The Activation of a Carbon–Hydrogen Bond in a Dimolybdenumcyclononatetraene by Oxidation of a Metal Centre; *X*-Ray Crystal Structures of $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2][CF_3SO_3]$ and $[Mo_2(\mu\text{-}C_8Me_8)(\mu\text{-}Cl)(\eta\text{-}C_5H_5)_2][SbCl_4]\cdot CH_2Cl_2$

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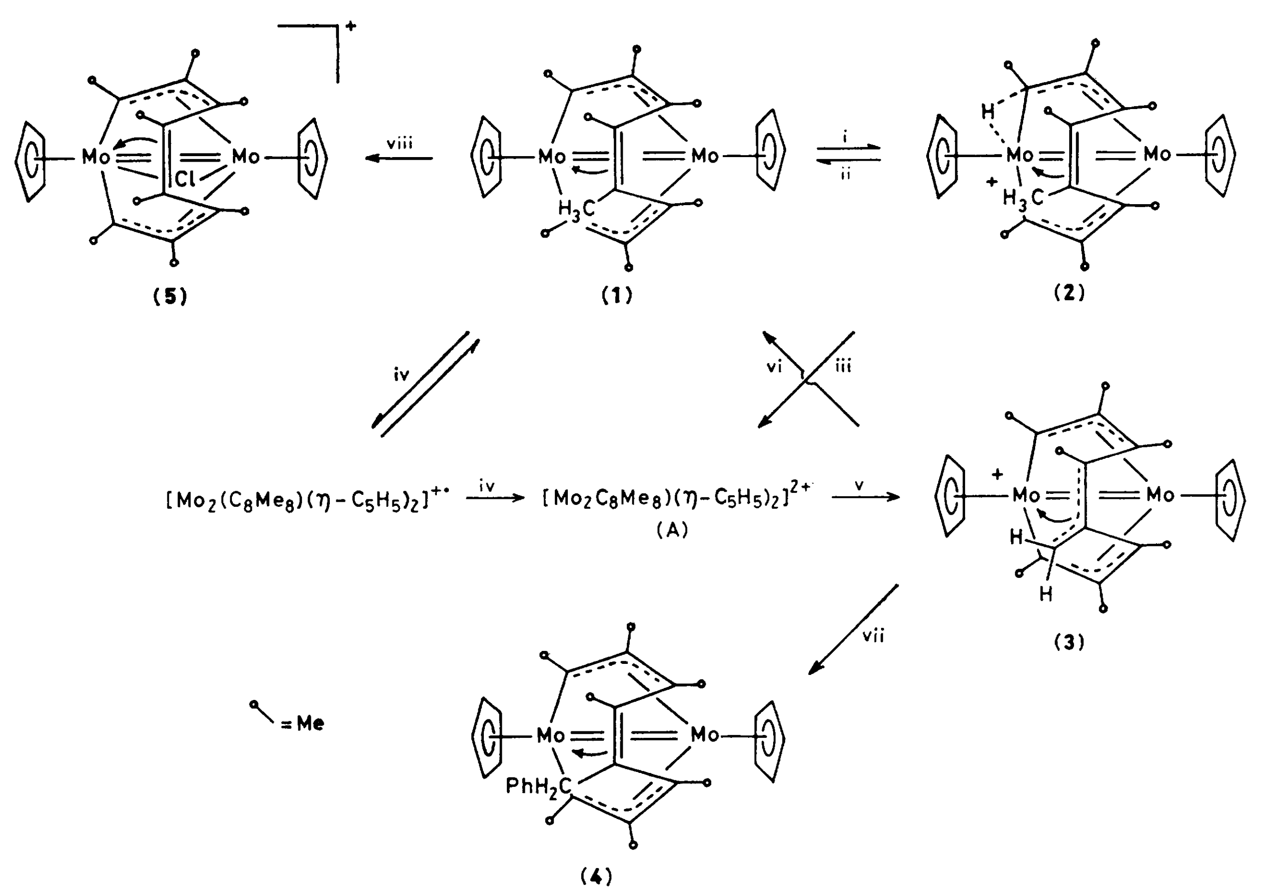
Protonation of $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$ in CH_2Cl_2 with an excess of CF_3SO_3H or reaction with $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ leads to the formation of the cation $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^+$, whereas, oxidation with $SbCl_6^-$ affords $[Mo_2(\mu\text{-}C_8Me_8)(\mu\text{-}Cl)(\eta\text{-}C_5H_5)_2][SbCl_4]$; both structures are established by *X*-ray crystallography.

We have previously reported[1,2] a simple synthesis of the complex $[Mo(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$ (**1**) by reduction of the cation $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$. This unusual dinuclear complex contains an electron rich metallacyclononatetraene ring system, which reacts with $HBF_4\cdot Et_2O$ or CF_3CO_2H in CH_2Cl_2 to form the cation $[Mo_2(\mu\text{-}C_8Me_8)(\mu_{Mo,C}\text{-}H)(\eta\text{-}C_5H_5)_2]^+$ (**2**) containing a μ-C–H–Mo system.[1] The observation of low concentrations of a second dimolybdenum species in these reactions led us to examine the reaction of (**1**) with a stronger acid.

Treatment (room temperature, 12 h) of (**1**) with an excess of CF_3SO_3H in CH_2Cl_2 afforded a purple solution, which upon addition of diethyl ether gave purple crystals of (**3**) as its $[CF_3SO_3]^-$ (triflate) salt. The same purple complex was ob-



Scheme 1. *Reagents:* i, $HBF_4 \cdot Et_2O$ or CF_3CO_2H in CH_2Cl_2; ii, $NaBH_4$; iii, CF_3SO_3H–CH_2Cl_2, $-H_2$; iv, $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ in CH_2Cl_2; v, Et_2O; vi, $K[BHBu^s_3]$; vii, $Li_2[Cu_2Ph_4]$; viii, $SbCl_6^-$.

tained on addition of CF_3SO_3H to the cation (**2**). N.m.r. spectroscopy† and chemical evidence indicated a structure for (**3**) in which one methyl hydrogen had been abstracted leaving the basic framework of (**1**) essentially intact. Thus regeneration of (**1**) from (**3**) by treatment with $K[BHBu^s_3]$ is quantitative and treatment with $Li[BDEt_3]$ confirmed (n.m.r. spectroscopy) hydrogen incorporation into one methyl group of (**1**). Similarly, reaction of (**3**) with lithium diphenylcuprate afforded a phenyl substituted derivative of (**1**), $[Mo(\mu\text{-}C_8Me_7CH_2Ph)(\eta\text{-}C_5H_5)_2]$ (**4**)† (see Scheme 1).

In order to characterise the nature of (**3**) fully an *X*-ray diffraction study‡ was carried out with a suitable crystal of the triflate salt. The two crystallographically independent cations show the same stereochemistry, which is illustrated diagramatically in Scheme 1 and fully in Figure 1. As in the parent complex (**1**), the cation (**3**) has a formal Mo–Mo bond order of two, consonant with the observed Mo(1)–Mo(2) distance 2.652(2) Å. One hydrogen has indeed been abstracted, from the methyl substituent of an olefinic carbon in (**1**), to give an allyl moiety, attached to Mo(2), whose contact carbons are C(4), C(5), and C(9). The remainder of the C_8 chain is bound to the $Mo_2(\eta\text{-}C_5H_5)_2$ unit as in (**1**) and (**2**).

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† N.m.r. data for (**3**) in $CDCl_3$: ^1H (303 K), δ 5.71 (s, 5 H, C_5H_5), 4.60 (s, 5 H, C_5H_5), 2.89 (s, 3 H, Me), 2.69 (s, 3 H, Me), 2.61 (s, 3 H, Me), 2.39 (s, 3 H, Me), 2.23 (s, 3 H, Me), 1.96 (s, 3 H, Me), 0.71 (s, 3 H, Me), 1.78 (s, 1 H), and 0.07 (s, 1 H, CH_2). ^{13}C {^1H} (303 K), δ 195.9, 183.0, 135.8, 116.2, 113.8, 98.8, 84.2, 70.7 (C_8 chain carbons); 100.7, 96.7 (C_5H_5); 59.4 (CH_2); 37.1, 34.0, 22.9, 22.1, 19.7, 19.5, 18.9 (CH_3) p.p.m. N.m.r. data for (**4**) in C_6D_6: ^1H (303 K), δ 7.6—6.8 (m, 5 H, Ph), 5.14 (s, 5 H, C_5H_5), 3.75 (s, 5 H, C_5H_5), 2.48 (s, 3 H, Me), 2.39 (s, 3 H, Me), 2.30 (s, 3 H, Me), 2.05 (s, 3 H, Me), 1.88 (s, 3 H, Me), 1.67 (s, 3 H, Me), 1.09 (s, 3 H, Me), 3.18 (d, 1 H, CH_2, $^2J_{HH}$ 15.6 Hz), and 1.80 (d, 1 H, CH_2, $^2J_{HH}$ 15.6 Hz). ^{13}C {^1H} δ 175.6, 174.3, 122.0, 120.2, 74.3, 71.7, 69.5, 68.2 (C_8 chain carbons); 143.4 (Ph, *ipso C*); 130.5—125.3 (*C*H of Ph); 98.4, 91.8 (C_5H_5); 44.6 (CH_2); 56.7, 33.1, 26.3, 23.5, 21.9, 18.5, 18.1 (CH_3) p.p.m. N.m.r. data for (**5**) in CD_2Cl_2: ^1H (303 K) δ 5.16 (s, 5 H, C_5H_5), 4.93 (s, 5 H, C_5H_5), 2.43 (s, 6 H, 2 × Me), 2.35 (s, 6 H, 2 × Me), 2.07 (s, 6 H, 2 × Me), 1.51 (s, 6 H, 2 × Me). ^{13}C {^1H} (303 K) 188.4, 129.2, 96.3, 92.6 (C_8 chain carbons); 100.5, 100.35 (C_5H_5), 30.1, 25.3, 22.5, 18.0 (CH_3) p.p.m.

‡ *Crystal data* for $[CF_3SO_3]^-$ salt of (**3**): $C_{27}H_{33}F_3Mo_2O_3S$, $M = 686.5$, monoclinic, space group $P2_1/c$, $a = 19.251(9)$, $b = 18.078(8)$, $c = 16.963(8)$ Å, $\beta = 113.79(4)°$, $U = 5\,402(4)$ Å^3, $D_c = 1.69$ g cm^{-3}, $Z = 8$, $F(000) = 2\,768$ electrons. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(Mo\text{-}K_\alpha) = 10.27$ cm^{-1}. Current *R* 0.058 for 5 159 unique, absorption corrected, observed $[I > 2\sigma(I)]$ reflections measured at 298 K on a Nicolet P3m diffractometer in the range $3 < 2\theta < 50°$. The structure was solved by direct and Fourier methods and refined by blocked cascade full matrix least squares with programs of the SHELXTL package on a Nicolet R3m/E structure determination system. One of two crystallographically independent molecular cations shows disorder affecting atoms C(59) and C(63), which correspond to atoms C(9) and C(13) shown for the other molecule in Figure 1. These atoms adopt two conformations of occupancy 0.51(1) and 0.49(1) such that in each one atom is bonded to Mo(2) and the other is not.

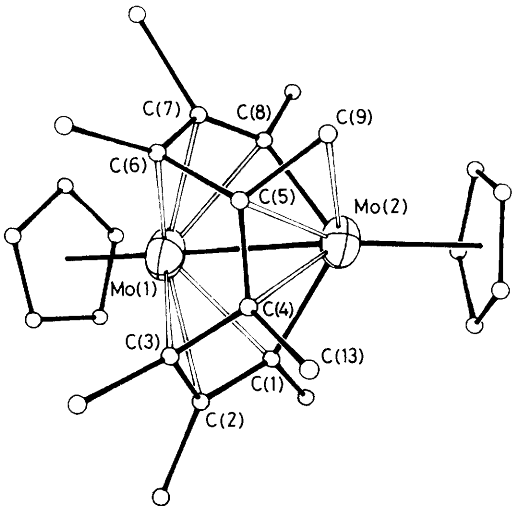

Figure 1. Molecular structure of $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^+$ (**3**); one molecule is shown, the second crystallographically independent cation is similar. Important geometric parameters are: Mo(1)–Mo(2) 2.655(1), Mo(1)–C(1) 2.205(10), Mo(1)–C(2) 2.285(13), Mo(1)–C(3) 2.266(12), Mo(1)–C(6) 2.180(12), Mo(1)–C(7) 2.172(17), Mo(1)–C(8) 2.218(12), Mo(2)–C(1) 2.132(10), Mo(2)–C(4) 2.239(15), Mo(2)–C(5) 2.276(14), Mo(2)–C(9) 2.416(13), and Mo(2)–C(8) 2.015(9) Å.

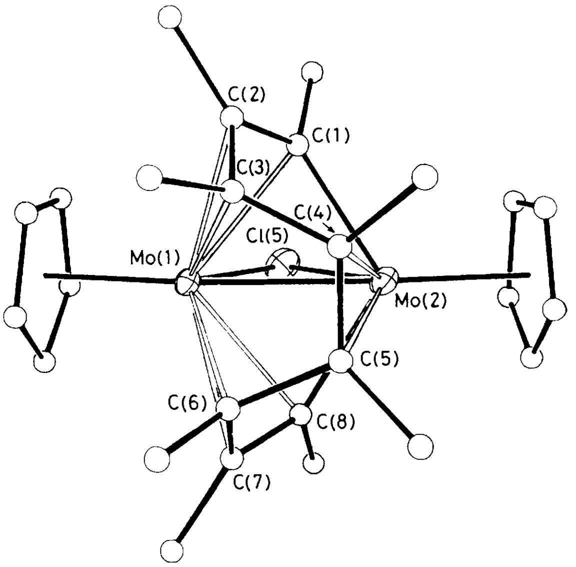

Figure 2. Molecular structure of $[Mo_2(\mu\text{-}C_8Me_8)(\mu\text{-}Cl)(\eta\text{-}C_5H_5)_2]^+$ (**5**). Important geometric parameters are: Mo(1)–Mo(2) 2.628(2), Mo(1)–C(1) 2.349(13), Mo(1)–C(2) 2.427(15), Mo(1)–C(3) 2.384(16), Mo(1)–C(6) 2.384(14), Mo(1)–C(7) 2.429(13), Mo(1)–C(8) 2.404(13), Mo(2)–C(1) 2.151(13), Mo(2)–C(4) 2.354(15), Mo(2)–C(5) 2.382(14), Mo(2)–C(8) 2.185(15), Mo(1)–Cl(5) 2.533(4), and Mo(2)–Cl(5) 2.580(5) Å.

An insight into the nature of this reaction was provided by the cyclic voltammogram§ of (**1**). In CH_2Cl_2 as solvent (**1**) undergoes a diffusion controlled reversible one-electron oxidation ($E^\circ = -0.02$ V) followed by a second irreversible one electron process with $E_{\frac{1}{2}}^{ox} = 0.70$ V (at a scan rate of 100 mV s^{-1}). Chemical oxidation of (**1**) with two equivalents of $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ (-78 °C, CH_2Cl_2) gave instantaneously a red solution, and on allowing to warm to room temperature (12 h), afforded a purple solution from which the BF_4 salt of (**3**) was obtained in good yield by addition of diethyl ether.

The weak oxidising agent $SbCl_6^-$ (cation NPr^n_4 or PhCO) reacted with (**1**) to give a quantitive yield of the cation (**5**) $[Mo_2(\mu\text{-}C_8Me_8)(\mu\text{-}Cl)(\eta\text{-}C_5H_5)_2]^+$ as its tetrachloroantimonate salt.† The structure of this salt as its methylene chloride solvate was established by *X*-ray crystallography.¶ As illustrated in Figure 2 the cation shows the same conformation for the $Mo_2(\mu\text{-}C_8Me_8)$ core as (**1**) with approximate C_s symmetry. The chlorine bridges the Mo–Mo vector preserving the Mo–Mo double bond seen in (**1**), (**2**), and (**3**). The anion is dimerised around a crystallographic inversion centre, each Sb atom being co-ordinated by five Cl atoms in a square pyramidal fashion sharing one edge of the pyramid with the other antimony. It is, therefore, likely that (**5**) is formed by one-electron oxidation of (**1**) by $SbCl_6^-$ (ref. 3) followed by chlorination of the resulting radical cation.

These observations suggest that activation of a methyl group in (**1**) initially involves stepwise two-electron oxidation of one of the molybdenum centres. In the reaction with CF_3SO_3H access to the same doubly charged intermediate (A) (Scheme 1) could be gained by further protonation of the monocation (**2**). This is supported by extended Hückel M.O. calculations which show build-up of negative charge on the (unprotonated) α-carbon atoms of the C_8 chain in both (**1**) and (**2**).** Thus it is suggested that in the reaction with the strong acid CF_3SO_3H consecutive protonation of the α-carbon atoms of (**1**) occurs to give a dicationic species with two μ-C–H–Mo linkages. If both these α-hydrogens are abstracted and H_2 eliminated from the metal centre, the same dicationic species (A) accessible *via* direct oxidation of (**1**) is formed (reactions involving abstraction of α-hydrogen atoms are known[4] for mononuclear complexes). Subsequent attack of the activated molybdenum centre on a methyl group (partly or wholly abstracting a β-hydrogen) followed by deprotonation on work-up with a basic solvent then affords (**3**).

The oxidative activation of (**1**) by direct and indirect means affords a route to further chemistry of these dimolybdenum species and is potentially applicable to other electron rich organometallic species.

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§ At a Pt electrode, with 0.1 M $[NBu^n_4][BF_4]$ as base electrolyte, and a saturated calomel electrode as reference. Under these conditions E° for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+/[Fe(\eta\text{-}C_5H_5)_2]$ is 0.57 V.

¶ *Crystal data* for (**5**) as $[SbCl_4]^-$ salt, dichloromethane solvate. $C_{27}H_{36}Mo_2SbCl_7$, $M = 922.3$, monoclinic, space group $P2_1/n$, $a = 14.557(6)$, $b = 13.224(3)$, $c = 17.032(4)$ Å, $\beta = 105.93(3)°$, $U = 3\,152(2)$ Å^3, $D_c = 1.94$ g cm^{-3}, $Z = 4$, $F(000) = 1\,808$ electrons, Mo-K_α radiation, $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 22.4 cm^{-1}. Current R 0.066 for 2 544 unique, observed $[I > 1.5\sigma(I)]$ reflections measured at 200 K in the range $4 < 2\theta < 40°$, solution and refinement as for (**3**). The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

** Calculations were carried out with program ICON8, J. Howell, A. Rossi, D. Wallace, K. Haraki, and R. Hoffmann, Quantum Chemistry Program Exchange, 1977, **10**, 344, using geometric parameters derived from the crystal structures of (**1**) and (**2**).[1] Net atomic charges were not corrected by charge iteration calculations. In (**1**) the net charge on C_8 chain terminal carbons was -0.54 e and in (**2**) -0.55 e for the unprotonated α-carbon.

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References

1 M. Green, N. C. Norman, and A. G. Orpen, *J. Am. Chem. Soc.*, 1981, **103**, 1269.

2 The dinuclear complex (**1**) can also be readily prepared by reduction (Na–Hg) of $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$; M. Green, K. E. Paddick, A. G. Orpen, and C. J. Schaverien, unpublished results.

3 N. G. Connelly and M. D. Kitchen, *J. Chem. Soc., Dalton Trans.*, 1977, 931.

4 R. R. Schrock, *Acc. Chem. Res.*, 1979, **12**, 98.