Reactions of Co-ordinated Ligands. Part 48.[1] Reactivity Studies of the Octatrienediylidenedimolybdenum Complexes $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$ and $[Mo_2(\mu\text{-}C_8H_4Bu^t{}_4)(\eta\text{-}C_5H_5)_2]$. Crystal Structures of $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2][CF_3SO_3]$, $[Mo_2(\mu\text{-}C_8Me_8)(\mu\text{-}Cl)(\eta\text{-}C_5H_5)_2][SbCl_4]\cdot CH_2Cl_2$, and $[Mo_2(\mu\text{-}C_8H_4Bu^t{}_4)(\mu_{Mo,C}\text{-}H)(\eta\text{-}C_5H_5)_2][BPh_4]\cdot CH_2Cl_2$ §

Simon G. Bott, Lee Brammer, Neil G. Connelly, Michael Green,*† A. Guy Orpen, Jill F. Paxton, and Colin J. Schaverien
Department of Inorganic Chemistry, The University, Bristol BS8 1TS
Stuart Bristow and Nicholas C. Norman‡
Department of Chemistry, The University, Manchester M13 9PL

Double protonation of $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$, (**1**), with excess CF_3SO_3H or hydride abstraction with $[CPh_3][BF_4]$ affords the cationic complex $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^+$, (**4**), which has been characterised as the triflate (CF_3SO_3) salt by *X*-ray crystallography. The structure of (**4**) is similar to that of (**1**) in having a C_8 chain bridging a Mo–Mo bond, the chain beginning and ending with σ bonds to Mo(2). Carbons C(1)—C(3) and C(6)—C(8) each form an η^3-allylic interaction with Mo(1) and C(4), C(5), and C(9) bond in a similar manner to Mo(2) [in contrast to an η^2-alkene-type interaction involving C(4) and C(5) found in (**1**)]. Mechanistic and electrochemical studies pertinent to the formation of (**4**) are discussed. Compound (**4**) reacts with the nucleophiles $K[BHBu^s{}_3]$, $K[BDBu^s{}_3]$, $Li[CuMe_2]$, $Li[CuPh_2]$, and Na[SMe] affording the neutral complexes $[Mo_2(\mu\text{-}C_8Me_7CH_2R)(\eta\text{-}C_5H_5)_2]$ [R = H, (**1**); D, (**1d**); Me, (**5**); Ph, (**6**); or SMe, (**7**)] thereby enabling a modification of the δ-ring substituent in the original complex (**1**). Subsequent hydride abstraction from (**5**) results in the cation $[Mo_2(\mu\text{-}C_8Me_6EtCH_2)(\eta\text{-}C_5H_5)_2]^+$, (**8**), analogous to (**4**), which on treatment with $Li[CuMe_2]$ affords the diethyl derivative $[Mo_2(\mu\text{-}C_8Me_6Et_2)(\eta\text{-}C_5H_5)_2]$, (**9**). The reaction of (**1**) with $[NPr^n{}_4][SbCl_6]$ affords the chloro cationic species $[Mo_2(\mu\text{-}C_8Me_8)(\mu\text{-}Cl)(\eta\text{-}C_5H_5)_2]^+$, (**11**), which was characterised by *X*-ray crystallography. Its structure is very similar to that of (**1**) except in containing a chlorine bridging the Mo–Mo vector. Protonation of the unsymmetrically substituted complex $[Mo_2(\mu\text{-}C_8H_4Bu^t{}_4)(\eta\text{-}C_5H_5)_2]$, (**3**), has also been studied and shown to afford a cationic complex containing an agostic CH interaction $[Mo_2(\mu\text{-}C_8H_4Bu^t{}_4)(\mu_{Mo,C}\text{-}H)(\eta\text{-}C_5H_5)_2]^+$, (**12**). Compound (**12**) was characterised by *X*-ray crystallography which reveals the site of protonation on a δ-ring carbon in contrast to the α-protonation observed in $[Mo_2(\mu\text{-}C_8Me_8)(\mu_{Mo,C}\text{-}H)(\eta\text{-}C_5H_5)_2]^+$, (**2**). Proton and ^{13}C n.m.r. studies indicate, however, that the proton in (**12**) is fluxional between the α and δ sites analogous to that seen in (**2**). Details of the spectroscopic studies are presented and discussed.

Alkyne linkage reactions at transition metal centres continue to attract the attention of synthetic chemists and have resulted in a wide variety of complexes. Of particular interest herein are those compounds resulting from the coupling of four alkynes, which contain a C_8 chain bonded to two metal centres. Our own work in this area derived from the observation that reduction of the bis(alkyne) cation $[Mo(NCMe)(\eta^2\text{-}RC_2R')_2(\eta\text{-}C_5H_5)]^+$ resulted in octatrienediylidenedimolybdenum complexes $[Mo_2\{\mu\text{-}(\sigma,\eta^3\text{:}\eta^2\text{:}\eta^3,\sigma\text{-}C_8R_4R'_4)\}(\eta\text{-}C_5H_5)_2]$ (R = R′ = Me; R = H, R′ = Bu^t)[2–4] and for R = H, R′ = Bu^t, a branched chain isomer $[Mo_2\{\mu\text{-}(\sigma,\eta^3\text{:}\eta^3,\sigma\text{-}CH{=}CHBu^tC_6H_2Bu^t{}_3)\}(\eta\text{-}C_5H_5)_2]$.[4] Similar octatrienediylidene complexes have also been characterised by Stone and Knox and co-workers[5–8] from reactions of alkynes with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (Mo≡Mo); $[Mo_2(\mu\text{-}C_8R_4R'_2R''_2)(\eta\text{-}C_5H_5)_2]$ (R = R′ = R″ = CO_2Me; R = R′ = CO_2Me, R″ = H; R = Ph, R′ = H, R″ = CO_2Me) together with an isomeric C_8 'flyover' or dimetallacyclodecapentaene complex, $[Mo_2\{\mu\text{-}[\sigma,\eta^4\text{:}\eta^4,\sigma\text{-}C_8(CO_2Me)_8]\}(\eta\text{-}C_5H_5)_2]$.[6,7] The ditungsten complex $[W\{\mu\text{-}C_8(CO_2Me)_8\}(\eta\text{-}C_5H_5)_2]$ has also been described.[8] This latter type of complex has also been reported by Wilke and co-workers,[9] *viz.* $[Cr_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]$, from the reaction of $[Cr(\eta\text{-}C_5H_5)_2]$ with $Na_2[C_8H_8]$, and more recently by Geiger and co-workers in $[Ru_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]^{2+}$ [10] resulting from oxidation of a complex containing a bridging cyclo-octatetraene (cot) ligand. Many examples of bridging cot compounds are known *e.g.* $[Rh_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]^{2+}$ [11] and the relationship between the above-mentioned complexes, cyclo-octatetraene, and alkyne linkage has been discussed by Wilke.[12] We note also that a dirhenium octatrienediylidene complex, $[Re_2(CO)_5(\mu\text{-}C_8Me_8)]$, has been reported by Mays *et al.*[13] though it has not been structurally characterised.

Despite the range of compounds described above and the various synthetic routes whereby they are formed, few reactivity studies have been reported. Our own studies on the protonation of $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$, (**1**) resulting in $[Mo_2(\mu\text{-}C_8Me_8)(\mu_{Mo,C}\text{-}H)(\eta\text{-}C_5H_5)_2]^+$ (**2**), which contains an

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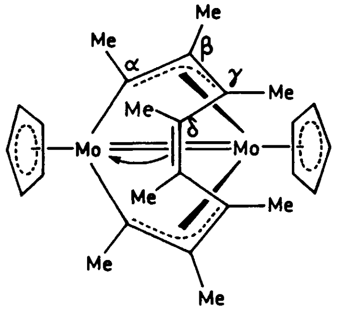
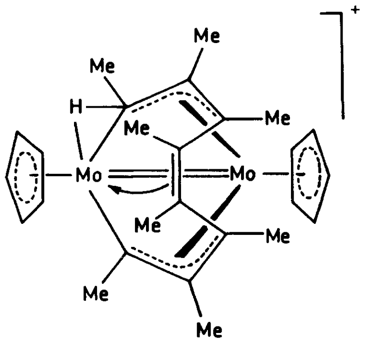
† *Present address:* Department of Chemistry, Kings College, London, Strand, London WC2R 2LS

‡ *Present address:* Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU.

§ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



(1)



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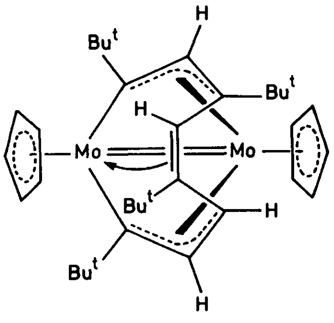

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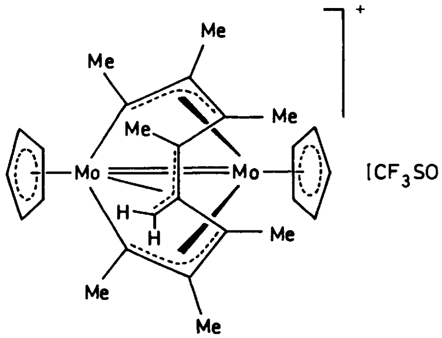

(4)

'agostic' CH interaction, have been reported in detail.[3] Herein we describe the further protonation of (2), together with other aspects of the reactivity of (1), and protonation studies of the unsymmetrical complex $[Mo_2(\mu\text{-}C_8H_4Bu^t{}_4)(\eta\text{-}C_5H_5)_2]$ (3) some aspects of which have been the subject of a preliminary communication.[14]

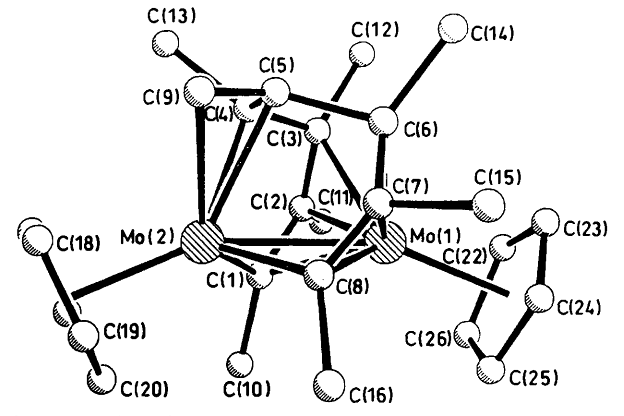

Figure 1. A view of the molecular structure of complex (4) showing the atom numbering scheme. One cation is shown, the second crystallographically independent cation being similar. Hydrogen atoms are omitted for clarity

Results and Discussion

Protonation of (1) with $HBF_4{\cdot}Et_2O$ or CF_3CO_2H affords the monoprotonated complex (2), containing an 'agostic' CH interaction as mentioned in the Introduction and described in detail in ref. 3. It was observed, however, that whilst formation of (2) was immediate and quantitative, prolonged reaction with $HBF_4{\cdot}Et_2O$ resulted in a second complex as evidenced by ^1H n.m.r. spectroscopy. Reasoning that this additional product might result from further protonation of (2), a reaction with the stronger acid CF_3SO_3H was carried out. Treatment of (1) with an excess of CF_3SO_3H in dichloromethane caused an immediate reaction from which (2) could be isolated as its $CF_3SO_3^-$ salt if work up occurred within 1—2 h, but if the reaction was allowed to proceed for prolonged periods (overnight) a new product, (4), could be isolated as purple crystals. N.m.r. spectroscopy (Table 1) and chemical evidence indicated a structure for (4) in whch one methyl hydrogen had been abstracted from (1) (as hydride) but leaving the basic framework of (1) essentially intact. In order to characterise the nature of (4) fully, an *X*-ray diffraction study was carried out the results of which are presented in Figure 1 and Tables 2 and 3. The two crystallographically independent cations show the same stereochemistry, the overall structure being very similar to that found in (1).[3] The Mo–Mo bond length [av. 2.654(1) Å] is consistent with a bond order of two as required by electron-counting procedures. One hydrogen has indeed been abstracted from (1) from a δ-methyl group resulting in an allyl moiety attached to Mo(2) whose contact carbons are C(4), C(5), and C(9). This is illustrated schematically in the diagram.

An insight into the nature of the reaction by which complex (4) is formed from (1) was provided by electrochemical studies using cyclic voltammetry.* 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 2 equivalents of $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ at −78 °C in CH_2Cl_2 gave instantaneously a red solution [presumably $(1)^{\bullet+}$] which, on being allowed to warm to room temperature and on stirring for 12 h, afforded a purple solution from which (4) was isolated as a tetrafluoroborate salt in good yield by addition of diethyl ether. These observations, deriving from protonation and chemical and electrochemical oxidation, are presented in Scheme 1. We

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* At a platinum electrode, with 0.1 mol dm^{-3} $[NBu^n{}_4][BF_4]$ 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.

Table 1. Proton and ^{13}C n.m.r. data for complexes **(4)**—**(9)**, **(11)**, and **(12)**[a]

Compound	^{1}H (δ)	^{13}C-{^{1}H} (δ)
(4)[b]	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), 1.78 (s, 1 H, CH_2), 0.71 (s, 3 H, Me), 0.07 (s, 1 H, CH_2)	195.9, 183.0, 135.8, 116.2, 113.8, 98.8, 84.2, 70.7 (C_8 ring 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 (Me)
(5)[c]	5.07 (s, 5 H, C_5H_5), 3.80 (s, 5 H, C_5H_5), 2.42 (q, 2 H, CH_2, $^{3}J_{HH}$ = 7.4), 2.41 (s, 3 H, Me), 2.30 (s, 3 H, Me), 2.29 (s, 3 H, Me), 2.26 (s, 3 H, Me), 2.01 (s, 3 H, Me), 1.87 (s, 3 H, Me), 0.99 (s, 3 H, Me), 0.74 (t, 3 H, CH_3, $^{3}J_{HH}$ = 7.4)	174.7, 173.9, 120.1, 119.7, 76.8, 71.7, 68.0, 67.8 (C_8 ring carbons); 97.3, 91.4, (C_5H_5), 33.3, 32.8, 25.3, 21.9, 21.6, 18.5, 17.3, 12.7 (Me); 25.3 (CH_2)
(6)[c]	7.6—6.8 (m, 5 H, Ph), 5.14 (s, 5 H, C_5H_5), 3.75 (s, 5 H, C_5H_5), 3.18 (d, 1 H, CH_2, $^{2}J_{HH}$ = 15.6), 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), 1.80 (d, 1 H, CH_2, $^{2}J_{HH}$ = 15.6), 1.67 (s, 3 H, Me), 1.09 (s, 3 H, Me)	175.6, 174.3, 122.0, 120.2, 74.3, 71.7, 69.5, 68.2 (C_8 ring carbons); 143.4, (Ph, *ipso* C), 130.5—125.3 (CH 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 (Me)
(7)[c]	5.23 (s, 5 H, C_5H_5), 3.82 (s, 5 H, C_5H_5), 3.33 (d, 1 H, CH_2, $^{2}J_{HH}$ = 11.4), 2.44 (s, 3 H, Me), 2.40 (s, 3 H, Me), 2.29 (s, 3 H, Me), 2.01 (s, 3 H, Me), 1.81 (s, 6 H, 2 × Me), 1.55 (s, 3 H, Me), 1.48 (d, 1 H, CH_2, $^{2}J_{HH}$ = 11.4), 1.01 (s, 3 H, Me)	175.0, 174.4, 121.8, 119.9, 70.9, 70.7, 68.9, 68.0 (C_8 ring carbons); 98.0, 91.5 (C_5H_5), 30.2 (CH_2), 46.7, 33.1, 32.8, 21.8, 18.5, 17.6, 16.4, 14.3 (Me)
(8)[b]	5.64 (s, 5 H, C_5H_5), 4.57 (s, 5 H, C_5H_5), 2.84 (s, 3 H, Me), 2.67 (s, 3 H, Me), 2.58 (s, 3 H, Me), 2.35 (s, 3 H, Me), 2.20 (s, 3 H, Me), 1.97 [q, 2 H, CH_2 (Et), $^{3}J_{HH}$ = 7.6], 1.80 (s, 3 H, Me), 1.75 (s, 1 H, CH_2), 0.08 (s, 1 H, CH_2)	196.1, 183.4, 136.2, 116.9, 112.7, 107.6, 96.9, 71.5 (C_8 ring carbons); 100.4, 96.8 (C_5H_5), 59.6 (CH_2), 37.0, 34.2, 22.1, 19.6, 18.9, 13.8 (Me); 25.8 (CH_2, Et)
(9)[c]	5.03 (s, 5 H, C_5H_5), 3.79 (s, 5 H, C_5H_5), 2.43 (q, 4 H, 2 × CH_2, $^{3}J_{HH}$ = 7.3), 2.37 (s, 6 H, 2 × Me), 2.26 (s, 6 H, 2 × Me), 1.89 (s, 6 H, 2 × Me), 0.77 (t, 6 H, 2 × Me $^{3}J_{HH}$ = 7.3)	
(11)[d]	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)	188.4, 129.2, 96.3, 92.6 (C_8 ring carbons); 100.5, 100.4 (C_5H_5), 30.1, 25.3, 22.5, 18.0 (Me)
(12)[b,e]	Ring protons: 7.45 [ddd, 1 H, H(6)], 7.15 [s, 1 H, H(2)], 4.89 [dd, 1 H, H(7)], 2.29 [s, 1 H, H(4)], −10.81 [ddd, 1 H, H(5)] Coupling constants: ^{3}J[H(6)H(7)] 5.1, ^{3}J[H(7)H(5)] 3.8, ^{4}J[H(6)H(5)] 3.0, ^{3}J[H(4)H(5)] 3.0, ^{4}J[H(6)H(4)] 3.0, ^{4}J[H(2)H(4)] unresolved <1.0, 5.73 [s, 5 H, C_5H_5(A)], 5.07 [s, 5 H, C_5H_5(B)], 1.35 (s, 9 H, Bu^t(A)], 1.31 [s, 9 H, Bu^t(B)], 1.28 [s, 9 H, Bu^t(C)], 0.82 [s, 9 H, Bu^t(D)]	C_8 ring carbons: 211.2 [C(1)], 197.0 [C(8)], 103.5 {C(2), ^{1}J[C(2)H(2)] 154}, 102.4 [C(3)], 99.8 {C(6), ^{1}J[C(6)H(6)] 168}, 69.3 [C(5)], 61.0 {C(4), ^{1}J[C(4)H(4)] 154}, 60.2 {C(7), ^{1}J[C(7)H(7)] 165}, 98.2 [C_5H_5(A), ^{1}J(CH), 190], 91.6 [C_5H_5(B), ^{1}J(CH), 190], 46.4, 44.3, 39.3, 38.5 (Bu^t quaternary carbons), 34.7(C), 33.8(B), 32.9(A), 30.6(D), (Bu^t methyl carbons)[f]

[a] Chemical shifts in p.p.m. relative to $SiMe_4$, positive values to high frequency, coupling constants in Hz, measurements at 303 K. [b] Measured in *$CDCl_3$ solution.* [c] Measured in C_6D_6 solution. [d] Recorded in CD_2Cl_2 solution. [e] Measured at 292 ± 1 K. The numbering scheme adopted is shown in the diagram of complex **(12)** (see text) and is the same as that used in the *X*-ray crystallographic study. The letters A—D for the C_5H_5 and Bu^t signals refer to correlations between the peaks in the ^{1}H and ^{13}C n.m.r. spectra as determined by two-dimensional experiments (see Experimental section). This was also the basis for the assignments of the C_8 ring carbons. ^{95}Mo N.m.r. −352 p.p.m. (one signal observed, see Experimental section for details). [f] Additional C–H couplings observed: C(4), 10, ^{3}J[C(4)H(6)] or ^{3}J[C(4)H(2)]; C(7), 11 and 6, ^{2}J[C(7)H(6)] and ^{4}J[C(7)H(4)].

propose that double protonation of **(1)** [or monoprotonation of **(2)**] affords an intermediate diprotonated dication, **(A)**, which subsequently loses H_2 to afford the dication $(\mathbf{1})^{2+}$ which may also be generated electrochemically or by addition of >2 equivalents of $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$. The species $(\mathbf{1})^{2+}$ then loses a proton from one of the δ-methyl carbons affording **(4)** possibly by means of a β-hydrogen abstraction process involving the doubly charged, and hence activated, molybdenum centre. Support for the proposed intermediate, **(A)**, is provided by extended-Hückel molecular-orbital (m.o.) calculations which show a build up of negative charge on the unprotonated α-ring carbon in both **(1)** and **(2)**. These are discussed in more detail in ref. 3. We note also that similar reactions involving double oxidation followed by proton loss from organic fragments at dimetal centres have been reported by Knox and Connelly.[15]

Since complex **(4)** derives from **(1)** by formal loss of hydride, an alternative synthetic route to **(4)** involving this process directly was thought possible. Accordingly, a reaction between **(1)** and $[CPh_3][BF_4]$ was carried out (CH_2Cl_2, 24 h) which does indeed afford **(4)** in high yield. The precise mechanism by which this reaction occurs is unclear. One possibility involves double oxidation of **(1)** by $[CPh_3][BF_4]$ affording **(4)** *via* the route $(\mathbf{1}) \longrightarrow (\mathbf{1})^{\cdot+} \longrightarrow (\mathbf{1})^{2+} \longrightarrow (\mathbf{4})$. An alternative pathway, however, is shown in equation (1). The fact that complex

$$(\mathbf{1}) \xrightarrow[-Ph_3C^{\cdot}]{+[CPh_3]^+} (\mathbf{1})^{\cdot+} \xrightarrow[-Ph_3CH]{+Ph_3C^{\cdot}} (\mathbf{4}) \qquad (1)$$

(4) is formed in high yield from the reaction between equimolar quantities of **(1)** and $[CPh_3][BF_4]$ supports the latter mechanism.

The availability of complex **(4)** in high yield from **(1)** enabled a number of reactivity studies to be carried out. Specifically, the addition of nucleophiles to **(4)** regenerates **(1)** or derivatives thereof allowing modification of the δ substituents on the C_8 ring.

Treatment of complex **(4)** with $K[BHBu^s_3]$ affords **(1)** quantitatively whilst use of the deutero borohydride $K[BDBu^s_3]$ affords **(1d)**. The ^{1}H n.m.r. spectrum of **(1d)** is identical to **(1)** except that the methyl signal at δ 0.99[3] has a reduced intensity from 6 to 5 in accordance with two CH_3 groups becoming CH_3 and CH_2D. Corresponding reactions with $Li[CuMe_2]$, $Li[CuPh_2]$, and Na[SMe] afforded the derivatives **(5)**—**(7)** respectively, n.m.r. data for which are presented in Table 1.

This synthetic approach resulting in modification of the δ-carbon substituent can be carried further so as to modify the substituent at the other δ position (δ′). Thus treatment of the monoethyl derivative, **(5)**, with 1 equivalent of $[CPh_3][BF_4]$ afforded the cationic species **(8)** analogous to **(4)** which, on treatment with $Li[CuMe_2]$ gave the δ,δ′-diethyl complex **(9)**

Table 2. Selected bond lengths (Å) and angles (°) for complex (**4**)

Mo(1)–Mo(2)	2.655(1)	Mo(1)–C(1)	2.205(10)	C(6)–C(14)	1.543(24)	C(7)–C(8)	1.212(23)
Mo(1)–C(2)	2.283(13)	Mo(1)–C(3)	2.266(12)	C(7)–C(15)	1.764(20)	C(8)–C(16)	1.592(20)
Mo(1)–C(6)	2.180(13)	Mo(1)–C(7)	2.172(17)	C(17)–C(18)	1.355(20)	C(17)–C(21)	1.374(17)
Mo(1)–C(8)	2.218(12)	Mo(1)–C(22)	2.357(12)	C(18)–C(19)	1.410(21)	C(19)–C(20)	1.423(19)
Mo(1)–C(23)	2.342(10)	Mo(1)–C(24)	2.312(11)	C(20)–C(21)	1.436(18)	C(22)–C(23)	1.334(17)
Mo(1)–C(25)	2.365(18)	Mo(1)–C(26)	2.329(16)	C(22)–C(26)	1.419(28)	C(23)–C(24)	1.370(22)
Mo(2)–C(1)	2.132(10)	Mo(2)–C(4)	2.239(15)	C(24)–C(25)	1.366(29)	C(25)–C(26)	1.366(31)
Mo(2)–C(5)	2.276(14)	Mo(2)–C(8)	2.015(9)	C(51)–C(52)	1.383(17)	C(51)–C(60)	1.578(17)
Mo(2)–C(9)	2.416(13)	Mo(2)–C(17)	2.387(10)	C(52)–C(53)	1.350(17)	C(52)–C(61)	1.575(16)
Mo(2)–C(18)	2.403(12)	Mo(2)–C(19)	2.371(16)	C(53)–C(54)	1.513(15)	C(53)–C(62)	1.558(22)
Mo(2)–C(20)	2.329(16)	Mo(2)–C(21)	2.354(12)	C(54)–C(55)	1.442(14)	C(54)–C(63)	1.554(22)
Mo(3)–Mo(4)	2.653(1)	Mo(3)–C(51)	2.196(10)	C(54)–C(63′)	1.433(25)	C(55)–C(56)	1.503(13)
Mo(3)–C(52)	2.255(10)	Mo(3)–C(53)	2.266(11)	C(55)–C(59)	1.463(23)	C(55)–C(59′)	1.492(23)
Mo(3)–C(56)	2.280(10)	Mo(3)–C(57)	2.311(10)	C(56)–C(57)	1.389(16)	C(56)–C(64)	1.560(20)
Mo(3)–C(58)	2.183(12)	Mo(3)–C(72)	2.313(10)	C(57)–C(58)	1.384(18)	C(57)–C(65)	1.521(15)
Mo(3)–C(73)	2.317(11)	Mo(3)–C(74)	2.348(15)	C(58)–C(66)	1.618(18)	C(67)–C(68)	1.350(16)
Mo(3)–C(75)	2.345(16)	Mo(3)–C(76)	2.339(12)	C(67)–C(71)	1.379(18)	C(68)–C(69)	1.353(19)
Mo(4)–C(51)	2.075(10)	Mo(4)–C(54)	2.283(12)	C(69)–C(70)	1.379(23)	C(70)–C(71)	1.427(23)
Mo(4)–C(55)	2.295(12)	Mo(4)–C(58)	2.069(10)	C(72)–C(73)	1.385(20)	C(72)–C(76)	1.373(20)
Mo(4)–C(59)	2.546(21)	Mo(4)–C(63′)	2.567(23)	C(73)–C(74)	1.381(28)	C(74)–C(75)	1.307(25)
Mo(4)–C(67)	2.328(14)	Mo(4)–C(68)	2.350(13)	C(75)–C(76)	1.372(25)	S(1)–O(1)	1.406(9)
Mo(4)–C(69)	2.408(13)	Mo(4)–C(70)	2.420(15)	S(1)–O(2)	1.326(12)	S(1)–O(3)	1.387(11)
Mo(4)–C(71)	2.334(18)	C(1)–C(2)	1.383(20)	S(1)–C(27)	1.750(20)	S(2)–O(4)	1.381(12)
C(1)–C(10)	1.548(18)	C(2)–C(3)	1.350(19)	S(2)–O(5)	1.391(10)	S(2)–O(6)	1.250(13)
C(2)–C(11)	1.555(19)	C(3)–C(4)	1.401(16)	S(2)–C(28)	1.759(24)	C(27)–F(1)	1.270(18)
C(3)–C(12)	1.605(23)	C(4)–C(5)	1.426(17)	C(27)–F(2)	1.303(18)	C(27)–F(3)	1.266(21)
C(4)–C(13)	1.654(15)	C(5)–C(6)	1.541(14)	C(28)–F(4)	1.270(23)	C(28)–F(5)	1.247(23)
C(5)–C(9)	1.464(19)	C(6)–C(7)	1.274(23)	C(28)–F(6)	1.315(19)		

Mo(2)–Mo(1)–C(2)	74.9(3)	Mo(2)–Mo(1)–C(1)	51.0(3)	Mo(1)–C(3)–C(12)	129.0(7)	C(2)–C(3)–C(4)	112.7(12)
Mo(2)–Mo(1)–C(3)	74.9(3)	C(1)–Mo(1)–C(2)	35.9(5)	C(4)–C(3)–C(12)	118.3(11)	C(2)–C(3)–C(12)	119.4(12)
C(2)–Mo(1)–C(3)	34.5(5)	C(1)–Mo(1)–C(3)	62.3(5)	Mo(2)–C(4)–C(5)	73.0(8)	Mo(2)–C(4)–C(3)	109.3(9)
C(1)–Mo(1)–C(6)	118.5(3)	Mo(2)–Mo(1)–C(6)	75.5(3)	Mo(2)–C(4)–C(13)	116.9(9)	C(3)–C(4)–C(5)	116.9(10)
C(3)–Mo(1)–C(6)	78.0(5)	C(2)–Mo(1)–C(6)	111.0(5)	C(5)–C(4)–C(13)	115.8(9)	C(3)–C(4)–C(13)	117.1(11)
C(1)–Mo(1)–C(7)	119.3(5)	Mo(2)–Mo(1)–C(7)	68.4(4)	Mo(2)–C(5)–C(6)	101.1(8)	Mo(2)–C(5)–C(4)	70.2(8)
C(3)–Mo(1)–C(7)	107.5(5)	C(2)–Mo(1)–C(7)	134.2(4)	Mo(2)–C(5)–C(9)	77.1(8)	C(4)–C(5)–C(6)	118.0(10)
Mo(2)–Mo(1)–C(8)	47.8(2)	C(6)–Mo(1)–C(7)	34.0(6)	C(6)–C(5)–C(9)	114.1(11)	C(4)–C(5)–C(9)	122.2(10)
C(2)–Mo(1)–C(8)	122.7(4)	C(1)–Mo(1)–C(8)	93.8(4)	Mo(1)–C(6)–C(7)	72.6(10)	Mo(1)–C(6)–C(5)	95.7(8)
C(6)–Mo(1)–C(8)	61.5(5)	C(3)–Mo(1)–C(8)	114.5(4)	Mo(1)–C(6)–C(14)	127.5(8)	C(5)–C(6)–C(7)	107.3(12)
Mo(1)–Mo(2)–C(1)	53.5(3)	C(7)–Mo(1)–C(8)	32.0(6)	C(7)–C(6)–C(14)	134.7(13)	C(5)–C(6)–C(14)	109.6(11)
C(1)–Mo(2)–C(4)	72.7(4)	Mo(1)–Mo(2)–C(4)	68.2(3)	Mo(1)–C(7)–C(8)	76.1(10)	Mo(1)–C(7)–C(6)	73.3(9)
C(1)–Mo(2)–C(5)	101.4(5)	Mo(1)–Mo(2)–C(5)	68.5(3)	Mo(1)–C(7)–C(15)	126.8(9)	C(6)–C(7)–C(8)	129.5(15)
Mo(1)–Mo(2)–C(8)	54.7(3)	C(4)–Mo(2)–C(5)	36.8(4)	C(8)–C(7)–C(15)	121.4(14)	C(6)–C(7)–C(15)	109.1(14)
C(4)–Mo(2)–C(8)	104.5(5)	C(1)–Mo(2)–C(8)	102.2(4)	Mo(1)–C(8)–C(7)	71.9(10)	Mo(1)–C(8)–Mo(2)	77.5(4)
Mo(1)–Mo(2)–C(9)	99.4(3)	C(5)–Mo(2)–C(8)	76.3(5)	Mo(1)–C(8)–C(16)	125.4(7)	Mo(2)–C(8)–C(7)	114.0(10)
C(4)–Mo(2)–C(9)	65.7(5)	C(1)–Mo(2)–C(9)	137.0(5)	C(7)–C(8)–C(16)	122.3(11)	Mo(2)–C(8)–C(16)	123.2(9)
C(8)–Mo(2)–C(9)	78.7(4)	C(5)–Mo(2)–C(9)	36.2(5)	Mo(3)–C(51)–Mo(4)	76.7(4)	Mo(2)–C(9)–C(5)	66.7(7)
Mo(4)–Mo(3)–C(52)	74.3(3)	Mo(4)–Mo(3)–C(51)	49.6(3)	Mo(4)–C(51)–C(52)	117.6(8)	Mo(3)–C(51)–C(52)	74.2(6)
Mo(4)–Mo(3)–C(53)	74.8(3)	C(51)–Mo(3)–C(52)	36.2(4)	Mo(4)–C(51)–C(60)	123.5(8)	Mo(3)–C(51)–C(60)	127.0(6)
C(52)–Mo(3)–C(53)	34.7(4)	C(51)–Mo(3)–C(53)	62.5(4)	Mo(3)–C(52)–C(51)	69.6(6)	C(52)–C(51)–C(60)	118.1(9)
C(51)–Mo(3)–C(56)	116.7(3)	Mo(4)–Mo(3)–C(56)	75.9(3)	C(51)–C(52)–C(53)	115.7(10)	Mo(3)–C(52)–C(53)	73.1(6)
C(53)–Mo(3)–C(56)	75.7(4)	C(52)–Mo(3)–C(56)	109.0(3)	C(51)–C(52)–C(61)	122.0(11)	Mo(3)–C(52)–C(61)	132.5(7)
C(51)–Mo(3)–C(57)	123.9(4)	Mo(4)–Mo(3)–C(57)	74.3(3)	Mo(3)–C(53)–C(52)	72.2(6)	C(53)–C(52)–C(61)	121.9(12)
C(53)–Mo(3)–C(57)	108.9(4)	C(52)–Mo(3)–C(57)	137.7(3)	C(52)–C(53)–C(54)	115.3(11)	Mo(3)–C(53)–C(54)	96.7(7)
Mo(4)–Mo(3)–C(58)	49.5(3)	C(56)–Mo(3)–C(57)	35.2(4)	C(52)–C(53)–C(62)	122.6(10)	Mo(3)–C(53)–C(62)	126.2(7)
C(52)–Mo(3)–C(58)	123.8(4)	C(51)–Mo(3)–C(58)	94.2(4)	Mo(4)–C(54)–C(53)	102.7(7)	C(54)–C(53)–C(62)	114.9(9)
C(56)–Mo(3)–C(58)	62.8(4)	C(53)–Mo(3)–C(58)	115.4(4)	C(53)–C(54)–C(55)	116.4(8)	Mo(4)–C(54)–C(55)	72.1(7)
C(51)–Mo(4)–C(55)	104.3(4)	C(57)–Mo(3)–C(58)	35.7(5)	C(53)–C(54)–C(63)	124.1(12)	Mo(4)–C(54)–C(63)	112.4(13)
Mo(3)–Mo(4)–C(58)	53.3(3)	C(54)–Mo(4)–C(55)	36.7(4)	Mo(4)–C(55)–C(54)	71.2(7)	C(55)–C(54)–C(63)	115.1(11)
C(54)–Mo(4)–C(58)	103.1(5)	C(51)–Mo(4)–C(58)	101.5(4)	C(54)–C(55)–C(56)	116.7(8)	Mo(4)–C(55)–C(56)	104.8(7)
Mo(3)–Mo(4)–C(59)	98.8(5)	C(55)–Mo(4)–C(58)	74.5(4)	C(54)–C(55)–C(59)	125.8(11)	Mo(4)–C(55)–C(59)	82.1(11)
C(54)–Mo(4)–C(59)	64.5(6)	C(51)–Mo(4)–C(59)	138.7(6)	Mo(3)–C(56)–C(55)	95.9(7)	C(56)–C(55)–C(59)	115.3(10)
C(58)–Mo(4)–C(59)	76.1(5)	C(55)–Mo(4)–C(59)	34.7(6)	C(55)–C(56)–C(57)	111.6(10)	Mo(3)–C(56)–C(57)	73.6(6)
Mo(1)–C(1)–C(2)	75.1(7)	Mo(1)–C(1)–Mo(2)	75.5(3)	C(55)–C(56)–C(64)	117.3(9)	Mo(3)–C(56)–C(64)	126.3(7)
Mo(1)–C(1)–C(10)	125.2(6)	Mo(2)–C(1)–C(2)	116.6(8)	Mo(3)–C(57)–C(56)	71.2(6)	C(57)–C(56)–C(64)	122.6(9)
C(2)–C(1)–C(10)	122.3(10)	Mo(2)–C(1)–C(10)	120.7(9)	C(56)–C(57)–C(58)	114.1(9)	Mo(3)–C(57)–C(58)	67.1(6)
Mo(1)–C(2)–C(3)	72.0(7)	Mo(1)–C(2)–C(1)	69.0(7)	C(56)–C(57)–C(65)	119.1(11)	Mo(3)–C(57)–C(65)	130.3(7)
Mo(1)–C(2)–C(11)	131.7(7)	C(1)–C(2)–C(3)	115.5(12)	Mo(3)–C(58)–Mo(4)	77.1(4)	C(58)–C(57)–C(65)	126.8(11)
C(3)–C(2)–C(11)	123.9(14)	C(1)–C(2)–C(11)	120.4(13)	Mo(4)–C(58)–C(57)	120.0(8)	Mo(3)–C(58)–C(57)	77.2(7)
Mo(1)–C(3)–C(4)	94.9(8)	Mo(1)–C(3)–C(2)	73.4(7)	Mo(4)–C(58)–C(66)	121.4(9)	Mo(3)–C(58)–C(66)	127.2(7)

Table 2 (*continued*)

Mo(4)–C(59)–C(55)	63.2(8)	C(57)–C(58)–C(66)	117.4(9)	S(1)–C(27)–F(2)	113.4(11)	S(1)–C(27)–F(1)	114.4(14)
O(1)–S(1)–O(3)	114.4(6)	O(1)–S(1)–O(2)	114.7(8)	S(1)–C(27)–F(3)	114.0(13)	F(1)–C(27)–F(2)	105.1(13)
O(1)–S(1)–C(27)	104.6(7)	O(2)–S(1)–O(3)	115.4(7)	F(2)–C(27)–F(3)	103.5(16)	F(1)–C(27)–F(3)	105.5(14)
O(3)–S(1)–C(27)	104.8(8)	O(2)–S(1)–C(27)	100.7(8)	S(2)–C(28)–F(5)	116.0(15)	S(2)–C(28)–F(4)	115.3(14)
O(4)–S(2)–O(6)	117.8(8)	O(4)–S(2)–O(5)	110.0(7)	S(2)–C(28)–F(6)	113.7(15)	F(4)–C(28)–F(5)	106.2(18)
O(4)–S(2)–C(28)	102.4(9)	O(5)–S(2)–O(6)	116.9(8)	F(5)–C(28)–F(6)	102.6(16)	F(4)–C(28)–F(6)	101.4(16)
O(6)–S(2)–C(28)	105.2(10)	O(5)–S(2)–C(28)	102.0(8)				

Table 3. Atomic co-ordinates (× 10^4) for complex (**4**)

Atom	*x*	*y*	*z*
Mo(1)	3 511(1)	8 265(1)	4 913(1)
Mo(2)	2 010(1)	8 380(1)	4 308(1)
Mo(3)	8 530(1)	8 218(1)	−170(1)
Mo(4)	7 054(1)	7 959(1)	−700(1)
C(1)	2 650(5)	7 380(5)	4 557(7)
C(2)	3 056(6)	7 249(8)	4 059(8)
C(3)	3 078(6)	7 816(7)	3 551(7)
C(4)	2 410(6)	8 236(6)	3 248(8)
C(5)	2 483(6)	9 002(7)	3 466(7)
C(6)	3 248(5)	9 276(7)	4 147(9)
C(7)	3 151(9)	9 411(9)	4 833(9)
C(8)	2 757(6)	9 094(5)	5 130(7)
C(9)	1 831(7)	9 455(7)	3 401(9)
C(10)	2 574(7)	6 794(6)	5 183(8)
C(11)	3 411(8)	6 476(7)	4 064(10)
C(12)	3 524(8)	7 716(9)	2 937(9)
C(13)	1 760(8)	8 026(8)	2 284(8)
C(14)	3 715(8)	9 636(9)	3 694(10)
C(15)	3 718(9)	10 175(7)	5 362(11)
C(16)	2 758(7)	9 306(7)	6 042(8)
C(17)	698(6)	8 074(8)	3 571(8)
C(18)	715(6)	8 769(8)	3 878(11)
C(19)	1 065(7)	8 758(8)	4 786(9)
C(20)	1 268(7)	8 009(7)	5 034(8)
C(21)	1 017(6)	7 591(7)	4 248(8)
C(22)	4 705(6)	7 702(7)	5 280(10)
C(23)	4 820(5)	8 431(7)	5 347(9)
C(24)	4 625(6)	8 673(8)	5 996(8)
C(25)	4 391(12)	8 100(12)	6 354(13)
C(26)	4 413(8)	7 488(11)	5 892(13)
C(51)	7 587(5)	8 978(6)	−355(6)
C(52)	7 946(5)	9 257(6)	−852(6)
C(53)	7 983(6)	8 796(6)	−1 460(7)
C(54)	7 320(6)	8 271(6)	−1 852(8)
C(55)	7 484(5)	7 496(5)	−1 681(6)
C(56)	8 298(6)	7 292(5)	−1 157(7)
C(57)	8 388(6)	6 955(5)	−386(7)
C(58)	7 928(6)	7 244(6)	−10(7)
C(59)*	6 929(11)	6 917(10)	−1 758(13)
C(59′)	6 972(13)	6 965(12)	−2 329(15)
C(60)	7 498(6)	9 501(6)	343(7)
C(61)	8 213(8)	10 087(6)	−784(9)
C(62)	8 383(8)	9 012(7)	−2 063(8)
C(63)*	6 592(13)	8 448(12)	−2 668(16)
C(63′)	6 600(13)	8 640(12)	−2 149(15)
C(64)	8 796(7)	7 089(7)	−1 658(7)
C(65)	8 963(7)	6 333(6)	−36(8)
C(66)	7 990(8)	6 879(7)	886(7)
C(67)	6 356(6)	7 998(6)	145(7)
C(68)	6 020(6)	8 484(6)	−502(8)
C(69)	5 697(7)	8 110(9)	−1 254(10)
C(70)	5 834(8)	7 365(9)	−1 090(12)
C(71)	6 282(8)	7 293(8)	−189(11)
C(72)	9 406(6)	8 520(7)	1 195(7)
C(73)	9 657(6)	7 878(8)	950(9)
C(74)	9 839(8)	8 030(9)	258(12)
C(75)	9 719(8)	8 735(11)	84(11)
C(76)	9 467(6)	9 056(8)	653(9)
S(1)	338(2)	5 779(2)	2 676(2)
S(2)	4 807(2)	−468(2)	2 026(2)
O(1)	761(6)	5 769(5)	3 573(6)
O(2)	−192(6)	5 260(7)	2 384(8)
O(3)	114(7)	6 480(6)	2 332(7)
O(4)	4 863(7)	210(6)	2 423(7)
O(5)	4 109(6)	−527(7)	1 327(8)
O(6)	5 034(8)	−1 025(7)	2 497(9)
C(27)	974(9)	5 480(8)	2 242(10)
F(1)	1 243(6)	4 838(6)	2 482(7)
F(2)	677(6)	5 455(7)	1 403(6)
F(3)	1 544(8)	5 898(8)	2 416(11)
C(28)	5 436(10)	−368(10)	1 516(12)
F(4)	5 485(7)	−927(7)	1 087(7)
F(5)	5 324(7)	176(7)	1 028(8)
F(6)	6 148(6)	−280(7)	2 055(8)

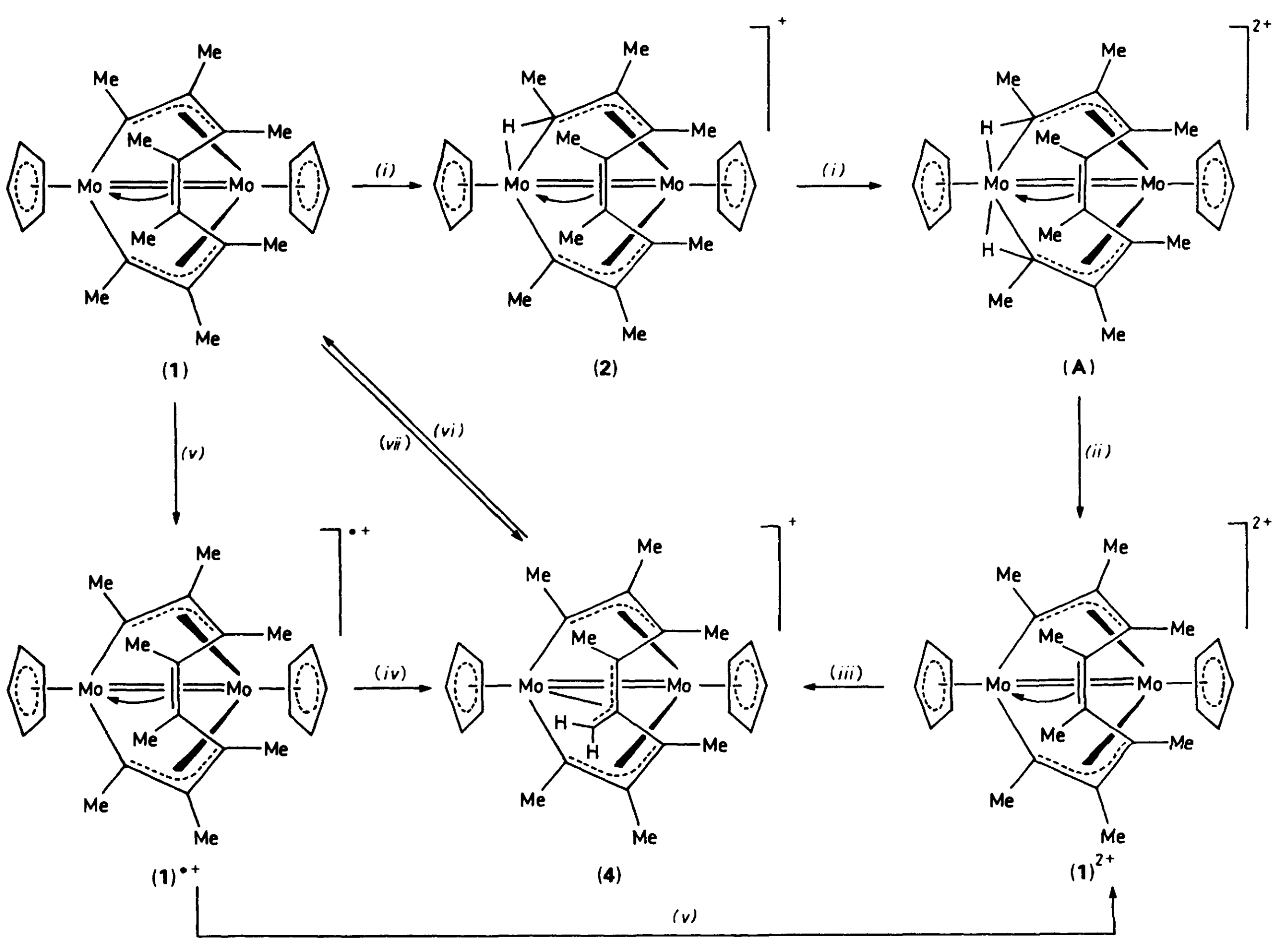
* Atomic site occupancy 0.51(1); primed atoms have occupancy 0.49(1).

(Scheme 2). Protonation of (**9**) with 1 equivalent of $HBF_4{\cdot}Et_2O$ resulted in complex (**10**) containing an agostic CH interaction analogous to that in (**2**). Full details of the preparation and n.m.r. spectroscopic characterisation of (**10**) are reported in ref. 3.

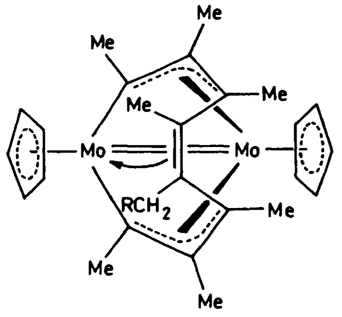
In addition to the reactivity studies carried out on complex (**4**) we have also examined further aspects of the reactivity of (**1**). Treatment of (**1**) with 1 equivalent of the weak oxidising agent $[NPr^n_4][SbCl_6]$ resulted in a quantitative yield of the chloro cationic complex (**11**). The structure of this salt, containing the octachlorodiantimonate dianion and methylene chloride of crystallisation, was established by *X*-ray crystallography. As illustrated in Figure 2, the cation shows the same configuration as the $Mo_2(\mu\text{-}C_8Me_8)$ core of (**1**)^3 with approximate C_s symmetry and the bonding description advanced for (**1**)^3 applies with equal validity to (**11**). The chlorine bridges the Mo–Mo vector preserving the formal double bond found in this class of molecule by acting as a formal, neutral one-electron donor. This is rather unusual since bridging chlorines are normally three-electron donors. The anion resides on a crystallographic inversion centre, each antimony atom being co-ordinated by five chlorine atoms with a square-pyramidal co-ordination geometry sharing one basal edge of the pyramid with the other antimony (Figure 3). We suggest that complex (**11**) is formed by initial one-electron oxidation of (**1**) followed by chlorination (*i.e.* reaction with Cl$^{\bullet}$) of the resulting radical cation, *i.e.* (**1**)$^{\bullet +}$.

A study of the reactivity of (**11**) towards the reagents $K[BHBu^s_3]$ and $Li[CuMe_2]$ resulted in the regeneration of (**1**) as determined by ^1H n.m.r. spectroscopy in both cases.

In addition to the reactions of complexes (**1**) and (**4**) described above, we also examined the protonation of (**3**). Treatment with 1 equivalent of $HBF_4{\cdot}Et_2O$ afforded high yields of the monoprotonated complex (**12**) as its $[BF_4]^-$ salt. Metathesis



Scheme 1. (*i*) $HBF_4{\cdot}Et_2O$ or CF_3SO_3H; (*ii*) $-H_2$; (*iii*) $-H^+$; (*iv*) $Ph_3C^{\cdot}$, $-Ph_3CH$; (*v*) $[Fe(\eta\text{-}C_5H_5)_2]^+$; (*vi*) $K[BHBu^s{}_3]$; (*vii*) $[CPh_3][BF_4]$



	R
(1)	H
(1d)	D
(5)	Me
(6)	Ph
(7)	SMe

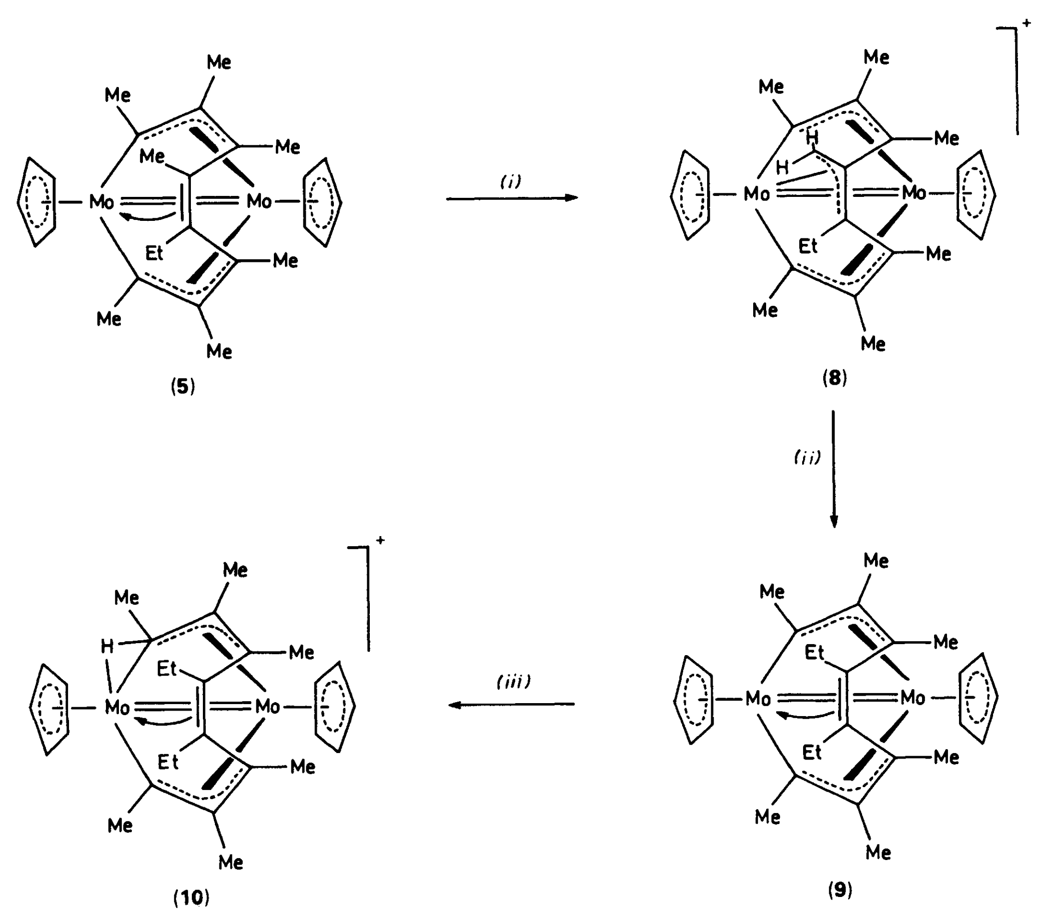
with $Na[BPh_4]$ afforded crystals of the CH_2Cl_2 adduct which was characterised by *X*-ray crystallography, the results of which are shown in Figure 4 with parameters presented in Tables 6 and 7.

The structure of the cation of (**12**) is grossly similar to that of the neutral parent compound (**3**)[4] and a detailed comparison of [Mo(2)–C(5) 2.419(6) Å in (**12**) *vs.* Mo(2)–C(5) 2.293(2) Å in (**3**)[4]]. A similar Mo–C bond lengthening on protonation is observed for (**1**) and (**2**)[3] in which the Mo–C_α bond is bridged. The hydrogen atom, H(5), was directly located and is bonded to both C(5) [C(5)–H(5) 1.10(8) Å] and Mo(2) [Mo(2)–H(5) 1.81(6) Å] and, as such, may be described as agostic.[17]

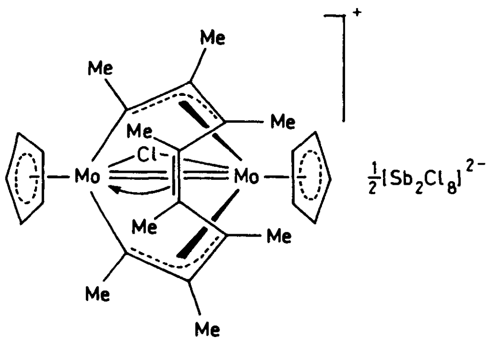
Other consequences of protonation on the geometry of the $Mo_2(\mu\text{-}C_8)$ core of (**12**) [as compared with (**3**)[4]] are notable. The Mo–C distances involving Mo(2) [other than Mo(2)–C(5)] are lengthened [by 0.013(8)—0.061(6) Å] and the Mo(1)–Mo(2) bond length by 0.020(1) Å, presumably as a consequence of increased positive charge on Mo(2). The C(4)–C(5) bond length is markedly lengthened by protonation at C(5) [from 1.432(4) to 1.479(9) Å] but does not reach alkyl proportions (*ca.* 1.54 Å), remaining intermediate between co-ordinated alkene and alkyl values. As in other β-agostic species, the Mo–C(4)–C(5)–H(5) system shows a relatively small deviation from strict planarity [Mo–C(4)–C(5)–H(5) torsion angle = −25(4)°].

Thus the site of protonation in complex (**2**), as revealed by *X*-ray crystallography, is found to be an α-ring carbon whilst that observed in (**12**) is on a δ-ring carbon. Those factors which determine the protonation site of lowest energy are subtle and difficult to gauge, but n.m.r. studies carried out for (**12**) indicate that the proton is fluxional between the α and δ sites as has been observed and discussed in detail for (**2**).[3]

Proton and ^{13}C n.m.r. data obtained at 292 K for complex (**12**) are listed in Table 1, and the variable temperature ^{13}C and ^1H n.m.r. data in Tables 8 and 9 respectively. In view of the more



Scheme 2. (*i*) $[CPh_3][BF_4]$; (*ii*) $Li[CuMe_2]$; (*iii*) $HBF_4 \cdot Et_2O$



(11)

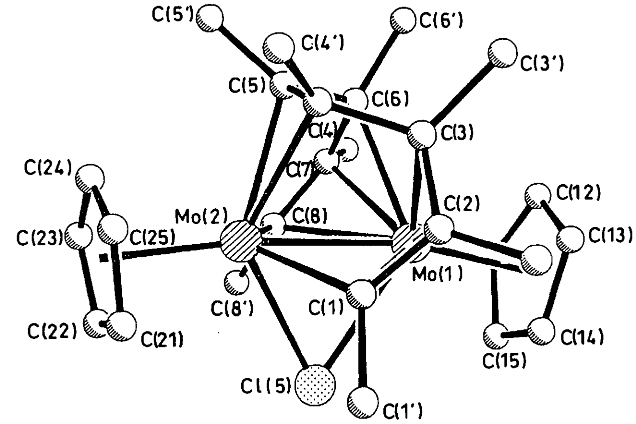


Figure 2. A view of the molecular structure of complex (**11**) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity

analysis of the variation in ^{13}C chemical shifts was attempted [*cf.* (**2**) for which such analyses were carried out, making use of simplifying assumptions made possible by the symmetry of the C_8Me_8 ligand]. Nevertheless, several qualitative points emerge from these data when taken together with the observed $^1J_{CH}$ data involving H(5) {at 292 K, *J*[C(5)H(5)] = 45, *J*[C(8)H(5)] < 20, and *J*[C(6)H(5)] and *J*[C(7)H(5)] < 5 Hz}. It is clear that, as in (**2**), (**12**) consists of an equilibrium mixture of two isomers in solution and equilibration remains fast on the n.m.r. time-scale above 223 K. The two isomers have H(5) directly bonded to a δ carbon, C(5), as in the solid-state structure, and to an α carbon, C(8), respectively. In both isomers this hydrogen is further co-ordinated in an agostic manner to Mo(2). The observed coupling constants and chemical shifts are therefore time averages weighted according to the concentrations of the two isomers. In contrast to (**2**), the δ-protonated isomer of (**12**) is the higher-concentration species at all temperatures {*cf.* $^1J_{CH}$ values for (**2**) are *J*[C(5)H] = 24 and *J*[C(8)H] = 48 Hz}. As in (**2**) the effect of protonation is to cause an upfield change on the carbon atom's chemical shift. The ^{13}C chemical shifts of all C(1)—C(8) are temperature dependent (Table 8) but those of C(5) and C(8) most notably so, as observed for (**2**). The temperature dependence of the chemical shifts of C(5) and C(8) are in the same sense as for (**2**) with that for the δ carbon, C(5), falling with decreased temperature and that for the α carbon, C(8), rising. The quantitative analysis applied to the variable-temperature ^{13}C n.m.r. data for complex (**2**) revealed that the temperature dependence of the equilibrium position led to the α-protonated isomer predominating

Table 4. Selected bond lengths (Å) and angles (°) for complex (**11**)

Sb–Cl(1)	2.364(4)	Sb–Cl(2)	2.979(3)	Mo(2)–C(5)	2.362(12)	Cl(6)–C(99)	1.707(21)
Sb–Cl(3)	2.422(3)	Sb–Cl(4)	2 530(4)	Cl(7)–C(99)	1.832(19)	C(11)–C(12)	1.420(23)
Sb–Cl(2^{I})	2.749(4)	Mo(1)–Mo(2)	2.625(2)	C(11)–C(15)	1.391(19)	C(12)–C(13)	1.390(20)
Mo(1)–Mo(3)	2.623(20)	Mo(1)–Cl(5)	2.533(4)	C(13)–C(14)	1.414(21)	C(14)–C(15)	1.392(19)
Mo(1)–C(11)	2.352(17)	Mo(1)–C(12)	2.340(15)	C(21)–C(22)	1.460(28)	C(21)–C(25)	1.359(26)
Mo(1)–C(13)	2.322(15)	Mo(1)–C(14)	2.323(14)	C(22)–C(23)	1.315(31)	C(23)–C(24)	1.288(29)
Mo(1)–C(15)	2.362(17)	Mo(1)–C(1)	2.347(12)	C(24)–C(25)	1.338(22)	C(1)–C(2)	1.383(17)
Mo(1)–C(2)	2.420(14)	Mo(1)–C(3)	2.392(15)	C(1)–C(1′)	1.517(16)	C(2)–C(3)	1.399(18)
Mo(1)–C(8)	2.408(12)	Mo(1)–C(7)	2.425(11)	C(2)–C(2′)	1.507(17)	C(3)–C(4)	1.491(19)
Mo(1)–C(6)	2.387(13)	Mo(2)–Cl(5)	2.585(5)	C(3)–C(3′)	1.544(17)	C(4)–C(5)	1.396(18)
Mo(2)–C(21)	2.291(17)	Mo(2)–C(22)	2.346(20)	C(4)–C(4′)	1.533(23)	C(8)–C(7)	1.379(15)
Mo(2)–C(23)	2.360(16)	Mo(2)–C(24)	2.317(20)	C(8)–C(8′)	1.539(20)	C(7)–C(6)	1.410(21)
Mo(2)–C(25)	2.338(17)	Mo(2)–C(1)	2.153(12)	C(7)–C(7′)	1.492(20)	C(6)–C(5)	1.544(21)
Mo(2)–C(4)	2.353(14)	Mo(2)–C(8)	2.180(13)	C(6)–C(6′)	1.505(16)	C(5)–C(5′)	1.509(19)
Cl(1)–Sb–Cl(2)	79.8(1)	Cl(1)–Sb–Cl(3)	90.6(1)	Mo(1)–Cl(5)–Mo(2)	61.7(1)	Mo(1)–C(1)–Mo(2)	71.2(3)
Cl(2)–Sb–Cl(3)	169.8(1)	Cl(1)–Sb–Cl(4)	92.3(1)	Mo(2)–C(1)–Mo(3)	27.7(1)	Mo(1)–C(1)–C(2)	76.0(7)
Cl(2)–Sb–Cl(4)	93.7(1)	Cl(3)–Sb–Cl(4)	90.2(1)	Mo(2)–C(1)–C(2)	118.3(8)	Mo(1)–C(1)–C(1′)	131.2(10)
Cl(1)–Sb–Cl(2^{I})	86.4(1)	Cl(2)–Sb–Cl(2^{I})	87.4(1)	Mo(2)–C(1)–C(1′)	123.1(9)	C(2)–C(1)–C(1′)	118.0(11)
Cl(3)–Sb–Cl(2^{I})	88.5(1)	Cl(4)–Sb–Cl(2^{I})	178.1(1)	Mo(1)–C(2)–C(1)	70.3(7)	Mo(1)–C(2)–C(3)	72.0(8)
Mo(2)–Mo(1)–Cl(5)	60.1(1)	Mo(2)–Mo(1)–Cl(1)	51.0(3)	C(1)–C(2)–C(3)	113.3(11)	Mo(1)–C(2)–C(2′)	127.8(11)
Cl(5)–Mo(1)–C(1)	66.4(3)	Mo(2)–Mo(1)–C(2)	74.6(3)	C(1)–C(2)–C(2′)	121.8(11)	C(3)–C(2)–C(2′)	124.8(11)
Cl(5)–Mo(1)–C(2)	98.9(3)	C(1)–Mo(1)–C(2)	33.7(4)	Mo(1)–C(3)–C(2)	74.2(9)	Mo(1)–C(3)–C(4)	98.4(9)
Mo(2)–Mo(1)–C(3)	73.9(3)	Cl(5)–Mo(1)–C(3)	123.1(3)	C(2)–C(3)–C(4)	116.1(10)	Mo(1)–C(3)–C(3′)	121.8(9)
C(1)–Mo(1)–C(3)	58.7(4)	C(2)–Mo(1)–C(3)	33.8(4)	C(2)–C(3)–C(3′)	120.9(11)	C(4)–C(3)–C(3′)	116.3(11)
Mo(2)–Mo(1)–C(8)	51.1(3)	Cl(5)–Mo(1)–C(8)	66.1(3)	Mo(2)–C(4)–C(3)	101.2(9)	Mo(2)–C(4)–C(5)	73.1(8)
C(1)–Mo(1)–C(8)	100.8(4)	C(2)–Mo(1)–C(8)	124.5(5)	C(3)–C(4)–C(5)	116.8(12)	Mo(2)–C(4)–C(4′)	119.2(8)
C(3)–Mo(1)–C(8)	109.4(5)	Mo(2)–Mo(1)–C(7)	75.4(3)	C(3)–C(4)–C(4′)	112.1(11)	C(5)–C(4)–C(4′)	125.5(13)
Cl(5)–Mo(1)–C(7)	97.5(3)	C(1)–Mo(1)–C(7)	125.5(5)	Mo(1)–C(8)–Mo(2)	69.6(3)	Mo(1)–C(8)–C(7)	74.1(7)
C(2)–Mo(1)–C(7)	132.0(5)	C(3)–Mo(1)–C(7)	101.6(5)	Mo(2)–C(8)–C(7)	119.0(10)	Mo(1)–C(8)–C(8′)	128.4(9)
C(8)–Mo(1)–C(7)	33.1(4)	Mo(2)–Mo(1)–C(6)	75.3(3)	Mo(2)–C(8)–C(8′)	122.9(8)	C(7)–C(8)–C(8′)	118.1(11)
Cl(5)–Mo(1)–C(6)	122.9(3)	C(1)–Mo(1)–C(6)	111.4(5)	Mo(1)–C(7)–C(8)	72.8(7)	Mo(1)–C(7)–C(6)	71.5(7)
C(2)–Mo(1)–C(6)	101.7(5)	C(3)–Mo(1)–C(6)	68.8(5)	C(8)–C(7)–C(6)	113.7(12)	Mo(1)–C(7)–C(7′)	128.6(10)
C(8)–Mo(1)–C(6)	58.3(4)	C(7)–Mo(1)–C(6)	34.1(5)	C(8)–C(7)–C(7′)	123.7(12)	C(6)–C(7)–C(7′)	122.4(10)
Mo(1)–Mo(2)–Cl(5)	58.2(1)	Mo(1)–Mo(2)–C(1)	57.8(3)	Mo(1)–C(6)–C(7)	74.4(7)	Mo(1)–C(6)–C(5)	97.8(7)
Cl(5)–Mo(2)–C(1)	68.1(4)	Mo(1)–Mo(2)–C(4)	73.8(4)	C(7)–C(6)–C(5)	113.6(11)	Mo(1)–C(6)–C(6′)	129.5(9)
Cl(5)–Mo(2)–C(4)	129.4(4)	C(1)–Mo(2)–C(4)	73.8(5)	C(7)–C(6)–C(6′)	121.7(12)	C(5)–C(6)–C(6′)	113.3(3)
Mo(1)–Mo(2)–C(8)	59.3(3)	Cl(5)–Mo(2)–C(8)	68.4(4)	Mo(2)–C(5)–C(4)	72.4(7)	Mo(2)–C(5)–C(6)	101.4(8)
C(1)–Mo(2)–C(8)	115.5(5)	C(4)–Mo(2)–C(8)	101.5(4)	C(4)–C(5)–C(6)	114.1(11)	Mo(2)–C(5)–C(5′)	119.9(8)
Mo(1)–Mo(2)–C(5)	74.1(3)	Cl(5)–Mo(2)–C(5)	128.9(4)	C(4)–C(5)–C(5′)	125.7(14)	C(6)–C(5)–C(5′)	113.9(10)
C(1)–Mo(2)–C(5)	102.7(4)	C(4)–Mo(2)–C(5)	34.4(4)	Cl(6)–C(99)–Cl(7)	110.2(8)	Cl(2)–Sb^{I}–Cl(2^{I})	87.4(1)
C(8)–Mo(2)–C(5)	72.3(5)	Sb–Cl(2)–Sb^{I}	92.6(1)	Sb–Cl(2^{I})–Sb^{I}	92.6(1)		

Symmetry operation: I $1 - x, 3 - y, -z$.

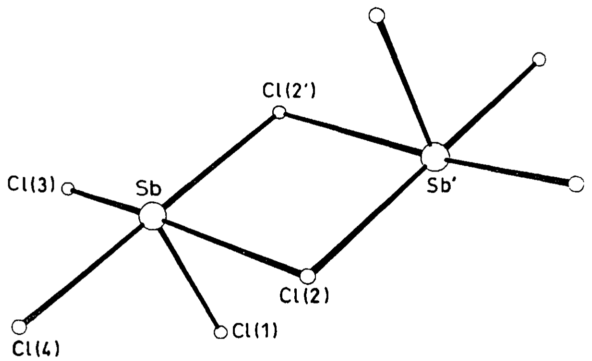
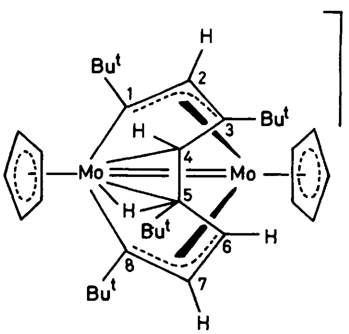


Figure 3. A view of the molecular structure of the $[Sb_2Cl_8]^{2-}$ dianion of (**11**)



(**12**)

increasingly at higher temperatures, despite the δ-protonated isomer being of lower enthalpy. In the case of (**12**) the δ-protonated isomer is predominant at all temperatures by virtue of an increased enthalpy difference (in favour of δ protonation) between the isomers. This predominance is sufficient to allow isolation and characterisation of (**12**) in the solid state as the δ-protonated isomer, thereby supporting the postulate made in ref. 3 that δ- and α-protonated isomers of (**2**) exist in equilibrium.

Experimental

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry oxygen-free dinitrogen. All solvents were distilled over suitable drying agents immediately prior to use.

Proton and ^{13}C n.m.r. spectra were recorded on JEOL

Table 5. Atomic co-ordinates (× 10^4) for complex (**11**)

Atom	*x*	*y*	*z*
Sb	4 519(1)	15 824(1)	843(1)
Mo(1)	4 430(1)	10 272(1)	2 741(1)
Mo(2)	5 797(1)	11 625(1)	2 957(1)
Mo(3)*	5 519(17)	11 775(15)	3 455(14)
Cl(1)	3 720(3)	14 278(2)	890(2)
Cl(2)	3 882(3)	15 325(3)	−929(2)
Cl(3)	4 999(4)	15 912(3)	2 319(2)
Cl(4)	3 037(3)	16 847(3)	802(2)
Cl(5)	4 801(3)	11 402(3)	3 989(2)
Cl(6)	1 566(4)	9 289(4)	−497(3)
Cl(7)	−296(4)	8 510(4)	−485(3)
C(11)	2 787(12)	9 942(11)	2 502(8)
C(12)	3 178(11)	9 193(11)	2 091(9)
C(13)	3 829(12)	8 640(11)	2 685(10)
C(14)	3 860(10)	9 043(9)	3 461(7)
C(15)	3 199(11)	9 828(10)	3 337(9)
C(21)	7 098(15)	12 298(14)	3 890(8)
C(22)	6 383(16)	13 100(15)	3 687(14)
C(23)	6 333(15)	13 303(11)	2 921(11)
C(24)	6 872(14)	12 727(13)	2 628(9)
C(25)	7 394(12)	12 123(12)	3 212(10)
C(1)	6 023(9)	10 166(9)	3 540(7)
C(2)	5 904(10)	9 315(9)	3 050(8)
C(3)	5 641(10)	9 536(10)	2 216(7)
C(4)	6 043(10)	10 486(10)	1 973(7)
C(8)	4 308(9)	12 050(9)	2 428(7)
C(7)	3 787(10)	11 565(9)	1 731(7)
C(6)	4 331(11)	10 887(9)	1 403(7)
C(5)	5 387(10)	11 206(9)	1 556(7)
C(1′)	6 446(11)	10 031(11)	4 452(7)
C(2′)	6 083(12)	8 267(9)	3 407(8)
C(3′)	5 415(11)	8 683(9)	1 573(7)
C(4′)	7 057(11)	10 337(11)	1 890(8)
C(8′)	3 808(11)	12 879(10)	2 793(8)
C(7′)	2 766(12)	11 798(10)	1 312(8)
C(6′)	3 925(11)	10 386(10)	588(7)
C(5′)	5 555(12)	11 959(10)	945(7)
C(99)	962(15)	8 661(14)	82(9)

* Atomic site occupancy 0.061(3).

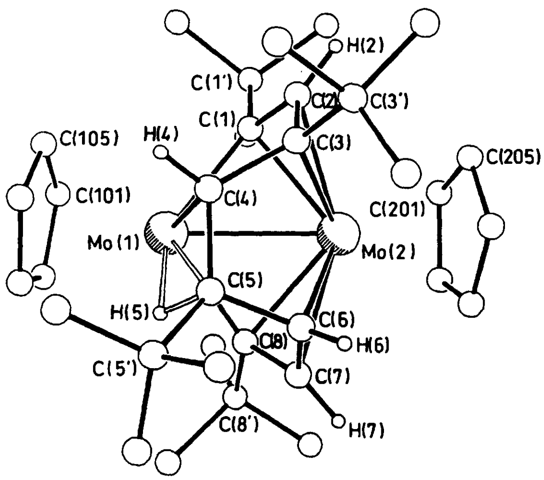


Figure 4. A view of the molecular structure of complex (**12**) showing the atom numbering scheme. Methyl and cyclopentadienyl hydrogens are omitted for clarity

FX90Q, FX200, and Varian XL300 spectrometers as appropriate and are recorded in Table 1.

Preparations.—$[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2][CF_3SO_3]$, (**4**). *Method A, double protonation.* To a solution of complex

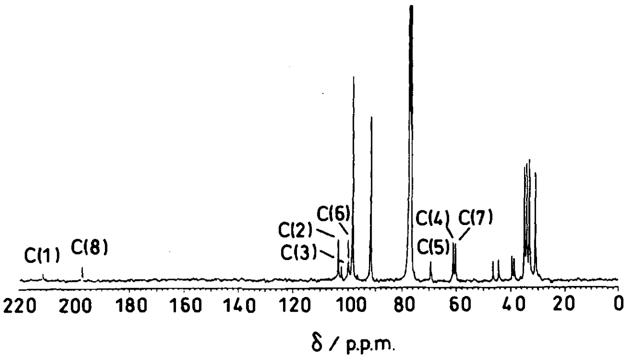


Figure 5. Proton-decoupled ^{13}C n.m.r. spectrum of complex (**12**) measured at 292 K

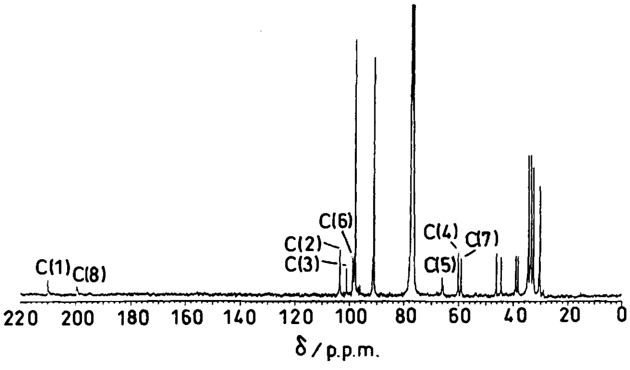


Figure 6. Proton-decoupled ^{13}C n.m.r. spectrum of complex (**12**) measured at 223 K

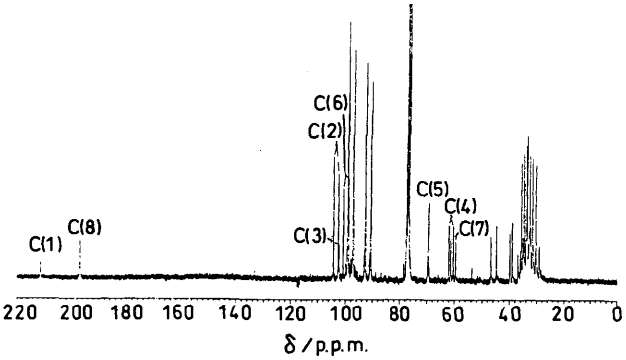


Figure 7. Proton-coupled ^{13}C n.m.r. spectrum of complex (**12**) with selective irradiation of H(5) (−10.81 p.p.m.) measured at 292 K

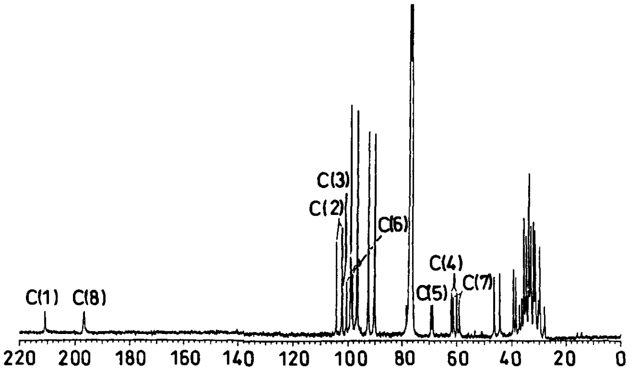


Figure 8. Fully proton-coupled ^{13}C n.m.r. spectrum of complex (**12**) measured at 292 K

Table 6. Selected bond lengths (Å) and angles (°) for complex (**12**)

Mo(1)–Mo(2)	2.659(1)	Mo(1)–C(1)	2.251(5)	C(5′)–C(53)	1.560(13)	C(6)–C(7)	1.422(10)
Mo(1)–C(2)	2.310(6)	Mo(1)–C(3)	2.381(6)	C(7)–C(8)	1 425(9)	C(8)–C(8′)	1.569(9)
Mo(1)–C(6)	2.253(7)	Mo(1)–C(7)	2.270(7)	C(8′)–C(81)	1.522(11)	C(8′)–C(82)	1.539(12)
Mo(1)–C(8)	2.293(7)	Mo(1)–C(101)	2.421(7)	C(8′)–C(83)	1.517(11)	C(201)–C(202)	1.419(10)
Mo(1)–C(102)	2.398(8)	Mo(1)–C(103)	2.355(8)	C(201)–C(205)	1.389(11)	C(202)–C(203)	1.384(10)
Mo(1)–C(104)	2.351(7)	Mo(1)–C(105)	2.392(7)	C(203)–C(204)	1.390(11)	C(204)–C(205)	1.413(10)
Mo(1)–C(106)	2.343(9)	Mo(1)–C(107)	2.326(9)	B–C(301)	1.625(11)	B–C(401)	1.665(8)
Mo(1)–C(108)	2.356(10)	Mo(1)–C(109)	2.392(11)	B–C(501)	1.660(10)	B–C(601)	1.662(9)
Mo(1)–C(110)	2.384(10)	Mo(2)–C(1)	2.173(6)	C(301)–C(302)	1.411(8)	C(301)–C(306)	1.407(9)
Mo(2)–C(4)	2.226(7)	Mo(2)–C(5)	2.419(6)	C(302)–C(303)	1.391(11)	C(303)–C(304)	1.374(10)
Mo(2)–C(8)	2.178(6)	Mo(2)–H(5)	1.81(6)	C(304)–C(305)	1.374(9)	C(305)–C(306)	1.390(10)
H(5)–C(5)	1.10(8)	Mo(2)–C(201)	2.392(6)	C(401)–C(402)	1.399(9)	C(401)–C(406)	1.415(8)
Mo(2)–C(202)	2.388(6)	Mo(2)–C(203)	2.377(7)	C(402)–C(403)	1.386(9)	C(403)–C(404)	1.368(10)
Mo(2)–C(204)	2.368(7)	Mo(2)–C(205)	2.394(8)	C(404)–C(405)	1.398(11)	C(405)–C(406)	1.383(9)
C(1)–C(1′)	1.537(8)	C(1)–C(2)	1.422(9)	C(501)–C(502)	1.398(10)	C(501)–C(506)	1.390(10)
C(1′)–C(11)	1.531(9)	C(1′)–C(12)	1.549(11)	C(502)–C(503)	1.399(10)	C(503)–C(504)	1.362(12)
C(1′)–C(13)	1.524(9)	C(2)–C(3)	1.434(9)	C(504)–C(505)	1.373(13)	C(505)–C(506)	1.407(11)
C(3)–C(3′)	1.562(10)	C(3)–C(4)	1.464(11)	C(601)–C(602)	1.388(8)	C(601)–C(606)	1.392(10)
C(3′)–C(31)	1.512(11)	C(3′)–C(32)	1.539(14)	C(602)–C(603)	1.409(8)	C(603)–C(604)	1.364(10)
C(3′)–C(33)	1.539(12)	C(4)–C(5)	1.479(9)	C(604)–C(605)	1.417(11)	C(605)–C(606)	1.377(10)
C(5)–C(5′)	1.569(10)	C(5)–C(6)	1.503(9)	C–Cl(1)	1.680(11)	C–Cl(2)	1.678(14)
C(5′)–C(51)	1.521(11)	C(5′)–C(52)	1.478(14)	C′–Cl(1)	1.679(18)	C′–Cl(2′)	1.679(25)

Mo(2)–Mo(1)–C(1)	51.7(2)	Mo(2)–Mo(1)–C(2)	73.0(2)	C(2)–C(3)–C(3′)	119.7(6)	Mo(1)–C(3)–C(4)	94.4(4)
C(1)–Mo(1)–C(2)	36.3(2)	Mo(2)–Mo(1)–C(3)	72.7(2)	C(2)–C(3)–C(4)	113.5(6)	C(3′)–C(3)–C(4)	117.8(6)
C(1)–Mo(1)–C(3)	64.5(2)	C(2)–Mo(1)–C(3)	35.6(2)	C(3)–C(3′)–C(31)	113.3(6)	C(3)–C(3′)–C(32)	111.3(7)
Mo(2)–Mo(1)–C(6)	74.6(2)	C(1)–Mo(1)–C(6)	117.9(2)	C(31)–C(3′)–C(32)	109.6(7)	C(3)–C(3′)–C(33)	106.7(7)
C(2)–Mo(1)–C(6)	106.5(2)	C(3)–Mo(1)–C(6)	72.3(2)	C(31)–C(3′)–C(33)	109.7(7)	C(32)–C(3′)–C(33)	106.0(7)
Mo(2)–Mo(1)–C(7)	74.5(2)	C(1)–Mo(1)–C(7)	126.0(2)	Mo(2)–C(4)–C(3)	106.7(4)	Mo(2)–C(4)–C(5)	78.7(4)
C(2)–Mo(1)–C(7)	136.9(2)	C(3)–Mo(1)–C(7)	107.0(2)	C(3)–C(4)–C(5)	118.7(6)	Mo(2)–C(5)–C(4)	64.4(3)
C(6)–Mo(1)–C(7)	36.6(2)	Mo(2)–Mo(1)–C(8)	51.5(1)	Mo(2)–C(5)–C(5′)	131.9(5)	C(4)–C(5)–C(5′)	126.0(6)
C(1)–Mo(1)–C(8)	96.1(2)	C(2)–Mo(1)–C(8)	124.5(2)	Mo(2)–C(5)–C(6)	96.7(4)	C(4)–C(5)–C(6)	110.5(6)
C(3)–Mo(1)–C(8)	115.8(2)	C(6)–Mo(1)–C(8)	65.1(2)	C(5′)–C(5)–C(6)	115.8(5)	C(5)–C(5′)–C(51)	113.5(6)
C(7)–Mo(1)–C(8)	36.4(2)	Mo(1)–Mo(2)–C(1)	54.4(1)	C(5)–C(5′)–C(52)	109.5(7)	C(4)–C(5)–H(5)	102(3)
Mo(1)–Mo(2)–C(4)	71.9(2)	C(1)–Mo(2)–C(4)	79.7(2)	Mo(2)–C(5)–H(5)	45(3)	C(5′)–C(5)–H(5)	91(4)
Mo(1)–Mo(2)–C(5)	72.4(2)	C(1)–Mo(2)–C(5)	108.1(2)	C(6)–C(5)–H(5)	106(4)	C(51)–C(5′)–C(52)	110.7(8)
C(4)–Mo(2)–C(5)	36.8(2)	Mo(1)–Mo(2)–C(8)	55.5(2)	C(5)–C(5′)–C(53)	108.6(7)	C(51)–C(5′)–C(53)	104.9(7)
C(1)–Mo(2)–C(8)	101.9(2)	C(4)–Mo(2)–C(8)	107.0(2)	C(52)–C(5′)–C(53)	109.4(7)	Mo(1)–C(6)–C(5)	104.4(4)
C(5)–Mo(2)–C(8)	78.5(2)	Mo(1)–C(1)–Mo(2)	73.9(2)	Mo(1)–C(6)–C(7)	72.3(4)	C(5)–C(6)–C(7)	116.4(6)
Mo(1)–C(1)–C(1′)	129.1(4)	Mo(2)–C(1)–C(1′)	130.2(4)	Mo(1)–C(7)–C(6)	71.0(4)	Mo(1)–C(7)–C(8)	72.7(4)
Mo(1)–C(1)–C(2)	74.1(3)	Mo(2)–C(1)–C(2)	109.7(4)	C(6)–C(7)–C(8)	118.6(5)	Mo(1)–C(8)–Mo(2)	72.9(2)
C(1′)–C(1)–C(2)	118.7(6)	C(1)–C(1′)–C(11)	110.6(5)	Mo(1)–C(8)–C(7)	70.9(4)	Mo(2)–C(8)–C(7)	111.0(4)
C(1)–C(1′)–C(12)	113.1(6)	C(11)–C(1′)–C(12)	105.5(6)	Mo(1)–C(8)–C(8′)	136.0(5)	Mo(2)–C(8)–C(8′)	129.0(5)
C(1)–C(1′)–C(13)	110.9(5)	C(11)–C(1′)–C(13)	109.1(6)	C(7)–C(8)–C(8′)	117.9(5)	C(8)–C(8′)–C(81)	112.4(6)
C(12)–C(1′)–C(13)	107.5(6)	Mo(1)–C(2)–C(1)	69.6(3)	C(8)–C(8′)–C(82)	106.5(5)	C(81)–C(8′)–C(82)	105.3(6)
Mo(1)–C(2)–C(3)	74.9(3)	C(1)–C(2)–C(3)	120.1(6)	C(8)–C(8′)–C(83)	112.0(5)	C(81)–C(8′)–C(83)	109.2(6)
Mo(1)–C(3)–C(2)	69.5(3)	Mo(1)–C(3)–C(3′)	132.3(4)	C(82)–C(8′)–C(83)	111.4(7)	Mo(2)–H(5)–C(5)	110(5)

(**1**)[3,*] (0.5 g, 0.93 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C, an excess of freshly distilled CF_3SO_3H (0.1 cm^3) was added dropwise with continuous stirring. After 12 h, pentane (10 cm^3) was added to the reaction mixture resulting in the separation of a dark purple oil. All solvents were then removed by syringe and Et_2O (10 cm^3) was added to the purple oil in which most of it dissolves. Further addition of pentane resulted in the precipitation of a purple powder leaving the excess of CF_3SO_3H in solution. Further washing in Et_2O and pentane produced (**4**) as a purple crystalline powder (0.45 g, 70% yield) (Found: C, 47.1; H, 4.8. $C_{27}H_{33}F_3Mo_2O_3S$ requires C, 47.2; H, 4.8%). Crystals suitable for *X*-ray diffraction were obtained by solvent diffusion of Et_2O into a CH_2Cl_2 solution of (**4**) at −30 °C over a period of days.

Method B, reaction with ferrocenium cation. A suspension of $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ (0.26 g, 0.93 mmol) in CH_2Cl_2 (5 cm^3) was added to a stirred (−78 °C) solution of complex (**1**) (0.25 g, 0.46 mmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was allowed to warm to room temperature and after 12 h diethyl ether (5 cm^3) was added resulting in the precipitation of the purple crystalline material (**4**) (BF_4 salt) (0.20 g, 85%), which was identified by comparison of the n.m.r. spectra.

Method C, reaction with $[CPh_3][BF_4]$. Trityl tetrafluoroborate (0.31 g, 0.93 mmol) was added to a stirred (room temperature) solution of complex (**1**) (0.50 g, 0.93 mmol) in CH_2Cl_2 (15 cm^3). After 24 h diethyl ether (10 cm^3) was added resulting in a purple crystalline precipitate of (**4**) (BF_4 salt) (0.41 g, 80%) which was washed with further diethyl ether (10 cm^3) and dried under vacuum.

$[Mo_2(\mu\text{-}C_8Me_7Et)(\eta\text{-}C_5H_5)_2]$, (**5**). A freshly prepared solution of $Li[CuMe_2]$ (0.3 mmol) in Et_2O (10 cm^3) was added to a solution of complex (**4**) (0.15 g, 0.272 mmol) in CH_2Cl_2 (10 cm^3) at −78 °C. After stirring for 30 min the solvent was removed *in vacuo* and the crude product dissolved in Et_2O (20 cm^3). After filtration through alumina to remove all particulate matter the Et_2O was removed *in vacuo* and the product dissolved in the minimum of hexane. Purification by

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[*] An alternative and higher yield preparation of (**1**), compared to that reported in ref. 3, involves magnesium amalgam reduction of $[Mo(NCMe)(\eta\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$; C. J. Schaverien, unpublished work.

Table 7. Atomic co-ordinates (× 10^4) for complex (**12**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	2 990(1)	2 725(1)	2 553(1)	C(201)	2 652(5)	−640(4)	2 421(6)
Mo(2)	2 277(1)	1 084(1)	2 178(1)	C(202)	2 502(5)	−594(4)	1 306(6)
C(1)	3 624(4)	1 194(4)	1 801(4)	C(203)	1 607(5)	−175(5)	1 109(6)
C(1′)	4 542(4)	558(5)	2 082(5)	C(204)	1 193(5)	42(4)	2 076(6)
C(11)	4 657(5)	−471(5)	1 409(6)	C(205)	1 841(5)	−254(4)	2 895(6)
C(12)	5 350(5)	1 013(6)	1 846(7)	B	7 646(5)	2 814(5)	4 898(6)
C(13)	4 637(5)	425(5)	3 263(5)	C(301)	6 870(4)	2 545(4)	5 555(5)
C(2)	3 566(5)	1 827(5)	997(5)	C(302)	6 610(5)	3 102(4)	6 541(5)
C(3)	2 709(5)	2 384(4)	669(4)	C(303)	5 871(5)	2 999(5)	7 066(6)
C(3′)	2 648(6)	3 040(5)	−251(6)	C(304)	5 350(5)	2 316(5)	6 622(6)
C(31)	2 002(7)	4 024(6)	−56(7)	C(305)	5 588(5)	1 730(5)	5 678(5)
C(32)	3 582(7)	3 229(7)	−459(8)	C(306)	6 326(4)	1 840(5)	5 157(5)
C(33)	2 333(9)	2 423(8)	−1 278(6)	C(401)	8 065(4)	1 824(4)	4 048(5)
C(4)	1 952(5)	1 887(5)	751(4)	C(402)	7 638(4)	1 593(5)	3 045(5)
C(5)	1 217(5)	2 403(4)	1 442(5)	C(403)	7 951(5)	736(5)	2 364(6)
C(5′)	180(5)	2 525(5)	1 128(6)	C(404)	8 708(5)	77(5)	2 631(7)
C(51)	−67(6)	1 672(6)	328(7)	C(405)	9 161(5)	285(5)	3 623(6)
C(52)	−323(7)	2 652(9)	2 104(9)	C(406)	8 850(4)	1 138(5)	4 306(6)
C(53)	−115(7)	3 471(7)	547(10)	C(501)	8 466(4)	3 174(4)	5 726(5)
C(6)	1 508(5)	3 256(4)	2 179(5)	C(502)	8 912(4)	3 945(5)	5 609(6)
C(7)	1 628(5)	3 146(5)	3 284(5)	C(503)	9 601(5)	4 214(5)	6 334(7)
C(8)	2 048(4)	2 199(5)	3 582(5)	C(504)	9 871(5)	3 722(6)	7 198(7)
C(8′)	2 048(5)	2 043(5)	4 785(5)	C(505)	9 461(6)	2 948(6)	7 335(7)
C(81)	2 115(7)	2 992(7)	5 546(6)	C(506)	8 758(5)	2 688(5)	6 616(6)
C(82)	1 117(5)	1 813(6)	4 939(6)	C(601)	7 161(4)	3 710(4)	4 175(5)
C(83)	2 802(6)	1 212(7)	5 084(6)	C(602)	6 266(4)	4 183(4)	4 247(5)
C(101)[a]	4 402(4)	3 120(5)	3 369(6)	C(603)	5 859(4)	4 951(4)	3 644(5)
C(102)[a]	4 230	3 530	2 390	C(604)	6 351(5)	5 263(5)	2 950(5)
C(103)[a]	3 426	4 259	2 469	C(605)	7 268(6)	4 802(5)	2 851(6)
C(104)[a]	3 102	4 299	3 497	C(606)	7 630(5)	4 042(5)	3 444(5)
C(105)[a]	3 705	3 596	4 054	C[c]	7 049(7)	3 107(13)	10 569(5)
C(106)[b]	3 202(6)	4 007(7)	3 927(6)	C′[d]	6 477(11)	4 026(19)	9 666(28)
C(107)[b]	4 045	3 360	3 763	Cl(1)	7 478(2)	3 278(3)	9 444(4)
C(108)[b]	4 301	3 428	2 727	Cl(2)[c]	6 039(4)	2 764(5)	10 333(5)
C(109)[b]	3 617	4 117	2 251	Cl(2′)[d]	5 462(8)	4 385(15)	10 183(13)
C(110)[b]	2 937	4 475	2 993				

[a] Atomic site occupancy 0.55(1). [b] Atomic site occupancy 0.45(1). [c] Atomic site occupancy 0.68(1). [d] Atomic site occupancy 0.32(1).

Table 8. Variation in ^{13}C n.m.r. chemical shifts with temperature for complex (**12**)*

T	C(1)	C(8)	C(2)	C(3)	C(6)	C(5)	C(4)	C(7)	C_5H_5 (A)	C_5H_5 (B)
292	211.2	197.0	103.5	102.4	99.8	69.3	61.0	60.2	98.2	91.6
273	210.6	197.5	103.3	101.8	99.3	68.2	60.5	59.7	97.9	91.3
253	210.4	198.2	103.4	101.5	99.1	67.3	60.3	59.4	97.9	91.2
233	210.2	199.1	103.5	101.2	98.9	66.4	60.2	59.1	98.0	91.2
223	210.0	199.6	103.6	101.1	98.8	66.0	60.1	59.0	98.0	91.2
	−1.2	**2.6**	+ −0.1	−1.3	−1.0	**−3.3**	−0.9	−1.2	−0.2	−0.4

* The signals for C(8) and C(5) broaden as the temperature is lowered and show the largest change in chemical shift.

Table 9. Variation in ^1H n.m.r. chemical shifts with temperature for complex (**12**)

T	H(2)	H(4)	H(6)	H(7)	H(5)	$CHCl_3$
293	7.15	2.29	7.45	4.89	−10.81	7.23
273	7.14	2.28	7.43	4.85	−10.85	7.23
253	7.13	2.27	7.42	4.80	−10.89	7.23
233	7.12	2.26	7.41	4.76	−10.93	7.23
218	7.11	2.25	7.39	4.72	−10.96	7.24
	−0.04	−0.04	−0.06	−0.17	−0.15	0.00

* Negative denotes a shift to high field (low frequency) as temperature is lowered. One ^1H–^1H coupling varies measurably with temperature, namely $^4J[H(6)H(5)]$ = 3.0 (293), 2.4 (273), 1.8 (253), 1.2 (233), and < 1.0 Hz (218 K). Measured T_1 for H(5) is 0.35(2) s.

column chromatography (alumina/hexane) afforded a purple solution of complex (**5**). Reduction of the solvent volume and cooling to −78 °C afforded pure (**5**) as purple crystals (Found: C, 58.6; H, 6.6. $C_{27}H_{36}Mo_2$ requires C, 58.7; H, 6.5%). Mass spectrum: *m*/*z* 552, *P*.

Compound (**6**) was prepared in an analogous manner using Li[$CuPh_2$] (yield 74%) (Found: C, 62.8; H, 6.1. $C_{31}H_{36}Mo_2$ requires C, 62.5; H, 6.2%). Mass spectrum: *m*/*z* 614, *P*.

[Mo_2(μ-$C_8Me_7CH_2SMe$)(η-C_5H_5)$_2$], (**7**). A solution of Me_2S_2 (0.1 g, 0.106 mmol) was reduced over a sodium amalgam in tetrahydrofuran (thf) (10 cm^3) by stirring overnight. A fraction of the resulting solution of Na[SMe] (2 cm^3) was added to a suspension of complex (**4**) (0.1 g, 0.146 mmol) in thf (10 cm^3) and the mixture was stirred at room temperature for 12 h. The thf was removed *in vacuo* and the resulting purple residue was dissolved in Et_2O (5 cm^3) and purified by low-temperature column chromatography (alumina/Et_2O) which afforded a purple solution. Removal of the solvent *in vacuo* followed by recrystallisation (−78 °C) from hexane afforded purple crystals

Table 10. Structure analyses of compounds (**4**), (**11**), and (**12**)*

Crystal data	(**4**)	(**11**)	(**12**)
Formula	$C_{27}H_{33}F_3Mo_2O_3S$	$C_{27}H_{36}Cl_7Mo_2Sb$	$C_{59}H_{73}BCl_2Mo_2$
M	686.5	922.4	1 055.8
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group (no.)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	19.251(9)	14.549(7)	15.149(4)
b/Å	18.078(8)	13.231(4)	13.793(3)
c/Å	16.963(8)	17.040(4)	12.660(2)
α/°	90	90	98.37(2)
β/°	113.79(4)	105.95(3)	94.90(2)
γ/°	90	90	78.72(2)
U/Å^3	5 402(4)	3 154(2)	2 562(1)
T/K	295	205	205
Z	8	4	2
D_c/g cm^{-3}	1.69	1.94	1.37
F(000)	2 768	1 808	1 200
μ(Mo-K_α)/cm^{-1}	10.3	22.4	6.2
Data collection and reduction			
Crystal dimensions (mm)	0.7 × 0.45 × 0.3	*ca.* 0.4 diameter	0.6 × 0.25 × 0.2
2θ range (°)	3—50	3—40	4—56
Scan width, ω °	$1.0 + \Delta\alpha_1\alpha_2$	$1.0 + \Delta\alpha_1\alpha_2$	$1.2 + \Delta\alpha_1\alpha_2$
Total data	7 087	3 504	7 962
Unique data	5 573	2 544	7 522
'Observed' data (N_O)	5 159	2 493	6 407
Observation criterion [$F^2 > n\sigma(F^2)$]	2	2	2.5
No. azimuthal scan data	213	—	—
Min., max. transmission coefficients	0.584, 0.683	—	—
Refinement			
Disordered atoms	C(59), C(63)	[partial occupancy Mo(3)]	C_5H_5 on Mo(1), CH_2Cl_2
Least-squares variables (N_V)	648	333	619
R	0.058	0.059	0.053
R'	0.065	0.076	0.067
S	2.04	3.06	1.58
g	0.0002	0.000 22	0.0008
Final difference map features (e Å^{-3})	+1.2, −0.6	+1.6, −1.2	+1.1, −1.4

* Details in common: λ(Mo-K_α) 0.710 69 Å; scan method, ω—2θ; $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_O - N_V)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$; $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$; $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics.

of complex (**7**) (0.07 g, 78%) (Found: C, 54.5; H, 6.5. $C_{27}H_{36}Mo_2S$ requires C, 55.5; H, 6.2%).

[$Mo_2(\mu$-$C_8Me_6EtCH_2)(\eta$-$C_5H_5)_2$][BF_4], (**8**). Trityl tetrafluoroborate (0.31 g, 0.93 mmol) was added to a stirred (room temperature) solution of complex (**5**) (0.51 g, 0.93 mmol) in CH_2Cl_2 (15 cm^3). After 24 h diethyl ether (10 cm^3) was added and the resulting purple precipitate collected. Recrystallisation (0 °C) from CH_2Cl_2–Et_2O (1:2) afforded purple crystals of complex (**8**) (0.51 g, 86%) (Found: C, 50.2; H, 5.1. $C_{27}H_{35}BF_4Mo_2$ requires C, 50.8; H, 5.5%).

[$Mo_2(\mu$-$C_8Me_6Et_2)(\eta$-$C_5H_5)_2$], (**9**). This was prepared and purified in a manner identical to the preparation of complex (**5**) from (**4**) (yield 79%) (Found: C, 60.0; H, 6.7. $C_{28}H_{38}Mo_2$ requires C, 60.4; H, 6.8%). Mass spectrum: *m*/*z* 566, *P*.

[$Mo_2(\mu$-$C_8Me_8)(\mu$-Cl$)(\eta$-$C_5H_5)_2$][$SbCl_4$], (**11**). A solution of complex (**1**) (0.2 g, 0.372 mmol) was dissolved in Et_2O (15 cm^3) and cooled to −78 °C. To this a solution of [NPr^n_4][$SbCl_6$] (0.19 g, 0.370 mmol) in CH_2Cl_2 (5 cm^3) was slowly added with continuous stirring, resulting in the immediate formation of a red-brown precipitate of (**11**). The mother-liquor was removed by syringe and the solid product washed with Et_2O (3 × 10 cm^3). Crystallisation by solvent diffusion of Et_2O (10 cm^3) into a CH_2Cl_2 (2 cm^3) solution of complex (**11**) at −30 °C over a period of days afforded crystals suitable for *X*-ray diffraction (yield 48%) (Found: C, 35.0; H, 4.1. $C_{26}H_{34}Cl_4Mo_2Sb{\cdot}CH_2Cl_2$ requires C, 36.6; H, 4.1%). The low observed carbon value is attributed to slow loss of solvent from the crystals.

[$Mo_2(\mu$-$C_8H_4Bu^t_4)(\mu_{Mo,C}$-H$)(\eta$-$C_5H_5)_2$][BF_4], (**12**). To a solution of [$Mo_2(\mu$-$C_8H_4Bu^t_4)(\eta$-$C_5H_5)_2$] (0.4 g, 0.62 mmol) in ether (5 cm^3) an excess of $HBF_4{\cdot}Et_2O$ (0.5 cm^3) was added dropwise and the solution stirred. Stirring was continued for 2—3 h at room temperature after which time the ether was removed *in vacuo* giving a purple oily residue. Further washings with fresh ether (3 × 10 cm^3) were carried out to remove excess of $HBF_4{\cdot}Et_2O$ resulting in a purple powder. Recrystallisation by solvent diffusion of Et_2O (10 cm^3) into a CH_2Cl_2 (3 cm^3) solution of complex (**12**) gave purple crystals of [$Mo_2(\mu$-$C_8H_4Bu^t_4)(\mu_{Mo,C}$-H$)(\eta$-$C_5H_5)_2$][BF_4] (0.3 g, 65% yield).

Crystals suitable for *X*-ray diffraction were obtained by metathesis with Na[BPh_4]. Equimolar quantities of [$Mo_2(\mu$-$C_8H_4Bu^t_4)(\mu_{Mo,C}$-H$)(\eta$-$C_5H_5)_2$][BF_4] and Na[BPh_4] were dissolved in 90% CH_2Cl_2–10% MeOH over which an equivalent volume of Et_2O was layered. Slow diffusion at −20 °C produced crystals of [$Mo_2(\mu$-$C_8H_4Bu^t_4)(\mu_{Mo,C}$-H$)(\eta$-$C_5H_5)_2$][BPh_4]${\cdot}CH_2Cl_2$.

N.M.R. Spectroscopic Studies for Complex (**12**).—All n.m.r. spectra for complex (**12**) as its BF_4 salt were recorded on a Varian XL 300 spectrometer using the pulse Fourier-transform technique at 299.92, 75.42, and 19.55 MHz for ^1H, ^{13}C, and ^{95}Mo respectively. Proton n.m.r. data were collected for samples dissolved in degassed $CDCl_3$ (*ca.* 0.2 mol dm^{-3}) and contained in tubes (outside diameter 5 mm) rotated at *ca.* 20 Hz, ^{13}C and ^{95}Mo data were obtained from similar solutions ($CDCl_3$, *ca.* 0.2 mol dm^{-3}) in tubes (outside diameter 10 mm) rotated at *ca.* 15 Hz. The ^1H and ^{13}C chemical shifts are reported downfield of $SiMe_4$ while the ^{95}Mo spectrum is referenced externally to a 2 mol dm^{-3} solution of $Na_2[MoO_4]$ in D_2O at apparent pH 11.

The two-dimensional ^1H—^{13}C chemical shift correlation was acquired using the following parameters: ^{13}C 90° pulse, 18 μs; ^1H 90° pulse, 27 μs; 128 transients; 128 increments; spectral widths 6 000 × 2 200 Hz; Fourier-transform size, 1 024 × 512 points; total experiment time, *ca.* 14 h.

X-Ray Crystallographic Studies.—Structure determinations for complexes **(4)** (CF_3SO_3 *salt*), **(11)** ($SbCl_4$ *salt*)·CH_2Cl_2, *and* **(12)** (BPh_4 *salt*)·CH_2Cl_2. Many of the details of the structure analyses carried out are listed in Table 10. *X*-Ray diffraction measurements were made using Nicolet four-circle P3m diffractometers on single crystals mounted in thin-walled glass capillaries. For **(11)** and **(12)** data were collected at reduced temperature using a Nicolet LT-1 crystal-cooling device. Cell dimensions for each analysis were determined from the setting-angle values of 15 centred reflections.

For each structure analysis, intensity data were collected by ω—2θ scans for unique portions of reciprocal space and corrected for Lorentz, polarisation, crystal decay (of *ca.* 0, 40, and 0% respectively), and long-term intensity fluctuations, on the basis of the intensities of three check reflections repeatedly measured during data collection. Corrections for *X*-ray absorption effects were applied for complex **(4)** only. For **(11)** crystal decomposition prevented both measurement of the crystal faces (and therefore absorption correction) and any useful data collection for $2\theta > 40°$. Only those reflections with pre-scan counts above a low threshold of 20 counts s^{-1} and having $2\theta > 40°$ were measured for **(12)** and above 30 counts s^{-1} (for all 2θ) were measured for **(4)**. The structures were solved by heavy-atom (Patterson and difference Fourier) methods, and refined by blocked-cascade least squares against *F*. For **(12)** one cyclopentadienyl ring [on Mo(1)] showed a two-site disorder, as did the dichloromethane solvent. In **(4)** there are two crystallographically distinct cations, one of which displays disorder affecting atoms C(59) and C(63), corresponding to atoms C(9) and C(13) in Figure 1. These atoms adopt two conformations: one of occupancy 0.51(1) in which C(59) is bonded to Mo(4) (*i.e.* is a methylene carbon), and one of occupancy 0.49(1) in which C(63′) is bonded to Mo(4). In complex **(11)** there is evidence of a second, low-occupancy, site for Mo(2), labelled Mo(3), which may be associated with the product of crystal decomposition. Although some sign of carbon-atom sites correspond to a molecule centred around Mo(1) and Mo(3) was observed in difference Fourier maps, no satisfactory model could be developed for those sites.

All non-hydrogen atoms were assigned anisotropic displacement parameters with the exception of the disordered carbons C(101)—C(110) of complex **(12)**, the disordered methyl/methylene carbons C(59), C(59′), C(63), and C(63′) of **(4)**, and C(11) and the low-occupancy Mo(3) of **(11)**. All hydrogen atoms were constrained to ideal geometries (with C–H 0.96 Å) except H(2,4-7) of **(12)** for which the C–H distances of H(2,4,6,7) were restrained to be close to 0.96 Å and H(5) not constrained at all. All hydrogen atoms were assigned fixed isotropic displacement parameters. Positional constraints were applied to the disordered cyclopentadienyl carbons of **(12)** (C–C 1.42 Å) and the C–Cl distances of the disordered dichloromethane in **(12)**.

Final difference syntheses showed no chemically significant features, the largest being close to the metal, solvent, or anion atoms. Refinements converged smoothly to residuals given in Table 10. All calculations were made with programs of the SHELXTL[18] system as implemented on a Nicolet R3m/E structure-determination system. Complex neutral-atom scattering factors were taken from ref. 19.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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