SOME STUDIES ON A μ^3-INDYNE COMPLEX OF TRIOSMIUM RELATING TO ALKYNE ROTATION IN M_3C_2 CLUSTERS *

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Summary

Direct evidence is presented for a fluxional M_3C_2 cluster $H_2Os_3(\mu^3\text{-indyne})$-$(CO)_9$ in which indyne rotation with respect to the metal triangle is accompanied by flipping, so that η^2-coordination of the hydrocarbon alternates between opposite ligand faces. This process is somewhat slower than an independent hydride exchange.

Introduction

Clusters of type $M_3(\mu^3\text{-alkyne})L_n$ have been structurally characterised in two distinct geometries: the M_3C_2 skeleton may be approximately square pyramidal (A) or trigonal bipyramidal (B). The more common form (A) is frequently described as containing two M—C σ-bonds and an η^2-alkene to metal interaction and as such may be considered to contain a di-metal substituted alkene (C). The skeletons of $Os_3(PhC_2Ph)(CO)_{10}$ [1,2], $H_2M_3(\text{alkyne})(CO)_9$ (M = Ru or Os) [3, 4] and $Rh_3(CO)(C_5H_5)_3(\text{alkyne})$ [5] with geometry (A) may be considered as *nido* and based on octahedra ($n + 2$ skeletal electron pairs). In contrast, $Fe_3(PhC_2Ph)$-

(A)   (B)   (C)   (D)
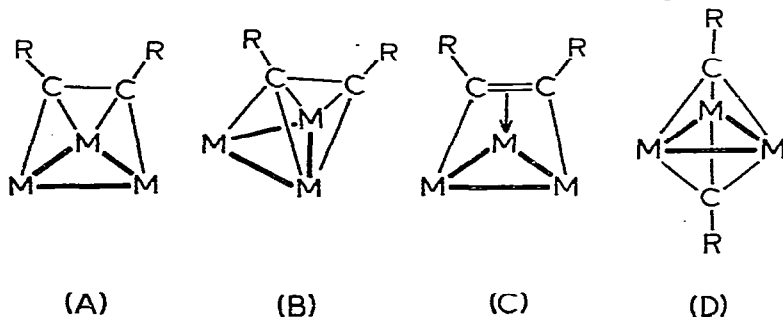
$(CO)_9$ [6] with geometry (B) is a *closo* cluster ($n + 1$ skeletal electron pairs) and

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* No reprints available.

since it contains a five-coordinate carbon atom there is no simple bonding description comparable with (C). The compounds $Rh_3(C_5H_5)_3$(alkyne) might also be expected to adopt structure (B), but where alkyne = $Et_2NC_2NEt_2$ [7] the alternative trigonal bipyramidal structure (D) is found. The PhC_2Ph analogue has been described as an alkyne cluster [8] but the NMR spectrum is rather more consistent with structure (D). Evidence is presented here for non-rigidity of type (A) clusters involving interconversions of geometries (A) and (B), which amount to alkyne rotations with respect to the M_3 triangle.

Results and discussion

The complexes H_2M_3(alkyne)$(CO)_9$ (M = Ru or Os) [3, 4] adopt the same structure in solution (Fig. 1) as established in the crystal (where M = Ru and alkyne = cyclooctyne) and these undergo several distinct fluxional processes [3, 9, 10].

(a) Hydride H^a transfer across the cluster to the vacant M—M bond. This is the fastest process and leads to a time-averaged plane of symmetry. On raising the temperature, $^{13}C(CO)$ NMR signals collapse and coalesce in pairs from nine to five (intensity ratio 2/2/2/2/1) [10] and the alkyne then appears symmetrical. For example, $H_2Os_3(H^1C^1C^2H^2)(CO)_9$ shows T_c for H^1—H^2 exchange at $-100 \pm 15°C$ (H^1 and H^2 signals at $\delta 10.14$ and 8.36 ppm at $-120°C$; Me_2O solution; $\Delta G^{\ddagger}(T_c)$ 33 ± 5 kJ mol^{-1}) [11].

(b) Axial—equatorial CO exchange at a single metal atom (local exchange).

(c) Other processes leading to total CO exchange, site exchange within the alkyne other than that resulting from (a) above, and hydride exchange. For $H_2Os_3(HC_2H)(CO)_9$ the hydride signals at $\delta -18.00$ and -21.41 ppm coalesce at $45 \pm 15°C$; $\Delta G^{\ddagger}(T_c)$ 61 ± 3 kJ mol^{-1}, Me_2O solution.

If (b) is occurring, total CO exchange could result from CO migration between metal atoms or by a combination of hydride exchange (unrestricted hydride migration about the metal triangle) and alkyne rotation. Without ligand—metal spin—spin coupling, as in rhodium cases, [8] direct observation of the latter is difficult. However, in an earlier paper [12] we described rotation of a μ^3-benzyne with respect to the Os_3 triangle in $Os_3(C_6H_4)(PMe_3)_2(CO)_7$ and
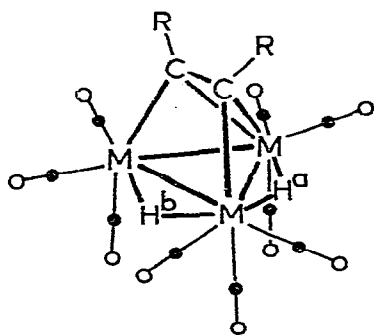

Fig. 1. Structure of H_2M_3(alkyne)$(CO)_9$. Although the hydrides were not located in the X-ray diffraction study of $H_2Ru_3(C_8H_{12})(CO)_9$ [16]. ^1H and ^{13}C NMR results confirm their positions, for example see ref. 10. The location of both hydrides along one M—M bond as preferred in some earlier papers [13] is incorrect.

suggested that this could occur by a series of 60° rotations associated with ligand flips so that each face of the carbon ring is successively coordinated. To test this hypothesis for the hydridoalkyne compounds an indyne complex of triosmium was prepared.

Indene reacts with $Os_3(CO)_{12}$ in refluxing nonane (150°C) to give a good yield of $H_2O_3(C_9H_6)(CO)_9$, in which both vinylic hydrogen atoms of the five-membered ring have been transferred to the metal. A ^1H NMR spectrum at −50°C shows an AB quartet for the CH_2 group (in CD_3COCD_3, 50/50 CD_3COCD_3/CD_2Cl_2 or $CDCl_3$ but not $CD_3C_6D_5$ in which there is accidental coincidence of signals) as well as separate hydride signals as expected for a structure with μ^3-indyne as in Fig. 1. Process (a) above would only freeze out well below −50°C by comparison with $H_2Os_3(HC_2H)(CO)_9$ and related species, so that diastereomers resulting from site exchange of the two alkyne carbon atoms were not observed; we only detected slower processes. Figure 2 shows that on raising the temperature broadening and coalescence of both the hydride and the methylene signals occur. Coalescence of the AB quartet can only mean that the M_3(indyne) skeleton is fluxional and we feel that the process illustrated in Fig. 3 is the most
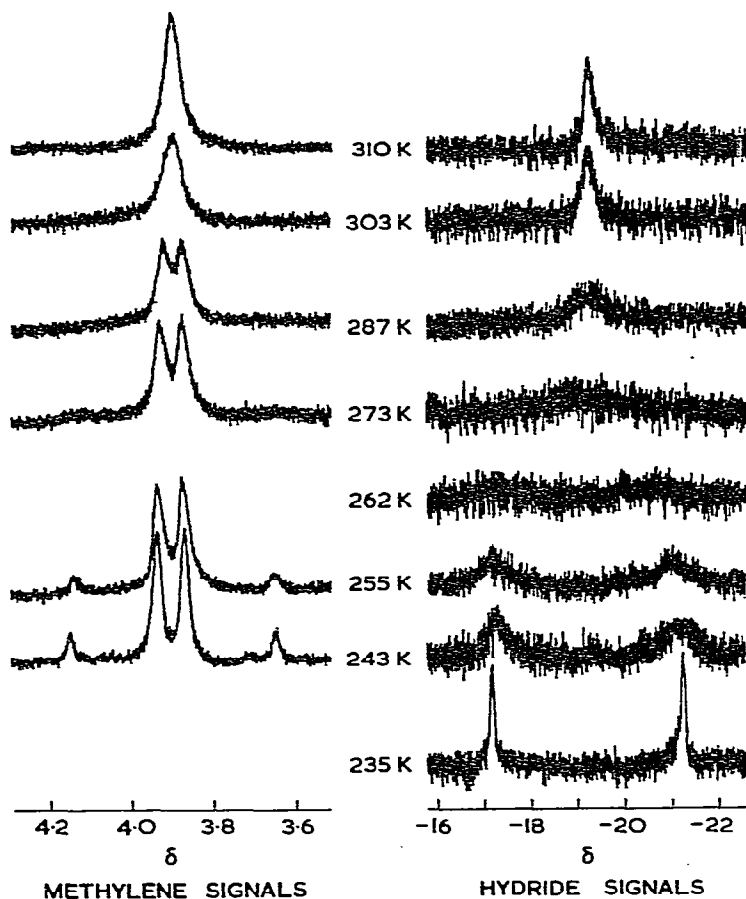

Fig. 2. ^1H NMR spectra ($C\underline{H}_2$ and Os$\underline{H}$ regions) of $H_2Os_3(C_9H_6)(CO)_9$ recorded in CD_3COCD_3/CD_2Cl_2 (1/1 by volume) at 100 MHz; temperature calibrated from methanol shifts.
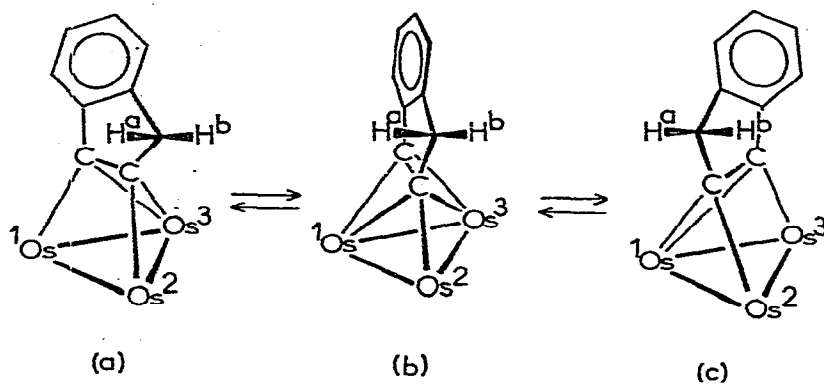
Fig. 3. Alkyne rotation/flipping mechanism.

likely representation of atom movements (the metal-bound carbons could be interchanged in Fig. 3). Hydride ligands could exchange by a faster independant process but not slower than alkyne rotation and for the indyne compound we have found that $\Delta G^{\ddagger}$ (268 K; hydride exchange) = 50 ± 1 kJ mol^{-1} (δ −17.63 and −21.26 ppm; T_c 268 K) while $\Delta G^{\ddagger}$ (295 K; CH$_2$ exchange) = 60 ± 2 kJ mol^{-1} (δ 3.81 and 4.00 ppm, J_{AB} 21.7 Hz; T_c 295 K) in CD$_3$COCD$_3$/CD$_2$Cl$_2$ (1/1 by volume). The faster hydride exchange most likely occurs by an unrestricted hydride migration between Os—Os bonds, and although one might envisage this exchange to occur by alkyne rotation without flipping this seems an unnecessary complication in view of the k·:own ability of hydrides to migrate in clusters. Thus with alkyne rotation, unrestricted hydride migration and localised CO scrambling (b) there is no need to invoke CO transfer between metals to obtain total CO scrambling as has been identified in these systems [10].

It was earlier believed [13] that alkyne rotation would not allow opposite faces of the ligand to be coordinated and the variable temperature ^{1}H NMR of the ligand in H$_2$M$_3$(cyclooctyne)(CO)$_9$ (M = Ru or Os) was accordingly interpreted in terms of conformational changes (Fig. 4). However, conformational changes about C^3 and C^8 cannot give H^a—H^b exchange as long as only one face of the ligand remains coordinated. A mechanism as in Figure 3 provides a better interpretation. After a 60° rotation/flip the opposite face of the cyclooctyne is
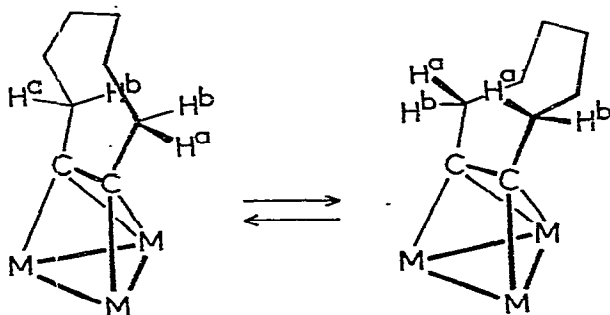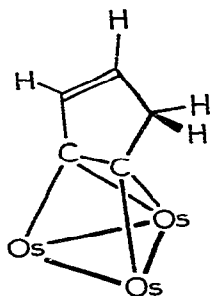

Fig. 4. Organic ring flipping in H$_2$M$_3$(C$_8$H$_{12}$)(CO)$_9$ (M = Ru or Os) [13].

Fig. 5. Skeleton of $H_2Os_3(C_5H_4)(CO)_9$ [14].

coordinated but the ligand is in the other conformation shown in Fig. 4. Rapid carbon ring flipping (Fig. 4) would then complete H^a—H^b exchange but this may actually be concerted with alkyne rotation/flipping. From data given in ref. 13, alkyne rotation/flipping in osmium and ruthenium clusters must have similar rates unlike most other dynamic processes. We were unable to prepare the corresponding ruthenium μ^3-indyne complex to establish the generality of this. Further for M = Os, alkyne = cyclooctyne, $\Delta G^{\ddagger} = 71$ kJ mol^{-1} for hydride exchange but 67 kJ mol^{-1} for H^a—H^b exchange. Hydride exchange cannot be slower than alkyne rotation, but this is not the case if these $\Delta G^{\ddagger}$ values are considered to be the same within experimental error.

For the cluster $H_2Os_3(C_5H_4)(CO)_9$ (Fig. 5) obtained in very low yield from cyclopentadiene [14], the observation of magnetic non-equivalence of the methylene hydrogens at —90°C but equivalence at room temperature was ascribed to temperature dependence of chemical shifts. Site exchange via a rotation/flipping mechanism as in Fig. 3 is more probable.

The μ^3-cyclopentyne complex $H_2Os_3(C_5H_6)(CO)_9$ (Fig. 6) [3] also shows temperature dependent ligand as well as hydride resonances; for the latter $T_c = 35°C$ and $\Delta G^{\ddagger}(T_c) = 58$ kJ mol^{-1}. The H^a and H^b atoms give a well-resolved 1/2/1 triplet (δ 2.76 ppm) at 65°C but at —45°C this resonance is somewhat broader but shows greater multiplicity indicating magnetic non-equivalence of these atoms at this lower temperature. Similarly the other CH_2 group gives a broad resonance centred on δ 1.75 ppm (65°C) but two broad signals (δ ~2.15 and 1.42 ppm) at —45°C. These changes can only be interpreted in terms of M_3C_2
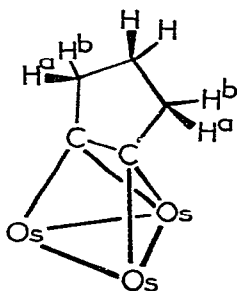

Fig. 6. Skeleton of $H_2Os_3(C_5H_6)(CO)_9$ [3].

fluxionality. These few examples seem to indicate that this rotation/flipping behaviour is general in μ^3-alkynes.

Therefore there is contrast in behaviour between μ^3-alkyne (1,2-disubstituted alkene) and μ^3-vinylidene (1,1-disubstituted form), for example $H_2Os_3(C=CH_2)$-$(CO)_9$ [3], in that the latter are rigidly bound to the metal triangle [3,15]; by use of prochiral substituents it was shown that coordination of the alkene did not rapidly alternate between the faces. These differences must be born in mind when considering stereospecificity of reactions involving these μ^3-ligands.

Experimental

Reaction of indene with $Os_3(CO)_{12}$. A solution of osmium carbonyl (0.51 g) and indene (2 cm^3) in nonane (30 cm^3) was refluxed under nitrogen for 24 h. After removal of the solvent from the brown solution under reduced pressure, the residue was chromatographed on TLC plates (silica), eluting with distilled pentane. A pale yellow band gave $H_2Os_3(C_9H_6)(CO)_9$ as thermally and air stable pale yellow crystals (0.285 g, 54%). (Found: C, 23.15; H, 0.85. $C_{18}H_8O_9Os_3$ calcd.: C, 23.05; H, 0.85%). ν(CO) (cyclohexane) 2112 m, 2084 s, 2060 vs, 2038(sh), 2035 s, 2026 s, 2013 s, 2004(sh), 2001 m, 1990(sh), 1987 m cm^{-1}. ^{1}H NMR (CDCl$_3$, −60°C) δ 7.0—7.6 m ppm ($C_6\underline{H}_4$); 3.80 d and 3.92 d ppm, J_{AB} 22.0 Hz ($C\underline{H}_2$); −17.35 s and −21.38 s ppm ($Os\underline{H}_2$). $\Delta\nu_{AB}$ (low temperature) for the $C\underline{H}_2$ AB quartet 12.4 Hz (CDCl$_3$), 25.9 Hz (CD$_3$COCD$_3$), 18.8 Hz (CD$_3$COCD$_3$/CD$_2$Cl$_2$; 1/1 by volume), 0 Hz (CD$_3$C$_6$D$_5$/CD$_2$Cl$_2$; 1/1 by volume). Although the shift is greatest in acetone, dichloromethane/acetone mixtures were required to obtain sufficient solubility for reasonably good spectra. These were recorded at 100 HMz on a Varian HA100 spectrometer.

An orange band from the TLC plate above gave a small amount of a mixture of an Os$_3$ and an Os$_2$ compound. These two predominate at the expense of H_2Os_3-$(C_9H_6)(CO)_9$ from a reaction in refluxing indene and these are now under investigation.

Acknowledgements

References

1 M. Tachikawa, J.R. Shapley and C.G. Pierpont, J. Amer. Chem. Soc., 97 (1975) 7172.
2 C.G. Pierpont, Inorg. Chem., 16 (1977) 636.
3 A.J. Deeming and M. Underhill, J. Chem. Soc. Dalton, (1974) 1415.
4 B.F.G. Johnson and J. Lewis, Pure Appl. Chem., 44 (1975) 43.
5 Trinh-Toan, R.W. Broach, S.A. Gardner and M.D. Rausch, Inorg. Chem., 16 (1977) 279.
6 J.F. Blount, L.F. Dahl, G. Hoogzand and W. Hübel, J. Amer. Chem. Soc., 88 (1966) 292.
7 R.B. King and C.A. Harman, Inorg. Chem., 15 (1976) 879.
8 L.J. Todd, J.R. Wilkinson, M.D. Rausch, S.A. Gardner and R.S. Dickson, J. Organometal. Chem., 101 (1975) 133.
9 W.G. Jackson, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 139 (1977) 125.
10 J. Evans, B.F.G. Johnson, J. Lewis and T.W. Matheson, J. Organometal. Chem., 97 (1975) C16.
11 A. Bury and A.J. Deeming, unpublished results.
12 A.J. Deeming, R.E. Kimber and M. Underhill, J. Chem. Soc. Dalton, (1973) 2589.
13 A.J. Canty, A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1973) 2056.
14 A.P. Humphries and S.A.R. Knox, J. Chem. Soc. Dalton, (1975) 1710.
15 W.G. Jackson, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 90 (1975) C13.
16 R. Mason and K.M. Thomas, Ann. N.Y. Acad. Sci., 239 (1974) 225.