode is observed in Os₃-(CO)₁₀(RC₂R),³ H₂M₃(CO)₉(RC₂R) (M = Ru,Os),⁴ and several heterometallic cluster-alkyne complexes.⁵ The reaction of terminal alkynes, HC=CR, with trinuclear metal clusters usually leads to hydrogen transfer to the metal. We report here the first structurally characterised example of the μ_3 - $\eta^2(\bot)$ co-ordination mode of an alkyne to an Os₃ framework.

Treatment of the unsaturated cluster $Os_3(CO)_8(H)$ -{ $Ph_2PCH_2P(Ph)C_6H_4$ } (1)⁶ with diphenylacetylene in toluene at 80 °C for 24 h produced a red solution from which, after



purification by t.l.c., a red crystalline solid, $Os_3(CO)_7(Ph_2PCH_2PPh_2)(PhC\equiv CPh)$ (2), was obtained in 40% yield. The spectroscopic data for (2) [i.r. v_{CO} (in CH₂Cl₂) 2052m, 1980s, 1960sh, and 1920sh cm⁻¹; ³¹P{¹H} n.m.r., (CDCl₃): δ 3.77 p.p.m. (s)] did not allow a full structural characterisation to be made, so an X-ray crystallographic study was carried out.[†] The structure of (2) is shown in Figure 1.

The X-ray structural analysis shows that the reaction of (1)with PhC=CPh resulted in the de-metallation of the phenyl group on the phosphine ligand to regenerate co-ordinated Ph2PCH2PPh2 (dppm), and the co-ordination of the PhC=CPh group in a μ_3 - $\eta^2(\perp)$ mode to the Os₃ triangle producing a stable, 46-electron cluster. The structure of (2) is analogous to those of Fe₃(CO)₉(PhC=CPh)¹ and Fe₂Ru(CO)₉(PhC=CPh).² In particular, the two short Fe-Fe and Fe-Ru distances found in these latter complexes, suggested to be due to optimisation of the alkyne-cluster interaction, are parallelled in complex (2) by the two short Os–Os distances [Os(1)-Os(3) 2.680(1)]and Os(2)-Os(3) 2.689(1) Å]. These Os-Os bond lengths are very similar to those found in the unsaturated clusters Os₃H₂(CO)₁₀ [Os-Os 2.681(1) Å]⁹ and Os₃H₂(CO)₈(dppm) [Os-Os 2.681(1) Å],¹⁰ and may be due, at least in part, to the fact that (2) is a 46-electron cluster, as well as to the requirements of co-ordination to the diphenylacetylene ligand.

The interaction between trinuclear clusters and alkynes has recently been the subject of a number of theoretical and spectroscopic studies.¹¹⁻¹³ The conclusions of these studies are that the preference for the perpendicular orientation of the alkyne ligand in 46-electron clusters is a consequence of the symmetry properties of the alkyne π orbitals and the cluster fragment levels,11 with back-donation from the two equivalent metal atoms to the alkyne playing an important role,12 such that for ruthenium and osmium, the previous failure to isolate stable complexes analogous to Fe₃(CO)₉(PhC=CPh) can be related to the decreased back-donation ability of these metals compared to iron.² The preference for the formation of the 46-electron cluster of iron, in contrast to the 48-electron clusters for ruthenium and osmium, has been relationalised in terms of charge equilibration in the M3 triangle, and it has been suggested that the μ_3 - $\eta^2(||)$ mode may even be favoured for a 46-electron Ru₃ compound.¹³ This may explain the great difference in reactivity between the highly reactive $Os_3(CO)_9(PhC \equiv CPh)^{14}$ (the structure of which is unknown) and the stable complex (2). If the co-ordination mode of the alkyne in Os₃(CO)₉(PhC=CPh) is $\mu_3 - \eta^2(||)$, the cluster would have a low-lying LUMO leading to ready reaction to produce a 48-electron species. If the co-ordination mode is μ_3 - $\eta^2(\perp)$, poor back-donation from the osmium atoms to the alkyne would lead to an unstable structure and ready reaction with two-electron donors to give a 48-electron cluster where the $\mu_3 - \eta^2(\parallel)$ co-ordination mode is favoured.

We therefore rationalise the formation of (2) in terms of the presence of the good σ -donor, poor π -acceptor phosphine



Figure 1. The structure of $Os_3(CO)_7(PhC\equiv CPh)$ (dppm) (2); (a) with phenyl rings omitted and (b) with H atoms omitted. Important bond lengths (Å) and angles (°): Os(1)-Os(2) 2.850(1), Os(1)-Os(3) 2.680(1), Os(2)-Os(3) 2.689(1), Os(1)-P(1) 2.333(5), Os(2)-P(2) 2.311(5), Os(1)-C(33) 2.116(16), Os(2)-C(33) 2.100(16), Os(1)-C(34) 2.199(15), Os(2)-C(34) 2.260(15), Os(3)-C(34) 2.205(15): Os(1)-Os(2)-Os(3) 57.8(1), Os(1)-Os(3) -Os(2) 64.1(1), Os(2)-Os(3) -Os(3) -Os(3) -C(34) 124.8(14), C(40)-C(34)-C(33) 119.4(13).

groups providing osmium atoms Os(1) and Os(2) with sufficient electron density to allow them to act as good back-donators to the alkyne ligand, and thus stabilise the μ_3 - $\eta^2(\perp)$ co-ordination mode and achieve charge equilibration on the Os₃ triangle. Certainly there appear to be no steric constraints on the co-ordination mode of the alkyne. This indicates that it is possible to control the co-ordination mode of an alkyne to a metal framework (metal surface) by modifying the electronic properties of the ligands attached to the metal atoms involved in the interaction with the alkyne.

The unsaturated cluster (1) appears to undergo de-metallation reactions readily, allowing the addition of two or four electrons to the cluster framework to occur under mild conditions, and is proving to be a useful starting material for a number of substituted Os₃ clusters. For example, we have also found that (1) reacts smoothly with $P(OMe)_3$ to produce $Os_3(CO)_8(dppm){P(OMe)_3}_2$.¹⁵

[†] Crystal data for (2): C₄₆H₃₂O₇Os₃P₂, M = 1329, monoclinic, space group P2₁/n, a = 10.972(2), b = 19.216(2), c = 20.325(3) Å, $\beta = 100.013(17)^\circ$, U = 4220 Å³, Mo-K_α radiation, $\lambda = 0.71069$ Å, Z = 4, $D_c = 2.09$ g cm⁻³, $D_o = 2.20$ g cm⁻³, μ (Mo-K_α) = 92.0 cm⁻¹. The structure was solved by Patterson and heavy atom phased Fourier methods (SHELX)⁷ using 5908 reflections with $F > 6\sigma(F)$. Leastsquares refinement with anisotropic Os, P and O atoms, and an empirical absorption correction,⁸ converged to R = 0.063. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We thank Dr M. Hursthouse (Queen Mary College, London) for the diffraction data collection, and the S.E.R.C. (P.A.D.) and the Isle of Man Government (J.A.C.) for financial support.

Received, 21st August 1987; Com. 1237

References

- 1 J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hübel, J. Am. Chem. Soc., 1966, 88, 292.
- 2 V. Busetti, G. Granozzi, S. Aime, R. Gobetto, and D. Osella, Organometallics 1985, 3, 1510.
- 3 M. Tachikawa, J. R. Shapley, and C. G. Pierpont, J. Am. Chem. Soc., 1975, 97, 7172; A. J. Deeming, S. Hasso, and M. Underhill, J. Chem. Soc., Dalton Trans., 1975, 1614.
- 4 A. J. P. Domingos, B. F. G. Johnson, and J. Lewis J. Organomet. Chem., 1972, 36, C43.

- 5 E. Sappa, A. Tiripicchio, and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203.
- 6 J. A. Clucas, D. F. Foster, M. M. Harding, and A. K. Smith, J. Chem. Soc., Chem. Commun., 1984, 949.
- 7 G. M. Sheldrick, SHELX program for Crystal Structure Determination, University Chemical Laboratory, Cambridge, 1976.
- N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
 M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, 1977, **16**, 2697.
- 10 J. A. Clucas, M. M. Harding, and A. K. Smith, J. Chem. Soc., Chem. Commun., 1985, 1280.
- 11 B. E. R. Schilling and R. Hoffmann, J. Am. Chem. Soc., 1979, 101, 3456; Acta Chem. Scand., Ser. A, 1979, 33, 231.
- 12 G. Granozzi, E. Tondello, M. Casarin, S. Aime, and D. Osella, Organometallics, 1983, 2, 430.
- 13 S. Aime, R. Bertoncello, V. Busetti, R. Gobetto, G. Granozzi, and D. Osella, *Inorg. Chem.*, 1986, **25**, 4004.
- 14 A. D. Clauss, J. R. Shapley, and S. R. Wilson, J. Am. Chem. Soc., 1981, 103, 7387.
- 15 J. A. Clucas, P. A. Dolby, M. M. Harding, and A. K. Smith, unpublished results.