Reactions of Co-ordinated Ligands. Part 53.[1] Synthesis of Dimolybdenum and Ditungsten μ-σ,η^2-(4e)-Vinylidene and -Allenylidene Complexes; Crystal Structures of $[N(PPh_3)_2][Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta^5\text{-}C_9H_7)_2]$, $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}C(Ph)(CH_2)_4OMe\}(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ ‡

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Addition of RC≡CLi to $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ affords the anionic 1:1 adducts $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2R\}(CO)_4(\eta\text{-}C_5H_5)_2]$, the structure of the analogous η^5-indenyl analogue being confirmed by a single-crystal X-ray diffraction study with the relatively stable complex $[N(PPh_3)_2][Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta^5\text{-}C_9H_7)_2]$. The same anionic species are also formed on deprotonation ($LiBu^t$) of the transversally bridged alkyne complexes $[Mo_2(\mu\text{-}RC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$. Variable-temperature NMR studies suggest that the μ-acetylide ligand in these anions readily switches from one metal centre to the other. Protonation of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ affords a relatively unstable 'side-on' bonded vinylidene $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}CHPh\}(CO)_4(\eta\text{-}C_5H_5)_2]$, which in solution at room temperature rearranges into $[Mo_2(\mu\text{-}PhC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$. Reaction of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ with $MeOSO_2CF_3$ in tetrahydrofuran (thf) affords *via* ring opening of the thf, the crystallographically identified stable complex $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}C(Ph)(CH_2)_4OMe\}(CO)_4(\eta\text{-}C_5H_5)_2]$. This is the first structurally characterised 'side-on' bonded vinylidene. The vinylidene fragment donates four electrons to the dimolybdenum centre with Mo(1)–C(1) 1.909(5), Mo(2)–C(1) 2.179(5) and Mo(2)–C(2) 2.443(6) Å. The corresponding alkylation reaction in dichloromethane affords $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$, and in this way a wide range of 'side-on' bonded vinylidene complexes were synthesised, extension of the synthetic procedure affording the corresponding ditungsten systems. Variable-temperature NMR studies show that in solution some of these complexes exhibit interesting dynamic behaviour and these observations are discussed. In solution the compound $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ undergoes an unusual thermal rearrangement into $[Mo_2\{\mu\text{-}\sigma:\eta^3\text{-}CHC(Ph)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$, and it is shown that a variety of β-substituted vinylidenes undergo analogous rearrangement reactions to form μ-allylidene complexes. Protonation of the adduct $Li[Mo\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2C(Me){=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ formed between $CH_2{=}C(Me)C{\equiv}CLi$ and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ affords the first 'side-on' bonded allenylidene $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$, which was structurally characterised by X-ray crystallography. The molecule contains an asymmetrically bridged allenylidene, the first such molecule to be structurally identified. The Mo(1)–C(1) distance of 1.912(3) Å indicates the presence of a Mo=C double bond.

There is considerable interest in the reaction chemistry of molecules containing an organic moiety bridging two metal centres. This interest has been stimulated by the belief that such studies could lead to the discovery of organic transformations, which are unique to dinuclear systems. With the aim of developing new synthetic strategies for the formation of such species we focused on the known[2] reactivity of the unsaturated dinuclear complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ towards a range of donor ligands. This dinuclear molecule reacts with carbon monoxide or cyanide anion to form adducts by making use of vacant low-lying σ and π acceptor orbitals,[3] and we reasoned that acetylide anions, delivered by RC≡CLi, should react with the molecules $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ or $[M_2(CO)_4(\eta^5\text{-}C_9H_7)_2]$ (M = Mo or W) to form anionic 1:1 adducts, which could then be treated with electrophiles. This paper describes details of our work[4,5] which has led to the synthesis and structural characterisation of 'side-on' bonded dinuclear vinylidene and allenylidene complexes.

Results and Discussion

Treatment of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with a molar equivalent of PhC≡CLi in tetrahydrofuran (thf) at −78 °C led to a rapid change in colour (purple to red) and formation of a reactive, moisture-sensitive, anionic species isolable as the dark red

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‡ Bis(triphenylphosphoranylidene)ammonium μ-1(η^2)-phenylethynyl-2κC^1-bis[dicarbonyl(η^5-indenyl)molybdenum] (*Mo–Mo*), μ-1(η^2)-4-methoxybutyl(phenyl)vinylidene-2κC^1-bis[dicarbonyl(η-cyclopentadienyl)molybdenum] (*Mo–Mo*) and μ-1(1,2-η)-3-methylbuta-1,2-dienylidene-2κC^1-bis[dicarbonyl(η-cyclopentadienyl)molybdenum] (*Mo–Mo*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

moderately air-stable crystalline salt $[N(PPh_3)_2][Mo_2(\mu\text{-}\sigma{:}\eta^2\text{-}C_2Ph)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1**. Interestingly, the same anionic species is also formed by deprotonation (LiBu^t, thf, −78 °C) of the transversally bridged alkyne complex $[Mo_2(\mu\text{-}PhC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$. Attempts to obtain crystals of **1** suitable for X-ray crystallography were unsuccessful, however crystals of the indenyl analogue **2** were readily obtained by layer diffusion and found to diffract satisfactorily. This led to the establishment of the molecular geometry of the anion shown in Fig. 1, selected bond lengths and interbond angles being listed in Table 1.

The X-ray structure confirmed that a 1:1 adduct had indeed been formed between the unsaturated molecule $[Mo_2(CO)_4(\eta^5\text{-}C_9H_7)_2]$ and the acetylide anion $PhC{\equiv}C^-$. The acetylide ligand adopts a μ-η^2 bonding mode and bridges two molybdenum atoms whose separation [3.102(2) Å] is consistent with the presence of a Mo–Mo single bond.[6] Each molybdenum carries two terminal carbonyl ligands and an η^5-indenyl ligand. Both indenyl ligands show some degree of distortion from η^5 to η^3 co-ordination. A convenient measurement of this distortion is Δ, the 'slip' parameter of the metal across the bonded face.[7] In complex **2** the slip is more marked in the case of the indenyl ligand bonded to Mo(2) (Δ = 0.29 Å) compared with Mo(1) (Δ = 0.05 Å). This can be understood in terms of the difference between the σ and π interactions of the acetylide ligand with the molybdenum centres. Since the indenyl co-ordinated to Mo(1) is less slipped this suggests that the σ interaction is comparable to the *trans* influence of the terminal carbonyls, *i.e.* the σ interaction is greater than the π interactions. Regarding the geometry of the μ-η^2 bonded acetylide ligand the Mo(1)–C(1)–C(2) angle is 158.7(4)°, which is within the range (158–162°) previously[8] observed for acetylides bound in a similar manner. The short Mo(1)–C(1) bond [2.018(4) Å] implies some delocalisation of the negative charge centred on Mo(1), and is within the range (1.83–2.06 Å) observed[9] for molybdenum to carbon double bonds suggesting a contribution from canonical form **II** (as well as **I**) to the electronic structure of **2**. Canonical form **II** is likely to be efficiently stabilised by the phenyl substituent at C(2), whose orientation, close (11.9°) to coplanar with the Mo(2)C(1)C(2) plane, allows delocalisation of the partial charge on C(2).

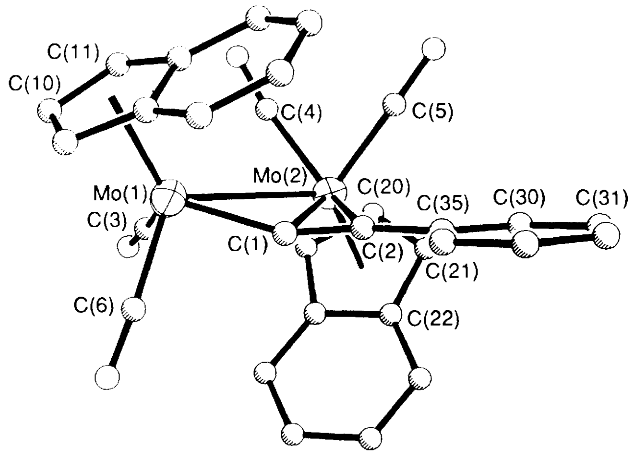
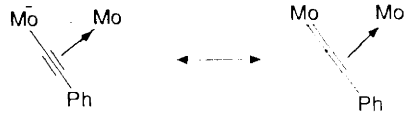
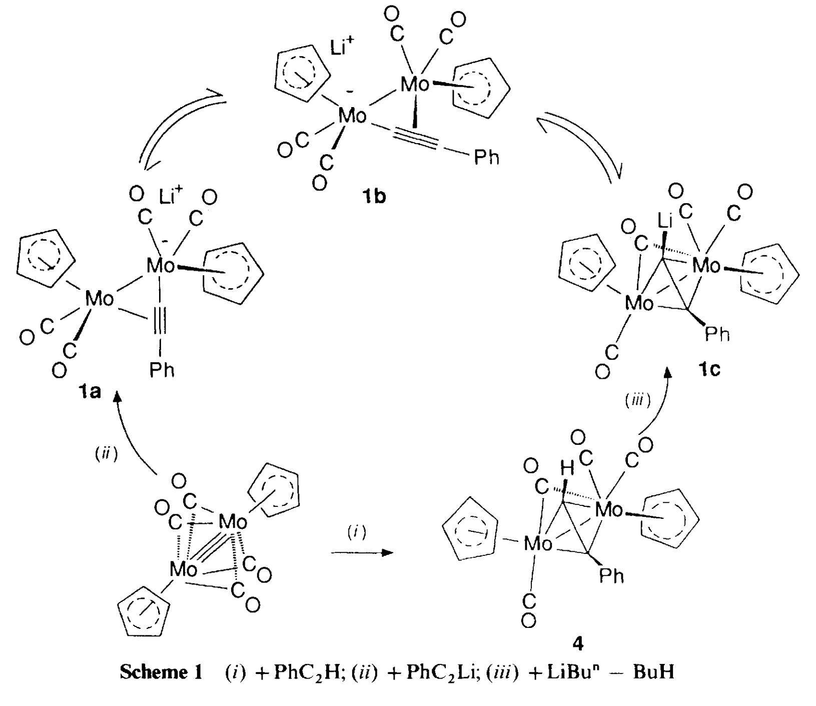


Fig. 1 Molecular structure of compound **2** showing the labelling scheme; all hydrogen atoms have been omitted for clarity



I **II**

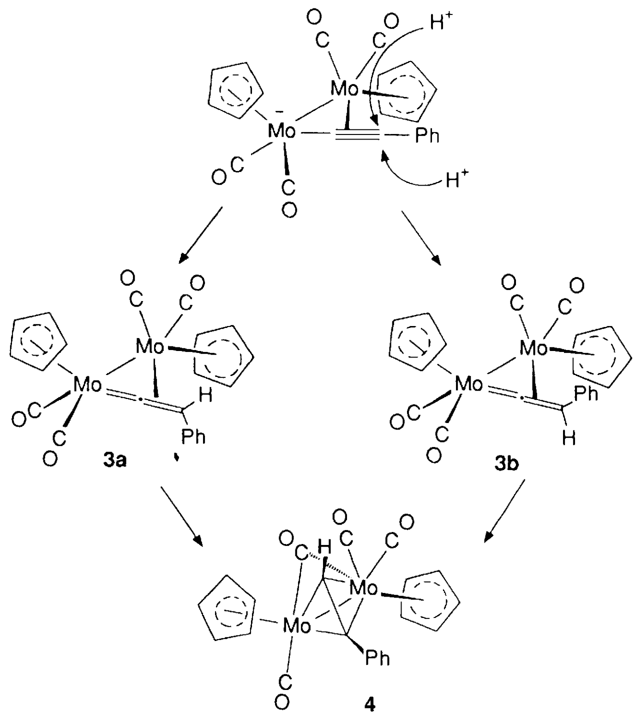
The $N(PPh_3)_2{}^+$ salts are sufficiently stable to be studied by NMR spectroscopy and at ambient temperatures compound **1** has a very simple ^1H spectrum, showing a phenyl region dominated by the counter ion and a single cyclopentadienyl resonance at δ 5.08, which integrates as ten hydrogens. This is clearly inconsistent with the solid-state structure, established for **2** and suggests that the molecule is fluxional in solution at room temperature. In agreement the ^1H NMR spectrum at −60 °C shows two singlets at δ 5.17 and 5.15. Upon warming these signals coalesced to a singlet, and from the NMR data $\Delta G^*_{T_c}$ was calculated at 51 ± 2 kJ mol^{-1}. At −60 °C the $^{13}C\text{-}\{^1H\}$ NMR spectrum showed four terminal carbonyl resonances and two cyclopentadienyl signals. In addition signals were also observed at δ 182.6 and 100.3 which can be assigned to C_α and C_β of the acetylide respectively. Upon warming, the four carbonyl resonances (δ 248.4, 247.2, 244.4, 242.8) coalesced to two (230.8, 229.6) and the two (δ 91.8, 90.6) cyclopentadienyl signals coalesced to a singlet (91.9) as expected. The marked temperature effect on the chemical shifts of the terminal carbonyls is interesting and suggests that at ambient temperature one is not simply seeing a time-averaging spectrum



Scheme 1 (*i*) $+PhC_2H$; (*ii*) $+PhC_2Li$; (*iii*) $+LiBu^n - BuH$

Table 1 Selected bond lengths (Å) and angles (°) for compound **2**

Mo(1)–Mo(2)	3.102(2)	Mo(1)–C(1)	2.018(4)	C(5)–O(5)	1.168(7)	C(6)–O(6)	1.166(8)
Mo(2)–C(1)	2.234(4)	Mo(2)–C(2)	2.281(4)	N–P(1)	1.577(3)	N–P(2)	1.581(4)
C(1)–C(2)	1.258(6)	Mo(1)–C(3)	1.911(6)	C(100)–C(101)	1.382(7)	C(101)–C(102)	1.364(10)
Mo(2)–C(4)	1.920(4)	Mo(2)–C(5)	1.909(6)	C(102)–C(103)	1.365(8)	C(103)–C(104)	1.381(7)
Mo(1)–C(6)	1.926(6)	Mo(1)–C(10)	2.382(6)	P(1)–C(105)	1.793(4)	C(100)–C(105)	1.385(6)
Mo(1)–C(11)	2.349(6)	C(10)–C(11)	1.403(9)	C(104)–C(105)	1.392(8)	C(110)–C(111)	1.379(7)
Mo(1)–C(12)	2.415(7)	C(11)–C(12)	1.423(9)	C(111)–C(112)	1.374(8)	C(112)–C(113)	1.374(7)
C(12)–C(13)	1.402(10)	C(13)–C(14)	1.341(12)	C(113)–C(114)	1.385(7)	P(1)–C(115)	1.801(5)
C(14)–C(15)	1.440(13)	C(15)–C(16)	1.319(15)	C(110)–C(115)	1.393(5)	C(114)–C(115)	1.396(7)
Mo(1)–C(17)	2.414(8)	C(12)–C(17)	1.452(8)	C(120)–C(121)	1.380(6)	C(121)–C(122)	1.375(6)
C(16)–C(17)	1.412(11)	Mo(1)–C(18)	2.370(7)	C(122)–C(123)	1.363(6)	C(123)–C(124)	1.379(6)
C(10)–C(18)	1.384(10)	C(17)–C(18)	1.401(10)	P(1)–C(125)	1.802(4)	C(120)–C(125)	1.381(5)
Mo(2)–C(20)	2.288(6)	Mo(2)–C(21)	2.355(5)	C(124)–C(125)	1.390(5)	C(200)–C(201)	1.386(6)
C(20)–C(21)	1.407(6)	Mo(2)–C(22)	2.544(5)	C(201)–C(202)	1.364(9)	C(202)–C(203)	1.372(8)
C(21)–C(22)	1.431(7)	C(22)–C(23)	1.406(7)	C(203)–C(204)	1.379(6)	P(2)–C(205)	1.804(4)
C(23)–C(24)	1.365(9)	C(24)–C(25)	1.410(8)	C(200)–C(205)	1.389(6)	C(204)–C(205)	1.378(8)
C(25)–C(26)	1.360(7)	Mo(2)–C(27)	2.519(6)	C(210)–C(211)	1.389(7)	C(211)–C(212)	1.349(8)
C(22)–C(27)	1.427(6)	C(26)–C(27)	1.413(7)	C(212)–C(213)	1.381(8)	C(213)–C(214)	1.368(7)
Mo(2)–C(28)	2.307(6)	C(20)–C(28)	1.393(7)	P(2)–C(215)	1.800(4)	C(210)–C(215)	1.376(7)
C(27)–C(28)	1.449(6)	C(30)–C(31)	1.390(7)	C(214)–C(215)	1.383(7)	C(220)–C(221)	1.388(10)
C(31)–C(32)	1.365(8)	C(32)–C(33)	1.354(9)	C(221)–C(222)	1.355(12)	C(222)–C(223)	1.351(10)
C(33)–C(34)	1.372(7)	C(2)–C(35)	1.450(6)	C(223)–C(224)	1.395(11)	P(2)–C(225)	1.798(6)
C(30)–C(35)	1.384(6)	C(34)–C(35)	1.393(7)	C(220)–C(225)	1.387(6)	C(224)–C(225)	1.385(8)
C(3)–O(3)	1.179(8)	C(4)–O(4)	1.177(6)				
Mo(2)–Mo(1)–C(1)	46.0(1)	Mo(2)–Mo(1)–C(3)	76.7(2)	Mo(2)–C(1)–C(2)	75.9(3)	Mo(2)–C(2)–C(1)	71.8(3)
C(1)–Mo(1)–C(3)	110.9(2)	Mo(2)–Mo(1)–C(6)	110.6(2)	Mo(2)–C(2)–C(35)	136.2(3)	C(1)–C(2)–C(35)	151.8(4)
C(1)–Mo(1)–C(6)	88.1(2)	C(3)–Mo(1)–C(6)	78.4(3)	Mo(1)–C(3)–O(3)	175.8(4)	Mo(2)–C(4)–O(4)	172.0(4)
Mo(1)–C(1)–Mo(2)	93.5(1)	Mo(1)–C(1)–C(2)	158.7(4)	Mo(2)–C(5)–O(5)	176.0(4)	Mo(1)–C(6)–O(6)	176.4(5)

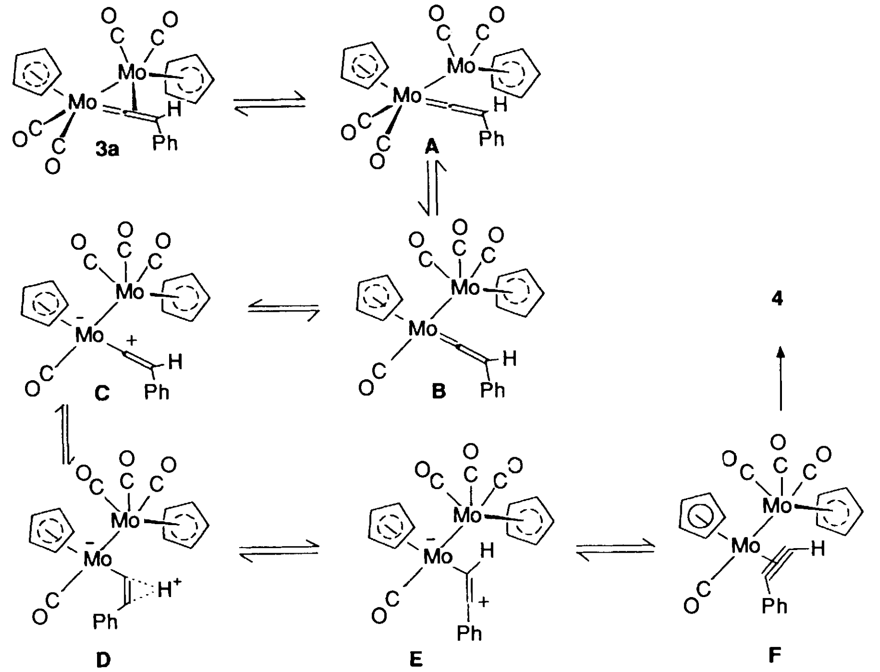


Scheme 2

of **1a** and **1b** (Scheme 1), but that there is a third species present in solution which could be the transversally bridged lithium complex **1c**. This is consistent with the fact that as mentioned earlier the same Mo_2 μ-acetylide anion is also formed on deprotonation of the corresponding Mo_2 μ-alkyne complex, and it is suggested that in the case of the phenyl-substituted system, **1c** (Scheme 1) is thermodynamically less stable than **1a**/**1b**.

In order to begin to explore the reactivity of electrophiles towards these Mo_2 μ-acetylide anionic species the reaction of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ with proton sources was examined. From a practical standpoint this was most readily achieved by passing a dichloromethane solution of the anion through a pad of alumina. This gave a dark blue solution, which on low-temperature crystallisation afforded a high yield of the dark blue crystalline complex **3**. This was thermally unstable rearranging in solution at room temperature (10 h) to the red μ-alkyne complex $[Mo_2(\mu\text{-}PhC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$ **4**. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of **3** measured at −60 °C exhibited resonances consistent with a 'side-on' bonded μ-σ:η^2-(4e)-vinylidene. The ^1H spectrum showed inequivalent cyclopentadienyl resonances at δ 4.93 and 4.62, a singlet hydrogen at δ 5.08, together with a phenyl multiplet. The $^{13}C\text{-}\{^1H\}$ spectrum showed four carbonyl resonances at δ 243.8, 235.8, 233.5 and 226.3, two inequivalent cyclopentadienyl ligands at δ 95.7 and 92.0, and a CH resonance at δ 66.1. There was also a quaternary carbon at δ 333.2, an extremely high-frequency chemical shift consistent with the presence of a metal–carbon multiple bond. Thus, the NMR data for **3** suggest that protonation takes place at the β-carbon, and results in the selective formation of a μ-σ:η^2-(4e)-vinylidene complex (either **3a** or **3b**, see below), which then slowly rearranges at room temperature to the Mo_2 μ-alkyne complex **4** shown in Scheme 2. It is interesting that UV irradiation of $[Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ in the presence of ethyne has been reported[10] to form a 1:1 adduct, which has also to be formulated as a 'side-on' bonded vinylidene $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}CH_2\}(CO)_4(\eta\text{-}C_5Me_5)_2]$. Similarly as in the case of **3**, the vinylidene α-carbon is reported to resonate at low field at δ 337.3, and the β-carbon at δ 45.3. As with complex **3** these shifts are very different from those expected for a symmetrically bridged μ-σ:σ-(2e)-vinylidene, where C_α would resonate in the range δ 280–240 and C_β at *ca.* δ 125. Like **3** the complex $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}CH_2\}(\eta\text{-}C_5Me_5)_2]$ is reported to rearrange to a μ-alkyne complex.

These rearrangement reactions of a 'side-on' bonded vinylidene into a μ-alkyne complex, *e.g.* **3** ⟶ **4**, are most unusual, and involve an apparent 1,2-hydrogen shift from the β-to the α-carbon. They are especially interesting because the reverse reaction, that is co-ordinated RC_2H into CCHR, is known in mono-,[11,12] di-[13] and tri-nuclear[14] chemistry. When



Scheme 3

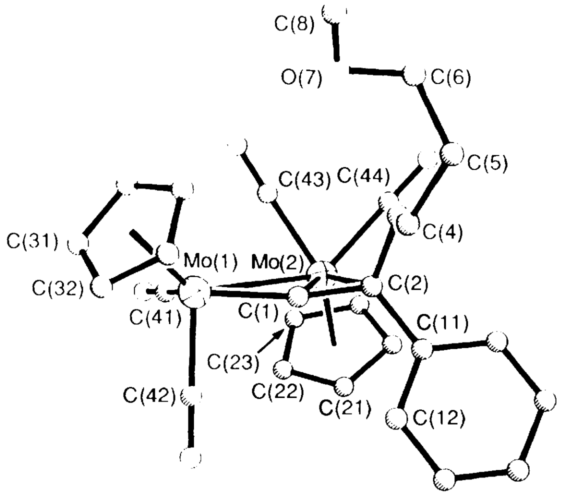


Fig. 2 Molecular structure of compound **5** showing the labelling scheme; all hydrogen atoms have been omitted for clarity

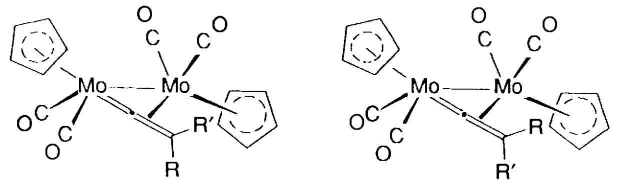
Table 2 Selected bond lengths (Å) and angles (°) for compound **5**

Mo(2)–Mo(1)	3.120(1)	Mo(2)–C(1)	2.179(5)
Mo(1)–C(1)	1.909(5)	Mo(2)–C(2)	2.443(6)
C(1)–C(2)	1.380(7)	C(2)–C(3)	1.529(7)
Mo(1)–C(41)	2.001(6)	Mo(1)–C(42)	1.968(6)
Mo(2)–C(43)	1.962(6)	Mo(2)–C(44)	1.948(5)
C(2)–C(11)	1.499(7)	C(11)–C(12)	1.394(8)
C(12)–C(13)	1.390(10)	C(13)–C(14)	1.349(10)
C(14)–C(15)	1.393(11)	C(11)–C(16)	1.395(7)
C(15)–C(16)	1.399(9)	Mo(2)–C(21)	2.391(6)
Mo(2)–C(22)	2.410(5)	C(21)–C(22)	1.391(9)
Mo(2)–C(23)	2.353(6)	C(22)–C(23)	1.400(10)
Mo(2)–C(24)	2.326(6)	C(23)–C(24)	1.390(8)
Mo(2)–C(25)	2.327(5)	C(21)–C(25)	1.409(8)
C(24)–C(25)	1.412(10)	Mo(1)–C(31)	2.369(6)
Mo(1)–C(32)	2.349(6)	C(31)–C(32)	1.382(11)
Mo(1)–C(33)	2.364(6)	C(32)–C(33)	1.386(9)
Mo(1)–C(34)	2.343(6)	C(33)–C(34)	1.398(10)
Mo(1)–C(35)	2.357(7)	C(31)–C(35)	1.400(10)
C(34)–C(35)	1.405(10)	C(3)–C(4)	1.529(9)
C(4)–C(5)	1.515(9)	C(5)–C(6)	1.480(11)
C(6)–O(7)	1.385(10)	O(7)–C(8)	1.307(15)
C(41)–O(41)	1.144(8)	C(42)–O(42)	1.152(8)
C(43)–O(43)	1.151(7)	C(44)–O(44)	1.159(7)
Mo(1)–Mo(2)–C(1)	37.1(1)	Mo(1)–Mo(2)–C(2)	70.9(1)
C(1)–Mo(2)–C(2)	34.1(2)	Mo(1)–Mo(2)–C(43)	75.5(2)
C(1)–Mo(2)–C(43)	98.9(2)	C(2)–Mo(2)–C(43)	112.6(2)
Mo(1)–Mo(2)–C(44)	123.9(1)	C(1)–Mo(2)–C(44)	103.7(2)
C(2)–Mo(2)–C(44)	77.1(2)	C(43)–Mo(2)–C(44)	76.1(2)
Mo(2)–C(1)–Mo(1)	99.3(2)	Mo(2)–C(1)–C(2)	83.5(3)
Mo(1)–C(1)–C(2)	168.5(4)	Mo(2)–C(2)–C(1)	62.4(3)
Mo(2)–C(2)–C(3)	118.4(4)	C(1)–C(2)–C(3)	117.6(4)
Mo(2)–C(2)–C(11)	113.1(3)	C(1)–C(2)–C(11)	120.4(4)
C(3)–C(2)–C(11)	114.8(4)	C(2)–C(3)–C(4)	112.6(5)
Mo(1)–C(41)–O(42)	173.3(4)	Mo(1)–C(42)–O(42)	178.4(6)
Mo(2)–C(43)–O(43)	176.3(5)	Mo(2)–C(44)–O(44)	176.5(5)

the rearrangement of **3** into **4** was followed by ^{1}H NMR spectroscopy in C_6D_6 there was no evidence for intermediate species.

If it is assumed that the rearrangement of compound **3** into **4** is thermodynamically driven then invoking the principle of microscopic reversibility the insights gained by Silvestre and Hoffmann (SH) in their analysis[15] of the alkyne to vinylidene rearrangement at a mononuclear centre can be extended to explain this rearrangement. As shown in Scheme 3 an initial switch in the bonding mode of the vinylidene ligand from μ-σ:η^2-(4e)- to σ-(2e), *i.e.* $\mathbf{3} \rightleftharpoons \mathbf{A}$, allows access *via* CO transfer to the co-ordinatively unsaturated species **B**. Then by the series of steps $\mathbf{B} \rightleftharpoons \mathbf{C} \rightleftharpoons \mathbf{D} \rightleftharpoons \mathbf{E} \rightleftharpoons \mathbf{F}$ which model those discussed by SH for reactions at a mononuclear centre, **3** can be transformed into **4**. In this reaction sequence the second metal centre serves as a temporary home for one of the carbonyl ligands.

Since the protonation reaction indicated that the β-carbon of the anionic μ-σ:η^2-(3e)-acetylide complex **1** was nucleophilic, the reactivity towards methyl trifluoromethanesulphonate was next investigated, in the expectation that β-methylation would occur. Initially, this methylation was carried out in tetrahydrofuran, the solvent in which the salt Li[Mo$_2${μ-σ:η^2-(3e)-C$_2$Ph}(CO)$_4$(η-C$_5$H$_5$)$_2$] was formed. On warming from −78 °C the initial red colour of the reaction mixture changed to dark blue, and on chromatographic work-up dark blue crystals of [Mo$_2${μ-σ:η^2-C=C(Ph)(CH$_2$)$_4$OMe}(CO)$_4$(η-C$_5$H$_5$)$_2$] **5**



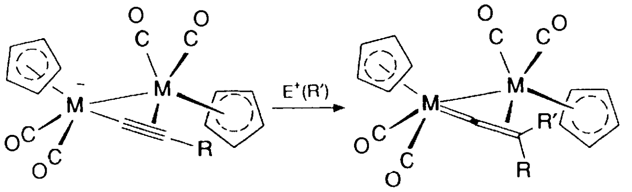
Scheme 4

were obtained in moderate (60%) yield. However, examination of the mass spectrum, elemental analysis, and subsequently the NMR spectra indicated a molecule of thf had become incorporated into the vinylidene complex. To investigate the structure of **5** further a single-crystal X-ray diffraction study was undertaken. The geometry of **5** is shown in Fig. 2, selected bond lengths and angles in Table 2.

This structure established for the first time a detailed structural characterisation of a μ-σ:η^2-(4e)-vinylidene ligand, in which the ligand adopts an asymmetric, 'side-on' coordination geometry. Thus, in **5** a Mo–Mo single bond [Mo(1)–Mo(2) 3.120(1) Å] is asymmetrically bridged by a vinylidene, which carries at the β-carbon phenyl and $(CH_2)_4OMe$ substituents, the latter derived from 'methylated' thf. The vinylidene ligand donates four electrons to the dimolybdenum centre, and may be regarded as binding to Mo(1) by a Mo=C double bond [Mo(1)–C(1) 1.909(5) Å] and to Mo(2) *via* interaction with the C=C double bond [Mo(2)–C(1) 2.179(5), Mo(2)–C(2) 2.443(6), C(1)–C(2) 1.380(7) Å]. The η^5-C_5H_5 ligands of **5** are mutually *trans* to one another, a feature carried through from the structure of the μ-acetylide anionic complex. The phenyl substituent is projected over the cyclopentadienyl ligand of Mo(2). In addition Fig. 2 further shows the non-planarity of the Mo(1), Mo(2), C(1), C(2) system [the C–C bond lies 11.3° out of the Mo(1), Mo(2), C(1) plane]. The Mo(1)–C(1)–C(2) bond angle is 168.5(4)°. Further discussion of the geometries of **2** and **5** is deferred for the moment.

An important point about these μ-σ:η^2-(4e)-vinylidenes **3** and **5** formed by either protonation or alkylation of the anionic species $Li[Mo_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ is that only one of a possible two diastereoisomers is generated (Scheme 4), and as noted from the crystal structure of **5**, that isomer is the one in which the R group of the acetylide is projected over the cyclopentadienyl ligand of the π-coordinated molybdenum. The implication, then, is that there is a preferred orientation of electrophilic attack by H^+ or the oxonium salt formed by O-methylation of thf upon the β-carbon of the μ-acetylide, namely *trans* to the C_5H_5 ligand. Also of interest is that when $R \neq R^1$ (Scheme 4) the β-carbon of the μ-σ:η^2-vinylidene is chiral.

With the realisation that methyl triflate could not be used in thf to methylate Mo_2(μ-acetylide) anions, because of the problem of thf ring opening, the solvent for the alkylation step was changed to dichloromethane. In this solvent good yields of the blue crystalline μ-σ:η^2-(4e)-vinylidenes **6**–**11** (Scheme 5) were obtained, and were characterised by elemental analysis, mass spectrometry, IR and NMR spectroscopy. The simple dihydro complex **12** was also synthesised by protonation of $Li[Mo_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-(3e)-}C_2H\}(CO)_4(\eta\text{-}C_5H_5)_2]$. Representative examples of the corresponding ditungsten complexes were prepared by a simple extension of these procedures. Thus, reaction of $[W_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with PhC≡CLi in thf at −78 °C gave a deep green solution,† which on warming underwent an irreversible colour change to red. Protonation of either the green or the red solution with CF_3CO_2H gave blue **13**



	M	R	R^1
5	Mo	Ph	$(CH_2)_4OMe$
6	Mo	Ph	Me
7	Mo	Me	Me
8	Mo	Pr^i	Me
9	Mo	Bu^t	Me
10	Mo	Ph	Et
11	Mo	Ph	C_3H_5
12	Mo	H	H
13	W	Ph	H
14	W	Ph	Me
15	W	Me	Me

Scheme 5

together with a small amount of the isomeric red μ-alkyne complex. Methylation of $Li[W_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-(3e)-}C_2R\}(CO)_4(\eta\text{-}C_5H_5)]$ (R = Me or Ph) with methyl triflate in CH_2Cl_2 gave **14** and **15**. In contrast with the corresponding Mo_2 reactions, significant amounts of the μ-alkyne complexes $[W_2(\mu\text{-}MeC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$ were also formed. In the reactions, which afforded **6**, **8**–**11**, **13** and **14**, there was no evidence for the formation of more than one diastereoisomer.

Examination of the variable-temperature solution NMR spectra of these complexes revealed interesting dynamic behaviour. For example, the ground-state structure of the dimethyl-substituted vinylidene **7** has two methyl and two η-C_5H_5 environments. However, at ambient temperature the 400 MHz ^1H NMR spectrum shows single broad cyclopentadienyl and methyl resonates at δ 5.45 and 1.70 respectively, which are resolved at −60 °C into two sharp cyclopentadienyl signals at δ 5.55 and 5.40 and two sharp methyl resonances at δ 1.73 and 1.67 in agreement with the illustrated structure. The ^{13}C-$\{^1H\}$ NMR spectrum measured at −60 °C is as expected with the μ-vinylidene α-carbon at δ 342.9, the β-carbon at δ 79.8, four carbonyl resonances at δ 243.6, 237.0, 236.6 and 226.1, two cyclopentadienyl signals at δ 96.1 and 92.8 and two inequivalent methyl groups which resonate at δ 28.7 and 27.9. Thus, **7** undergoes an exchange process in solution, which renders both the cyclopentadienyl and methyl groups equivalent, the calculated $\Delta G^*_{T_c}$ values for this equilibrium being 59 ± 2 and 61 ± 2 kJ mol^{-1} respectively. The corresponding dimethyl-substituted ditungsten complex **15** showed similar behaviour with $\Delta G^*_{T_c}(C_5H_5) = 66 \pm 2$ and $\Delta G^*_{T_c}(Me) = 68 \pm 2$ kJ mol^{-1}. At ambient temperatures the isopropyl-substituted complex **8** showed NMR resonances in accord with the expected ground-state structure, the methyls of the Pr^i group showing inequivalence (δ 1.09 and 0.96) due to diastereotopic splitting caused by the chirality of **8**. On warming to 70 °C the two cyclopentadienyl resonances coalesced with $\Delta G^*_{T_c}$ = 68 ± 2 kJ mol^{-1}, the diastereotopic Pr^i methyl groups coalesced with $\Delta G^*_{T_c}$ = 68 ± 2 kJ mol^{-1} while the signals due to the methyl substituent of the β-carbon and the Pr^i hydrogen remained unchanged. A similar fluxional process to that undergone by **8** is also observed with **9** ($\Delta G^*_{T_c}$ = 50 ± 2 kJ mol^{-1}); the η-C_5H_5 resonances coalesce to a singlet, while the methyl resonance (δ 1.60) and the Bu^t resonance (δ 0.93) remain sharp.

The implications of these observations are either (*i*) that a single synchronous process [Scheme 6(*a*)] allows inversion of chirality in compound **8** and 'flipping' of the μ-σ:η^2-vinylidene ligand or (*ii*) that there exists a high-energy rate-limiting step giving access to intermediates which collapse to either

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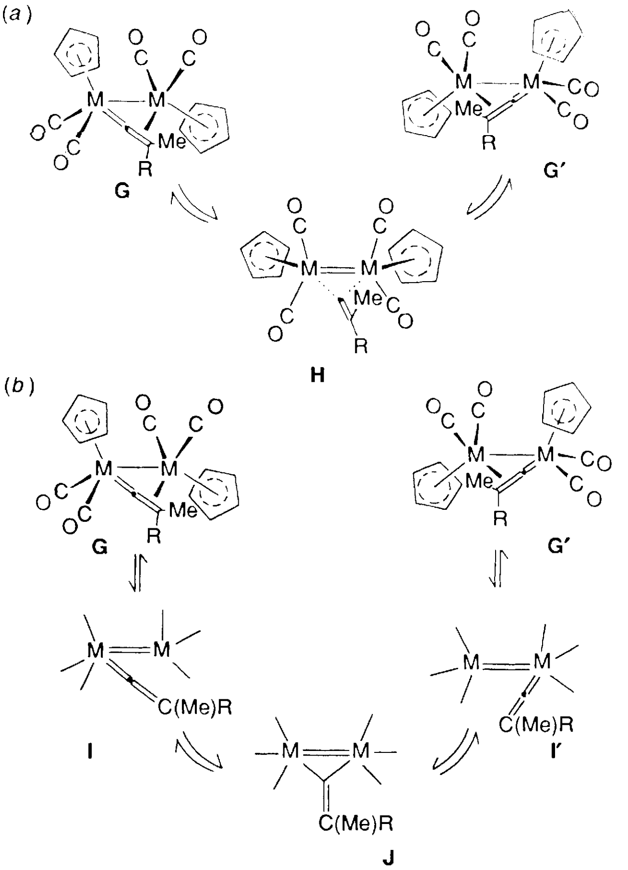
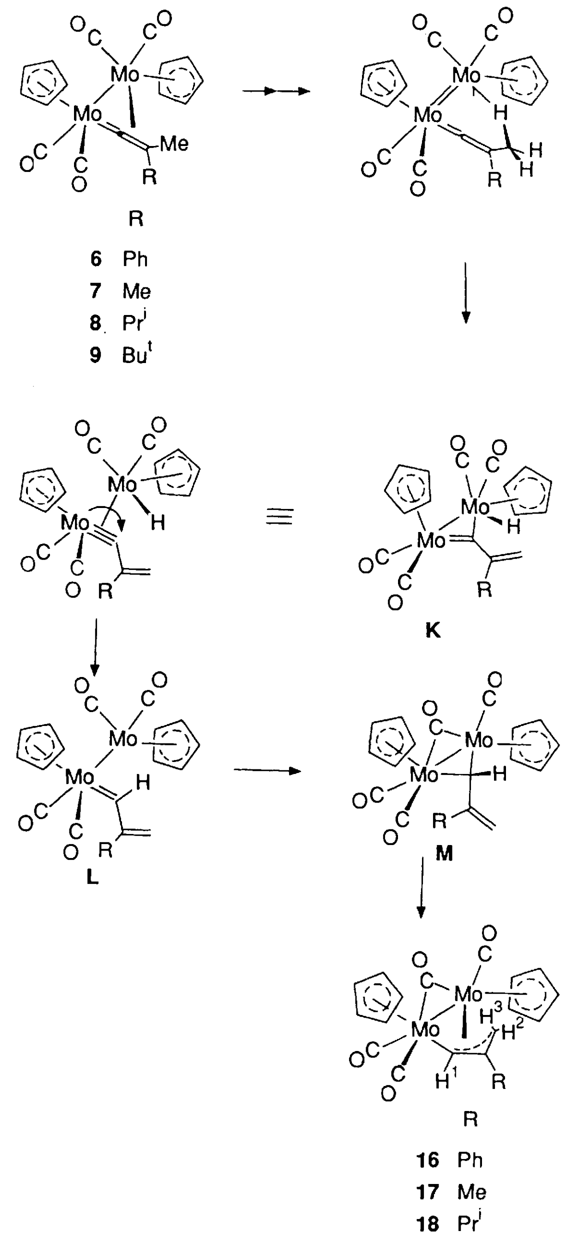
† Significantly, on cooling the red solution does not revert to green. Further experiments are needed to clarify the nature of these colour changes. The same red acetylide adduct may alternatively be prepared by deprotonating a thf solution of $[W_2(\mu\text{-}PhC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$ with LiBu^t at −78 °C. A transient green colour was not observed.



Scheme 6 H ≈ J and no implication is intended for orientations of the $M(CO)_2(\eta-C_5H_5)$ units in **I**, **I′**, **J**. Route (*b*) could be considered as an expanded form of (*a*) in that **J** might be the same as **H**

enantiomer of the thermodynamically preferred diastereoisomer [Scheme 6(*b*)]. Route (*a*) implies a symmetrical intermediate or transition state of the sort **H**, in which the change from $\mu-\sigma:\eta^2$-(4e) to $\mu-\sigma:\sigma$-(2e) bonding for the vinylidene ligand, is accompanied by rotation of the $M(CO)_2(\eta-C_5H_5)$ unit about the M–M bond. In contrast, route (*b*) allows for other intermediate species **I**, **I′** and **J** in which low-energy rearrangements such as rotation about the M=C[16] and M–M bonds provide access to either **G** or **G′** after initial cleavage of $M(2)-C_\beta$ contact. As is illustrated such a rearrangement involves a rotational movement of the vinylidene, which can in principle occur in either a clockwise or anticlockwise direction, resulting in an exchange process which simultaneously averages $\eta-C_5H_5$ environments and in the case of, for example compound **8**, inverts chirality at C(2). The $\mu-\sigma:\sigma$-(2e) bonded vinylidene species which results from this rotational process contains a metal–metal double bond either with or without bridging carbonyls (only the latter is illustrated for the sake of simplicity). In the case of the β,β′-dimethyl-substituted vinylidene complexes **7** and **15** clockwise or anticlockwise rotation affords the same $\mu-\sigma:\sigma$-(2e)-vinylidene intermediate, which can collapse to identical species with the $C=CMe_2$ fragment $\mu-\sigma:\eta^2$-(4e) bonded to either of the two $M(CO)_2(\eta-C_5H_5)$ centres, with the result that the methyl and cyclopentadienyl environments are equivalanced on the NMR time-scale. The variable-temperature ^1H NMR spectrum of **8** suggests that a similar process occurs in solution resulting in the equivalencing of the $\eta-C_5H_5$ environments and loss of the diastereotopic splitting of the isopropyl methyl groups. However, the β and β′ sites occupied by the methyl and isopropyl groups do not observably exchange, presumably because such a process would result in the formation of a higher-energy species, *i.e.* the other diastereoisomer, a species where the Pr^i group projects over the cyclopentadienyl ligand.



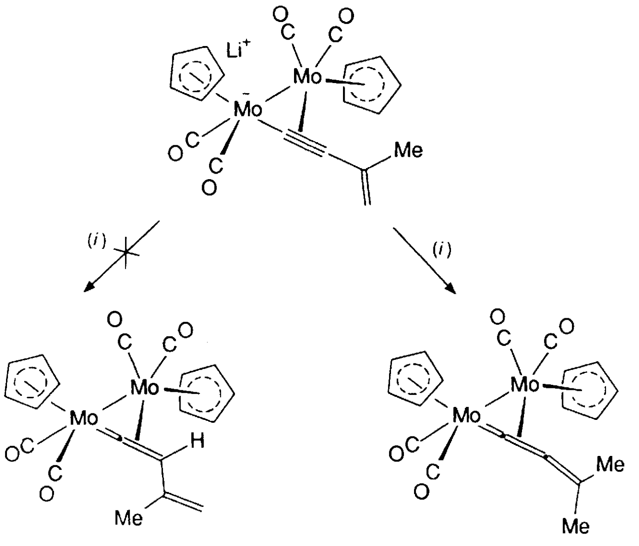
Scheme 7

Thus, these observations raise an interesting question about the stereoselectivity of the $\mu-\sigma:\eta^2$-(4e)-vinylidene-forming reactions. As mentioned earlier in this paper only one of the two possible diastereoisomers (see Scheme 4) are formed in both protonation and alkylation reactions, which might suggest that the electrophile is selectively delivered across the face where the two carbonyl ligands of the second metal centre are projected, *i.e.* selective formation of **3a** in Scheme 2. However, because of the observed dynamic behaviour of these molecules we cannot exclude the possibility that the electrophile approaches in the opposite direction, *i.e.* across the face of the $\eta-C_5H_5$ ligand, the resulting kinetic product rearranging under thermodynamic control *via* the sort of processes depicted in Scheme 6.

When an attempt was made to investigate the variable-temperature NMR spectra of compounds **6**–**9** at higher temperatures (> 80 °C) unusual isomerisation reaction occurred leading to the formation in good yield of the bright orange crystalline dimolybdenum complexes **16**–**19**. Comparison of the spectroscopic data observed for these complexes (see Experimental section) with those reported[17] for the μ-allylidene

Table 3 Selected bond lengths (Å) and angles (°) for compound **20**

Mo(1)–Mo(2)	3.145(1)	Mo(1)–C(1)	1.912(3)
Mo(1)–C(10)	2.358(3)	Mo(1)–C(11)	2.353(3)
Mo(1)–C(12)	2.349(4)	Mo(1)–C(13)	2.342(3)
Mo(1)–C(14)	2.346(3)	Mo(1)–C(30)	1.993(3)
Mo(1)–C(31)	1.975(3)	Mo(2)–C(1)	2.209(3)
Mo(2)–C(2)	2.240(3)	Mo(2)–C(20)	2.399(3)
Mo(2)–C(21)	2.402(3)	Mo(2)–C(22)	2.353(3)
Mo(2)–C(23)	2.322(3)	Mo(2)–C(24)	2.331(3)
Mo(2)–C(32)	1.949(3)	Mo(2)–C(33)	1.973(3)
C(1)–C(2)	1.336(3)	C(2)–C(3)	1.348(4)
C(3)–C(4)	1.491(4)	C(3)–C(5)	1.505(5)
C(10)–C(11)	1.406(6)	C(10)–C(14)	1.393(5)
C(11)–C(12)	1.414(5)	C(12)–C(13)	1.401(5)
C(13)–C(14)	1.407(6)	C(20)–C(21)	1.396(5)
C(20)–C(24)	1.410(4)	C(21)–C(22)	1.425(5)
C(22)–C(23)	1.399(4)	C(23)–C(24)	1.404(5)
C(30)–O(30)	1.151(4)	C(31)–O(31)	1.141(4)
C(32)–O(32)	1.146(4)	C(33)–O(33)	1.155(4)
Mo(2)–Mo(1)–C(1)	43.9(1)	Mo(2)–Mo(1)–C(30)	70.5(1)
Mo(2)–Mo(1)–C(31)	101.8(1)	C(1)–Mo(1)–C(30)	112.6(1)
C(1)–Mo(1)–C(31)	91.4(1)	C(31)–Mo(1)–C(30)	87.5(1)
Mo(1)–Mo(2)–C(1)	36.9(1)	Mo(1)–Mo(2)–C(2)	71.4(1)
Mo(1)–Mo(2)–C(32)	119.6(1)	Mo(1)–Mo(2)–C(33)	74.1(1)
C(1)–Mo(2)–C(32)	101.6(1)	C(1)–Mo(2)–C(33)	99.0(1)
C(2)–Mo(2)–C(32)	76.4(1)	C(2)–Mo(2)–C(33)	115.1(1)
C(32)–Mo(2)–C(33)	75.6(1)	Mo(1)–C(30)–O(30)	172.0(2)
Mo(1)–C(31)–O(31)	177.9(3)	Mo(2)–C(32)–O(32)	177.9(3)
Mo(2)–C(33)–O(33)	175.9(2)	Mo(1)–C(1)–C(2)	167.2(2)
Mo(2)–C(1)–C(2)	73.8(2)	Mo(2)–C(2)–C(1)	71.3(2)
Mo(2)–C(2)–C(3)	144.2(2)	C(1)–C(2)–C(3)	144.5(3)
C(2)–C(3)–C(4)	123.4(3)	C(2)–C(3)–C(5)	120.4(3)
C(5)–C(3)–C(4)	116.2(3)		



Scheme 8 (i) + H$^+$

complex [$Mo_2(\mu$-$\sigma:\eta^3$-CHCHCMe$_2$)(CO)$_4$(η-C_5H_5)$_2$] suggested that these molecules were also μ-allylidene complexes (Scheme 7); for example, in [$Mo_2(\mu$-$\sigma:\eta^3$-CH^{1}CH^{2}CMe$_2$)(CO)$_4$(η-C_5H_5)$_2$] H^1 resonates at δ 10.93 and the carbon σ-bound to the molybdenum has a ^{13}C chemical shift of δ 174.9. This compares well with the NMR data for **16** where H^1 occurs at δ 10.53 [d, ^4J(HH) 3.1], H^2 at 3.78 [dd, ^4J(HH) 3.1, ^2J(HH) 1.3 Hz] and H^3 at 0.84 [d, ^2J(HH) = 1.3 Hz]. The CH carbon resonance resonates at δ 166.5, the *C*Ph carbon at δ 110.0, and the CH$_2$ carbon at δ 59.5. The alkyl-substituted μ-allylidenes **17**–**19** show similar NMR spectra to that of **16**, a point of interest being that the isopropyl group of **18** shows diastereotopic methyl groups at δ 1.49 and 0.94. This occurs because the quaternary carbon of the μ-allylidene is chiral, as is the β-carbon of the parent μ-σ:η^2-(4e)-vinylidene **8**.

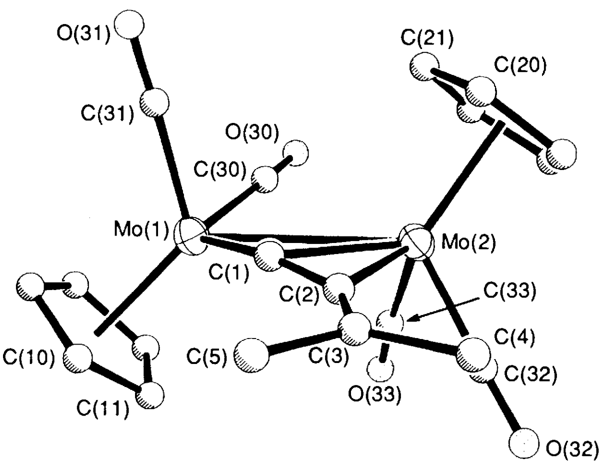
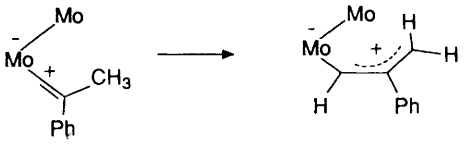


Fig. 3 Molecular structure of compound **20** showing the labelling scheme; all hydrogen atoms have been omitted for clarity

Thus, μ-σ:η^2-(4e)-vinylidenes with a β-methyl substituent undergo a smooth thermal rearrangement to a μ-allylidene, *via* a 1,3-hydrogen shift from the methyl carbon to the α-carbon. At first sight a possible mechanism for this isomerisation reaction involves a concerted 1,3-H shift to an electron-deficient α-carbon of the vinylidene moiety, in a process which relates to the rarrangement of β-hydrogen substituted μ-σ:η^2-(4e)-vinylidenes into a μ-alkyne complex (Scheme 3). This is however, most unlikely as such a process would correspond to a disallowed rearrangement of a β-methyl-substituted vinyl carbonium ion into an allylic carbonium ion. A more likely reaction pathway is shown in Scheme 7 and involves both metal centres.



If as was previously suggested (Scheme 3) a σ-(2e) bonded vinylidene species can be accessed, then as is shown in Scheme 7 the resulting co-ordinatively unsaturated molybdenum centre would be in close proximity to the β-methyl group of the vinylidene ligand. This could lead to an initial agostic Mo(μ-H)C interaction resulting in complete hydrogen transfer to the molybdenum centre and formation of the intermediate **K**. This species is essentially a complex in which a carbyne functions as a two-electron donor, and rotation of the carbyne moiety allows the carbyne carbon and hydride ligand to assume the correct orientation for C–H bond formation to occur. This process generates the vinylcarbene **L** which collapses *via* the μ-vinylcarbene **M** to the observed μ-allylidene.

Returning to the synthesis of μ-σ:η^2-(4e)-vinylidene complexes by electrophilic attack on the β position of a μ-acetylide, we also examined the protonation of the adduct formed between $CH_2{=}C(Me)C{\equiv}CLi$ and [$Mo_2(CO)_4(\eta$-$C_5H_5)_2$]. Examination of Scheme 8 shows that in this system proton attack can occur conventionally to give a β-vinyl-substituted μ-σ:η^2-(4e)-vinylidene, or alternatively on the δ position to form a dinuclear μ-σ:η^2-(4e)-allenylidene, a type of molecule that had not previously been reported. When a solution in tetrahydrofuran of the deep purple adduct was added directly to an alumina-packed column the colour changed immediately to deep green. Although an attempt to purify this material by column chromatography was not successful, fractional crystallisation allowed the separation of red [$Mo_2\{\mu$-HC$_2$C(Me)=CH$_2\}$(CO)$_4$(η-C_5H_5)$_2$] (9% yield) and a dark green crystalline material **20** in good yield (49%).

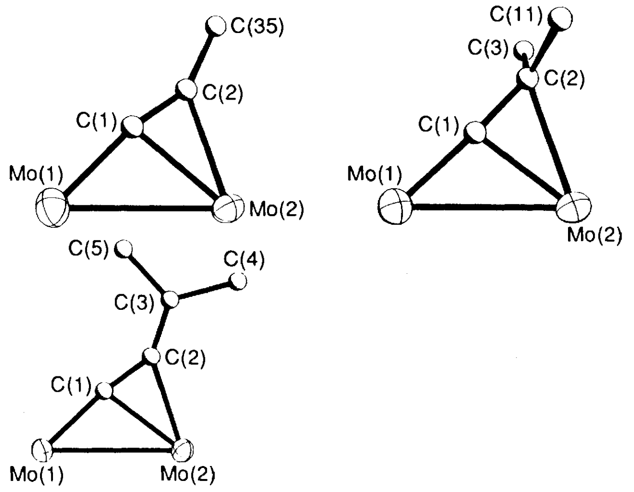
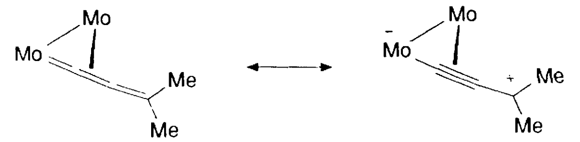


Fig. 4 The $Mo_2(\mu\text{-}C_2R_n)$ portions of compounds **2**, **5** and **20** viewed perpendicular to the $Mo_2(\mu\text{-}C)$ plane. Only the contact carbons of the R groups are shown

Elemental analysis, IR and NMR spectroscopy indicated that **20** was a μ-σ:η^2-(4e)-allenylidene complex. In particular the ^1H NMR spectrum showed the presence of two methyl groups and two inequivalent cyclopentadienyl ligands. The $^{13}C\text{-}\{^1H\}$ spectrum contained corresponding signals as well as a resonance at δ 287.7 assignable to a carbenoid carbon, *i.e.* C_α. In view of the novelty of this complex a single-crystal X-ray diffraction study was undertaken. This established the structure illustrated in Fig. 3, selected bond lengths and angles being listed in Table 3.

The dinuclear complex contains an asymmetrically bridged allenylidene ligand acting as a four-electron donor. Each metal is ligated by two terminal carbonyl ligands and a η^5-cyclopentadienyl ring arranged in an approximately mutually *trans* orientation. The Mo–Mo distance of 3.145(1) Å is appropriate for a single bond. The short Mo(1)–C(1) separation of 1.912(3) Å [*cf.* that in **5**, 1.909(5) Å] may be regarded as indicating a Mo=C double bond. Two further electrons are donated to Mo(2) by means of the C(1)–C(2) double bond. The methyl substituents both lie close to the Mo(1), Mo(2), C(1) plane, as do C(2) and C(3). Compared to μ-σ:σ-(2e)-allenylidenes, which are linear, the C_3Me_2 fragment present in **20** is distinctly kinked with C(1)–C(2)–C(3) 144.5°. This 'bend back' is reminiscent of that found in mononuclear allene complexes. Compared to the related vinylidene complex, two notable features are the short C(1)–C(2) distance of 1336(3) Å [*cf.* 1.380(7) Å in **5**] and the shorter Mo(2)–C(2) separation of 2.240(3) Å [*cf.* 2.443(6) Å in **5**]. The former distance is particularly striking since it is slightly *less* than the C(2)–C(3) length of 1.348(4) Å (indicating a C=C double bond), rather than longer as might be expected since η^2 co-ordination of a C=C unit is usually observed to lead to bond elongation. An explanation for these observations is shown in Scheme 9, *i.e.* there is a contribution to the bonding from the polar structure. This provides an explanation for the ^{13}C NMR chemical shift of the carbenoid C(1) being rather upfield of the position observed for the related vinylidene complexes, a situation that might suggest that C(1) of **20** is less electron deficient than for example compound **7**. A short C_α–C_β bond distance of *ca.* 1.250 Å has been found[18–20] for mononuclear allenylidenes and 1.280 Å for a dinuclear[21] μ-σ:σ-(2e)-allenylidene.

Unlike the dimethyl-substituted vinylidene complexes **7** and **15**, the ^1H NMR spectrum of **20** showed no evidence of line broadening, however a spin-saturation-transfer experiment showed that an exchange process was occurring in solution. Irradiation (gated) at the resonance frequency of one of the methyl groups led to a partial collapse of the other methyl signal indicating that at ambient temperatures site exchange is occurring. It is reasonable to suggest that analogous processes to those discussed for the μ-σ:η^2-(4e)-vinylidenes also occur with symmetrically substituted μ-σ:η^2-(4e)-allenylidenes.



Scheme 9

The generality of this synthetic approach to μ-σ:η^2-(4e)-allenyidenes was demonstrated by the simple extension of this procedure to the synthesis of $[Mo_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-(4e)-}C{=}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5Me_5)_2]$ **21** and $[W_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-(4e)-}C{=}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **22**. These complexes were isolated in reasonable yield as green crystalline materials characterised by elemental analysis, IR and NMR spectroscopy.

Finally, it is interesting to compare the geometries of the dinuclear μ-acetylide, μ-vinylidene and μ-allenylidene complexes. Fig. 4 shows the $Mo_2(\mu\text{-}CCR_n)$ units of **2**, **5** and **20** viewed perpendicular to the $Mo_2(\mu\text{-}C)$ plane. In each case the formally sp hybridised bridging carbon, C(1), is slightly nonlinear [Mo(1)–C(1)–C(2) 158.7(4), 168.5(4) and 167.2(2)° respectively] and the C(1)–C(2) bond lies somewhat out of the $Mo_2C(1)$ plane (by 18.2, 11.3 and 11.6° respectively). As noted above these deviations must in part be due to the bulk of the substituents at C(2), and the variation in Mo(2)–C(2) distances [2.281(4), 2.443(6), 2.240(3) Å] reflects the variation in encumbrance between formally sp (in **2** and **20**) and sp^2 (in **5**) hybridised C(2) atoms. As may be observed in Fig. 4 the bonding at C(1) in **2** and **20** is (in part) in the direction allowing C(2) to move *towards* Mo(2). In contrast, for **5** the Mo(1)–C(1)–C(2) distortion is almost entirely perpendicular to the Mo(2)(μ-C) plane.

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 NMR spectra were recorded on a Bruker AM360 instrument operating at 360.1 and 90.55 MHz respectively for ^1H and ^{13}C. Chemical shifts are quoted as positive to high frequency of $SiMe_4$, with coupling constants in Hz. Data are given for room-temperature measurements unless stated otherwise. Infrared spectra were measured using a Perkin-Elmer 983 G spectrometer.

Preparations.—$[N(PPh_3)_2][Mo_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **1**. Solid $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.5 g, 1.15 mmol) was added to a stirred (−78 °C) solution of PhC_2Li [1.15 mmol, prepared from PhC_2H (0.12 g) and LiBu^t (640 μl of 1.8 mol dm^{-3} LiBu^t in hexane)] in tetrahydrofuran (70 cm^3). Within minutes a deep red solution formed and this was allowed to warm to room temperature before removal of the thf *in vacuo*. The residual red oil was dissolved in CH_2Cl_2 (50 cm^3) and $[N(PPh_3)_2]Cl$ added, at room temperature. The mixture was stirred for *ca.* 10 min and then stirred for 30 min with activated charcoal (*ca.* 0.30 g) and the solution filtered through a Celite pad (3 × 5 cm). The resulting red solution gave a red-brown powder following removal of the CH_2Cl_2 *in vacuo*. Recrystallisation by layer diffusion (−30 °C, diethyl ether–CH_2Cl_2) afforded dark red *crystals* of compound **1** (0.85 g, 70%) (Found: C, 64.5; H, 4.2; N, 1.2. $C_{58}H_{45}Mo_2NO_4P_2$ requires C, 64.9; H, 4.2; N, 1.3%); $\nu_{CO}(CH_2Cl_2)$ 1847s, 1819m, 1787m and 1765w cm^{-1}. NMR (CD_2Cl_2): ^1H (−80 °C), δ 7.76–7.05 (m, 35 H, Ph), 5.17 (s, 5 H, C_5H_5) and 5.15 (s, 5 H, C_5H_5); (25 °C), δ 7.8–7.1 (m, 35 H, Ph) and 5.07 (s, 10 H, C_5H_5); $^{13}C\text{-}\{^1H\}$ (−60 °C), δ 248.4, 247.2, 244.4, 242.8 (CO), 128.6 (C_α), 136–123 (Ph), 100.3 (C_β), 91.8 (C_5H_5) and 90.5 (C_5H_5); $^{13}C\text{-}\{^1H\}$ (25 °C), δ 230.8, 229.6 (CO), 185.1 (C_α), 136–123 (Ph), 101.0 (C_β) and 91.9 (C_5H_5).

$[N(PPh_3)_2][Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2Ph\}(CO)_4(\eta^5\text{-}C_9H_7)_2]$ **2**. Similarly, reaction of $[Mo_2(CO)_4(\eta^5\text{-}C_9H_7)_2]$[22] (1.0 mmol) with PhC_2Li (1.0 mmol) in thf (−78 °C) followed by addition of $[N(PPh_3)_2]Cl$ gave deep red *crystals* of compound **2** (75%) (Found: C, 67.7; H, 4.2. $C_{66}H_{49}Mo_2NO_4P_2$ requires C, 67.5; H, 4.1%).

$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}CH(Ph)\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **3**. A solution of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.50 g, 1.15 mmol) in thf (70 cm^3) was prepared as described above. The thf solvent was then removed *in vacuo*, the dark red anion dissolved in CH_2Cl_2 (30 cm^3) and the resultant solution passed through an alumina pad (3 × 8 cm). Protonation in this manner yielded a dark blue solution. Removal of the solvent *in vacuo* followed by recrystallisation (−30 °C) from hexane–diethyl ether (1:1) afforded dark blue *crystals* of compound **3** (0.53 g, 85%) (Found: C, 49.0; H, 3.0. $C_{22}H_{16}Mo_2O_4$ requires C, 49.3; H, 3.0%), ν_{CO}(hexane) 1971m, 1923s, 1899s and 1867m, cm^{-1}. NMR ($C_6D_5CD_3$, −60 °C): ^1H, δ 7.1 (m, 5 H, Ph), 5.08 (s, 1 H, C*H*Ph), 4.93 (s, 5 H, C_5H_5) and 4.62 (s, 5 H, C_5H_5); $^{13}C\text{-}\{^1H\}$, δ 333.2 (C_α), 243.7, 235.8, 233.5, 226.3 (CO), 136.4 (Ph), 128.0, 127.2, 124.3 (Ph), 95.7 (C_5H_5), 92.0 (C_5H_5) and 66.1 (*C*HPh) *m*/*z* = 536, $[M]^+$; 480, $[M-2CO]^+$; 452, $[M-3CO]^+$; and 424, $[M-4CO]^+$.

Thermal rearrangement of compound **3**. Complex **3** (0.04 g, 0.08 mmol) was dissolved in C_6H_6 (5 cm^3) to form a dark blue solution. After 10 h at room temperature the solvent was removed *in vacuo* from the red solution. Recrystallisation of the resultant product from diethyl ether afforded red *crystals* of $[Mo_2(\mu\text{-}PhC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$ **4** (95%) (Found: C, 48.9; H, 2.9. $C_{22}H_{16}Mo_2O_4$ requires C, 49.3; H, 3.0%), ν_{CO}(hexane) 1995m, 1931s and 1847m, cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 7.2 (m, 5 H, Ph), 5.52 (s, 1 H, CH) and 5.30 (s, 10 H, C_5H_5); $^{13}C\text{-}\{^1H\}$, δ 231.5, 230.1 (CO), 146.5 (Ph), 130.3, 128.3, 125.8 (Ph), 92.5 (H*C*CPh), 92.2 (C_5H_5) and 75.0 (HC*C*Ph); *m*/*z* = 536, $[M]^+$; 480, $[M-2CO]^+$; 452, $[M-3CO]^+$; and 424, $[M-4CO]^+$.

Methylation of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ *in tetrahydrofuran*. The salt $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.50 g, 1.15 mmol) was prepared in thf (50 cm^3) solution. To the solution was added, at −78 °C $MeOSO_2CF_3$ (130 μl, 0.189 g, 1.15 mmol), the mixture allowed to warm to room temperature and stirred for *ca.* 1 h. The initially red solution became deep blue and following removal of the volatiles *in vacuo* the dark blue oil remaining was dissolved in the minimum of hexane and the resultant solution chromatographed on alumina. Elution with hexane–diethyl ether (9:1) followed by recrystallisation (−30 °C) from dichloromethane–pentane afforded dark blue *crystals* of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Ph)(CH_2)_4OMe\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **5** (0.43 g, 60%) (Found: C, 51.9; H, 4.3. $C_{27}H_{26}Mo_2O_5$ requires C, 52.1; H, 4.2%), ν_{CO}(hexane) 1958m, 1923s, 1898s and 1868w cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 7.20 (m, 5 H, Ph), 5.58 (s, 5 H, C_5H_5), 4.90 (s, 5 H, C_5H_5), 3.28 (m, 2 H, CH_2), 3.23 (s, 3 H, Me) and 1.52 (m, 6 H, CH_2); $^{13}C\text{-}\{^1H\}$, δ 338.7 (C_α), 244.1, 235.0, 233.6, 226.8 (CO), 144.7 (Ph), 128.6, 126.6, 126.4 (Ph), 97.4 (C_5H_5), 93.3 (C_5H_5), 83.8 (C_β), 72.0, 42.0, 30.0, 28.8 (CH_2) and 58.2 (Me, OMe): *m*/*z* = 566, $[M-2CO]^+$; 538, $[M-3CO]^+$; and 510, $[M-4CO]^+$.

$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **6**. The salt $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.50 g, 1.15 mmol) was prepared as described above in thf (50 cm^3) solution. Once the anion had formed the solution was allowed to warm from −78 °C to room temperature and the thf was then removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (50 cm^3) and the resultant solution cooled (−78 °C). One molar equivalent of $MeOSO_2CF_3$ (130 μl, 0.189 g, 1.15 mmol) was added and the mixture allowed to warm to room temperature. After stirring at room temperature for 1 h the dark blue solution was filtered through an alumina pad (3 × 6 cm) and the CH_2Cl_2 removed *in vacuo*. The blue solid thus obtained was dissolved in the miminum volume of hexane and chromatographed on alumina. Elution with hexane afforded a red band, which on collection and recrystallisation (−30 °C, hexane–diethyl ether) gave red *crystals* of $[Mo_2(\mu\text{-}MeC_2Ph)(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.07 g, 10%) (Found: C, 50.1; H, 3.4. $C_{23}H_{18}Mo_2O_4$ requires C, 50.2; H, 3.3%), ν_{CO}(hexane) 1983m, 1959s, 1915s and 1831w cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.2 (m, 5 H, Ph), 5.16 (s, 10 H, C_5H_5) and 2.56 (s, 3 H, Me): *m*/*z* = 550, $[M]^+$; 494, $[M-2CO]^+$; 466, $[M-3CO]^+$; and 438 $[M-4CO]^+$. Further elution afforded a major dark blue band. Collection and recrystallisation (−30 °C, hexane–diethyl ether) gave dark blue *crystals* of compound **6** (70%) (Found: C, 50.2; H, 3.4. $C_{23}H_{18}Mo_2O_4$ requires C, 50.2; H, 3.3%), ν_{CO}(hexane) 1971m, 1923s, 1903s and 1871w cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 7.15 (m, 5 H, Ph), 5.59 (s, 5 H, C_5H_5), 4.96 (s, 5 H, C_5H_5) and 2.01 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 340.7 (C_α), 235.6, 233.6, 231.3, 230.6 (CO), 146.1 (Ph), 128.6, 126.5, 126.0 (Ph), 97.1 (C_5H_5), 93.1 (C_5H_5), 78.9 (C_β) and 27.0 (Me): *m*/*z* = 550, $[M]^+$; 494, $[M-2CO]^+$; 466, $[M-3CO]^+$; and 438, $[M-4CO]^+$.

$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **7**. Similarly, reaction of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (1.15 mmol) with $MeOSO_2CF_3$ (130 μl, 0.189 g, 1.15 mmol) in CH_2Cl_2 afforded a blue-purple solid, which was dissolved in the minimum of hexane and chromatographed on alumina. Elution with hexane afforded red *crystals* of $[Mo_2(\mu\text{-}MeC_2Me)(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.11 g, 20%) (Found: C, 44.1; H, 3.3. $C_{18}H_{16}Mo_2O_4$ requires C, 44.3; H, 3.3%), ν_{CO}(hexane) 1981m, 1918s, 1913s and 1842m, cm^{-1}. NMR (C_6D_6): ^1H, δ 4.83 (s, 10 H, C_5H_5) and 2.38 (s, 6 H, Me); $^{13}C\text{-}\{^1H\}$, δ 231.2 (CO), 91.6 (C_5H_5), 82.5 (*C*Me) and 22.4 (Me). Further elution with hexane gave a blue-black band. Recrystallisation (−30 °C) from hexane gave black *crystals* of compound **7** (0.23 g, 40%) (Found: C, 44.1; H, 3.3. $C_{18}H_{16}Mo_2O_4$ requires C, 44.3; H, 3.3%), ν_{CO}(hexane) 1967w, 1927s, 1895s and 1867w cm^{-1}. NMR (CD_2Cl_2): ^1H (−60 °C), δ 5.55 (s, 5 H, C_5H_5), 5.40 (s, 5 H, C_5H_5), 1.73 (s, 3 H, Me) and 1.67 (s, 3 H, Me); (25 °C), δ 5.45 (br s, 10 H, C_5H_5) and 1.70 (br s, 6 H, Me); $^{13}C\text{-}\{^1H\}$ (−60 °C), δ 342.9 (C_α), 243.6, 237.0, 236.6, 226.1 (CO), 96.1 (C_5H_5), 92.8 (C_5H_5), 79.8 (C_β), 28.7 (Me) and 27.9 (Me): *m*/*z* = 488, $[M]^+$; 460, $[M-CO]^+$; 432, $[M-2CO]$; 404, $[M-3CO]$; and 376, $[M-4CO]^+$.

$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Pr^i)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **8**. In the same way reaction of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2Pr^i\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (1.15 mmol) with $MeOSO_2CF_3$ (1.15 mmol) in CH_2Cl_2 (30 cm^3) afforded red *crystals* of $[Mo_2(\mu\text{-}MeC_2Pr^i)(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.18 g, 30%) (Found: C, 46.9; H, 4.0. $C_{20}H_{20}Mo_2O_4$ requires C, 46.5; H, 3.9%), ν_{CO}(hexane) 1984m, 1925s, 1917s and 1847m, cm^{-1}. NMR: ^1H (C_6D_6), δ 4.85 (s, 10 H, C_5H_5), 2.73 [q, 1 H, C*H*Me₂, ^3J(HH) 6.8], 2.61 (s, 3 H, Me) and 0.93 [d, 6 H, CH*Me*₂, ^3J(HH) 6.8 Hz]; $^{13}C\text{-}\{^1H\}$(CD_2Cl_2), δ 234.5, 228.6 (CO), 103.8, 70.7 (MeC_2Pr^i), 92.3 (C_5H_5), 33.6 (Me), 24.8 (*C*HMe₂) and 24.0 (CH*Me*₂): *m*/*z* = 516, $[M]^+$. Further elution afforded purple *crystals* of compound **8** (0.19 g, 31%) (Found: C, 46.3; H, 3.9. $C_{20}H_{20}Mo_2O_4$ requires C, 46.5; H, 3.9%), ν_{CO}(hexane) 1967m, 1921s, 1895s and 1864m, cm^{-1}. NMR: ^1H (C_6D_6, 25 °C), δ 5.05 (s, 5 H, C_5H_5), 4.99 (s, 5 H, C_5H_5), 1.42 (s, 3 H, Me), 1.35 [m, 1 H, C*H*Me₂, ^3J(HH) 6.6], 1.09 [d, 3 H, CH*Me*₂, ^3J(HH) 6.6] and 0.96 [d, 3 H, CH*Me*₂, ^3J(HH) 6.6]; (C_6D_6, 70 °C), δ 5.09 (s, 10 H, C_5H_5), 1.46 (s, 3 H, Me) and 1.41 [m, 1 H, C*H*Me₂, ^3J(HH) 6.6] and 1.06 [d, 6 H, CH*Me*₂, ^3J(HH) 6.6 Hz]; $^{13}C\text{-}\{^1H\}$ (C_6H_6, 25 °C), δ 344.5 (C_α), 242.5, 236.2, 235.5, 226.1 (CO), 95.3 (C_5H_5), 92.3 (C_5H_5), 91.6 (C_β), 38.3 (*C*Me), 23.2 (CH*Me*₂), 20.6 (*C*HMe₂) and 20.1 (CH*Me*₂).

$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Bu^t)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **9**. The same procedure involving methylation ($MeOSO_2CF_3$, 1.15 mmol) of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2Bu^t\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (1.15 mmol) in CH_2Cl_2 afforded green *crystals* (−30 °C, hexane) of $[Mo_2(\mu\text{-}MeC_2Bu^t)(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.18 g, 30%) (Found: C,

Table 4 Structure analyses for compounds **2**, **5** and **20***

	2	**5**	**20**
Crystal data			
Formula	$C_{66}H_{49}Mo_2NO_4P_2$	$C_{27}H_{26}Mo_2O_5$	$C_{19}H_{16}Mo_2O_4$
M	1174.0	622.4	500.2
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	10.576(7)	11.828(3)	8.138(2)
b/Å	14.626(8)	12.663(4)	10.022(2)
c/Å	19.136(9)	17.422(4)	11.495(3)
α/°	73.79(4)	90	85.41(2)
β/°	77.58(4)	105.20(2)	84.35(2)
γ/°	73.95(4)	90	73.54(2)
U/Å^3	2701(2)	2518(1)	893.3(3)
Z	2	4	2
D_c/g cm^{-3}	1.44	1.64	1.87
$F(000)$	1196	1248	492
μ(Mo-Kα)/cm^{-1}	5.6	9.9	13.9
Data collection and reduction			
Crystal dimensions (mm)	0.58 × 0.25 × 0.4	0.22 × 0.25 × 0.13	0.45 × 0.4 × 0.3
2θ range (°)	4–50	4–50	4–55
Scan method	Wyckoff ω	ω–2θ	ω–2θ
Scan width (ω°)	1.0	$1.0 + \Delta\alpha_1\alpha_2$	$1.0 + \Delta\alpha_1\alpha_2$
Total data	9733	3539	4267
Unique data	9398	3368	4109
'Observed' data (N_o) [$F^2 > 1.5\sigma(F^2)$]	7224	2834	3750
Crystal faces [distance from origin (mm)]		$(001)[0.063]$, $(00\bar{1})[0.063]$, $(110)[0.113]$, $(1\bar{1}\bar{1})[0.125]$, $(\bar{1}11)[0.125]$, $(\bar{1}\bar{1}0)[0.113]$	$(100)[0.213]$, $(\bar{1}00)[0.213]$, $(011)[0.075]$, $(0\bar{1}\bar{1})[0.075]$, $(0\bar{1}1)[0.175]$, $(01\bar{1})[0.175]$
No. of azimuthal scan data	400		
Minimum, maximum transmission coefficients	0.729, 0.835	0.759, 0.892	0.698, 0.749
Refinement			
Least-squares variables (N_v)	676	307	242
R	0.049	0.032	0.31
R'	0.051	0.038	0.41
S	1.20	1.07	1.39
Final difference map features (e Å^{-3})	+0.87, −0.35	+0.5, −0.3	+1.1, −1.0

* Details in common: $T = 295$ K; λ(Mo-Kα) 0.710 69 Å; no disordered atoms; $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$; $w = [\sigma_c^2(F_o) + 0.0005F_o^2]^{-1}$, $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics.

47.1; H, 4.0. $C_{21}H_{22}Mo_2O_4$ requires C, 47.6; H, 4.2%), ν_{CO}(hexane) 1989m, 1980m, 1928w, 1919s and 1845m cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.95 (s, 10 H, C_5H_5), 2.63 (s, 3 H, Me) and 1.08 (s, 9 H, C*Me*$_3$): m/z = 530, $[M]^+$; 474, $[M - 2CO]^+$; and 418, $[M - 4CO]^+$. Further elution and recrystallisation (−30 °C, hexane) gave dark purple *crystals* of compound **9** (0.12 g, 20%) (Found: C, 47.2; H, 4.2. $C_{21}H_{22}Mo_2O_4$ requires C, 47.6; H, 4.2%), ν_{CO}(hexane) 1961w, 1919s, 1889s and 1863w cm^{-1}. NMR (C_6D_6): ^{1}H, δ 5.17 (s, 5 H, C_5H_5), 5.05 (s, 5 H, C_5H_5), 1.60 (s, 3 H, Me) and 0.93 (s, 9 H, CMe_3); ^{13}C-{^{1}H}, δ 348.6 (C_α), 243.9, 234.5, 226.6 (CO), 107.3 (C_β), 94.6 (C_5H_5), 92.0 (C_5H_5), 38.5 (C*Me*$_3$), 30.4 (*C*Me$_3$) and 27.3 (*C*Me): m/z = 530, $[M]^+$; 474, $[M - 2CO]^+$; 446, $[M - 3CO]^+$; and 418, $[M - 4CO]^+$.

$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}C(Et)Ph\}(CO)_4(\eta\text{-}C_5H_5)]$ **10**. Reaction (−78 °C) of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (2.0 mmol) with $EtOSO_2CF_3$ (0.26 cm^3, 2.0 mmol) in CH_2Cl_2 followed by column chromatography gave a dark blue band. Recrystallisation (twice, −30 °C, CH_2Cl_2–hexane) gave a trace of the corresponding μ-alkyne complex followed by dark blue *crystals* of compound **10** (0.53 g, 47%) (Found: C, 51.0; H, 3.6. $C_{24}H_{20}Mo_2O_4$ requires C, 51.1; H, 3.6%), ν_{CO}(hexane) 1957w, 1920w, 1894m, and 1856w cm^{-1}. NMR: ^{1}H ($CDCl_3$), δ 7.28 (m, 5 H, Ph), 5.56 (s, 5 H, C_5H_5), 4.90 (s, 5 H, C_5H_5) and 3.3 (m, 1 H, CH_2); ^{13}C-{^{1}H} (CD_2Cl_2), δ 337.7 (C_α), 244.4, 234.8, 233.7, 227.5 (CO), 144.5, 128.8, 126.7, 126.5 (Ph), 97.4 (C_5H_5), 93.4 (C_5H_5), 85.2 (C_β), 35.4 (CH_2) and 16.2 (Me): m/z = 563, $[M - H]^+$; 506, $[M - 2H - 2CO]^+$; and 450, $[M - 2H - 4CO]^+$.

$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}C(CH_2CH{=}CH_2)Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **11**. Similarly, reaction of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(3e)-}C_2Ph\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (1.0 mmol) with a large excess of freshly distilled allyl bromide (2 cm^3, 23 mmol) in CH_2Cl_2 (20 cm^3) followed by column chromatography gave a blue band. Recrystallisation (−30 °C, hexane–diethyl ether) gave dark blue *crystals* of compound **11** (0.250 g, 43%) (Found: C, 52.0; H, 3.5. $C_{25}H_{20}Mo_2O_4$ requires C, 52.1; H, 3.5%), ν_{CO}(hexane) 1965w, 1924s, 1901m, and 1867w cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 7.27–7.00 (m, 5 H, Ph), 5.80 (m, 1 H, C*H*=CH$_2$), 5.55 (s, 5 H, C_5H_5), 5.10 (m, 2 H, CH=C*H*$_2$), 4.92 (s, 5 H, C_5H_5), 4.0 [dd, 1 H, C*H*$_2$CH=CH$_2$, ^2J(HH), 15.3, ^3J(HH) 6.1] and 1.70 [dd, 1 H, C*H*$_2$CH=CH$_2$, ^2J(HH) 15.3, ^3J(HH) 5.7 Hz]; ^{13}C-{^{1}H}, δ 337.6 (C_α), 244.0, 234.5, 233.1, 226.1 (CO), 137.6 (*C*H=CH$_2$), 144.3, 128.4, 126.3 (Ph), 116.2 (CH=*C*H$_2$), 97.1 (C_5H_5), 93.1 (C_5H_5), 82.1 (C_β) and 45.6 (*C*H$_2$CH=CH$_2$).

$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-(4e)-}C{=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **12**. A solution of LiBu^t[2.0 mmol, in pentane (2.5 mol dm^{-3})] was added dropwise with stirring to a cooled (−78 °C) solution of $[Mo_2(\mu\text{-}HC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.92 g, 2.0 mmol) in thf. The colour of the reaction mixture changed to purple. Addition (−78 °C) of CF_3CO_2H (0.15 cm^3, 2.0 mmol) afforded a dark purple solution, which was filtered through a pad (2 × 3 cm) of alumina. The solvent was removed *in vacuo* and the residue

Table 5 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Mo(1)	3 812(1)	2 512(1)	1 795(1)
Mo(2)	1 848(1)	2 561(1)	3 251(1)
C(1)	3 541(4)	1 521(3)	2 755(2)
C(2)	2 956(4)	976(3)	3 279(2)
C(3)	3 749(6)	3 751(4)	1 965(3)
C(4)	962(5)	3 444(3)	2 460(3)
C(5)	277(5)	2 118(3)	3 320(3)
C(6)	5 606(5)	2 340(5)	1 958(3)
C(10)	3 772(7)	3 040(5)	503(3)
C(11)	2 467(6)	3 045(5)	863(3)
C(12)	2 350(6)	2 068(5)	1 201(3)
C(13)	1 295(7)	1 648(6)	1 608(3)
C(14)	1 523(9)	672(6)	1 846(4)
C(15)	2 825(12)	61(6)	1 690(5)
C(16)	3 839(10)	436(6)	1 314(5)
C(17)	3 673(7)	1 459(5)	1 056(3)
C(18)	4 502(7)	2 081(6)	643(3)
C(20)	879(5)	3 529(4)	4 067(3)
C(21)	1 319(5)	2 589(4)	4 506(3)
C(22)	2 739(5)	2 387(3)	4 426(2)
C(23)	3 687(6)	1 605(4)	4 770(3)
C(24)	4 998(6)	1 638(4)	4 584(3)
C(25)	5 405(6)	2 422(4)	4 045(3)
C(26)	4 523(5)	3 187(4)	3 693(3)
C(27)	3 156(5)	3 190(3)	3 893(3)
C(28)	1 970(5)	3 880(3)	3 649(3)
C(30)	1 902(5)	−112(3)	4 358(3)
C(31)	1 738(6)	−1 040(4)	4 744(3)
C(32)	2 459(6)	−1 841(4)	4 487(4)
C(33)	3 340(6)	−1 735(4)	3 858(4)
C(34)	3 507(5)	−821(3)	3 474(3)
C(35)	2 783(4)	19(3)	3 709(3)
O(3)	3 770(5)	4 524(3)	2 032(2)
O(4)	283(4)	3 991(3)	2 035(2)
O(5)	−727(4)	1 903(3)	3 367(2)
O(6)	6 701(4)	2 274(4)	2 024(3)
N	259(3)	2 785(3)	7 914(2)
P(1)	749(1)	2 842(1)	7 067(1)
P(2)	791(1)	2 541(1)	8 672(1)
C(100)	2 669(5)	1 122(3)	7 020(3)
C(101)	3 121(5)	174(4)	6 931(3)
C(102)	2 340(6)	−229(4)	6 680(3)
C(103)	1 121(6)	301(4)	6 506(3)
C(104)	652(5)	1 252(3)	6 586(3)
C(105)	1 428(4)	1 668(3)	6 854(2)
C(110)	3 000(4)	3 398(3)	6 132(2)
C(111)	3 799(5)	4 056(3)	5 832(3)
C(112)	3 545(5)	4 911(4)	6 057(3)
C(113)	2 482(5)	5 125(3)	6 589(3)
C(114)	1 656(4)	4 480(3)	6 893(2)
C(115)	1 920(4)	3 605(3)	6 671(2)
C(120)	−503(4)	3 838(3)	5 857(2)
C(121)	−1 599(4)	4 295(3)	5 503(2)
C(122)	−2 862(4)	4 325(3)	5 885(3)
C(123)	−3 038(4)	3 905(3)	6 621(3)
C(124)	−1 961(4)	3 448(3)	6 988(2)
C(125)	−683(4)	3 418(3)	6 603(2)
C(200)	1 989(5)	858(3)	9 634(3)
C(201)	2 290(5)	−143(4)	9 926(3)
C(202)	1 858(5)	−748(4)	9 649(3)
C(203)	1 128(5)	−375(4)	9 079(3)
C(204)	816(5)	620(3)	8 785(3)
C(205)	1 246(4)	1 241(3)	9 058(2)
C(210)	−1 729(5)	3 631(4)	9 055(3)
C(211)	−2 798(6)	3 998(5)	9 542(3)
C(212)	−2 683(6)	3 810(4)	10 260(3)
C(213)	−1 505(6)	3 271(4)	10 512(3)
C(214)	−452(5)	2 908(4)	10 031(3)
C(215)	−550(4)	3 084(3)	9 294(2)
C(220)	3 486(5)	2 480(4)	8 447(3)
C(221)	4 574(6)	2 888(5)	8 337(4)
C(222)	4 388(7)	3 825(6)	8 383(3)
C(223)	3 150(8)	4 367(5)	8 541(3)
C(224)	2 035(6)	3 976(4)	8 670(3)
C(225)	2 209(5)	3 020(3)	8 622(2)

dissolved in the minimum volume of toluene. Column chromatography on alumina and elution with hexane–diethyl ether (5:1) gave a purple band. Collection and recrystallisation (−78 °C) from hexane–diethyl ether gave purple *crystals* of compound **12** (0.50 g, 55%) (Found: C, 41.6; H, 2.7. $C_{16}H_{12}Mo_2O_4$ requires C, 41.8; H, 2.6%), ν_{CO}(hexane) 1976w, 1928s, 1905m, and 1868w cm^{-1}. NMR ($CDCl_3$): ^1H, δ 5.44 (s, 5 H, C_5H_5), 5.30 (s, 5 H, C_5H_5), 3.44 [d, 1 H, ^2J(HH) 14.2] and 2.83 [d, 1 H, C=C*H*H, ^2J(HH) 14.2 Hz]; ^{13}C-{^1H}, δ 329.5 (C_α), 241.8, 231.6, 231.0, 230.3 (CO), 94.6 (C_5H_5), 93.0 (C_5H_5) and 40.0 (CH_2): *m*/*z* = 459, [*M* − H]$^+$; 432, [*M* − CO]$^+$; 404, [*M* − 2CO]$^+$; 376, [*M* − 3CO]$^+$.

[W_2{μ-σ:η^2-(4e)-C=CH(Ph)}$(CO)_4(\eta$-$C_5H_5)_2$] **13**. The (red) acetylide complex Li[$W_2(C_2Ph)(CO)_4(\eta$-$C_5H_5)_2$] was prepared by addition (−78 °C) of PhC_2Li (0.5 mmol) to a solution of [$W_2(CO)_4(\eta$-$C_5H_5)_2$] (0.5 mmol) in thf (30 cm^3). This initially gave a green solution which on warming to −65 °C became deep red. The red solution was then filtered through a short pad of alumina (3 × 2 cm) held at −30 °C. The resultant blue solution was evaporated to dryness *in vacuo*, and the residue recrystallised (−30 °C) from hexane–diethyl ether to give dark blue *crystals* of compound **13** (0.25 g, 70%) (Found: C, 37.2; H, 2.3. $C_{22}H_{16}O_4W_2$ requires C, 37.1; H, 2.3%), ν_{CO}(hexane) 1961w, 1915s, 1887m and 1853w cm^{-1}. NMR (C_6D_6): ^1H, δ 7.1 (m, 5 H, Ph), 4.94 (s, 5 H, C_5H_5), 4.84 (s, 5 H, C_5H_5) and 4.51 (s, 1 H, C*H*Ph); ^{13}C-{^1H}, δ 305.8 (C_α), 234.0, 231.2, 219.2, 216.0 (CO), 142.5, 128.9, 126.5, 126.0 (Ph), 96.1 (C_5H_5), 92.0 (C_5H_5) and 63.1 (*C*HPh).

[W_2{μ-σ:η^2-(4e)-C=C(Ph)Me}$(CO)_4(\eta$-$C_5H_5)_2$] **14**. The salt Li[$W_2(C_2Ph)(CO)_4(\eta$-$C_5H_5)_2$] (red isomer) (1.0 mmol) was prepared as described above in thf (50 cm^3) solution. The solvent was removed *in vacuo* and the residue redissolved in CH_2Cl_2 (20 cm^3). After cooling this solution to −78 °C, $MeOSO_2CF_3$ (0.11 cm^3, 1.0 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h during which time it became dark blue. The solvent was removed *in vacuo* and the residue dissolved in Et_2O and chromatographed on alumina. Elution with hexane–diethyl ether (3:1) afforded a blue band which was collected. The following minor red band was discarded. Recrystallisation (−30 °C) from hexane–diethyl ether gave dark blue *crystals* of compound **14** (0.24 g, 33%) (Found: C, 38.0; H, 2.4. $C_{23}H_{18}O_4W_2$ requires C, 38.1; H, 2.5%), ν_{CO}(CH_2Cl_2) 1955w, 1903s, 1877m and 1825w cm^{-1}. NMR: ^1H (C_6D_6), δ 7.1 (m, 5 H, Ph), 5.03 (s, 5 H, C_5H_5), 4.88 (s, 5 H, C_5H_5) and 2.15 (s, 3 H, Me); ^{13}C-{^1H} (CD_2Cl_2), δ 312.8 (C_α) 234.4, 230.0, 219.4, 215.7 (CO), 146.0–125.3 (Ph), 96.6 (C_5H_5), 91.7 (C_5H_5), 72.4 (C_β) and 27.9 (Me).

[W_2{μ-σ:η^2-(4e)-C=CMe$_2$}$(CO)_4(\eta$-$C_5H_5)_2$] **15**. The salt Li[$W_2(C_2Me)(CO)_4(\eta$-$C_5H_5)_2$] (2.0 mmol) was prepared as above as a cherry-red thf solution (30 cm^3). The solvent was removed *in vacuo* and the residue redissolved in CH_2Cl_2 (20 cm^3). The compound $MeOSO_2CF_3$ (0.22 cm^3, 2.0 mmol) was then added at −78 °C, and stirred for 2 h at room temperature. The solvent was removed *in vacuo*, the residue dissolved in the minimum of diethyl ether and the resultant solution chromatographed on alumina. Separation of the blue vinylidene complex from the red μ-alkyne complex [W_2(μ-$MeC_2Me)(CO)_4(\eta$-$C_5H_5)_2$] was difficult. Elution with hexane–diethyl ether produced a red band tailing with a blue band. The latter was collected and the volume of the solvent reduced *in vacuo* until

Table 6 Atomic coordinates (× 10^4) for compound **5**

Atom	*x*	*y*	*z*
Mo(1)	4587(1)	605(1)	3015(1)
Mo(1)	2961(1)	1107(1)	1333(1)
C(1)	4455(4)	461(4)	1748(3)
C(2)	5413(4)	−193(4)	2005(3)
C(3)	5230(5)	−1375(4)	1841(3)
C(41)	2398(5)	1873(4)	2167(3)
C(42)	3761(5)	2425(4)	1184(3)
C(43)	3068(5)	−8(4)	3028(3)
C(44)	4975(5)	−820(4)	3420(3)
C(11)	6620(4)	201(4)	2037(3)
C(12)	6785(5)	1081(5)	1598(3)
C(13)	7900(6)	1428(6)	1598(5)
C(14)	8852(6)	901(6)	2020(5)
C(15)	8732(5)	16(6)	2467(5)
C(16)	7612(5)	−336(5)	2471(4)
C(21)	5889(5)	2084(4)	3229(3)
C(22)	4810(6)	2472(4)	3279(4)
C(23)	4516(6)	1971(5)	3917(4)
C(24)	5428(6)	1294(5)	4273(3)
C(25)	6280(5)	1334(4)	3839(3)
C(31)	1035(9)	1042(6)	486(4)
C(32)	1806(6)	1076(5)	12(3)
C(33)	2473(6)	162(5)	121(3)
C(34)	2126(6)	−441(5)	692(4)
C(35)	1231(5)	100(6)	922(4)
C(4)	5402(6)	−1693(5)	1033(3)
C(5)	5458(6)	−2877(5)	923(4)
C(6)	4413(7)	−3511(6)	939(6)
O(7)	3437(6)	−3208(6)	347(5)
C(8)	3065(11)	−3981(11)	−152(7)
O(41)	1979(3)	2335(3)	2586(3)
O(42)	4245(5)	3182(3)	1088(3)
O(43)	2201(4)	−376(3)	3078(3)
O(44)	5205(4)	−1649(3)	3700(2)

the μ-alkyne complex began to crystallise. The red complex was separated (0.33 g, 25%) and the blue solution cooled to −30 °C to afford blue *crystals* of compound **15** (0.43 g, 32%) (Found: C, 32.6; H, 2.5. $C_{18}H_{16}O_4W_2$ requires C, 32.6; H, 2.4%), ν_{CO}(hexane) 1957w, 1913s, 1885m and 1855w cm^{-1}. NMR ($CDCl_3$): ^1H, δ 5.99 (s, 5 H, C_5H_5), 5.50 (s, 5 H, C_5H_5), 1.93 (s, 3 H, Me) and 1.75 (s, 3 H, Me); ^{13}C-{^1H}, δ 315.2 (C_α), 232.2, 230.9, 220.3, 215.2 (CO), 94.8 (C_5H_5), 91.0 (C_5H_5), 72.2 (C_β), 29.4 (Me) and 27.5 (Me).

Thermolysis of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Ph)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **6**. A solution of compound **6** (0.03 g, 0.05 mmol) in C_6H_6 (1 cm^3) contained in a small Young's tube was heated at 80 °C for 12 h, the initial deep blue colour changing to orange. The volatile material was removed *in vacuo* and the residue extracted into CH_2Cl_2. Column chromatography of the extract on an alumina-packed column gave on elution with CH_2Cl_2 a bright orange-red band. This was collected and recrystallised (−30 °C) from hexane–dichloromethane to give orange *needles* of $[Mo_2\{\mu\text{-}\sigma:\eta^3\text{-}CHC(Ph)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **16** (0.02 g, 72%) (Found: C, 50.2; H, 3.3. $C_{23}H_{18}Mo_2O_4$ requires C, 50.2; H, 3.3%), $\nu_{CO}(CH_2Cl_2)$ 1955s, 1915s, 1849s and 1771m cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 10.53 [d, 1 H, H^1, ^4J(HH) 3.1], 7.5 (m, 5 H, Ph), 5.35 (s, 5 H, C_5H_5), 4.81 (s, 5 H, C_5H_5), 3.78 [dd, 1 H, H^2, ^4J(HH) 3.1, ^2J(HH) 1.3] and 0.84 [d, 1 H, H^3, ^2J(HH) 1.3 Hz]; ^{13}C-{^1H}, δ 243.1, 242.5, 242.0, 236.0 (CO), 166.5 (CH), 142.0 (*C*Ph), 129.0, 128.2, 125.4 (CH, Ph), 111.0 (*C*Ph), 95.3 (C_5H_5), 94.0 (C_5H_5) and 59.5 (CH_2).

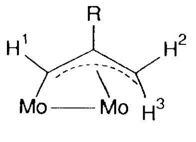


Table 7 Atomic coordinates (× 10^4) for compound **20**

Atom	*x*	*y*	*z*
Mo(1)	7 486(1)	1 529(1)	2 773(1)
Mo(2)	3 753(1)	3 573(1)	2 779(1)
C(1)	6 500(3)	3 504(3)	2 673(2)
C(2)	5 649(3)	4 823(3)	2 399(2)
C(3)	5 813(4)	6 112(3)	2 110(2)
C(4)	4 322(5)	7 362(3)	1 946(4)
C(5)	7 564(5)	6 357(4)	1 943(3)
C(10)	9 721(4)	1 691(4)	1 346(3)
C(11)	8 428(4)	1 394(4)	773(3)
C(12)	8 291(4)	63(4)	1 197(3)
C(13)	9 499(4)	−445(3)	2 029(3)
C(14)	10 374(4)	564(4)	2 119(3)
C(20)	2 877(4)	4 717(3)	4 584(3)
C(21)	3 357(4)	3 287(4)	4 873(3)
C(22)	2 220(4)	2 697(4)	4 357(3)
C(23)	1 064(4)	3 770(4)	3 753(3)
C(24)	1 479(4)	5 015(3)	3 880(3)
C(30)	5 786(4)	507(3)	3 400(3)
C(31)	8 028(4)	1 578(3)	4 404(3)
C(32)	3 008(4)	4 689(3)	1 359(3)
C(33)	3 868(4)	2 190(3)	1 622(3)
O(30)	4 944(3)	−221(3)	3 713(2)
O(31)	8 391(4)	1 604(3)	5 334(2)
O(32)	2 520(4)	5 342(3)	534(2)
O(33)	3 859(3)	1 439(3)	913(2)

Thermolysis of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **7**. Similarly, thermolysis of compound **7** (0.03 g, 0.06 mmol) gave on recrystallisation (−30 °C) of the product from hexane–dichloromethane orange *crystals* of $[Mo_2\{\mu\text{-}\sigma:\eta^3\text{-}CHC(Me)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **17** (0.025 g, 80%) (Found: C, 43.8; H, 3.3. $C_{18}H_{16}Mo_2O_4$ requires C, 44.3; H, 3.3%), $\nu_{CO}(CH_2Cl_2)$ 1951s, 1915s, 1843s and 1767m cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 9.77 [d, 1 H, H^1, ^4J(HH) 2.9], 5.29 (s, 5 H, C_5H_5), 5.10 (s, 5 H, C_5H_5), 3.15 [d, 1 H, H^2, *J*(HH) 2.9 Hz], 2.24 (s, 3 H, Me) and 0.64 (s, 1 H, H^3); ^{13}C-{^1H}, δ 252.2, 244.0, 240.6, 236.2 (CO), 170.0 (CH), 111.2 (*C*Me), 94.6 (C_5H_5), 92.5 (C_5H_5), 60.4 (CH_2) and 29.3 (C*Me*).

Thermolysis of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Pr^i)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **8**. In the same way thermolysis of compound **8** (0.025 g, 0.05 mmol) afforded orange *crystals* of $[Mo_2\{\mu\text{-}\sigma:\eta^3\text{-}CHC(Pr^i)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **18** (0.02 g, 80%) (Found: C, 46.2; H, 3.8. $C_{20}H_{20}Mo_2O_4$ requires C, 46.5; H, 3.9%), $\nu_{CO}(CH_2Cl_2)$ 1947s, 1911s, 1843s and 1769m cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 9.93 [d, 1 H, H^1, ^4J(HH) 3.0], 5.28 (s, 5 H, C_5H_5), 3.16 [d, 1 H, H^2, ^4J(HH) 3.0], 2.42 [m, 1 H, C*H*Me_2, ^3J(HH) 6.8], 1.49 [d, 3 H, CH*Me*$_2$, ^3J(HH) 6.8], 0.94 [d, 3 H, CH*Me*$_2$, ^3J(HH) 6.8 Hz] and 0.39 (s, 1 H, H^3); ^{13}C-{^1H}, δ 252.2, 242.6, 240.0, 236.8 (CO), 167.8 (CH), 122.2 (*C*Pr^i), 94.5 (C_5H_5), 91.9 (C_5H_5), 57.6 (CH_2), 39.8 (*C*HMe_2), 27.0 (CH*Me*$_2$) and 20.3 (CH*Me*$_2$).

Thermolysis of $[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C(Bu^t)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **9**. Similarly, thermolysis of compound **9** (0.025 g, 0.05 mmol) afforded orange *crystals* of $[Mo_2\{\mu\text{-}\sigma:\eta^3\text{-}CHC(Bu^t)CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **19** (0.02 g, 80%) (Found: C, 47.3; H, 4.2. $C_{21}H_{22}Mo_2O_4$ requires C, 47.6; H, 4.2%), $\nu_{CO}(CH_2Cl_2)$ 1951s, 1915s, 1847s and 1715m cm^{-1}. NMR (C_6D_6): ^1H, δ 9.62 [d, 1 H, H^1, ^4J(HH), 3.4], 4.81 (s, 5 H, C_5H_5), 4.46 (s, 5 H, C_5H_5), 2.93 [dd, 1 H, H^2, ^2J(HH) 1.0, ^4J(HH) 3.4], 1.00 (s, 9 H, CMe_3) and 0.49 [d, 1 H, H^3, ^2J(HH) 1.0 Hz]; ^{13}C-{^1H}, δ 251.9, 243.2, 239.8, 238.0 (CO), 161.7 (CH), 100.6 (*C*Bu^t), 94.3 (C_5H_5), 91.1 (C_5H_5), 57.6 (CH_2), 38.4 (*C*Me_3) and 30.7 (C*Me*$_3$).

$[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(4e)\text{-}C{=}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **20**. A thf (20 cm^3) solution of $Li[Mo_2\{\mu\text{-}\sigma:\eta^2\text{-}(3e)\text{-}C_2C(Me){=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (2.3 mmol) was prepared by addition (−78 °C) of $CH_2{=}C(Me)C_2Li$ to $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$. This solution was protonated at ambient temperature by adding the solution directly to an alumina-packed column, whereupon the colour changed from purple to deep green. Eluting the column with Et_2O gave a dark green band containing a mixture of compound **20** and $[Mo_2\{\mu\text{-}HC_2C(Me){=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$. It was not possible to resolve this mixture by column chromatography, but this was readily achieved by fractional crystallisation. Slow evaporation, under partial vacuum, of a hexane–dichloromethane (10:1) solution afforded first a green material. This was collected and recrystallised (−30 °C) from hexane to give dark green *crystals* of compound **20** (0.56 g, 49%) (Found: C, 45.5; H, 3.3. $C_{19}H_{16}Mo_2O_4$ requires C, 45.6; H, 3.2%), ν_{CO}(hexane) 1969w, 1925s, 1905m and 1869w cm^{-1}. NMR: ^1H ($CDCl_3$), δ 5.47 (s, 5 H, C_5H_5), 5.29 (s, 5 H, C_5H_5), 2.42 [q, 3 H, Me, ^4J(HH) 0.7] and 2.17 [q, 3 H, Me, ^4J(HH) 0.7 Hz]; $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 287.7 (C_α), 238.2, 233.0, 231.5, 230.8 (CO), 149.4, 148.9 (C), 95.0 (C_5H_5), 93.7 (C_5H_5), 33.1 (Me) and 25.2 (Me): $m/z = 500$, $[M]^+$; 442, $[M - 2H - 2CO]^+$; and 414, $[M - 2H - 3CO]^+$. Evaporation of the mother-liquor gave a red material, which on recrystallisation (−30 °C) from hexane gave red *crystals* of $[Mo_2\{\mu\text{-}HC_2C(Me){=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.10 g, 9%) (Found: C, 45.5; H, 3.1. $C_{19}H_{16}Mo_2O_4$ requires C, 45.6; H, 3.2%), ν_{CO}(hexane) 1993m, 1937 (sh), 1929s and 1849m cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.60 (s, 1 H, CH), 5.30 (s, 10 H, C_5H_5), 4.96 [dq, 1 H, H, ^2J(HH), 2.2, ^4J(MeH) 1.3], 4.75 [dq, 1 H, H, ^2J(HH) 2.2, ^4J(MeH) 0.7] and 1.81 [dd, 3 H, Me, ^4J(MeH) 1.3, ^4J(MeH) 0.7 Hz].

$[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}(4e)\text{-}C{=}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5Me_5)_2]$ **21**. The salt $Li[Mo_2\{\mu\text{-}\sigma{:}\eta^2\text{-}(3e)\text{-}C_2C(Me){=}CH_2\}(CO)_4(\eta\text{-}C_5Me_5)_2]$ 1.0 mmol) was prepared as a purple thf (10 cm^3) solution in the normal way except insofar as the reaction between $[Mo_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ and $CH_2{=}C(Me)C_2Li$ was slow (0.5 h) even at room temperature. It was then protonated on an alumina column using the same procedure as for compound **15**. The yield of the isomeric μ-alkyne complex was negligible. Recrystallisation (−39 °C) from hexane afforded green *crystals* of compound **21** (0.17 g, 26%) (Found: C, 54.2; H, 5.6. $C_{29}H_{36}Mo_2O_4$ requires C, 54.4; H, 5.7%), ν_{CO}(hexane) 1954m, 1897s and 1845w cm^{-1}. NMR ($CDCl_3$): ^1H, δ 2.41 [q, 3 H, Me, ^4J(MeH) 0.7], 2.14 [q, 3 H, ^4J(MeH) 0.7], 1.87 (s, 15 H, C_5Me_5) and 1.81 (s, 15 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 302.5 (C_α), 243.0, 240.0, 235.1, 233.8 (CO), 156.5, 141.9 (C), 105.5 (C_5Me_5), 105.1 (C_5Me_5), 34.5 (Me), 24.9 (Me), 10.8 ($C_5\mathit{Me}_5$) and 10.7 ($C_5\mathit{Me}_5$).

$[W_2\{\mu\text{-}\sigma{:}\eta^2\text{-}(4e)\text{-}C{=}C{=}CMe_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **22**. An identical procedure to that described for the preparation of the analogous Mo_2 complex was used. Formation and protonation of $Li[W_2\{\mu\text{-}\sigma{:}\eta^2\text{-}(3e)\text{-}C_2C(Me){=}CH_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.5 mmol) afforded a dark green solid, which on recrystallisation (−30 °C) from hexane gave dark green *crystals* of compound **22** (0.16 g, 48%) (Found: C, 33.7; H, 2.5. $C_{19}H_{16}O_4W_2$ requires C, 33.8; H, 2.4%), ν_{CO}(CH_2Cl_2) 1961w, 1925s, 1905s, 1885w and 1841w cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 5.57 (s, 5 H, C_5H_5), 5.43 (s, 5 H, C_5H_5), 2.26 [q, 3 H, Me, ^4J(MeH) 0.9] and 1.93 [q, 3 H, Me, ^4J(MeH) 0.9 Hz]; $^{13}C\text{-}\{^1H\}$, δ 260.2 (C_α), 228.5, 226.3, 219.3, 216.9 (CO), 146.1, 145.6 (C), 94.6 (C_5H_5), 92.5 (C_5H_5), 33.4 (Me) and 25.6 (Me): $m/z = 676$, $[M]^+$; 620, $[M - 2CO]^+$; and 592, $[M - 3CO]^+$.

Structure Determinations of Compounds **2**, **5** *and* **20**.—Many of the details of the structure analyses are listed in Table 4. X-Ray diffraction measurements were made at room temperature using Nicolet four-circle P3m diffractometers on single crystals mounted in thin-walled glass capillaries under N_2. Cell dimensions for the analyses were determined from the setting angle values of 23, 15 and 24 centred reflections respectively.

For each structure analysis, intensity data were collected for unique portions of reciprocal space and corrected for Lorentz, polarisation, crystal decay (negligible in each case) and long-term intensity fluctuations, on the basis of the intensities of three check reflections repeatedly measured during data collection. For compound **20**, only reflections with intensity above a low threshold were recorded for $2\theta > 40°$. Corrections for X-ray absorption effects were applied on the basis of the indexed crystal faces and dimensions for **5** and **20** and on the basis of azimuthal scan data for **2**. The structures were solved by heavy-atom (Patterson and Fourier difference) methods and refined by blocked-cascade least squares against F until shift/e.s.d. values were <0.1. All non-hydrogen atoms were assigned anisotropic displacement parameters. All hydrogen atoms were constrained to ideal geometries (with C–H 0.96 Å) and assigned isotropic displacement parameters; these were fixed and related to those of their attached carbon atoms. Final difference syntheses showed no chemically significant features, the largest being close to the metal atoms. Refinements converged smoothly to residuals given in Table 4. Tables 5–7 report the positional parameters for these structure determinations.

All calculations were made with programs of the SHELXTL [23] system as implemented on a Nicolet R3m/E structure determination system. Complex neutral-atom scattering factors were taken from ref. 24.

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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