Reactions of Co-ordinated Ligands. Part 54.[1] Synthesis of (1,2,3-η)-*trans*-Butadienyl Complexes by Deprotonation or Desilylation of Cationic Molybdenum 1,3-Diene Complexes; Formation of η⁴-Vinylketene Complexes and Crystal Structures of $[Mo\{(1,2,3\text{-}\eta)\text{-}trans\text{-}CH_2CHC{=}CH_2\}(CO)_2(\eta\text{-}C_5Me_5)]$, $[Mo\{\eta^3\text{-}CH_2\overline{CC(Me)CH_2C}O\}(CO)_2(\eta\text{-}C_5Me_5)]$ and $[MoI\{\eta^4\text{-}CH_2{=}CHC(Me){=}C{=}O\}(CO)(\eta\text{-}C_5Me_5)]$†

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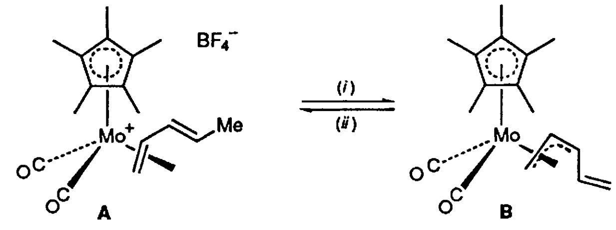
One of the products of the reaction of the base $Li[N(SiMe_3)_2]$ with $[Mo(\eta^4\text{-}C_4H_6)(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$ is the *exo*-orientated (1,2,3-η)-*trans*-butadienyl complex $[Mo\{(1,2,3\text{-}\eta)\text{-}trans\text{-}CH_2CHC{=}CH_2\}(CO)_2(\eta\text{-}C_5Me_5)]$. A single-crystal X-ray diffraction study of the latter has revealed that the two adjacent π systems, allyl and $C{=}CH_2$ within the butadienyl fragment are orthogonal to each other. This complex can be formed selectively and in high yield by reaction of $[NBu^n_4]F$ with the cation $[Mo\{\eta^4\text{-}CH_2{=}CHC(SiEt_3){=}CH_2\}(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$. The desilylation reaction has also been used to transform $[Mo\{\eta^4\text{-}syn\text{-}CH(Ph){=}CHC(SiMe_3){=}CH_2\}(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$ into a mixture of *exo*- and *endo*-$[Mo\{(1,2,3\text{-}\eta)\text{-}trans\text{-}syn\text{-}CH(Ph)CHC{=}CH_2\}(CO)_2(\eta\text{-}C_5Me_5)]$. An alternative synthetic route to (1,2,3-η)-*trans*-butadienyl complexes was explored involving reaction of $Li[Mo(CO)_3(\eta\text{-}C_5Me_5)]$ with $CH_2{=}C{=}C(Me)CH_2Cl$. In the event an unusual cyclisation reaction occurred leading to the formation of the X-ray crystallographically identified complex $[Mo\{\eta^3\text{-}CH_2\overline{CC(Me)CH_2C}O\}(CO)_2(\eta\text{-}C_5Me_5)]$. Extended Hückel molecular orbital calculations on $[Mo\{(1,2,3\text{-}\eta)\text{-}trans\text{-}CH_2CHC{=}CH_2\}(CO)_2(\eta\text{-}C_5Me_5)]$ using the complete set of crystallographic coordinates shows that reaction with protons should occur on the end carbon of the butadienyl ligand to form a cationic η³-vinylcarbene complex. However, protonation with CF_3SO_3H affords a vinylketene complex $[Mo(OSO_2CF_3)\{\eta^4\text{-}CH_2{=}CHC(Me){=}C{=}O\}(CO)(\eta\text{-}C_5Me_5)]$ the structural identity of which was established by an X-ray crystallographic study of the analogue $[MoI\{\eta^4\text{-}CH_2{=}CHC(Me){=}C{=}O\}(CO)(\eta\text{-}C_5Me_5)]$ obtained from the triflate complex *via* metathesis. The mechanisms of these reactions are discussed.

During the course of an investigation into the chemistry of cationic molybdenum η⁴-1,3-diene complexes a serendipitous discovery of a novel deprotonation reaction focused our attention on a group of molecules containing the (1,2,3-η)-*trans*-butadienyl ligand, *i.e.* derivatives of (1,2,3-η)-*trans*-$CH_2CHC{=}CH_2$. The first example of such a molecule was reported by Nesmeyanov *et al.*[2] in 1976 when it was observed that tetrakis(trifluoromethyl)allene reacted with metal carbonyl anions such as $Na[Fe(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ to give initially a σ-bonded complex, which on thermolysis or UV irradiation afforded the X-ray crystallographically identified molecule $[Fe\{(1,2,3\text{-}\eta)\text{-}trans\text{-}C(CF_3)_2C(CF_3)C{=}CF_2\}(PPh_3)(\eta\text{-}C_5H_5)]$. Subsequent work by Benaim,[3] Bruce,[4-9] Hughes,[10] Brisdon[11-13] and Herrmann,[14] and their respective co-workers led to the preparation and characterisation of a range of substituted (1,2,3-η)-*trans*-butadienyl complexes. A limitation of these studies, however, is that they cannot be extended to simple, *i.e.* unsubstituted (1,2,3-η)-*trans*-butadienyls with obvious restrictions on reactivity studies. This encouraged us to develop our initial investigations[15] to other systems, W, Fe, Ru,[16] Pd and Pt,[17] and in this paper are details of work with molybdenum complexes.



Scheme 1 (*i*) NEt_3, CH_2Cl_2; (*ii*) $HBF_4{\cdot}Et_2O$, CH_2Cl_2

Results and Discussion

As part of our earlier study,[18] which established that protonation of η³-pentadienyl molybdenum complexes gives cationic η⁴-1,3-diene species, it was observed that addition of triethylamine to the *trans*-penta-1,3-diene cation **A** (Scheme 1) resulted in a smooth conversion into the neutral *anti*-pentadienyl complex **B** as the sole isolable product. However, use of the more powerful amide base $Li[N(SiMe_3)_2]$ gave

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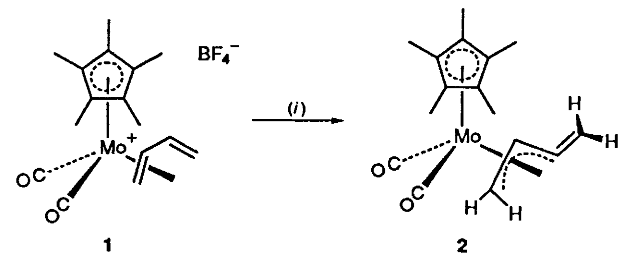
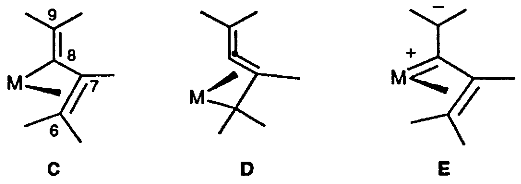
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 2 (*i*) Li[N(SiMe$_3$)$_2$], thf, −78 °C



Scheme 3

instead a mixture of **B** and a second species, which on the basis of spectroscopic data appeared to be the butadienyl complex [Mo{(1,2,3-η)-*trans*-CH(Me)CHC=CH$_2$}(CO)$_2$(η-C$_5$Me$_5$)]. With the objective of eliminating the former reaction pathway and the possible formation of *syn* and *anti* isomers due to the presence of the methyl substituent, the deprotonation of the corresponding buta-1,3-diene cation **1** was therefore examined. Treatment with Li[N(SiMe$_3$)$_2$] in tetrahydrofuran (thf) at −78 °C afforded on column chromatography a yellow crystalline complex **2**, which on the basis of elemental analysis, IR and NMR spectroscopy appeared to be an unsubstituted (1,2,3-η)-*trans*-butadienyl complex (Scheme 2). In view of the unusual nature of this deprotonation reaction, and also because of the need to confirm unequivocally the molecular geometry of **2**, a single-crystal X-ray diffraction study was carried out with a crystal obtained from diethyl ether. Fig. 1 shows the geometry of the molecule and the atomic numbering scheme used. Selected bond lengths and angles are given in Table 1.

The central molybdenum atom can be described as seven-co-ordinate, being bonded to two terminal carbonyl ligands, an (1,2,3-η)-*trans*-butadienyl fragment and a pentamethylcyclopentadienyl ligand, which is considered to occupy three co-ordination sites. Both metal carbonyl groups are essentially linear, within experimental error, with O–C–Mo angles of 177 and 175°, the Mo–C and C–O bond lengths being typical. The two carbonyl ligands lie at an angle of 82° to one another. The C$_5$Me$_5$ ligand is essentially planar, with methyl substituents pushed up out of the plane by a mean angle of 4.7°.

The butadienyl ligand is bound *via* C(6), C(7) and C(8) to the metal, with C(9) bent away from the molybdenum atom at a non-bonding distance of 3.43 Å, and with the C(7)–C(8)–C(9) angle opened out to 139°. The 'η^3-allyl' type backbone can be seen to adopt an *exo* orientation with respect to the η^5-C$_5$Me$_5$ ligand, the C(6)–C(7)–C(8) angle of 120° being typical[19] of η^3-allyl complexes. The relative stereochemistry of the butadienyl ligand itself is transoid. The C(6)–C(7)–C(8) fragment lies symmetrically opposite the two carbonyl ligands as illustrated by the fact that the two angles C(16)–Mo–C(7) and C(17)–Mo–C(7) are almost identical. The non-co-ordinated butadienylic double bond [C(8)–C(9)] distance of 1.35 Å is only slightly longer than the terminal C–C bond length in free buta-1,3-diene,[20] and is also within the range found[21] for the unco-ordinated C=CH$_2$ bond of ligated allene complexes. Using low-angle data, three of the butadienyl fragment hydrogen atoms were located; H(6a), H(6b) and H(9b). The coordinates of H(9a) could be generated by assuming sp^2 hybridisation of C(9). Fig. 1 shows clearly that H(6a) and H(6b) lie orthogonal to the pair H(9a) and H(9b). This established that the two adjacent π systems, allyl and C=CH$_2$ bond, are not conjugated and that the bonding can be considered analogous to that found in allenes. Finally, it is interesting that carbon–carbon interatomic distances of 1.35 and 1.39 Å within the metal-bound part of the ligand are somewhat unsymmetrical. This, together with the metal–carbon separations of 2.33, 2.21 and 2.20 Å, implies some degree of localised bonding from the metal to C(8) as shown in formalism **C** in Scheme 3. It is interesting that all of the substituted (1,2,3-η)-*trans*-butadienyl complexes whose structures have been established by X-ray crystallography also show a short metal to carbon bond consistent with a contribution from structure **C**, however, it is important to note that examination of the C–C distances within the butadienyl moiety implies a contribution from structure **D** in many cases. Whether **C** or **D** predominates is clearly dependent on the metal as well as ligand substituents.

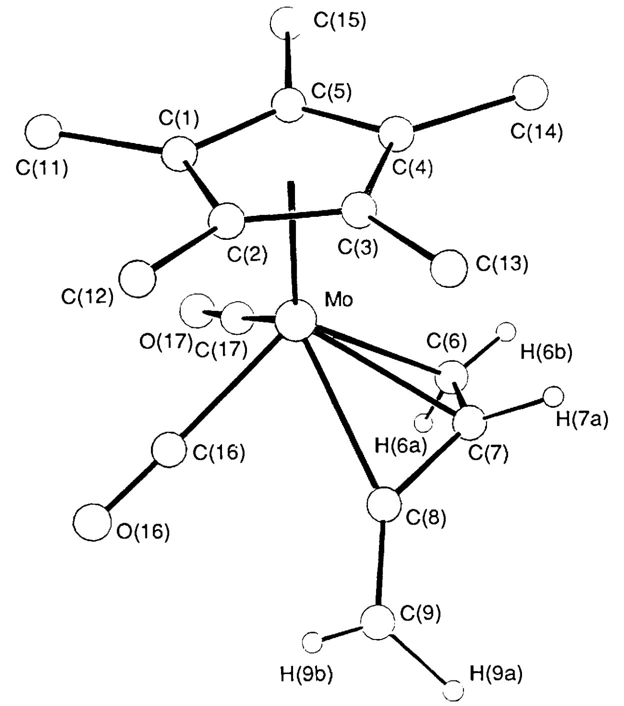


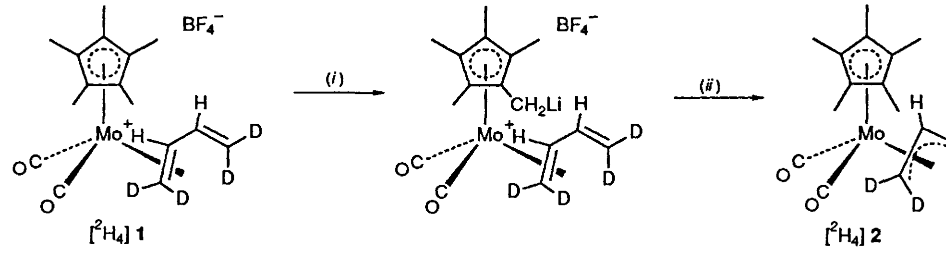
Fig. 1 Molecular structure of complex **2** showing labelling scheme, which with the exception of η-C$_5$Me$_5$ ligand, includes all hydrogen atoms

Carbon-13 NMR spectroscopy has also proved diagnostic in characterising these complexes and in understanding the bonding. The quaternary carbon C(8) in **2** was found to resonate at surprisingly low field, typically δ 170 for these unsubstituted systems. In the complexes characterised by Bruce *et al.*,[9] which carry electron-withdrawing cyano substituents, the quaternary carbon is deshielded further and resonates in the range δ 210–240, leading to the suggestion of a major contribution from structure **E** (Scheme 3).

There is no precedent for the deprotonation reaction involved in the transformation **1** ⟶ **2**, and it is obviously interesting to consider possible reaction pathways. The failure of the deprotonation reaction with the corresponding η^5-indenyl and η^5-cyclopentadienyl system implicated the η^5-C$_5$Me$_5$ ligand as a necessary participant in this reaction, and an insight into its role was provided by the observation that when a solution of complex **1** in (CD$_3$)$_2$CO was treated with an excess of NEt$_3$, and the cation **1** reisolated after several days, the ^{2}H NMR spectrum showed that an average of *ca.* 1.2 atoms of deuterium per molecule had been incorporated into the methyl groups of the C$_5$Me$_5$ ligand. This suggests that the reaction **1** ⟶ **2** proceeds *via* an initial deprotonation of one of the methyl groups of the η^5-C$_5$Me$_5$ ligand, for which there are many precedents. Subsequent *intramolecular* deprotonation then affords **2** (see Scheme 4). This suggestion is supported by the observation that the corresponding deprotonation reaction with the 1,1,4,4-

Table 1 Bond lengths (Å) and angles (°) for complex **2**

Mo–C(1)	2.293(11)	Mo–C(2)	2.323(13)	C(2)–C(12)	1.502(19)	C(3)–C(4)	1.433(20)
Mo–C(3)	2.393(12)	Mo–C(4)	2.420(12)	C(3)–C(13)	1.536(23)	C(4)–C(5)	1.393(18)
Mo–C(5)	2.312(13)	Mo–C(16)	1.926(13)	C(4)–C(14)	1.536(18)	C(5)–C(15)	1.512(20)
Mo–C(17)	1.934(14)	Mo–C(6)	2.328(13)	C(16)–O(16)	1.155(17)	C(17)–O(17)	1.179(18)
Mo–C(7)	2.208(14)	Mo–C(8)	2.198(15)	C(6)–C(7)	1.348(22)	C(7)–C(8)	1.391(20)
C(1)–C(2)	1.477(19)	C(1)–C(5)	1.426(16)	C(8)–C(9)	1.353(24)		
C(1)–C(11)	1.511(19)	C(2)–C(3)	1.373(18)				
C(2)–Mo–C(1)	37.3(5)	C(3)–Mo–C(1)	59.2(5)	C(8)–Mo–C(17)	109.0(6)	C(8)–Mo–C(6)	63.0(5)
C(3)–Mo–C(2)	33.8(4)	C(4)–Mo–C(1)	59.2(4)	C(8)–Mo–C(7)	36.8(5)	C(2)–C(1)–Mo	72.5(7)
C(4)–Mo–C(2)	57.8(4)	C(4)–Mo–C(3)	34.6(5)	C(5)–C(1)–Mo	72.7(7)	C(5)–C(1)–C(2)	104(1)
C(5)–Mo–C(1)	36.1(4)	C(5)–Mo–C(2)	59.1(5)	C(11)–C(1)–Mo	124.8(8)	C(11)–C(1)–C(2)	129(1)
C(5)–Mo–C(3)	57.4(5)	C(5)–Mo–C(4)	34.1(5)	C(11)–C(1)–C(5)	127(1)	C(1)–C(2)–Mo	70.2(6)
C(16)–Mo–C(1)	97.8(5)	C(16)–Mo–C(2)	90.9(5)	C(3)–C(2)–Mo	75.9(7)	C(3)–C(2)–C(1)	109(1)
C(16)–Mo–C(3)	116.7(5)	C(16)–Mo–C(4)	148.6(5)	C(12)–C(2)–Mo	126(1)	C(12)–C(2)–C(1)	122(1)
C(16)–Mo–C(5)	132.9(5)	C(17)–Mo–C(1)	97.9(5)	C(12)–C(2)–C(3)	128(1)	C(2)–C(3)–Mo	70.3(7)
C(17)–Mo–C(2)	133.4(5)	C(17)–Mo–C(3)	150.8(6)	C(4)–C(3)–Mo	73.7(7)	C(4)–C(3)–C(2)	110(1)
C(17)–Mo–C(4)	119.7(6)	C(17)–Mo–C(5)	93.3(5)	C(13)–C(3)–Mo	122(1)	C(13)–C(3)–C(2)	125(1)
C(17)–Mo–C(16)	82.0(6)	C(6)–Mo–C(1)	145.1(5)	C(13)–C(3)–C(4)	126(1)	C(3)–C(4)–Mo	71.7(7)
C(6)–Mo–C(2)	149.1(5)	C(6)–Mo–C(3)	115.3(5)	C(5)–C(4)–Mo	68.7(7)	C(5)–C(4)–C(3)	106(1)
C(6)–Mo–C(4)	96.1(5)	C(6)–Mo–C(5)	109.7(5)	C(14)–C(4)–Mo	124.1(8)	C(14)–C(4)–C(3)	128(1)
C(6)–Mo–C(16)	113.1(5)	C(6)–Mo–C(17)	71.9(5)	C(14)–C(4)–C(5)	125(1)	C(1)–C(5)–Mo	71.2(7)
C(7)–Mo–C(1)	150.5(5)	C(7)–Mo–C(2)	122.8(5)	C(4)–C(5)–Mo	77.2(8)	C(4)–C(5)–C(1)	111(1)
C(7)–Mo–C(3)	93.4(5)	C(7)–Mo–C(4)	92.3(5)	C(15)–C(5)–Mo	123.8(9)	C(15)–C(5)–C(1)	123(1)
C(7)–Mo–C(5)	121.5(5)	C(7)–Mo–C(16)	105.0(6)	C(15)–C(5)–C(4)	125(1)	O(16)–C(16)–Mo	177(1)
C(7)–Mo–C(17)	103.5(5)	C(7)–Mo–C(6)	34.5(6)	O(17)–C(17)–Mo	175(1)	C(7)–C(6)–Mo	67.9(7)
C(8)–Mo–C(1)	148.1(4)	C(8)–Mo–C(2)	111.6(5)	C(6)–C(7)–Mo	77.7(9)	C(8)–C(7)–Mo	71.2(8)
C(8)–Mo–C(3)	98.9(5)	C(8)–Mo–C(4)	117.1(5)	C(8)–C(7)–C(6)	120(1)	C(7)–C(8)–Mo	72.0(9)
C(8)–Mo–C(5)	151.2(5)	C(8)–Mo–C(16)	70.1(6)	C(9)–C(8)–Mo	149(1)	C(9)–C(8)–C(7)	139(1)

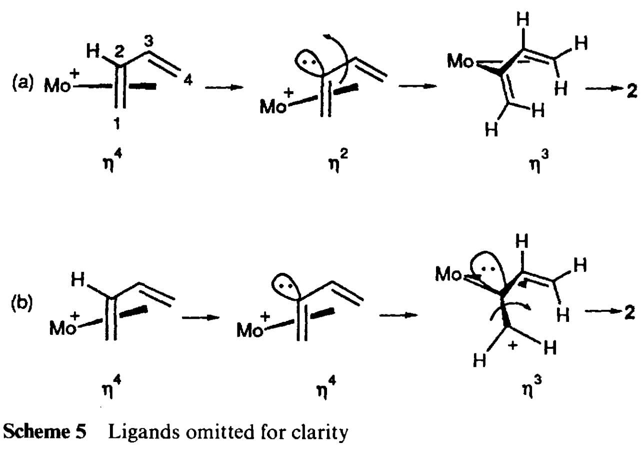


Scheme 4 (*i*) $+\mathrm{Li[N(SiMe_3)_2]}$, $-\mathrm{NH(SiMe_3)_2}$; (*ii*) $-\mathrm{LiBF_4}$

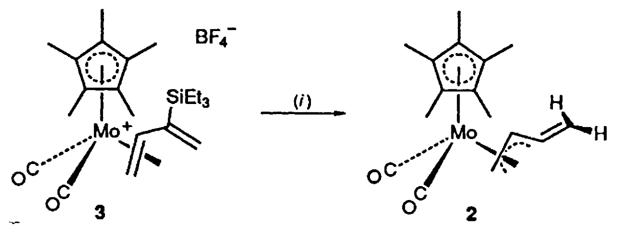
tetradeuteriobuta-1,3-diene cation [$^2H_4$]**1** afforded **2** with the deuterium in the positions shown in Scheme 4.

A further point of interest arising from this reaction is the origin of the geometry observed for the butadienyl ligand present in complex **2**. The η^3-allyl backbone of the ligand can be seen in Fig. 1 to adopt an *exo* orientation with respect to the η^5-C_5Me_5 ligand. This feature is unsurprising in that according to the mechanism proposed in Scheme 4 it is necessary for the protons attached to C^2 or C^3 of the 1,3-diene to be in close proximity to the internal base provided by the lithiated C_5Me_5 ligand. For this to occur, the 1,3-diene must therefore adopt an *exo* orientation, this relative geometry being retained in the product **2**. Although it has previously[18] been noted that for **1** an equilibrium[22] exists in solution at 25 °C with the *endo* isomer predominating, it can be assumed that the *exo* species maintains an equilibrium concentration sufficient to permit the deprotonation to take place.

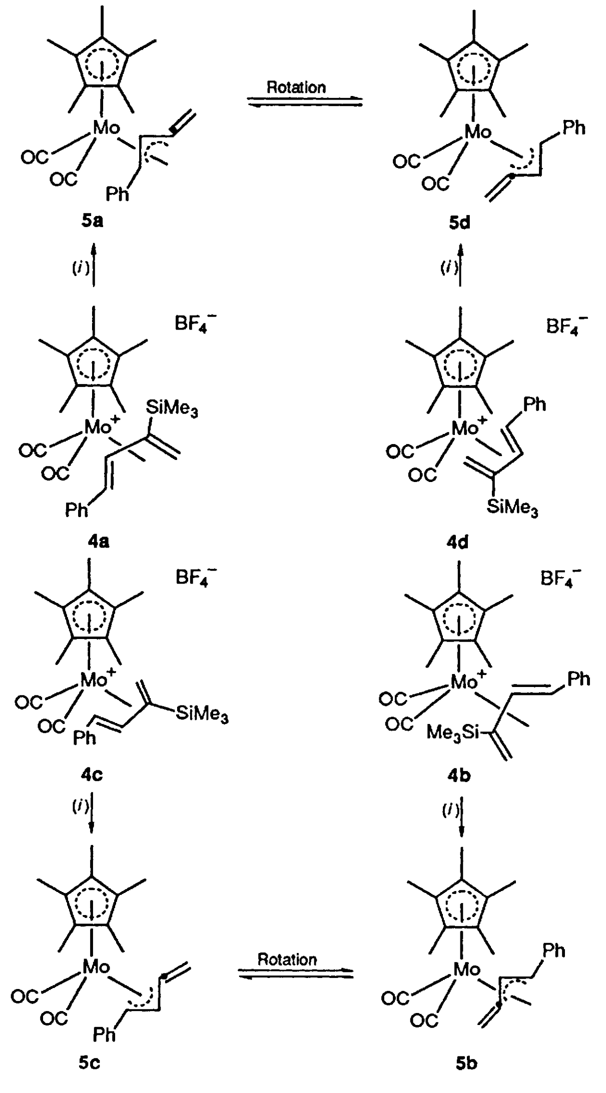
More intriguing is the matter of the relative stereochemistry of the butadienyl ligand itself. The solid-state structure of complex **2** shows the gross conformation of the ligand to be transoid in nature, as has also been the case for all of the other examples of (1,2,3-η)-butadienyl complexes characterised in this manner. This is in contrast with the 1,3-diene cation precursor **1**, in which the diene is present wholly in an *s-cis* conformation, there being no evidence suggesting any *s-cis* $\rightleftharpoons$ *s-trans* interconversion in solution. It is thus evident that during the conversion of **1** into **2** a rotation about the C^2–C^3 axis of the 1,3-diene ligand must occur in order to explain this change in stereochemistry. The geometrical changes accompanying this reaction are, however, more subtle than a simple rotation, in that the two terminal CH_2 groups of the parent 1,3-diene end up orthogonal to each other. There are two seemingly distinct ways of achieving this (Scheme 5). The first pathway (a) involves initial deprotonation followed by a η^4 to η^2 change in the bonding mode of the 1,3-diene and rotation about the C^2–C^3 axis so that the lone pair on C^2 can interact with the



Scheme 5 Ligands omitted for clarity



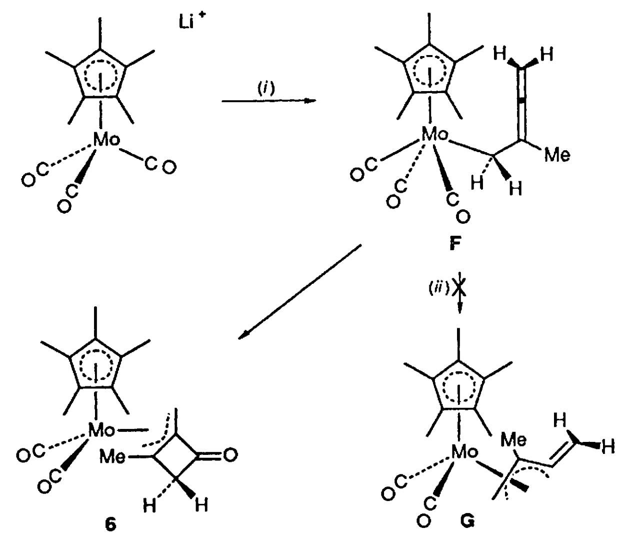
Scheme 6 (*i*) $[NBu^n_4]F$, thf, $-SiEt_3F$



Scheme 7 (*i*) $+[NBu^n_4]F$, $-SiMe_3F$

molybdenum centre. The second pathway (b) involves a η^4 to η^3 change of the bonding and a net transfer of the positive charge from the metal to carbon. At present it is difficult to differentiate between these two possibilities.

From a synthetic standpoint the deprotonation route to (1,2,3-η)-*trans*-butadienyl complexes is clearly limited to η-C_5Me_5 substituted systems, and therefore we sought to avoid this limitation by examining a potentially related fluoride anion-induced desilylation reaction. Thus, a suspension of $[Mo(NCMe)_2(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$ in thf was treated with an excess of 2-triethylsilylbuta-1,3-diene and the resulting mixture heated to form in excellent yield the 1,3-diene substituted cation $[Mo\{\eta^4\text{-}CH_2{=}CHC(SiEt_3){=}CH_2\}(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$ **3**. The presence, in solution at 25 °C, of a single isomeric species was demonstrated by ^1H NMR spectroscopy, although the broadness of the signals suggested some degree of *endo–exo* equilibration. Neutral complexes containing 2-silyl-1,3-dienes co-ordinated at tricarbonyliron centres have previously been prepared by Pearson[23] and Paquette[24] and their co-workers.



Scheme 8 (*i*) $+CH_2{=}C{=}C(Me)CH_2Cl$; (*ii*) thermolysis, $-CO$

Treatment of the silyldiene substituted cation **3** with a stoichiometric quantity of tetra-*n*-butylammonium fluoride in tetrahydrofuran effected smooth desilylation, affording, after chromatographic work-up, **2** (the η-C_5H_5 substituted complexes of Mo and W can also be prepared by the desilylation route) in yields of up to 90% (Scheme 6). The mechanistic implications of this reaction are likely to be broadly analogous to those postulated for the original deprotonation reaction, with the action of the fluoride anion mirroring that of the base. Formation of **2** is virtually instantaneous at room temperature, and represents a marked activation of the silyldiene towards nucleophilic attack on silicon upon co-ordination to the cationic metal centre.

The possibility of preparing other structural analogues of complex **2** was also explored. The cation $[Mo\{\eta^4\text{-}CH(Ph){=}CHC(SiMe_3){=}CH_2\}(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$ **4** was prepared (82% yield) by treating 1-*syn*-1-phenyl-3-trimethylsilylbuta-1,3-diene[25] with $[Mo(CNMe)_2(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$. As is shown in Scheme 7 the cation **4** can exist as the *exo* and *endo* enantiomeric pairs **4a**/**4b** and **4c**/**4d**. The NMR spectra cannot distinguish between these pairs, however the peaks are sharp suggesting that only one pair is present in solution. Treatment of **4** with tetra-*n*-butylammonium fluoride again resulted in a smooth desilylation reaction and the formation of a yellow crystalline material, which was identified by elemental analysis, IR and NMR spectroscopy as a mixture of *exo-syn* and *endo-syn* isomers **5a**/**5b** and **5c**/**5d** (4:1) (Scheme 7).

The formation of *exo-syn* (**5a**/**5b**) and *endo-syn* (**5e**/**5d**) from one of the pairs **4a**/**4b** or **4c**/**4d** suggests that the mixture of *exo* and *endo* isomers is formed by subsequent rotation of the butadienyl ligand about an axis through the Mo and the plane of the butadienyl fragment. Isomerisation *via* a π–σ–π conversion would cause the phenyl and H^e substituents to exchange their positions, and this does not occur.

In order to complete our initial synthetic investigation one other possible route to (1,2,3-η)-*trans*-butadienyl complexes was examined. Thus, in analogous fashion to conventional η^3-allyl synthesis, a study of the reaction of 4-chloro-3-methylbuta-1,2-diene with the nucleophile $Li[Mo(CO)_3(\eta\text{-}C_5Me_5)]$ was undertaken. As is shown in Scheme 8 such a reaction might have been expected to afford initially the complex F, which on thermolysis would be expected to lose a molecule of carbon monoxide to form the (1,2,3-η)-*trans*-

Table 2 Bond lenghts (Å) and angles (°) for complex **6**

Mo–C(16)	1.935(8)	Mo–C(17)	1.942(6)	C(2)-C(12)	1.489(7)	C(3)–C(4)	1.414(7)
Mo–C(1)	2.419(7)	Mo–C(2)	2.404(6)	C(3)–C(13)	1.498(12)	C(4)–C(5)	1.424(11)
Mo–C(3)	2.323(7)	Mo–C(4)	2.312(6)	C(4)–C(14)	1.503(10)	C(5)–C(15)	1.501(8)
Mo–C(5)	2.353(5)	Mo–C(6)	2.330(4)	C(6)–C(7)	1.405(10)	C(7)–C(8)	1.441(8)
Mo–C(7)	2.213(5)	Mo–C(8)	2.402(6)	C(7)–C(18)	1.489(11)	C(8)–C(9)	1.535(11)
C(16)–O(16)	1.163(11)	C(17)–O(17)	1.162(7)	C(8)–C(10)	1.503(10)	C(9)–C(18)	1.539(9)
C(1)–C(2)	1.438(9)	C(1)–C(5)	1.414(8)	C(18)–O(18)	1.208(8)		
C(1)–C(11)	1.493(12)	C(2)–C(3)	1.428(11)				
C(17)–Mo–C(16)	81.43(3)	C(1)–Mo–C(16)	149.9(3)	C(5)–C(1)–Mo	70.2(4)	C(5)–C(1)–C(2)	107.4(6)
C(1)–Mo–C(17)	108.8(2)	C(2)–Mo–C(16)	125.1(3)	C(11)–C(1)–Mo	129.7(4)	C(11)–C(1)–C(2)	127.0(5)
C(2)–Mo–C(17)	142.3(2)	C(2)–Mo–C(1)	34.7(2)	C(11)–C(1)–C(5)	125.1(5)	C(1)–C(2)–Mo	73.2(3)
C(3)–Mo–C(16)	93.7(3)	C(3)–Mo–C(17)	133.9(2)	C(3)–C(2)–Mo	69.3(4)	C(3)–C(2)–C(1)	107.6(4)
C(3)–Mo–C(1)	58.4(3)	C(3)–Mo–C(2)	35.1(3)	C(12)–C(2)–Mo	128.1(4)	C(12)–C(2)–C(1)	126.0(7)
C(4)–Mo–C(16)	92.6(3)	C(4)–Mo–C(17)	98.6(2)	C(12)–C(2)–C(3)	126.1(6)	C(2)–C(3)–Mo	75.6(4)
C(4)–Mo–C(1)	58.4(2)	C(4)–Mo–C(2)	58.5(2)	C(4)–C(3)–Mo	71.8(4)	C(4)–C(3)–C(2)	108.3(6)
C(4)–Mo–C(3)	35.5(2)	C(5)–Mo–C(16)	123.4(2)	C(13)–C(3)–Mo	124.8(5)	C(13)–C(3)–C(2)	125.5(5)
C(5)–Mo–C(17)	85.9(2)	C(5)–Mo–C(1)	34.4(2)	C(13)–C(3)–C(4)	125.7(7)	C(3)–C(4)–Mo	72.6(3)
C(5)–Mo–C(2)	57.8(2)	C(5)–Mo–C(3)	58.7(2)	C(5)–C(4)–Mo	73.8(3)	C(5)–C(4)–C(3)	107.8(6)
C(5)–Mo–C(4)	35.5(3)	C(6)–Mo–C(16)	76.0(2)	C(14)–C(4)–Mo	124.8(5)	C(14)–C(4)–C(3)	125.9(7)
C(6)–Mo–C(17)	123.2(2)	C(6)–Mo–C(1)	116.7(2)	C(14)–C(4)–C(5)	126.0(5)	C(1)–C(5)–Mo	75.3(3)
C(6)–Mo–C(2)	91.4(2)	C(6)–Mo–C(3)	99.3(2)	C(4)–C(5)–Mo	70.7(3)	C(4)–C(5)–C(1)	108.9(5)
C(6)–Mo–C(4)	133.4(2)	C(6)–Mo–C(5)	148.9(2)	C(15)–C(5)–Mo	126.1(4)	C(15)–C(5)–C(1)	124.6(7)
C(7)–Mo–C(16)	102.8(2)	C(7)–Mo–C(17)	104.8(2)	C(15)–C(5)–C(4)	126.1(6)	C(7)–C(6)–Mo	67.5(3)
C(7)–Mo–C(1)	101.7(2)	C(7)–Mo–C(2)	95.1(2)	C(6)–C(7)–Mo	76.6(3)	C(8)–C(7)–Mo	79.1(3)
C(7)–Mo–C(3)	120.8(2)	C(7)–Mo–C(4)	153.5(2)	C(8)–C(7)–C(6)	128.4(6)	C(18)–C(7)–Mo	108.9(3)
C(7)–Mo–C(5)	133.7(2)	C(7)–Mo–C(6)	35.9(3)	C(18)–C(7)–C(6)	140.6(5)	C(18)–C(7)–C(8)	90.4(5)
C(8)–Mo–C(16)	101.2(3)	C(8)–Mo–C(17)	69.0(2)	C(7)–C(8)–Mo	64.8(3)	C(9)–C(8)–Mo	108.9(4)
C(8)–Mo–C(1)	108.9(2)	C(8)–Mo–C(2)	121.7(2)	C(9)–C(8)–C(7)	93.3(5)	C(10)–C(8)–Mo	121.4(5)
C(8)–Mo–C(3)	154.9(2)	C(8)–Mo–C(4)	159.5(2)	C(10)–C(8)–C(7)	127.2(6)	C(10)–C(8)–C(9)	124.5(6)
C(8)–Mo–C(5)	124.7(2)	C(8)–Mo–C(6)	65.5(2)	C(18)–C(9)–C(8)	85.1(5)	C(9)–C(18)–C(7)	91.2(5)
C(8)–Mo–C(7)	36.1(2)	O(16)–C(16)–Mo	177.1(6)	O(18)–C(18)–C(7)	135.0(6)	O(18)–C(18)–C(9)	133.2(7)
O(17)–C(17)–Mo	177.9(5)	C(2)–C(1)–Mo	72.1(4)				

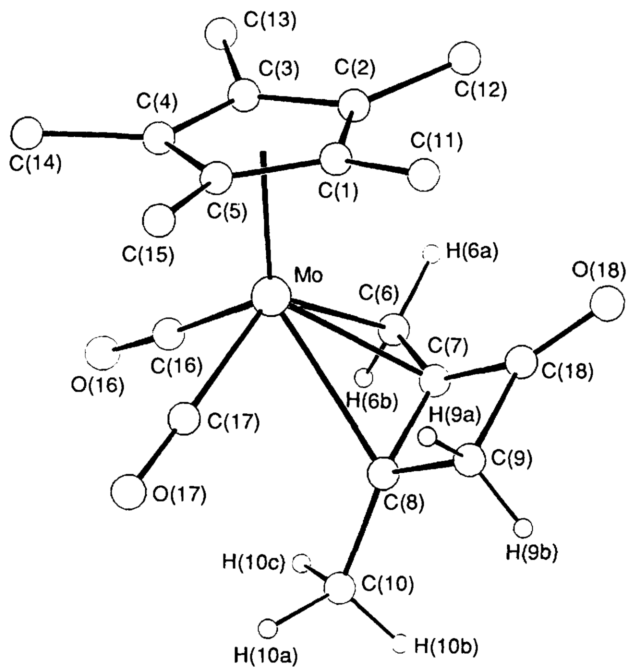
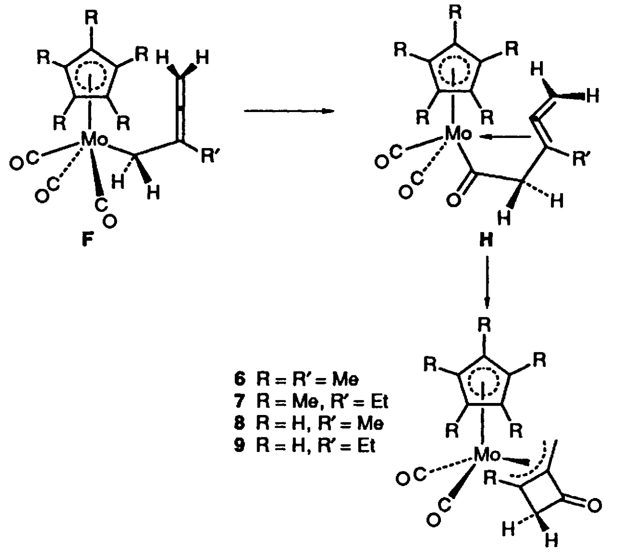


Fig. 2 Molecular structure of complex **6** showing labelling scheme, which with the exception of the η-C_5Me_5 ligand, includes all hydrogen atoms

butadienyl complex **G**. In the event **F** was not formed, instead an unusual orange-yellow crystalline compound **6** was obtained by chromatographic work-up of the reaction mixture. The IR spectrum showed two terminal carbonyl bands at 1940 and 1862, and an organic type CO stretch at 1738 cm^{-1}. The ^{1}H NMR spectrum did not show the low-field signals typical of the (1,2,3-η)-*trans*-butadienyl ligand, and the ^{13}C-{^{1}H} spectrum revealed signals characteristic of two methylenes and one methyl centre, in addition to three quaternary centres at δ 193.0, 98.3 and 93.0. The large upfield shift observed for the olefinic protons (δ 2.03 and 1.68) of the organic ligand suggested that the corresponding CH_2 was involved in bonding with the metal.

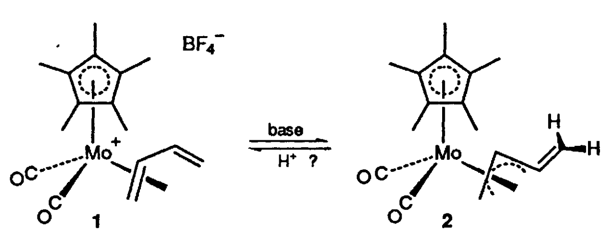
In order to establish the structure of **6** a single-crystal X-ray diffraction study was undertaken. The molecular geometry and atomic numbering scheme used are shown in Fig. 2. Selected bond lengths and angles are listed in Table 2. The molybdenum atom can be described as formally seven-co-ordinate, bound to two carbonyl ligands, a pentamethylcyclopentadienyl ring, and a six-carbon organic fragment bonded *via* three carbon atoms in an η^3-allylic fashion. The metal carbonyl groups are essentially linear [Mo–C(16)–O(16) 177.1, Mo–C(17)–O(17) 177.9°] with unexceptional Mo–C and C–O interatomic distances. The η^5-C_5Me_5 ring is almost planar and is bound at a mean distance of 1.26 Å from the metal atom, the methyl groups being pushed out of the plane of the ring away from the metal at a mean angle of 7.3°. The organic ligand is most interesting and to our knowledge unique. It has formally resulted from incorporation of one carbonyl ligand into the allenyl fragment. The ligand is bound *via* three carbon atoms in a manner analogous to that observed for η^3-allylic complexes. This C(6)–C(7)–C(8) moiety is bonded *exo* with respect to the η^5-C_5Me_5 ring with Mo–C distances of 2.33, 2.21 and 2.40 Å and a bond angle of 127° typical for η^3-allylic molybdenum complexes. The C(7)–C(8) vector makes up one side of a four-membered ring, which is completed by methylene C(9) and the carbonyl, C(18)–O(18), groups. The four-membered ring is planar and internal angles of 90 ± 5° imply that the system is strained. The bond lengths within the ring of 1.54, 1.54 and 1.49 Å are typical for C–C single bonds. The C(7)–C(8) distance of 1.44 Å is commensurate with a η^3-allylic bonding arrangement.

This unusual cyclobutenone ring-forming reaction proved



6 R = R' = Me
7 R = Me, R' = Et
8 R = H, R' = Me
9 R = H, R' = Et

Scheme 9



Scheme 10

to be capable of generalisation allowing the synthesis in good yield of $[\mathrm{Mo}\{\eta^3\text{-}\mathrm{CH_2\overline{CC(Et)CH_2C}O}\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5Me_5})]$ **7**, $[\mathrm{Mo}\{\eta^3\text{-}\mathrm{CH_2\overline{CC(Me)CH_2C}O}\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$ **8** and $[\mathrm{Mo}\{\eta^3\text{-}\mathrm{CH_2\overline{CC(Et)CH_2C}O}\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})]$ **9**. In terms of mechanism the formation of these molecules can be understood by the interception of the postulated intermediate **F** (Scheme 8) *via* an intramolecular η^2-co-ordination of the allenyl ligand and concomitant migration of the allenyl fragment onto a co-ordinated CO ligand. The resulting intermediate **H** (Scheme 9) could then collapse *via* a formal insertion of the co-ordinated allenic double bond into the metal–acyl bond to form the four-membered ring present in **6**–**9**.

With the synthesis and structural characterisation of the simple (1,2,3-η)-*trans*-butadienyl complex **2** it was now possible to begin to explore its chemical reactivity. Recalling the manner in which **2** was originally obtained it was important to ascertain the reversibility of this reaction (Scheme 10), and as a first step it was clearly of interest to use the structural parameters now available for **2** to assess *via* an extended Hückel molecular orbital (EHMO) calculation the relative reactivity of the different sites present on the (1,2,3-η)-butadienyl ligand towards protons. Such calculations were therefore carried out using the complete set of crystallographic coordinates. No geometry idealisations have been made save that all the C–H bond lengths were fixed at 1.08 Å. The global coordinate frame was chosen with Z along the Mo–C^7 bond (see Fig. 1) and X lying in the plane of the Z axis and the OC–Mo–CO bisection. The standard EHMO method was employed as implemented in Hoffmann's ICON8 program.[26] Charge interation calculations were also performed but did not produce significantly different results to those from the standard method. Only the latter are therefore described below. The weighted H_{ij} formula was used throughout with default parameters for all atoms except Mo where values from Curtis and Eisenstein[27] were taken.

Theoretical predictions of reactivity focus on the atomic charges if the mechanism is charge controlled or on MO coefficients if the mechanism is frontier-orbital controlled. A detailed analysis of the bonding and reactivity for a substituted molybdenum η^3-butadienyl species has appeared recently.[13] Given that **2** possesses an unsubstituted ligand and that it can be obtained by deprotonation, we seek here to examine only the susceptibility of **2** towards electrophilic attack.

Electrophilic attack on the butadienyl ligand is predicted at the site with the largest negative charge, if charge controlled, or at the site with the largest MO coefficient in the highest occupied molecular orbital (HOMO), if frontier-orbital controlled. In both instances,the EHMO calculations indicate attack at C^9 (see Fig. 1). The Mulliken population analysis gives a charge of −0.35 for C^9 which is over twice as large as the value of −0.15 for C^6. Both C^7 and C^8 have small positive charges of about 0.03. The only significant HOMO coefficients on the butadienyl moiety are on C^9 where the p_x and p_y atomic orbitals have coefficients of −0.25 and 0.15 respectively. The remaining butadienyl carbon atomic coefficients have magnitudes less than 0.09. It is thus clear from the calculations that the deprotonation reaction which generates complex **2** would not be expected to be reversible. Instead attack should occur on the methylene carbon C^9 to give an η^3-vinylcarbene fragment.

Addition of $\mathrm{HBF_4{\cdot}Et_2O}$ to a cooled (−78 °C) solution of complex **2** in $\mathrm{CH_2Cl_2}$ resulted in an immediate reaction as evidenced by IR spectroscopy. After warming to room temperature, the mixture was worked up according to standard procedures, but did not yield a stable, identifiable product, although the regeneration of **1** could be dismissed from the IR data. Continuing our investigation, the use of trifluoromethanesulfonic acid proved to be more fruitful. Dropwise addition to a cooled (−78 °C) solution of **2** in dichloromethane caused an instantaneous change in colour from yellow to deep orange-red. The reaction mixture was warmed to room temperature and filtered through Celite. Removal of the solvent gave the crude product as a brownish orange solid. The IR data revealed a single terminal carbonyl absorption band at 2007 cm^{-1}, in addition to a second band at 1677 cm^{-1}, indicating that an unexpected reaction had taken place. The protonation product **10** was found to be soluble in diethyl ether, and was clearly not cationic. The NMR spectra for this material showed it to be a single complex, and it was initially[15] identified as the η^3-vinylcarbene complex $[\mathrm{Mo(OSO_2CF_3)}\{\eta^3\text{-}\mathrm{C(Me)CH{=}CH_2}\}(\mathrm{CO})(\eta\text{-}\mathrm{C_5Me_5})]$, however inconsistencies in the data cast doubt over the proposed structure and therefore more definitive information was sought. Crystals suitable for an X-ray analysis could not be procured, leading us to examine the possibility of preparing structural analogues by replacement of the triflate ligand. Addition of a large excess of lithium iodide to a solution of the triflate **10** in dichloromethane effected smooth conversion into a single new species **11** as shown by IR spectroscopy. The product was purified by column chromatography on alumina, elution with diethyl ether affording, upon recrystallisation, orange crystals that were effectively air-stable in the solid state. The replacement of the co-ordinated triflate ligand was confirmed by ^{13}C NMR spectroscopy with its substitution by iodide anion assumed. Both the ^{1}H and ^{13}C-{^{1}H} NMR spectra of **11** bore a close resemblance to those of their triflate precursor, demonstrating their common structural identity. The greater stability of the iodo complex allowed high-quality crystals to be obtained, and a single-crystal X-ray diffraction analysis was carried out.

This revealed the solid-state structure to be that of the η^4-vinylketene complex as illustrated in Scheme 11. The solid-state structure of **11** (Fig. 3, selected bond lengths and angles in Table 3) shows a typical piano-stool type arrangement with the vinylketene ligand orientated *endo* with respect to the $\eta\text{-}\mathrm{C_5Me_5}$ ligand. The iodo ligand is bound to the metal at a distance of 2.88 Å and lies *trans* to the carbonyl terminus of the organic ligand. The angle between the terminal and cumulated carbon atoms, C(17)–Mo–C(16), is 83.9°. The terminal carbonyl ligand deviates slightly from linearity [Mo–C(16)–O(16) 174.5°], but the interatomic distances of Mo–C(16) 2.00 Å and C(16)–O(16) 1.13 Å are unremarkable. The pentamethylcyclopentadienyl ligand is bound at a mean distance of 2.32 Å from the metal centre with the methyl substituents pushed up and out of the plane of the ring by an average angle of 9.24°.

Comparison (Table 4) of the structural parameters observed for the vinylketene ligand present in **11** with those observed for related complexes shows a good agreement. The metal–carbon separation of 2.08 Å for Mo–C(17) is considerably shorter than the other metal–ligand distances (2.38, 2.41, 2.33 Å). This suggests that C(17) participates more strongly in the metal–ligand back bonding than the other three carbon atoms of the η^4 system. The C(17)–C(18) distance of 1.46 Å implies a substantial decrease in bond order. This, together with the other two C–C separations of 1.41 Å, indicates a more delocalised structure than the vinylketene formalism suggests. This arises through contributions from the alternative bonding descriptions **J** and **K** (Scheme 12). Formalisms **J** and **K** are termed σ,η^3-allylcarbonyl and 1-metallacyclopent-3-en-2-one respectively. Both **J** and **K** result in a rehybridisation of C^1 from sp to sp^2 which causes the C^2–C^1–O angle to approach 120°. The cumulated double bond does indeed show a significant deviation from linearity of nearly 50° with the bond angle found to be 130.5°. The angle C(18)–C(19)–C(20) of 122° is typical of that found with η^3-allyl complexes. The torsion angle C(17)–C(18)–C(19)–C(20) of $-3.9°$ indicates that the vinylketene moiety in **11** is almost planar. The carbonyl group oxygen atom lies out of the plane as illustrated by the dihedral angles C(21)–C(18)–C(17)–O(17) $-46.2°$ and C(19)–C(18)–C(17)–O(17) 134.5°.

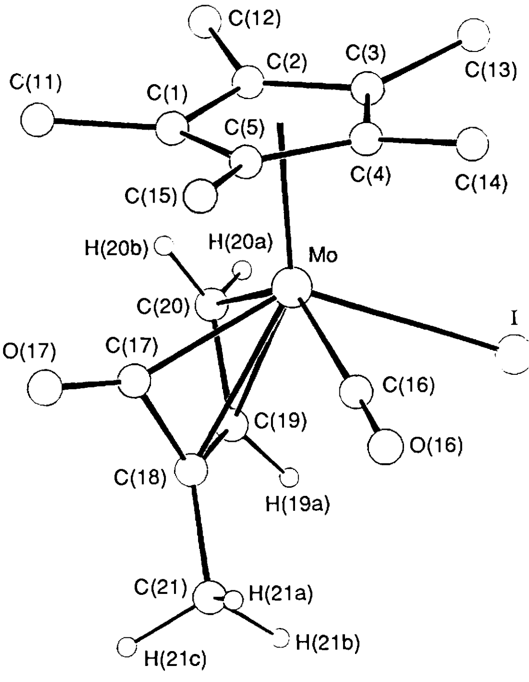
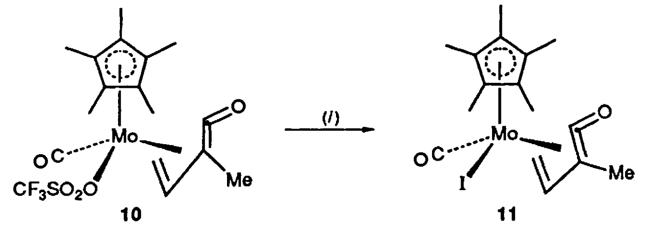


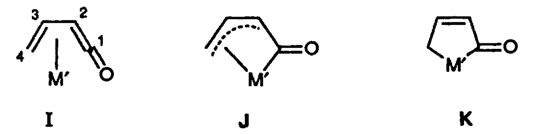
Fig. 3 Molecular structure of **11** showing labelling scheme, which with the exception of the η-C_5Me_5 ligand, includes all hydrogen atoms



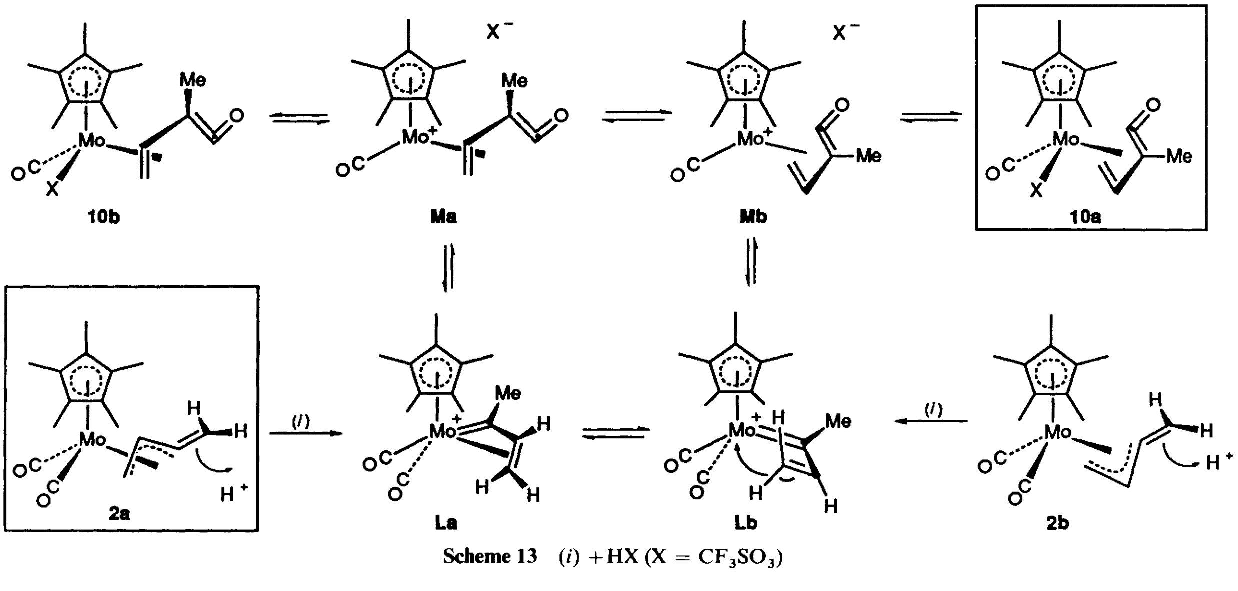
Scheme 11 (*i*) + LiI, CH_2Cl_2

The ^{13}C-{^{1}H} NMR spectra of complexes **10** and **11** each show a pair of low-field signals (δ 255.9 and 223.4 **10**, 256.4 and 223.8 **11**) attributed to C^1 of the vinylketene and the carbonyl ligand (see Experimental section for numbering scheme). A ^{1}H-coupled spectrum recorded for **10** revealed a 9 Hz *J*(CH) coupling for the signal at δ 255.9, identifying it as the ketene C^1 resonance. Signals deriving from C^2–C^4 of the vinylketene (δ 85.0, 133.5, 62.8 **10**; 64.3, 130.8, 57.9 **11**) for C^2, C^3, C^4 respectively, were unremarkable in magnitude, although the C^3 resonances are somewhat deshielded, perhaps due to electronic effects associated with other contributing resonance structures. The attached proton is similarly observed at low field (δ 6.48 **10**, 6.54 **11**) in contrast to the remaining vinylic protons.

The formation of an η^4-vinylketene complex by protonation of an (1,2,3-η)-*trans*-butadienyl complex is a unique observation. It is reasonable to propose that the reaction proceeds *via* an η^3-vinylcarbene intermediate and involves the three steps depicted in Scheme 13: (*i*) protonation of the butadienyl ligand under



Scheme 12



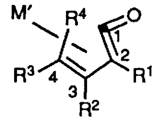
Scheme 13 (*i*) + HX (X = CF_3SO_3)

Table 3 Bond lengths (Å) and angles (°) for complex **11**

Mo–I	2.882(1)	Mo–C(1)	2.310(7)	C(2)–C(3)	1.426(12)	C(2)–C(12)	1.532(12)
Mo–C(2)	2.376(8)	Mo–C(3)	2.374(9)	C(3)–C(4)	1.427(11)	C(3)–C(13)	1.498(13)
Mo–C(4)	2.289(7)	Mo–C(5)	2.257(7)	C(4)–C(5)	1.424(11)	C(4)–C(14)	1.492(12)
Mo–C(16)	2.004(8)	Mo–C(17)	2.082(8)	C(5)–C(15)	1.521(10)	C(16)–O(16)	1.126(10)
Mo–C(18)	2.377(8)	Mo–C(19)	2.414(8)	C(17)–O(17)	1.205(10)	C(17)–C(18)	1.463(11)
Mo–C(20)	2.327(7)	C(1)–C(2)	1.441(11)	C(18)–C(19)	1.409(12)	C(18)–C(21)	1.498(13)
C(1)–C(5)	1.420(10)	C(1)–C(11)	1.513(12)	C(19)–C(20)	1.409(12)		

C(1)–Mo–I	144.5(2)	C(2)–Mo–O	110.4(2)	C(20)–Mo–C(5)	130.7(3)	C(20)–Mo–C(16)	139.9(3)
C(2)–Mo–C(1)	35.8(3)	C(3)–Mo–I	85.9(2)	C(20)–Mo–C(17)	77.8(3)	C(20)–Mo–C(18)	63.2(3)
C(3)–Mo–C(1)	59.4(3)	C(3)–Mo–C(2)	35.0(3)	C(20)–Mo–C(19)	34.6(3)	C(2)–C(1)–Mo	74.6(5)
C(4)–Mo–I	96.5(2)	C(4)–Mo–C(1)	60.3(3)	C(5)–C(1)–Mo	69.9(4)	C(5)–C(1)–C(2)	107.4(7)
C(4)–Mo–C(2)	59.2(3)	C(4)–Mo–C(3)	35.6(3)	C(11)–C(1)–Mo	129.4(6)	C(11)–C(1)–C(2)	124.6(7)
C(5)–Mo–I	132.4(2)	C(5)–Mo–C(1)	36.2(3)	C(11)–C(1)–C(5)	127.1(7)	C(1)–C(2)–Mo	69.6(4)
C(5)–Mo–C(2)	59.6(3)	C(5)–Mo–C(3)	59.7(3)	C(3)–C(2)–Mo	72.5(5)	C(3)–C(2)–C(1)	108.1(6)
C(5)–Mo–C(4)	36.5(3)	C(16)–Mo–I	81.3(2)	C(12)–C(2)–Mo	130.0(6)	C(12)–C(2)–C(1)	125.1(8)
C(16)–Mo–C(1)	117.5(3)	C(16)–Mo–C(2)	139.7(3)	C(12)–C(2)–C(3)	126.3(8)	C(2)–C(3)–Mo	72.6(5)
C(16)–Mo–C(3)	113.4(3)	C(16)–Mo–C(4)	81.6(3)	C(4)–C(3)–Mo	68.9(5)	C(4)–C(3)–C(2)	107.8(7)
C(16)–Mo–C(5)	83.6(3)	C(17)–Mo–I	133.3(2)	C(13)–C(3)–Mo	130.4(6)	C(13)–C(3)–C(2)	124.7(7)
C(17)–Mo–C(1)	80.8(3)	C(17)–Mo–C(2)	109.5(3)	C(13)–C(3)–C(4)	126.9(8)	C(3)–C(4)–Mo	75.5(4)
C(17)–Mo–C(3)	140.2(3)	C(17)–Mo–C(4)	124.7(3)	C(5)–C(4)–Mo	70.5(4)	C(5)–C(4)–C(3)	108.0(7)
C(17)–Mo–C(5)	89.0(3)	C(17)–Mo–C(16)	83.9(3)	C(14)–C(4)–Mo	128.2(6)	C(14)–C(4)–C(3)	124.4(8)
C(18)–Mo–I	96.2(2)	C(18)–Mo–C(1)	115.7(3)	C(14)–C(4)–C(5)	126.7(7)	C(1)–C(5)–Mo	73.9(4)
C(18)–Mo–C(2)	133.0(3)	C(18)–Mo–C(3)	165.9(3)	C(4)–C(5)–Mo	73.0(4)	C(4)–C(5)–C(1)	108.6(6)
C(18)–Mo–C(4)	156.3(3)	C(18)–Mo–C(5)	125.4(3)	C(15)–C(5)–Mo	127.1(6)	C(15)–C(5)–C(1)	124.4(7)
C(18)–Mo–C(16)	80.6(3)	C(18)–Mo–C(17)	37.6(3)	C(15)–C(5)–C(4)	126.2(7)	O(16)–C(16)–Mo	174.5(7)
C(19)–Mo–I	77.2(2)	C(19)–Mo–C(1)	120.8(3)	O(17)–C(17)–Mo	146.3(6)	C(18)–C(17)–Mo	82.2(5)
C(19)–Mo–C(2)	114.8(3)	C(19)–Mo–C(3)	134.5(3)	C(18)–C(17)–O(17)	130.5(8)	C(17)–C(18)–Mo	60.2(4)
C(19)–Mo–C(4)	169.5(3)	C(19)–Mo–C(5)	150.4(3)	C(19)–C(18)–Mo	74.3(5)	C(19)–C(18)–C(17)	114.8(7)
C(19)–Mo–C(16)	105.4(3)	C(19)–Mo–C(17)	64.6(3)	C(21)–C(18)–Mo	133.0(5)	C(21)–C(18)–C(17)	121.8(7)
C(19)–Mo–C(18)	34.2(3)	C(20)–Mo–I	85.9(2)	C(21)–C(18)–C(19)	123.4(7)	C(18)–C(19)–Mo	71.5(4)
C(20)–Mo–C(1)	94.5(3)	C(20)–Mo–C(2)	80.4(3)	C(20)–C(19)–Mo	69.4(4)	C(20)–C(19)–C(18)	122.0(7)
C(20)–Mo–C(3)	103.2(3)	C(20)–Mo–C(4)	137.8(3)	C(19)–C(20)–Mo	76.1(4)		

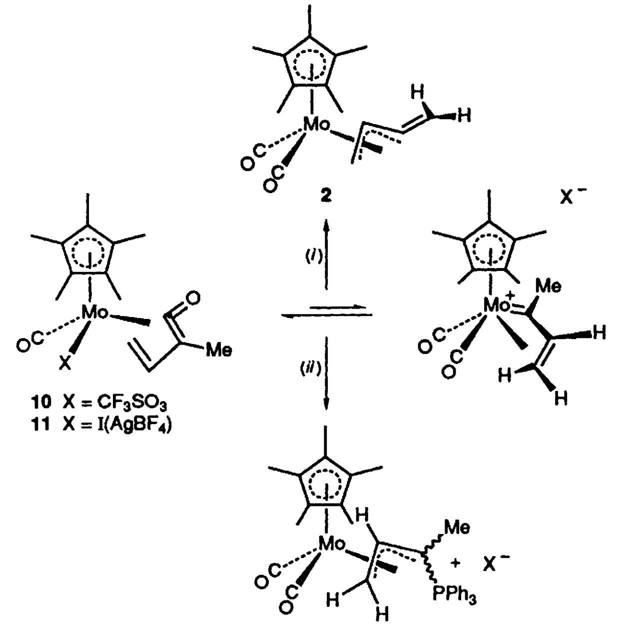
Table 4 X-Ray crystallographic data (bond lengths in Å, angles in °) for η^4-vinylketene complexes



M′	R^1	R^2	R^3	R^4	M–C^1	M–C^2	M–C^3	M–C^4	C^1–C^2	C^2–C^3	C^3–C^4	C^1–O	C^2–C^1–O	Ref.
Fe(CO)$_3$	Me	H	Ph	H	1.93	2.10	2.09	2.18	1.44	1.40	1.42	1.19		30
Fe(CO)$_2$(PPh$_3$)	OMe	CO$_2$Me	H	H	1.90	2.18	2.10	2.11	1.48	1.41	1.43	1.21		33
Fe(CO)$_3$	Me	H	Me	Me	1.92	2.11	2.09	2.20	1.44	1.40	1.41		137	28
Fe(CO)$_3$	Ph	Ph	Ph	H	1.92	2.14	2.13	2.17	1.47	1.42	1.43	1.19	137.4	31
Mn(CO)(η-C$_5$H$_5$)	Ph	Ph	Ph	H	1.90	2.12	2.13	2.22	1.48	1.43	1.42	1.20	134.7	32
					1.88	2.12	2.14	2.18	1.47	1.44	1.40	1.23	132.7	29
Co(η-C$_5$H$_5$)	Ph	Ph	Ph	H	1.84	2.03	2.01	2.09	1.44	1.41	1.42	1.21	139.5	32
Mo(η-C$_5$H$_5$)O	Me	Me	Me		2.09	2.47	2.43	2.29	1.47	1.40	1.45	1.22	131.0	35
C(CF$_3$)=C(Me)					2.08	2.43	2.44	2.30	1.48	1.38	1.48	1.21	130.5	
W(CO)(S$_2$CNEt$_2$)$_2$	Ph	H	Me	H	2.19	2.36	2.26	2.39	1.43	1.49	1.35	1.20	138.9	34
MoI(CO)(η-C$_5$Me$_5$)	Me	H	H	H	2.08	2.38	2.41	2.33	1.46	1.41	1.41	1.21	130.5	This work

charge or frontier orbital control to give a cationic η^3(4e)-vinylcarbene intermediate **L**, (*ii*) CO 'insertion' into the metal–carbon double bond[34] affording a 16-electron species **M** and (*iii*) capture of the unsaturated species by triflate anion. As is illustrated in Scheme 13 protonation of the *exo* isomer **2a**, *i.e.* the isomer used in the reaction, would be expected to give the η^3(4e)-vinylcarbene cation **La**, which could isomerise *via* a $\eta^3(4e) \rightleftharpoons \sigma(2e)$ change in bonding mode and rotation about the C^1–C^2 bond to the isomeric species **Lb**. The isomer **Lb** could in principle also be formed by protonation of the corresponding unknown *endo*-(1,2,3-η)-*trans*-butadienyl complex **2b**. Isomerisation of **La** and **Lb** by reversible coupling of a *cis* co-ordinated CO and the carbene accesses the unobserved *exo*- and *endo*-vinylketene cations **Ma** and **Mb**, which are then captured by X^- to form the isolated neutral vinylketene complex **10**. It is particularly interesting that **2a** gives **10a** selectively, in a reaction which is possibly thermodynamically controlled. Attempts to detect by low-temperature NMR spectroscopy formation of **L** on protonation of **2** were unsuccessful, and this is unusual in view of the report[36] that a tungsten analogue of **L**, the complex [W{=C(Ph)C(Ph)=CH(C$_6$H$_4$Me-4)}(CO$_2$)(η-C$_5$H$_5$)][BF$_4$] prepared by protonation of [W{≡C(C$_6$H$_4$Me-4)}(CO)$_2$(η-C$_5$H$_5$)] in the presence of PhC$_2$Ph and structurally identified by X-ray crystallography, does not incorporate CO into the vinylcarbene fragment either under pressure or upon addition of iodide anion.

The reverse transformation, *i.e.* the regeneration of the (1,2,3-η)-*trans*-butadienyl complex **2** from **10**, was also examined. Treatment of a solution of **10** in dichloromethane with triethylamine at room temperature resulted in a rapid conversion into **2**, in essentially quantitative yield. This reaction is interesting in that an *endo*-vinylketene is converted



10 X = CF_3SO_3
11 X = I($AgBF_4$)

12 X = BF_4
13 X = CF_3SO_3

Scheme 14 (*i*) +NEt_3; (*ii*) +PPh_3

into an *exo*-(1,2,3-η)-*trans*-butadienyl fragment. The simplest explanation for this observation is that the postulated step **Mb** ⟶ **10a** (Scheme 13) in the protonation reaction is reversible, and that **2a** is reformed by capture of **La** *via* proton abstraction from the methyl group.

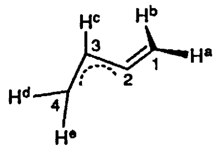
A preliminary study of the behaviour of complexes **10** and **11** towards nucleophiles is also consistent with the reversibility of the step **Mb** ⟶ **10a**, the reactivity pattern being characteristic of η^3-vinylcarbenes rather than η^4-vinylketenes. Thus, Thomas and co-workers[30,37] have shown that upon treatment with nucleophiles the η^4-vinylketene complexes [Fe{PhCH=CHC(R)=C=O}$(CO)_3$] (R = Me or Bu^t) undergo attack at C^1 of the vinylketene ligand leading to the formation on quenching with Bu^tBr or $MeCO_2H$ of β,γ-unsaturated ketones. In contrast to this observation, addition of triphenylphosphine to **10** leads to a rapid reaction and formation of a bright yellow crystalline solid **13**, which was identified on the basis of elemental analysis, IR and NMR spectroscopy as the phosphonium-substituted η^3-allyl complex illustrated in Scheme 14. Similarly, reaction of the iodo-substituted η^4-vinylketene **11** with $AgBF_4$ and PPh_3 in dichloromethane afforded **12**, the tetrafluoroborate analogue of **13**. It is suggested that both **12** and **13** are formed by capture of **La** accessed by the equilibrium processes **10** $\rightleftharpoons$ **Mb** $\rightleftharpoons$ **Lb** $\rightleftharpoons$ **La**, *via* nucleophilic attack of PPh_3 on the C^1 or carbenoid carbon. Support for this suggestion is provided by the report that the η^3-vinylcarbene cation [W{=C(Ph)C(Ph)=CH(C_6H_4Me-4)}$(CO)_2(\eta$-$C_5H_5)$][BF_4] prepared by Geoffrey and co-workers[36] reacts with phosphines to form the analogous phosphonium-substituted η^3-allyl complex [W{η^3-CH(C_6H_4Me-4)C(Ph)C(Ph)PBu_3}$(CO)_2(\eta$-$C_5H_5)$][BF_4].

To summarise, the fluoride-induced desilylation of 2-silylbuta-1,3-diene cations (deprotonation of buta-1,3-diene cations) gives novel (1,2,3-η)-*trans*-butadienyl complexes. Protonation of the molybdenum butadienyl **2** affords the neutral η^4-vinylketene complex **10** *via* intramolecular insertion of CO. This transformation is readily reversible upon addition of base, with an intermediate η^3-vinylcarbene cation implicated (Scheme 13). Vinylketene complexes **10** and **11** undergo a pattern of reactivity towards nucleophiles characteristic of a masked or latent vinylcarbene complex. Complexes **10** and **11** represent intermediates in a mechanism postulated for the Dötz annulation reaction, and are the key to a wide-ranging chemistry. Preliminary studies[16] indicate that the preparative strategies established for molybdenum may be extended to other systems.

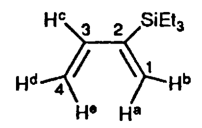
Experimental

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 services unless otherwise indicated. The ^1H and ^{13}C-{^1H} NMR spectra were recorded on Bruker AM360 and JEOL EX270 spectrometers. Chemical shifts are cited as positive to high frequency of $SiMe_4$, with coupling constants in Hz. Data are given for room-temperature measurements unless otherwise stated. Infrared spectra were measured using a Perkin Elmer 983G spectrometer. Mass spectra and analytical data were obtained courtesy of the University of London and the University of Bath Analytical Services.

Deprotonation of [Mo(η^4-C_4H_6)$(CO)_2(\eta$-$C_5Me_5)$][BF_4] **1**.—A tetrahydrofuran (thf) suspension of the buta-1,3-diene substituted cation (0.25 g, 0.58 mmol) was cooled to −78 °C, and treated with Li[N$(SiMe_3)_2$] (1 mol dm^{-3} solution in hexane, 610 μl, 1.05 mol equivalents). The reaction mixture was stirred for 0.5 h at this temperature, and was then warmed to ambient to give a homogeneous orange-yellow solution. Solvent was removed under reduced pressure, and the solid residue was chromatographed on alumina. Elution with Et_2O gave a yellow band, yielding after removal of solvent, a yellow solid, which on recrystallisation (−40 °C) from Et_2O afforded air-stable, bright yellow, *crystals* of [Mo{(1,2,3-η)-*trans*-CH_2CHC=CH_2}(CO_2)-$(\eta$-$C_5Me_5)$] **2** (0.053 g, 27%) (Found: C, 56.5; H, 5.9. $C_{16}H_{20}MoO_2$ requires C, 56.5; H, 5.9%), $\nu_{CO}(CH_2Cl_2)$ 1941s and 1862s cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 6.09 [d, 1 H, JH^aH^b) 2.3, $H^{a/b}$], 5.20 [d, 1 H, $J(H^aH^b)$ 2.0, $H^{b/a}$], 2.60 [dd, 1 H, $J(H^cH^e)$ 10.1, $J(H^cH^d)$ 7.8, H^c], 2.37 [d, 1 H, $J(H^dH^c)$ 7.7, H^d], 1.86 (s, 15 H, C_5Me_5) and 1.46 [d, 1 H, $J(H^eH^c)$ 10.3, H^e]; ^{13}C-{^1H}, δ 238.1 (CO), 235.1 (CO), 174.8 (C^2), 104.8 (C_5Me$_5$), 102.5 (C^1), 53.0 (C^3), 44.6 (C^4) and 10.4 (C_5Me_5). *m*/*z* = 342 ([*M*]$^+$) and 314 ([*M* − CO]$^+$). Further elution with Et_2O–thf (1:1) afforded an orange band which was not characterised.

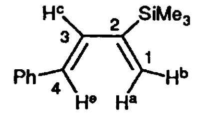


Preparation of [Mo{η^4-CH_2=CHC($SiEt_3$)=CH_2}$(CO)_2(\eta$-$C_5Me_5)$][BF_4] **3**.—A suspension of [Mo$(NCMe)_2(CO)_2(\eta$-$C_5Me_5)$][BF_4] (0.534 g, 1.09 mmol) in thf (20 cm^3) was treated with 2 triethylsilylbuta-1,3-diene (0.75 cm^3, excess) and was then heated to reflux for 2 h. The resulting dark green suspension was cooled, and solvent was removed under reduced pressure. The green solid residue was triturated with several portions of diethyl ether, and the washings were discarded. The residue was taken up in CH_2Cl_2 and the solution filtered through Celite. Addition of Et_2O afforded pale green *crystals* of complex **3** (0.51 g, 88%) (Found: C, 48.9; H, 6.5. $C_{22}H_{35}BF_4$-MoO_2Si requires C, 48.7; H, 6.5%), $\nu_{CO}(CH_2Cl_2)$ 2030s and 1969s cm^{-1}. NMR (CD_2Cl_2): ^1H (233 K), δ 5.85 [dd, 1 H, $J(H^cH^e)$ 10.2, $J(H^cH^d)$ 7.4, H^c], 2.92 [d, 1 H, $J(H^dH^c)$ 7.2, H^d], 2.35 (br s, 1 H, $H^{a/b}$), 1.97 (s, 15 H, C_5Me_5), 1.26 [d, 1 H, $J(H^eH^c)$ 10.3, H^c], 10.1 [t, 9 H, J(HH) 7.9, CH_2CH_3] and 0.79 (m, 6 H, CH_2CH_3); ^{13}C-{^1H} (298 K), δ 225.8 (CO), 221.8 (CO), 110.0 (C^2), 105.2 (C_5Me$_5$), 104.9 (C^3), 66.3 ($C^{1/4}$), 61.0 ($C^{1/4}$), 11.1 (C_5Me_5), 7.6 (CH_2CH_3) and 3.6 (CH_2CH_3).



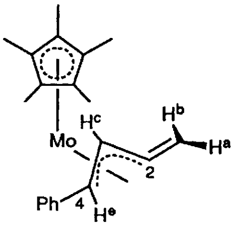
Reaction of Complex **3** *with Tetra*-n-*butylammonium Fluoride*.—A solution of the diene cation **3** (0.349 g, 0.64 mmol) in dichloromethane (15 cm^3) was treated with [NBu^n_4]F (1 mol dm^{-3} in thf, 2 cm^3) causing an immediate change from dark green to deep orange-brown. The mixture was stirred for 5 min and then evaporated to dryness under reduced pressure. Purification of the oily residue by column chromatography gave a bright yellow band which was eluted with diethyl ether. Upon removal of solvent a bright yellow powder was obtained, identified (IR and NMR spectra) as complex **2** (0.209 g, 95%) by comparison with an authentic sample.

Preparation of [Mo{η^4-CH(Ph)=CHC($SiMe_3$)=CH_2}$(CO)_2$(η-C_5Me_5)][BF_4] **4**.—A suspension of [Mo$(NCMe)_2(CO)_2$(η-C_5Me_5)][BF_4] (0.40 g, 0.88 mmol) in thf (15 cm^3) was treated with 1-phenyl-3-trimethylsilylbuta-1,3-diene (0.243 g, 1.2 mmol). The solution was heated to reflux for 5 h after which time the IR spectrum indicated that the reaction was complete. The green suspension was cooled, and the solvent was removed under reduced pressure. The residue was redissolved in CH_2Cl_2 (5 cm^3) and the resulting solution filtered through Celite. Addition of Et_2O (20 m^3) afforded pale yellow *crystals* of complex **4** (0.414 g, 82%) (Found: C, 52.1; H, 5.8. $C_{24}H_{33}BF_4MoO_2Si$ requires C, 52.1; H, 5.8%). ν_{CO}(CH_2Cl_2) 2038s and 1987s cm^{-1}. NMR [$(CD_3)_2CO$]: ^{1}H, δ 7.61–7.46 (m, 5 H, Ph), 6.81 [d, 1 H, J(H^cH^e) 10.8, H^c], 3.64 [d, 1 H, J(H^cH^e) 10.8, H^e], 2.88 (br s, 1 H, H^b), 2.07 (s, 15 H, C_5Me_5), 1.67 (br s, 1 H, H^a) and 0.59 (s, 9 H, $SiMe_3$); ^{13}C-{^{1}H}, δ 229.1 (CO), 225.1 (CO), 129.7, 129.1, 128.4, 125.1 (Ph), 105.7 (C^3), 103.1 (C^2), 100.1 (C_5Me$_5$), 91.2 (C^4), 58.2 (C^1), 9.5 (C_5Me_5) and −2.1 ($SiMe_3$).

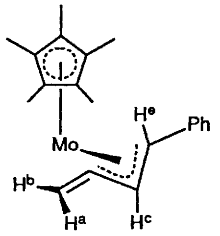


Preparation of [Mo{(1,2,3-η)-*trans*-CH(Ph)CHC=CH_2}$(CO)_2$(η-C_5Me_5)] **5a** + **5b**.—A solution of complex **3** (0.25 g, 0.43 mmol) in CH_2Cl_2 (10 cm^3) was treated with [NBu^n_4]F (1 mol dm^{-3} in thf, 0.65 cm^3) causing an immediate darkening of the solution. After stirring at room temperature for 20 min the volatiles were removed under reduced pressure and the residue was purified by column chromatography on alumina. Elution with diethyl ether afforded, after removal of the solvent, a yellow solid. Recrystallisation from pentane gave bright yellow *crystals* of **5a**/**5b** (4:1 mixture) (0.126 g, 70%) (Found: C, 63.5; H, 5.8. $C_{21}H_{24}MoO_2$ requires C, 63.5; H, 5.8%), ν_{CO}(CH_2Cl_2) 1953s and 1876s cm^{-1}. NMR [$(CD_3)_2CO$]: ^{1}H, **5a**, δ 7.60–7.27 (m, 5 H, Ph), 6.29 [d, 1 H, J($H^{a/b}H^c$) 2.6, $H^{a/b}$], 5.37 [d, 1 H, J($H^{b/a}H^c$) 2.6, $H^{b/a}$], 3.98 [dt, 1 H, J(H^cH^e) 10.4, J($H^cH^{a/b}$) 2.6, H^c], 3.40 [d, 1 H, $J$$H^eH^c$) 10.4, H^e] and 1.88 (s, 15 H, C_5Me_5); **5b**, δ 7.60–7.27 (m, 5 H, Ph), 6.27 [d, 1 H, J($H^{a/b}H^c$) 2.2, $H^{a/b}$], 5.12 [d, 1 H, J($H^{b/a}H^c$) 2.2, $H^{b/a}$], 4.64 [dt, 1 H, J(H^cH^e) 10.6, J($H^cH^{a/b}$) 2.2, H^c], 3.16 [d, 1 H, J(H^eH^c) 10.6, H^e] and 2.00 (s, 15 H, C_5Me_5); ^{13}C-{^{1}H}, **5a**, δ 242.2 (CO), 234.8 (CO), 172.4 (C^2), 128.3, 126.8, 126.6, 126.0 (Ph), 103.8 (C_5Me$_5$), 103.2 (C^1), 66.9 (C^4), 53.4 (C^3) and 9.9 (C_5Me_5).

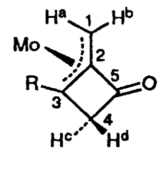
Preparation of [Mo{η^3-$CH_2CC(Me)CH_2CO$}$(CO)_2$(η-C_5Me_5)] **6**.—An excess of 4-chloro-3-methylbuta-1,2-diene (1.5 mmol) was added to a solution of Li[Mo$(CO)_3$(η-C_5Me_5)] (0.258 g, 0.50 mmol) in thf (20 cm^3). The reaction mixture was stirred at room temperature for 2 h, and then concentrated under reduced pressure to give an orange-red oil. Chromatography on alumina afforded two fractions, both eluted with toluene–hexane (1:1). The first, red band was discarded. The second, slower-moving orange-yellow band was collected, concentrated and chromatographed twice further to give an orange-yellow solid. Recrystallisation from hexane gave large, orange-yellow *crystals* of complex **6** (0.19 g, 60%) (Found: C, 56.5; H, 5.8. $C_{18}H_{22}MoO_3$ requires C, 56.6; H, 5.8%), ν_{CO}(CH_2Cl_2) 1940s, 1862s and 1738m cm^{-1}. NMR (CD_2Cl_2): ^{1}H, δ 3.31 [d, 1 H, J(H^cH^d) 14.98, $H^{c/d}$], 3.12 [d, 1 H, J(H^cH^d) 14.98, $H^{c/d}$], 2.03 [d, 1 H, J(H^bH^a) 4.13, H^b], 1.83 (s, 15 H, C_5Me_5), 1.68 [d, 1 H, J(H^aH^b) 4.13, H^a] and 1.57 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 241.96 (CO), 236.88 (CO), 193.02 (C^5), 107.74 (C_5Me$_5$), 98.32 (C^2), 93.01 (C^3), 60.28 (C^1), 31.41 (C^4), 20.19 (Me) and 9.96 (C_5Me_5).



5a, *exo-syn*



5b, *endo-syn*



Preparation of [Mo{η^3-$CH_2CC(Et)CH_2CO$}(CO_2)(η-C_5Me_5)] **7**.—Similarly, a reaction of 4-chloro-3-ethylbuta-1,2-diene (1.2 mmol) with Li[Mo$(CO)_3$(η-C_5Me_5)] (0.258 g, 0.80 mmol) in thf (8 cm^3) afforded on chromatography and recrystallisation from hexane orange-yellow *crystals* of complex **7** (0.234 g, 74%) (Found: C, 57.0; H, 6.2. $C_{19}H_{24}MoO_3$ requires C, 57.6; H, 6.1%), ν_{CO}(CH_2Cl_2) 1951s, 1874s and 1735m cm^{-1}. NMR (CD_2Cl_2): ^{1}H, δ 3.55 [d, 1 H, J(H^cH^d) 15.02, $H^{c/d}$], 3.03 [d, 1 H, J(H^cH^d) 15.02, $H^{c/d}$], 2.42 (apparent sxt, 1 H, J 14.84, 7.33, C*H*HCH$_3$), 2.04 [d, 1 H, J(H^aH^b) 4.22, H^b], 1.84 (s, 15 H, C_5Me_5), 1.75 [d, 1 H, J(H^aH^b) 4.22, H^a], 1.29 (apparent sxt, 1 H, J 14.84, 7.33, CH*H*CH$_3$) and 0.90 (t, 3 H, J 7.33, Me); ^{13}C-{^{1}H}, δ 241.88 (CO), 237.28 (CO), 192.80 (C^5) 104.39 (C_5Me$_5$), 99.08 (C^2), 96.97 (C^3), 56.56 (C^1), 32.24 (C^4), 27.76 (CH_2CH_3), 13.95 (CH_3) and 9.72 (C_5Me_5).

Preparation of [Mo{η^3-$CH_2CC(Me)CH_2CO$}$(CO)_2$(η-C_5H_5)] **8**.—Reaction under similar conditions of 4-chloro-3-methylbuta-1,2-diene with Li[Mo$(CO)_3$(η-C_5H_5)] in thf afforded yellow *crystals* of complex **8** (68%) (Found: C, 50.2; H, 3.9. $C_{13}H_{12}MoO_3$ requires C, 50.0; H, 3.9%), ν_{CO}(CH_2Cl_2) 1965s, 1888s and 1744m cm^{-1}. NMR (CD_2Cl_2): ^{1}H, δ 5.22 (s, 5 H, C_5H_5), 3.42 (s, 2 H, $H^{c/d}$), 3.05 [d, 1 H, J(H^aH^b) 4.22, H^b], 1.65 (s, 3 H, Me) and 1.62 [d, 1 H, J(H^aH^b) 4.22, H^a]; ^{13}C-{^{1}H}, δ 238.66 (CO), 233.75 (CO) 195.68 (C^5), 96.31 (C^2), 94.79 (C_5H_5), 91.91 (C^3), 61.73 (C^1), 26.85 (C^4) and 19.40 (Me).

Preparation of [Mo{η^3-$CH_2CC(Et)CH_2CO$}$(CO)_2$(η-C_5H_5)] **9**.—A similar procedure afforded yellow *crystals* of complex **9** (52%) (Found: C, 51.7; H, 4.4. $C_{14}H_{14}MoO_3$ requires C, 51.6; H, 4.3%), ν_{CO}(CH_2Cl_2) 1962s, 1885s and 1746m cm^{-1}. NMR (CD_2Cl_2): ^{1}H, δ 4.64 (s, 5 H, C_5H_5), 3.42 [d, 1 H, J(H^cH^d) 15.02, $H^{c/d}$], 3.06 [d, 1 H, J(H^cH^d) 15.02, $H^{c/d}$], 2.87 [d, 1 H, J(H^aH^b) 4.39, H^b], 2.40 (apparent sxt, 1 H, J 14.97, 7.33, C*H*HCH$_3$), 1.61 [d, 1 H, J(H^aH^b) 4.39, H^a], 1.36 (apparent sxt,

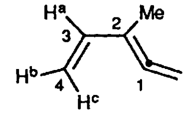
Table 5 Structure analyses for compounds **2**, **6** and **11**

Crystal data	**2**	**6**	**11**
Formula	$C_{16}H_{20}MoO_2$	$C_{18}H_{22}MoO_3$	$C_{16}H_{21}IMoO_2$
M	340.23	382.31	486.18
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	14.686(3)	9.010(1)	14.266(3)
b/Å	8.961(1)	13.137(2)	11.866(2)
c/Å	12.172(2)	8.761(3)	10.160(1)
α/°		106.67(3)	—
β/°	100.63(2)	116.46(2)	100.11(2)
γ/°	—	93.70(1)	—
U/Å^3	1574.36	867.67	1693.18
Z	4	2	4
D_c/g cm^{-3}	1.44	1.46	1.82
F(000)	696	392	1048
μ(Mo-Kα)/cm^{-1}	8.19	7.53	25.82
Data collection and reduction			
Crystal dimensions (mm)	0.32 × 0.18 × 0.16	0.39 × 0.24 × 0.13	0.52 × 0.40 × 0.10
2θ range/°	3–25	3–25	3–25
Scan width, ω/°	0.90	0.80	0.90
Scan speed/° s^{-1}	0.05	0.05	0.05
Total data	1630	2741	2489
Unique data	1443	2436	2182
Systematic absences	$0k0, k = 2n + 1$ $h0l, l = 2n + 1$	—	$0k0, k = 2n + 1$ $h0l, l = 2n + 1$
R	0.0560	0.0450	0.0408
R'	0.0566	0.0456	0.0431

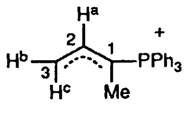
1 H, *J* 14.97, 7.33, $CHHCH_3$) and 0.72 (t, 3 H, *J* 7.33, Me); $^{13}C-\{^1H\}$, δ 234.58 (CO), 239.52 (CO), 194.46 (C^5), 103.06 (C^2), 94.96 (C_5H_5), 94.56 (C^3), 58.84 (C^1), 28.17 (C^4), 27.79 (CH_2CH_3) and 14.03 (Me).

Protonation of $[Mo\{(1,2,3-\eta)$-*trans*-$CH_2CHC{=}CH_2\}(CO)_2(\eta-C_5Me_5)]$ **2**.—A solution of complex **2** (0.17 g, 0.50 mmol) in CH_2Cl_2 (30 cm^3) was cooled to −78 °C, and to this was added dropwise trifluoromethanesulfonic acid (44 μl, 0.50 mmol). An immediate change in colour from yellow to a deep amber was observed. The reaction mixture was warmed to ambient and stirred for 30 min. It was then filtered through Celite and the solvent removed under reduced pressure. The resulting pale orange powder was recrystallised (0 °C) from CH_2Cl_2–Et_2O to give orange *microcrystals* of $[Mo(SO_3CF_3)\{\eta^4-CH_2{=}CHC(Me){=}C{=}O\}(CO)(\eta-C_5Me_5)]$ **10** (0.20 g, 82%) (Found: C, 40.6; H, 4.3. $C_{17}H_{21}F_3MoO_5S$ requires C, 41.6; H, 4.3%), $\nu_{CO}(CH_2Cl_2)$ 2007s and 1677m cm^{-1}. NMR (CD_2Cl_2): ^1H (298 K), δ 6.48 [dd, 1 H, $J(H^aH^c){=}J(H^aH^b)$ 8.8, H^a], 2.99 [dd, 1 H, $J(H^cH^a)$ 8.3, $J(H^bH^c)$ 1.3, H^c], 2.41 (s, 3 H, Me), 1.98 [dd, 1 H, $J(H^bH^a)$ 9.0, $J(H^bH^c)$ 1.4, H^b] and 1.88 (s, 15 H, C_5Me_5); ^{13}C (203 K), δ 255.9 (d, *J* 9, C^1), 223.4 (s, CO), 133.5 (d, *J* 163, C^3), 118.0 (q, *J* 319, CF_3SO_3), 105.5 (s, C_5Me_5), 85.0 (d, *J* 4, C^2), 62.8 (t, *J* 162, C^4), 14.8 [dq, *J* 3 (q), 130 (q), Me] and 9.3 (q, *J* 129, C_5Me_5).

Preparation of $[MoI\{\eta^4-CH_2{=}CHC(Me){=}C{=}O\}(CO)(\eta-C_5Me_5)]$ **11**.—An excess of anhydrous LiI (2.0 mmol) was added to a solution of complex **3** (0.20 g, 0.41 mmol) in CH_2Cl_2 (20 cm^3) and the reaction mixture stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue chromatographed on alumina. Elution with diethyl ether gave an orange band which was collected. Removal of the solvent and recrystallisation (−30 °C) from diethyl ether gave orange *crystals* of complex **11** (0.16 g, 84%) (Found: C, 41.0; H, 4.5. $C_{16}H_{21}IMoO_2$ requires C, 41.0; H, 4.5%), $\nu_{CO}(CH_2Cl_2)$ 1996s and 1665m cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 6.54 [ddq, 1 H, $J(H^aH^c){=}J(H^aH^b)$ 8.5, $J(H^aMe)$ 0.7, H^a], 3.16 [dd, 1 H, $J(H^cH^a)$ 8.1, $J(H^bH^c)$ 0.5, H^c], 2.17 [ddq, 1 H, $J(H^bH^a)$ 8.5, $J(H^bH^c)$ 0.7, $J(H^bMe)$ 0.7, H^b], 2.02 (q, 3 H, Me) and 1.96 (s, 15 H, C_5Me_5); $^{13}C-\{^1H\}$, δ 256.4 (C^1), 223.8 (CO), 130.8 (C^3), 103.65 (C_5Me_5), 64.3 (C^2), 57.9 (C^4), 14.7 (Me) and 10.8 (C_5Me_5).



Preparation of $[Mo\{\eta^3-CH_2CHC(Me)PPh_3\}(CO)_2(\eta-C_5Me_5)][BF_4]$ **12**.—To a stirred solution of complex **11** (0.10 g, 0.21 mmol) in CH_2Cl_2 was added PPh_3 (0.06 g, 0.23 mmol). On addition of $AgBF_4$ (0.45 g, 0.23 mmol) the solution rapidly changed from bright orange to yellow. The reaction mixture was allowed to stir at room temperature for 0.5 h, during which time it darkened. Filtration through Celite and slow addition of diethyl ether afforded a brilliant yellow powder. Recrystallisation from CH_2Cl_2–Et_2O afforded yellow *crystals* of complex **12** (0.122 g, 83%) (Found: C, 58.6; H, 5.0. $C_{34}H_{36}BF_4MoO_2P$ requires C, 59.2; H, 5.3%), $\nu_{CO}(CH_2Cl_2)$ 1960s and 1885s cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 7.82–7.60 (complex m, 15 H, PPh_3), 4.08 [ddd, 1 H, $J(H^aH^c)$ 10.0, $J(H^aH^b)$ 7.76, $J(H^aP)$ 22.0, H^a], 2.03 [d, 3 H, $J(CH_3P)$ 14.1, Me], 1.91 (s, 15 H, C_5Me_5), 1.76 [ddd, 1 H, $J(H^bH^a)$ 8.2, $J(H^bH^c)$ 3.7, $J(H^bP)$ 1.51, H^b] and 0.42 [ddd, 1 H, $J(H^cH^a)$ 10.3, $J(H^cH^b)$ 3.8, $J(H^cP)$ 1.1, H^c]; $^{13}C-\{^1H\}$, δ 242.7 [d, J(CP) 6.8, CO], 236.7 (CO), 134.6 [d, J(CP) 8.2, PPh_3], 129.8 [d, J(CP) 12.2, PPh_3], 120.1 [d, J(CP) 84.1, PPh_3], 106.6 (C_5Me_5), 85.8 [d, J(CP) 8.2, C^2], 45.3 (C^3), 27.4 [d, J(CP) 8.2, Me] and 10.6 [d, J(CP) 2.0, C_5Me_5]; $^{31}P-\{^1H\}$, δ 32.4 (PPh_3).



Reactions of Complex **10**.—*With triphenylphosphine*. To a solution of complex **10** (0.113 g, 0.23 mmol) in CH_2Cl_2 (20 cm^3)

Table 6 Fractional atomic coordinates for complex **2**

Atom	*x*	*y*	*z*
Mo	0.236 11(7)	−0.013 48(10)	0.121 26(8)
C(1)	0.224 7(8)	0.015 7(14)	0.305 3(9)
C(2)	0.316 4(10)	0.072 7(14)	0.291 9(11)
C(3)	0.304 0(10)	0.197 8(13)	0.225 8(10)
C(4)	0.207 0(10)	0.229 4(13)	0.194 5(10)
C(5)	0.161 0(8)	0.117 3(14)	0.241 9(10)
C(11)	0.202 4(12)	−0.108 0(16)	0.380 5(10)
C(12)	0.405 1(10)	0.009 3(19)	0.356 0(12)
C(13)	0.382 8(12)	0.288 6(17)	0.191 2(16)
C(14)	0.159 7(12)	0.358 5(15)	0.122 8(13)
C(15)	0.057 6(10)	0.111 6(16)	0.237 9(13)
C(16)	0.307 6(11)	−0.195 0(14)	0.136 9(11)
C(17)	0.134 8(10)	−0.152 3(15)	0.079 7(11)
O(16)	0.350 2(9)	−0.303 9(12)	0.150 9(9)
O(17)	0.071 5(7)	−0.235 3(12)	0.062 0(9)
C(6)	0.166 2(11)	0.036 0(17)	−0.062 8(11)
C(7)	0.255 1(11)	0.082 0(17)	−0.040 3(10)
C(8)	0.325 2(9)	−0.021 2(16)	−0.005 2(12)
C(9)	0.399 7(13)	−0.079 6(20)	−0.040 6(14)

Table 7 Fractional atomic coordinates for complex **6**

Atom	*x*	*y*	*z*
Mo	0.761 40(6)	0.243 16(4)	0.027 18(6)
C(16)	0.900 7(7)	0.226 2(5)	−0.090 4(8)
O(16)	0.979 7(6)	0.217 8(5)	−0.166 3(7)
C(17)	0.701 7(7)	0.085 4(5)	−0.082 5(8)
O(17)	0.661 4(6)	−0.008 8(4)	−0.152 3(7)
C(1)	0.523 3(7)	0.305 1(4)	0.051 9(7)
C(2)	0.641 5(7)	0.398 5(4)	0.086 2(8)
C(3)	0.657 3(7)	0.382 1(5)	−0.073 8(8)
C(4)	0.548 1(7)	0.281 7(5)	−0.206 4(7)
C(5)	0.467 4(6)	0.234 1(4)	−0.127 8(7)
C(11)	0.451 2(8)	0.291 3(5)	0.170 6(8)
C(12)	0.718 2(8)	0.499 4(5)	0.250 6(9)
C(13)	0.754 4(9)	0.464 1(5)	−0.104 1(11)
C(14)	0.508 7(8)	0.239 5(6)	−0.401 9(8)
C(15)	0.328 9(8)	0.132 6(5)	−0.225 0(9)
C(6)	1.032 0(7)	0.341 0(4)	0.259 8(7)
C(7)	0.948 6(7)	0.277 9(4)	0.316 0(7)
C(8)	0.895 8(7)	0.161 1(4)	0.252 4(7)
C(9)	0.798 9(8)	0.165 1(5)	0.359 5(8)
C(11)	1.000 3(9)	0.079 2(5)	0.229 9(9)
C(18)	0.857 6(7)	0.289 5(5)	0.424 0(7)
O(18)	0.848 9(6)	0.364 5(3)	0.535 4(6)

Table 8 Fractional atomic coordinates for complex **11**

Atom	*x*	*y*	*z*
Mo	0.248 26(4)	−0.005 28(5)	0.144 70(6)
I	0.138 75(4)	0.199 57(5)	0.134 97(6)
C(1)	0.266 6(6)	−0.184 7(6)	0.233 6(7)
C(2)	0.169 6(5)	−0.153 7(7)	0.238 5(8)
C(3)	0.171 3(5)	−0.058 4(7)	0.324 3(8)
C(4)	0.268 6(5)	−0.029 5(7)	0.371 4(7)
C(5)	0.326 6(5)	−0.108 0(6)	0.316 4(7)
C(11)	0.296 0(7)	−0.292 2(7)	0.171 8(9)
C(12)	0.081 6(6)	−0.222 2(9)	0.177 6(10)
C(13)	0.085 7(7)	−0.009 6(8)	0.370 1(10)
C(14)	0.301 1(7)	0.054 7(8)	0.478 7(9)
C(15)	0.433 9(5)	−0.121 4(7)	0.356 6(9)
C(16)	0.355 5(6)	0.103 8(7)	0.197 9(8)
O(16)	0.420 3(5)	0.157 9(7)	0.230 0(7)
C(17)	0.336 9(5)	−0.072 7(7)	0.022 5(8)
O(17)	0.401 7(4)	−0.136 2(5)	0.014 9(6)
C(18)	0.296 5(6)	0.019 1(6)	−0.065 9(7)
C(19)	0.196 3(6)	0.023 1(7)	−0.092 1(8)
C(20)	0.140 2(6)	−0.059 6(7)	−0.043 5(8)
C(21)	0.358 3(6)	0.104 3(8)	−0.118 1(9)

was added PPh_3 (0.06 g, 0.23 mmol). After stirring at room temperature for 1 h the bright yellow solution was filtered through Celite. The volume of the solvent was reduced *in vacuo* and diethyl ether was added. The resultant precipitate was collected and recrystallised from CH_2Cl_2–Et_2O to give bright yellow *crystals* of $[Mo\{\eta^3\text{-}CH_2CHC(Me)PPh_3\}(CO)_2(\eta\text{-}C_5Me_5)][CF_3SO_3]$ (0.13 g, 90%) (Found: C, 55.4; H, 4.7. $C_{35}H_{36}F_3MoO_5PS$ requires C, 55.9; H, 4.8%), $\nu_{CO}(CH_2Cl_2)$ 1957s and 1883s cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 7.78–7.58 (complex m, 15 H, CH_3P), 4.10 [ddd, 1 H, $J(H^aH^c)$ 11.2, $J(H^aH^b)$ 8.2, $J(H^aP)$ 14.0, H^a], 2.02 [d, 3 H, $J(CH_3P)$ 14.0, Me], 1.91 (s, 15 H, C_5Me_5), 1.75 [ddd, 1 H, $J(H^bH^a)$ 8.2, $J(H^bH^c)$ 3.7, $J(H^bP)$ 1.5, H^b] and 0.41 [ddd, 1 H, $J(H^cH^a)$ 11.3, $J(H^cH^b)$ 3.7, $J(H^cP)$ 1.1, H^c]; $^{13}C\text{-}\{^1H\}$, δ 242.9 [d, $J(CP)$ 6.4, CO], 236.9 (CO), 134.8 [d, $J(CP)$ 9.2, PPh_3], 130.0 [d, $J(CP)$ 12.1, PPh_3], 120.2 [d, $J(CP)$ 84.0, PPh_3], 106.7 (C_5Me$_5$), 85.9 [d, $J(CP)$ 8.1, C^2], 47.5 [d, $J(CP)$ 65.5, C^1], 45.5 [d, $J(CP)$ 3.0, C^3], 27.7 [d, $J(CP)$ 9.0, Me] and 10.8 (C_5Me_5); $^{31}P\text{-}\{^1H\}$, δ 36.5 (PPh_3).

With triethylamine. To a solution of complex **10** (0.113 g, 0.23 mmol) in CH_2Cl_2 at −20 °C was added dropwise triethylamine (0.30 mmol). The reaction mixture was allowed to warm to room temperature over 0.5 h. Removal of the solvent and column chromatography of the residue afforded complex **2** (98%), identified by IR and NMR spectroscopy.

Structure Determinations of Complexes **2**, **6** *and* **11**.—Many details of the structure analyses are listed in Table 5. X-Ray diffraction measurements were made at room temperature using a Phillips PW 1100 diffractometer on single crystals mounted on a glass fibre. 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 fluctuations, on the basis of the intensities of three check reflections repeatedly measured during the data collection. 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. After absorption corrections had been applied, all non-hydrogen atoms were assigned anisotropic thermal parameters before the final cycles of full-matrix least-squares refinement which converged to the residuals given in Table 5. Tables 6–8 report the atomic coordinates for these structure determinations. All calculations were made with programs of the SHELXTL[38] system. Complex neutral-atom scattering factors were taken from ref. 39.

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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