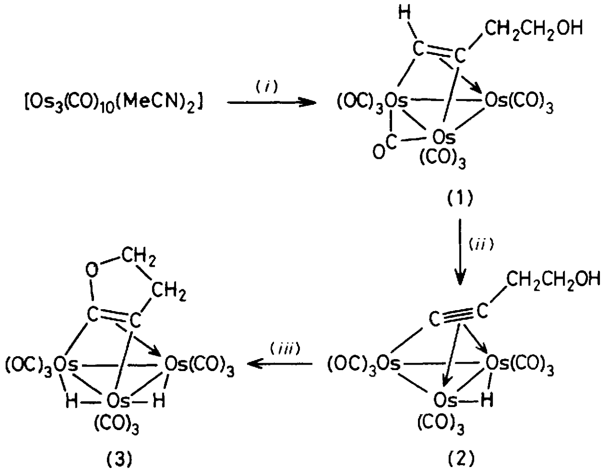
Intramolecular Nucleophilic Attack at the α-Carbon Atom of a μ_3-Alkynyl Ligand in a Triosmium Cluster

Silvio Aime *
Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino, Italy
Antony J. Deeming *
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ

The cluster $[Os_3(CO)_{12}]$ reacts with but-3-yn-1-ol, $HC{\equiv}CCH_2CH_2OH$, in hydrocarbon solvent at 130 °C to give the 2,3-dihydrofuran-4,5-diyl complex $[Os_3H_2(CO)_9(\mu_3\text{-}\overline{C{=}CCH_2CH_2O})]$ (3) (yield 48%). The probable route to this compound is indicated by the formation of the simple alkyne compound $[Os_3(CO)_{10}(\mu_3\text{-}HC{\equiv}CCH_2CH_2OH)]$ (1) from $[Os_3(CO)_{10}(MeCN)_2]$ and the alkynol at room temperature which at higher temperatures converts to compound (3) probably *via* its isomer $[Os_3H(CO)_9(\mu_3\text{-}C{\equiv}CCH_2CH_2OH)]$ (2). This isomerisation occurs because α-carbon atoms of μ_3-alkynyl ligands are susceptible to nucleophilic attack which in this case occurs intramolecularly with cyclisation. The dynamic behaviour of clusters (1) and (3) is described; in both cases inversion of the chiral Os_3(alkyne) group is observed.

Several examples of triruthenium and triosmium clusters derived from acetylenic alcohols have been described. In some cases the effect of the OH function is not immediately obvious because clusters are formed which are directly comparable with those of simple alkynes. Complexes $[M_3H(CO)_9(\mu_3\text{-}C{\equiv}CCR_2OH)]$ (R = Me or Ph; M = Ru [1,2] or Os [2]) and $[Os_3(CO)_{10}(\mu_3\text{-}HOCH_2C{\equiv}CCH_2OH)]$ [3] are examples. When the OH group is adjacent to the carbon–carbon multiple bond as in these cases, the metal atoms have great influence on the reactivity of the alcohol. Hydroxide ion is readily lost from the $\mu_3\text{-}C{\equiv}CCR_2OH$ complexes and when R = Ph there is an acid-catalysed isomerisation to give $[Os_3H(\mu\text{-}OH)(CO)_9(\mu_3\text{-}C{=}C{=}CPh_2)]$.[4] The diol $[Os_3(CO)_{10}(\mu_3\text{-}HOCH_2C{\equiv}CCH_2OH)]$ thermally converts by C–O bond cleavage to $[Os_3H(CO)_9(\mu_3\text{-}CH_2{=}C{=}CCHO)]$ and hence by isomerisation to $[Os_3H(CO)_9(\mu_3\text{-}CHCHCCHO)]$.[3] While these effects are novel and interesting, we wished to establish whether a hydroxy-function and the metal atoms could be made essentially non-interacting. By moving the OH group further from the alkyne function, for example by using $HC{\equiv}CCH_2CH_2OH$, the above transformations would be prevented but at the same time the greater flexibility of the $HOCH_2CH_2$ chain might allow OH to attack at metal atoms, CO ligands, or elsewhere in the cluster. Intramolecular attack does indeed occur.



Scheme. (*i*) 20 °C, $HC{\equiv}CCH_2CH_2OH$; (*ii*) 96 °C, – CO; (*iii*) 96 °C, isomerisation

Results and Discussion

Reaction of $[Os_3(CO)_{12}]$ in refluxing hydrocarbon at 130 °C with $HC{\equiv}CCH_2CH_2OH$ (L) in excess gave a fairly clean reaction to give one major product (3) (48% isolated yield) which was shown to have the stoicheiometry $[Os_3(CO)_9L]$. The ^1H n.m.r. spectrum showed it to be the dihydride $[Os_3H_2(CO)_9(C_4H_4O)]$ and the i.r. spectrum [ν(CO)] is extremely similar to that of alkyne or benzyne complexes such as $[Os_3H_2(CO)_9(\mu_3\text{-}C_6H_4)]$.[5] The ^1H n.m.r. spectrum at low temperatures showed four multiplets at δ 2.64, 2.92, 3.97, and 4.90 p.p.m. (Table 1), each corresponding to one hydrogen atom of the $\text{-}CH_2CH_2\text{-}$ group. No ^1H n.m.r. or i.r. absorption was present that could be assigned to an OH group. These data are only consistent with (3) being the 2,3-dihydrofuran-4,5-diyl complex illustrated in the Scheme. No other product, such as an alkynyl complex of type $[Os_3H(CO)_9(\mu_3\text{-}C{\equiv}CR)]$, commonly formed from terminal alkynes, was formed in any significant amount.

To define the route to (3) from the butynol, we attempted to co-ordinate the alkyne to triosmium under mild conditions so that subsequent thermal transformations could be observed. Thus $[Os_3(CO)_{10}(MeCN)_2]$ reacts rapidly at room temperature in dichloromethane with the butynol to give $[Os_3(CO)_{10}(\mu_3\text{-}HC{\equiv}CCH_2CH_2OH)]$ (1) in reasonable yield (47%). This complex has spectral properties such as a ν(CO) absorption at 1 852 cm^{-1} (Table 2) for a bridging CO group and a low-field $HC{\equiv}C\text{-}$ ^1H n.m.r. signal at δ 9.28 p.p.m. quite characteristic of a complex with a structure as shown in the Scheme (for examples, see ref. 2). No cyclisation had occurred at this stage. Compound (1) readily converts as shown in the Scheme through (2) to (3), identical with the compound formed directly from the butynol and $[Os_3(CO)_{12}]$. There is spectroscopic evidence for the formation of (2) as an intermediate but

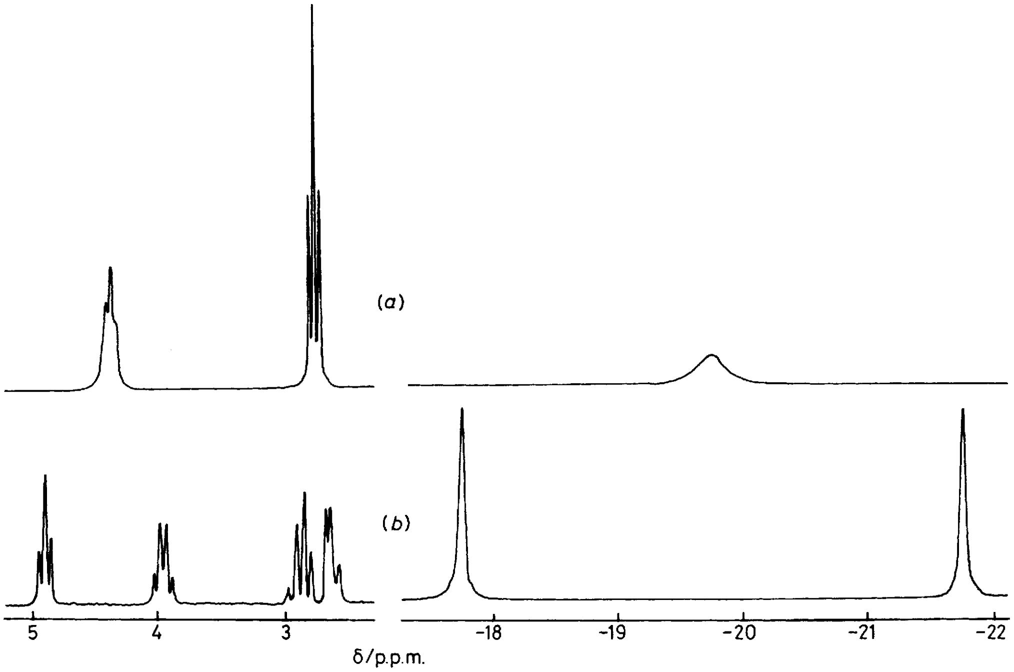


Figure. Proton n.m.r. spectra of compound (3) in $CDCl_3$ (200 MHz) (*a*) at 22 °C and (*b*) at −50 °C

Table 1. Proton n.m.r. data *

Complex	*T*/°C	CH^x_2	CH^y_2	CH^z	OH	OsH
(1) $[Os_3(CO)_{10}(H^zC{\equiv}CCH^x_2CH^y_2OH)]$	40	2.62 (br)	3.79 (m)	9.28 (s)	1.40 (br)	
	−40	2.70 (m), 2.45 (m)	3.79 (m)	9.17 (s)	1.95 (br)	
(3) $[Os_3H_2(CO)_9(\overline{C{=}CCH^x_2CH^y_2O})]$	22	2.73 (t)	4.41 (t)			−19.7 (br)
	−50	2.92 (m), 2.64 (m)	4.90 (t), 3.97 (q)			−17.75 (s), −21.78 (s)

* Recorded in $CDCl_3$ at 200 MHz; δ values relative to $SiMe_4$ in p.p.m.; br = broad, s = singlet, m = complex multiplet, q = quintet, t = triplet.

Table 2. Selected i.r. data *

Compound	$\tilde{\nu}(CO)/cm^{-1}$
(1)	2 102(2), 2 063(10), 2 057(9), 2 027(8), 2 009(6), 2 001(5), 1 852(1)
(2)	2 101(1), 2 075(10), 2 052(9), 2 021(10), 2 011(7), 1 981(4)
(3)	2 110(2), 2 083(9), 2 058(10), 2 031(9), 2 025(5), 2 013(8), 2 000(6), 1 986(4)

* Recorded in cyclohexane solution; relative intensities are given in parentheses.

it could not be obtained analytically pure, partly because of an apparent isomerisation of (2) to (3) on silica.

It has previously been demonstrated that nucleophilic addition at the α-carbon atom of a μ_3-C≡CR group in a tri-osmium cluster can readily occur [6] and that this is consistent with the relatively low electron-population density at this carbon atom.[7] We therefore propose that the cyclisation reaction results from an intramolecular nucleophilic attack to give the zwitterionic compound $[Os_3{}^-H(CO)_9(\overline{C{=}CCH_2CH_2OH^+})]$ followed by proton transfer from O to Os to give (3). Cyclisation of $HC{\equiv}CCH_2CH_2OH$ resulting from co-ordination to a metal atom has been seen before but only in cationic complexes. Co-ordination of this alkyne to $[Fe(\eta\text{-}C_5H_5)(CO)_2]^+$, for example, results in cyclisation to give two isomeric complexes of type $[Fe(\eta\text{-}C_5H_5)(CO)_2L]^+$, where L = η^2-2,3-dihydrofuran or σ-2-oxacyclopentylidene.[8] Cyclisation of $HC{\equiv}CCH_2CH_2OH$ also occurs in its reaction with $[PtMeCl(PMe_2Ph)_2]$ and $AgPF_6$ in methanol to give exclusively a complex containing the cycloalkylidene ligand.[9]

Compounds (1) and (3) are both fluxional; the Figure shows the ^1H n.m.r. spectra of $[Os_3H_2(CO)_9(\overline{C{=}CCH_2CH_2O})]$ (3) at −50 and 22 °C. The $^-CH_2CH_2{}^-$ group of (3) shows two well resolved triplets above 22 °C consistent with an AA′BB′ spectrum and a time-averaged plane of symmetry through the five atoms of the organic ring. Similar spectra and changes with temperature are observed for the $^-CH_2CH_2{}^-$ group of compound (1). Again a time-averaged plane is generated through the C_4 chain. In each case the low-temperature spectra (Table 1) are consistent with the static structures shown in the Scheme. These are rather attractive examples to illustrate that the μ_3-alkyne ligands rotate and that as they do so the opposite faces of the alkyne ligands interchange and the observed time-averaged planes of symmetry are generated. The Os_3(alkyne) cages in (1) and (3) are chiral. Although mechanisms of alkyne rotation without inversion could be envisaged, our spectra clearly show that rapid inversion occurs, that is, the asymmetric osmium-bound carbon atoms undergo inversion.

References 10—12 give other examples of this behaviour in which a 60° rotation of the alkyne with respect to the metal triangle is associated with the ligand passing through a vertical orientation in the transition state or intermediate.

Experimental

The but-3-yn-1-ol was used as purchased from Aldrich Chemical Co. Ltd.

*Action of But-*3-*yn*-1-*ol on* $[Os_3(CO)_{12}]$.—The alkynol (0.058 g) was added to a solution of $[Os_3(CO)_{12}]$ (0.225 g) in light petroleum (b.p. 120—160 °C; 50 cm^3) and the mixture refluxed under nitrogen for 1.25 h. The cooled solution was decanted from a little insoluble brown deposit, the solvent removed under vacuum, and the residue chromatographed on SiO_2 (t.l.c.) eluting with a pentane–diethyl ether mixture (1 : 1 v/v). Several very minor bonds were eluted together with one main almost colourless band which yielded $[Os_3H_2(CO)_9(C_4H_4O)]$ (3) as pale yellow crystals (0.100 g). Rechromatography gave a rather purer product (0.082 g) (Found: C, 18.0; H, 0.9. $C_{13}H_6O_{10}Os_3$ requires C, 17.5; H, 0.7%).

*Action of But-*3-*yn*-1-*ol on* $[Os_3(CO)_{10}(MeCN)_2]$.—The reagent $Me_3NO{\cdot}2H_2O$ (0.160 g) in acetonitrile (80 cm^3) was added over 1 h to a refluxing solution of $[Os_3(CO)_{12}]$ (0.570 g) in dichloromethane (300 cm^3) and acetonitrile (30 cm^3) under nitrogen. The solution was passed through an SiO_2 column twice and the solvent removed under vacuum. The solid $[Os_3(CO)_{10}(MeCN)_2]$ was dissolved in dichloromethane (20 cm^3) to give a yellow solution and the alkynol (0.141 g) added. After 15 min at room temperature the solvent was removed from the orange-red solution and the residue chromatographed on SiO_2 (t.l.c.) eluting with pentane–diethyl ether (1 : 1 v/v). The faster orange band gave $[Os_3(CO)_{10}(HC{\equiv}CCH_2CH_2OH)]$ (1) as orange-red crystals (0.265 g) (Found: C, 18.65; H, 0.8. $C_{14}H_6O_{11}Os_3$ requires C, 18.25; H, 0.65%).

Thermolysis of Compound (1).—Thermolysis of compound (1) in refluxing heptane for 20 min gave a solution with an i.r. spectrum showing *ca.* 90% of a compound of type $[Os_3H(CO)_9(C{\equiv}CR)]$, which we presume to have $R = CH_2CH_2OH$. Chromatography on SiO_2 gave a little of compound (3) (4%) while compound (2) could not be obtained pure. Similar treatments of (1) in refluxing hexane or cyclohexane (2 h) gave variable results. Up to 52% of compound (3) and up to 20% of compound (2) (albeit impure) could be isolated. We believe that compound (2) partially converts to (3) on silica since successive elutions gave separate fast-moving bands of (3) in front of a slowly moving band of (2). An analytically pure sample of (2) was not obtained.

Acknowledgements

We thank Johnson-Matthey Ltd. for a loan of OsO_4 and N.A.T.O. for support.

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Received 24*th November* 1982; *Paper* 2/1974