Activation of a μ_3-Ethylidyne Ligand through Oxidation–Deprotonation: *X*-Ray Structure of $[Ru_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3][BF_4]$

Neil G. Connelly, Nigel J. Forrow, Selby A. R. Knox, Kirsty A. Macpherson, and A. Guy Orpen
Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

Oxidation of the μ_3-ethylidyne complex $[Ru_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]$ yields $[Ru_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]^+$ (characterised by *X*-ray diffraction) and $[Ru_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]^{2+}$; the latter deprotonates to give the μ_3-vinylidene cation $[Ru_3(\mu_3\text{-}CCH_2)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]^+$ which reacts with methyl-lithium to form $[Ru_3(\mu_3\text{-}CEt)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]$, completing a μ_3-CMe to μ_3-CEt homologation.

In the preceding communication we described how μ-alkylidene ligands were rendered susceptible to deprotonation through oxidation of their electron-rich diruthenium complexes.[1] We now report that activation of a hydrocarbon species (μ_3-ethylidyne) bound at a triruthenium centre can be achieved similarly.

The cyclic voltammogram of $[Ru_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]$ (**1**)[2] differs from that of diruthenium μ-alkylidene complexes in having two diffusion-controlled *reversible* oxidation waves with E° = 0.17 and 0.86 V, and both mono- and di-cations are isolable. Thus, treatment of (**1**) with one equivalent of $AgBF_4$ or an excess of less powerful oxidants such as H^+, Ph_3C^+, or I_2, rapidly generates $[Ru_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]^+$ (**2**).† No e.s.r. signal has yet been observed for (**2**), but a magnetic moment of 2.0 μ_B was determined by Evans' method.[3] Reaction of (**1**) with two equivalents of $AgBF_4$ yields $[Ru_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]^{2+}$ (**3**)† equally rapidly. Regeneration of (**1**) is achieved by addition of $LiBHEt_3$ to either (**2**) or (**3**).

N.m.r. spectroscopic data† characterise (**1**) as having three-fold symmetry, and *X*-ray diffraction reveals that the

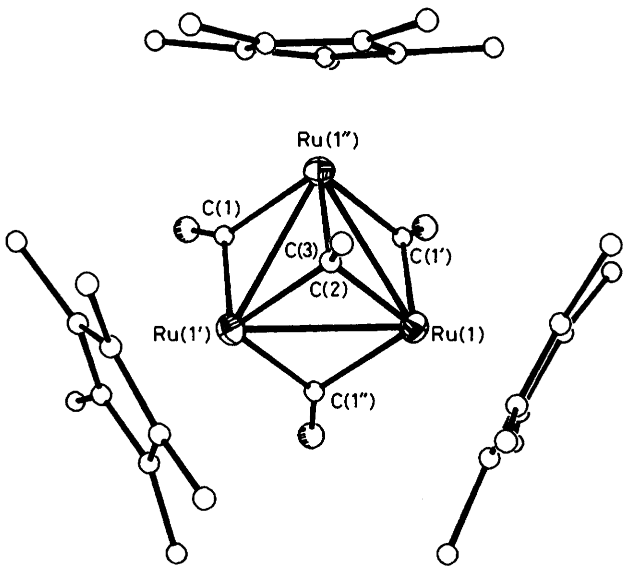

Figure 1. Molecular structure of the cation (**2**). Hydrogen atoms omitted for clarity. Selected distances: Ru(1)–C(1′) 2.027(9), Ru(1)–C(1″) 2.053(9), Ru(1)–C (of C_5Me_5), 2.250(8)—2.284(9), C(2)–C(3) 1.49(2) Å;

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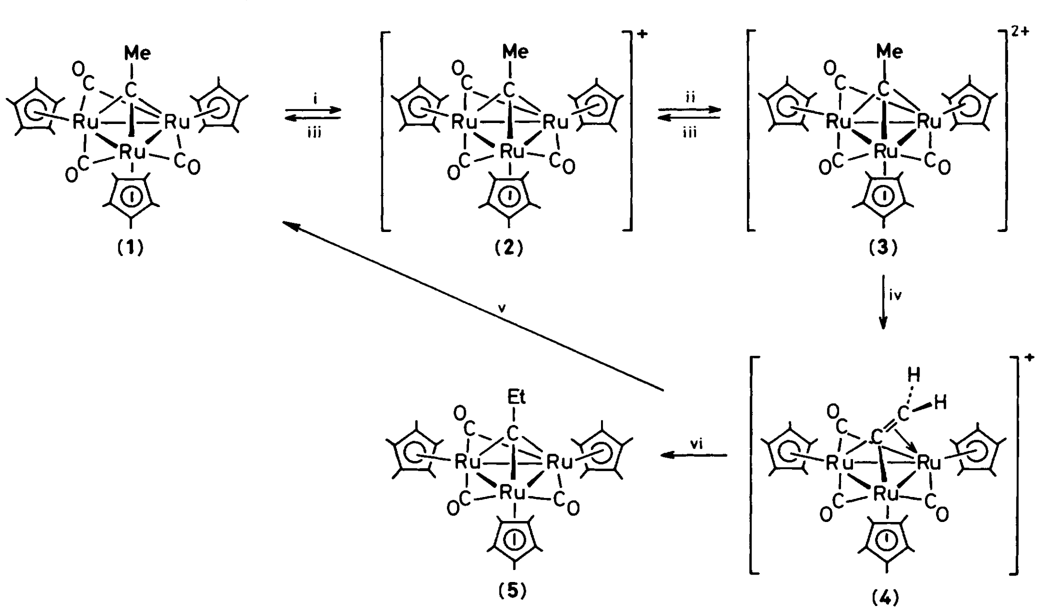
† The new species (**2**)—(**5**) were characterised by elemental analyses, and i.r. and n.m.r. spectroscopy. Selected spectroscopic data (i.r. in CH_2Cl_2, n.m.r. in $CDCl_3$, coupling constants in Hz): (**1**) (data given for comparison), red crystals, ν(CO) 1 775s and 1 723m cm^{-1}; ^{1}H n.m.r. δ 1.71 (45 H) and 4.57 (3 H). (**2**), green crystals, ν(CO) 1 834s and 1 788s cm^{-1}. (**3**), green powder, ν(CO) 1 883s and 1 846s cm^{-1}; ^{1}H n.m.r. δ 2.06 (s, 45 H) and 4.37 (3 H). (**4**), orange crystals, ν(CO) 1 860s, 1 818sh, and 1 802m cm^{-1}; ^{1}H n.m.r. δ 1.77 (s, 45 H) and 6.20 (s, 2 H) (fluxional complex). (**5**), red crystals, ν(CO) 1 777s and 1 726s cm^{-1}; ^{1}H n.m.r. δ 1.34 (t, *J* 7, 3 H), 1.70 (s, 45 H), and 4.53 (q, *J* 7, 2 H).



Cations as BF_4^- salts

Scheme 1. *Reagents:* i, H^+, Ph_3C^+, Ag^+, or I_2; ii, Ag^+; iii, $LiBHEt_3$; iv, solid state or in CD_3NO_2, $-H^+$; v, $NaBH_4$; vi, MeLi.

same holds for paramagnetic (**2**).‡ The structure of the radical cation is illustrated in Figure 1, showing a crystallographic three-fold rotation axis and approximate C_{3v} symmetry. One-electron oxidation of (**1**) does not therefore appear to cause major disruption of the metal–metal or metal–ligand bonding and the orbital depopulated is probably singly degenerate, there being no indication of Jahn–Teller distortion in (**2**).

Whereas solid (**2**) is stable apparently indefinitely in air, solid (**3**) slowly deprotonates over several days (and more rapidly in nitromethane solution) to give the μ_3-vinylidene complex $[Ru_3(\mu_3\text{-}CCH_2)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3][BF_4]$ (**4**)† in good yield. The cation is highly reactive towards nucleophiles, regenerating (**1**) smoothly with $NaBH_4$ and giving the μ_3-propylidyne analogue $[Ru_3(\mu_3\text{-}CEt)(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_3]$ (**5**) with methyl-lithium. The sequence (**1**) → (**2**) → (**3**) → (**4**) → (**5**) (Scheme 1) represents a new and efficient route for homologation of a μ_3-alkylidyne species, and should be applicable to higher homologues, and to other trinuclear metal systems.

Maitlis has pointed out that in the Fischer–Tropsch synthesis the surface on which a metal is supported may play the role of an electron acceptor in the carbon chain growth stage.[4] It can be seen from this and the preceding communication[1] that oxidation does promote pathways which lead to homologation of simple hydrocarbon species co-ordinated at polynuclear metal centres.

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‡ *Crystal data for* (**2**): $C_{35}H_{48}O_3Ru_3BF_4$, $M = 906$, cubic, space group $P\bar{4}3n$ (No. 218), $a = 19.102(5)$ Å, $U = 6970(3)$ Å^3, $Z = 8$, $D_c = 1.73\,g\,cm^{-3}$, $F(000) = 3648$ electrons, graphite-monochromated Mo-K_α X-radiation, $\lambda = 0.71069$ Å. $\mu(\text{Mo-}K_\alpha) = 13.1\,cm^{-1}$; $R = 0.045$ for 1296 independent reflections collected at 200 K in the range $4 \leqslant 2\theta \leqslant 55°$ with $I \geqslant 2\sigma(I)$ on a Nicolet P3m diffractometer. The anions lie at sites of 23 (ordered) and 222 (disordered) symmetry. The atomic co-ordinates for this work 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.

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