Reactions of Co-ordinated Ligands. Part 58.[1] The Reaction of Dimolybdenum μ-σ:η²-(4e)-Vinylidene Complexes with Proton Sources and Diazomethane; Synthesis and Crystal Structure of the Mo≡Mo Bonded Complex [Mo_2{μ-σ:η²-$CH_2C(Ph)CH_2$}$(CO)_3$(η-$C_5H_5)_2$][CF_3SO_3] *

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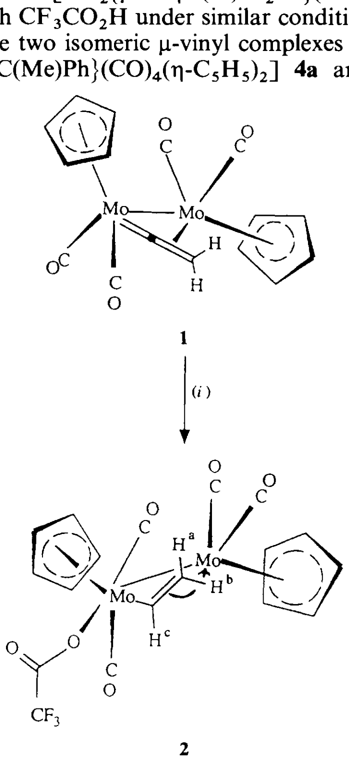
Protonation (CF_3CO_2H) of the 'side-on' bonded dinuclear vinylidene complexes [Mo_2{μ-σ:η²-(4e)-C=CR_2}$(CO)_4$(η-$C_5H_5)_2$] (R = H or Me) afforded the bridged μ-vinyl complexes [Mo_2{OC(O)CF_3}(μ-CH=CR_2)$(CO)_4$(η-$C_5H_5)_2$], whereas a similar reaction of one of the isomers of [Mo_2{μ-σ:η²-(4e)-C=C(Ph)Me}$(CO)_4$(η-$C_5H_5)_2$] afforded the isomeric complexes [Mo_2{OC(O)CF_3}{μ-CH=C(Me)Ph}$(CO)_4$(η-$C_5H_5)_2$] and [Mo_2{OC(O)CF_3}{μ-CH=C(Ph)Me}$(CO)_4$(η-$C_5H_5)_2$]. Deuterium-labelling experiments and extended-Hückel molecular-orbital (EHMO) calculations suggest that these reactions involve delivery of a proton by CF_3CO_2H to the α-carbon of the vinylidene complex in a direction perpendicular to the plane containing the β-carbon substituents. Protonation of the α-carbon is also implicated in the reaction of [Mo_2{μ-σ:η²-(4e)-C=CMe_2}$(CO)_4$(η-$C_5H_5)_2$] with HBF_4·Et_2O or CF_3SO_3H where the products are the unusual cationic species [Mo_2{μ-σ:η²-$CH_2C(Me)CH_2$}$(CO)_3$(η-$C_5H_5)_2$][X] (X = BF_4 or CF_3SO_3). The same cations are also produced by α protonation of the μ-allylidene complex [Mo_2{μ-σ:η³-CHC(Me)CH_2}$(CO)_4$(η-$C_5H_5)_2$]. Similarly, protonation (CF_3SO_3H) of [Mo_2{μ-σ:η³-CHC(Ph)CH_2}$(CO)_4$(η-$C_5H_5)_2$] (formed on thermolysis of [Mo_2{μ-σ:η²-(4e)-C=C(Ph)-Me}$(CO)_4$(η-$C_5H_5)_2$] afforded the X-ray crystallographically identified complex [Mo_2{μ-σ:η²-CH_2C-(Ph)CH_2}$(CO)_3$(η-$C_5H_5)_2$][CF_3SO_3]. In the solid state the complex contains an unusual bonding mode for a dinuclear allyl complex, the $CH_2C(Ph)CH_2$ fragment being bonded *via* η² co-ordination to one molybdenum atom and a three-centre two-electron interaction between one of the CH_2 groups of the allyl and both metal atoms, which are bonded to each other by a formal triple bond. In solution this cation and the related methyl-substituted species show dynamic behaviour resulting in equivalencing on the NMR time-scale of the two *anti*- and two *syn*-protons of the allyl ligand. The reaction of diazomethane with [Mo_2{μ-σ:η²-(4e)-C=CR_2}$(CO)_4$(η-$C_5H_5)_2$] (R = H or Me) has also been studied. The reactions lead respectively to the formation of the μ-allene complexes [Mo_2(μ-η²:η²-CH_2=C=CR_2)$(CO)_4$(η-$C_5H_5)_2$]. A similar reaction between CH_2N_2 and the unsymmetrical labile 'side-on' bonded vinylidene [Mo_2{μ-σ:η²-(4e)-C=C(Ph)H}$(CO)_4$(η-$C_5H_5)_2$] gave [Mo_2{μ-η²:η²-CH_2=C=C(Ph)H}$(CO)_4$(η-$C_5H_5)_2$], whereas, in contrast, [Mo_2{μ-σ:η²-(4e)-C=C(Ph)Me}$(CO)_4$(η-$C_5H_5)_2$] affords the diastereoisomers [Mo_2{μ-η²:η²-CH_2=C=C(Ph)Me}$(CO)_4$(η-$C_5H_5)_2$] and [Mo_2{μ-η²:η²-CH_2=C=C(Me)Ph}-$(CO)_4$(η-$C_5H_5)_2$]. The EHMO calculations implicate dipolar intermediates in these reactions formed by nucleophilic attack under frontier-orbital control on the lowest unoccupied molecular orbital of the vinylidene ligand located on the α-carbon.

We have previously[2] shown that 'side-on' bonded dinuclear vinylidene complexes of the type [M_2{μ-σ:η²-(4e)-C=C(R^1)R^2}$(CO)_4$(η-$C_5H_5)_2$] (M = Mo or W; R^1 = R^2 = H; R^1 = aryl or alkyl, R^2 = H; R^1 = R^2 = alkyl) can readily be synthesised by protonation or alkylation of the anionic acetylide species Li[M_2{μ-σ:η²-(3e)-C_2R^1}$(CO)_4$-(η-$C_5H_5)_2$], which in turn can be conveniently accessed either by addition of R^1C≡CLi to the unsaturated dinuclear complexes [$M_2(CO)_4$(η-$C_5H_5)_2$], or by deprotonation (LiR) of [M_2(μ-R^1C_2H)$(CO)_4$(η-$C_5H_5)_2$]. Thus, with simple synthetic access and structural characterisation of 'side-on' bonded vinylidenes, it has become possible to begin to explore the reactivity of these unusual molecules, and in particular to compare the chemistry of μ-σ:η²-(4e)-vinylidene complexes with that of the more common 'upright' μ-σ:σ-(2e)-vinylidenes.[3] We chose initially to explore reactions with proton sources,[4] and with the potential 1,3-dipolarophile diazomethane, because there was already some understanding[3] of the corresponding reactions of dinuclear 'upright' vinylidene complexes.

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Results and Discussion

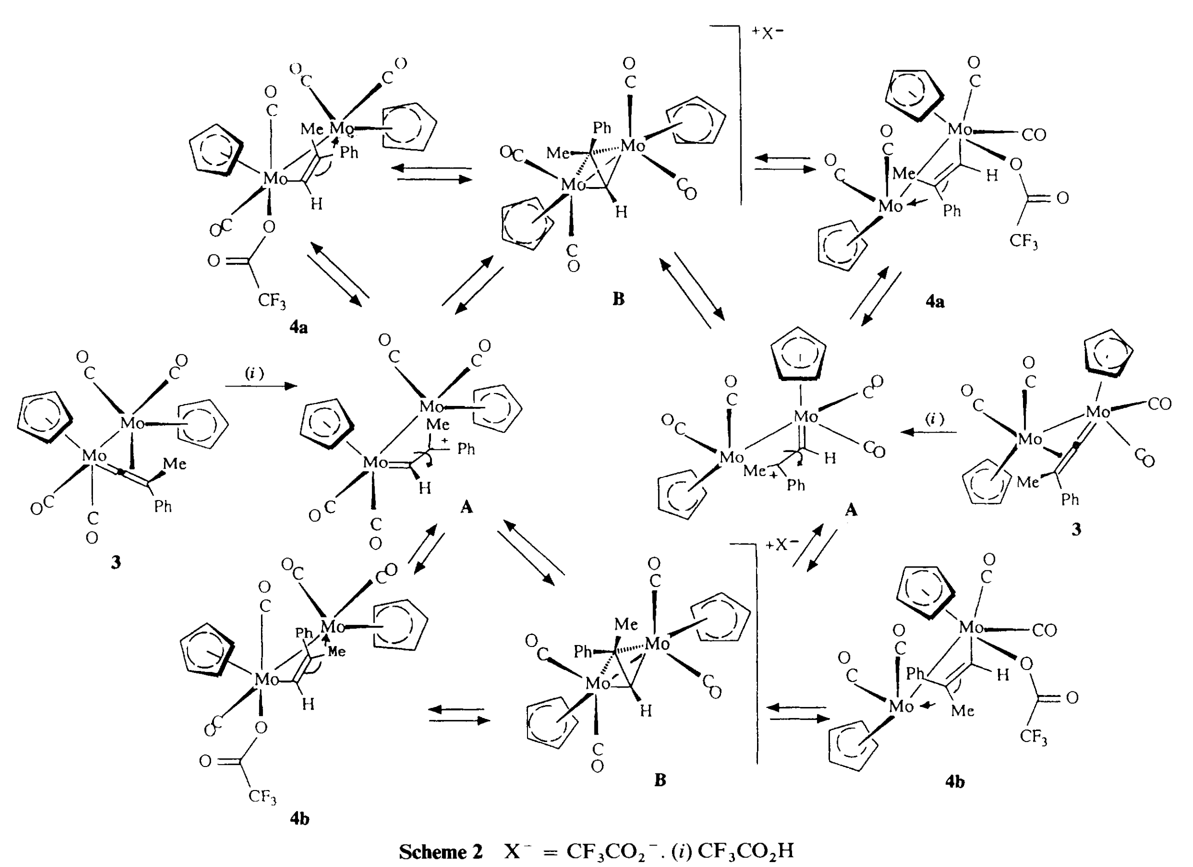
Addition of trifluoroacetic acid to a cooled (−78 °C) toluene solution of the purple complex [Mo_2{μ-σ:η²-(4e)-C=CH_2}-$(CO)_4$(η-$C_5H_5)_2$] **1** on warming to room temperature resulted in a change in colour to bright red and the formation in good yield of the red crystalline complex **2**, identified by elemental analysis, IR and NMR spectroscopy as a bridged μ-vinyl complex [Mo_2{OC(O)CF_3}{μ-CH=CH_2}$(CO)_4$(η-$C_5H_5)_2$] (Scheme 1). Comparison of the spectroscopic data for **2** with those reported[5,6] for the X-ray crystallographically identified μ-vinyl complex obtained by reaction of CF_3CO_2H with $[Mo_2(\mu\text{-}HC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$ showed these to be identical. When this reaction was extended to the unsymmetrically substituted 'side-on' bonded vinylidene $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **3** obtained[2] as one isomer on methylation of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$, treatment with CF_3CO_2H under similar conditions afforded a mixture of the two isomeric μ-vinyl complexes $[Mo_2\{OC(O)CF_3\}\{\mu\text{-}CH{=}C(Me)Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **4a** and $[Mo_2\{OC(O)CF_3\}\{\mu\text{-}CH{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **4b** (Scheme 2). Initially the ratio of the isomers **4a** and **4b** as determined by NMR spectroscopy was 2.5 : 1, however in solution (CD_2Cl_2) at room temperature isomerisation occurred (24 h) to give only one isomer, which is presumed on the basis of possible steric interactions between the phenyl and $\eta\text{-}C_5H_5$ substituents to be **4a**.



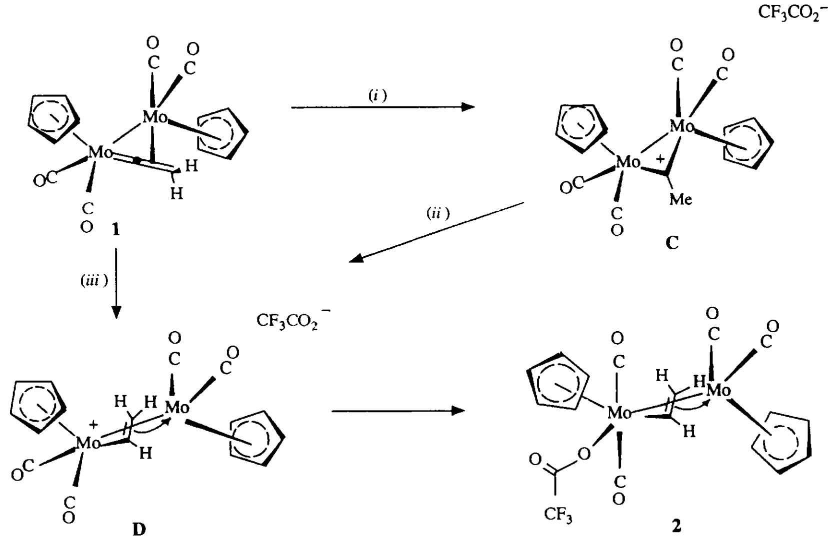
Scheme 1 (*i*) CF_3CO_2H, toluene

An explanation for these observations is shown in Scheme 2, and assumes (see below) that a proton is delivered by the trifluoroacetic acid to the α-carbon of complex **3** in a direction perpendicular to the plane containing the methyl and phenyl substituents. This results in the formation of the cation **A** (Scheme 2) carrying a phenyl-substituted carbonium ion. Rotation can obviously occur about the $C_\alpha\text{–}C_\beta$ bond, and then either by direct capture by trifluoroacetate anion of the cation **A**, or the symmetrically bound μ-vinyl cation **B**, the isomers **4a** and **4b** can be accessed. In dichloromethane as solvent, thermodynamic control could occur leading *via* the equilibrium process depicted to the exclusive formation of **4a**. Support for the suggested involvement of the symmetrically bound vinyl cation **B** derives from the report[5] that the ^1H NMR spectrum of the cationic precursor of **2** shows at ambient temperature rapid exchange of the two μ-vinyl methylene-proton environments, with the apparent simultaneous time averaging of the two $\eta\text{-}C_5H_5$ environments.

Thus, it is suggested that the proton directly attacks the α-carbon of the $\mu\text{-}\sigma:\eta^2$-(4e)-vinylidene moiety. However, it is interesting that it has been shown[7] that protonation of the 'upright' diiron complexes $[Fe_2\{\mu\text{-}\sigma:\sigma\text{-(2e)-}C{=}CR_2\}(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ proceeds under kinetic control *via* β protonation to form a cationic μ-alkylidyne complex, which then under thermodynamic control isomerises by a 1,2-H shift to the isolated μ-vinyl cation. As is illustrated in Scheme 3 such an alternative pathway is also in principle available for the conversion of complex **1** into **2**, β protonation of **1** affording the cation **C** which then undergoes a 1,2-H shift to form **D** before capture by a trifluoroacetate anion. In order to distinguish



Scheme 2 $X^- = CF_3CO_2^-$. (*i*) CF_3CO_2H

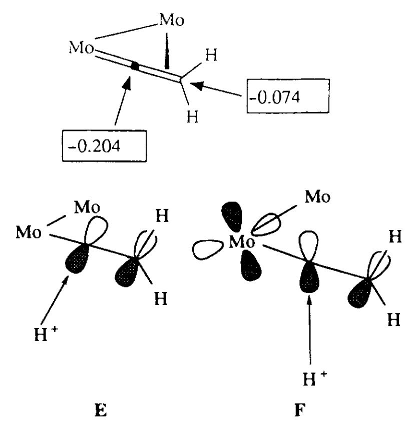


Scheme 3 (*i*) β Protonation; (*ii*) 1,2-H shift; (*iii*) α protonation

between these two distinct pathways it was decided first to conduct suitable deuterium-labelling experiments, and secondly carry out extended-Hückel molecular-orbital calculations to see if there were fundamental reasons for preferring initial α or β protonation.

Reaction of complex 2 with CF_3CO_2D (less than 5% H) afforded red crystals of $[Mo_2\{OC(O)CF_3\}(\mu\text{-}CD{=}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ $[^2H]$**2**, the ^1H NMR spectrum of which indicated an upper limit of 5% residual proton occupancy on C_α. Had β protonation occurred, then since the μ-alkylidyne intermediate **C** (Scheme 3) would have contained a methyl (CH_2D) group, scrambling of the deuterium would have been observed. More specifically, because the 1,2-H shift would have been subject to a primary isotope effect, the ^1H NMR spectrum would have indicated a greater than 66% proton occupancy at C_α of the vinyl group, and indirectly a greater than 33% deuterium occupancy at the vinyl-methylene position. This was not observed and, moreover, a ^2H NMR spectrum of $[^2H]$**2** showed no evidence of deuterium located on the β-carbon of the μ-vinyl system. It was also found that reaction of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}CD_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (prepared[2] from $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2D\}(CO)_4(\eta\text{-}C_5H_5)_2]$ and CF_3CO_2D) led to the selective formation of $[Mo_2\{OC(O)CF_3\}(\mu\text{-}CH{=}CD_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ $[^2H_2]$**2**. Thus, both experiments show that protonation occurs on C_α, and not at C_β followed by a hydrogen shift.

Further insight into the factors controlling the protonation reaction was gained from theoretical considerations. Simple extended-Hückel molecular-orbital (EHMO) theory has repeatedly demonstrated an ability to rationalise the sites of nucleophilic and electrophilic attack in organometallic systems. Accordingly, we carried out EHMO calculations on the complex $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ using standard parameters and the crystallographically determined coordinates obtained[2] for $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Ph)(CH_2)_4\text{-}OMe\}(CO)_4(\eta\text{-}C_5H_5)_2]$, the η-$C_5H_5$ hydrogen atoms being idealised at a C–H contact distance of 1.10 Å. If we make the reasonable assumption that protonation is charge controlled, the site of such electrophilic attack should correlate with the carbon atom having the largest negative charge. The α-carbon carries a charge of −0.204, significantly larger than the β-carbon value of −0.074 (Scheme 4). Thus, the α-carbon is predicted to be the site of protonation, in accord with the deuterium-labelling experiments. Interestingly, from an examination of the detailed charge distribution on the α-carbon, the direction of attack, *i.e.* **E** or **F** in Scheme 4, can also be inferred. Both p orbitals lying in the Mo_2C_2 plane have unit populations while the p orbital perpendicular to this plane has a reduced population of only 0.79. This implies a relatively larger negative charge in the plane, and the favoured direction of proton attack will therefore also lie in this plane perpendicular to the Mo–C σ bond, *i.e.* the direction in **E**.



Scheme 4

Further insight and support for the α-protonation pathway came from a study of the related reactions of β,β-disubstituted vinylidenes. As was expected from our study of the protonation of complexes **1** and **3**, addition of trifluoroacetic acid to a toluene solution of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **5** or $[W_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **7** gave good yields of the μ-vinyl complexes $[Mo_2\{OC(O)\text{-}CF_3\}(\mu\text{-}CH{=}CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **6** and $[W_2\{OC(O)CF_3\}\text{-}(\mu\text{-}CH{=}CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **8** respectively. However, it was recognised[4] that if trifluoroacetate anion was not available for capture of the co-ordinatively unsaturated μ-vinyl cations assumed to be formed on α protonation of **5** and **7** then the β-methyl substituents might become involved in further reactions. It was therefore important to examine the protonation of a β,β-dimethyl-substituted vinylidene using $HBF_4{\cdot}Et_2O$ and trifluoromethanesulfonic acid. Addition of $HBF_4{\cdot}Et_2O$ to a CH_2Cl_2 solution of $[Mo\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **5** at −78 °C caused a rapid reaction as evidenced by a subtle change in colour from blue to purple. With the exception of the apparent presence of dissolved carbon monoxide, the IR spectrum of this solution was typical of those containing μ-vinyl complexes. Upon warming to room temperature a further reaction occurred as evidenced by the gradual appearance of a red precipitate of the complex **9**. The IR spectrum of **9** showed only two broad ν(CO) absorbances, one of which had a shoulder. Examination of the ^1H NMR spectrum revealed the

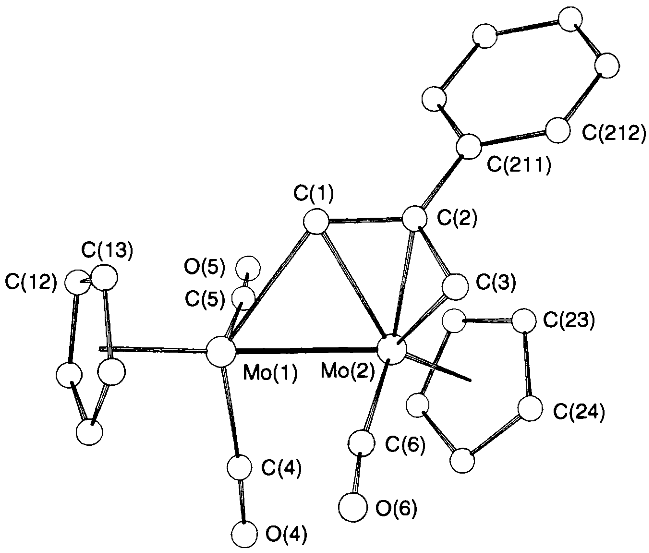


Fig. 1 Molecular structure of the cation associated with the complex $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}CH_2C(Ph)CH_2\}(CO)_3(\eta\text{-}C_5H_5)_2][CF_3SO_3]$ **13**

presence of only one methyl group. The spectrum also showed resonances attributable to two inequivalent η-C_5H_5 ligands, which appeared as two broad singlets. Clearly a rearrangement, of an initially formed μ-vinyl complex, had occurred. The poor solubility of **9**, a salt, in either CH_2Cl_2 or acetone, and its reactivity towards other polar solvents rendered it impossible at this stage to obtain an adequate $^{13}C\text{-}\{^1H\}$ NMR spectrum. However, the characterisation of **9** was greatly facilitated by the discovery that protonation of the μ-allylidene complex $[Mo_2\{\mu\text{-}\sigma:\eta^3\text{-}CHC(Me)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$,[2] obtained by thermal rearrangement of **5**, with either $HBF_4{\cdot}Et_2O$ or CF_3SO_3H gave high yields of cations identical (IR, ^1H NMR) to **9** and **10**. The triflate salt **10** was significantly more soluble in CH_2Cl_2, and it was now possible to obtain the necessary NMR spectra including a $^{13}C\text{-}\{^1H\}$ (-60 °C) spectrum. This provided evidence that **10**, and by analogy **9**, carries only three CO ligands, thereby explaining the detection of the free CO noted earlier. Furthermore, apart from the resonances attributable to the two η-C_5H_5 ligands and the methyl group, three other ^{13}C resonances at δ 25.0, 43.1 and 111.5 were apparent. These, together with the four signals in the low-temperature (-60 °C) ^1H NMR spectrum at δ 1.53, 2.36, 2.43 and 2.56, each integrating for one proton, suggested the presence in **9** and **10** of a 2-substituted allyl fragment lying in a low-symmetry environment.

In order fully to elucidate the structure of complexes **9** and **10** attempts were made to grow crystals suitable for X-ray crystallography. These attempts were unsuccessful, however the 2-phenyl-substituted analogue $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}CH_2C(Ph)CH_2\}(CO)_3(\eta\text{-}C_5H_5)_2][CF_3SO_3]$ **13**, which was formed in high yield by protonation (CF_3SO_3H) of the μ-allylidene complex $[Mo_2\{\mu\text{-}\sigma:\eta^3\text{-}CHC(Ph)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$[2] (available by thermolysis of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$) formed X-ray-quality crystals on layer diffusion. The structure of the cation present in **13** is shown in Fig. 1, and fractional coordinates, selected bond lengths and angles are given in Tables 1 and 2 respectively. The structure consists of one independent molecule in the asymmetric unit. Ignoring the metal–metal bond and regarding the cyclopentadienyl ligands as occupying three co-ordination sites, the geometry around each molybdenum atom is close to octahedral. The relatively short metal–metal bond length of 2.561(2) Å is comparable to that found[8] for other formally triply bonded dimolybdenum structures. A formal triple bond is in fact required on the basis of the 18-electron rule. This compound is the first structurally characterised cationic species with a μ-allyl ligand, which adopts a markedly different bridging role to that previously observed[9] where the central allyl carbon atom bonds symmetrically to both metal atoms.

The metal–metal axis is almost symmetrical bridged by C(1) of the allyl fragment [Mo(1)–C(1) 2.462(18) and Mo(2)–C(1) 2.364(18) Å], with the remaining two carbon atoms bonding solely to Mo(2). The bonding may be considered as η^2 co-ordination to Mo(2) [Mo(2)–C(2) 2.197(17) and Mo(2)–C(3) 2.317(16) Å], and a three-centre two-electron interaction between the α-carbon of the fragment and both metal atoms. This type of three-centred bonding is rare for alkyl ligands,[10] and has not been previously observed for an allyl group. It is more common for one of the C–H bonds of the bridging alkyl also to interact with one of the metals forming a M(μ-H)C interaction.[11–13] Alternatively the bonding of this organo-fragment can also be described as $\mu\eta^3\delta_{4a}$, which describes the bonding to each molybdenum succinctly.[14] Each molybdenum atom has an η^5-co-ordinated cyclopentadienyl ligand and these are in a *trans* configuration relative to one another. Both cyclopentadienyls bond relatively symmetrically [Mo–C (C_5H_5) 2.303(14)–2.378(14) Å]. Atom Mo(1) has two terminally bonded carbonyl ligands whilst Mo(2) has one carbonyl ligand. All three CO ligands are essentially linear [Mo–C (carbonyl) 1.937(2)–2.106(18), C–O 1.123(23)–1.171(25) Å, Mo–C–O 172(2)–175(2)°]. The deviation in the Mo–C–O bond angles from 180° may be due to steric effects as proposed[15,16] for related dimolybdenum complexes. There is also a weak interaction between the carbonyl on Mo(2) and Mo(1) [Mo(1)–C(6) 2.692(29) Å], a type which has been noted in previous Mo_2 compounds.

Thus, with these structural insights we can now summarise

Table 1 Fractional atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}CH_2C(Ph)CH_2\}(CO)_3(\eta\text{-}C_5H_5)_2][CF_3SO_3]$ **13**

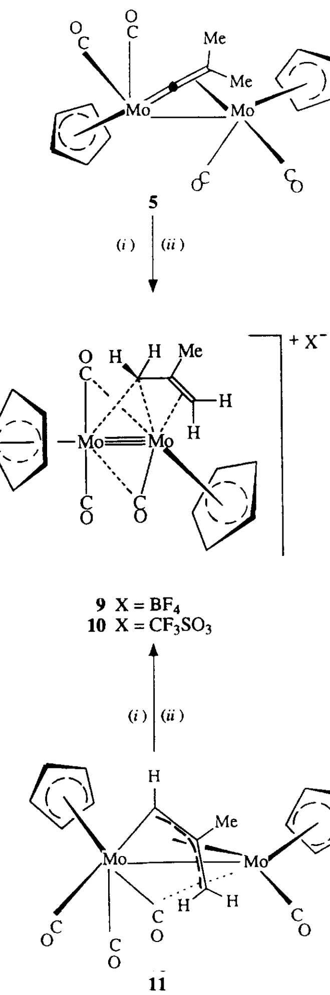
Atom	*x*	*y*	*z*
Mo(1)	0.164 08(6)	0.109 63(6)	0.247 91(14)
Mo(2)	0.043 02(7)	0.090 30(7)	0.214 37(12)
C(4)	0.149 7(9)	0.035 4(9)	0.356 7(16)
O(4)	0.145 7(8)	−0.008 5(7)	0.421 1(12)
C(5)	0.122 4(7)	0.163 9(9)	0.374 8(17)
O(5)	0.104 4(7)	0.196 7(8)	0.446 9(12)
C(6)	0.089 9(9)	0.018 2(10)	0.142 3(17)
O(6)	0.111 0(7)	−0.029 5(7)	0.099 1(12)
C(1)	0.096 0(8)	0.179 6(9)	0.122 3(15)
C(2)	0.031 2(8)	0.166 5(9)	0.079 5(14)
C(3)	0.022 5(8)	0.104 6(9)	0.017 0(14)
S	0.173 8(3)	0.364 9(3)	0.312 7(4)
O(30)	0.173 8(8)	0.428 2(7)	0.365 7(11)
O(31)	0.212 4(7)	0.316 7(8)	0.374 4(12)
O(32)	0.111 7(6)	0.344 5(9)	0.271 2(17)
C(33)	0.222 8(13)	0.376 4(11)	0.180 8(16)
F(1)	0.278 0(6)	0.398 8(8)	0.204 5(13)
F(2)	0.195 0(8)	0.420 5(8)	0.112 6(11)
F(3)	0.223 4(8)	0.320 8(8)	0.117 7(11)
C(11)	0.265 3(7)	0.117 3(7)	0.332 5(8)
C(12)	0.255 4(7)	0.177 0(7)	0.270 0(8)
C(13)	0.250 5(7)	0.161 3(7)	0.149 5(8)
C(14)	0.257 3(7)	0.091 9(7)	0.137 5(8)
C(15)	0.266 4(7)	0.064 7(7)	0.250 6(8)
C(21)	−0.000 9(7)	0.066 7(9)	0.399 6(11)
C(22)	−0.034 6(7)	0.122 7(9)	0.356 6(11)
C(23)	−0.069 0(7)	0.103 4(9)	0.254 8(11)
C(24)	−0.056 6(7)	0.035 4(9)	0.234 9(11)
C(25)	−0.014 5(7)	0.012 7(9)	0.324 3(11)
C(211)	−0.020 9(5)	0.216 3(6)	0.087 0(11)
C(212)	−0.074 9(5)	0.210 1(6)	0.014 7(11)
C(213)	−0.124 7(5)	0.256 3(6)	0.020 9(11)
C(214)	−0.120 6(5)	0.308 7(6)	0.099 5(11)
C(215)	−0.066 7(5)	0.314 9(6)	0.171 8(11)
C(216)	−0.016 8(5)	0.268 7(6)	0.165 6(11)

Table 2 Selected bond distances (Å) and angles (°) for $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}CH_2C(Ph)CH_2\}(CO)_3(\eta\text{-}C_5H_5)_2][CF_3SO_3]$ **13**

Mo(1)–Mo(2)	2.561(2)	Mo(1)–C(4)	1.975(19)
Mo(1)–C(5)	2.016(18)	Mo(1)–C(6)	2.692(20)
Mo(1)–C(1)	2.462(18)	Mo(2)–C(6)	1.937(20)
Mo(2)–C(1)	2.364(18)	Mo(2)–C(2)	2.197(17)
Mo(2)–C(3)	2.317(16)	C(4)–O(4)	1.159(24)
C(5)–O(5)	1.123(23)	C(6)–O(6)	1.171(25)
C(1)–C(2)	1.450(23)	C(2)–C(3)	1.455(25)
C(2)–C(211)	1.478(20)	S–O(30)	1.421(15)
S–O(31)	1.446(17)	S–O(32)	1.429(16)
S–C(33)	1.834(22)	C(33)–F(1)	1.26(3)
C(33)–F(2)	1.32(3)	C(33)–F(3)	1.34(3)
C(4)–Mo(1)–Mo(2)	80.3(5)	C(5)–Mo(1)–Mo(2)	76.9(5)
C(5)–Mo(1)–C(4)	84.1(8)	C(6)–Mo(1)–Mo(2)	43.2(4)
C(6)–Mo(1)–C(4)	70.9(7)	C(6)–Mo(1)–C(5)	117.1(6)
C(1)–Mo(1)–Mo(2)	56.1(4)	C(1)–Mo(1)–C(4)	136.2(7)
C(1)–Mo(1)–C(5)	82.1(7)	C(1)–Mo(1)–C(6)	79.0(6)
C(6)–Mo(2)–Mo(1)	72.0(6)	C(1)–Mo(2)–Mo(1)	59.8(4)
C(1)–Mo(2)–C(6)	99.0(7)	C(2)–Mo(2)–Mo(1)	96.1(4)
C(2)–Mo(2)–C(6)	106.6(7)	C(2)–Mo(2)–C(1)	36.8(6)
C(3)–Mo(2)–Mo(1)	107.8(4)	C(3)–Mo(2)–C(6)	76.7(7)
C(3)–Mo(2)–C(1)	63.5(6)	C(3)–Mo(2)–C(2)	37.5(6)
O(4)–C(4)–Mo(1)	175(2)	O(5)–C(5)–Mo(1)	174(1)
Mo(2)–C(6)–Mo(1)	64.8(6)	O(6)–C(6)–Mo(1)	123(1)
O(6)–C(6)–Mo(2)	172(2)	Mo(2)–C(1)–Mo(1)	64.1(5)
C(2)–C(1)–Mo(1)	128(1)	C(2)–C(1)–Mo(2)	65.3(9)
C(1)–C(2)–Mo(2)	78(1)	C(3)–C(2)–Mo(2)	76(1)
C(3)–C(2)–C(1)	116(1)	C(2)–C(3)–Mo(2)	66.8(9)
O(31)–S–O(30)	113.7(9)	O(32)–S–O(30)	114(1)
O(32)–S–O(31)	117(1)	C(33)–S–O(30)	103.7(9)
C(33)–S–O(31)	101(1)	C(33)–S–O(32)	105(1)
F(1)–C(33)–S	112(1)	F(2)–C(33)–S	109(2)
F(2)–C(33)–F(1)	106(2)	F(3)–C(33)–S	110(1)
F(3)–C(33)–F(1)	114(2)	F(3)–C(33)–F(2)	105(2)

our synthetic findings as illustrated in Scheme 5. With the establishment of the solid-state structure of the cation **13** it was also possible to interpret the variable-temperature solution NMR spectra of the cations **9**, **10** and **13**. As previously noted and detailed in the Experimental section, the low-temperature (−60 °C) ^1H NMR spectrum exhibits two inequivalent $\eta\text{-}C_5H_5$ signals and four signals due to the allyl protons, a pair of *syn*-proton signals lying downfield of the two *anti*-proton signals. On warming to room temperature each pair of allyl signals undergoes a coalescence [$\Delta G^{\ddagger}_{318}$(*syn*-H) 61 ± 2 kJ mol^{-1}; $\Delta G^{\ddagger}_{300}$(*anti*-H) 59 ± 2 kJ mol^{-1}] to give two broad signals there being no change in the appearance of the cyclopentadienyl resonances. This implies that a dynamic process occurs in solution whereby the two *anti*-allylic protons become equivalent on the NMR time-scale as do the two *syn*-protons. The broadness of the two signals present in the room-temperature spectrum suggests that *syn*/*anti* exchange is also beginning to occur, however attempts to observe further coalescence at high temperatures were prevented by decomposition in the solvents available. Thus, these observations can be rationalised by the processes shown in Scheme 6, where equivalencing of the two ends of the allylic ligand, *i.e.* $H^a \rightleftharpoons H^c$, $H^b \rightleftharpoons H^d$ occurs *via* the symmetrically η^3-bonded allylic species **G**. The *syn*/*anti* exchange presumably involves the higher-energy σ-bonded intermediates **H**–**J**.

With the establishment of the structural identity of the cationic complexes **9**, **10** and **13**, both in the solid state and solution, it was also possible to rationalise their formation on protonation of β,β-disubstituted $\mu\text{-}\sigma:\eta^2$-(4e)-vinylidene complexes. As is shown in Scheme 7, α protonation of **5** would be expected to give the co-ordinatively unsaturated cation **K**. Although this might be partially stabilised by interaction ($Mo\text{–}F\text{–}BF_3$) with the tetrafluoroborate anion there is now the possibility of a δ-hydrogen interaction, which could lead to the successive formation of the intermediates **L** and **M**, *via* transfer

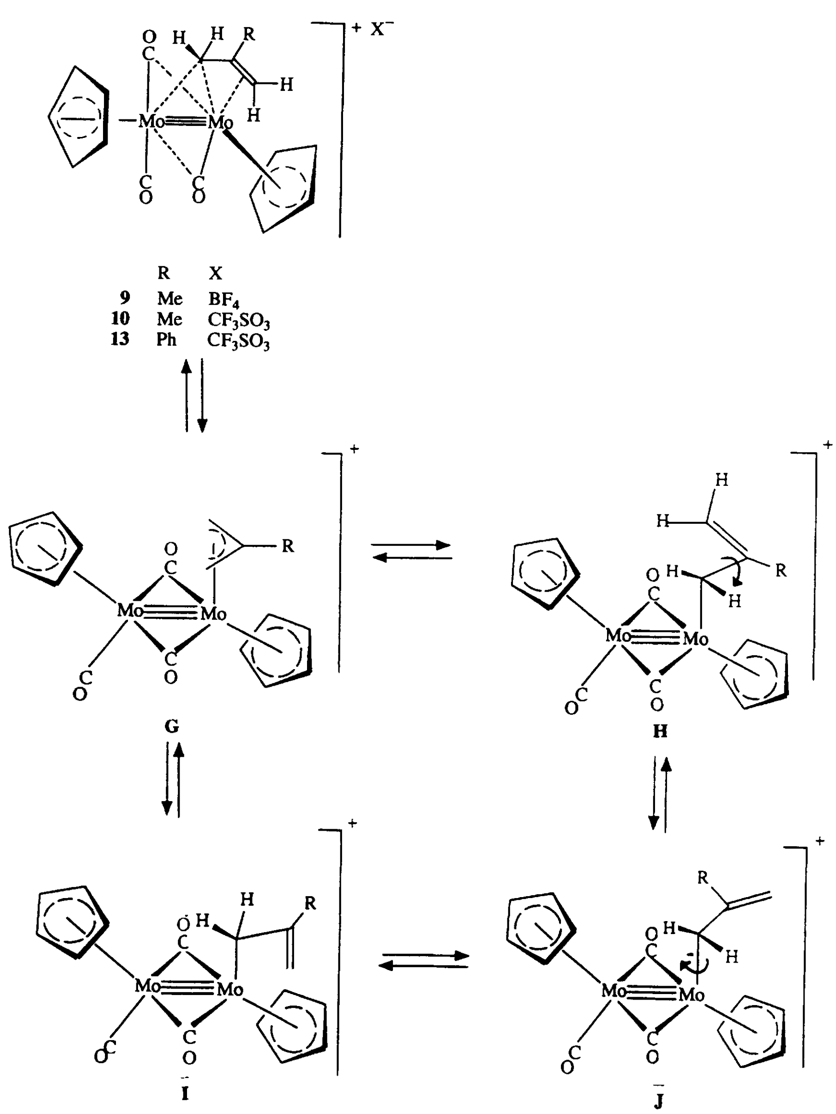


Scheme 5 $X^- = BF_4$ or $CF_3SO_3^-$. (*i*) $HBF_4{\cdot}Et_2O$ or CF_3SO_3H; (*ii*) −CO

of hydrogen from the methyl group to the molybdenum centre. Further transfer of the hydrogen, which is bonded to the metal, to what was originally the α-carbon of the μ-vinylidene, thus accesses the intermediates **N** and **O**. These same species should also, according to EHMO calculations,[17,*] be formed on charge-controlled protonation of the α-carbon of the μ-allylidene complex $[Mo_2\{\mu\text{-}\sigma:\eta^3\text{-}CHC(Me)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **11**, a prediction which is borne out by experiment (see above) for both **11** and the phenyl-substituted analogue **12**. Surprisingly the intermediate **O** carrying an agostic Mo(μ-H)C interaction is unstable, losing a molecule of carbon monoxide to form the bridged allyl complexes **9** and **10**.

In exploring the reactivity of these dinuclear cations it was observed that when complex **9** was treated with 1 mol equivalent of $K[BHBu^s_3]$ the μ-allylidene complex **11** (47% yield) was reformed, suggesting that in the presence of a donor ligand (thf) **9** is in equilibrium with a thf-substituted analogue of **O**, and that the borohydride functions as a base abstracting a proton from the Mo(μ-H)C system leading to the reformation of **11** on transfer of CO *via* a disproportionation reaction. A disproportionation reaction also occurred on reaction of **9** with

* EHMO Calculations on the double μ-allylidene complex $[Mo_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]$ indicate a build-up of negative charge on C_α as does a similar calculation (R. J. Deeth) with the complex $[Mo_2(\mu\text{-}\sigma:\eta^3\text{-}CHCHCH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ using parameters from the X-ray crystallographically defined complex $[Mo_2(\mu\text{-}\sigma:\eta^3\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$.[18]

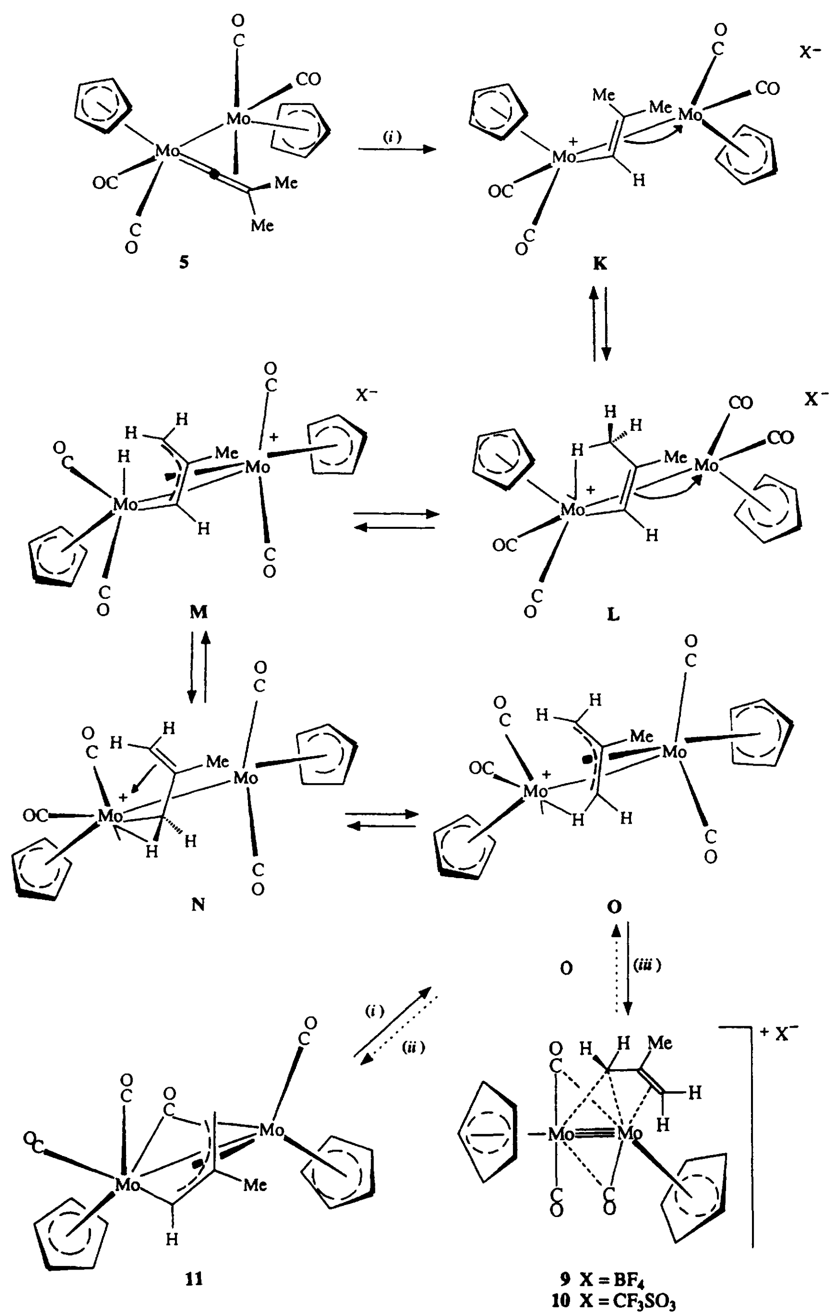


Scheme 6

an excess of but-2-yne leading to the formation of the known[19] cation $[Mo(\eta^2-MeC_2Me)_2(CO)(\eta-C_5H_5)][BF_4]$. In the former reaction attempts to identify the other molybdenum-containing products were unsuccesssful, however in the case of the but-2-yne reaction the other product was the known complex $[Mo\{\eta^3-CH_2C(Me)CH_2\}(CO)_2(\eta-C_5H_5)]$.

As indicated in the Introduction we have also explored the reactivity of 'side-on' bonded vinylidene complexes towards diazomethane. Previously it has been shown[20] that the 'upright' vinylidene complex $[Fe_2\{\mu-\sigma:\sigma-(2e)-C=CH_2\}(\mu-CO)_2(\eta-C_5H_5)_2]$ reacts with CH_2N_2 in the presence of copper(I) chloride to give the μ-cyclopropylidene complex $[Fe_2\{\mu-\sigma:\sigma-(2e)-CCH_2CH_2\}(\mu-CO)(CO)_2(\eta-C_5H_5)_2]$, which on heating or UV irradiation affords the μ-allene complex $[Fe_2(\mu-\eta^2:\eta^2-CH_2=C=CH_2)(CO)_2(\eta-C_5H_5)_2]$. In a related study[21] the same diiron 'upright' vinylidene on UV irradiation in the presence of N_2CHCO_2Et was shown to give directly the μ-allene complex $[Fe_2\{\mu-\eta^2:\eta^2-CH_2=C=CH(CO_2Et)\}(CO)_2(\eta-C_5H_5)_2]$. In this instance it was suggested that a μ-cyclopropylidene intermediate was not formed, but rather that loss of CO led to the formation of an alkylidenevinylidene complex, which collapsed to form a μ-allene *via* an intramolecular coupling reaction. To an extent this proposition is supported by the report[22] that UV irradiation of $[Ru_2\{\mu-\sigma:\sigma-(2e)-C=CH_2\}(\mu-CO)(CO)_2(\eta-C_5H_5)_2]$ in acetonitrile affords $[Ru_2\{\mu-\sigma:\sigma-(2e)-C=CH_2\}(\mu-CO)(CO)(NCMe)(\eta-C_5H_5)_2]$, which on treatment with CH_2N_2 gives $[Ru_2(\mu-\eta^2:\eta^2-CH_2=C=CH_2)(CO)_2(\eta-C_5H_5)_2]$; however, it is important to note that the μ-alkylidene/vinylidene complex $[Ru_2(\mu-CMe_2)\{\mu-\sigma:\sigma-(2e)-C=CH_2\}(CO)_2(\eta-C_5H_5)_2]$ is reported to be thermally stable and does not rearrange to a μ-allene complex. Against this background it was obviously of interest to examine the reactivity of a range of dimolybdenum $\mu-\sigma:\eta^2-(4e)$-vinylidene complexes towards diazomethane; indeed it had already been reported in a preliminary communication[23] that $[Mo_2\{\mu-\sigma:\eta^2-(4e)-C=CH_2\}(CO)_4(\eta-C_5Me_5)_2]$ reacts with CH_2N_2 to form $[Mo_2(\mu-\eta^2:\eta^2-CH_2=C=CH_2)(CO)_4(\eta-C_5Me_5)_2]$.

The starting point for our investigation was the EHMO calculation, mentioned earlier in the context of charge-controlled protonation. In principal, diazomethane should behave as a soft nucleophile and react with a $\mu-\sigma:\eta^2-(4e)$-vinylidene complex under frontier-orbital control. A plot of the lowest unoccupied molecular orbital (LUMO) (Fig. 2) of $[Mo_2\{\mu-\sigma:\eta^2-(4e)-C=CH_2\}(CO)_4(\eta-C_5H_5)_2]$ reveals that the α-carbon of the vinylidene fragment carries a substantial p-orbital component perpendicular to the Mo_2C_2 plane, approximately parallel to the vinylidene plane. The β-carbon has no LUMO component, hence EHMO theory predicts that nucleophilic attack should



Scheme 7 X = BF_4^- or $CF_3SO_3^-$. (*i*) + $HBF_4{\cdot}Et_2O$ or CF_3SO_3H; (*ii*) –CO; (*iii*) =[$BHBu^s_3$]

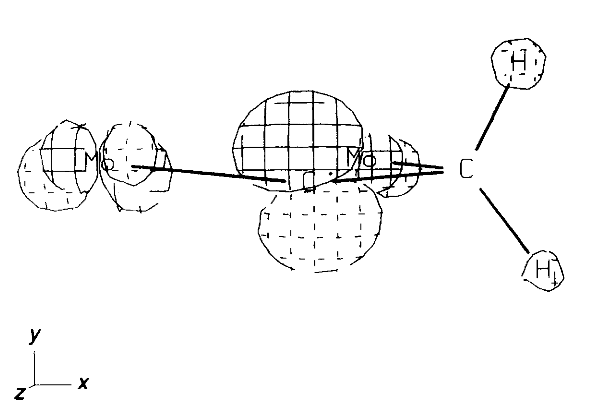
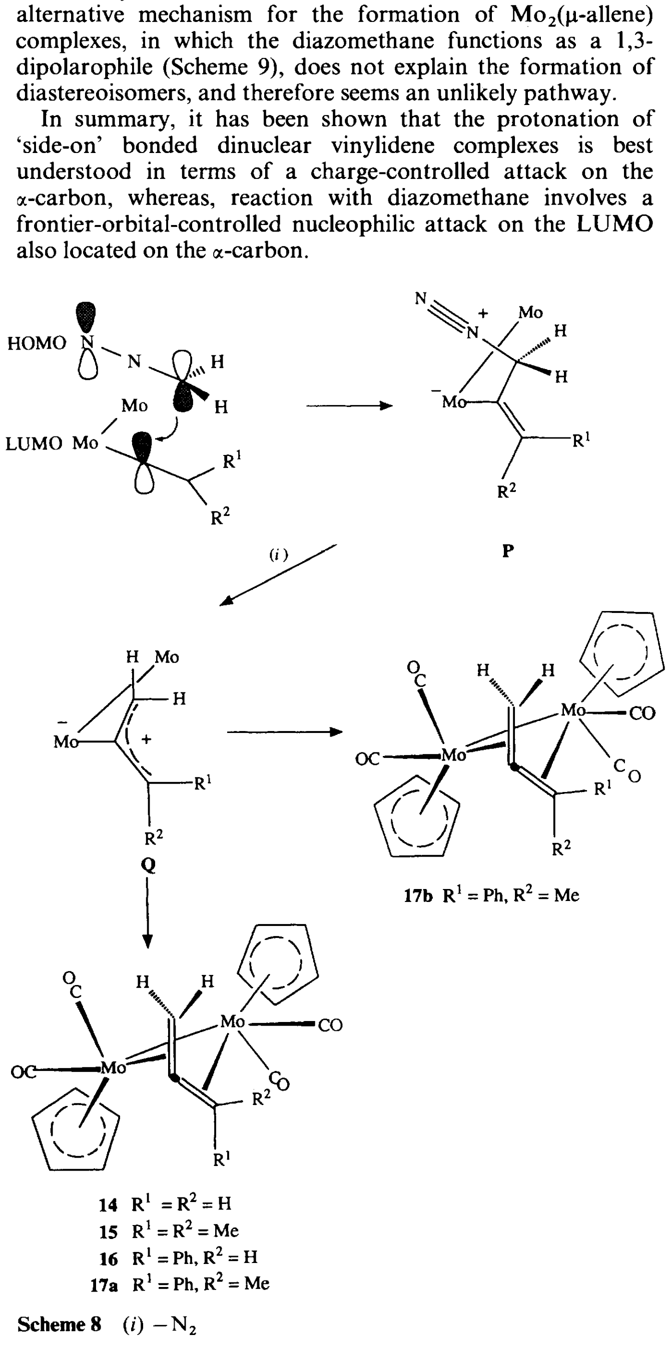


Fig. 2 The LUMO associated with the complex [$Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-(4e)-}C{=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2$]

occur at the vinylidene α-carbon. This prediction is consistent with our earlier report[24] that phosphines and isocyanides attack the α-carbon atom of the vinylidenes [$Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-(4e)-}C{=}C(R^1)R^2\}(CO)_4(\eta\text{-}C_5H_5)_2$]. Addition of an excess of an ether solution of diazomethane to a diethyl ether solution (−78 °C) of [$Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-(4e)-}C{=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2$] **1** led to a change in colour from purple to orange and the formation in high yield of the known[15] μ-allene complex [$Mo_2(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_2{=}C{=}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2$] **14**, previously obtained by reaction of $CH_2{=}C{=}CH_2$ with [$Mo_2(CO)_4(\eta\text{-}C_5H_5)_2$]. In a similar way treatment of [$Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-(4e)-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2$] **5** with CH_2N_2 gave an orange crystalline complex, which was characterised by elemental analysis, IR and NMR spectroscopy (see Experimental section) as the μ-allene complex [$Mo_2(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_2{=}C{=}CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2$] **15**. It is interesting that previous attempts[15] to make this complex by reaction of $CH_2{=}C{=}CMe_2$ with [$Mo_2(CO)_4(\eta\text{-}C_5H_5)_2$] failed, even under forcing conditions. The unsymmetrical labile 'side-on' bonded vinylidene $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-C=C(Ph)H}\}(CO)_4(\eta\text{-}C_5H_5)_2]$ also reacted with an excess of CH_2N_2 to give orange crystals of $[Mo_2\{\mu\text{-}\eta^2:\eta^2\text{-}CH_2\text{=C=C(Ph)H}\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **16**. In contrast, a similar reaction of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-C=C(Ph)Me}\}(CO)_4(\eta\text{-}C_5H_5)_2]$ gave under kinetic control an inseparable mixture of the two red crystalline diastereoisomers $[Mo_2\{\mu\text{-}\eta^2:\eta^2\text{-}CH_2\text{=C=C(Ph)Me}\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **17a** and $[Mo_2\{\mu\text{-}\eta^2:\eta^2\text{-}CH_2\text{=C=C(Me)Ph}\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **17b** (2.3:1).

All of these observations can be explained if we assume that as is illustrated in Scheme 8, the diazomethane attacks the LUMO located on the α-carbon of the vinylidene fragment to form the dipolar intermediate **P**. Loss of N_2 then leads to the formation of the dipolar species **Q**, carrying an allylic carbonium ion. Providing **Q** has a long enough lifetime then rotation about a carbon–carbon bond within the allylic carbonium ion could occur allowing the formation of the diastereoisomers **17a** and **17b**. Presumably, in the case of the formation of **16**, only one isomer is formed because one isomer of the allylic cation is more stable for steric reasons. The alternative mechanism for the formation of Mo_2(μ-allene) complexes, in which the diazomethane functions as a 1,3-dipolarophile (Scheme 9), does not explain the formation of diastereoisomers, and therefore seems an unlikely pathway.

In summary, it has been shown that the protonation of 'side-on' bonded dinuclear vinylidene complexes is best understood in terms of a charge-controlled attack on the α-carbon, whereas, reaction with diazomethane involves a frontier-orbital-controlled nucleophilic attack on the LUMO also located on the α-carbon.



17b R^1 = Ph, R^2 = Me

14 R^1 = R^2 = H
15 R^1 = R^2 = Me
16 R^1 = Ph, R^2 = H
17a R^1 = Ph, R^2 = Me

Scheme 8 (*i*) $-N_2$

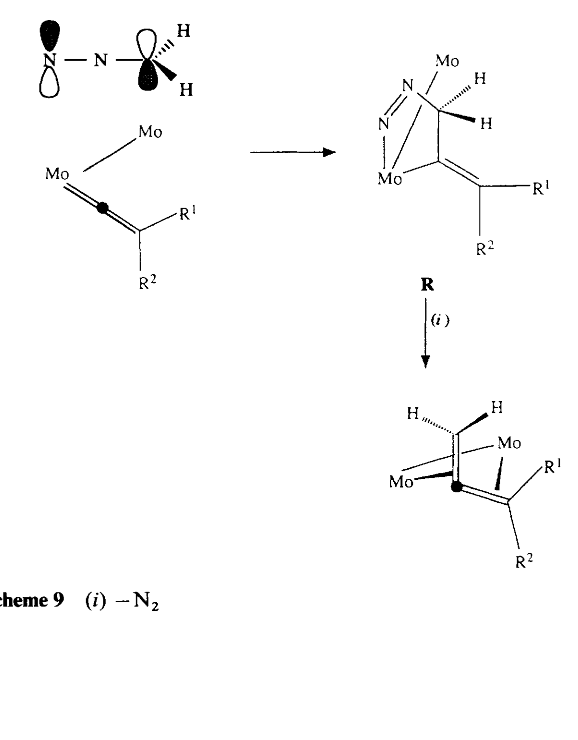
Experimental

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 ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker AM360 spectrometer. Chemical shifts are quoted as positive to high frequency of tetramethylsilane. Data given are for room-temperature measurements unless stated otherwise. The IR spectra were measured using a Perkin-Elmer 983G spectrometer. Mass spectra and analytical data were obtained courtesy of the University of London Services.

Reactions of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-C=CH}_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **1**.—(*a*) *Trifluoroacetic acid.* A toluene (5 cm^3) solution of complex **1** (0.15 g, 0.33 mmol) at −78 °C was treated with CF_3CO_2H (26 μl, 0.33 mmol). The stirred solution was allowed to warm to room temperature, whereupon it gradually changed from deep purple to bright red. The volatile material was removed *in vacuo* and the residue redissolved in dichloromethane. The solution was filtered through Celite, the volume reduced to 2 cm^3 and hexane (2 cm^3) added resulting in the formation of red *crystals* of $[Mo_2\{OC(O)CF_3\}(\mu\text{-CH=CH}_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **2** (0.16 g, 85%) (Found: C, 51.5; H, 2.3. Calc. for $C_{18}H_{13}F_3Mo_2O_6$ C, 51.6; H, 2.3%); $\nu_{CO}(CH_2Cl_2)$ 2029m, 1957s, 1888m and 1689w cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.05 [dd, 1 H, CH^c=CH_2, $J(H^aH^c)$ 12.0, $J(H^bH^c)$ 8.0], 5.32 (s, 5 H, C_5H_5), 5.16 (s, 5 H, C_5H_5), 4.00 [d, 1 H, CH^c=$C(H^a)H^b$, $J(H^bH^c)$ 8.0] and 3.30 [d, 1 H, CH=$C(H^a)H^b$, $J(H^aH^c)$ 12.0 Hz].

(*b*) *Deuteriotrifluoroacetic acid.* Similarly, reaction (−78 °C) of complex **1** (0.15 g, 0.33 mmol) with CF_3CO_2D (26 μl, 0.33 mmol) in toluene (5 cm^3) gave red *crystals* of $[Mo_2\{OC(O)CF_3\}(\mu\text{-CD=CH}_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ [^{2}H]**2** (0.16 g, 85%); $\nu_{CO}(CH_2Cl_2)$ 2029m, 1957s and 1888m cm^{-1}. NMR: ^1H ($CDCl_3$): δ 9.05 [dd, H < 5%, CH=CH_2, $J(H^aH^c)$ 12.0, $J(H^bH^c)$ 8.0 Hz], 5.32 (s, 5 H, C_5H_5), 5.16 (s, 5 H, C_5H_5), 4.00 (br s, 1 H, CD=CH_2), 3.30 (br s, 1 H, CD=CH_2); ^2H (CH_2Cl_2), δ 9.05 (br s, CD=CH_2).

Other Reactions with Trifluoroacetic Acid.—$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-C=CD}_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$. Reaction (−78 °C) of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-C=CD}_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.15 g, 0.33 mmol) with



Scheme 9 (*i*) $-N_2$

CF_3CO_2H (26 µl, 0.33 mmol) in toluene (5 cm^3) afforded red *crystals* of $[Mo_2\{OC(O)CF_3\}(\mu\text{-}CH{=}CD_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ $[^2H_2]$**2** (0.16 g, 85%); $\nu_{CO}(CH_2Cl_2)$ 2029m, 1957s and 1888m cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.05 (br s, 1 H, $CH{=}CD_2$), 5.32 (s, 5 H, C_5H_5), 5.16 (s, 5 H, C_5H_5), 4.00 [d, H < 5%, $CH{=}CDH$, J(HH) 8.0], 3.30 [d, H < 5%, $CH{=}CHD$, J(HH) 12.0 Hz].

$[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}(4e)\text{-}C{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **3**. Following the same procedure a toluene solution (5 cm^3) of complex **3** (0.193 g, 0.35 mmol) was treated (−78 °C) with CF_3CO_2H (28 µl, 0.35 mmol) to give red *crystals* of $[Mo_2\{OC(O)CF_3\}\{\mu\text{-}CH{=}C(Me)Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **4a** and $[Mo_2\{OC(O)CF_3\}\{\mu\text{-}CH{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **4b** (0.18 g, 80%) (Found: C, 41.3; H, 2.5. $C_{25}H_{19}F_3Mo_2O_6{\cdot}CH_2Cl_2$ requires C, 41.7; H, 2.8%); ν_{CO}(CH_2Cl_2 1995m, 1980m, 1960s, 1925s, 1895m and 1850m cm^{-1}. On isolation the ratio of isomers was 2.5:1 (**4a**:**4b**), however on standing at room temperature in solution (dichloromethane) isomerisation occurs (24 h) to give only **4a**. NMR (CD_2Cl_2) data for **4a**: ^1H, δ 9.60 (s, 1 H, CH), 7.63–7.09 (m, 5 H, Ph), 5.47 (s, 5 H, C_5H_5), 4.70 (s, 5 H, C_5H_5) and 2.33 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 241.1, 238.5, 238.4, 231.9 (CO), 167.0 (CH), 162.5 [q, CF_3CO_2, J(CF) 40.0], 150.1, 128.8, 127.7, 125.2 (Ph), 116.5 [q, CF_3CO_2, J(CF) 29.0 Hz], 106.3 [C(Ph)Me], 95.1 (C_5H_5), 94.3 (C_5H_5) and 29.4 (Me). ^1H NMR data (CD_2Cl_2) for **4b**: δ 8.71 (s, 1 H, CH), 7.63–7.03 (m, 5 H, Ph), 5.17 (s, 5 H, C_5H_5), 5.13 (s, 5 H, C_5H_5) and 2.31 (s, 3 H, Me).

$[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}(4e)\text{-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **5**. To a toluene (5 cm^3) solution of complex **5** (0.40 g, 0.82 mmol) at −78 °C was added CF_3CO_2H (64 µl, 0.82 mmol). No reaction was apparent until the reaction mixture warmed to room temperature when it changed from deep blue to bright red. Removal of the solvent *in vacuo* and recrystallisation of the residue from dichloromethane–hexane gave red *crystals* of $[Mo_2\{OC(O)CF_3\}(\mu\text{-}CH{=}CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **6** (0.45 g, 96%) (Found: C, 39.4; H, 2.8. $C_{20}H_{17}F_3Mo_2O_6$ requires C, 39.9; H, 2.9%); $\nu_{CO}(CH_2Cl_2)$ 2014m, 1948s and 1869m cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 8.54 (s, 1 H, CH), 5.39 (s, 5 H, C_5H_5), 5.09 (s, 5 H, C_5H_5), 1.99 (s, 3 H, Me) and 1.97 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 240.9, 239.0, 238.5, 234.2 (CO), 166.7 (CH), 162.5 [q, CF_3CO_2, J(CF) 40.0], 115.7 [q, CF_3, J(CF) 292 Hz], 111.9 (CMe$_2$), 94.5 (C_5H_5), 93.9 (C_5H_5), 37.2 (Me) and 29.8 (Me).

$[W_2\{\mu\text{-}\sigma{:}\eta^2\text{-}(4e)\text{-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **7**. Similarly, reaction of complex **7** (0.113 g, 0.17 mmol) with CF_3CO_2H (13 µl, 0.17 mmol) in toluene (2 cm^3) gave red *crystals* of $[W_2\{OC(O)CF_3\}(\mu\text{-}CH{=}CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **8** (0.09 g, 70%) (Found: C, 30.5; H, 2.1. $C_{20}H_{17}F_3O_6W_2$ requires C, 30.9; H, 2.2%); $\nu_{CO}(CH_2Cl_2)$ 2008m, 1936s, 1890 (sh), 1858m and 1694 cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 7.57 (s, 1 H, CH), 5.51 (s, 5 H, C_5H_5), 5.18 (s, 5 H, C_5H_5), 2.13 (s, 3 H, Me) and 2.12 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 228.6, 226.6, 225.9, 224.1 (CO), 162.7 [q, CF_3CO_2, J(CF) 40.0], 141.6 [s, with satellites, CH, ^1J(CW) 90, 35], 114.0 [q, CF_3, J(CF) 290 Hz], 100.2 (CMe$_2$), 92.3 (C_5H_5), 92.0 (C_5H_5), 39.1 (Me) and 29.8 (Me).

Reactions of $[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}(4e)\text{-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **5**.—(*a*) *Tetrafluoroboric acid.* Addition of $HBF_4{\cdot}OEt_2$ (52 µl, 0.37 mmol) to a cooled (−78 °C) solution of complex **5** (0.18 g, 0.37 mmol) in dichloromethane (5 cm^3) initially gave a deep purple solution [$\nu_{CO}(CH_2Cl_2)$ 2025m, 1958s and 1885m cm^{-1}], which on warming to room temperature and stirring for 1 h changed to red. Addition of diethyl ether (5 cm^3) gave a red precipitate which on recrystallisation (0 °C) from CH_2Cl_2–Et_2O gave red *crystals* of $[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}CH_2C(Me)CH_2\}(CO)_3(\eta\text{-}C_5H_5)_2][BF_4]$ **9** (0.125 g, 60%), $\nu_{CO}(CH_2Cl_2)$ 1999w, 1938m and 1920 (sh) cm^{-1}. Identical ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra to those observed for the CF_3SO_3 salt (see below).

(*b*) *Trifluoromethanesulfonic acid.* A similar reaction between complex **5** (0.37 mmol) and CF_3SO_3H (0.37 mmol) gave the more soluble red crystalline complex $[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}CH_2C(Me)CH_2\}(CO)_3(\eta\text{-}C_5H_5)_2][CF_3SO_3]$ **10** (0.14 g, 70%) (Found: C, 35.4; H, 2.8. $C_{18}H_{17}F_3Mo_2O_6S$ requires C, 35.4; H, 2.8%); $\nu_{CO}(CH_2Cl_2)$ 1999w, 1938m and 1920 (sh) cm^{-1}, (KBr disc) 1983m, 1921m and 1904m cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 5.66 (s, 5 H, C_5H_5), 5.41 (s, 5 H, C_5H_5), 3.05 (br s, 2 H), 2.56 (s, 3 H, Me) and 1.9 (br s, 2 H); (−60 °C), δ 5.72 (s, 5 H, C_5H_5), 5.47 (s, 5 H, C_5H_5), 3.59 [d, 1 H, H^a, $J(H^aH^c)$ 3.3], 2.56 (s, 3 H, Me), 2.43 [dd, 1 H, H^c, $J(H^aH^c)$ 3.3, $J(H^cH^d)$ 1.9], 2.36 [d, 1 H, H^d, $J(H^dH^c)$ 1.9] and 1.53 (br s, 1 H, H^b); $^{13}C\text{-}\{^1H$, gate decoupled$\}$; (−60 °C), δ 233.4 (CO), 228.8 (CO), 228.1 (CO), 111.5 (s, CMe), 98.5 (m, C_5H_5), 95.3 (m, C_5H_5), 43.1 [at, CH_2, ^1J(CH) 160], 29.6 [q, Me, ^1J(CH) 130] and 25.0 [at, CH_2, ^1J(CH) 150 Hz].

Other Reactions with Trifluoromethanesulfonic Acid.—$[Mo_2\{\mu\text{-}\sigma{:}\eta^3\text{-}CHC(Me)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **11**. Addition of CF_3SO_3H (0.5 mmol) to complex **11** (0.224 g, 0.05 mmol) in CH_2Cl_2 (5 cm^3) at −78 °C led to an instantaneous darkening of the orange colour. Warming to room temperature and addition of diethyl ether (5 cm^3) gave an orange precipitate. Recrystallisation (0 °C) from CH_2Cl_2–Et_2O gave orange crystals of **10** (90%), identical (IR, NMR spectra) with that prepared above.

$[Mo_2\{\mu\text{-}\sigma{:}\eta^3\text{-}CHC(Ph)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **12**. In a similar way addition of CF_3SO_3H (0.5 mmol) to complex **12** (0.5 mmol) in CH_2Cl_2 (5 cm^3) gave on addition of Et_2O an orange precipitate. Recrystallisation (0 °C) from CH_2Cl_2–Et_2O gave orange *crystals* of $[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}CH_2C(Ph)CH_2\}(CO)_3(\eta\text{-}C_5H_5)_2][CF_3SO_3]$ **13** (90%) (Found: C, 41.3; H, 2.7. $C_{23}H_{19}F_3Mo_2O_6S$ requires C, 41.1; H, 2.7%); $\nu_{CO}(CH_2Cl_2)$ 1994w, 1937m and 1919 (sh) cm^{-1}. ^1H NMR [$(CD_3)_2CO$, 45 °C], δ 7.76–7.36 (m, 5 H, Ph), 6.02 (s, 5 H, C_5H_5), 5.27 (s, 5 H, C_5H_5), 3.9 (br s, 2 H, H^a, H^c) and 2.22 (br s, 2 H, H^b, H^d); (25 °C), δ 7.76–7.36 (m, 5 H, Ph), 6.02 (s, 5 H, C_5H_5), 5.27 (s, 5 H, C_5H_5), 4.4 (br s, 1 H, $H^{a/c}$), 3.25 (br s, 1 H, $H^{a/c}$) and 2.20 (br s, 2 H, H^b, H^d); (CD_2Cl_2, −40 °C), δ 7.61–7.40 (m, 5 H, Ph), 5.78 (s, 5 H, C_5H_5), 5.07 (s, 5 H, C_5H_5), 4.12 [d, 1 H, H^a, $J(H^aH^c)$ 3.9], 2.85 [dd, 1 H, H^c, $J(H^cH^a)$ 3.9, $J(H^cH^d)$ 2.8], 2.37 [d, 1 H, H^d, $J(H^dH^c)$ 2.8 Hz] and 1.83 (br s, 1 H, H^b).

Reactions of $[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}CH_2C(Me)CH_2\}(CO)_3(\eta\text{-}C_5H_5)_2][BF_4]$ **9**. (*a*) $K[BHBu^s_3]$. A solution of $K[BHBu^s_3]$ (1 mol dm^{-3} in thf, 0.22 mmol) was added dropwise with stirring to a suspension of complex **9** (0.125 g, 0.22 mmol) in thf at −78 °C. On warming to room temperature the mixture changed from red to dark orange. Volatile material was removed *in vacuo* and the residue extracted into toluene. Chromatography on alumina and elution with CH_2Cl_2–Et_2O (1:1) gave an orange band. This was collected and identified by IR and NMR spectroscopy as $[Mo_2\{\mu\text{-}\sigma{:}\eta^3\text{-}CHC(Me)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **11** (0.06 g, 57%).

(*b*) *But-2-yne.* An excess of MeC≡CMe (0.05 cm^3) was added to a solution of complex **9** (0.10 g, 0.16 mmol) in CH_2Cl_2 (95 cm^3) contained in a Young's tube. Over 7 d at room temperature the mixture changed from red to dark yellow. Addition of diethyl ether (5 cm^3) gave a yellow precipitate (0.07 mmol) of $[Mo(\eta^2\text{-}MeC_2Me)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ identified by IR and NMR spectroscopy. Removal of the solvent from the mother-liquor followed by chromatography on alumina (elution with hexane) gave bright yellow *crystals* of $[Mo\{\eta^3\text{-}CH_2C(Me)CH_2\}(CO)_2(\eta\text{-}C_5H_5)]$ (0.07 mmol) which was identified by IR and NMR spectroscopy.

Reactions of Diazomethane.—(*a*) $[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}(4e)\text{-}C{=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **1**. A solution of complex **1** (0.20 g, 0.44 mmol) in diethyl ether (10 cm^3) was cooled to −78 °C and treated on stirring with an ether solution of diazomethane (0.80 mmol in 5 cm^3 of Et_2O) added dropwise over 30 min. The reaction mixture was allowed to warm to room temperature, whereupon it changed from purple to orange. The solvent was removed *in vacuo* and the residue dissolved in toluene (2 cm^3) and chromatographed on an alumina-packed column. Elution with hexane–diethyl ether (9:1) afforded an orange band, which on recrystallisation (0 °C) from hexane–diethyl ether gave orange *crystals* of $[Mo_2(\mu\text{-}\eta^2:\eta^2\text{-}CH_2{=}C{=}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **14** (0.166 g, 80%) (Found: C, 43.0; H, 3.1. Calc. for $C_{17}H_{14}Mo_2O_4$: C, 43.1; H, 3.0%); ν_{CO}(toluene) 1915 (allene), 1995w, 1960m, 1860s and 1830m cm^{-1}. NMR (C_6D_6): ^1H, δ 4.54 (s, 10 H, C_5H_5), 3.67 [t, 2 H, $=CH_2$, *J*(HH) 4.0] and 2.52 [t, 2 H, $=CH_2$, *J*(HH) 4.0 Hz]; $^{13}C\text{-}\{^1H\}$, δ 237.16, 233.48 (CO), 196.96 (CH_2CCH_2), 93.06 (C_5H_5) and 36.66 (CH_2CCH_2).

(*b*) $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **5**. In a similar way reaction of complex **5** (0.20 g, 0.40 mmol) with CH_2N_2 (1.0 mmol) in diethyl ether (10 cm^3) gave, on column chromatography and recrystallisation (0 °C) from hexane–diethyl ether, orange *crystals* of $[Mo_2(\mu\text{-}\eta^2:\eta^2\text{-}CH_2{=}C{=}CMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **15** (0.16 g, 80%) (Found: C, 45.4; H, 3.5. $C_{19}H_{18}Mo_2O_4$ requires C, 45.5; H, 3.6%); ν_{CO}(hexane) 1953m, 1921s, 1879s and 1854m cm^{-1}. NMR (C_6D_6): ^1H, δ 4.68 (s, 5 H, C_5H_5), 4.52 (s, 5 H, C_5H_5), 30.8 [d, 1 H, CH_2, *J*(HH) 2.80], 1.95 [d, 1 H, CH_2, *J*(HH) 2.75 Hz], 1.75 (s, 3 H, Me) and 1.67 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 243.5, 236.15, 235.1, 232.5 (CO), 222.38 (CH_2CCMe_2), 94.12 (C_5H_5), 92.07 (C_5H_5), 73.45 (CH_2CCMe_2), 37.82 (C*Me*), 32.53 (CH_2CCMe_2) and 32.01 (C*Me*).

(*c*) $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Ph)H\}(CO)_4(\eta\text{-}C_5H_5)_2]$. In the same way reaction (−78 °C) of a solution of the thermally labile complex $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Ph)H\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.05 g, 0.09 mmol) in diethyl ether (5 cm^3) with CH_2N_2 (0.20 mmol in 5 cm^3 of Et_2O) gave an orange solution on warming to room temperature. Removal of the solvent *in vacuo* and chromatography of the residue on alumina gave on elution with hexane–diethyl ether (2:1) an orange band. Crystallisation (0 °C) from hexane–diethyl ether gave orange *crystals* of $[Mo_2\{\mu\text{-}\eta^2:\eta^2\text{-}CH_2{=}C{=}C(Ph)H\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **16** (0.037 g, 75%) (Found: C, 50.0; H, 3.3. $C_{23}H_{18}Mo_2O_4$ requires C, 50.2; H, 3.3%); ν_{CO}(toluene) 1923 (allene), 1956w, 1877m, 1854w and 1802w cm^{-1}. NMR (C_6D_6): ^1H, δ 7.20 (m, 5 H, Ph), 5.98 (s, 1 H, C*H*Ph), 5.06 (s, 5 H, C_5H_5), 4.76 (s, 5 H, C_5H_5), 3.49 [d, 1 H, CH_2, *J*(HH) 1.90] and 2.37 [d, 1 H, CH_2, *J*(HH) 1.90 Hz]; $^{13}C\text{-}\{^1H\}$, δ 237.8, 236.8, 235.7, 234.2 (CO), 203.6 [CH_2CC(Ph)H], 142.6, 131.9, 127.9, 126.3 (Ph), 93.9 (C_5H_5), 92.4 (C_5H_5), 61.5 [CH_2CC(Ph)H] and 32.0 [CH_2CC(Ph)H].

(*d*) $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **3**. Similarly, reaction of a solution (diethyl ether, 10 cm^3) of complex **3** (0.31 g, 0.56 mmol) with CH_2N_2 (1.0 mmol in 10 cm^3 Et_2O) gave a red solution. Removal of solvent *in vacuo* and column chromatography gave on elution with hexane–diethyl ether (4:1) a red band. Collection and recrystallisation (0 °C) from hexane–diethyl ether gave red *crystals* of $[Mo_2\{\mu\text{-}\eta^2:\eta^2\text{-}CH_2{=}C{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **17a** and **17b** (2.3:1) (0.15 g, 48%) (Found: C, 51.6; H, 3.4. $C_{24}H_{20}Mo_2O_4$ requires C, 51.8; H, 3.6%); ν_{CO}(CH_2Cl_2) 1948m, 1914s, 1868m and 1822w cm^{-1}. NMR data ($CDCl_3$) for **17a**; ^1H, δ 7.94–7.15 (m, 5 H, Ph), 5.26 (s, 5 H, C_5H_5), 4.73 (s, 5 H, C_5H_5), 3.99 [d, 1 H, CH_2, *J*(HH) 3.3], 2.75 [d, 1 H, CH_2, *J*(HH) 3.3 Hz] and 2.23 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 244.3, 235.4, 234.1, 232.2 (CO), 197.0 [CH_2CC(Ph)Me], 148.6, 128.0, 126.3, 125.5 (Ph), 95.1 (C_5H_5), 92.6 (C_5H_5), 73.3 [*C*(Ph)Me], 37.1 [CH_2CC(Ph)Me] and 31.7 (Me). NMR data ($CDCl_3$) for **17b**: ^1H, δ 7.94–7.15 (m, 5 H, Ph), 5.05 (s, 5 H, C_5H_5), 4.51 (s, 5 H, C_5H_5), 3.64 [d, 1 H, CH_2, *J*(HH) 3.4], 2.48 [d, 1 H, CH_2, *J*(HH) 3.4 Hz] and 2.42 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 245.2, 239.9, 237.0, 232.1 (CO), 204.8 [CH_2CC(Ph)Me], 146.6, 131.5, 127.7, 126.4 (Ph), 94.6 (C_5H_5), 92.4 (C_5H_5), 66.0 [*C*(Ph)Me], 39.9 (Me) and 33.4 [CH_2CC(Ph)Me].

Structure Determination of Complex **13**.—*Crystal data*. $C_{23}H_{19}F_3Mo_2O_6S$, $M = 672.25$, orthorhombic, space group *Pbca*, $a = 20.665(4)$, $b = 20.274(4)$, $c = 11.446(2)$ Å, $U = 4795.44$ Å^3, $F(000) = 2656$, μ(Mo-Kα) = 10.70 cm^{-1}, $Z = 8$, $D_c = 1.86$ g cm^{-3}.

Data collection. Data were collected in the range θ 3–25°, with a scan width of 0.70° using the technique described previously.[25] Equivalent reflections were merged to give 1757 data with $I/\sigma(I) > 3.0$.

Structure solution and refinement.[26] The coordinates of both metal atoms were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms located from subsequent Fourier-difference synthesis. The phenyl hydrogen atoms were included in geometrically idealised positions and constrained to 'ride' on the relevant carbon atoms with common group isotropic thermal parameters fixed at 0.08 Å^2. Some disorder of both cyclopentadienyl rings was evident, making location of these ligand hydrogens impossible. The allylic hydrogens attached to carbon atoms C(1) and C(3) were not located. Detailed Fourier maps of the counter ion $CF_3SO_3^-$ revealed rotational disorder, which accounts for the somewhat large anisotropic thermal parameters of these atoms. The metal atoms, three carbonyl ligands, C(1), C(2) and C(3) of the allyl fragment, and all eight atoms of the counter ion CF_3SO_3 were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement which converged at *R* 0.0619 and *R′* 0.0582 with weights of $w = 1/\sigma(F_o)^2$ assigned to the individual reflections.

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

EHMO Calculations.—All EHMO calculations employed the program system developed by Mealli and Proserpio.[27] The structure of the model complex **1** employed the crystallographically determined coordinates of the substituted vinylidene species $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Ph)(CH_2)_4OMe\}(CO)_4(\eta\text{-}C_5H_5)_2]$ with the vinylidene β-carbon substituents replaced by hydrogens. All C–H distances were idealised to 1.10 Å. The calculations were carried out on an IBM compatible 486 DX2-66 personal computer using the atomic parameters supplied. Careful examination of the charge distribution and orbital populations revealed no anomalous effects from so-called counter-intuitive orbital mixing.[28]

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