Synthesis and Reactivity of Trinuclear Osmium and Dinuclear and Trinuclear Ruthenium Compounds derived from Hydroxyalkynes

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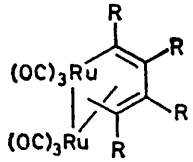
3-Hydroxy-3-methylbut-1-yne ($HC{\equiv}CCMe_2OH$) reacts with $[Ru_3(CO)_{12}]$ to give $[Ru_3H(CO)_9(C{\equiv}CCMe_2OH)]$ in very low yield as already described, but we can now report that the main products are isomeric compounds with empirical formula $[Ru_2(CO)_6(alkyne)_2]$, which contain ruthenacyclopentadiene groups, and substituted benzenes formed by oligomerisation of three alkyne molecules. Much better yields of $[Os_3H(CO)_9(C_2CMe_2OH)]$ are obtained in a similar way with no evidence for alkyne trimerisation or complex dimer formation. The complex $[Os_3H_2(CO)_{10}]$ reacts at room temperature with HC_2CMe_2OH to give $[Os_3(CO)_{10}(HC_2CMe_2OH)]$ and $[Os_3H(CO)_{10}(CH{=}CHCMe_2OH)]$. The dynamic n.m.r. behaviour of the first of these and the thermal decarbonylations of both are described. The ^1H n.m.r. spectra of cationic clusters formed by hydroxide-ion loss in acidic solution are reported and the involvement of such cations in substitution and dehydration reactions of the η^3 ligands.

TERMINAL alkynes of type $HC{\equiv}CCRR'(OH)$ have recently been shown to react with $[Ru_3(CO)_{12}]$ to give trinuclear clusters of type $[Ru_3H(CO)_9(C_2CRR'OH)]$ (1) [1] in a manner well established for $HC{\equiv}CBu^t$.[2] The hydroxy-function allows reactions to occur at the side chain, such as acid-induced dehydration to give $[Ru_3H(CO)_9(C_2CPh{=}CH_2)]$ (2) where R = Me and R' = Ph, the *X*-ray structure of which was established.[1] Compounds (1) were obtained in very low yield and we report here that most of the $[Ru_3(CO)_{12}]$ is converted into dimeric species of type $[Ru_2(CO)_6(alkyne)_2]$, compounds (3), containing



metallacyclopentadiene rings. We will also describe here related chemistry for osmium based on $HC{\equiv}CCMe_2OH$.

These are among the first attempts to prepare osmium and ruthenium clusters with hydrocarbon ligands functionalised at a side chain to see how the cluster modifies the chemistry of the particular function. Hydroxy-functionalised alkyne clusters also have the potential of being easily supported on metal oxide surfaces.

RESULTS AND DISCUSSION

Ruthenium.—The complex $[Ru_3(CO)_{12}]$ reacts readily with $HC{\equiv}CCMe_2OH$ in aliphatic solvents leading to increasingly turbid solutions as the reaction proceeds. When all the initial carbonyl had reacted, the insoluble material was removed by filtration. This orange-brown powder is not a metal carbonyl as it is transparent around 2 000 cm^{-1} and there are no mass spectral peaks corresponding to a mass higher than 253. On the basis of spectral data we think the material is a mixture (approximate mol ratio 1 : 4) of benzene derivatives $C_6H_3R_3$-1,2,4 and -1,3,5 ($R = CMe_2OH$) corresponding to different patterns of oligomerisation of $HC{\equiv}CCMe_2OH$ and with the 1,2,4-isomer predominant.

The mass spectrum shows a fragmentation pattern involving loss of H_2O molecules and the ^1H n.m.r. spectrum contains two sets of singlets in the aromatic region (δ 7.20—7.55, intensity 1) and in the aliphatic region (δ 1.30—1.70, intensity 6). The ^{13}C (^1H-coupled) n.m.r. spectrum contains four distinct sets of resonances. There are four singlets (δ 145.5—150.8), four doublets (J = 156 Hz, δ 120.6—129.6, aromatic *C*H), four singlets (δ 73.0—75.9, *C*Me_2OH), and a set of overlapping quartets (J = 127 Hz, δ 32.0—34.1, *C*H_3).

Chromatography of the yellow-brown filtrate gave two bands which yielded metal carbonyl compounds, one of which is the cluster (1) (R = R' = Me). The other carbonyl compound is poorly volatile, gave no mass spectrum, while ^1H and ^{13}C n.m.r. spectra gave several resonances indicating the presence of more than one species; the ^1H n.m.r. spectrum showed three clear sets of resonances at δ 7.40—7.60, 5.40—5.60, and 1.30—1.60.

These spectra are consistent with ruthenacyclopentadiene derivatives with the empirical formula $[Ru_2(CO)_6L_2]$ (L = alkyne) but the stoicheiometry of the material was only adequately established by comparison with the directly analogous material obtained from the reaction of $[Ru_3(CO)_{12}]$ with $HC{\equiv}CCH_2OH$. A brown band was obtained similarly with an indistinguishable ν(CO) spectrum (2 086m, 2 054vs, 2 015vs, 1 992s cm^{-1}) but which in this case gave crystals with a very clear mass spectrum corresponding to $[Ru_2(CO)_6(alkyne)_2]$. The origin of the mixture for the ruthenacyclopentadiene compounds $[Ru_2(CO)_6L_2]$ (L = $HC{\equiv}CCMe_2OH$) (3) is almost certainly in the orientations of asymmetric alkyne coupling in the formation of the ruthenacyclopentadiene rings (*i.e.* head to head, head to tail, and tail to tail).

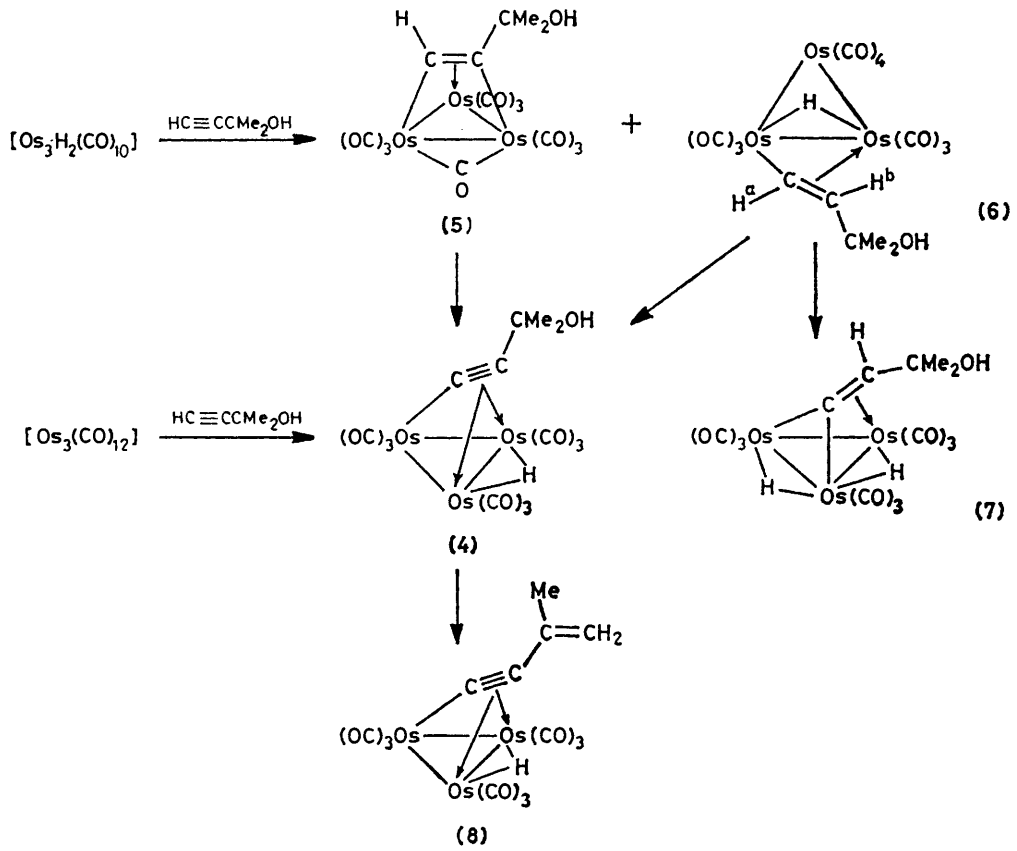
The synthesis of simple triruthenium clusters derived from $HC{\equiv}CCMe_2OH$ is difficult and we hoped that the triosmium system would be simpler.

Osmium.—Scheme (1) summarises the syntheses of compounds (4) to (8). While $[Ru_3(CO)_{12}]$ gives compound (1) (R = R' = Me) in only low yield (<5%) on thermal reaction with $HC{\equiv}CCMe_2OH$ with most of the cluster breaking down into the dimers (3), $[Os_3(CO)_{12}]$ gives only trinuclear species. Reaction with a 10-fold

excess of the alkyne at 130 °C gives up to 60% crude yield of $[Os_3H(CO)_9(C_2CMe_2OH)]$, compound (4), within 1 h. The chemistry of Ru differs from that of Os partly because the Os_3 rings are more robust but possibly also because with osmium, alkynyl ligand formation is faster than alkyne coupling. The μ_3-alkynyl ligand would stabilise the cluster while alkyne coupling presumably facilitates cluster breakdown.

The complex $[Os_3H_2(CO)_{10}]$ is more reactive than $[Os_3(CO)_{12}]$ and reacts with $HC{\equiv}CCMe_2OH$ at room temperature to give $[Os_3(CO)_{10}(HC_2CMe_2OH)]$, compound (5) (66%), and a low yield of $[Os_3H(CO)_{10}(CH{=}CHCMe_2OH)]$, compound (6) (8%), which were easily separated by thin-layer chromatography (t.l.c.) (SiO_2). Compounds (5) and (6) are analogous to the μ_3-C_2H_2 and μ-$CH{=}CH_2$ compounds formed similarly from acetylene,[3] and have the structures shown (Scheme 1). Compound (5) adopts the common bridging CO structure [ν(CO) = 1 850 cm^{-1}], rather than the form without bridging CO as found for $[Os_3(CO)_{10}(PhC_2Ph)]$,[4] while (6) contains the *trans* alkene (*cis* addition of Os–H to the alkyne) [$J(H^aH^b)$ = 14.2 Hz].

Ready decarbonylation of complexes (5) and (6) occurs above 120 °C. The formation of (4) from (5) is essentially quantitative whereas (6) gives both compounds (4) and (7) (Scheme 1). Interestingly compound (6) is a substituted derivative of $[Os_3H(CO)_{10}(CH{=}CH_2)]$ which decarbonylates exclusively to $[Os_3H_2(CO)_9(C{=}CH_2)]$.[3] Bulky alkyl substituents at the vinyl group may radically change the chemistry; for example, $[Os_3H(CO)_{10}(CH{=}CHBu^t)]$ gives $[Os_3H(CO)_9(C_2Bu^t)]$ alone in good yields by loss of H_2 and CO on thermolysis.[5] Compound (6) therefore gives both types of product. Further studies are being carried out on the mechanism of H-transfer reactions associated with decarbonylation. We favour the idea that for loss of H_2, H-atom transfer from C to Os atoms must occur prior to decarbonylation, but we will develop this idea elsewhere.



SCHEME 1

Dynamic N.M.R. Behaviour of $[Os_3(CO)_{10}(HC{\equiv}CCMe_2OH)]$.—Compound (5) shows interesting variable-temperature ^1H and ^{13}C n.m.r. spectra. A single process leading to coalescence in the range −30 to 60 °C is observed in the ^1H n.m.r. spectrum but in addition at least two other faster processes may be identified from the ^{13}C n.m.r. spectra in the range −90 to −25 °C. The process observed in the ^1H spectra requires motion of the alkyne ligand with respect to the metal triangle. Thus at −30 °C the alkyne ligand shows four singlets in intensity ratio 1 : 1 : 3 : 3 at δ 9.25, 1.56, 1.48, and 1.47 respectively as expected for the static structure shown in Scheme 1. The Me groups are diastereotopic since, regarding the μ_3 ligand as a substituted alkene, one face of the alkene is bound in a η^2 manner to one osmium atom. Figure 1 shows how the O*H* signal shifts steadily

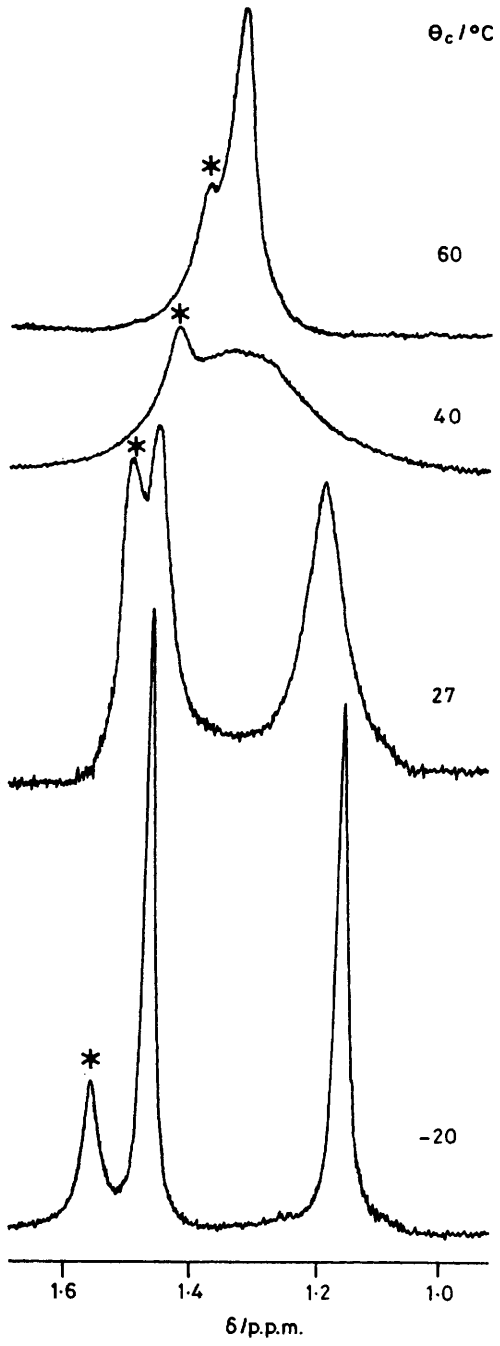


FIGURE 1 ^{1}H N.m.r. spectra for $[Os_3(CO)_{10}(CH{\equiv}CCMe_2OH)]$, compound (5). O*H* peaks are marked with an asterisk. Solvent $CDCl_3$

upfield as expected and the two Me singlets coalesce as the temperature is increased from −30 °C to 60 °C. There must be a rapid process leading to interchange of the two alkene faces which would require a non-rigid Os_3C_2 skeleton. We have made similar observations on $[Os_3H_2(CO)_9(\mu_3\text{-indyne})]$ [6] and related μ_3-aryne complexes [7,8] and have proposed a ligand rotation–flipping mechanism. The fluxionality of complexes of type $[Os_3(CO)_{10}(alkyne)]$ has already been noted,[4] but no details at all were given. The rotation of the μ_3 ligand with respect to the Os_3 triangle requires positional changes of the CO ligands and to analyse these more clearly the variable-temperature ^{13}C n.m.r. spectra of a ^{13}CO-enriched (*ca.* 65%) sample of cluster (5) were recorded (Figure 2). Temperatures as low as −90 °C (CD_2Cl_2 solution) were required to resolve eight resonances at δ 205.7, 182.0, 181.4, 180.6, 177.7, 175.8, 174.2, and 173.3 p.p.m. in relative ratio 1 : 1 : 1 : 1 : 1 : 3 : 1 : 1 which is consistent with the proposed static structure (Scheme 1) with ten different carbonyl groups, if three signals are overlapping. The assignment is straightforward only for the μ-CO group resonance at δ 205.7 p.p.m. Based on several observations reporting axial CO resonances at lower field than equatorial ones (for examples see ref. 9), we tentatively assign the group of three signals at 182.0, 181.4, and 180.6 p.p.m., each of intensity one, to the axial carbonyls, one for each of the three $Os(CO)_3$ units. The remaining absorptions are

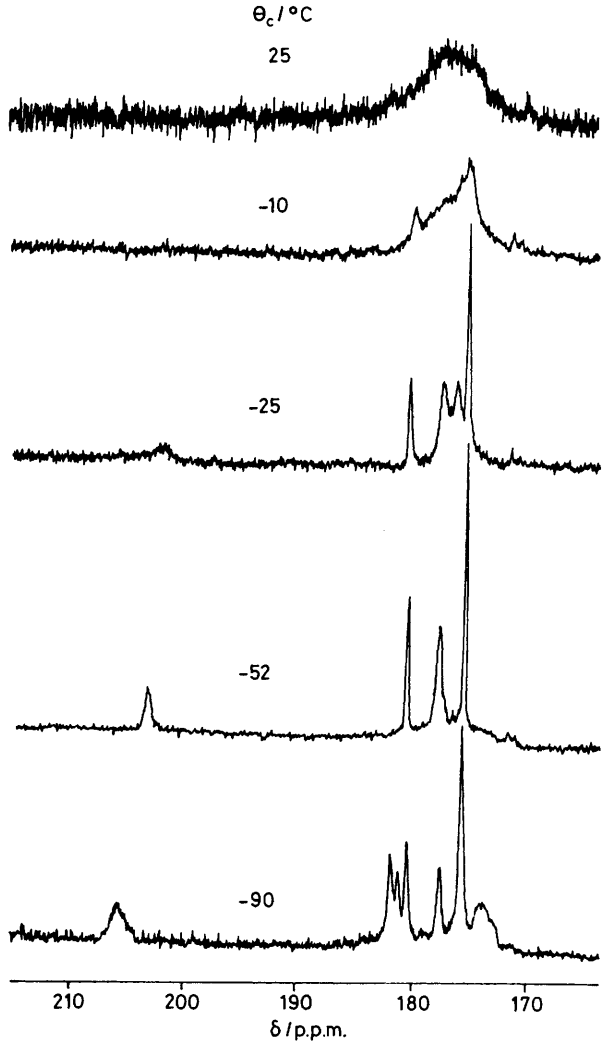
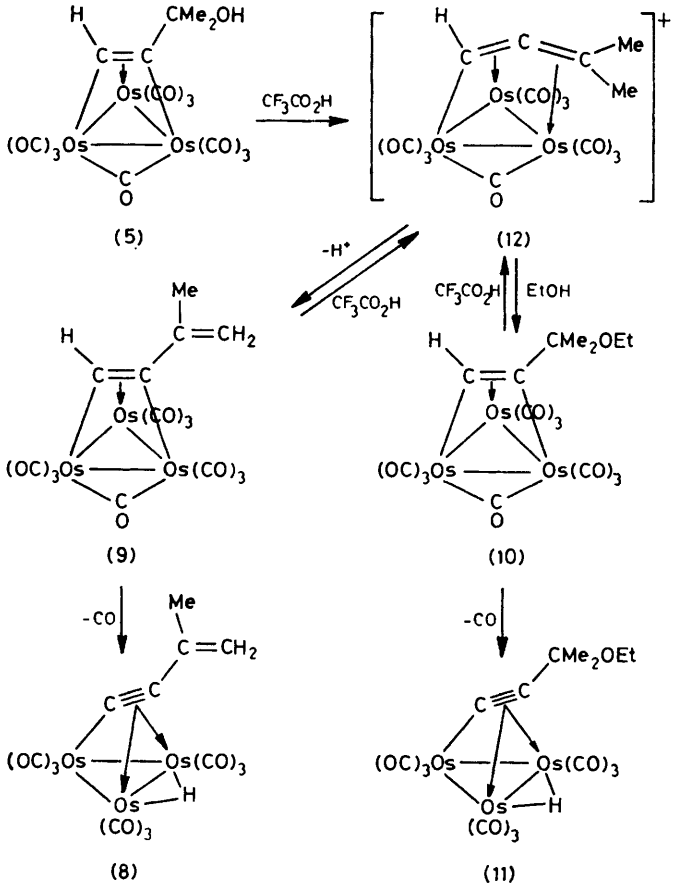


FIGURE 2 ^{13}C N.m.r. spectra for $[Os_3(CO)_{10}(CH{\equiv}CCMe_2OH)]$, compound (5), in the carbonyl region; solvent $CDCl_3$. The resonances of the organic ligand are unobserved since there is *ca.* 60% ^{13}C enrichment for the CO ligands

then assigned to the six equatorial carbonyls with three signals overlapping.

A feature of the spectrum at −90 °C is the broadness of the μ-CO resonance and the two highest field equatorial resonances, the μ-CO signal being significantly broader than at −52 °C. This could possibly be ascribed to unresolved C–C coupling, large for mutually *trans* CO groups, but also possibly to the start of a very fast but undefined dynamic process being frozen out. The complex is too insoluble, however, in CF_2Cl_2 to obtain



SCHEME 2

spectra at lower temperatures. This process could involve oscillation between symmetric and asymmetric μ-CO positions and the fairly large shift (*ca.* 3 p.p.m. downfield) between −52 and −90 °C might relate to such behaviour. The possibility of adopting different structures is indicated by the diphenylacetylene analogue which has no bridging CO.[4]

As the temperature is raised from −90 to −25 °C two signals at δ 180.6 and 175.8 remain sharp but the other terminal-CO resonances coalesce. Firstly signals at δ 182.0, 177.7, and 174.2 coalesce to a new peak at δ 178.0 by −52 °C and then the signals at δ 181.4, 175.8 (a component of the signal of intensity three), and 173.3 coalesce so that by −25 °C there are five signals with intensities 1 : 1 : 3 : 3 : 2. This is totally consistent with two mechanistically distinct localised CO exchanges at separate $Os(CO)_3$ units, which we presume to be those σ-bonded to the alkyne.

At higher temperatures there is total CO scrambling and certainly this is related to the non-rigidity of the Os_3C_2 framework deduced from ^1H n.m.r. spectra. One could envisage a procession of the equatorial CO groups including the μ-CO group around the cluster as the alkyne rotates, but, since there is already a fast localised exchange at two $Os(CO)_3$ units, total scrambling occurs. Total scrambling is quite an unusual feature of triosmium clusters but is facilitated by alkyne rotation in this case.

Reactions of Co-ordinated Hydroxy-ligands with Acid.—Compound (4) slowly dehydrates to (8) after several hours in hydrocarbon solvents at above 120 °C but dehydrations of this sort are possible at room temperature under acid-catalysed conditions. This, of course, is expected for a $RCMe_2OH$ group but the main feature of these μ_3 ligands is that intermediate carbocations are stabilised in the cluster and are observed to be formed totally in CF_3CO_2H solution (Scheme 2). Thus compound (5) dissolves in CF_3CO_2H to give a non-hydridic species, the 60 MHz ^1H n.m.r. spectrum of which at room temperature shows only two signals apart from those of the solvent (δ 9.63 and δ 1.82; 1 : 6 intensity ratio) but at lower temperatures at 100 MHz the Me signal may just be resolved into two peaks separated by *ca.* 2 Hz. The two non-equivalent Me signals are almost coincident. The same ^1H n.m.r. spectrum in CF_3CO_2H solution is observed for compound (5) as for (9) and (10) [which were obtained from (5) under acid-catalysed conditions (see Experimental section)].

Complex (4) also dissolves readily in neat CF_3CO_2H. Like (4), the solute is a mono-hydride and there are two separate Me signals (^1H n.m.r. δ 1.98 and 2.22) which indicate the species in solution is $[Os_3H(CO)_9(C_3Me_2)]^+$, compound (13). The cation is presumably an intermediate in the dehydration of (4) to (8) but we have not yet isolated (13). We wish to study it further because the C_3Me_2 ligand should be a six-electron donor but as an allenediyl ($C{=}C{=}CMe_2$) with orthogonal π orbitals the bonding is not so easy to envisage.

The formation of cationic complexes by loss of OH^- has synthetic potential especially where there are no hydrogen atoms suitable for deprotonation, which tends to dominate here. We are further examining the electrophilic behaviour of complexes such as (12) and (13) with various nucleophilic reagents.

EXPERIMENTAL

Spectroscopic data for the new compounds are given in the Table.

Reaction of HC_2CMe_2OH *with* $[Ru_3(CO)_{12}]$.—A solution of $[Ru_3(CO)_{12}]$ (0.600 g) and the alkyne (1.2 cm^3) in cyclohexane (250 cm^3) was heated under reflux under N_2 for 2 h. After cooling, the reaction mixture was filtered to separate the insoluble organic material (0.5 g). Chromatography of the filtrate (t.l.c., SiO_2; eluant: light petroleum–diethyl ether) gave $[Ru_3H(CO)_9(C{\equiv}CCMe_2OH)]$, compound (1), (*ca.* 0.025 g, 4%) and $[Ru_2(CO)_6(HC_2CMe_2OH)_2]$ compound (3) (0.150 g, 30%) as a brown oil.

Infrared, ^{1}H n.m.r., and analytical data for the trinuclear compounds

Compound	ν(CO)[a]/cm^{-1}	^{1}H n.m.r.[b] OsH	CH_3	OH	Others	Analysis (%)[c] C	H
(1) (R = R′ = Me)	2 102w, 2 075vs, 2 056vs, 2 020s, 1 989ms	−21.0(s)	1.60(s)	2.2(s)			
(4)	2 103w, 2 077vs, 2 056vs, 2 024vs, 2 016s, 1 984m	−23.68(s)	1.80(s)	1.1(br)		18.75(18.55)	1.0(0.9)
(5)	2 103m, 2 065vs, 2 058vs, 2 026s, 2 009m, 2 003m, 1 850w		1.49(s)[d] 1.18(s)[d]	1.56(s)	9.25(s)	19.6(19.3)	1.25(0.9)
(6)	2 106w, 2 064vs, 2 054s, 2 023vs, 2 016m, 2 005m, 1 996m, 1 986w, 1 979w	−18.37[d]	1.48(s)	[e]	7.58(dd) 4.41(d)	19.8(19.25)	1.3(1.1)
(7)	2 105w, 2 081vs, 2 059s, 2 054m, 2 025vs, 2 016s, 2 013(sh), 2 005m, 1 983m, 1 976w	−18.37[f] −21.68[f]	1.27(s) 1.43(s)	1.68	5.32(s)	19.1(18.5)	1.25(1.1)
(8)	2 103w, 2 077vs, 2 055vs, 2 023vs	−23.44(s)	2.21(t)[g]		5.33(m)[h]	19.3(18.9)	0.85(0.7)
(9)[i]	2 102m, 2 063vs, 2 058vs, 2 027vs, 2 016m, 2 010m, 2 003m, 1 984m, 1 850m		1.57(s)		5.01(m) 4.81(m) 9.39(s)		
(11)	2 102w, 2 075vs, 2 054vs, 2 022vs, 2 014vs, 2 981m	−23.74(s)	1.63(s)		3.49(q) 1.12(t)	23.0(20.55)[j]	1.9(1.3)
(12)			1.82(s)[k]		9.63(s)		
(13)		−20.22	1.98(s) 2.18(s)				

[a] Recorded in cyclohexane. [b] Recorded in $CDCl_3$ at 30 °C unless stated otherwise. q = Quartet, dd = double doublet. [c] Calculated figures are given in parentheses. [d] At −30 °C. [e] Not assigned. [f] Broad at 30 °C. [g] J *ca.* 1.2 Hz. [h] The CH_2 signals overlap. [i] Contaminated with compound (10). [j] Probably contaminated with some hydrocarbon. [k] Just resolved into two peaks at 100 MHz.

Reaction of HC_2CMe_2OH *with* $[Os_3(CO)_{12}]$.—A solution of $[Os_3(CO)_{12}]$ (0.45 g) and the alkyne (0.400 g) in light petroleum (b.p. 120—160 °C) (200 cm^3) was heated under reflux under nitrogen for 1 h. The i.r. spectrum of the reaction mixture showed *ca.* 50% reaction in 20 min. Chromatography (t.l.c., SiO_2) of the mixture after removal of the solvent gave one main band which gave brown impure $[Os_3H(CO)_9(C_2CMe_2OH)]$, compound (4), (0.279 g). Careful re-chromatography was necessary to give the completely pure compound (0.128 g, 28%) as colourless crystals. Prolonged reflux times gave some dehydration to $[Os_3H(CO)_9(C_2CMe{=}CH_2)]$, compound (8).

Reaction of HC_2CMe_2OH *with* $[Os_3H_2(CO)_{10}]$.—A solution of $[Os_3H_2(CO)_{10}]$ (0.435 g) and the alkyne (4 cm^3) in pentane solution (10 cm^3) was allowed to stand for 3 d at room temperature. Removal of solvent and t.l.c. (SiO_2; eluant: toluene) gave $[Os_3(CO)_{10}(HC_2CMe_2OH)]$, compound (5) (0.317 g, 66%), as orange-red crystals and $[Os_3H(CO)_{10}(CH{=}CHCMe_2OH)]$, compound (6) (0.038 g, 8%), as bright yellow crystals.

Decarbonylation of (5).—An orange solution of $[Os_3(CO)_{10}(HC_2CMe_2OH)]$ (0.073 g) in light petroleum (b.p. 120—160 °C) when refluxed under N_2 became very pale yellow in 15 min. Thin-layer chromatographic (SiO_2) work-up gave colourless crystals of compound (4) (0.063 g, 83%).

Thermolysis of Compound (6).—A solution of $[Os_3H(CO)_{10}(CH{=}CHCMe_2OH)]$ (0.038 g) in light petroleum (b.p. 120—160 °C) was heated under reflux under nitrogen for 15 min. Chromatographic work-up (SiO_2) gave compound (4) (0.006 g), $[Os_3H_2(CO)_9(C{=}CHCMe_2OH)]$, compound (7) (0.011 g), and $[Os_3(CO)_{12}]$ (0.006 g).

Treatment with CF_3CO_2H.—$[Os_3(CO)_{10}(HC_2CMe_2OH)]$. The compound CF_3CO_2H (0.2 cm^3) was added to a solution of compound (5) (0.162 g) in $CDCl_3$ (2 cm^3). Hydrogen-1 n.m.r. signals around δ 5 indicated that complete dehydration had rapidly occurred. After 15 min the solution was diluted with chloroform (containing 1% ethanol) and treated with solid $K[HCO_3]$. Chromatography (SiO_2), after removal of solvent from the filtered solution, gave some recovered compound (5) (0.021 g) but mainly a mixture (0.100 g) of $[Os_3(CO)_{10}(HC_2CMe{=}CH_2)]$ (9) and $[Os_3(CO)_{10}(HC_2CMe_2OEt)]$ (10) (2.8 : 1.0 mol ratio). Although these could not be separated by t.l.c., ^{1}H n.m.r. strongly indicated their presence. Decarbonylation of some of this mixture (0.033 g) in refluxing light petroleum for 15 min gave a mixture of $[Os_3H(CO)_9(C_2CMe{=}CH_2)]$, compound (8) (0.023 g), and $[Os_3H(CO)_9(C_2CMe_2OEt)]$, compound (11) (0.011 g). These were easily separated by t.l.c. and were fully characterised as colourless crystals.

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