Formation of Triosmium μ-Carbyne Complexes by Ring-opening and Carbon–Hydrogen Activation of 3,3-Dimethylcyclopropene; Rearrangement of an Alkyl μ-Carbyne to a μ-Vinyl Complex *via* a 1,2-Hydrogen Shift

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Reaction of 3,3-dimethylcyclopropene with $[H_2Os_3(CO)_{10}]$ affords $[Os_3(\mu\text{-}H)(\mu\text{-}CCH_2CHMe_2)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)(\mu\text{-}CCH{=}CMe_2)(CO)_{10}]$; the former on thermolysis rearranges successively to $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CHCHMe_2)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C{=}CHCHMe_2)(CO)_9]$.

There is at present considerable interest in the chemistry of metal complexes which contain μ_2- and μ_4-bridged carbyne (alkylidyne) ligands. Such species have been synthesised by hydride anion abstraction[1] or protonation[2] of bridged methylene complexes, protonation of μ-vinylidene complexes,[3] *O*-alkylation of μ-carbonyl ligands,[4,5] reaction of mononuclear carbyne complexes with further metal fragments,[6] α-hydrogen abstraction reactions,[7] and protonation of carbidic carbon atoms.[8] Each synthetic approach is limited to certain carbyne carbon substituents. In exploring the reactions of cyclopropenes with di-[9,10] and tri-metal centres we have discovered a new route to alkyl substituted bridged carbyne complexes, one of which on thermolysis undergoes an unusual molecular rearrangement to a μ-vinyl complex.

Reaction (room temp., 16 h) of 3,3-dimethylcyclopropene with $[H_2Os_3(CO)_{10}]$ in hexane affords the yellow crystalline complexes (**1**) (80% yield) and (**2**) (10%) characterised by i.r. and n.m.r. spectroscopy.† The molecular structure of the major product (**1**) was established by single crystal *X*-ray diffraction,‡ and is illustrated in Figure 1.

Complex (**1**) is, surprisingly, a triosmium bridged carbyne complex where three osmium atoms define an approximate equilateral triangle [Os(1)–Os(2) 2.870(2), Os(1)–Os(3) 2.827(2), Os(2)–Os(3) 2.861(2) Å]. The μ-carbyne group (CCH_2CHMe_2) bridges the Os(1)–Os(2) edge almost symmetrically with Os(1)–C(11) 2.020(24) and Os(2)–C(11) 1.966(22) Å. The carbyne carbon also interacts with the $Os(CO)_4$ unit, although to a lesser extent than observed in the related molecule $[Os_3(\mu\text{-}H)(\mu\text{-}CH)(CO)_{10}]$. Thus, in (**1**) the Os(3)–C(11) distance is 2.640(26) Å, and the acute dihedral angle between the Os_3 and Os(1)–C(11)–Os(2) planes is 82.1°.

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† Spectroscopic data for (**1**): ν_{CO} 2 105w, 2 059vs, 2 023m, 2 013s, 2 001m, and 1 989s cm^{-1} (hexane); n.m.r. ^1H ($CDCl_3$), δ 4.51 [d, 2 H, CCH_2, $^3J(HH)$ 5.6 Hz], 1.79 [m, 1 H, CCH_2CHMe_2, $^3J(HH)$ 6.6, $^3J(HH)$ 5.6 Hz], 1.10 [d, 6 H, $CHMe_2$, $^3J(HH)$ 6.6 Hz], −16.73 [s, 1 H, Os(μ-H)Os]; ^{13}C (CD_2Cl_2), δ 319.44 [dt, μ-C, $^2J(CH)$ 5.4, $^2J(CH)$ 4.9 Hz], 174.64, 174.29, 174.05, 169.70 (CO), 73.1 [t, CH_2, $^1J(CH)$ 128 Hz], 36.76 [d, CH, $^1J(CH)$ 128 Hz], and 23.40 p.p.m. (2 × Me). Spectroscopic data for (**2**): ν_{CO} 2 105w, 2 058vs, 2 021(sh), 2 015s, and 1 989s cm^{-1} (hexane); n.m.r. ^1H ($CDCl_3$), δ 8.42 (br.s, 1 H, CH=), 2.13 (s, 3 H, Me), 2.05 (s, 3 H, Me), −16.26 [s, 1 H, Os(μ-H)Os]; ^{13}C (CD_2Cl_2), δ 332.3 (μ-C), 184.9, 176.6, 175.7, 174.7, 174.1, 169.8 (CO), 152.5 [d, $CH{=}CMe_2$, $^1J(CH)$ 150 Hz], 148.9 (CMe_2), 28.85 (Me), and 20.60 p.p.m. (Me).

‡ *Crystal data* for (**1**): $C_{15}H_{10}O_{10}Os_3$, $M = 920.6$, triclinic, space group $P\bar{1}$, $a = 9.226(3)$, $b = 9.333(5)$, $c = 13.136(7)$ Å, $\alpha = 89.70(4)$, $\beta = 74.18(4)$, $\gamma = 78.00(3)°$, $U = 1\,062.9(9)$ Å^3, $Z = 2$, $D_c = 2.88\ g\ cm^{-3}$, $F(000) = 815.67$, $\mu(Mo\text{-}K_\alpha) = 179.6\ cm^{-1}$, $\lambda = 0.710\,69$ Å. Current R 0.070 for 2 931 unique observed $[I > 1.5\sigma(I)]$ reflections measured at 293 K on a Nicolet P3m diffractometer in the range $4 < 2\theta < 50°$. The structure was solved by heavy atom (Patterson and difference Fourier) methods and refined using a full matrix blocked cascade least squares procedure. Lorentz, polarisation, and empirical absorption corrections were applied. The hydrogen atoms of the s-butyl group were placed in idealised geometries using a riding model. The bridging hydride position was calculated using the program HYDEX, all other atoms were refined without constraints and with anisotropic thermal parameters. The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

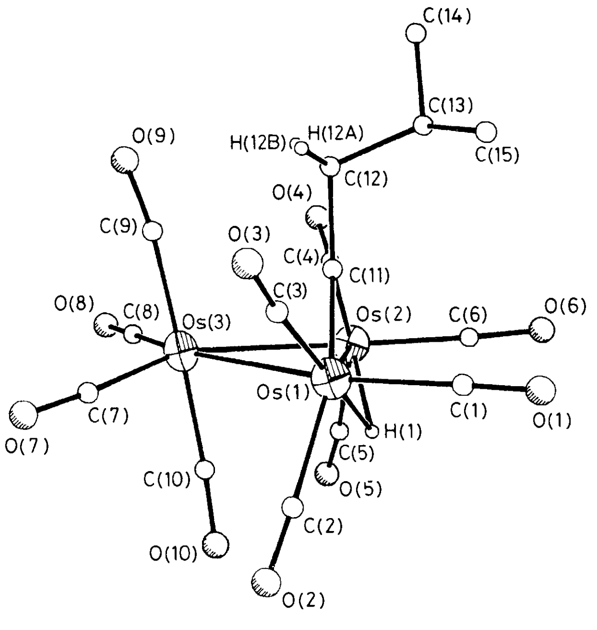
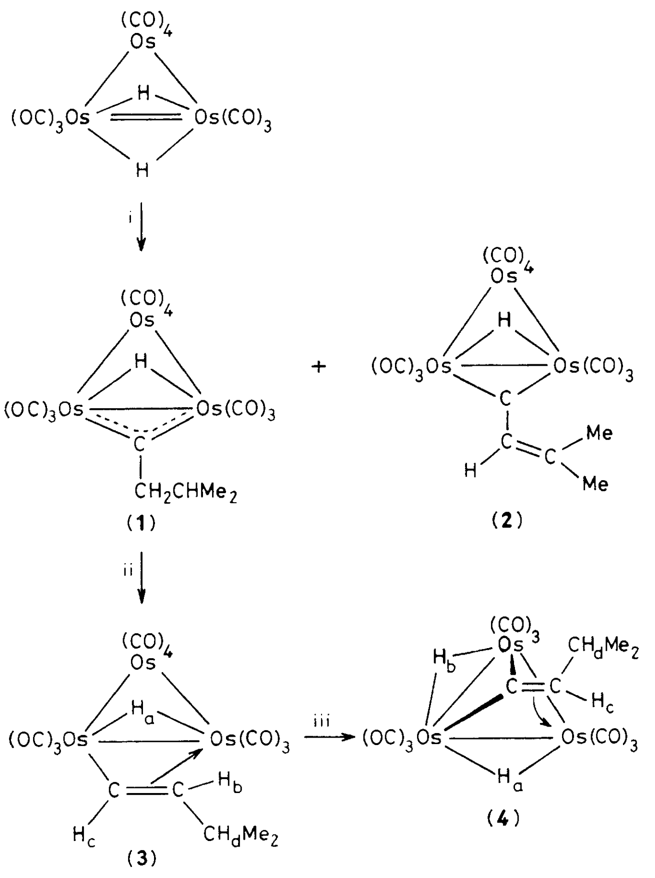
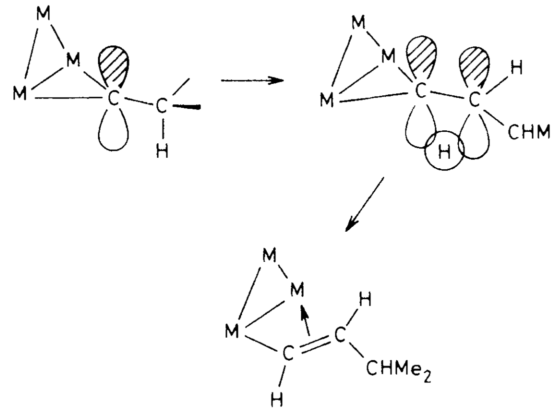


Figure 1. Molecular structure of $[Os_3(\mu\text{-H})(\mu\text{-CCH}_2\text{CHMe}_2)(CO)_{10}]$ (**1**). Important geometric parameters are: C(11)-C(12) 1.528(28), Os(1)-H(1) 1.854, Os(2)-H(1) 1.855 Å; Os(1)-C(11)-Os(2) 92.2(8), Os(1)-Os(3)-C(10) 82.6(8), Os(2)-Os(3)-C(10) 77.3(11), Os(3)-Os(1)-C(11) 63.5(7), Os(3)-Os(2)-C(11) 63.1(8)°. Hydrogen atoms of the $CHMe_2$ group are omitted for clarity.



Scheme 1. i, +3,3-Dimethylcyclopropene; ii, reflux, hexane–octane; iii, –CO, reflux, hexane–octane.



Scheme 2

This compares with the same parameters in $[Os_3(\mu\text{-H})(\mu\text{-CH})(CO)_{10}]$ (2.35 Å, 69.7°),[5] $[Fe(\mu\text{-H})(\mu\text{-COMe})(CO)_{10}]$ (2.70 Å, 91°),[4] $[Ru_3(\mu\text{-H})(\mu\text{-COMe})(CO)_{10}]$ (2.90 Å, 94.7°),[11] and $[Ru_3(\mu\text{-H})(\mu\text{-CNMe}_2)(CO)_{10}]$ (—, 100°).[12] This difference in geometry is also reflected in the ^{13}C n.m.r. spectra. The chemical shift of the carbyne carbon present in (**1**) is temperature dependent [δ 312.0 (−80 °C), 320.5 p.p.m. (40 °C)] unlike the μ-CH system, which occurs[5] at higher field (δ 219.0 p.p.m.). This implies a possible equilibrium in solutions of (**1**), and a weaker donor interaction between the $Os(CO)_4$ group and the $\mu\text{-CCH}_2\text{CHMe}_2$ carbyne carbon compared with μ-CH.

The minor product (**2**) was identified by i.r. and n.m.r. spectroscopy† as a vinyl substituted μ-carbyne, and in contrast with (**1**) the ^{13}C carbyne chemical shift (δ 332.3 p.p.m.) is not temperature dependent.

The formation of (**1**) and (**2**) under mild conditions is unusual in that both carbon–carbon and olefinic carbon–hydrogen bond cleavage occurs. The reaction is regioselective in that treatment of $[D_2Os_3(CO)_{10}]$ with 3,3-dimethylcyclopropene leads to the formation of (**1**) with selective deuterium incorporation only into the Os(μ-D)Os and Os(μ-CCHDCHMe$_2$)Os sites. There is no deuterium incorporation into the minor product (**2**), suggesting that this is formed by capture of $[Os_3(CO)_{10}]$ generated by competing hydrogenation of the cyclopropene. This is supported by the observation that (**2**) is also formed on displacement of CH_4 from $[Os_3(\mu\text{-H})_2(\mu\text{-CH}_2)(CO)_{10}]$[13] by 3,3-dimethylcyclopropene. The reaction pathways by which the μ-carbyne ligands are generated from the cyclopropene are clearly complex, and will be discussed in a full paper.

The alkyl substituted μ-carbyne complex (**1**) undergoes an unusual thermal rearrangement. In refluxing hexane–octane (1:1) the μ-vinyl complex (**3**)§ is formed, and then rearranges[14] to a μ-vinylidene complex (**4**)§ (see Scheme 1). The first reaction is particularly interesting, and involves a

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§ Spectroscopic data for (**3**): n.m.r. ^1H ($CDCl_3$), δ 7.25 [dddd, 1 H, H_c, $^3J(H_cH_b)$ 14.04, $^3J(H_cH_a)$ 1.7, $^4J(H_cH_d)$ 0.61 Hz], 4.39 [dd, 1 H, H_b, $^3J(H_bH_c)$ 14.04, $J(H_bH_a)$ 7.08 Hz], 1.8 [m, 1 H, H_d], 1.30 [d, 6 H, 2 × Me, $^3J(HH_d)$ 6.6 Hz], −18.95 [d, 1 H, H_a, $^3J(H_aH_c)$ 1.7 Hz]; ^{13}C (CD_2Cl_2), δ 112.48 [*C*H, ^1J(CH) 153 Hz], 95.8 [*C*H, ^1J(CH) 149 Hz], and 39.80 p.p.m. [*C*HMe$_2$, ^1J(CH) 127 Hz]. Spectroscopic data for (**4**): n.m.r. ^1H ($CDCl_3$), δ 6.74 [d, 1 H, H_c, $^3J(H_cH_d)$ 9.03 Hz], 1.8 [m, 1 H, H_d], 1.18 [d, 6 H, 2 × Me, $^3J(HH_d)$ 6.84 Hz], −18.27 [d, 1 H, H_b, $^2J(H_bH_a)$ 1.28 Hz], −21.35 [d, 1 H, H_a, $^2J(H_aH_b)$ 1.28 Hz]; ^{13}C (CD_2Cl_2), δ 201.7 (*C*=CHPr^i), 103.34 [d, *C*H$_c$CHMe$_2$, ^1J(CH) 155 Hz], 43.81 [d, *C*HMe$_2$, ^1J(CH) 128 Hz], 23.64 (Me), and 23.15 p.p.m. (Me).

μ-carbyne to μ-vinyl rearrangement[15] a type of reaction which has not been previously observed. It is suggested that this rearrangement is not directly metal assisted, but involves a 1,2-hydrogen shift to an electron deficient carbon atom, *i.e.* the carbyne carbon (see Scheme 2). In organic chemistry this type of reaction is a well known 'allowed' process,[16] and it is interesting that these ideas apparently carry over to reactions at multimetal centres. This rearrangement may be viewed as a homogeneous model for hydrocarbon rearrangement on a metal surface.[17]

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