Chemistry of Phosphido-bridged Dimolybdenum Complexes. Part 6.[1] The Insertion of Allene into Co-ordinated μ-Vinyl and η^3-Allyl Ligands; *X*-Ray Crystal Structures of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)\{\eta^3\text{-}CH_2C(CH_2)C(Me){=}CH_2\}(CO)_3]$ and $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^5\text{-}CH_2C(CH_2)C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)_2]$†

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Prolonged photolysis of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_4]$ in the presence of allene gives the new complexes $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^5\text{-}CH_2C(CH_2)C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)_2]$ and $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)\{\eta^3\text{-}CH_2C(CH_2)C(Me){=}CH_2\}(CO)_3]$ the structures of which in the solid state have been determined by single-crystal *X*-ray analyses. The former of these new complexes is also obtained in the reaction of the μ-vinyl complex $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)_3]$ with allene but not in the reaction of the isomeric η^3-allyl complex $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)(\eta^3\text{-}C_3H_5)(CO)_3]$ with allene. On the other hand the *syn*-methylallyl complex $[Mo(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)(\eta^3\text{-}syn\text{-}MeCHCH_2CH_2)(CO)_3]$ does react with allene to give a *ca.* 1:2 inseparable mixture of $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^5\text{-}CH_2C(CH_2)C(Me){=}CHMe\}(\mu\text{-}PMe_2)(CO)_2]$ and $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^5\text{-}CH_2C(CH_2)C(Et){=}CH_2\}(\mu\text{-}PMe_2)(CO)_2]$. These complexes may be obtained separately from reactions of the appropriate μ-vinyl complexes with allene. The mechanism of formation of the new complexes is discussed in the light of the above experimental results.

In previous papers we have described the reactions of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4]$ (**1**)[2,3] [R = Me, (**1a**); Ph, (**1b**)] with alkynes[4] and dienes[5] which lead to the synthesis of a number of dinuclear μ-vinyl and η^3-allyl complexes of molybdenum of the type $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-vinyl})(\mu\text{-}PR_2)(CO)_3]$ (**2**)[4,5] and $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PR_2)(\eta^3\text{-allyl})(CO)_3]$ (**3**)[5] (R = Me or Ph). The proposed structures of these complexes are shown in Figure 1, the structure for a complex of type (**2**) [μ-vinyl = μ-C(Me)=CHMe, R = Me] having been confirmed by *X*-ray analysis.[4] We now find that, on prolonged photolysis in the presence of excess of allene, the mixture of complexes $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)_3]$ (**2a**) and $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)(\eta^3\text{-}C_3H_5)(CO)_3]$ (**3a**) obtained in the initial reaction of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_4]$ (**1a**) with allene reacts further to give new products. In this paper we report the characterisation of these new products and our studies on the reactions of complexes of types (**2**) and (**3**) with allene, which we have undertaken in order to explore the mechanism of formation of the new species.

Results and Discussion

Prolonged Photolysis of Complex (**1a**) *with Excess of Allene.*—Reaction of complex (**1a**) with a *ca.* two-fold excess of allene for 4 h under photolysis (Hanovia 125-W medium-pressure immersion lamp) gave (**2a**) (22), (**3a**) (12), unreacted (**1a**) (60%), and traces of at least three other products.[5] We now find that prolonged photolysis of (**1a**) with a large excess of allene (saturated solution in benzene–hexane, 1:1) for 3 d results in a reduction in the yields of (**2a**) (7), (**3a**) (10), and unreacted (**1a**) (20%) and the appearance of two new orange complexes in 45 and 7% yield. These new major and minor products have been characterised on the basis of i.r. and ^1H n.m.r. spectroscopy, mass spectrometry, microanalysis, and *X*-ray structural studies (see below) as, respectively, $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^5\text{-}CH_2C(CH_2)C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)_2]$ (**4a**) and $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)\{\eta^3\text{-}CH_2C(CH_2)C(Me){=}CH_2\}(CO)_3]$ (**5a**) (Figure 1).

Crystals of (**4a**) and (**5a**) suitable for the *X*-ray studies were grown by slow evaporation of hexane–CH_2Cl_2 (1:1) solutions at 0 °C. The molecular structure of the minor product, (**5a**), is shown in Figure 2. Table 1 lists the atomic co-ordinates; selected bond lengths and interbond angles are given in Table 2. Complex (**5a**) crystallizes with the η^3-allyl ligand in the *exo* conformation relative to the cyclopentadienyl ligand on Mo(2). If the Mo–Mo bond is ignored, the ligands on Mo(2) adopt a similar geometry to that found in the mononuclear complex $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CO)_2]$.[6] Thus the four atoms P(1), C(21), and the two terminal allyl carbons C(1) and C(3) form the irregular base of an approximate square-pyramidal geometry. The Mo–C (terminal, allyl) bond distances of 2.315(8) and 2.309(7) Å are identical within error limits, hence implying that the bonding of the η^3-allyl ligand is normal and not of the σ–π type observed for the ligand in the asymmetric electronic environment of $[Mo(\eta\text{-}C_5H_5)I(\eta^3\text{-}C_3H_5)(NO)]$.[6] As in $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CO)_2]$,[6] the average Mo–C (terminal, allyl) bond length is significantly greater than the Mo–C (central, allyl) bond length of 2.261(7) Å, although the difference is less than in the mononuclear complex. The structure of the η^3-C_6H_9 ligand may be compared to that of the η^3-C_6H_8Cl ligand in $[\{Pd(\eta^3\text{-}C_6H_8Cl)\}_2]$,[7] which differs formally only in

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† μ-Carbonyl-1,1-dicarbonyl-1,2-bis(η-cyclopentadienyl)-μ-dimethylphosphido-2-(2′-isopropenylallyl-$C^{1'-3'}$)dimolybdenum (*Mo–Mo*) and μ-dimethylphosphido-μ-[2′-(isopropenyl-2$\kappa^2C^{1,2}$)allyl-1$\kappa(\eta^3)$]-bis-[carbonyl(η-cyclopentadienyl)molybdenum] (*Mo–Mo*).

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

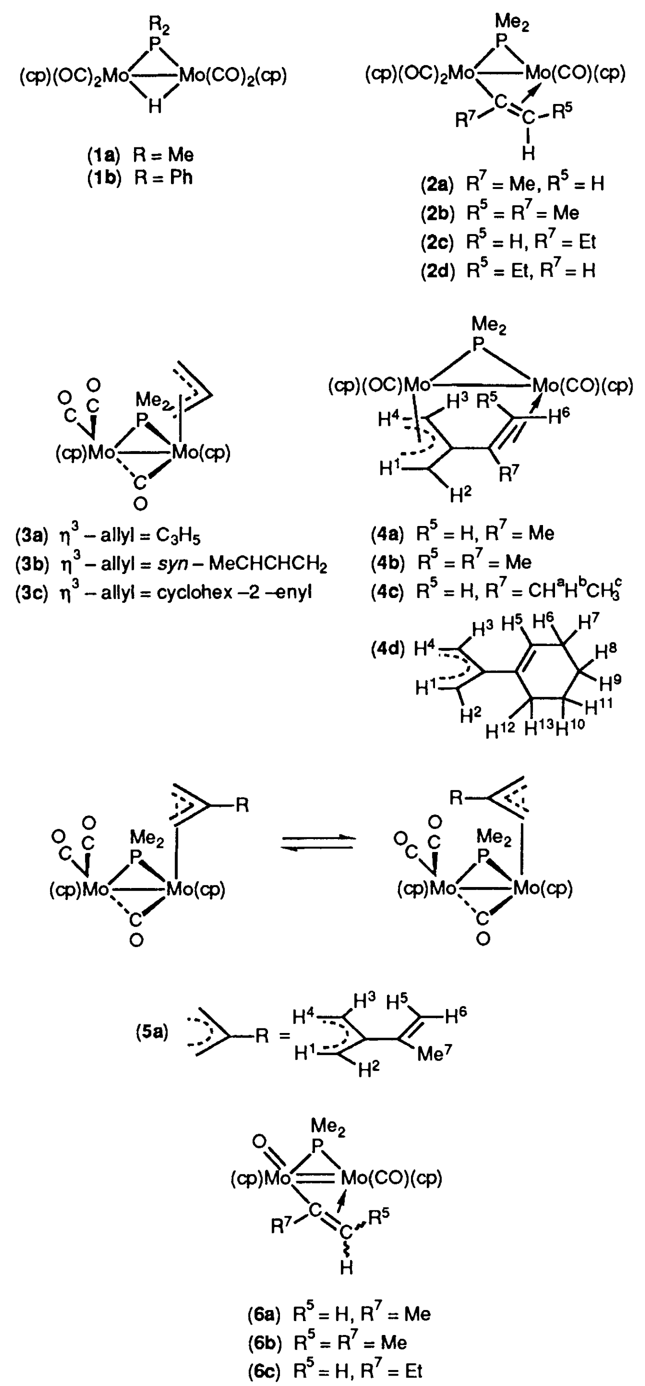


Figure 1. Structures of the dimolybdenum complexes (cp = η^5-C_5H_5)

the replacement of one of the ethyl hydrogens by chlorine. The dihedral angle between the planes containing C(1)–C(2)–C(3) and C(5)–C(4)–C(6) is *ca.* 8° in (**5a**) compared to 27° in the palladium compound, implying a greater element of electron delocalization over the two parts of the ligand in the former complex. The C=C double bond length in (**5a**), 1.336(14) Å, is, however, equal within error limits to the 1.38(6) Å for the corresponding bond in the palladium complex.

Complex (**5a**) has a semi-bridging carbonyl, CO(21), as evidenced by the Mo(2)–C(21)–O(21) interbond angle of 155.9(6)° and Mo–CO(21) distances of 1.963(7) and 2.629(7) Å for Mo(2) and Mo(1) respectively. The slightly shorter Mo(2)–P bond length of 2.408(2) Å, compared to 2.426(2) Å for Mo(1)–P, may reflect the reduced π-acid character of the η^3-allyl group compared to a carbonyl ligand, this then increasing the electron density available to Mo(2) for π-back bonding to phosphorus. The Mo–Mo bond length of 3.285(1) Å is slightly greater than that in $[Mo_2(\eta-C_5H_5)_2(\mu-H)(\mu-PMe_2)(CO)_4]$ (**1a**)[8] [3.267(1) Å] but is within the range normally observed for Mo–Mo single bonds.[9] The shorter Mo–P bonds and longer Mo–Mo bond in (**5a**) compared to complex (**1a**) result in a slightly larger bite angle at phosphorus of 85.6(1) compared to 84.8(1)°. The geometry of the ligands at Mo(1) is similar in both complexes except that in (**5a**) a μ-CO group replaces the μ-H group in (**1a**). In contrast to (**1a**), the two cyclopentadienyl ligands in (**5a**) adopt a relative *cis* orientation with respect to the Mo–Mo vector.

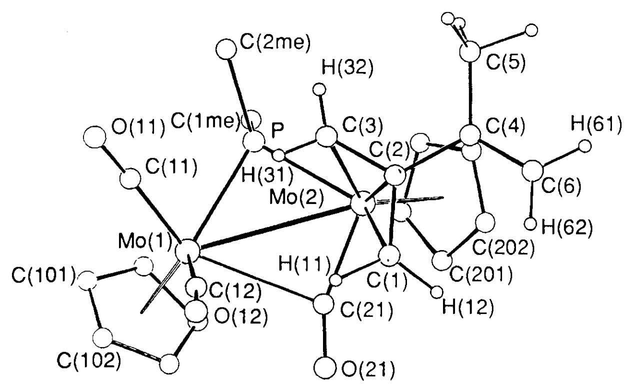


Figure 2. Molecular structure of $[Mo_2(\eta-C_5H_5)_2(\mu-PMe_2)\{\eta^3-CH_2C(CH_2)C(Me)=CH_2\}(CO)_3]$ (**5a**) showing the crystallographic numbering

The i.r. [ν(CO)] spectrum of complex (**5a**) is similar to those of other η^3-allyl complexes of type (**3**)[5] with two terminal carbonyl absorptions and a semi-bridging carbonyl absorption at 1 798 cm^{-1} as expected on the basis of the crystal structure. However, the ^{1}H n.m.r. spectrum of (**5a**) in $CDCl_3$ at 238 K indicates the presence in solution of two isomers in a ratio of *ca.* 1.1:1. Thus four cyclopentadienyl resonances are observed in addition to twelve resonances with relative intensity corresponding to one hydrogen each and two resonances corresponding to methyl groups. On the basis of a series of selective-decoupling experiments the resonances have been assigned to specific hydrogens in the C_6H_9 ligand in each of the two isomers. For each isomer, four resonances in the region δ 3.0 to −0.9 correspond to the *syn* and *anti* allyl hydrogens and two resonances in the range δ 5.3—4.6 correspond to the alkene hydrogens. The assignments are given in the Experimental section and the numbering scheme for the ligand hydrogen atoms is shown in Figure 1. Presumably one isomer corresponds to an *exo* configuration for the allyl ligand and the other to an *endo* configuration (Figure 1). It is not, however, possible to determine from the ^{1}H n.m.r. data which set of resonances corresponds to the *exo* isomer and which to the *endo*. Similar isomerism has been observed in other η^3-allyl complexes of type (**3**).[5]

The molecular structure of the major product (**4a**), from the reaction of (**1a**) with excess of allene is shown in Figure 3. Table 3 lists the atomic co-ordinates; selected bond lengths and interbond angles are given in Table 4. The C_6H_9 ligand bridges the Mo–Mo bond *via* coordination of the η^3-allyl group to Mo(2) and of the η^2-alkene group to Mo(1). The non-coplanarity of the η^3-allyl and the η^2-alkene groups, the dihedral angle between the two planes being 52.35°, contrasts strongly with the structure of the ligand in (**5a**) in which the corresponding angle is *ca.* 8°. However the similarity in C–C 'backbone' bond distances in the C_6H_9 ligand in (**4a**), 1.498(6) Å, and (**5a**), 1.494(12) Å, argues against any significant

Table 1. Fractional atomic co-ordinates for complex (**5a**)

Atom	*x*	*y*	*z*
Mo(1)	0.158 93(3)	0.290 53(7)	0.128 69(8)
Mo(2)	0.132 68(2)	−0.027 25(6)	0.058 76(7)
P	0.090 4(1)	0.141 7(2)	0.217 4(3)
C(1)	0.150 7(3)	−0.023 7(10)	−0.209 9(9)
C(2)	0.097 8(3)	−0.047 4(8)	−0.186 5(8)
C(3)	0.070 8(3)	0.057 1(8)	−0.113 5(9)
C(4)	0.072 4(3)	−0.176 9(9)	−0.231 3(10)
C(5)	0.016 9(4)	−0.191 5(13)	−0.183 1(13)
C(6)	0.095 3(4)	−0.270 1(11)	−0.321 5(13)
C(11)	0.098 6(3)	0.392 4(8)	0.067 3(13)
O(11)	0.063 6(3)	0.456 1(7)	0.026 5(12)
C(12)	0.167 8(4)	0.307 0(10)	−0.102 4(13)
O(12)	0.173 6(4)	0.326 4(10)	−0.232 2(9)
C(21)	0.199 7(3)	0.062 7(7)	0.031 4(9)
O(21)	0.244 2(2)	0.069 0(6)	0.008 6(7)
C(101)	0.185 0(4)	0.461 1(11)	0.300 7(13)
C(102)	0.220 7(4)	0.453 6(10)	0.184 6(15)
C(103)	0.244 8(4)	0.332 3(10)	0.192 8(15)
C(104)	0.225 1(4)	0.257 3(11)	0.316 6(14)
C(105)	0.186 1(5)	0.342 8(13)	0.389 7(11)
C(201)	0.188 2(3)	−0.187 9(8)	0.165 1(11)
C(202)	0.155 8(3)	−0.254 0(7)	0.057 1(12)
C(203)	0.105 8(3)	−0.246 0(8)	0.114 5(10)
C(204)	0.105 6(3)	−0.175 8(8)	0.257 6(9)
C(205)	0.157 9(3)	−0.137 6(8)	0.291 2(10)
C(1me)	0.088 6(4)	0.115 3(12)	0.434 6(11)
C(2me)	0.022 6(3)	0.186 1(11)	0.194 3(13)

Table 2. Selected bond lengths (Å) and angles (°) for complex (**5a**)*

Mo(1)–Mo(2)	3.285(1)	Mo(2)–P–Mo(1)	85.6(1)
Mo(1)–P	2.426(2)	C(2me)–P–C(1me)	96.7(5)
Mo(1)–C(11)	1.930(9)	C(2)–C(1)–Mo(2)	70.3(4)
Mo(1)–C(12)	1.965(11)	C(1)–C(2)–Mo(2)	74.0(4)
Mo(1)–C(21)	2.629(7)	C(3)–C(2)–Mo(2)	74.4(4)
Mo(2)–P	2.408(2)	C(3)–C(2)–C(1)	115.1(7)
Mo(2)–C(1)	2.309(7)	C(4)–C(2)–Mo(2)	118.8(5)
Mo(2)–C(2)	2.261(7)	C(4)–C(2)–C(1)	122.6(7)
Mo(2)–C(3)	2.315(8)	C(4)–C(2)–C(3)	122.3(7)
Mo(2)–C(21)	1.963(7)	C(2)–C(3)–Mo(2)	70.2(4)
P–C(1me)	1.847(10)	C(5)–C(4)–C(2)	115.9(8)
P–C(2me)	1.817(9)	C(6)–C(4)–C(2)	123.1(8)
C(1)–C(2)	1.402(10)	C(6)–C(4)–C(5)	120.7(9)
C(2)–C(3)	1.394(11)	O(11)–C(11)–Mo(1)	177.4(9)
C(2)–C(4)	1.494(12)	O(12)–C(12)–Mo(2)	175(1)
C(4)–C(5)	1.496(13)	Mo(2)–C(21)–Mo(1)	90.2(3)
C(4)–C(6)	1.336(14)	O(21)–C(21)–Mo(1)	113.6(5)
C(11)–O(11)	1.157(12)	O(21)–C(21)–Mo(2)	155.9(6)
C(12)–O(12)	1.119(13)		
C(21)–O(21)	1.167(8)		
Range Mo(1)–Cp	2.320(10)—2.363(10)		
Range Mo(2)–Cp	2.326(8)—2.339(8)		

* Cp = Cyclopentadienyl ring carbon atoms.

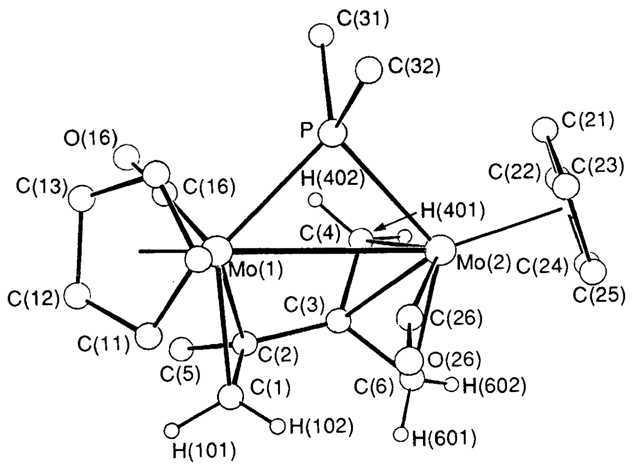


Figure 3. Molecular structure of $[Mo_2(\eta-C_5H_5)_2\{\mu-\eta^5-CH_2C(CH_2)C(Me)=CH_2\}(\mu-PMe_2)(CO)_2]$ (**4a**) showing the crystallographic numbering

difference in electron delocalisation between the allyl and alkene groups in the two complexes. Co-ordination of the alkene to Mo(1) results in an increase in the C=C double bond distance from 1.336(14) Å in (**5a**) to 1.384(6) Å in (**4a**) which may be rationalised on the basis of metal back bonding into the alkene π^* antibonding orbitals. Although the mean Mo–C (allyl, terminal) bond distance is only slightly reduced, at 2.296(5) Å in (**4a**) compared to 2.312(8) Å in (**5a**), the corresponding bond to the central allyl carbon is significantly longer in (**4a**), at 2.315(4) compared to 2.261(7) Å in (**5a**). The η^3-allyl group in (**4a**) is constrained, by the co-ordination of the alkene to the adjacent molybdenum centre, to adopt an *endo* conformation relative to the cyclopentadienyl group on Mo(2). The large separation of the central allyl carbon and Mo(2) may thus reflect the requirement of the alkene group to be in reasonable proximity to Mo(1).

Although overall the complex obeys the effective atomic number (e.a.n.) rule, Mo(1) is electron poor and Mo(2) is electron rich. The electron deficiency at Mo(1) may be partially compensated by the reduced Mo(1)–P bond distance of 2.392(1) Å compared to Mo(2)–P 2.421(1) Å. The lack of a significant semi-bridging carbonyl interaction in (**4a**) in comparison to (**5a**) may reflect the replacement of a carbonyl by an η^2-alkene on Mo(1) which, due to the reduced π-acid character of the alkene, results in an increase in the electron density at Mo(1). However, at least equally important in hindering a semi-bridging carbonyl interaction is the steric crowding at Mo(1). The non-linearity of CO(26) [Mo(2)–C(26)–O(26) interbond angle 167.1(4)°] may reflect the steric crowding in the molecule; the large Mo(1)–CO(26) separation of 3.00 Å indicates that there is no significant bonding interaction. The two cyclopentadienyl ligands adopt an approximate relative *cis* orientation with respect to to the Mo–Mo vector.

The Mo–Mo bond distance, 3.333(1) Å in (**4a**) is significantly longer than in (**5a**), 3.285(1) Å, although it is still consistent with the presence of a Mo–Mo single bond. The longer Mo–Mo bond may reflect an attempt to reduce the steric crowding in the molecule. The slightly reduced average Mo–P bond distance, together with the increased Mo–Mo distance, result in an increased bite angle at phosphorus of 87.7(1) compared to 85.6(1) in (**5a**).

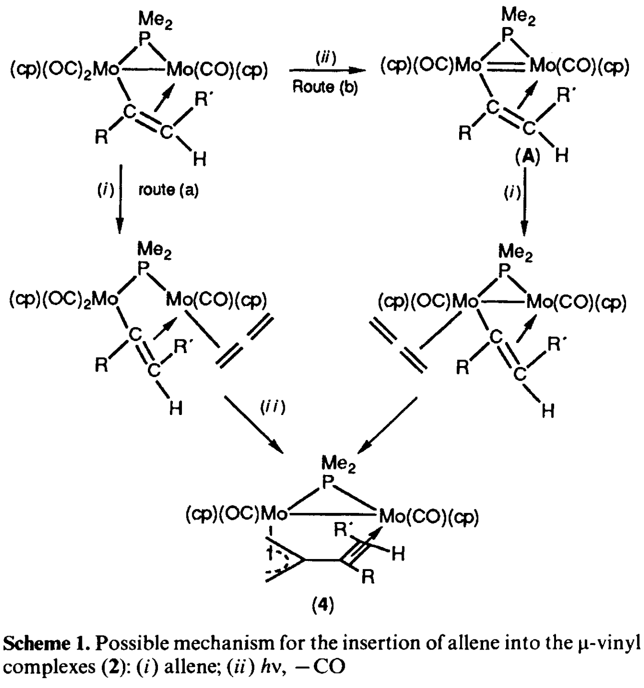
Spectroscopic studies indicate that the solid-state structure of complex (**4a**) is retained in solution. Thus two carbonyl absorption bands are observed in the i.r. [ν(CO)] spectrum and the ^1H n.m.r. spectrum contains six resonances of relative intensity 1 and one of relative intensity 3 in the range δ 3.0—1.0 corresponding to the hydrogens in the C_6H_9 ligand. The assignment of the complex ^1H n.m.r. spectrum of the C_6H_9 ligand has been confirmed by a series of selective-decoupling experiments. The numbering scheme for the ligand hydrogen atoms is shown in Figure 1. The upfield chemical shifts of the two alkene hydrogens, δ 1.84 (H^5) and 1.73 (H^6), imply that the

Table 3. Fractional atomic co-ordinates for complex (**4a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	0.337 28(3)	0.146 51(2)	0.184 06(2)	C(26)	0.281 7(5)	0.077 8(2)	0.393 8(3)
Mo(2)	0.169 59(3)	0.005 30(2)	0.297 59(2)	O(26)	0.345 2(4)	0.111 4(2)	0.466 6(2)
P	0.370 26(11)	0.011 64(5)	0.188 91(8)	C(11)	0.465 3(5)	0.246 4(3)	0.277 8(4)
C(1)	0.150 4(5)	0.213 0(3)	0.241 8(4)	C(12)	0.453 9(5)	0.260 4(2)	0.166 6(4)
C(2)	0.077 3(4)	0.166 0(2)	0.163 1(3)	C(13)	0.537 2(5)	0.205 6(3)	0.121 1(4)
C(3)	0.016 9(4)	0.091 7(2)	0.196 2(3)	C(14)	0.599 8(5)	0.157 1(3)	0.201 5(5)
C(4)	0.021 4(5)	0.025 4(3)	0.135 5(3)	C(15)	0.557 4(5)	0.181 7(3)	0.298 8(4)
C(31)	0.354 7(6)	−0.049 1(3)	0.068 1(4)	C(21)	0.229 5(5)	−0.124 0(2)	0.304 2(4)
C(32)	0.547 2(5)	−0.025 1(3)	0.258 4(5)	C(22)	0.074 6(6)	−0.120 4(3)	0.286 0(4)
C(6)	−0.033 1(5)	0.082 6(3)	0.297 2(4)	C(23)	0.278 9(6)	−0.090 2(3)	0.404 5(4)
C(5)	−0.009 1(6)	0.199 7(3)	0.061 7(4)	C(24)	0.025 0(6)	−0.084 8(3)	0.374 0(5)
C(36)	0.266 5(4)	0.132 2(2)	0.034 5(3)	C(25)	0.150 5(7)	−0.065 6(3)	0.447 8(4)
O(16)	0.236 1(3)	0.127 7(2)	−0.058 9(2)				

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

Mo(1)–Mo(2)	3.333(1)	Mo(2)–P–Mo(1)	87.7(1)
Mo(1)–P	2.392(1)	C(32)–P–C(31)	98.6(3)
Mo(1)–C(16)	1.913(4)	C(2)–C(1)–Mo(1)	76.6(3)
Mo(1)–C(1)	2.258(5)	C(1)–C(2)–Mo(1)	68.6(2)
Mo(1)–C(2)	2.360(4)	C(3)–C(2)–Mo(1)	103.9(2)
Mo(2)–P	2.421(1)	C(3)–C(2)–C(1)	118.8(4)
Mo(2)–C(3)	2.315(4)	C(5)–C(2)–Mo(1)	122.8(3)
Mo(2)–C(4)	2.303(4)	C(5)–C(2)–C(1)	120.3(4)
Mo(2)–C(6)	2.285(5)	C(5)–C(2)–C(3)	114.0(3)
Mo(2)–C(26)	1.943(4)	C(2)–C(3)–Mo(2)	120.7(2)
P–C(31)	1.843(5)	C(4)–C(3)–Mo(2)	71.9(2)
P–C(32)	1.834(5)	C(4)–C(3)–C(2)	122.6(4)
C(1)–C(2)	1.384(6)	C(6)–C(3)–Mo(2)	71.0(2)
C(2)–C(3)	1.498(6)	C(6)–C(3)–C(2)	121.5(4)
C(3)–C(4)	1.396(6)	C(6)–C(3)–C(4)	115.5(4)
C(3)–C(6)	1.412(6)	C(3)–C(4)–Mo(2)	72.9(2)
C(16)–O(16)	1.169(5)	C(3)–C(6)–Mo(2)	73.3(2)
C(26)–O(26)	1.170(5)	O(16)–C(16)–Mo(1)	172.9(3)
Range Mo(1)–Cp	2.290(4)—2.375(5)	O(26)–C(26)–Mo(2)	167.1(4)
Range Mo(2)–Cp	2.286(5)—2.371(5)		



Scheme 1. Possible mechanism for the insertion of allene into the μ-vinyl complexes (**2**): (*i*) allene; (*ii*) *hν*, −CO

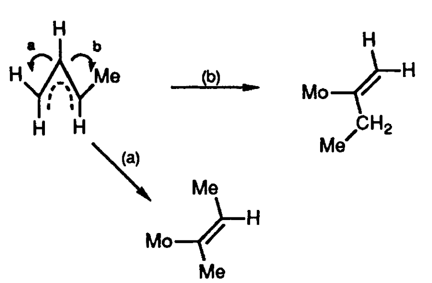
alkene remains co-ordinated to the Mo in solution. The ^{13}C n.m.r. spectrum of (**4a**) which contains six resonances in the range δ 100—20 due to the C_6H_9 ligand, assigned on the basis of ^{13}C–^{1}H coupling constants, is also consistent with the retention of the solid-state structure in solution.

The formation of (**4a**) and (**5a**) from the reaction of (**1a**) with excess of allene could proceed either *via* the μ-vinyl complex (**2a**) or *via* the allyl complex (**3a**), which are both formed initially. In order to determine the reaction pathway which is followed we have investigated separately the reactions of the μ-vinyl complexes (**2**) and the allyl complexes (**3**) with allene.

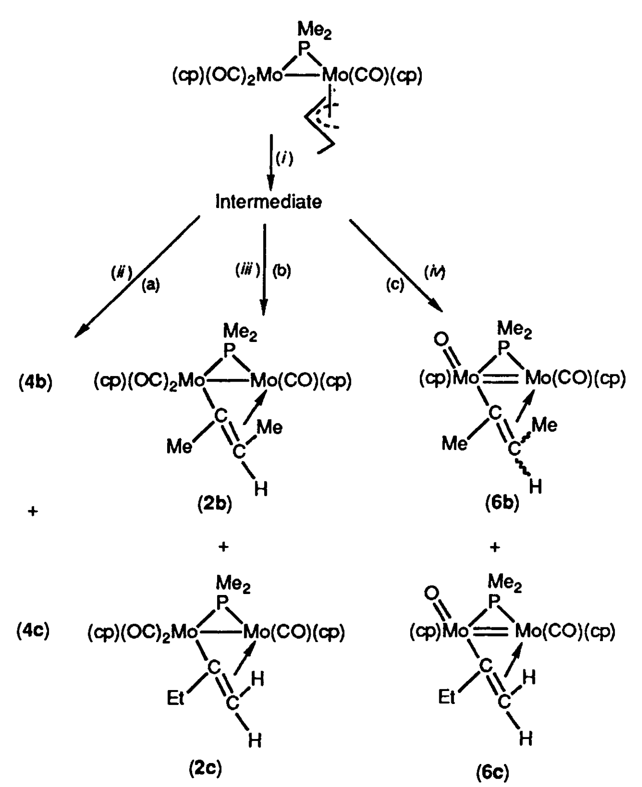
Reaction of the Vinyl Complexes (**2**) *with Allene*.—Photolysis of an allene-saturated hexane solution of complex (**2a**) for 1.5 h gave (**4a**) in high yield (68%) as the only significant product. Photolysis of the dimolybdenum μ-vinyl complexes $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(R^7){=}CHR^5\}(\mu\text{-}PMe_2)(CO)_3]$ [$R^5 = R^7 =$ Me, (**2b**); $R^5 =$ H, $R^7 =$ Et, (**2c**)] with allene similarly gave $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^5\text{-}CH_2C(CH_2)C(R^7)\text{-}CHR^5\}(\mu\text{-}PMe_2)(CO)_2]$ [$R^5 = R^7 =$ Me, (**4b**); $R^5 =$ H, $R^7 =$ Et, (**4c**)]. The proposed structures of (**4a**)—(**4c**) (Figure 1) are based on i.r. and ^{1}H n.m.r. spectroscopy, mass spectrometry, and, in the case of (**4a**) and (**4c**), microanalysis. Complex (**4b**) is always obtained contaminated with other unidentified products and it has not proved possible to identify resonances in the ^{1}H n.m.r. spectrum of (**4b**) associated with all of the hydrogens in the C_7H_{11} bridging ligand. It has been assumed in Figure 1 that the two methyl groups on the alkene part of the ligand in (**4b**) adopt the same relative *trans* orientation as in the μ-vinyl complex, (**2b**), from which it is derived, although the ^{1}H n.m.r. spectrum does not prove this.

It is clear, from the positioning of the alkyl substituents in the complexes (**4b**) and (**4c**), that the η^2-alkene part of the bridging organic ligand in the complexes (**4**) is derived in the above reaction from the μ-vinyl ligand in the complexes (**2**). The overall process by which the complexes (**4**) are obtained from the μ-vinyl complexes (**2**) may therefore be described as an insertion of allene into the Mo–C σ bond. Related insertion reactions of allene in which carbon–carbon bond formation involving the central carbon atom of the allene molecule takes place have been described previously.[10,11]

Two possible mechanisms for the insertion of allene are shown in Scheme 1. These differ according to whether co-ordination of allene takes place before [route (a)] or after [route (b)] the loss of CO induced by u.v. irradiation. Stirring a hexane solution of complex (**2a**) with allene in the dark results in no change in the i.r. spectrum. There is therefore no evidence for the formation of an adduct as proposed for route (a). However, u.v. irradiation of a solution of (**2a**) in the absence of allene results in a rapid colour change from orange to orange-green. Subsequent



Scheme 2. 1,2-Hydrogen shift in the allyl ligand in complex (**3b**) required to give (a) (**2b**) and (b) (**2c**)



Scheme 3. Reactions of the intermediate obtained on irradiation of the η^3-allyl complex (**3b**): (*i*) *hv*; (*ii*) allene; (*iii*) CO; (*iv*) no CO or allene

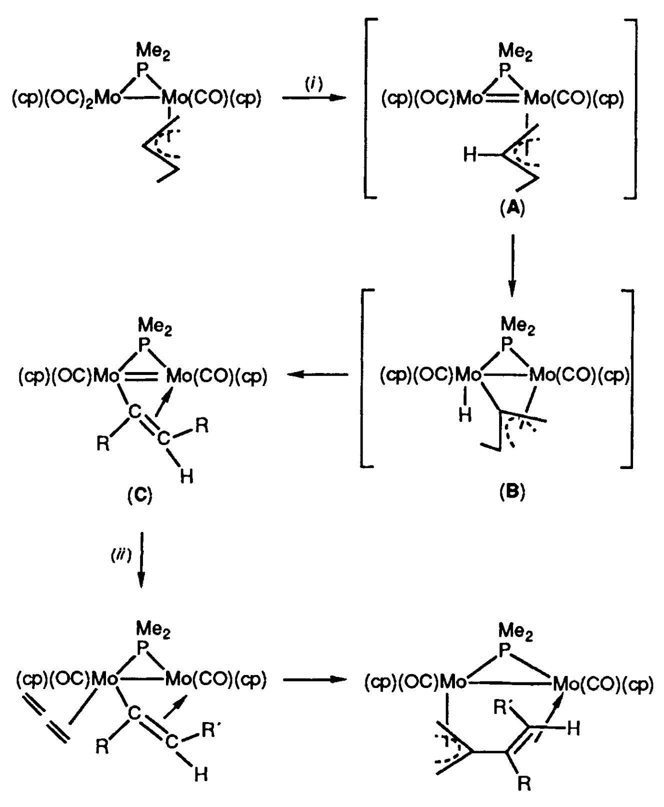
stirring of the irradiated solution in the dark with allene gives (**4a**) in *ca.* 20% yield. If no allene is added the only product isolated from the irradiated solution is a trace of the red μ-vinyl oxo complex $[Mo_2O(\eta\text{-}C_5H_5)_2\{\mu\text{-}\sigma:\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)]$ (**6a**).[4] The structure proposed for intermediate (**A**) in Scheme 1, route (b), is closely related to that of $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2(CO)_2]$,[12a] which also contains an Mo–Mo double bond. We cannot, however, exclude the possibility that CO loss from (**2a**) is accompanied by co-ordination of a solvent molecule rather than an increase in the metal–metal bond order. The fact that (**A**) reacts rapidly with allene suggests that it is the likely intermediate. Further evidence that the intermediate is an unsaturated complex formed by loss of CO is provided by the fact that stirring of the irradiated solution with CO enables some (**2a**) to be recovered which is not the case if CO is absent. It thus appears that the loss of CO from (**2a**) on irradiation may be reversible. Once allene has reacted with (**A**) insertion presumably occurs rapidly as no simple allene adduct may be isolated.

Nubel and Brown[12b] have shown that the first step in the insertion reaction of ethene with the μ-vinyl complex $[Re_2(\mu\text{-}H)\{\mu\text{-}\sigma:\eta^2\text{-}C(H){=}CH_2\}(CO)_8]$, involves photochemical loss of CO and formation of an ethene adduct. There is therefore some precedent for the formation of the allene adduct in route (b). It is noteworthy that the yields of the allene insertion products, (**4**) decrease for the μ-vinyl complexes, (**2a**), (*ca.* 70% conversion) > (**2c**) (*ca.* 50%) > (**2b**) (*ca.* 30%). Thus (**2c**), with an α-ethyl substituent on the μ-vinyl ligand, gives a lower yield of insertion product than that of the α-methyl complex, (**2a**). Complex (**2b**), with methyl substituents on the α- and β-carbon atoms, gives a lower yield still and $[Mo_2(C_5H_5)_2\{\mu\text{-}\sigma:\eta^2\text{-}C(H){=}CHEt\}(\mu\text{-}PMe_2)(CO)_3]$, which was also present in the reaction mixture when (**2c**) was treated with allene, does not give an insertion product at all. The dependence of the yield of the complexes (**4**) on the steric bulk of the μ-vinyl substituents, particularly the β-alkyl groups, may be a result of steric crowding in the allene adduct in route (b).

Reaction of the Allyl Complexes (**3**) *with Allene*.—The unsubstituted allyl complex $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)(\eta^3\text{-}C_3H_5)(CO)_3]$ (**3a**) does not react with allene even after prolonged periods of u.v. irradiation. Thus (**2a**) rather than (**3a**) is the precursor of (**4a**) in the reaction of (**1a**) with excess of allene. On the other hand the methyl allyl complex $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)(\eta^3\text{-}syn\text{-}MeCHCHCH_2)(CO)_3]$ (**3b**)[5] *does* react with allene under photolysis to give an inseparable mixture (*ca.* 1:2) of the two complexes (**4b**) and (**4c**). These complexes may, of course, be obtained separately from, respectively, the reactions of the μ-vinyl complexes (**2b**) and (**2c**) with allene. The most likely explanation for the formation of (**4b**) and (**4c**) in the reaction of (**3b**) with allene is that the allyl ligand in (**3b**) undergoes an initial 1,2-hydrogen atom shift to give a mixture of (**2b**) and (**2c**) (Scheme 2) which then reacts with allene as previously described. This explanation has been confirmed by a number of experiments. Thus u.v. irradiation of a solution of complex (**3b**) results in a colour change from red to red-green. On stirring the irradiated solution with allene in the dark a mixture of (**4b**) and (**4c**) is formed in *ca.* 50% yield. Similar treatment of the irradiated solution with CO for 1 h, followed by stirring with allene, gives the μ-vinyl complexes (**2b**) and (**2c**) in *ca.* 30% combined yield with only traces of (**4b**), (**4c**), and other unidentified products. Under similar conditions, but using N_2 rather than CO, (**2b**) and (**2c**) are formed with a lower combined yield (*ca.* 10%); in addition the complexes $[Mo_2O(\eta\text{-}C_5H_5)_2\{\mu\text{-}C(R^7){=}CHR^5\}(\mu\text{-}PMe_2)(CO)]^4$ $[R^5 = R^7 = Me$, (**6b**); $R^7 = Et$, $R^5 = H$, (**6c**)] (*ca.* 20% combined yield) and traces of other unidentified species are obtained. From these results it is clear that u.v. irradiation of (**3b**) gives an unstable intermediate which may participate in three competing reactions (Scheme 3): (a) with allene to give (**4b**) and (**4c**); (b) with CO to give (**2b**) and (**2c**); and (c) with air in the absence of allene or CO, to give (**6b**) and (**6c**).

Any mechanism proposed to explain the reaction of complex (**3b**) with allene must account for the overall 1,2-hydrogen atom shift and the C–C bond formation in the reaction. The latter may occur *via* insertion of allene into a Mo–C σ bond as proposed for the reaction of allene with the μ-vinyl complexes. It is proposed (Scheme 4) that u.v. irradiation of (**3b**) induces CO loss from the molybdenum atom adjacent to the one to which the allyl ligand is co-ordinated giving a co-ordinatively unsaturated intermediate (**A**). Carbon–hydrogen bond cleavage, perhaps *via* an initial CHMo agostic interaction, gives (**B**) and readdition of the hydride to one or other of the two terminal allyl carbon atoms then gives two isomers of an unsaturated μ-vinyl intermediate, (**C**), similar to that proposed to be formed on u.v. irradiation of the μ-vinyl complexes (**2**). Addition of allene and insertion into the Mo–C σ-bond then proceeds as previously described.

Hydrogen-shift processes similar to the one described here have been observed previously in the rearrangement of μ-allylidene to μ-alkyne ligands at a dimolybdenum centre, and a



(4b) R = R' = Me
(4c) R = Et, R' = H

Scheme 4. Possible mechanism for the formation of complexes (**4b**) and (**4c**) from the η^3-allyl complex (**3b**); (*i*) *h*ν, −CO; (*ii*) allene

similar mechanism was postulated to account for the phenomenon.[13] In addition, the bridging $\sigma:\eta^3$-allyl ligand in the co-ordinatively unsaturated intermediate, (**B**), in Scheme 4 has been previously observed in stable di-iron complexes such as $[Fe_2(\mu\text{-}\sigma:\eta^3\text{-}C_3H_4)(CO)_7]$.[14] Finally, intramolecular attack of a metal hydride on an η^3-allyl ligand has been previously postulated to account for the variable-temperature ^1H n.m.r. behaviour of $[Mo(\eta^3\text{-}C_3H_5)(Ph_2PCH_2CH_2PPh_2)_2H]$.[15]

An alternative route to complexes (**4b**) and (**4c**) to that shown in Scheme 4 is the insertion of allene into the Mo–C σ bond in intermediate (**B**) prior to readdition of the hydride ligand. We cannot exclude this possibility but the formation of the unsaturated μ-vinyl intermediate (**C**), which is also proposed as an intermediate in the reaction of the μ-vinyl complexes (**2**) with allene, is perhaps in this case also the most likely route to (**4**).

The conversion of a σ-vinyl ligand into an η^3-allyl ligand has been proposed previously as part of the mechanism by which attack of H^- on a cationic molybdenum alkyne complex affords an allyl species.[16,17] That the reverse reaction, as observed in the dimolybdenum system described here, has not been previously documented can be ascribed to the fact that most known allyl complexes are mononuclear. Presumably the isomerisation of an allyl to a vinyl ligand requires the driving force provided by the presence of a second metal centre, which then enables the vinyl ligand to co-ordinate in a bridging 'σ,π' mode. Why this isomerisation takes place for the η^3-C_4H_7 ligand in (**3b**) [and for the η^3-C_6H_9 (cyclohex-2-enyl) ligand in (**3c**),[4] see Experimental section] but not for the η^3-C_3H_5 ligand in (**3a**) remains to be resolved.

Interconversion of Complexes (**4a**) *and* (**5a**). The mechanism of formation of complex (**4a**) from (**2a**) (Scheme 1) assumes that (**5a**), which contains an extra molecule of CO in place of the co-ordinated double bond in (**4a**), is not the initial product of the reaction. Although (**5a**) may be converted into (**4a**) on u.v. irradiation, the low conversion factor for this reaction is incompatible with it being on the primary route to (**4a**), since this latter complex is generated in *ca.* 70% conversion on reaction of (**2a**) with allene. Furthermore no (**5a**) is formed on reaction of (**2a**) with allene. However, although no reaction is observed between complex (**4a**) and CO under pressure [60 atm (*ca.* 6 × 10^6 Pa), room temperature (r.t.)], u.v. irradiation of a solution of (**4a**) under CO rapidly gives an equilibrium mixture of (**4a**) and (**5a**) in the ratio *ca.* 1:4. The most likely explanation of the formation of (**5a**) on reaction of (**1a**) with allene is therefore *via* the reaction of (**4a**) with scavenged CO under u.v. irradiation. The formation of (**4a**) involves loss of two molecules of CO from (**1a**) and the solution concentration of CO is clearly sufficient to give a significant yield of (**5a**) from (**4a**).

Experimental

General techniques and instrumentation were as described in Part 1 of this series.[3] The complex $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_4]$ was prepared by the literature method.[2] All other chemicals were obtained from commercial suppliers and used without further purification. I.r. spectra were recorded in n-hexane and all n.m.r. spectra in $CDCl_3$ unless otherwise stated. N.m.r. chemical shifts are in p.p.m. on the δ scale relative to $SiMe_4$ (0 p.p.m.) (for ^1H and ^{13}C) or to $P(OMe)_3$ for ^{31}P (upfield shifts negative).

(*i*) *Prolonged Photolysis of* $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_4]$ (**1a**) *with Excess of Allene.*—Complex (**1a**) (0.2 g, 0.4 mmol) was dissolved in hexane–benzene (1:1, 60 cm^3) and the solution saturated with allene in a glass photolysis vessel. A quartz vessel containing the u.v. filament was placed in the vessel and the solution irradiated with u.v. light (Hanovia 125-W medium-pressure immersion lamp) for 3 d. The solvent was removed on a rotary evaporator and the residue column chromatographed using hexane–CH_2Cl_2 (1:1) as eluant to separate unreacted (**1a**) (0.04 g, 20%). The remaining products were separated by t.l.c. using hexane–ethyl acetate (9:1) as eluant to give (in order of elution, decreasing R_f values) red $[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}\eta^5\text{-}CH_2C(CH_2)C(Me)\text{=}CH_2\}(\mu\text{-}PMe_2)(CO)_2]$ (**4a**) (0.095 g, 45%), orange $[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}PMe_2)\{\eta^3\text{-}CH_2C(CH_2)C(Me)\text{=}CH_2\}(CO)_3]$ (**5a**) (0.015 g, 7%), (**2a**) (0.015 g, 7%),[5] and (**3a**) (0.02 g, 10%).[5]

Complex (**4a**) (Found: C, 46.4; H, 4.9; P, 5.2. $C_{20}H_{25}Mo_2O_2P$ requires C, 46.2; H, 4.8; P, 6.0%); *m*/*z* 520 (M^+), $M^+ - n$CO (*n* = 0—2); $\nu_{max.}$(CO) at 1 854s and 1 829s cm^{-1}. N.m.r.: ^1H (303 K), δ 4.93 (s, 5 H, C_5H_5), 4.78 (s, 5 H, C_5H_5), 2.48 [m, $J(H^1H^3)$ 0.5, H^3], 2.37 (s, 3 H, Me^7), 1.84 [dd, $^3J(PH)$ 14, $J(H^5H^6)$ 3.7, 1 H, H^5], 1.80 [d, $^2J(PH)$ 9.2, 3 H, PMe^AMe^B], 1.73 (d, 1 H, H^6), 1.58 [d, $^2J(PH)$ 9.2, 3 H, PMe^AMe^B], 1.44 [m, J_{12} 1.7, J_{24} 0.5, 1 H, H^2], 1.41 [m, $^3J(PH)$ 3.9, 1 H, H^1], 0.99 [dd, $^3J(PH)$ 2.6, 1 H, H^4]; ^{13}C (243 K, ^1H gated decoupled), δ 250.2 [d, $^2J(PC)$ 15.5, 1 CO], 244.4 [d, $^2J(PC)$ 9.0, 1CO], 99.9, 73.9 [s, $CH_2C(CH_2)C(Me)CH_2$], 92.7 [d, $J(CH)$ 176.7, C_5H_5], 89.1 [d, $J(CH)$ 177.0, C_5H_5], 45.4 [t, $J(CH)$ 152.2, $CH_2C(CH_2)C(Me)CH_2$ or $CH_2C(CH_2)C(Me)CH_2$], 37.6 [t, $J(CH)$ 154.6, $CH_2C(CH_2)C(Me)CH_2$ or $CH_2C(CH_2)C(Me)CH_2$], 31.8 [q, $J(CH)$ 128.2, $CH_2C(CH_2)C(Me)CH_2$], 28.6 [qd, $J(CH)$ 128.2, $^2J(PC)$ 21.9, PMe^AMe^B], 23.6 [t, $J(CH)$ 160.9, $CH_2C(CH_2)C(Me)CH_2$], and 21.7 p.p.m. [qd, $J(CH)$ 127.6, $^2J(PC)$ 19.1 Hz, PMe^AMe^B]; ^{31}P (263 K), δ −25.2 (s, μ-PPh_2).

Complex (**5a**): *m*/*z* 548 (M^+), $M^+ - n$CO (*n* = 0—3); $\nu_{max.}$(CO) at 1 935s, 1 865s, and 1 798 m cm^{-1}. ^1H N.m.r. (238 K): rotamer 1 (52%), δ 5.25 [m, $J(H^5H^6)$ 1.6, 1 H, H^5], 5.09 (s, 5 H, C$_5$H$_5$), 4.68 [m, J(H^{6}H^7) 0.5, 1 H, H^6], 4.56 (s, 5 H, C$_5$H$_5$), 3.01 [m, J(H^{1}H^2) 4.5, J(H^{2}H^3) 2.5, 1 H, H^2], 2.25 [dd, ^3J(PH) 10.8, 1 H, H^1], 2.1—1.9 (m, 6 H, PMe$_2$), 1.78 (m, 3 H, Me^7), 0.91 (m, 1 H, H^3), and −0.68 [m, ^3J(PH) 5, 1 H, H^4]; rotamer 2 (48%), 5.20 (s, 5 H, C$_5$H$_5$), 5.09 [m, J(H^{5}H^6) 1.6, J(H^{5}H^7) 0.5, 1 H, H^5], 4.70 [m, J(H^{6}H^7) 0.5, 1 H, H^6], 4.69 (s, 5 H, C$_5$H$_5$), 2.88 [m, J(H^{1}H^2) 3.4, J(H^{2}H^3) 2.8, 1 H, H^2], 2.1—1.9 (m, 6H, PMe$_2$), 2.01 (obscured, H^1), 1.67 (m, 3 H, Me^7), 1.16 (m, 1 H, H^3), and −0.89 [d, ^3J(PH) 10.3 Hz, 1 H, H^4].

(*ii*) *Reaction of the Vinyl Complex* (**2a**) *with Allene.*—The complex [Mo$_2$(η-C$_5$H$_5$)$_2${μ-σ:η^2-C(Me)=CH$_2$}(μ-PMe$_2$)(CO)$_3$] (**2a**)^3 (0.02 g, 0.039 mmol) was dissolved in hexane (30 cm^3) and the solution saturated with allene. After u.v. irradiation for 1.5 h the solvent was removed on a rotary evaporator and the residue separated by t.l.c. Elution with hexane–ethyl acetate (9:1) gave (**4a**) (0.014 g, 68%) as the only significant product.

(*iii*) *Photolysis of Complex* (**2a**) *followed by Allene Addition.*—Complex (**2a**) (0.01 g, 0.02 mmol) was dissolved in hexane (15 cm^3) and irradiated with u.v. light for 1.5 h to give an orange-green solution. The solution was then saturated with allene and stirred in the dark for 1.5 h to give, after t.l.c. separation, (**4a**) (0.002 g, 19%) and a trace of the vinyl oxo complex [Mo$_2$O(η-C$_5$H$_5$)$_2${μ-σ:η^2-C(Me)=CH$_2$}(μ-PMe$_2$)(CO)] (**6a**)^4 (identified by mass spectrometry and i.r. spectroscopy). In a variation of the above reaction the same irradiated solution was treated with CO instead of allene, to give (**2a**) (0.002 g) and a trace of the vinyl oxo complex. In another reaction the same irradiated solution was stirred under N$_2$ for 1.5 h to give, after t.l.c. separation, a trace of the vinyl oxo complex (0.001 g) as the only significant product.

(*iv*) *Reaction of the Vinyl Complex* [Mo$_2$(η-C$_5$H$_5$)$_2${μ-σ:η^2-C(Me)=CHMe}(μ-PMe$_2$)(CO)$_3$] (**2b**) *with Allene.*—Complex (**2b**) (0.01 g, 0.02 mmol) and allene were treated as in (*ii*) above to give orange [Mo$_2$(η-C$_5$H$_5$)$_2${μ-σ:η^5-CH$_2$C(CH$_2$)C(Me)-CHMe}(μ-PMe$_2$)(CO)$_2$] (**4b**) (0.003 g, 30%) and [Mo$_2$O-(η-C$_5$H$_5$)$_2${μ-σ:η^2-C(Me)=CHMe}(μ-PMe$_2$)(CO)] (**6b**)^4 (0.001 g). Complex (**4b**): m/z 534 (M^+), $M^+ - n$CO (n = 0—2); $\nu_{\text{max.}}$(CO) 1 851s and 1 829s cm^{-1}. ^{1}H N.m.r. (303 K): δ 4.79 (m, 10 H, C$_5$H$_5$), 2.98 [q, J(H^{5}H^6) 6.4, 1 H, H^6], 2.66 (s, 1 H, H^3), 2.30 (s, 3 H, Me^7), 1.77 [d, ^2J(PH) 9.2, 3 H, P*Me*^{A}Me^B], 1.55 [d, ^2J(PH) 9.0 Hz, 3 H, PMe^A*Me*^{B}], and 1.33 (d, 3 H, Me^5).

(*v*) *Reaction of the Vinyl Complex* [Mo$_2$(η-C$_5$H$_5$)$_2${μ-σ:η^2-C(Et)=CH$_2$}(μ-PMe$_2$)(CO)$_3$] (**2c**) *with Allene.*—Complex (**2c**) was only available as a 5:1 mixture with [Mo$_2$(η-C$_5$H$_5$)$_2$-{μ-σ:η^2-C(H)=CHEt}(μ-PMe$_2$)(CO)$_3$] (**2d**).^{4} A solution of (**2c**)/(**2d**) (0.02 g, 0.04 mmol) in hexane (30 cm^3) was treated with allene as in (*ii*) above to give (**4c**) (0.008 g, 40%) and unreacted (**2d**) (0.002 g). Irradiation of 0.01 g of the mixture of (**2c**) and (**2d**) in the absence of allene gave, on t.l.c. separation, (**2d**) (0.001 g) and [Mo$_2$O(η-C$_5$H$_5$)$_2${μ-σ:η^2-C(Et)=CH$_2$}(μ-PMe$_2$)(CO)] (**6c**)^4 (0.001 g) as the only products. Complex (**4c**) (Found: C, 47.4; H, 5.2. C$_{21}$H$_{27}$Mo$_2$O$_2$P requires C, 47.3; H, 4.9%): m/z 534 (M^+), $M^+ - n$CO (n = 0—2); $\nu_{\text{max.}}$(CO) at 1 854s and 1 829s cm^{-1}. ^{1}H N.m.r. (303 K): δ 4.92 (s, 5 H, C$_5$H$_5$), 4.78 [d, ^3J(PH) 0.5, 5 H, C$_5$H$_5$], 3.01 (dq, J_{ab} 13.8, J_{ac} 7.3, 1 H^a), 2.43 [m, J(H^{3}H^4) 0.5, 1 H, H^3], 1.95 (dq, J_{bc} 7.3, 1 H, H^b), 1.83 [dd, ^3J(PH) 11.1, J_{56} 3.6, 1 H, H^6], 1.81 [d, ^2J(PH) 9.2, 3 H, P*Me*^{A}Me^B], 1.72 (d, 1 H, H^5), 1.59 [d, ^2J(PH) 9.2, 3 H, PMe^A*Me*^{B}], 1.43 (s, 1 H, H^2), 1.42 [d, ^3J(PH) 3.2, 1 H, H^1], 1.28 (t, 3 H, Me^c), and 1.02 [d, ^3J(PH) 2.7, 1 H, H^4].

(*vi*) *Reaction of the* η^3-*Allyl Complex* [Mo$_2$(η-C$_5$H$_5$)$_2$-(μ-PMe$_2$)(η^3-C$_3$H$_5$)(CO)$_3$] (**3a**) *with Allene.*—Complex (**3a**) (0.005 g, 0.01 mmol) was dissolved in hexane–benzene (10 cm^3:2 cm^3) and the solution saturated with allene. Irradiation with u.v. light for 1 h gave (**3a**) (0.003 g) as the only significant product on t.l.c. separation.

(*vii*) *Reaction of the* η^3-*Allyl Complex* [Mo$_2$(η-C$_5$H$_5$)$_2$-(μ-PMe$_2$)(η^3-*syn*-MeCHCHCH$_2$)(CO)$_3$] (**3b**) *with Allene.*—Complex (**3b**) (0.02 g, 0.04 mmol) was dissolved in hexane–benzene (10 cm^3:10 cm^3) and the solution saturated with allene. The mixture was irradiated with u.v. light for 1 h at 2 °C and then stirred for 1 h in the dark at 15 °C. The solvent was removed on a rotary evaporator and the products separated by t.l.c. using hexane–ethyl acetate (9:1) as eluant to give (**4b**) and (**4c**) (0.012 g, 55%) as an inseparable mixture in *ca.* 1:2 ratio, unreacted (**3b**) (0.002 g), and [Mo$_2$O(η-C$_5$H$_5$)$_2${μ-σ:η^2-C(Et)=CH$_2$}(μ-PMe$_2$)(CO)]^4 (0.001 g).

(*viii*) *Reaction of the Cyclohex-2-enyl Complex* [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PMe$_2$)(η^3-C$_6$H$_9$)(CO)$_3$] (**3c**)^5 *with Allene.*—Complex (**3c**) (0.025 g, 0.045 mmol) was treated with allene as in (*vii*) to give [Mo$_2$(η-C$_5$H$_5$)$_2${μ-η^5-CH$_2$C(CH$_2$)(C$_6$H$_9$)}(μ-PMe$_2$)(CO)$_2$] (0.008 g, 30%) (**4d**) and unreacted (**3c**) (0.003 g). Complex (**4d**): m/z 560 (M^+), $M^+ - n$CO (n = 0 or 2); $\nu_{\text{max.}}$(CO) at 1 854s and 1 829s cm^{-1}. ^{1}H N.m.r. (303 K): δ 5.44 [m, J(H^{6}H^7) 15.0, 1 H, H^7], 5.22 [m, J(H^{5}H^6) 10.1, 1 H, H^6], 4.82 (s, 5 H, C$_5$H$_9$), 4.60 (s, 5 H, C$_5$H$_5$), 3.53 (d, 1 H, H^5), 2.39 (s, 2 H, H^{12}, H^{13}), 2.37 (s, 1 H, H^5), 1.9—1.5 (m, 4 H, H^8, H^9, H^{10}, H^{11}), 1.74 [d, ^2J(PH) 9.1, 3 H, P*Me*^{A}Me^B], 1.56 [m, ^2J(PH) 9.3, 3 H, PMe^A*Me*^{B}], 1.47 (m, 2 H, H^1, H^2), and 0.93 [d, ^3J(PH) 2.4, 1 H, H^4].

Crystallography.—*Crystal data for* [Mo$_2$(C$_5$H$_5$)$_2${μ-η^5-CH$_2$C(CH$_2$)C(Me)=CH$_2$}(μ-PMe$_2$)(CO)$_2$], (**4a**) C$_{20}$H$_{25}$Mo$_2$-O$_2$P, M = 519.88, monoclinic, space group $P2_1/c$ (no. 14), a = 9.064(2), b = 17.595(4), c = 12.540(3), β = 97.93(3)°, U = 1 980.77 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), Z = 4, D_c = 1.740 g cm^{-3}. 2 816 Unique absorption-corrected data [$I > 3\sigma(I)$, $3 < \theta < 25°$, Mo-K_α radiation]. A burgundy red crystal of size 0.15 × 0.21 × 0.24 mm, μ(Mo-K_α) = 12.20 cm^{-1}, was used in the data collection; F(000) = 992.

Crystal data for [Mo$_2$(η-C$_5$H$_5$)$_2$(μ-PMe$_2$){η^3-CH$_2$C(CH$_2$)-C(Me)=CH$_2$}(CO)$_3$], (**5a**). C$_{21}$H$_{25}$Mo$_2$O$_3$P, M = 548.28, orthorhombic, space group $P2_12_12_1$, a = 25.839(4), b = 9.943(3), c = 8.415(3) Å, U = 2 161.96 Å^3, Z = 4, F(000) = 1 096, μ(Mo-K_α) = 11.26 cm^{-1}, D_c = 1.684 g cm^{-3}. 1 915 Unique absorption-corrected data, [$I > 3\sigma(I)$, $3 < \theta < 25°$, Mo-K_α radiation]. A deep orange crystal of size 0.18 × 0.15 × 0.10 mm was used in the data collection.

Data collection. Data for both structures were collected in the range θ 3—25°, with a scan width of 0.84° for (**4a**) and 0.86° for (**5a**), using the technique described previously.^{18} For both structures Lorentz and polarisation corrections were applied. Equivalent reflections were merged to give 2 816 data for (**4a**) and 1 915 for (**5a**) with $I/\sigma(I) > 3.0$.

Structure solution and refinement.^{19} The co-ordinates of both metal atoms in structures (**4a**) and (**5a**) were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent Fourier different syntheses. The hydrogen atoms of both organic fragments were located in a Fourier difference synthesis calculated using data with sin θ < 0.35. All remaining hydrogen atoms, in both structures, were included in geometrically idealised positions and were constrained to 'ride' on the relevant carbon atoms. Full-matrix refinement was carried out for both structures, with anisotropic thermal parameters assigned to all non-hydrogen atoms in the final stages of refinement. For both (**4a**) and (**5a**) weights of $w = 1/\sigma^2F_o$ were assigned to individual reflections. Refinement converged at R 0.0251 and R' 0.0269 for (**4a**) and R 0.0306 and R' 0.0312 for (**5a**).

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

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