The Stable Radical Cation $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]^+$: An Intermediate in the Redox Activation of an Alkyl C–H Bond and a Probe of Metal–Alkene Bonding

Neil G. Connelly,* Bernhard Metz and A. Guy Orpen

School of Chemistry, University of Bristol, Bristol UK BS8 1TS

An X-ray structure determination has shown that oxidation of $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$ **1** to $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]^+$ **1**$^+$ results in geometric changes consistent with the presence of a three-electron metal–alkene interaction; cation **1**$^+$ undergoes both H-atom abstraction (with the CPh_3 radical) and oxidative deprotonation {on addition of $[Fe(\eta\text{-}C_5H_5)_2]^+$} to give $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^+$ **2**$^+$ showing that the mechanism of the redox-activation of one C–H bond of **1** (EC or EEC) is critically dependent on the nature of the chemical oxidant.

Complex $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$ **1** reacts with either 1 equivalent of the trityl cation, $[CPh_3]^+$, or 2 equivalents of $[Fe(\eta\text{-}C_5H_5)_2]^+$ to give $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^+$ **2**$^+$ (Scheme 1), cyclic voltammetry suggesting two possible mechanisms for C–H bond activation.[1] The first involves an EC (E = electrochemical, C = chemical) pathway where one-electron oxidation is followed by H-atom abstraction; such a mechanism was proposed for the reaction[2] of mononuclear $[WMe_2(\eta\text{-}C_5H_5)_2]$ with $[CPh_3]^+$. The second involves an EEC pathway where the removal of two electrons is followed by proton loss, as has been proposed for the oxidation of $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\mu\text{-dppm})(\eta\text{-}C_5H_5)_2]$ to $[Ru_2(\mu\text{-}CH)(\mu\text{-}CO)(\mu\text{-dppm})(\eta\text{-}C_5H_5)_2]^+$[3] and of $[Ru_3(\mu_3\text{-}CCH_3)(CO)_3(\eta\text{-}C_5Me_5)_3]$ to $[Ru_3(\mu_3\text{-}CCH_2)(CO)_3(\eta\text{-}C_5Me_5)_3]$.[4] We now show, by an investigation of the reactions of the isolable radical cation **1**$^+$ with CPh_3 and $[Fe(\eta\text{-}C_5H_5)_2]^+$, that the mechanism of the redox-activation of **1** is critically dependent on the oxidant. Furthermore, **1** and **1**$^+$ constitute the first structurally characterised redox pair to allow a direct study of the effects of electron-transfer on metal–alkene bonding.

The hexafluorophosphate salt of cation **1**$^+$ was isolated following treatment of **1** with 1 equivalent of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2.† An X-ray crystal structure analysis‡ of this salt shows that the molecular geometry of **1**$^+$ (Fig. 1) is broadly similar to that of **1**[5] and has approximate C_s symmetry. In both **1** and **1**$^+$ the C_8 chain is η^3-coordinated to Mo(1) through C(1–3) and C(6–8) and σ-bonded to Mo(2) through C(1) and C(8), thereby acting as a double μ-allylidene ligand. In addition, it binds atom Mo(2) as an η-alkene through C(4) and C(5). As in **1** the Mo–Mo distance in **1**$^+$ is consistent with a bond order of two [Mo(1)–Mo(2) 2.620(1) Å; *cf.* 2.595(1) Å in **1** and 2.655(1) Å in **2**$^+$]. Furthermore the Mo–C distances for atoms C(1), C(2), C(3), C(6), C(7) and C(8) of the C_8 chain are remarkably similar in **1** and **1**$^+$ [bond lengths in **1**$^+$ averaged over C_s symmetry are Mo(1)–C(1) 2.252(5), Mo(1)–C(2) 2.343(5), Mo(1)–C(3) 2.298(5), Mo(2)–C(1) 2.096(5) Å, *cf.* 2.237(2), 2.348(2), 2.317(2), 2.093(2) Å respectively in **1**]. In contrast the Mo(2)–C(4) and Mo(2)–C(5) distances are significantly increased in **1**$^+$ [mean 2.405(5) Å] as compared with **1** [2.234(2) Å]. In **1** this interaction is essentially an isolated metal–alkene bond of the classic Dewar–Chatt–Duncanson type. In **1**$^+$ the metal–alkene bond is clearly weakened and the C(4)–C(5) bond shortened [1.394(6) *cf.* 1.442(3) Å in **1**] as a result of oxidation. These changes are consistent with one-electron oxidation leading to depopulation of the orbital involved in the metal–alkene-π* interaction. Thus the metal–alkene bond in **1**$^+$ may be described as a three-electron interaction (see Fig. 2) observable in this case because of the constraints imposed by the conformation of the C_8 chain. This model is also consistent with the EPR spectrum.†§

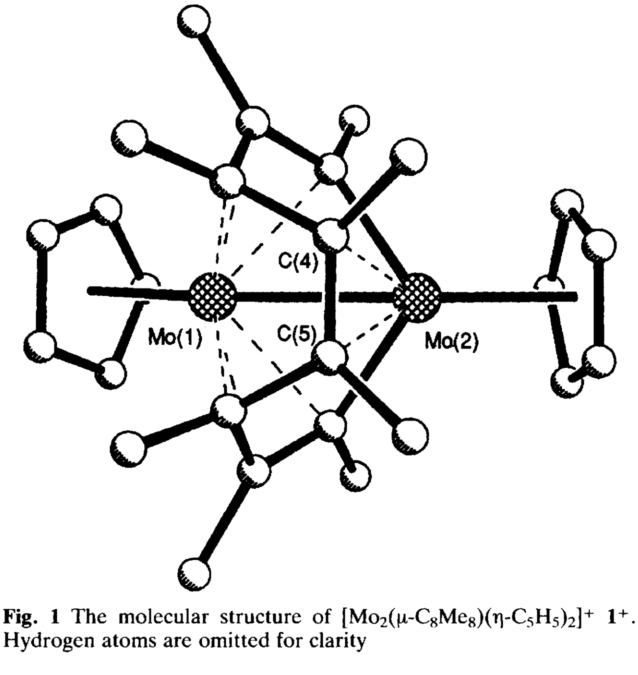
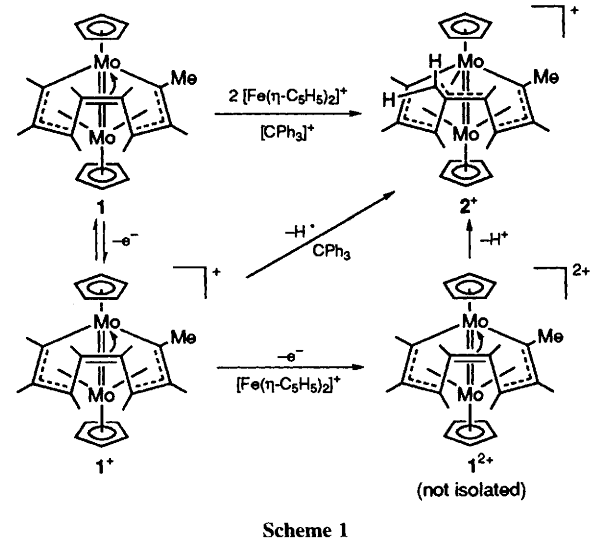


Fig. 1 The molecular structure of $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]^+$ **1**$^+$. Hydrogen atoms are omitted for clarity



Scheme 1

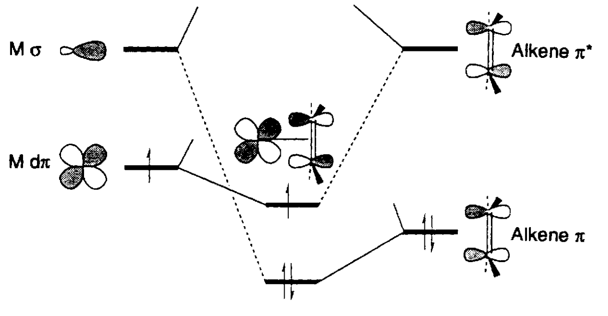


Fig. 2 Schematic orbital interaction diagram for the three-electron Dewar–Chatt–Duncanson metal–alkene bond in **1**$^+$

The isolation of a stable salt of **1**$^+$ allowed a detailed study of the mechanism of formation of **2**$^+$ from **1**. Thus cation **1**$^+$ reacts with 1 equivalent of either the CPh_3 radical[6] or $[Fe(\eta\text{-}C_5H_5)_2]^+$ to give, in both cases, near-quantitative yields of **2**$^+$. With CPh_3 the product is formed by hydrogen atom abstraction, this step being the second in the EC mechanism involved in the formation of **2**$^+$ from **1** and 1 equivalent of $[CPh_3]^+$. With $[Fe(\eta\text{-}C_5H_5)_2]^+$ removal of one electron (the second from **1**) is followed by proton loss, *i.e.* the final step of an EEC mechanism for the formation of **2**$^+$ from **1** and 2 equivalents of $[Fe(\eta\text{-}C_5H_5)_2]^+$. These results show that the mechanism for the oxidative activation of the C–H bonds of hydrocarbons coordinated to bi- and poly-nuclear centres can depend not only on the redox potential of the substrate but also on the oxidant chosen.

We thank the SERC for a post-doctoral research assistantship (B. M.) and for funds to purchase an EPR spectrometer.

Received, 24th June 1994; Com. 4/03843F

Footnotes

† Addition of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.12 g, 0.36 mmol) in CH_2Cl_2 (10 cm^3) to **1** (0.20 g, 0.37 mmol) in CH_2Cl_2 (30 cm^3) gave a brown solution from which **1**$^+$ was isolated as the analytically pure (C and H analysis) $[PF_6]^-$ salt after evaporation to dryness, washing the residue with hexane (50 cm^3) and recrystallisation from CH_2Cl_2–diethyl ether, yield 81%. The air-stable brown crystalline solid is paramagnetic, EPR (175 K, CH_2Cl_2) g_{iso} = 2.0132, hyperfine coupling to one metal atom, $A(^{95,97}Mo)$ = 28.5 G.

‡ *Crystal data* for $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2][PF_6]$ **1**$^+\cdot[PF_6]^-$: $C_{26}H_{34}F_6Mo_2P$, M = 638.4, orthorhombic, space group *Pbca* (no. 61), a = 16.847(5), b = 15.777(5), c = 19.679(6) Å, V = 5231(3) Å^3, Z = 8, D_c = 1.74 g cm^{-3}, λ = 0.71073 Å, μ = 1.08 mm^{-1}, $F(000)$ = 2744, T = 200 K. Data were collected on a Siemens R3m/V diffractometer at reduced temperature for $4 < 2\theta < 50°$. The structure was solved by heavy atom methods and refined by least-squares against F^2 to $R1$ 0.043 ($wR2$ = 0.106) for all 4595 unique intensity data corrected for absorption and extinction. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Details of the analysis of the anisotropic EPR spectrum of **1**$^+$ and of NMR spectroscopic studies of the electron exchange between **1** and **1**$^+$ will be presented at a later date. (N. G. Connelly, B. Metz and P. H. Rieger, work in progress).

References

1 S. G. Bott, L. Brammer, N. G. Connelly, M. Green, A. G. Orpen, J. F. Paxton, C. J. Schaverien, S. Bristow and N. C. Norman, *J. Chem. Soc., Dalton Trans.*, 1990, 1957.

2 J. C. Hayes and N. J. Cooper, *J. Am. Chem. Soc.*, 1982, **104**, 5570.

3 N. G. Connelly, N. J. Forrow, B. P. Gracey, S. A. R. Knox and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1985, 14.

4 N. G. Connelly, N. J. Forrow, S. A. R. Knox, K. A. Macpherson and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1985, 16.

5 M. Green, N. C. Norman, A. G. Orpen and C. J. Schaverien, *J. Chem. Soc., Dalton Trans.*, 1984, 2455.

6 H. Volz, W. Lotsch and H.-W. Schnell, *Tetrahedron*, 1970, **26**, 5343.