Reactions of Co-ordinated Ligands. Part 55.[1] Molybdenum-mediated Addition of Alkynes to Cyclooctatetraene; One-electron Oxidation and Protonation of η^3-Allyl(η^4-1,3-diene)-(η-cyclopentadienyl or η^5-indenyl) Molybdenum Complexes, and Crystal Structures of $[Mo(\eta^3,\eta^4-C_{12}H_{13})(\eta-C_5H_5)]$, $[Mo(\eta^2,\eta^4-C_{14}H_{17})(\eta-C_5H_5)][BF_4]$ and $[Mo(\eta^2,\eta^4-C_{12}H_{13})-(\mu_{Mo,C}-H)(\eta^5-C_9H_7)][CF_3SO_3]$ *

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Reaction of $[Mo(NCMe)(\eta^2-MeC_2Me)_2(\eta-C_5H_5)][BF_4]$ with cyclooctatetraene (cot) in acetonitrile in the presence of the proton scavenger Na_2CO_3 affords the neutral complex $[Mo(\eta^3,\eta^4-C_{12}H_{13})(\eta-C_5H_5)]$ **1**. Analogous reactions between cot and $[Mo(NCMe)(\eta^2-EtC_2Et)_2(\eta-C_5H_5)][BF_4]$, $[Mo(NCMe)(\eta^2-MeC_2Me)_2(\eta^5-C_9H_7)][BF_4]$ and $[Mo(NCMe)(\eta^2-EtC_2Et)_2(\eta^5-C_9H_7)][BF_4]$ give $[Mo(\eta^3,\eta^4-C_{14}H_{17})(\eta-C_5H_5)]$ **2**, $[Mo(\eta^3,\eta^4-C_{12}H_{13})(\eta^5-C_9H_7)]$ **3**, and $[Mo(\eta^3,\eta^4-C_{14}H_{17})(\eta^5-C_9H_7)]$ **4** in good yield. A single-crystal X-ray diffraction study on **1** established the presence of an unusual bicyclo[4.2.2]decane ligand, to which a $Mo(\eta-C_5H_5)$ fragment is η^3,η^4-bonded. Although this structure suggests that these complexes are formed *via* a $(6 + 2)\pi$ addition reaction, it is proposed that a stepwise process is involved. The chemical reactivity of the complexes **1**–**4** has been explored. Reaction of **1** or **3** with $[CPh_3][BF_4]$ affords respectively the cations $[Mo(\eta^4,\eta^4-C_{12}H_{12})(\eta-C_5H_5)][BF_4]$ **7** and $[Mo(\eta^4,\eta^4-C_{12}H_{12})(\eta^5-C_9H_7)][BF_4]$ **8**. Reaction of these bis(1,3-diene) cations with the nucleophiles 'H^-' and 'Ph^-' leads to regioselective attack on the *exo*-η^4-1,3-diene moiety. Treatment of **1**, **2** and **3** with $AgBF_4$ leads to a one-electron oxidation reaction and formation of the 17-electron species $[Mo(C_{12}H_{13})(\eta-C_5H_5)][BF_4]$ **10**, $[Mo(C_{14}H_{17})(\eta-C_5H_5)][BF_4]$ **11**, and $[Mo(C_{12}H_{13})(\eta^5-C_9H_7)[BF_4]$ **12**. A single crystal X-ray diffraction study on **11** indicates the absence of agostic $Mo(\mu-H)C$ interactions, the radical cation being best described as a carbon-centred radical η^2,η^4-bonded to a 16-electron cationic molybdenum centre. Finally, the protonation of **1**–**4** has been studied, being shown to afford cationic species which adopt different structures in the solid state and in solution. An X-ray crystallographic study on $[Mo(\eta^6-C_{12}H_{13})(\mu_{Mo,C}-H)(\eta^5-C_9H_7)][CF_3SO_3]$, which is formed on reaction of **3** with CF_3SO_3H, established the presence of an agostic $Mo(\mu-H)C$ interaction between a carbon–hydrogen bond β to an alkene moiety, representing an arrested 1,3-hydrogen shift of the type postulated in the initial stage of a metal-assisted isomerisation of an alkene.

A small group of transition-metal-centred reactions have been identified[2–7] which can lead to the formation of 1,3-dienes by addition of an alkene C–H bond to an alkyne. These reactions probably involve the initial oxidative coupling of a co-ordinated alkyne and alkene to form a metallacyclopent-2-ene, which then rearranges *via* a 1,3-hydrogen shift process to give a co-ordinated 1,3-diene. For example, we observed[3] that $[Mo(\eta^2-MeC_2Me)_2(CO)(\eta-C_5H_5)][BF_4]$ reacts with *o*-diphenylphosphinostyrene (dpps) to form $Mo(\eta^3\text{-dpps})(\eta^2-MeC_2Me)(\eta-C_5H_5)][BF_4]$, which on refluxing in MeCN forms $[Mo(NCMe)\{\eta^4\text{-MeCH=C(Me)CH=CHC}_6H_4PPh_2\text{-}o\}(\eta-C_5H_5)][BF_4]$. In seeking to understand this and apparently related reactions we treated the labile complexes $[Mo(NCMe)(\eta^2-MeC_2Me)_2(\eta-C_5H_5)][BF_4]$,[8] $[MoX(\eta^2-MeC_2Me)_2(\eta^5-C_9H_7)]$[9] (X = halide) and $[Mo(\eta^2-MeC_2Me)_2(CO)(\eta-C_5H_5)][BF_4]$[8] with cyclooctatetraene, a molecule which shows versatility in the range of its bonding modes with metal centres. This paper reports our detailed findings, and a study of the reactivity of the new complexes obtained.

Results and Discussion

In preliminary studies[10] we found that the but-2-yne complex $[Mo(NCMe)(\eta^2-MeC_2Me)_2(\eta-C_5H_5)][BF_4]$ reacted in refluxing acetonitrile with cyclooctatetraene (cot) to give a neutral rather than the expected cationic molybdenum complex. The formation of a neutral complex suggested that elimination of HBF_4 had occurred, and therefore with this in mind the proton scavenger anhydrous Na_2CO_3 was added to the reaction mixture. This resulted in an enhanced yield (31 to 79%) of **1**, which was isolated as a bright yellow air-stable crystalline material by column chromatography of the reaction mixture.

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Elemental analysis, NMR and mass spectral data suggested that an unusual reaction had occurred, and that **1** had the molecular formula [Mo($C_{12}H_{13}$)(η-C_5H_5)]. Similar reactions also occurred between cot and [Mo(NCMe)(η^2-EtC$_2$Et)$_2$(η-C_5H_5)][BF$_4$], [Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η^5-C_9H_7)[BF$_4$] and [Mo(NCMe)(η^2-EtC$_2$Et)$_2$(η^5-C_9H_7)][BF$_4$] to give respectively the fully characterised (analysis, NMR and mass spectra) crystalline complexes [Mo($C_{14}H_{17}$)(η-C_5H_5)] **2**, [Mo($C_{12}H_{13}$)(η^5-C_9H_7)] **3**, and [Mo($C_{14}H_{17}$)(η^5-C_9H_7)] **4** in good yield. It was also found that the more reactive (η^5 to η^3 slippage) indenyl-substituted cation [Mo(η^2-MeC$_2$Me)$_2$(CO)(η^5-C_9H_7)][BF$_4$] afforded **3** directly on reaction with cot in refluxing acetonitrile in the presence of anhydrous Na_2CO_3.

The neutral adduct [Mo($C_{12}H_{13}$)(η^5-C_9H_7)] **3** is also formed when [MoBr(η^2-MeC$_2$Me)$_2$(η^5-C_9H_7)] or [MoI(η^2-MeC$_2$Me)$_2$(η^5-C_9H_7)][9] are refluxed with cyclooctatetraene in tetrahydrofuran (thf) for several hours. A higher yield of **3** (48 compared with 28%) was obtained from the reaction of cot with the iodo-complex, an indication that the molybdenum–iodine bond is more labile than the molybdenum–bromine bond. Interestingly, when a solution of [MoBr(η^2-MeC$_2$Me)$_2$(η^5-C_9H_7)] in dichloromethane was treated with AgBF$_4$ and cot at room temperature a partial conversion (39%) into **3** was observed.

Examination of the ^{1}H and ^{13}C NMR spectra of compounds **1**–**4** revealed that the methyl and ethyl alkyne substituents originally present in the starting materials were no longer intact, and in order firmly to establish the structural identities of these adducts a single-crystal X-ray diffraction study on **1** was carried out. This established the unusual structure illustrated in Fig. 1, selected bond lengths and angles being listed in Table 1. Compound **1** contains a η^3,η^4-bonded bicyclic $C_{12}H_{13}$ moiety, and at first sight a likely mode of formation is (6 + 2)π addition of the co-ordinated but-2-yne to the cot followed by proton loss and a hydrogen-transfer process. Within the asymmetric η^3-allyl, which is present in the former cot ring, the distance from the molybdenum to the central carbon, Mo–C(13), is 2.235(5) Å while the distances from molybdenum to the outer carbons C(12) and C(6) are longer at 2.315(7) and 2.265(7) Å respectively. This arrangement is typical[11] of allyl complexes, which either show this pattern or have no significant differences in the molybdenum–carbon distances. The C–C distances within the η^3-allyl moiety, C(6)–C(13) and C(13)–C(12), are 1.421(10) and 1.403(10) Å respectively. These are similar to distances which have been observed in other molybdenum–allyl systems. There is obviously some distortion from sp^2 hybridisation at C(13), indicated by an increase in the bond angle C(6)–C(13)–C(12) to 130.5(6)°. The η^4-1,3-diene, formed from the four carbon atoms of the but-2-yne, is typical[11] of known co-ordinated diene systems. The four molybdenum–carbon distances are similar, Mo–C(14), Mo–C(15), Mo–C(16) and Mo–C(17) being 2.266(8), 2.284(7), 2.287(7) and 2.244(7) Å respectively. Carbon–carbon distances C(14)–C(15) and C(16)–C(17) are 1.424(11) and 1.439(10) Å while the central bond, C(15)–C(16) is shorter, at 1.371(10) Å, as expected. The distance C(9)–C(10) is 1.320(11) Å, indicative of a normal double bond.

Having established the structure of compound **1** by crystallography, assignment of the complex NMR spectra of **1**–**4** was much simplified. Selective decoupling and two-dimensional NMR techniques, correlation spectroscopy (COSY) and CH correlation, were used to establish the couplings and assignments listed in the Experimental section. One point of specific interest is the proton spectrum of **1** and of the η^5-indenyl analogue **3**. The spectra are broadly similar with differences in shifts of less than 0.01 ppm for most of the protons, with two notable exceptions. All the protons of the co-ordinated 1,3-diene are shifted, the *syn* protons downfield by approximately 0.4 ppm, but more significantly the *anti* protons are shifted upfield by nearly 1.5 ppm, to δ −0.59 and −0.93 for **3**. There is, surprisingly, no shift of the central allyl proton on the replacement of η-C_5H_5 by η^5-C_9H_7, a change which has been observed[12] to produce an upfield shift of about 4.0 ppm in other *exo*-allyl systems.

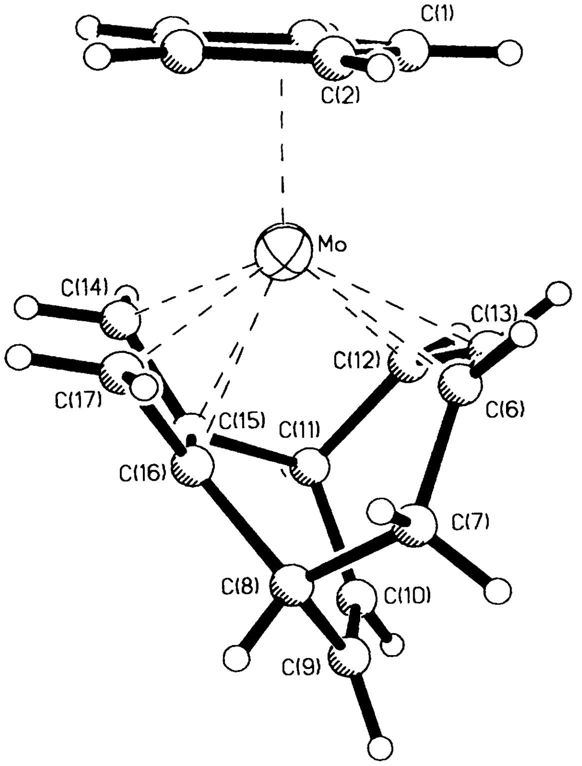
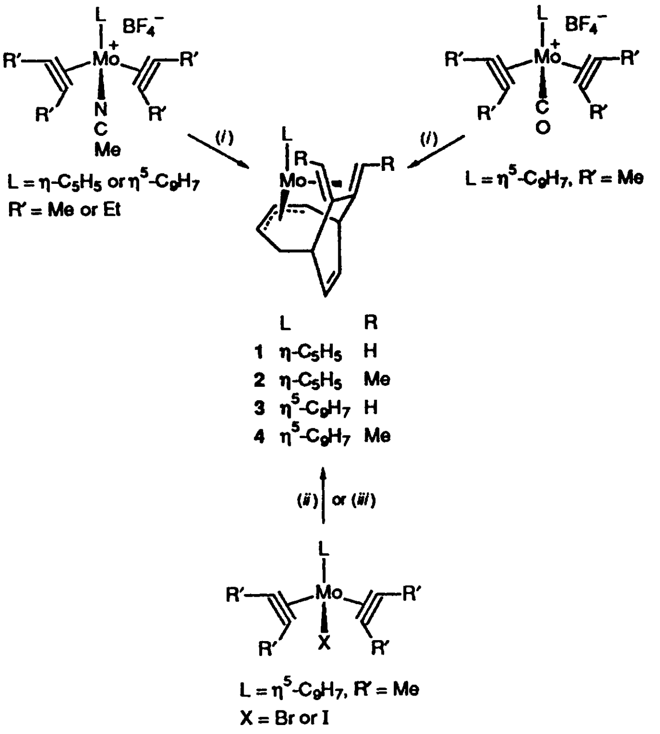


Fig. 1 Molecular structure of compound **1** showing labelling scheme

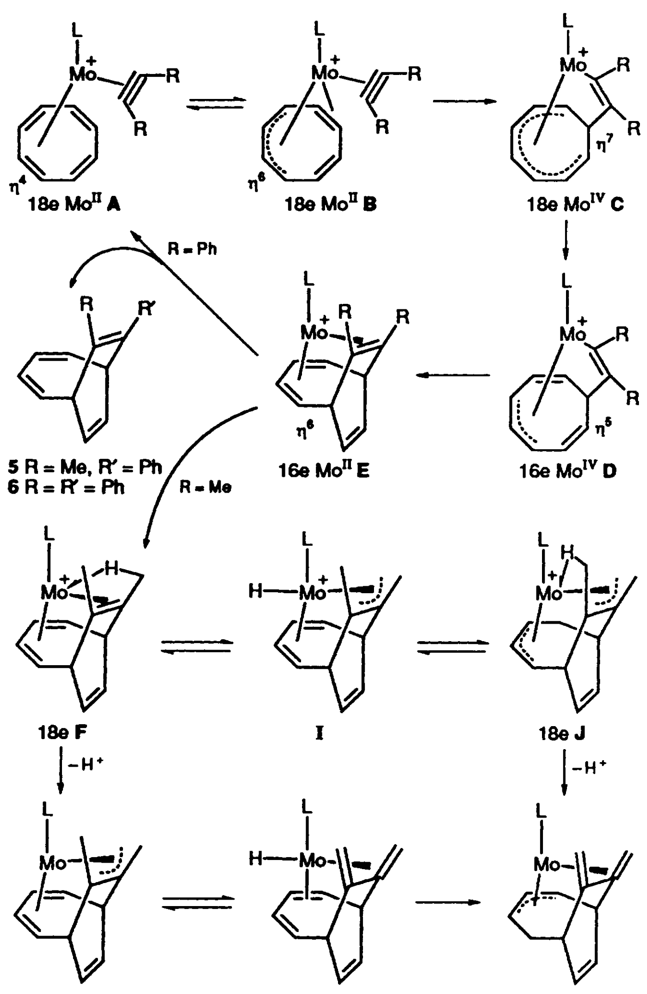
Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Mo–C(1)	2.262(7)	Mo–C(2)	2.286(8)
Mo–C(3)	2.326(9)	Mo–C(4)	2.360(8)
Mo–C(5)	2.299(8)	Mo–C(6)	2.265(7)
Mo–C(12)	2.315(7)	Mo–C(13)	2.235(5)
Mo–C(14)	2.266(8)	Mo–C(15)	2.284(7)
Mo–C(16)	2.287(7)	Mo–C(17)	2.244(7)
C(1)–C(2)	1.426(11)	C(1)–C(5)	1.394(11)
C(2)–C(3)	1.407(12)	C(3)–C(4)	1.371(14)
C(4)–C(5)	1.424(12)	C(6)–C(7)	1.515(10)
C(6)–C(13)	1.421(10)	C(8)–C(9)	1.492(11)
C(7)–C(8)	1.487(11)	C(9)–C(10)	1.320(11)
C(8)–C(16)	1.534(10)	C(11)–C(12)	1.522(10)
C(10)–C(11)	1.493(11)	C(15)–C(16)	1.371(10)
C(11)–C(15)	1.549(11)		
C(12)–C(13)	1.403(10)		
C(14)–C(15)	1.424(11)		
C(16)–C(17)	1.439(10)		
C(7)–C(6)–C(13)	131.5(6)	C(6)–C(7)–C(8)	111.2(6)
C(7)–C(8)–C(9)	111.0(6)	C(7)–C(8)–C(16)	107.0(6)
C(9)–C(8)–C(16)	113.9(6)	C(8)–C(9)–C(10)	122.8(7)
C(9)–C(10)–C(11)	121.3(7)	C(10)–C(11)–C(12)	114.2(6)
C(10)–C(11)–C(15)	109.4(6)	C(12)–C(11)–C(15)	100.1(6)
C(11)–C(12)–C(13)	126.6(6)	C(6)–C(13)–C(12)	130.5(6)
C(11)–C(15)–C(14)	115.7(7)	C(8)–C(16)–C(15)	118.0(6)
C(11)–C(15)–C(16)	119.4(6)	C(8)–C(16)–C(17)	122.6(6)
C(14)–C(15)–C(16)	117.2(6)	C(15)–C(16)–C(17)	118.4(6)

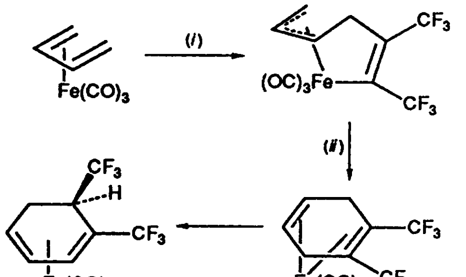
Thus, as summarised in Scheme 1 the η^3,η^4-C_{12} bicyclic ligand is accessed from cyclooctatetraene and a variety of labile bis(alkyne) complexes. Although the structures **1**–**4** might suggest a concerted thermally forbidden (6 + 2)π cycloaddition between cot and η^2-alkyne, followed by a hydrogen shift process, we believe the formation of **1**–**4** involves a stepwise process, unlike Pettit and co-workers[3] who have proposed



Scheme 1 (*i*) + C_8H_8, Na_2CO_3; (*ii*) + C_8H_8; (*iii*) + C_8H_8, $AgBF_4$, CH_2Cl_2



Scheme 2

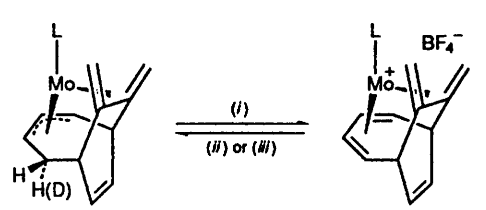


Scheme 3 (*i*) UV, $CF_3C_2CF_3$; (*ii*) heat

that the facile reaction of $C_2(CO_2Me)_2$ with $[Fe(CO)_3(\eta^4\text{-}1,3\text{-}C_8H_8)]$ involves a concerted (6 + 2)π cycloaddition.

In the case of the reaction between, for example, $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ and cyclooctatetraene it is likely that initially MeCN and MeC_2Me are displaced to form the cation **A** illustrated in Scheme 2. This supported by the observation[8] that phosphites or phosphines rapidly react with $[Mo(NCMe)(\eta^2\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ to give the cations $[MoL_2(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$ [L = PR_3 or $P(OR)_3$]. Since both cot and alkynes can readily switch their bonding modes, it is reasonable to expect that **A** could reversibly transform into **B** *via* a change in the bonding mode of the co-ordinated cot from η^4 to η^6, and the alkyne from a 4e to a 2e donor. Oxidative coupling of the 2e donor alkyne present in **B** with a double bond of the co-ordinated cot then leads to **C**, where the unsaturation at the molybdenum centre is relieved by a further switch in the bonding mode of the cot. A precedent for this coupling reaction is provided by the iron-centred reaction[14] of co-ordinated buta-1,3-diene and hexafluorobut-2-yne (Scheme 3). The last stage in the iron reaction, *i.e.* carbon–carbon coupling, is mirrored in the step **D** to **E** (Scheme 2) where, instead of forming a six-membered ring in the reductive elimination step, 1,6-coupling occurs to form the bicyclo[4.2.2]decatetraene ligand. Support for this suggestion is provided by the observation that when an excess of cyclooctatetraene is treated with $[Mo(NCMe)(\eta^2\text{-}PhC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$[8] or alternatively with the pair of diphenylacetylene cations $[Mo(NCMe)(\eta^2\text{-}PhC_2Ph)_2L][BF_4]$[8] (L = η-$C_5H_5$ or η^5-C_9H_7) the organic molecules 7-methyl-8-phenylbicyclo[4.2.2]deca-2,4,7,9-triene **5** and 7,8-diphenylbicyclo[4.2.2]deca-2,4,7,9-triene **6** are formed in yields of over 100% based on the molybdenum complex. Since a bis(alkyne) complex is used in the reaction the high yield obviously results from capture of the $Mo(\eta\text{-}C_5H_5)^+$ or $Mo(\eta^5\text{-}C_9H_7)^+$ fragments by the second molecule of alkyne and a molecule of cot with consequent reformation of intermediate **A**.

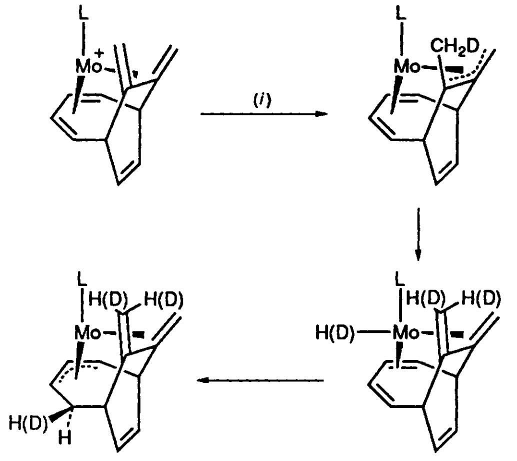
The step **E** ⟶ **A** involved in the formation of compounds **5** and **6** is facilitated by the fact that **E** is co-ordinatively unsaturated. However, when R = Me or Et, *i.e.* but-2-yne or hex-3-yne systems, an alternative competing reaction path is now available to the intermediate **E**. This involves the initial development of an agostic C(μ-H)Mo interaction, which leads to the formation of the species **F**. Once this occurs then **1** can be formed by either or both of the pathways shown in Scheme 2, *i.e.* **F** ⟶ **G** ⟶ **H** ⟶ **1**, or **F** ⟶ **I** ⟶ **J** ⟶ **1**. Proton loss from **F** to the acetonitrile solution, which contains sodium carbonate as an irreversible trap for protons, affords **G** a η^4-1,3-diene/η^3-allyl. Since **G** is an 18-electron species a $\eta^4 \longrightarrow \eta^2$ change in the bonding mode of the 1,3-diene is obviously a prerequisite for the H-shift process involved in the transformation **G** to **H**. In the alternative pathway the hydrogen atom originally attached to the methyl group transfers completely to the molybdenum to form first **I** and then **J** prior to proton loss.



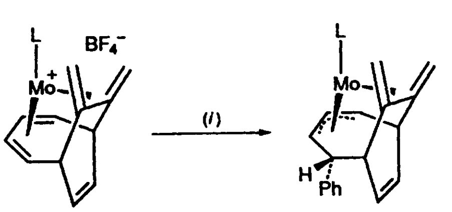
L
1 η-C_5H_5
3 η^5-C_9H_7

L
7 η-C_5H_5
8 η^5-C_9H_7

Scheme 4 (*i*) + $[CPh_3][BF_4]$; (*ii*) + $K[BHBu^s_3]$; (*iii*) $Na[BD_3(CN)]$

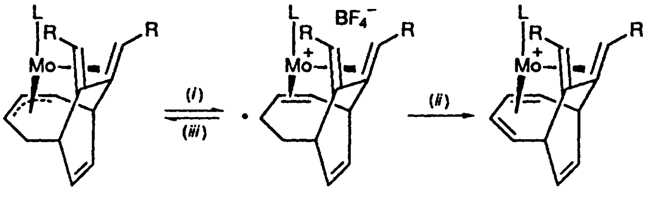


Scheme 5 L = η^5-C_9H_7. (*i*) + $Na[BD_3(CN)]$



8 L = η^5-C_9H_7 **9** L = η^5-C_9H_7

Scheme 6 (*i*) + MgPhBr, thf



L	R	L	R	L	R
1 η-C_5H_5	H	**10** η-C_5H_5	H	**7** η-C_5H_5	H
2 η-C_5H_5	Me	**11** η-C_5H_5	Me		
3 η^5-C_9H_7	H	**12** η^5-C_9H_7	H	**8** η^5-C_9H_7	H

Scheme 7 (*i*) + CPh_3^+, $-CPh_3^{\bullet}$; (*ii*) + $CPh_3^{\bullet}$, $-Ph_3CH$; (*iii*) + $Na[BH_3(CN)]$

Aside from the synthetic and structural interest in the molecules **1**–**4** they also offer considerable potential for reactivity studies. Since it is well known[15] that suitably substituted η^3-allyl complexes can be readily transformed into cationic η^4-1,3-diene complexes *via* a hydride-abstraction reaction with trityl tetrafluoroborate, it was obviously of interest to treat **1** with $[CPh_3][BF_4]$. In dichloromethane at −78 °C a rapid change in colour from yellow to green occurred resulting in the formation in excellent yield of the cation $[Mo(\eta^4,\eta^4\text{-}C_{12}H_{12})(\eta\text{-}C_5H_5)][BF_4]$ **7**. An analogous reaction between $[CPh_3][BF_4]$ and **3** afforded $[Mo(\eta^4,\eta^4\text{-}C_{12}H_{12})(\eta^5\text{-}C_9H_7)][BF_4]$ **8**. Elemental analysis and NMR spectroscopy (see Experimental section) confirmed the illustrated bis(1,3-diene) structures (Scheme 4).

Reaction of these bis(1,3-diene) cations **7** and **8** with $K[BHBu^s_3]$ in thf led respectively to the regeneration of the parent complexes **1** and **3**. This is a particularly interesting reaction in that **7** and **8** carry two potential sites for nucleophilic attack, *i.e.* at the *exo*- or the *endo*-orientated 1,3-diene. The transformations **7** ⟶ **1** and **8** ⟶ **3** strongly suggest that a regioselective reaction is occurring at the *exo*-η^4-1,3-diene moiety, however there is an alternative explanation for these observations which requires that 'H^-' is first delivered to an end carbon of the *endo*-1,3-diene on the face opposite to the metal thus generating in the case of the η-C_5H_5-substituted system the intermediate **G** in Scheme 2. This species then undergoes a H-shift process, *i.e.* $\mathbf{G} \rightleftharpoons \mathbf{H} \longrightarrow \mathbf{1}$, to regenerate the parent η^3-allyl/η^4-1,3-diene complex **1** (Scheme 5).

Deuterium-labelling experiments render this second possible reaction pathway less plausible. When compound **8** is treated with $Na[BD_3(CN)]$ in thf complex **3D** is formed. The ^2H NMR spectrum showed a single signal at δ 3.00, which is coincident with the assignment for the protons for the methylene group H^{5a}, H^{5b}. The ^1H NMR spectrum showed a reduction in the intensity of the multiplet centred at δ 2.99 assigned to H^s,H^1,H^{5a},H^{5b}. The proton-decoupled ^{13}C NMR spectrum of **3D** was identical to that of **3**, with the exception of the signal at δ 48.4 assigned to C^5, which was broader and weaker, as expected from coupling to ^2H. Treatment of **3D** with $[CPh_3][BF_4]$ in CH_2Cl_2 as solvent led to the formation of **8**, the ^2H NMR and mass spectra of which indicated complete removal of the deuterium. These observations are consistent with selective hydride (D^-) addition to the *exo*-η^4-1,3-diene and hydride (D^-) abstraction from H^{5b} (Scheme 4). If the η^5-indenyl analogue of **G** (Scheme 2) had been formed then H/D transfer from the CH_2D group *via* the molybdenum to C^5 would have given complex **3** with some deuterium in the positions H^{5a} and H^s/H^a (see Scheme 5). This is not observed, moreover $[CPh_3][BF_4]$ would be expected to remove H^- or D^- from only H^{5b}; again this is not observed.

Thus, 'H^-' or 'D^-' appears to be delivered selectively to the *exo*-η^4-1,3-diene moiety present in compound **3**. This same regioselectivity was also observed in the reaction of **8** with MgPhBr in thf solution. The product of the reaction **9**, a pink material, was characterised by elemental analysis, mass and NMR spectroscopy. Selective ^1H decoupling experiments along with the ^{13}C NMR spectrum established the couplings and chemical shifts listed in the Experimental section, which are consistent with the illustrated structure (Scheme 6). In agreement with this structure, treatment with $[CPh_3][BF_4]$ failed to abstract H^- from **9**. The origin of the regioselective nucleophilic attack on the *exo*-1,3-diene as opposed to the *endo*-1,3-diene is unclear, and further experiments are planned to clarify this question.

It was observed that when compound **1** was treated with $[CPh_3][BF_4]$ decomposition sometimes occurred together with the formation of a small quantity of a blue-green crystalline material, the NMR spectrum of which was broad and uninformative. Treatment, however, of this material with $Na[BH_3(CN)]$ led to the quantitative reformation of **1**. These observations suggested that the reaction with $[CPh_3][BF_4]$ did not lead to a simple hydride abstraction, but that an initial one-electron oxidation occurred to form a 17-electron species, which then underwent a hydrogen-abstraction reaction (see Scheme 7). This idea was reinforced by a cyclic voltammetry experiment with **1**, which showed a low-potential (−0.05 V), reversible, diffusion-controlled one-electron oxidation. This suggested that it might be possible to obtain an isolable 17-electron species by oxidation of **1** with a suitable oxidising agent. It was found that careful addition of a dichloromethane solution of **1** to a stirred suspension of $AgBF_4$ at room temperature led to an immediate change in colour from yellow to green and formation of a silver mirror. A conventional work-up and recrystallisation from

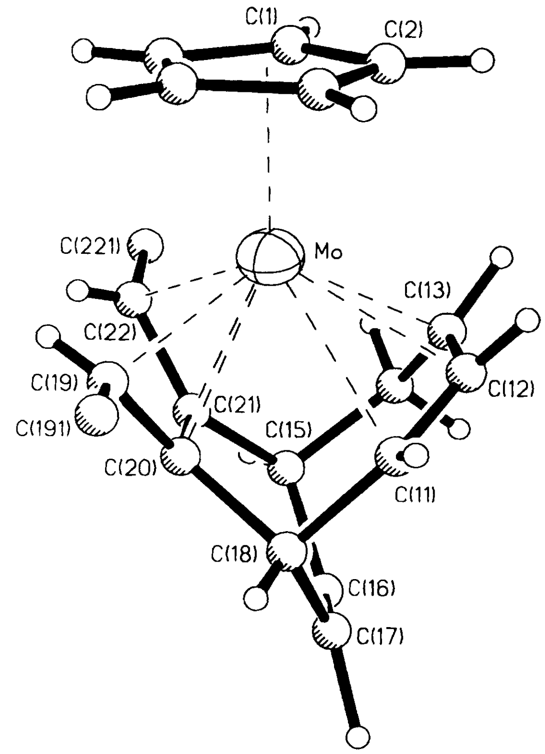


Fig. 2 Molecular structure of cation **11** showing labelling scheme; methyl group hydrogen atoms have been omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for compound **11**

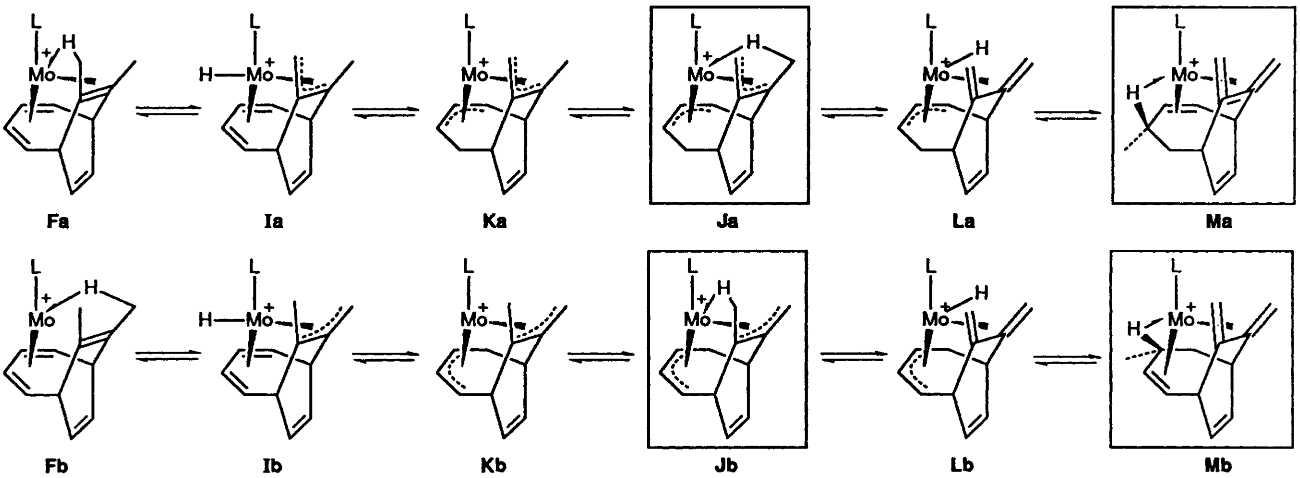
Mo–C(1)	2.300(6)	Mo–C(2)	2.309(7)
Mo–C(3)	2.322(6)	Mo–C(4)	2.325(6)
Mo–C(5)	2.309(8)	Mo–C(11)	2.571(8)
Mo–C(12)	2.310(7)	Mo–C(13)	2.288(6)
Mo–C(19)	2.260(6)	Mo–C(20)	2.276(5)
Mo–C(21)	2.274(5)	Mo–C(22)	2.264(6)
C(1)–C(2)	1.394(11)	C(1)–C(5)	1.403(12)
C(2)–C(3)	1.374(9)	C(3)–C(4)	1.383(10)
C(4)–C(5)	1.362(11)	C(11)–C(12)	1.343(11)
C(11)–C(18)	1.527(11)	C(14)–C(15)	1.514(10)
C(12)–C(13)	1.391(10)	C(15)–C(16)	1.497(11)
C(13)–C(14)	1.438(11)	C(191)–C(19)	1.516(8)
C(15)–C(21)	1.523(7)	C(19)–C(20)	1.415(7)
C(16)–C(17)	1.308(12)	C(21)–C(22)	1.430(8)
C(17)–C(18)	1.441(11)	C(22)–C(221)	1.492(10)
C(18)–C(20)	1.526(9)		
C(20)–C(21)	1.411(7)		
C(12)–C(11)–C(18)	128.5(7)	C(17)–C(18)–C(20)	114.4(6)
C(11)–C(12)–C(13)	132.8(7)	C(191)–C(19)–C(20)	123.8(5)
C(12)–C(13)–C(14)	133.7(7)	C(18)–C(20)–C(19)	118.4(5)
C(13)–C(14)–C(15)	119.7(7)	C(18)–C(20)–C(21)	117.7(5)
C(14)–C(15)–C(16)	111.1(6)	C(19)–C(20)–C(21)	119.4(5)
C(14)–C(15)–C(21)	105.7(5)	C(15)–C(21)–C(20)	118.1(5)
C(16)–C(15)–C(21)	112.9(6)	C(15)–C(21)–C(22)	122.1(5)
C(15)–C(16)–C(17)	122.0(6)	C(20)–C(21)–C(22)	118.2(5)
C(16)–C(17)–C(18)	121.0(7)	C(21)–C(22)–C(221)	124.6(5)
C(11)–C(18)–C(17)	144.0(7)		
C(11)–C(18)–C(20)	99.5(5)		

diethyl ether–dichloromethane afforded in high yield (88%) green crystals of **10**. Elemental analysis indicated that **10** had the molecular formula [Mo($C_{12}H_{13}$)(η-C_5H_5)][BF_4]. Similar oxidation reactions with **2** and **3** afforded the green crystalline 17-electron cations [Mo($C_{14}H_{17}$)(η-C_5H_5)][BF_4] **11** and [Mo($C_{12}H_{13}$)(η^5-C_9H_7)][BF_4] **12** respectively. A single-crystal X-ray diffraction study with suitable crystals of **11** established the structure shown in Fig. 2. Selected bond lengths and angles are listed in Table 2.

The 17-electron cation **11** has a similar overall geometry to that found for **1**, in which a Mo(η^5-C_5H_5) fragment is η^3,η^4-bonded to the bicyclic cage. As might be expected the unco-ordinated C(16)–C(17) double-bond distance of 1.308(12) Å is similar to that found for C(9)–C(10) [1.320(11) Å] in **1**, and although **11** has methyl substituents on the η^4-1,3-diene moiety compared with that in **1**, again the variations in the parameters of the η^4-1,3-diene on one-electron oxidation are minor. The most significant effects of oxidation are shown in the allyl moiety. All the molybdenum–carbon distances to the allyl have lengthened; that to the outer carbon adjacent to the bridgehead of the ring, Mo–C(11), is 2.571(8) Å, an increase of 0.256(10) Å compared with that found in **1**, *cf.* 2.315(7) Å. The bonds Mo–C(12) and Mo–C(13) have lengthened by smaller amounts to 2.310(7) and 2.288(6) Å respectively, increases of 0.065(9) and 0.023(9) Å by comparison with the neutral complex **1**. The carbon–carbon bond distances within the allyl are reduced; C(11)–C(12) is 1.343(11) Å, a reduction of 0.057(14) Å compared to that in **1**, and C(12)–C(13) is 1.391(10) Å, a reduction of 0.030(14) Å. The hydrogens on some of the carbons were clearly located: those on C(13) and C(12) of the allyl, the bridgehead carbons C(15) and C(18), the unco-ordinated double bond, C(16) and C(17), and on C(19) and C(22) of the 1,3-diene system. Interestingly, the structure shows no agostic interactions to alleviate the electron deficiency at the molybdenum. The shortest molybdenum–hydrogen distances are those to the hydrogens on C(19) and C(22) of the 1,3-diene. Each of these is, however, greater than 2.4 Å, and even these distances are likely to be underestimates of true internuclear distances. Thus, the radical cation **11** has a very distorted η^3-allyl system, or more likely is best described as a carbon-centred radical η^2,η^4 bonded to a 16-electron cationic molybdenum centre (Scheme 7).

The reactivity of the neutral complexes **1**–**4** is also interesting in another respect, that is protonation. As can be seen on examination of Scheme 2 there is the possibility that the intermediates, **F**, **I** and **J**, and related cations could be accessed by protonation. Addition of HBF_4·Et_2O to a solution of **1** in diethyl ether afforded the green crystalline cation **13**. Similarly, protonation of **1** or **2** by trifluoromethanesulfonic acid afforded the green crystalline compounds **14** and **15** respectively, while protonation of the analogous indenyl complex **3** with CF_3SO_3H in Et_2O gave dark brown-black crystals of **16**. A preliminary study of the ^1H NMR spectra of **14** and **16** at ambient temperature showed, in addition to signals due to the protons of an unco-ordinated double bond, the η^5-C_5H_5 or η^5-C_9H_7 ligand and several signals in the δ 1–4 region, a signal at −1.0 and −1.1 respectively, each integrating as three protons, which collapsed as the temperature was lowered. At lower temperatures (−70 to −80 °C) new signals emerged at high field, δ −8.15 to −11.55, for **14** (position depending on the temperature during acquisition) and at δ −7.86 for **16**, which integrated for one proton. The ^1H NMR spectrum of **15** was temperature invariant between −60 and +80 °C with a signal at δ −9.03 integrating for a single proton.

These high-field chemical shifts are indicative of the presence of an agostic metal–hydrogen interaction which relieves the unsaturation at the molybdenum centre caused by protonation of one of the electron-rich centres in the η^3,η^4-C_{12} ligand, or of a simple Mo–H bond. There are a number of possible structures for these cations, and these are illustrated in Scheme 8 as enantiomeric pairs. It would be expected that **F**, **I**, **K**, **J**, **L** and **M** could all interconvert, and therefore different structures might be preferred depending on the substituents and on the phase, *i.e.* the solid state or in solution. It should also be noted that because of these equilibrium processes the establishment of the location of the hydrogen delivered by the proton in either the solid state or in solution would not determine the initial site of protonation. In other words this is a problem of kinetic and



Scheme 8 L = η-C_5H_5 or η^5-C_9H_7

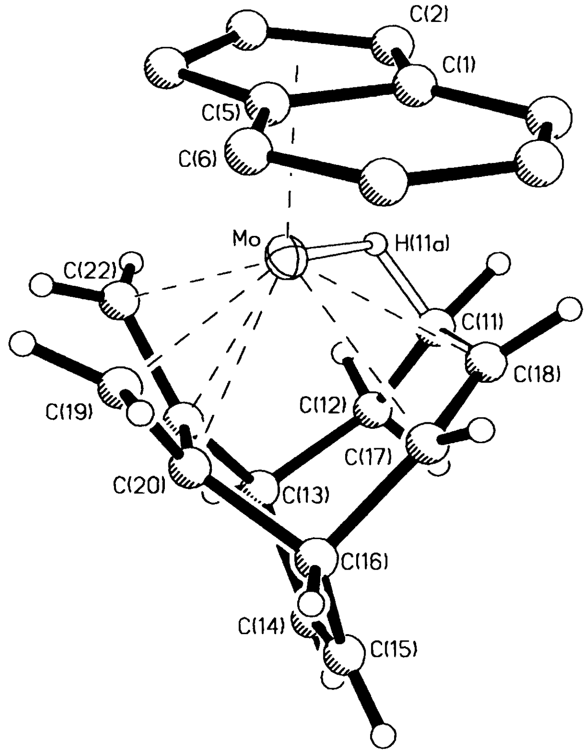


Fig. 3 Molecular structure of compound **16** showing labelling scheme; indenyl group hydrogen atoms have been omitted for clarity

thermodynamic control. In order to begin to study this problem, single-crystal X-ray diffraction studies were made on crystals of **13** and **16**.

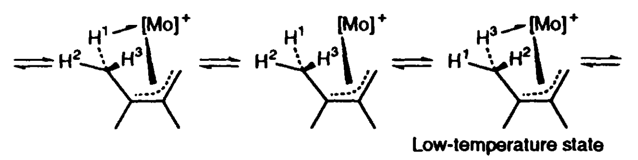
Unfortunately, the structure analysis of compound **13** was not satisfactory, despite data collection at both room and reduced temperature. In both cases the structure showed clear signs of disorder and the molecular parameters were obviously inaccurate as a result. However, the structure determination did confirm that the C_{12} carbon skeleton remained intact. The crystal structure determination of **16** (Fig. 3, selected bond lengths and angles Table 3) proved far more informative. All the hydrogen atoms were directly located, and with the exception of one of the methylene protons they were freely refined. This showed that protonation of **3** affords a cation, which in the solid state adopts a structure different from that suggested by the variable-temperature ^1H NMR data, *i.e.* **Ma/Mb** rather than **Ja/Jb** (see Scheme 8). Examination of the X-ray data for **16** shows that the most significant changes compared to the neutral complex **1** are observed within the η^3-allyl moiety. The Mo–C(17) bond has increased by 0.027(8) Å to 2.342(4) Å, and Mo–C(18) has shortened by 0.017(8) Å to 2.218(4) Å. There is a substantial increase in Mo–C(11) of 0.125(4) Å to 2.391(4) from 2.266(7) Å in the neutral complex. These changes are accompanied by an opening of Mo–C(18)–C(11) and closing of Mo–C(11)–C(18) angles of more than 5°, and by lengthening of C(18)–C(11) from 1.421(10) to 1.471(6) Å, a distance intermediate between a single bond length, *cf.* 1.518(6) Å for the adjacent bond C(11)–C(12), and a co-ordinated allylic carbon–carbon bond. These changes are consistent with a β-agostic system, *i.e.* structures **Ma/Mb**, Scheme 8, where C_α = C(18) and C_β = C(11), in which a hydrogen bridges the Mo–C(11) bond, and this bonding arrangement was confirmed by the direct location and refinement of the bridging hydrogen, H(11a). The geometry of the agostic interaction, Mo–H(11a) of 1.80(5) Å, C(11)–H(11a) of 1.08(5) Å and Mo–H(11a)–C(11) of 110(4)°, is consistent with a three-centre two-electron Mo(μ-H)C bond. The non-planar geometry of the four-centre Mo–$C_\alpha C_\beta$–H system with a dihedral angle of 27(3)° is in contrast to other β-agostic interactions in which M–$C_\alpha C_\beta$–H angles are typically closer to zero. β-Agostic interactions have previously only been spectroscopically and structurally characterised when adjacent to alkyl, allyl and 1,3-diene groups.[16] The system described in this paper is the first characterised example of a β-C–H–M bond adjacent to an alkene moiety, and represents an arrested 1,3-hydrogen shift, an intermediate postulated[17] in the initial stage of the metal-assisted isomerisation of alkenes.

Returning to the question of the structures adopted by the cations **13** to **16** in solution, a closer examination of the NMR data is justified. As noted in the Experimental section the ^1H spectra of **13** and **14** are identical. At ambient temperature, in addition to the familiar protons of the unco-ordinated double bond, H^7 and H^8, at δ 5.75 and 6.36, with a *cis* coupling of 9.52 Hz, the bridgehead proton, H^1, at δ 3.91 with an 8.3 Hz coupling to H^2, the proton at the end of the η^3-allyl, at δ 3.69, the most obvious feature is the broad signal at δ −1.00 for the three protons of the methyl group. As the temperature was lowered the latter signal collapsed and three new signals emerged, one at high field and two at lower fields. A further reduction in the temperature had little effect on the ^1H NMR spectrum indicating that in solution the most stable form of the cation present in **13** and **14** is **Ja/Jb** as depicted in Scheme 8. This structure is also consistent with the ^{13}C NMR spectrum, however attempts to obtain coupled ^{13}C spectra at a variety of temperatures were unsuccessful. Thus, the changes which occur in the high-field portion of the ^1H NMR spectrum as the temperature is lowered are consistent with the process depicted in Scheme 9.

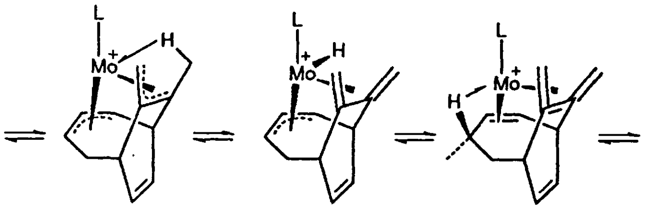
In sharp contrast the ^1H and ^{13}C NMR spectra of the cation

Table 3 Selected bond lengths (Å) and angles (°) for compound **16**

Mo–C(1)	2.401(4)	Mo–C(2)	2.316(4)	C(8)–C(9)	1.367(6)	C(9)–H(9)	1.013(50)
Mo–C(3)	2.298(4)	Mo–C(4)	2.290(4)	C(11)–H(11a)	1.080(51)	C(11)–H(11b)	1.016(47)
Mo–C(5)	2.361(4)	Mo–C(11)	2.391(4)	C(11)–C(12)	1.518(6)	C(11)–C(18)	1.471(6)
Mo–H(11a)	1.800(54)	Mo–C(17)	2.342(4)	C(12)–H(12a)	0.965(35)	C(12)–H(12b)	1.014(48)
Mo–C(18)	2.218(4)	Mo–C(19)	2.296(5)	C(12)–C(13)	1.544(6)	C(13)–H(13)	0.884(47)
Mo–C(20)	2.284(4)	Mo–C(21)	2.287(4)	C(13)–C(14)	1.499(6)	C(13)–C(21)	1.521(5)
Mo–C(22)	2.246(4)	C(1)–C(2)	1.435(6)	C(14)–H(14)	0.937(46)	C(14)–C(15)	1.315(6)
C(1)–C(5)	1.437(5)	C(1)–C(9)	1.423(6)	C(15)–H(15)	0.886(43)	C(15)–C(16)	1.497(6)
C(2)–H(2)	1.022(51)	C(2)–C(3)	1.411(6)	C(16)–H(16)	0.912(47)	C(16)–C(17)	1.531(6)
C(3)–H(3)	1.059(53)	C(3)–C(4)	1.414(6)	C(16)–C(20)	1.512(5)	C(17)–H(17)	0.863(45)
C(4)–H(4)	0.877(48)	C(4)–C(5)	1.440(5)	C(17)–C(18)	1.412(6)	C(18)–H(18)	0.979(46)
C(5)–C(6)	1.426(5)	C(6)–H(6)	1.006(51)	C(19)–H(19a)	0.995(46)	C(19)–H(19b)	1.010(48)
C(6)–C(7)	1.357(6)	C(7)–H(7)	0.917(51)	C(19)–C(20)	1.416(6)	C(20)–C(21)	1.412(5)
C(7)–C(8)	1.428(7)	C(8)–H(8)	0.967(48)	C(21)–C(22)	1.441(6)		
Mo–C(11)–H(11a)	45.1(28)	Mo–C(11)–H(11b)	118.2(25)	C(12)–C(13)–C(21)	110.5(3)	C(15)–C(16)–C(20)	112.4(3)
H(11a)–C(11)–H(11b)	83.5(37)	Mo–C(11)–C(12)	115.3(3)	C(14)–C(13)–C(21)	112.6(3)	C(17)–C(16)–C(20)	98.4(3)
H(11a)–C(11)–C(12)	111.5(29)	H(11b)–C(11)–C(12)	114.1(26)	C(13)–C(14)–C(15)	122.8(4)	C(16)–C(17)–C(18)	129.1(4)
Mo–C(11)–C(18)	65.1(2)	H(11a)–C(11)–C(18)	102.0(29)	C(14)–C(15)–C(16)	119.8(4)	C(11)–C(18)–C(17)	132.4(4)
H(11b)–C(11)–C(18)	107.6(25)	C(12)–C(11)–C(18)	128.3(4)	C(16)–C(20)–C(19)	120.0(3)	C(20)–C(21)–C(22)	117.4(3)
Mo–H(11a)–C(11)	110(4)	C(11)–C(12)–C(13)	112.7(3)	C(16)–C(20)–C(21)	116.4(3)	C(13)–C(21)–C(20)	119.6(3)
C(12)–C(13)–C(14)	108.8(3)	C(15)–C(16)–C(17)	116.2(4)	C(19)–C(20)–C(21)	117.8(3)	C(13)–C(21)–C(22)	122.3(3)



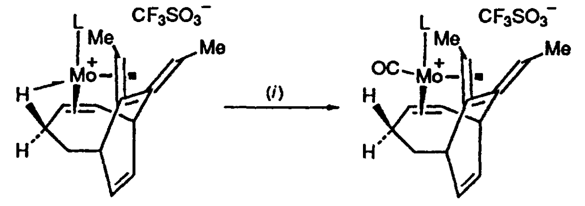
Scheme 9



Scheme 10 L = η^5-C_9H_7. Only one enantiomer is included for clarity

15 obtained by protonation of **2** with CF_3SO_3H are temperature invariant with no indication of dynamic behaviour. From proton, COSY and CH correlation NMR spectra (see Experimental section for details) it was possible to establish that in solution in the temperature range 213–353 K the cation **15** adopts a structure analogous to **Ma/Mb** (Scheme 8) with *syn*-methyl substituents on the 1,3-diene. Difficulty was again experienced in obtaining a ^1H-coupled ^{13}C NMR spectrum, frustrating attempts to measure *J*(CH) for Mo(μ-H)C.

At ambient temperature the ^1H NMR spectrum of the indenyl analogue **16** shows similarities to the corresponding spectrum of **13** and **14**, with a high-field signal at δ −1.10 for the three protons of the agostic methyl group. The allyl protons H^2, H^3 and H^4, lie at δ 3.05, 1.03 and 3.0, shifted upfield from those of the η-C_5H_5 substituted cation **13**/**14**. As the temperature was lowered the single agostic methyl signal disappeared and new signals emerged, including a high-field signal at δ −7.86 for the single agostic proton. The spectrum did not, however, remain as simple as that of **13**/**14**. The appearance of new signals in the spectrum was accompanied by several shifts. In particular, the signal assigned to the allyl proton H^3 was shifted upfield by at least 0.3 ppm, and there were also changes in the chemical shifts of both of the methylene protons, H^5, and in the region of H^4. This implies that as the temperature is lowered, in addition to the process shown in Scheme 9, the changes depicted in Scheme 10 also occur, these being analogous to **Ja/Jb** $\rightleftharpoons$ **La/Lb** $\rightleftharpoons$ **Ma/Mb** in Scheme 8. Interestingly, in the solid state structure **Ma/Mb** is preferred. Proton-coupled ^{13}C NMR spectra of **16** were obtained at ambient and reduced temperatures. They are consistent with these structures, but, neither DEPT (distortionless enhancement of polarisation transfer) nor off-resonance decoupling was able to locate conclusively the carbon attached to the agostic proton, and it is possible that these experiments were confused by rapid equilibria in solution between two or more isomeric forms of the cation **16**.



15 **17**

Scheme 11 L = η-C_5H_5. (*i*) + CO, CH_2Cl_2

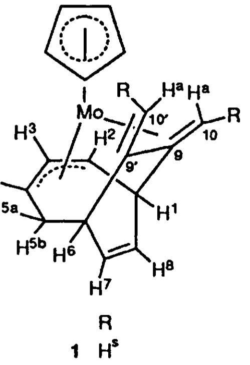
Finally, the reactivity of cations **15** and **16** was explored. Treatment of **16** with Li[BDEt$_3$] resulted in a deprotonation reaction and formation of **3** in high yield. Examination of the ^2H NMR spectrum showed that the product did not contain deuterium, and therefore the reaction can be viewed as involving the simple attack by 'D$^-$' on the relatively acidic Mo(μ-H)C bridging atom. Reaction of the cation **15** with carbon monoxide resulted in the formation of the orange crystalline complex **17**, which was readily identified by elemental analysis, IR and NMR spectroscopy as having the illustrated (Scheme 11) structure. This reaction is consistent with the structure shown for **15** where reaction at the molybdenum centre leads to displacement of the agostic Mo(μ-H)C ligand.

In conclusion the molybdenum-mediated cycloaddition of alkynes to cyclooctatetraene has been shown to provide access to novel bicyclo[4.2.2]decane systems carrying η^3-allyl and η^4-1,3-diene systems. The reaction chemistry of these molecules has been explored and particularly noteworthy are the observations that one-electron-transfer reactions can lead to unusual 17-electron cations, whereas protonation affords cations which have been shown to adopt structures involving Mo(μ-H)C bonds. Interestingly, it has been found that these cations adopt different structures in the solid phase and in solution.

Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and further degassed before use where necessary. Column chromatography was performed using BDH alumina, Brockman activity II as the solid support. Reagents were obtained from commercial sources unless otherwise indicated. The ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded on JEOL FX200 and Brucker AM360 spectrometers, as appropriate. Chemical shifts are quoted as positive to high frequency of tetramethylsilane, with coupling constants in Hz. Data given are for room-temperature measurements unless stated otherwise. Infrared spectra were measured using a Perkin Elmer 983G spectrometer. Mass spectra and analytical data were obtained courtesy of the University of Bristol and London Services.

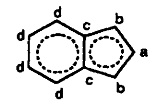
Reactions with Cylooctatetraene.—[Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$]. The cationic complex [Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$] (0.285 g, 0.72 mmol) was dissolved in acetonitrile (80 cm^3), to which cyclooctatetraene (0.40 g, 3.56 mmol) and anhydrous Na$_2$CO$_3$ (0.05 g, mmol) had been added. The resulting suspension was heated under reflux for 18 h. The solvent and volatiles were removed *in vacuo* and the residue extracted with dichloromethane (3 cm^3). The extract was chromatographed on an alumina-packed column. Elution with hexane–diethyl ether (9 : 1) gave a single yellow band, which was collected and recrystallised (–78 °C) from hexane to afford bright yellow *crystals* of [Mo(η^3,η^4-C$_{12}$H$_{13}$)(η-C$_5$H$_5$)] **1** (0.18 g, 79%) (Found: C, 64.1; H, 5.8. C$_{17}$H$_{18}$Mo requires C, 64.2; H, 5.7%). NMR (C$_6$D$_6$): ^{1}H, δ 6.16 [dd, 1 H, H^8, *J*(H^{1}H^8) 6.7, *J*(H^{7}H^8) 9.5], 5.59 [dd, 1 H, H^7, *J*(H^{6}H^7) 4.7, *J*(H^{7}H^8) 9.5], 4.37 (s, 5 H, C$_5$H$_5$), 3.04 [at, 1 H, H^1, *J*(H^{1}H^8) 6.7, *J*(H^{1}H^2) 8.06], 3.0 (cm, 3 H, H^6, H^{5a}, H^{5b}), 2.88 (br s, 1 H, H^s), 2.75 [dd, 1 H, H^2, *J*(H^{1}H^2) 8.06, *J*(H^{2}H^3) 8.55], 2.67 [dm, 1 H, H^4, *J*(H^{3}H^4) 11.0], 2.55 (br s, 1 H, H^s), 1.54 [dd, 1 H, H^3, *J*(H^{3}H^4) 11.0, *J*(H^{2}H^3) 8.55 Hz], 0.92 (br s, 1 H, H^a) and 0.51 (br s, 1 H, H^a); ^{13}C-{^{1}H}, δ 132.7 (C^7), 130.2 (C^8), 121.7 (C^9), 85.6 (C$_5$H$_5$), 81.1 (C$^{9'}$), 62.2 (C^3), 58.5 (C^4), 48.3 (C^5), 45.0 (C^{10}), 44.6 (C$^{10'}$), 40.2 (C^2), 37.3 (C^6) and 32.5 (C^1). Mass spectrum: *m*/*z* 318, [*M*]$^+$.



	R
1	H^s
2	Me

[Mo(NCMe)(η^2-EtC$_2$Et)$_2$(η-C$_5$H$_5$)][BF$_4$]. A similar reaction (18 h, reflux) between [Mo(NCMe)(η^2-EtC$_2$Et)$_2$(η-C$_5$H$_5$)][BF$_4$] (0.42 g, 0.95 mmol), cyclooctatetraene (0.40 cm^3, 3.56 mmol) and Na$_2$CO$_3$ (0.05 g) in acetonitrile (80 cm^3) afforded a single yellow band on column chromatography (eluted with hexane–diethyl ether, 4 : 1). Recrystallisation (–78 °C) from pentane afforded yellow *crystals* of [Mo(η^3,η^4-C$_{14}$H$_{17}$)(η-C$_5$H$_5$)] **2** (0.25 g, 67%) (Found: C, 65.9; H, 6.6. C$_{19}$H$_{22}$Mo requires C, 65.9; H, 6.4%). NMR (C$_6$D$_6$): ^{1}H, δ 6.24 [dd, 1 H, H^8, *J*(H^{1}H^8) 7.08, *J*(H^{7}H^8) 9.4], 5.79 [dd, 1 H, H^7, *J*(H^{6}H^7) 5.13, *J*(H^{7}H^8) 9.4], 4.24 (s, 5 H, C$_5$H$_5$), 3.37 [at, 1 H, H^1, *J*(H^{1}H^8) 7.10, *J*(H^{1}H^2) 8.3], 3.1 (cm, 3 H, H^6, H^{5a}, H^{5b}), 2.92 [dd, 1 H, H^2, *J*(H^{1}H^2) 8.3, *J*(H^{2}H^3) 8.31], 2.50 [dd, 1 H, H^4, *J*(H^{3}H^4) 10.57, *J*(H^{4}H^5) 5.18], 1.93 [d, 3 H, Me, *J*(H^{a}Me) 6.35], 1.82 [at, 1 H, H^3, *J*(H^{2}H^3) 8.3, *J*(H^{3}H^4) 10.5], 1.60 [d, 3 H, Me, *J*(H^{a}Me) 5.86 Hz], 1.35 (m, 1 H, H^a) and 0.70 (m, 1 H, H^a); ^{13}C-{^{1}H}, δ 134.6 (C^7), 129.5 (C^8), 119.0 (C^9), 87.1 (C$_5$H$_5$), 76.0 (C$^{9'}$), 67.7 (C^3), 59.5 (C^4), 56.7 (C^{10}), 54.3 (C$^{10'}$), 52.1 (C^5), 41.9 (C^2), 37.6 (C^6), 27.8 (C^1) and 18.8 (Me). Mass spectrum: *m*/*z* = 346, [*M*]$^+$.

[Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η^5-C$_9$H$_7$)][BF$_4$]. Reaction (18 h, reflux) of [Mo(NCMe)(η^2-MeC$_2$Me)$_2$(η^5-C$_9$H$_7$)][BF$_4$] (0.33 g, 0.73 mmol), cyclooctatetraene (0.3 cm^3, 2.67 mmol) and Na$_2$CO$_3$ (0.05 g) in acetonitrile (50 cm^3) followed by removal of the solvent *in vacuo*, extraction into CH$_2$Cl$_2$ (2 × 4 cm^3), and column chromatography, gave on elution with hexane–diethyl ether (4 : 1) a single bright red band. Collection and recrystallisation (–78 °C) from pentane gave red *crystals* of [Mo(η^3,η^4-C$_{12}$H$_{13}$)(η^5-C$_9$H$_7$)] **3** (0.15 g, 56%) (Found: C, 68.4; H, 5.8. C$_{21}$H$_{20}$Mo requires C, 68.5; H, 5.5%). NMR (C$_6$D$_6$): ^{1}H, δ 7.1–6.9 (m, 2 H, H^d), 6.8–6.7 (m, 2 H, H^d), 6.03 [dd, 1 H, H^8, *J*(H^{1}H^8) 6.6, *J*(H^{7}H^8) 9.5] 5.48 [dd, 1 H, H^7, *J*(H^{6}H^7) 5.5, *J*(H^{7}H^8) 9.5], 5.09 (m, 1 H, H^b), 4.65 (m, 1 H, H^b), 3.53 [t, 1 H, H^a, *J*(H^{a}H^b) 3.17], 3.23 (m, 1 H, H^s), 2.99 (m, 4 H, H^s, H^1, H^{5a}, H^{5b}), 2.8 (m, 2 H, H^6, H^2), 2.75 [dd, 1 H, H^4, *J*(H^{3}H^4) 11.3, *J*(H^{4}H^5) 3.2 Hz], 1.55 (m, 1 H, H^3), –0.59 (br s, 1 H, H^a) and –0.93 (br s, 1 H, H^a); ^{13}C-{^{1}H}, δ 132.7 (C^7), 130.2 (C^8), 126.1 (C^d), 123.9 (C^d), 123.7 (C^d), 122.0 (C^9), 109.8 (C^c), 109.1 (C^c), 88.9 (C^a), 82.1 (C^9), 73.1 (C^8), 71.9 (C^b), 65.3 (C^3), 61.8 (C^4), 54.9 (C^{10}), 48.5 (C^5), 44.8 (C^2), 37.6 (C^6) and 33.9 (C^1). Mass spectrum: *m*/*z* = 368, [*M*]$^+$.

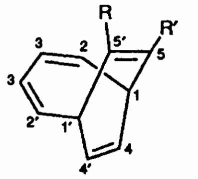


[Mo(CO)(η^2-MeC$_2$Me)$_2$(η^5-C$_9$H$_7$)][BF$_4$]. Reaction (18 h, reflux) of [Mo(CO)(η^2-MeC$_2$Me)$_2$(η^5-C$_9$H$_7$)][BF$_4$] (0.7 mmol) with C$_8$H$_8$ (0.3 cm^3) and Na$_2$CO$_3$ (0.05 g) in acetonitrile (50 cm^3) afforded a red solution. Removal of solvent and column chromatography on alumina gave a red band on elution with hexane–diethyl ether (4 : 1). Recrystallisation from pentane gave red *crystals* of compound **3** (56%).

[Mo(NCMe)(η^2-EtC$_2$Et)$_2$(η^5-C$_9$H$_7$)][BF$_4$]. A similar reaction afforded red *crystals* of [Mo(η^3,η^4-C$_{14}$H$_{17}$)(η^5-C$_9$H$_7$)] **4** (0.15 g, 54%) (Found: C, 69.5; H, 6.5. C$_{23}$H$_{24}$Mo requires C, 69.7; H, 6.1%). NMR (C$_6$D$_6$): ^{1}H, δ 7.1–7.05 (m, 2 H, H^d), 6.84–6.63 (m, 2 H, H^d), 6.07 [dd, 1 H, H^8, *J*(H^{1}H^8) 6.3, *J*(H^{7}H^8) 8.81], 5.66 [dd, 1 H, H^7, *J*(H^{6}H^7) 5.86, *J*(H^{7}H^8) 8.81], 4.81 (m, 1 H, H^b), 4.38 (m, 1 H, H^b), 3.46 (br m, 1 H, H^a), 3.36 [at, 1 H, H^1, *J*(H^{1}H^8) 6.3, *J*(H^{1}H^2) 8.1], 3.16–3.09 (m, 1 H, H^{5a} or H^{5b}), 2.96 (m, 3 H, H^2, H^{5a} or H^{5b}), 2.56 (m, 1 H, H^4), 1.91 [d, 3 H, Me, *J*(H^{a}Me), 5.53 Hz], 1.76 (m, 4 H, Me, H^3), –0.08 (br s, 1 H, H^a) and –0.40 (br s, 1 H, H^a); ^{13}C-{^{1}H}, δ 134.4 (C^7), 129.6 (C^8), 126.0 (C^d), 125.3 (C^d), 124.4 (C^d), 124.0 (C^d), 119.3 (C^9), 110.8 (C^c), 108.9 (C^c), 90.3 (C^a), 77.2 (C^9), 73.9 (C^b), 72.9 (C^b), 70.4 (C^{10}), 67.9 (C^{10}), 63.6 (C^3), 60.6 (C^4), 51.6 (C^5), 46.6 (C^2), 37.5 (C^6), 28.6 (C^1), 18.3 (Me) and 17.1 (Me). Mass spectrum: *m*/*z*, 396, [*M*]$^+$.

[Mo(NCMe)(η^2-PhC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$]. A solution of [Mo(NCMe)(η^2-PhC$_2$Me)$_2$(η-C$_5$H$_5$)][BF$_4$] (0.8 g, 1.53 mmol) and cyclooctatetraene (0.40 cm^3, 3.6 mmol) in acetonitrile (80 cm^3) together with Na$_2$CO$_3$ (0.05 g) was refluxed for 18 h. The solvent was removed *in vacuo* and the residue extracted into CH$_2$Cl$_2$ (2 × 4 cm^3). The extract was then chromatographed on alumina. Elution with hexane gave a single yellow band, which was collected, affording on low-temperature (–50 °C) crystallisation from hexane the yellow oil 7-methyl-8-phenylbicyclo[4.2.2]deca-2,4,7,9-triene **5** (0.38 g, 113%) (Found: C, 92.7; H, 7.3. C$_{17}$H$_{16}$ requires C, 92.7; H, 7.3%). NMR (CDCl$_3$): ^{1}H, δ 7.25–7.06 (m, 5 H, Ph), 6.26–6.0 (m, 2 H, H^2, H$^{2'}$), 5.8–5.6 (m, 4 H, H^3, H$^{3'}$, H^4, H$^{4'}$), 3.31 [dd, 1 H, H^1, *J*(HH) 8.8, 5.4], 3.14

[dd, 1 H, $H^{1'}$, J(HH) 8.8, 5.4 Hz] and 1.65 (s, 3 H, Me); $^{13}C-\{^1H\}$, δ 142.6 (C^2), 141.7 ($C^{2'}$), 141.5 (C^5), 140.1 (C^5), 131.6 (Ph), 129.0 (Ph), 127.8 (Ph), 126.0 (Ph), 125.0 (C^3), 124.3 ($C^{3'}$), 121.6 (C^4), 120.5 ($C^{4'}$), 41.5 ($C^{1'}$), 41.4 ($C^{1'}$) and 17.9 (Me). Mass spectrum: m/z 220, $[M]^+$; 205, $[M - Me]^+$; and 143 $[M - Ph]^+$.

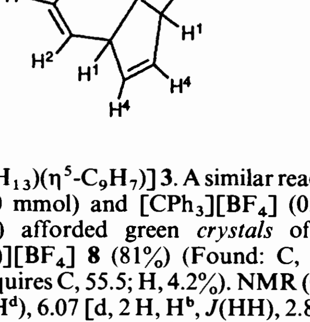


5 R = Me, R′ = Ph
6 R = R′ = Ph

$[Mo(NCMe)(\eta^2-PhC_2Ph)_2(\eta-C_5H_5)][BF_4]$. Reaction of $[Mo(NCMe)(\eta^2-PhC_2Ph)_2(\eta-C_5H_5)][BF_4]$ (1.5 mmol), C_8H_8 (3.5 mmol) and Na_2CO_3 (0.05 g) in MeCN (50 cm^3) afforded cream *crystals* of 7,8-diphenylbicyclo[4.2.2]deca-2,4,7,9-triene **6** (134% with respect to molybdenum complex) (Found: C, 93.1; H, 6.5. $C_{22}H_{18}$ requires C, 93.6; H, 6.4%). NMR ($CDCl_3$): ^1H, δ 7.04 (s, 10 H, Ph), 6.33 [dd, 2 H, H^2, $H^{2'}$, J(HH) 8.53, J(HH) 3.5], 5.97–5.79 (m, 4 H, H^4, $H^{4'}$, H^3, $H^{3'}$) and 3.63 [dm, 2 H, H^1, $H^{1'}$, J(HH) 8.53 Hz]; $^{13}C-\{^1H\}$, δ 141.7 (C^2), 141.2 (C^5), 133.2 (Ph), 129.8 (Ph), 127.7 (Ph), 126.0 (Ph), 125.0 (C^3), 121.2 (C^4) and 42.2 (C^1). Mass spectrum: m/z 282, $[M]^+$; and 205, $[M - Ph]^+$.

$[Mo(NCMe)(\eta^2-PhC_2Ph)_2(\eta^5-C_9H_7)][BF_4]$. Similarly, reaction of $[Mo(NCMe)(\eta^2-PhC_2Ph)_2(\eta^5-C_9H_7)][BF_4]$ (1.5 mmol), with C_8H_8 (4.0 mmol) and Na_2CO_3 (0.05 g) in MeCN (50 cm^3) afforded cream *crystals* of compound **6** (130% with respect to molybdenum complex).

Reactions with Trityl Tetrafluoroborate.—$[Mo(\eta^3,\eta^4-C_{12}H_{13})(\eta-C_5H_5)]$ **1**. A solution of $[CPh_3][BF_4]$ (0.11 g, 0.33 mmol) in CH_2Cl_2 (2 cm^3) was added dropwise to a stirred and cooled (−78 °C) solution of compound **1** (0.10 g, 0.31 mmol) in CH_2Cl_2 (9 cm^3). An immediate colour change from yellow to green occurred. The solution was stirred and allowed to warm slowly to room temperature. After 1 h the volume of solvent was reduced *in vacuo* and diethyl ether added. The resulting green precipitate was collected, redissolved in CH_2Cl_2 (10 cm^3) and filtered through Celite. Addition of diethyl ether and cooling (0 °C) afforded green *crystals* of $[Mo(\eta^4,\eta^4-C_{12}H_{12})(\eta-C_5H_5)][BF_4]$ **7** (0.09 g, 91%) (Found: C, 50.1; H, 4.3. $C_{17}H_{17}BF_4Mo$ requires C, 50.5; H, 4.2%). NMR: $^1H(CD_2Cl_2)$, δ 5.95 (br s, 2 H, H^4), 5.56 (s, 5 H, C_5H_5), 4.78 (cm, 2 H, H^2), 3.64 (cm, 2 H, H^3), 3.54 [d, 2 H, H^s, J(HH) 2.9], 3.35 (m, 2 H, H^1) and 2.31 [d, 2 H, H^a, J(HH) 2.9 Hz]; $^{13}C-\{^1H\}$ (CD_3NO_2), δ 129.9 (C^4), 93.2 (C_5H_5), 92.4 (C^5), 73.9 (C^3), 65.1 (C^2), 60.9 (C^6) and 29.6 (C^1).



$[Mo(\eta^3,\eta^4-C_{12}H_{13})(\eta^5-C_9H_7)]$ **3**. A similar reaction between compound **3** (0.30 mmol) and $[CPh_3][BF_4]$ (0.30 mmol) in CH_2Cl_2 (10 cm^3) afforded green *crystals* of $[Mo(\eta^4,\eta^4-C_{12}H_{12})(\eta^5-C_9H_7)][BF_4]$ **8** (81%) (Found: C, 55.5; H, 4.2. $C_{21}H_{19}BF_4Mo$ requires C, 55.5; H, 4.2%). NMR (CD_2Cl_2): ^1H, δ 7.5–7.2 (m, 4 H, H^d), 6.07 [d, 2 H, H^b, J(HH), 2.84], 5.74 (m, 3 H, H^4, H^a, indenyl), 4.15 [dd, 2 H, H^2, J(HH) 6.56, 3.5], 3.52–3.4 (m, 2 H, H^3), 3.49 [d, 2 H, H^s, J(HH) 3.5], 3.3–3.1 (m, 2 H, H^1) and 2.22 [d, 2 H, H^a, J(HH) 3.5 Hz]; $^{13}C-\{^1H\}$, δ 128.6 (C^d), 128.0 (C^4), 125.7 (C^d), 108.9 (C^c), 96.4 (C^a), 94.0 (C^5), 85.5 (C^b), 71.6 (C^3), 66.4 (C^2), 66.1 (C^6) and 29.2 (C^1).

Reactions with $K[BHBu^s_3]$.—$[Mo(\eta^4,\eta^4-C_{12}H_{12})(\eta-C_5H_5)][BF_4]$ **7**. A solution of potassium selectride® $K[BHBu^s_3]$ (0.3 cm^3, 0.3 mmol, 1 mol dm^{-3} solution in thf) was added dropwise with stirring to a cooled (−78 °C) suspension of compound **7** (0.10 g, 0.24 mmol) in thf (20 cm^3). On warming to room temperature a clear yellow solution was formed. The solvent was removed *in vacuo*, the residue dissolved in hexane and the extract chromatographed on an alumina-packed column. Elution with hexane afforded one yellow band, which on collection and recrystallisation (−78 °C) from hexane gave yellow *crystals* of $[Mo(\eta^3,\eta^4-C_{12}H_{13})(\eta-C_5H_5)]$ **1** (90%), identified by NMR and mass spectroscopy.

$[Mo(\eta^4,\eta^4-C_{12}H_{12})(\eta^5-C_9H_7)][BF_4]$ **8**. A similar reaction led to the formation in essentially quantitative yield of compound **3**.

Reactions of $[Mo(\eta^4,\eta^4-C_{12}H_{12})(\eta^5-C_9H_7)][BF_4]$ **8**.—*With* $Na[BD_3(CN)]$. Sodium cyanotrideuterioborate (0.02 g, 0.23 mmol) was added to a stirred and cooled (0 °C) suspension of compound **8** (0.11 g, 0.23 mmol) in thf (8 cm^3). The reaction mixture was allowed to warm to room temperature the colour changing from green to pinkish red. The solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 (1.5 cm^3) and the resulting extract chromatographed on alumina. Elution with diethyl ether–hexane (1:4) gave red *crystals* of $[Mo(\eta^3,\eta^4-C_{12}H_{12}D)(\eta^5-C_9H_7)]$ **3D** (0.05 g, 60%). NMR: ^1H (C_6D_6), δ 7.1–6.7 (m, 4 H, H^d), 6.05 [dd, 1 H, H^8, $J(H^1H^8)$, 6.1, $J(H^7H^8)$ 9.6], 5.50 [dd, 1 H, H^7, $J(H^6H^7)$ 5.3, $J(H^7H^8)$ 9.6], 5.11 (br s, 1 H, H^b), 4.67 (br s, 1 H, H^b), 3.57 [t, 1 H, H^a, $J(H^aH^b)$ 3.07], 3.21 (m, 1 H, H^5), 3.00 (m, 3 H, H^5, H^1, H^{5a}), 2.79 (m, 2 H, H^6, H^2), 2.75 [br d, 1 H, H^4, $J(H^3H^4)$ 11.2 Hz], 1.59 (br m, 1 H, H^3), −0.58 (br s, 1 H, H^a) and −0.94 (br s, 1 H, H^a); ^2H (C_6H_6), δ 3.00 (br s, D^5); $^{13}C-\{^1H\}$ (C_6D_6), δ 132.6 (C^7), 130.2 (C^8), 126.1 (C^d), 123.9 (C^d), 123.7 (C^d), 121.9 (C^9), 109.8 (C^c), 109.0 (C^c), 88.9 (C^a), 82.0 (C^9), 73.4 (C^b), 72.2 (C^b), 65.6 (C^3), 61.8 (C^4), 54.7 (C^{10}), 48.4 (br, C^5), 44.9 (C^2), 37.6 (C^6) and 33.9 (C^1). Mass spectrum: m/z 369, $[M]^+$.

With phenylmagnesium bromide. A solution of MgPhBr (1.5 cm^3, 1.5 mol dm^{-3} solution in thf) was added dropwise with stirring and cooling (0 °C) to a suspension of compound **8** (0.20 g, 0.44 mmol) in thf (5 cm^3). An immediate change in colour occurred. The reaction mixture was allowed to warm to room temperature, the solvent removed *in vacuo* and the residue chromatographed on alumina. Elution with diethyl ether–hexane (1:4) afforded a red band which was collected and recrystallised (−78 °C) from hexane to give pink *crystals* of $[Mo(\eta^3,\eta^4-C_{12}H_{12}Ph)(\eta^5-C_9H_7)]$ **9** (0.17 g, 86%) (Found: C, 73.1; H, 5.3. $C_{27}H_{24}Mo$ requires C, 73.0; H, 5.4%). NMR (C_6D_6): ^1H, δ 7.49–7.46 (m, 2 H, H^d), 7.42–6.95 (m, 5 H, Ph), 6.86–6.72 (m, 2 H, H^d), 5.95 [dd, 1 H, H^8, $J(H^7H^8)$ 9.62, $J(H^1H^8)$ 6.84], 5.06 (br s, 1 H, H^b), 5.04 [dd, 1 H, H^7, $J(H^6H^7)$ 5.61, $J(H^7H^8)$ 9.63], 4.72 (s, 1 H, H^b), 4.54 [dd, 1 H, H^5, $J(H^5H^6)$ 8.55, $J(H^5H^4)$ 3.94], 3.57 [t, 1 H, H^a, indenyl, J(HH) 3.07], 3.20 [d, 1 H, H^s, $J(H^sH^a)$ 2.62], 3.06 [dd, 1 H, H^6, $J(H^6H^5)$ 8.55, $J(H^6H^7)$ 5.61], 3.03 (br s, 1 H, H^s), 2.95 [dd, 1 H, H^1, $J(H^1H^8)$ 6.84, $J(H^1H^2)$ 7.81], 2.79 [dd, 1 H, H^2, $J(H^1H^2)$

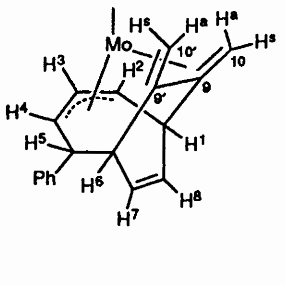


Table 4 Structure analyses for compounds **1**, **11** and **16**

	1	**11**	**16**
Crystal data			
Formula	$C_{17}H_{18}Mo$	$C_{19}H_{22}BF_4Mo$	$C_{22}H_{21}F_3MoO_3S$
M	318.3	433.1	518.4
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group (no)	$P2_12_12_1$ (19)	$P2_1/n$ (14)	$P2_1/c$ (14)
a/Å	7.848(6)	10.102(2)	10.558(6)
b/Å	11.339(7)	13.571(3)	15.605(8)
c/Å	14.378(13)	12.762(2)	12.023(7)
β/°	90	90.38(2)	94.37(4)
U/Å^3	1279(2)	1749.6(6)	1975(2)
Z	4	4	4
T/K	295	295	200
D_c/g cm^{-3}	1.65	1.64	1.74
$F(000)$	648	876	1048
μ(Mo-Kα)/cm^{-1}	9.8	7.7	8.0
Data collection and reduction			
Crystal dimensions (mm)	0.8 × 0.75 × 0.65	0.6 × 0.35 × 0.1	0.35 × 0.4 × 0.3
2θ range/°	4–50	4–55	3–55
Scan method	ω–2θ	ω–2θ	ω–2θ
Scan width (ω°)	$1.0 + \Delta\alpha_1\alpha_2$	$1.2 + \Delta\alpha_1\alpha_2$	$1.1 + \Delta\alpha_1\alpha_2$
Total data	2231	4438	4342
Unique data	2130	4027	4109
'Observed' data (N_o)	1974	3116	3563
Observation criterion [$F^2 > n\sigma(F^2)$]	2	1.5	1.5
Crystal faces [distances from origin (mm)]	(001)[0.35], $(00\bar{1})$[0.3], (110)[0.425], $(\bar{1}10)$[0.4], $(1\bar{1}0)$[0.4], $(\bar{1}\bar{1}0)$[0.425], (011)[0.2], $(0\bar{1}\bar{1})$[0.2]		
Minimum, maximum transmission coefficient	0.715, 0.499	—	—
Refinement			
Least-squares variables (N_v)	191	258	340
R*	0.049	0.055	0.045
R'*	0.047	0.056	0.045
S*	2.05	1.51	1.20
g	0.0005	0.0007	0.0011
Final difference map features (e Å^{-3})	+2.5, −1.3	+0.7, −0.5	+1.3, −0.9

* $R = \Sigma|\Delta|\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}|\Delta|/\Sigma w^{\frac{1}{2}}F_o$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$; $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics.

7.8, $J(H^2H^3)$ 7.9], 2.77 [dd, 1 H, H^4, $J(H^3H^4)$ 10.74, $J(H^4H^5)$ 3.94], 1.70 [dd, 1 H, H^3, $J(H^2H^3)$ 7.9, $J(H^3H^4)$ 10.7], −0.60 [d, 1 H, H^a, $J(H^aH^s)$ 2.62 Hz] and −0.82 (br m, 1 H, H^a); ^{13}C-{^1H}, δ 142.2 (Ph), 132.3 (C^7), 130.2 (C^8), 129.8 (Ph), 128.3 (Ph), 126.2 (C^d), 124.0 (C^d), 123.8 (C^d), 115.9 (C^9), 109.8 (C^c), 88.8 (C^a), 80.8 (C^9), 73.5 (C^b), 72.3 (C^b), 65.5 (C^3), 64.9 (C^4), 63.9 (C^5), 55.6 (C^{10}), 54.9 ($C^{10'}$), 44.5 (C^2), 41.5 (C^6) and 33.8 (C^1). Mass spectrum: *m*/*z*, 444, $[M]^+$.

Reactions with Silver Tetrafluoroborate.—[Mo(η^3,η^4-$C_{12}H_{13}$)(η-C_5H_5)] **1**. A solution of compound **1** (0.12 g, 0.36 mmol) in CH_2Cl_2 (4 cm^3) was added dropwise at room temperature to a stirred solution of $AgBF_4$ (0.07 g, 0.37 mmol) in CH_2Cl_2 (4 cm^3). An immediate colour change occurred from yellow to green and a silver mirror formed. The reaction mixture was filtered through Celite then reduced in volume *in vacuo*. Addition of diethyl ether gave a green precipitate. This was collected and recrystallised from diethyl ether–dichloromethane to give green *crystals* of [Mo(η^2,η^4-$C_{12}H_{13}$)(η-C_5H_5)][BF_4] **10** (0.14 g, 88%) (Found: C, 50.8; H, 4.4. $C_{17}H_{18}BF_4Mo$ requires C, 50.4; H, 4.5%). The NMR spectra were broad and featureless.

[Mo(η^3,η^4-$C_{14}H_{17}$)(η-C_5H_5)] **2**. A similar reaction between compound **2** (0.15 g, 0.43 mmol) and $AgBF_4$ (0.09 g, 0.43 mmol) gave green *crystals* of [Mo(η^2,η^4-$C_{14}H_{17}$)(η-C_5H_5)][BF_4] **11** (0.17 g, 90%) (Found: C, 52.3; H, 5.0. $C_{19}H_{22}BF_4Mo$ requires C, 52.7; H, 5.1%).

[Mo(η^3,η^4-$C_{12}H_{13}$)(η^5-C_9H_7)] **3**. Similarly, reaction between compound **3** (0.09 g, 0.23 mmol) and $AgBF_4$ (0.05 g, 0.26 mmol) gave green *crystals* of [Mo(η^2,η^4-$C_{12}H_{13}$)(η^5-C_9H_7)][BF_4] **12** (0.10 g, 90%) (Found: C, 52.3; H, 5.0. $C_{21}H_{20}BF_4Mo$ requires C, 52.6; H, 5.1%).

Reaction of [Mo(η^2,η^4-$C_{12}H_{13}$)(η^5-C_9H_7)][BF_4] **12** *with* Na[BH_3(CN)].—A suspension of compound **12** (0.02 g, 0.04 mmol) in thf (2 cm^3) was cooled in an ice-bath. Solid Na[BH_3(CN)] (0.12 g, 0.1 mmol) was added, the reaction mixture rapidly changing colour from green to pinkish red. Volatile material was removed *in vacuo* and the residue extracted into CH_2Cl_2 (1.5 cm^3). This extract was then chromatographed on alumina. Elution with diethyl ether–hexane (1:4) afforded a red band which was collected. Recrystallisation from hexane at −78 °C afforded *crystals* of compound **3** (70%), identified by NMR and mass spectroscopy.

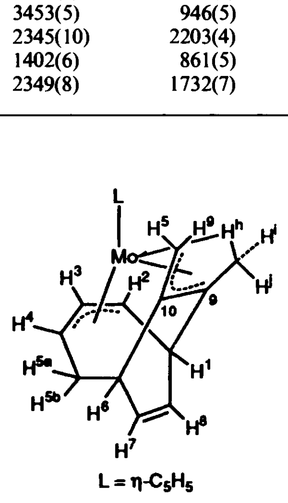
Protonation of [Mo(η^3,η^4-$C_{12}H_{13}$)(η-C_5H_5)] **1**.—(*a*) *With* $HBF_4 \cdot Et_2O$. Complex **1** (0.10 g, 0.31 mmol) was dissolved in diethyl ether (20 cm^3), the solution cooled to −78 °C and $HBF_4 \cdot Et_2O$ (excess, 10 drops) added slowly dropwise. The solution turned green after a few seconds and on warming to room temperature a green precipitate formed. Recrystallisation (ambient) from dichloromethane (diethyl ether) gave *green* crystals of [Mo(η^3,η^3-$C_{12}H_{13}$)($\mu_{Mo,C}$-H)(η-C_5H_5)][BF_4] **13**

Table 5 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Mo	10 126(1)	5 181(1)	6 032(1)
C(1)	9 628(9)	6 571(6)	4 937(5)
C(2)	9 123(11)	7 052(7)	5 810(6)
C(3)	7 729(11)	6 381(9)	6 124(7)
C(4)	7 347(9)	5 539(8)	5 472(8)
C(5)	8 547(10)	5 630(8)	4 733(6)
C(6)	12 760(8)	5 863(6)	6 386(5)
C(7)	13 426(10)	5 583(7)	7 349(5)
C(8)	12 913(10)	4 378(6)	7 645(4)
C(9)	14 127(9)	3 475(7)	7 283(5)
C(10)	13 837(10)	2 860(7)	6 520(5)
C(11)	12 233(10)	3 017(6)	5 975(5)
C(12)	12 245(8)	4 078(6)	5 327(4)
C(13)	12 826(6)	5 217(6)	5 540(4)
C(14)	9 099(10)	3 335(7)	6 255(6)
C(15)	10 770(8)	3 374(6)	6 640(5)
C(16)	11 069(8)	4 196(7)	7 321(4)
C(17)	9 713(9)	4 990(7)	7 569(5)

Table 6 Atomic coordinates (× 10^4) for compound **11**

Atom	*x*	*y*	*z*
Mo	2313(1)	2389(1)	4217(1)
C(1)	2516(9)	3056(5)	2569(5)
C(2)	3561(7)	3419(4)	3175(5)
C(3)	3037(7)	3993(4)	3956(6)
C(4)	1677(7)	3996(4)	3832(6)
C(5)	1338(8)	3420(5)	2997(7)
C(11)	3576(7)	1952(6)	5909(7)
C(12)	4223(6)	1806(5)	5006(7)
C(13)	3953(6)	1230(4)	4129(5)
C(14)	3287(7)	304(7)	3975(6)
C(15)	2104(6)	46(4)	4644(6)
C(16)	2531(6)	−301(5)	5707(7)
C(17)	2744(9)	312(6)	6481(7)
C(18)	2450(8)	1346(5)	6374(4)
C(191)	1037(8)	3298(5)	6415(5)
C(19)	855(6)	2552(4)	5541(4)
C(20)	1360(5)	1580(4)	5579(4)
C(21)	1261(5)	975(3)	4683(4)
C(22)	627(6)	1370(4)	3769(5)
C(221)	532(7)	853(5)	2740(6)
B	2375(8)	1439(5)	−537(6)
F(1)	3453(5)	946(5)	−705(6)
F(2)	2345(10)	2203(4)	−1157(5)
F(3)	1402(6)	861(5)	−776(6)
F(4)	2349(8)	1732(7)	419(5)



L = η-C_5H_5

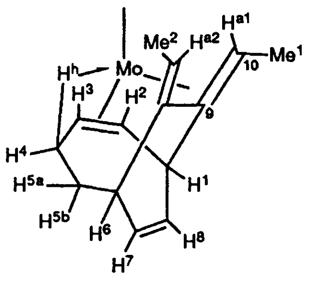
Table 7 Atomic coordinates (× 10^4) for compound **16**

Atom	*x*	*y*	*z*
Mo	2152(1)	826(1)	2633(1)
C(1)	2960(4)	2072(2)	1754(3)
C(2)	3152(4)	1317(3)	1107(3)
C(3)	1950(4)	990(3)	728(3)
C(4)	996(4)	1485(3)	1187(3)
C(5)	1615(3)	2168(2)	1823(3)
C(6)	1142(4)	2871(3)	2427(3)
C(7)	1980(5)	3428(3)	2944(4)
C(8)	3317(5)	3319(3)	2895(4)
C(9)	3815(4)	2653(3)	2333(4)
C(11)	3906(4)	−101(3)	3136(3)
C(12)	3561(4)	−964(3)	3609(3)
C(13)	2313(4)	−936(2)	4199(3)
C(14)	2623(4)	−759(2)	5415(3)
C(15)	2606(4)	16(3)	5843(3)
C(16)	2156(4)	756(2)	5124(3)
C(17)	3132(4)	1150(3)	4396(3)
C(18)	3958(4)	738(3)	3696(3)
C(19)	427(4)	1124(3)	3620(4)
C(20)	1173(4)	493(3)	4207(3)
C(21)	1405(4)	−280(2)	3647(3)
C(22)	922(4)	−349(3)	2497(4)
C	3272(4)	6587(3)	5032(3)
F(1)	4123(3)	7220(2)	5045(2)
F(2)	2304(3)	6870(2)	5568(3)
F(3)	3818(3)	5947(2)	5628(3)
S	2768(1)	6249(1)	3618(1)
O(1)	2191(4)	7004(2)	3130(3)
O(2)	3927(3)	5993(3)	3181(3)
O(3)	1888(3)	5565(2)	3788(3)

(0.96 g, 92%) (Found: C, 49.9; H, 4.6. $C_{17}H_{19}BF_4Mo$ requires C, 50.3; H, 4.7%). NMR (CD_2Cl_2): ^1H(ambient), δ 6.36 [dd, 1 H, H^8, $J(H^1H^8)$ 6.8, $J(H^7H^8)$ 9.52], 5.75 [dd, 1 H, H^7, $J(H^6H^7)$ 5.3, $J(H^7H^8)$ 9.52], 5.55 (s, 5 H, C_5H_5), 3.91 [dd, 1 H, H^1, $J(H^1H^8)$ 6.84, $J(H^1H^2)$ 8.30], 3.69 [dd, 1 H, H^2, $J(H^1H^2)$ 8.30, $J(H^2H^3)$, 8.50], 3.22–3.00 (m, 2 H, H^4, H^{5a}), 2.89 (br s, 1 H, H^s), 2.87–2.82 (m, 1 H, H^6), 2.62 [at, 1 H, H^3, $J(H^3H^2)$ 8.50, $J(H^3H^4)$, 8.50], 2.46 [d, 1 H, H^{5b}, $J(H^{5b}H^{5a})$ 14.2], 1.61 [d, 1 H, H^a, $J(H^aH^s)$ 1.23 Hz] and −1.00 (br s, 3 H, Me); (213 K), δ 6.37 (br s, 1 H, H^8), 5.77 (br s, 1 H, H^7), 5.57 (s, 5 H, C_5H_5), 3.93 (br s, 1 H, H^1), 3.68 (br s, 1 H, H^2), 3.30–3.00 (m, 2 H, H^4, H^{5a}), 3.23 (s, 1 H, H^j), 2.87 (br s, 1 H, H^s), 2.85 (br s, 1 H, H^6), 2.63 (br s, 1 H, H^3), 2.51 (br s, 1 H, H^{5b}), 1.74 (s, 1 H, H^i), 1.62 (s, 1 H, H^a) and −8.15 (br s, 1 H, H^h); ^{13}C-{^1H} (ambient), δ 133.2 (C^7), 130.1 (C^8), 124.7 (C^9), 92.2 (C_5H_5), 83.1 (C), 63.0 (C^3), 48.8, 47.2, 44.2, 36.4, 31.2 (C^6) and 29.8 (C^1).

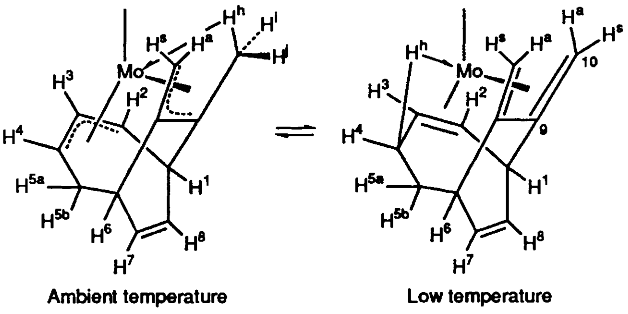
(*b*) *With trifluoromethanesulfonic acid*. Similarly, addition of CF_3SO_3H (0.31 mmol) to compound **1** (0.10 g, 0.31 mmol) afforded green *crystals* of [Mo(η^3,η^3-$C_{12}H_{13}$)($\mu_{Mo,C}$-H)(η-C_5H_5)][CF_3SO_3] **14** (0.11 g, 90%) (Found: C, 46.4; H, 4.1. $C_{18}H_{19}F_3MoO_3S$ requires C, 46.2; H, 4.1%). The ^1H and ^{13}C-{^1H} NMR spectra were identical to those of compound **13**.

Protonation of [Mo(η^3,η^4-$C_{14}H_{17}$)(η-C_5H_5)] **2** *with Trifluoromethanesulfonic Acid*.—A solution of compound **2** (0.11 g, 0.32 mmol) in diethyl ether (20 cm^3) was cooled to −78 °C. An excess of CF_3SO_3H (0.40 mmol) was added dropwise with stirring. On warming to room temperature a green precipitate was formed. This was collected and recrystallised from dichloromethane–diethyl ether to give dark green *crystals* of [Mo(η^2,η^4-$C_{14}H_{17}$)($\mu_{Mo,C}$-H)(η-C_5H_5)][CF_3SO_3] **15** (0.13 g, 78%) (Found: C, 47.9; H, 4.5. $C_{20}H_{23}F_3MoO_3S$ requires C, 48.4; H, 4.7%). NMR (CD_3NO_2, ambient): ^1H, δ 6.4 [at, 1 H, H^8, $J(H^1H^8)$ 7.5, $J(H^7H^8)$ 8.31], 5.95 [dd, 1 H, H^7, $J(H^6H^7)$ 5.64, $J(H^7H^8)$ 8.31], 5.39 (s, 5 H, C_5H_5), 4.27 [at, 1 H, H^1, $J(H^1H^2)$ 7.4, $J(H^1H^8)$ 7.5], 3.91 [at, 1 H, H^2, $J(H^2H^3)$ 7.4, $J(H^1H^2)$, 7.4], 3.29 [m, 1 H, H^{5a}, $J(H^{5a}H^{5b})$ 14.6, $J(H^{5a}H^6)$ 9.37], 3.04 [dd, 1 H, H^6, $J(H^{5a}H^6)$ 9.37, $J(H^6H^7)$ 5.64], 2.8 [m, 2 H, H^3, H^4, $J(H^2H^3)$ 7.4, $J(H^4H^h)$ 8.6], 2.55 [q, 1 H, H^{a1}, $J(H^{a1}Me)$ 6.1], 2.48 [dd, 1 H, H^{5b}, $J(H^{5b}H^{5a})$ 14.6, $J(H^{5b}H^H)$ 7.6], 2.26 [q, 1 H, H^{a2}, $J(H^{a2}Me)$ 5.3], 2.09 [d, 3 H, Me^1, $J(H^{a1}Me)$ 6.1], 1.75 [d, 3 H, Me^2, $J(H^{a2}Me^2)$ 5.5] and −9.03 [m, 1 H, H^h, $J(H^hH^4)$ 8.6, $J(H^hH^{5b})$ 7.8 Hz]; ^{13}C-{^1H}, δ 134.3 (C^7), 129.2 (C^8), 121.6 (C^9), 93.2 (C_5H_5), 79.0 (C^9), 67.2 (C^{10}), 65.6 (C^3), 63.4 (C^{10}),



51.7 (C^5), 48.9 (C^2), 34.6 (C^6), 26.7 (C^1), 25.2 (C^4), 20.2 (Me^1) and 18.0 (Me^2).

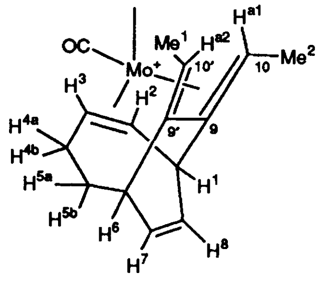
Protonation of [Mo(η^3,η^4-$C_{12}H_{13}$)(η^5-C_9H_7)] **3** *with* CF_3SO_3H.—Similarly, reaction (−78 °C) of compound **3** (0.20 g, 0.54 mmol) with CF_3SO_3H (1.08 mmol) in diethyl ether (10 cm^3) gave a dark brown oil, which on washing (2 × 10 cm^3) with Et_2O and recrystallisation (−78 °C) from dichloromethane–diethyl ether (1 : 1) gave dark brown *crystals* of [Mo(η^6-$C_{12}H_{13}$)($\mu_{Mo,C}$-H)(η^5-C_9H_7)][CF_3SO_3] **16** (0.16 g, 76%) (Found: C, 50.9; H, 3.9. $C_{22}H_{21}F_3MoO_3S$ requires C, 51.0; H, 4.1%). NMR (CD_2Cl_2): ^1H (ambient), δ 7.36–7.25 (m, 2 H, H^d), 7.22–7.12 (m, 2 H, H^d), 6.17 (s, 1 H, H^b), 6.13 [dd, 1 H, H^8, $J(H^7H^8)$ 9.27, $J(H^1H^8)$ 6.34], 5.96 (s, 1 H, H^b), 5.58 [dd, 1 H, H^7, $J(H^6H^7)$ 5.37, $J(H^7H^8)$ 9.27], 5.25 (s, 1 H, H^a), 3.78 [dd, 1 H, H^1, $J(H^1H^8)$ 6.34, $J(H^1H^2)$ 8.79], 3.12 (s, 1 H, H^s), 3.05 [dd, 1 H, H^2, $J(H^1H^2)$ 8.6, $J(H^2H^3)$ 8.6], 3.00–2.90 (cm, 2 H, H^4, H^{5a} or H^{5b}), 2.74 [dd, 1 H, H^6, $J(H^6H^5)$ 9.27 $J(H^6H^7)$ 5.37], 2.43 [d, 1 H, H^{5a} or H^{5b}, $J(H^{5a}H^{5b})$ 15.0], 1.03 (br s, 1H, H^3), 0.79 (br s, 1 H, H^a) and −1.10 (br s, 3 H, Me); (193 K), δ 7.27–7.11 (br s, 4 H, H^d), 6.16 (s, 1 H, H^b), 6.10 (m, 2 H, H^8, H^b), 5.53 (br s, 1 H, H^7), 5.25 (s, 1 H, H^a, indenyl), 3.76 (s, 1 H, H^1), 3.13 (br s, 1 H, H^s), 2.96 (br s, 1 H, H^2), 2.86 (s, 1 H), 2.71 (br s, 2 H), 2.22 (br s, 1 H, H^5), 0.77 (br s, 2 H, H^3, H^a), 0.69 (br s, 1 H, H^a) and −7.86 (s, 1 H, H^h); ^{13}C-{^1H} (ambient), δ 133.2 (C^7), 130.4 (C^8), 130.0 (C^d), 129.2 (C^d), 126.4 (C^d), 125.7 (C^9), 111.9 (C^c), 110.6 (C^c), 94.0 (C^a), 83.9 (C^b), 82.1 (C^b), 81.1 (C^9), 71.0 (C^3), 60.5 (C^{10}), 48.5 (C^2), 44.5 (C^5), 38.0 (C^6) and 33.2 (C^1); (200 K), δ 133.9 (C^7), 129.8 (C^8), 129.4 (C^d), 129.0 (C^d), 125.6 (C^d), 122.9 (C^9), 109.9 (C^c), 93.5 (C^a), 83.2 (C^9), 82.9 (C^b), 81.8 (C^b), 70.4 (C^3), 60.7 (C^{10}), 51.5 (C^2), 47.3 (C^5), 46.1 (C^{10}), 36.7 (C^6), 36.5 (C^4) and 32.2 (C^1).



Ambient temperature Low temperature

Reaction of Compound **16** *with* Li[BDEt$_3$].—A suspension of compound **16** (0.11 g, 0.23 mmol) in thf (10 cm^3) was cooled to −78 °C. A solution of Li[BDEt$_3$] (0.30 cm^3 of 1 mol dm^{-3} solution in thf) was then added dropwise with stirring. On warming to room temperature the reaction mixture turned red. Removal of the solvent, extraction with dichloromethane and column chromatography on alumina afforded on elution with diethyl ether a single red band, which on recrystallisation (−78 °C) gave red crystals of **3** (0.06 g, 75%). Proton, ^{13}C-{^1H} NMR and mass spectra confirmed this; ^2H NMR spectroscopy showed no evidence of deuterium incorporation.

Reaction of Compound **15** *with Carbon Monoxide*.—Complex **15** (0.183 g, 0.21 mmol) was dissolved in dichloromethane (40 cm^3) giving a dark green solution. Carbon monoxide was bubbled through the solution resulting (2 h) in a change in colour from green to orange. The solvent was removed *in vacuo* and the residue recrystallised (−30 °C) from dichloromethane–diethyl ether to give orange *crystals* of [Mo(CO)(η^2,η^4-$C_{14}H_{18}$)(η-C_5H_5)][CF_3SO_3] **17** (0.14 g, 72%) (Found: C, 48.2; H, 4.3. $C_{21}H_{23}F_3MoO_4S$ requires C, 48.1; H, 4.4%); ν_{CO}(CH_2Cl_2) 2003s cm^{-1}. NMR (CD_3NO_2): ^1H, δ 6.35 [dd, 1 H, H^8, $J(H^7H^8)$ 9.1, $J(H^1H^8)$ 7.1], 6.17 [dd, 1 H, H^7, $J(H^7H^8)$ 9.11, $J(H^6H^7)$ 5.38], 5.49 (s, 5 H, C_5H_5), 4.05 [at, 1 H, H^1, $J(H^1H^8)$ 7.2, $J(H^1H^2)$ 7.3], 3.80 (m, 1 H), 3.36 (m, 1 H, H^6), 3.29 [q, 1 H, H^{a1}, $J(H^{a1}Me)$ 6.3], 2.54 (m, 1 H), 2.24 (m, H, H^2), 2.17 (m, 1 H), 2.07 (m, 1 H), 1.93 [d, 3 H, Me, $J(HMe^1)$ 6.3], 1.83 (m, 1 H), 1.73 [d, 3 H, Me^2, $J(HMe^2)$ 5.96] and 1.63 [q, 1 H, H^{a2}, $J(H^{a2}Me)$ 5.96 Hz]; ^{13}C-{^1H}, δ 227.2 (CO), 134.8 (C^7), 127.8 (C^8), 96.3 (C^9), 95.3 (C_5H_5), 93.6 (C^9), 73.1 (C^{10}), 71.4 (C^3), 57.2 (C^2), 40.7 (C^5), 36.9 (C^{10}), 36.1 (C^6), 29.3 (C^1), 19.9 (C^4), 17.7 (Me) and 16.8 (Me).



Structure Determination of Compounds **1**, **11** *and* **16**.—Many of the details of the structure analyses carried out are listed in Table 4. X-Ray diffraction measurements were made using Nicolet four-circle P3m diffractometers with Mo-Kα X-radiation (λ = 0.710 69 Å) on single crystals mounted in thin-walled glass capillaries under N_2. Cell dimensions for the analyses were determined from the setting angle values of 15, 15 and 19 centred reflections respectively.

For each structure analysis, intensity data were collected for unique portions of reciprocal space and corrected for Lorentz, polarisation, crystal decay (negligible in each case) and long-term intensity fluctuations, on the basis of the intensities of three check reflections repeatedly measured during data collection. For compound **16** only reflections with intensity above a low threshold were recorded for $2\theta > 50°$. Corrections for X-ray absorption effects were applied on the basis of the indexed crystal faces and dimensions for the large (and only reasonable quality) crystal of **1**, which showed rather poor ω-scan profiles. The structures were solved by heavy-atom (Patterson and Fourier difference) methods, and refined by blocked-cascade least squares against *F* until shift/e.s.d. values were <0.1. All non-hydrogen atoms were assigned anisotropic displacement parameters. All hydrogen atoms were constrained to ideal geometries (with C–H 0.96 Å) except for those attached to C(14) and H(17) of **1** which were constrained to have C–H close to 0.96 Å, H(12), H(13), H(15)–H(19), and H(22) of **11** which were refined freely, and all hydrogens of **16** except H(12a) which were constrained to have C–H close to 0.96 Å. Hydrogens were assigned isotropic displacement parameters; these were fixed and related to those of their attached carbon atoms or refined either freely or in groups. The handedness of the crystal (and molecule) of **1** studied was assessed by refinement of the Rogers parameter η with the result that the configuration shown is tentatively assigned [η = 0.56(24)].[18] Final difference synthesis showed no chemically significant features, the largest being close to the metal or anion atoms. Refinements converged smoothly to residuals given in Table 4. Tables 5–7 report the positional parameters for these structure determinations.

All calculations were made with programs of the SHELXTL[19] system as implemented on a Nicolet R3m/E structure-determination system. Complex neutral-atom scattering factors were taken from ref. 20.

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

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