Acid-induced Displacement of Acetaldehyde from a μ-Vinyloxy-triosmium Cluster

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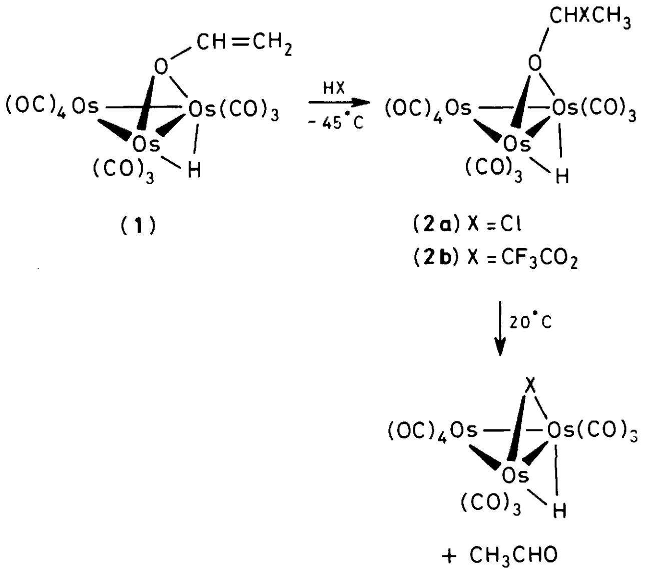
Protonation of the μ-vinyloxy-ligand in $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ with HX (X = Cl or CF_3CO_2) leads to the compounds $[Os_3H(X)(CO)_{10}]$ with liberation of acetaldehyde (ethanal). Several intermediates including the addition species $[Os_3H(\mu\text{-}OCHXCH_3)(CO)_{10}]$ (X = Cl or CF_3CO_2) have been identified (and isolated for X = Cl). These addition compounds readily undergo β-elimination of acetaldehyde. This reaction has been exploited as a synthetic route to the known complexes $[Os_3H(X)(CO)_{10}]$ (X = Cl, Br, I, CF_3CO_2, or OH) and the new compounds from potassium *O*-ethyl dithiocarbonate and *NN*-diethyldithiocarbamate, $[Os_3H(S_2COEt)(CO)_{10}]$ (two isomers) and $[Os_3H(S_2CNEt_2)(CO)_{10}]$. The complex $[Os_3H(S_2CNEt_2)(CO)_{10}]$ undergoes ready decarbonylation to $[Os_3H(S_2CNEt_2)(CO)_9]$.

The vinyloxy-compound $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**) was previously reported as a minor product from the reaction of $[Os_3H_2(CO)_{10}]$ with ketene.[1] We have found that a better route to compound (**1**) is from vinylene carbonate $OCH{=}CHOCO$ and the dihydrido-osmium compound. Wanting to use this compound as a starting material for the synthesis of compounds of the type $[Os_3H(X)(CO)_{10}]$, we have protonated compound (**1**) followed by displacement of the organic ligand by various anions.

Results and Discussion

Protonation of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**).—When gaseous HCl is bubbled into a $CDCl_3$ solution of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**) at −45 °C a new species $[Os_3H(\mu\text{-}OCHClCH_3)(CO)_{10}]$ (**2a**) immediately forms. Compound (**2a**) results from addition of HCl across the double bond of the vinyloxy-group and is rather unstable in solution at room temperature towards β-elimination of acetaldehyde to give $[Os_3H(Cl)(CO)_{10}]$[2] (see Scheme). Removal of solvent, under vacuum immediately after forming compound (**2a**), gave a yellow solid which was characterised by ^1H n.m.r. and i.r. spectroscopy although it could not be prepared sufficiently pure for satisfactory elemental analysis (see Table and Experimental section). The ^1H n.m.r. spectrum of (**2a**) shows the expected quartet (δ 5.19) and doublet (δ 1.66) for the $CHCH_3$ group but with chemical shifts and coupling constant (5.2 Hz) characteristic of $OHCClCH_3$ rather than co-ordinated acetaldehyde. Its ν(CO) spectrum around 2 000 cm^{-1} closely resembles that of the analogous μ-methoxy-compound $[Os_3H(OMe)(CO)_{10}]$.[3]

Analogously to the protonation by HCl, addition of trifluoroacetic acid to a $CDCl_3$ solution of compound (**1**) ultimately produces the known compound $[Os_3H(CF_3CO_2)(CO)_{10}]$[2] and free acetaldehyde quantitatively. Several intermediates were observed by ^1H n.m.r. at low temperature. At −45 °C addition of CF_3CO_2H immediately gives an intermediate associated with new CH and CH_3 signals [δ 5.31 (q), 1.40 (d), J_{HH} 3.9 Hz] and a new hydride signal at δ −12.54. This first intermediate is $[Os_3H\{\mu\text{-}OCH(OCOCF_3)CH_3\}(CO)_{10}]$ (**2b**) corresponding directly to that observed in the HCl case. As the solution is slowly warmed, acetaldehyde is liberated from (**2b**) to give two new hydrido-intermediates (δ −12.47 and −10.77) which increase and then decrease in concentration as the final hydride $[Os_3H(CF_3CO_2)(CO)_{10}]$ is formed. The same two intermediates and final product are seen when the hydroxy-compound $[Os_3H(OH)(CO)_{10}]$[3] in $CDCl_3$ is protonated with CF_3CO_2H at −45 °C under identical conditions. $[Os_3H(OH)(CO)_{10}]$ has been reported to react with HX to give $[Os_3H(X)(CO)_{10}]$ (X = Cl,[4] Br,[4] or RCO_2 where R = H, Me, or CF_3[5]) and when X is unco-ordinating (*e.g.*, HBF_4 in MeCN) the cation $[Os_3H(CO)_{10}(MeCN)_2]^+$ is formed.[4] We suggest that one of the intermediates on protonation of $[Os_3H(OH)(CO)_{10}]$ at −45 °C is $[Os_3H(\mu\text{-}OH_2)(CO)_{10}]^+$ but cannot present any evidence for this. $[Os_3H(CF_3CO_2)(CO)_{10}]$ is not protonated by CF_3CO_2H under the conditions of the experiment.



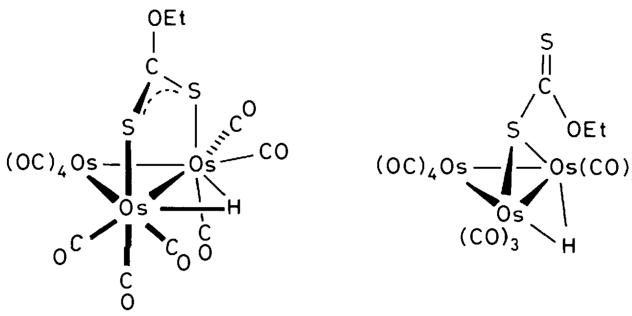
Scheme.

Protonation of Compound (**1**) *with* $HBF_4{\cdot}Et_2O$ *followed by Anion Addition.*—Treatment of compound (**1**) with $HBF_4{\cdot}Et_2O$ in $CDCl_3$ in the absence of any added anion leads to $[Os_3H(OH)(CO)_{10}]$ after chromatographic separation. Presumably protonation gives an intermediate which reacts with water on subsequent work-up. The low-temperature ^1H n.m.r. spectra of this reaction mixture are extremely complex, containing a number of unidentified hydrido-species, their concentrations dependent on temperature and acid concentration. We have found that when compound (**1**) in dichloro-

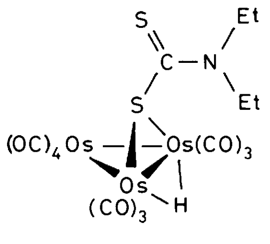
Table. Spectroscopic data for new compounds

Complex	ν(CO)/cm$^{-1\,a}$	^{1}H n.m.r.^{b}
(**2a**) $[Os_3H(OCHClCH_3)(CO)_{10}]^c$	2 109w, 2 072vs, 2 058s, 2 022vs 2 014s, 2 005s, 1 988w, 1 986w	5.19 (q, CH) 1.66 (d, CH_3, *J* 5.2) −12.81 (s, OsH)
(**2b**) $[Os_3H\{OCH(OCOCF_3)CH_3\}(CO)_{10}]^c$		5.31 (q, CH) 1.40 (d, CH_3, *J* 3.9) −12.54 (s, OsH)
(**3**) or (**4**) $[Os_3H(S_2COEt)(CO)_{10}]$	2 109m, 2 069vs, 2 060s, 2 024vs, 2 018s, 2 004s, 1 990m (sh), 1 987m	4.57 (q, CH_2) 1.43 (t, CH_3, *J* 7.2) −17.36 (s, OsH)
(**3**) or (**4**) $[Os_3H(S_2COEt)(CO)_{10}]$	2 110m, 2 071vs, 2 061s, 2 023vs, 2 015s, 2 006s, 2 000m (sh), 1 987m	4.27 (q, CH_2) 1.32 (t, CH_3, *J* 7.1) −17.54 (s, OsH)
(**5**) $[Os_3H(S_2CNEt_2)(CO)_{10}]$	2 105w, 2 065vs, 2 055m, 2 021vs, 2 010s, 2 003m, 1 985m	4.15 (q, CH_2) 4.00 (q, CH_2) 1.44 (t, CH_3, *J* 7.0) 1.26 (t, CH_3) −17.19 (s, OsH)
(**6**) $[Os_3H(S_2CNEt_2)(CO)_9]$	2 086w, 2 052s, 2 029s, 2 001s, 1 987m, 1 963w	3.96 (q, CH_2) 3.67 (q, CH_2) 1.38 (t, CH_3, *J* 7.1) 1.27 (t, CH_3) −14.71 (s, OsH)

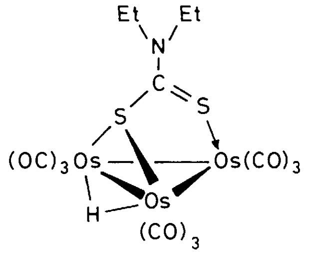
^{a} Recorded in cyclohexane solution. ^{b} Recorded in $CDCl_3$; *J* values in Hz; reference $SiMe_4$. ^{c} N.m.r. spectra at −45 °C.



(3) and (4)



(5)



(6)

methane is treated with $HBF_4{\cdot}Et_2O$ at −78 °C followed by treatment with the salt $[NEt_4]X$ (X = Cl, Br, or I) the known complexes $[Os_3H(X)(CO)_{10}]$ (X = Cl, Br, or I)[2] can be isolated in good yield following chromatographic work-up (see Experimental section for a typical preparation). Treatment with $[NBu^n{}_4]OH$ in methanol gives the methoxy-complex $[Os_3H(OMe)(CO)_{10}]$.[3] Similar reaction with tetrabutylammonium acetylacetonate gives the hydroxy-compound $[Os_3H(OH)(CO)_{10}]$.[3]

We have extended this synthetic route to form new sulphur ligand compounds. Thus, addition of potassium *O*-ethyl dithiocarbonate to the solution of protonated compound (**1**) at −78 °C leads to two separable, isomeric compounds of stoicheiometry $[Os_3H(S_2COEt)(CO)_{10}]$, (**3**) and (**4**), for which we propose the structures shown. Their i.r. and n.m.r. data (Table) clearly indicate that they have the form $[Os_3H(S_2COEt)(CO)_{10}]$ and both modes of ligand bonding have been found for other related systems of type $[Os_3H(X)(CO)_{10}]$. For instance, where X = $SCH{=}NC_6H_4F$-4,[6] $SCH{=}NC_6H_4Me$-4,[7] or cyclic thioamido-ligands such as SCH_2CH_2NCS[8] the ligand is bonded through a single sulphur atom but where X = HCS_2 (dithioformate)[9] the ligand bridges through both sulphur atoms. It is not always obvious which way the ligand will bridge because in $[Os_3H(SCHNPh)(CO)_{10}]$ there is a single sulphur atom bridging,[7] while in the $OCHNC_6H_4Me$-4 analogue the bridge is through the oxygen and nitrogen atoms,[10] and in $[Os_3H(SCHNPh)(CO)_9(PMe_2Ph)]$ the bridging is through the sulphur and nitrogen atoms.[7] In our case the isomers (**3**) and (**4**) are obtained but in the absence of *X*-ray structures we have been unable to tell which isomer has which structure.

A similar treatment of protonated compound (**1**) at −78 °C with tetraethylammonium *NN*-diethyldithiocarbamate gives $[Os_3H(S_2CNEt_2)(CO)_{10}]$, compound (**5**), as a single isomer. In this case we can be sure of the structure shown, with a single sulphur atom in the bridge, because of the non-equivalence of the Et groups. Compound (**5**) readily undergoes thermal decarbonylation in refluxing heptane to give $[Os_3H(S_2CNEt_2)(CO)_9]$, compound (**6**), also containing non-equivalent sulphur atoms and ethyl groups. This contrasts with the behaviour of compounds (**3**) and (**4**) neither of which decarbonylates under these conditions. However, we have shown that the major isomer does react with $Me_3NO{\cdot}2H_2O$ to give a product with an i.r. spectrum characteristic of a nonacarbonyl species (see Experimental section). However, this nonacarbonyl compound is unstable in solution and we have been unable to characterise it properly. Carbon–sulphur bond cleavage occurs with thioamido-triosmium clusters[6] and that may be the cause of decomposition in this case.

Experimental

$[Os_3H_2(CO)_{10}]$ was prepared according to the published procedure.[11] Vinylene carbonate, $[NEt_4]X$ (X = Cl, Br, or I), and $[NBu^t_4]OH$ (1 mol dm^{-3} solution in MeOH) were purchased from Aldrich. Potassium *O*-ethyl dithiocarbonate was prepared by the reaction of ethanol with potassium hydroxide and carbon disulphide (Found: C, 22.2; H, 3.1; S, 39.9. Calc. for $C_3H_5KOS_2$: C, 22.5; H, 3.1; S, 40.0%). Tetraethylammonium *NN*-diethyldithiocarbamate was prepared by reacting $[NEt_4]Cl$ with sodium *NN*-diethyldithiocarbamate. Tetrabutylammonium acetylacetonate was prepared from the reaction of $[NBu^n_4]OH$ (1 mol dm^{-3} in MeOH) and acetylacetone (Found: C, 73.0; H, 12.35; N, 4.05. Calc. for $C_{20}H_{41}NO_3$: C, 73.9; H, 12.6; N, 4.1%).

^1H N.m.r. spectra were recorded at 200 MHz on a Varian XL200 spectrometer.

Preparation of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**).—Vinylene carbonate (0.182 g, 8.75 mol per mol Os_3) was added to a solution of $[Os_3H_2(CO)_{10}]$ (0.206 g) in CH_2Cl_2 (90 cm^3). After 28 h the solvent was removed from the solution which had turned from purple to orange. The product was purified by t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–diethyl ether (10:3, v/v)] to give yellow crystals. Yield: 0.162 g (75%) (Found: C, 16.6; H, 0.55. $C_{12}H_4O_{11}Os_3$ requires C, 16.1; H, 0.45%). This compound has been reported earlier as a minor product from the reaction of $[Os_3H_2(CO)_{10}]$ with ketene.[1]

Protonation of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**) *with* HCl.—HCl gas was passed through concentrated H_2SO_4 and then into a solution of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (0.031 g) in $CDCl_3$ (0.5 cm^3) in an n.m.r. tube at −45 °C for 30 s. After recording the ^1H n.m.r. spectra at −45, −30, 0, and 24 °C the solution was allowed to stand at room temperature for several hours before work-up by t.l.c. (SiO_2; eluant, pentane) to give a quantitative yield of $[Os_3H(Cl)(CO)_{10}]$.

Reaction of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**) *with* HCl *in Cyclohexane*.—HCl Gas was bubbled into a solution of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**) (0.065 g) in cyclohexane (40 cm^3) for 40 s. After standing for 10 min removal of solvent gave compound (**2a**) as a yellow solid (0.060 g, 88%). This compound is fairly unstable in solution and could not be obtained analytically pure but was characterised by the data in the Table.

Protonation of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**) *with* CF_3CO_2H.—This was carried out in an n.m.r. tube in a similar way to the HCl experiment by adding trifluoroacetic acid (5 mol per mol Os_3) from a microsyringe to the $CDCl_3$ solution at −45 °C. Subsequent t.l.c. (SiO_2; eluant, pentane) gave the known compound $[Os_3H(CF_3CO_2)(CO)_{10}]$[2] in almost quantitative yield.

Protonation of $[Os_3H(OH)(CO)_{10}]$ *with* CF_3CO_2H.—This was carried out under identical conditions at −45 °C to give two unknown hydrido-species (δ −12.47 and −10.77). On warming to room temperature the cluster $[Os_3H(CF_3CO_2)(CO)_{10}]$ was obtained as the final product.

Attempted Protonation of $[Os_3H(CF_3CO_2)(CO)_{10}]$ *with* CF_3CO_2H.—A similar treatment of $[Os_3H(CF_3CO_2)(CO)_{10}]$ with CF_3CO_2H (5 mol per mol Os_3) at −45 °C in $CDCl_3$ led to no change in the ^1H n.m.r. spectrum.

Reaction of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**) *with* $HBF_4{\cdot}Et_2O$ *and* $[NEt_4]Cl$.—$HBF_4{\cdot}Et_2O$ (0.055 cm^3) was added under argon to a solution of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (0.051 g) in dry CH_2Cl_2 (10 cm^3) at −78 °C. After 30 min solid $[NEt_4]Cl$ (0.052 g) was added and after a further 30 min at this temperature the solution was allowed to warm to room temperature. Removal of solvent after 1 h followed by t.l.c. (SiO_2; eluant, pentane) gave $[Os_3H(Cl)(CO)_{10}]$[2] (0.033 g, 65%).

Similar reactions with $[NEt_4]Br$ and $[NEt_4]I$ gave the products $[Os_3H(X)(CO)_{10}]$ (X = Br or I)[2] in 55 and 81% yields respectively.

Similar reaction with $[NBu^n_4]OH$ (1 mol dm^{-3} solution in MeOH) gave $[Os_3H(OMe)(CO)_{10}]$ (57%) whilst the reaction with tetrabutylammonium acetylacetonate gave $[Os_3H(OH)(CO)_{10}]$ (36%). All yields are after chromatographic separation on silica.

Reaction of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**) *with* $HBF_4{\cdot}Et_2O$ *and Potassium* O-*Ethyl Dithiocarbonate*.—Using a similar procedure but adding potassium *O*-ethyl dithiocarbonate (0.042 g) to a mixture of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (0.114 g) and $HBF_4{\cdot}Et_2O$ (0.080 cm^3), removal of solvent and t.l.c. of the residue (SiO_2; eluant, pentane) gave a yellow solid, compound (**3**), which crystallised on treatment with hexane. Yield: 0.045 g, 36% (Found: C, 16.3; H, 0.6; S, 6.05. Calc. for $C_{13}H_6O_{11}Os_3S_2$: C, 16.05; H, 0.6; S, 6.05%). Eluting further with pentane–diethyl ether (10:1, v/v) gave an isomeric compound (**4**) (0.010 g, 8%) as a yellow solid which was characterised by data given in the Table.

Reaction of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (**1**) *with* $HBF_4{\cdot}Et_2O$ *and Tetraethylammonium* NN-*Diethyldithiocarbamate*.—Similarly use of $[Os_3H(\mu\text{-}OCH{=}CH_2)(CO)_{10}]$ (0.143 g), $HBF_4{\cdot}Et_2O$ (0.115 cm^3), and tetraethylammonium *NN*-diethyldithiocarbamate (0.200 g) gave a yellow solid which was separated by t.l.c. (SiO_2; eluant, pentane) to give two bands. The first gave $[Os_3H(Cl)(CO)_{10}]$ (0.055 g, 39%) (probably formed from $[NEt_4]Cl$ impurity present). The second band gave yellow crystals of compound $[Os_3H(S_2CNEt_2)(CO)_{10}]$ (**5**) on treatment with cyclohexane (0.035 g, 22%) (Found: C, 18.8; H, 1.2; N, 1.4; S, 6.4. Calc. for $C_{15}H_{11}NO_{10}Os_3S_2$: C, 18.0; H, 1.1; N, 1.4; S, 6.4%).

Thermolysis of $[Os_3H(S_2CNEt_2)(CO)_{10}]$ (**5**).—A solution of $[Os_3H(S_2CNEt_2)(CO)_{10}]$ (**5**) (0.019 g) in heptane (22 cm^3) was refluxed under argon for 1 h. Removal of solvent followed by t.l.c. [SiO_2; eluant, pentane–diethyl ether (9:1, v/v)] gave $[Os_3H(S_2CNEt_2)(CO)_9]$ (**6**) as red crystals. Yield: 0.010 g (56%) (Found: C, 17.05; H, 1.05; N, 1.45; S, 5.6. Calc. for $C_{14}H_{11}NO_9Os_3S_2$: C, 17.3; H, 1.15; N, 1.45; S, 6.6%).

Attempted Thermal Decarbonylation of $[Os_3H(S_2COEt)(CO)_{10}]$, *Compounds* (**3**) *and* (**4**).—Solutions of both isomers in heptane showed no change in their i.r. spectra after refluxing for 4 h under argon.

Reaction of $[Os_3H(S_2COEt)(CO)_{10}]$ (*major isomer*) *with* Me_3NO.—$Me_3NO{\cdot}2H_2O$ (0.016 g, 2 mol per mol Os_3) was added to a solution of $[Os_3H(S_2COEt)(CO)_{10}]$ (0.069 g) in CH_2Cl_2 (20 cm^3). The solution immediately changed from yellow to red. Removal of the solvent followed by t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–CH_2Cl_2 (10:3, v/v)] gave $[Os_3H(S_2COEt)(CO)_9]$ (0.010 g, 15%). This material could not be obtained pure and decomposed on attempted recrystallisation, ν(CO) (C_6H_{12}) at 2 087w, 2 053s, 2 027s, 2 004s, 1 976m, and 1 944m cm^{-1}.

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