Chemistry of Phosphido-bridged Dimolybdenum Complexes. Part 4.[1] Reactions of $[Mo_2(\eta^5-C_5H_5)_2(\mu-H)(\mu-PR_2)(CO)_4]$ (R = Ph or Me) with Dienes

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The photochemical reactions of $[Mo_2(\eta^5-C_5H_5)_2(\mu-H)(\mu-PR_2)(CO)_4]$ (R = Ph or Me) with allene, 1,3-butadiene, 2-methyl-1,3-butadiene, and 1,3-cyclohexadiene have been studied. In each of these reactions allyl complexes of general formula $[Mo_2(\eta^5-C_5H_5)_2(\mu-PR_2)(\eta^3\text{-allyl})(CO)_3]$ are obtained as major products. The ^1H n.m.r. spectra of these allyl complexes indicate that they exist in solution as an equilibrium mixture of *exo* and *endo* isomers. In the reactions with 1,3-butadiene the allyl complexes are accompanied by very low yields of other species which are assigned the formula $[Mo_2(\eta^5-C_5H_5)_2O(\mu\text{-vinyl})(\mu-PR_2)(CO)]$ on the basis of spectroscopic evidence. The reaction of $[Mo_2(\eta^5-C_5H_5)_2(\mu-H)(\mu-PMe_2)(CO)_4]$ with allene gives as a major product, in addition to the allyl species, the complex $[Mo_2(\eta^5-C_5H_5)_2\{\mu-\sigma:\eta^2-C(Me)=CH_2\}(\mu-PMe_2)(CO)_3]$.

Mononuclear η^3-allyl complexes of the type $[Mo(\eta^5-C_5H_5)(\eta^3\text{-allyl})(CO)_2]$ are well known[2] and exist in solution as an equilibrium mixture of conformational isomers with differing relative orientation of the allyl and cyclopentadienyl ligands (Figure 1). The position of equilibrium between the conformers has been studied by ^1H n.m.r.[2-4] and ^{95}Mo n.m.r.[5] spectroscopy and shown to depend critically on the nature of the substituents on the allyl ligand.

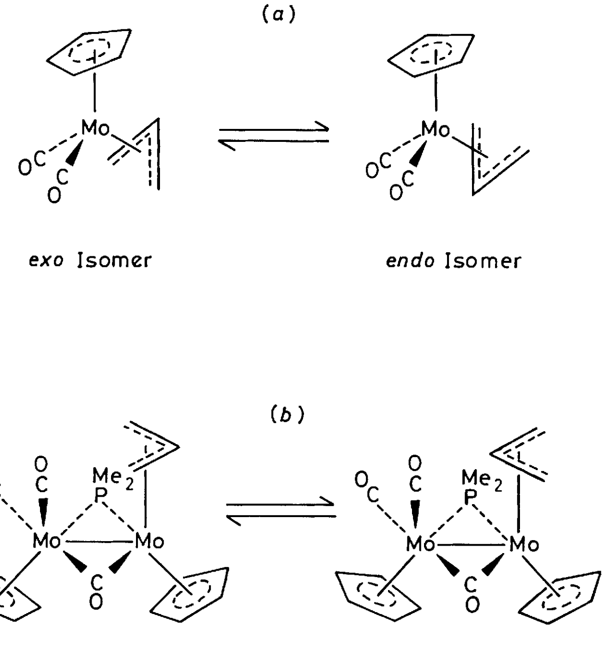

Figure 1. Proposed structures for *exo* and *endo* isomers of (*a*) mononuclear allyl complexes and (*b*) the dinuclear allyl complexes (**2**) and (**3**)

In this paper we report the synthesis of some dinuclear molybdenum allyl complexes from the photochemical reactions of $[Mo_2(\eta^5-C_5H_5)_2(\mu-H)(\mu-PR_2)(CO)_4]$ [R = Ph (**1a**) or Me (**1b**)] with dienes. These allyl complexes, in which the allyl ligand is bonded to only one of the metal atoms, also exist as a mixture of conformers in solution with the relative concentrations depending on the nature of the allyl and PR_2 groups. Other photochemical reactions of (**1a**) and (**1b**) to have been reported previously include those of (**1a**) with organophosphines[6] and those of (**1b**) with alkynes.[7]

Results and Discussion

U.v. irradiation of complexes (**1a**) and (**1b**) with dienes [allene, 1,3-butadiene, 2-methyl-1,3-butadiene, and 1,3-cyclohexadiene] in hexane–benzene solution gives respectively the green allyl complexes $[Mo_2(\eta^5-C_5H_5)_2(\mu-PR_2)(\eta^3\text{-allyl})(CO)_3]$ (**2**) and (**3**) [R = Ph; η^3-allyl = C_3H_5 (**2a**), C_4H_7 (**2b**), C_5H_9 (**2c**), or C_6H_9 (**2d**); R = Me; η^3-allyl = C_3H_5 (**3a**), C_4H_7 (**3b**), C_5H_9 (**3c**), or C_6H_9 (**3d**)]. Proposed structures in the solid state for these allyl complexes, in which the allyl ligand is assigned an *exo* configuration, are shown in Figure 2. These proposals are based on the structure of the closely related η^3-allyl complex $[Mo_2(\eta^5-C_5H_5)_2(\mu-PMe_2)\{\eta^3-CH_2C(CH_2)C(Me)=CH_2\}(CO)_3]$ which has been determined by *X*-ray analysis.[8] The *syn* stereochemistry of the allyl ligands in complexes (**2b**), (**2c**), (**3b**), and (**3c**) is deduced from the magnitude of the ^1H n.m.r. coupling constants for these derivatives (Table).

The ^1H n.m.r. spectrum of complex (**2a**) in the allyl region in CD_2Cl_2 at 203 K shows nine resonances (one representing two coincident signals) which may be assigned to two sets of five inequivalent allyl hydrogens on the basis of selective decoupling experiments. There are thus two isomers of (**2a**) in solution at low temperature which, from the ^1H n.m.r. intensities, are present in a concentration ratio of *ca.* 3:2. These isomers are assigned *exo* and *endo* configurations as shown in Figure 1. Faller *et al.*[3] have noted that for complexes $[Mo(\eta^5-C_5H_5)(\eta^3\text{-allyl})(CO)_2]$ the ^1H n.m.r. resonances of the *anti* allyl hydrogens are normally shifted δ *ca.* 0.6 upfield in the *exo* isomer compared to the *endo* isomer. For (**2a**) in CD_2Cl_2 the *anti* hydrogens of the major isomer give resonances at δ −0.86 and 1.15 whilst the corresponding resonances of the minor isomer are at δ 0.27 and 2.23. The tentative suggestion that the major and minor isomers of (**2a**) have respectively the *exo* and *endo* configurations is put forward on this basis, although the environment of the allyl ligand in the dinuclear complexes is clearly different from the environment of the allyl ligand in the mononuclear complexes studied by Faller.

On warming the solution of complex (**2a**) in CD_2Cl_2 all the allyl resonances broaden but no averaged ^1H n.m.r. spectrum is observed, even at 311 K. In toluene, pairs of corresponding allyl

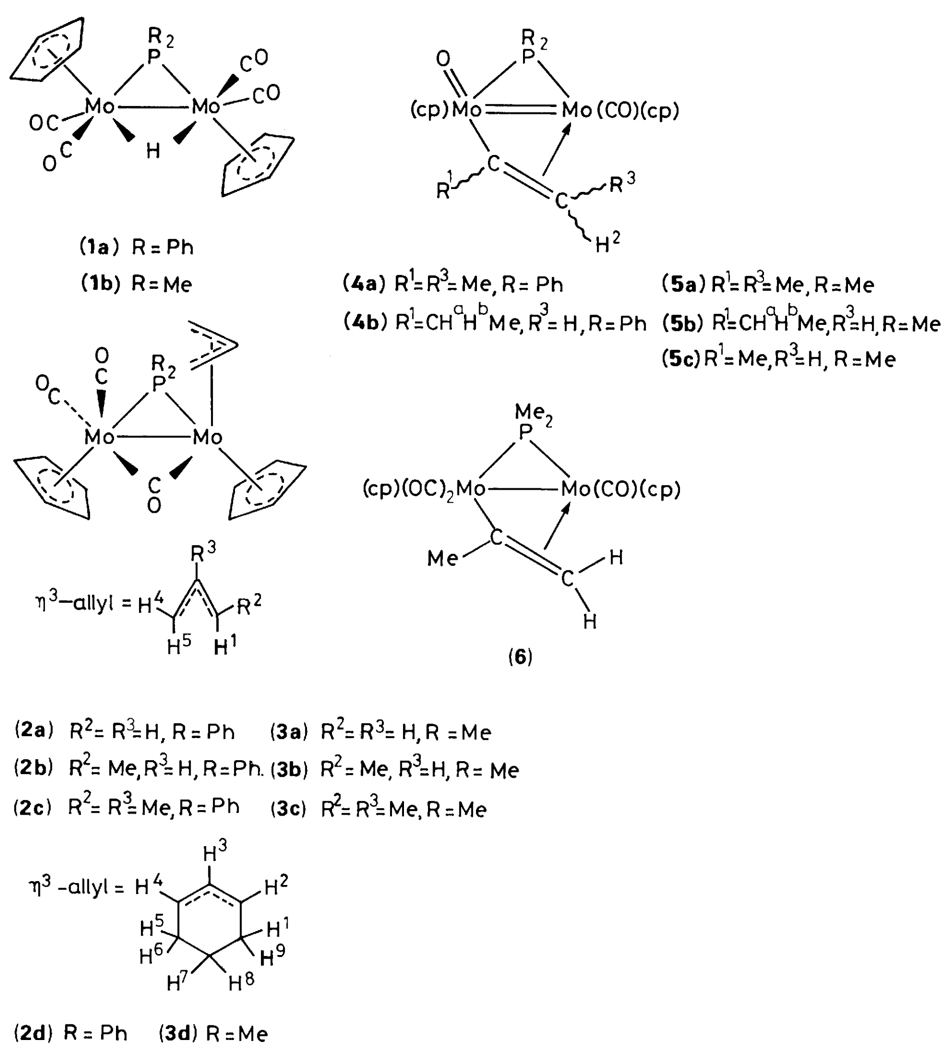

Figure 2. Proposed structures for the dimolybdenum complexes (1)—(6); cp = η^5-C_5H_5

resonances of the two isomers coalesce at *ca.* 377 K but there is significant decomposition above this temperature and again no averaged spectrum could be obtained.

Proton n.m.r. spectra of the remaining allyl complexes (**2b**)—(**2d**) and (**3a**)—(**3d**) (Table 1) all indicate the presence of two isomers in solution at low temperatures. For (**2a**)—(**2c**) and (**3a**)—(**3c**) the unique *anti* allyl hydrogen resonance (H^5) upfield of $SiMe_4$ (range δ -0.5 to -1.5) is associated with the major isomer. It may therefore be assumed that, for each of these complexes, the major isomer is of the same structural type and probably *exo*. It should be noted that for (**2b**), (**2c**), (**3b**), and (**3c**), in which the allyl ligand is unsymmetrically substituted, two *exo* and two *endo* isomers are possible. Each set of isomers differs according to whether R^2 is closer to the bridging CO or the bridging PR_2 ligand. The fact that all the allyl complexes, regardless of whether or not the ligand is symmetrical, give rise to only two isomers suggests, however, that an *exo–endo* pair is present rather than two *exo* or two *endo* isomers. The major isomer of the (μ-PMe_2) cyclohexenyl complex, (**3d**), shows similar ^1H n.m.r. cyclopentadienyl resonances to those of the major isomers of complexes (**3a**)—(**3c**) and, on this basis, it probably also has the same structure. The assignment of the C_6H_9 resonance of (**3d**) to individual protons is based on selective decoupling experiments, although it is not possible by this means to determine which of H^5/H^6, H^7/H^8, and H^1/H^9 are above and below the plane of the ring.

The relative values of the *exo*:*endo* isomer ratios in the series (**2a**)—(**2d**) and (**3a**)—(**3d**) are difficult to rationalise on the basis of any single factor. Thus although complexes (**2c**) and (**3c**), which contain the same η^3-*syn*-1,2-dimethylallyl ligand, each have an *exo*:*endo* isomer ratio of *ca.* 7:1 this is the highest observed in the series (**2a**)—(**2d**) and the lowest in (**3a**)—(**3d**). Faller *et al.*[3] have suggested that steric interaction of a central allyl methyl group and the cyclopentadienyl ligand in [(Mo(η^5-C_5H_5)(η^3-allyl)$(CO)_2$] complexes is a significant factor in determining isomer ratios. Such an interaction in (**3c**) would lead to the observed relatively low *exo*:*endo* isomer ratio, whereas for (**2c**) steric interactions between the allyl ligand and the bulky μ-PPh_2 group may be more important.

In addition to the allyl complexes the reactions of (**1a**) and (**1b**) with 1,3-butadiene gave rise respectively to low yields of the red μ-vinyl oxo complexes (**4**) and (**5**) of formula [$Mo_2(\eta^5$-$C_5H_5)_2$\{μ-σ:η^2-C(R^1)=CHR^3\}(μ-PR_2)(CO)] [R = Ph, R^1 = R^3 = Me (**4a**); R = Ph, R^1 = Et, R^3 = H (**4b**); R = Me, R^1 = R^3 = Me (**5a**); R^1 = Et, R^3 = H (**5b**)]. Complexes (**5a**) and (**5b**) have been obtained previously, as minor products in the reaction of (**1b**) with, respectively, the alkynes MeC≡CH and EtC≡CH.[7]

The proposed structures of (**4**) and (**5**) are shown in Figure 2, based on the spectroscopic data given in the Experimental section and on a comparison of the data with those for a related complex, [$Mo_2(\eta^5$-$C_5H_5)_2$O(μ-σ:η^2-CH=CHPh)-

Table. Infrared and ^{1}H n.m.r. data for the new compounds

Compound	ν(CO) cm^{-1} (hexane)	^{1}H N.m.r.[a]
(2a) [Mo$_2$(η^5-C$_5$H$_5$)$_2$(μ-PPh$_2$)(η^3-C$_3$H$_5$)(CO)$_3$]	1 948s, 1 940m, 1 879m, 1 861s, 1 831s, 1 804m	Major (60%): 7.7—6.6 (m, 10 H, Ph), 5.05 (s, 5 H, cp), 4.74 (s, 5 H, cp), 4.02 [dddd, *J*(H^{1}H^3) 10.8, *J*(H^{3}H^5) 10.8, *J*(H^{2}H^3) 7.3, *J*(H^{3}H^4) 7.3, 1 H, H^3], 2.55 [dd, *J*(H^{1}H^2) 2.1, 1 H, H^2], 1.67 [m, *J*(H^{4}H^5) 1.8, 1 H, H^4], 1.15 (dd, 1 H, H^1), −0.86 [ddd, ^{3}*J*(PH) 10.8, 1 H, H^5] Minor (40%): 5.08 (s, 5 H, cp), 4.73 (s, 5 H, cp), 3.93 [dddd, *J*(H^{1}H^3) 11.3, *J*(H^{3}H^5) 10.8, *J*(H^{3}H^4) 8.5, *J*(H^{2}H^3) 7.8, 1 H, H^3], 2.68 [dd, *J*(H^{1}H^2) 2.4, 1 H, H^2], 2.23 (dd, 1 H, H^1), 2.07 [dd, *J*(H^{4}H^5) 0.6, 1 H, H^4], 0.27 [ddd, ^{3}*J*(PH) 10.8, 1 H, H^5][b]
(2b) [Mo$_2$(η^5-C$_5$H$_5$)$_2$(μ-PPh$_2$)(η^3-C$_4$H$_7$)(CO)$_3$]	1 932s, 1 853s, 1 773w	Major (66%): 7.7—7.6 (m, 10 H, Ph), 5.07 (s, 5 H, cp), 4.80 (s, 5 H, cp), 3.91 [ddd, *J*(H^{1}H^3) 11.2, *J*(H^{3}H^5) 11, *J*(H^{3}H^4) 7.5, 1 H, H^3], 1.72 (s, 3 H, Me^2), 1.72 (obscured, H^1), 1.51 [ddd, ^{3}*J*(PH) 5, *J*(H^{4}H^5) 2.8, 1 H, H^4], −1.10 [ddd, *J*(PH) 11.2, 1 H, H^5] Minor (34%): 5.05 (s, 5 H, cp), 4.75 (s, 5 H, cp), 3.95 (obscured, H^3), 3.1 [dq, *J*(H^{1}H^3) 11, *J*(H^{1}H^2) 6.1, 1 H, H^1], 1.77 (d, 3 H, Me^2), 1.77 (obscured, H^4), 0.3 [ddd, ^{3}*J*(PH) 10.8, *J*(H^{3}H^5) 10.8, *J*(H^{4}H^5) 2.8, 1 H, H^5][c]
(2c) [Mo$_2$(η^5-C$_5$H$_5$)$_2$(μ-PPh$_2$)(η^3-C$_5$H$_9$)(CO)$_3$]	1 948s, 1 937m, 1 877s, 1 862m, 1 795 (sh), 1 786m	Major (88%): 7.8—6.8 (m, 10 H, Ph), 4.77 (s, 5 H, cp), 4.34 (s, 5 H, cp), 1.54 (s, 3 H, Me^3), 1.50 [d, *J*(H^{1}H^2) 6.7, 3 H, Me^2], 1.46 [d, *J*(H^{4}H^5) 2.9, 1 H, H^4], 1.25 (q, 1 H, H^1), −1.22 [dd, ^{3}*J*(PH) 12.6, 1 H, H^5] Minor (12%): 4.78 (s, 5 H, cp), 4.31 (s, 5 H, cp), 3.10 [q, *J*(H^{1}H^2) 6.3, 1 H, H^1], 1.75 (m, 1 H, H^4), 1.61 (d, 3 H, Me^2), 1.39 (s, Me^3), 0.37 (m, 1 H, H^5)[d]
(2d) [Mo$_2$(η^5-C$_5$H$_5$)(μ-PPh$_2$)(η^3-C$_6$H$_9$)(CO)$_3$]	1 948s, 1 936s, 1 879s, 1 862m, 1 795 (sh), 1 786m	Major (55%): 7.9—6.8 (m, 10 H, Ph), 5.80 (m, 2 H, C$_6$H$_9$), 5.12 (s, 5 H, cp), 4.89 (s, 5 H, cp), 4.32 (m, 1 H, H^3), 2.4—1.7 (m, 5 H, C$_6$H$_9$), −0.78 (m, 1 H, H^4) Minor (45%): 5.15 (s, 5 H, cp), 4.95 (s, 5 H, cp), 4.32 (m, 1 H, H^3), 3.55 (m, 1 H, H^2), 0.12 (m, 1 H, H^4)[e]
(3a) [Mo$_2$(η^5-C$_5$H$_5$)(μ-PMe$_2$)(η^3-C$_3$H$_5$)(CO)$_3$]	1 934s, 1 861s, 1 803m	Major (89%): 5.20 (s, 5 H, cp), 4.91 [d, ^{3}*J*(PH) 1.0, 5 H, cp], 3.84 [dddd, *J*(H^{3}H^5) 11.0, *J*(H^{1}H^3) 10.4, *J*(H^{3}H^4) 7.7, *J*(H^{2}H^3) 7.4, 1 H, H^3], 2.64 [dd, *J*(H^{1}H^2) 2.1, 1 H, H^2], 2.04 [d, ^{2}*J*(PH) 9.9, 3 H, P*Me*$^{\rm A}$Me$^{\rm B}$], 1.93 [d, ^{2}*J*(PH) 8.5, 3 H, PMe$^{\rm A}$*Me*$^{\rm B}$], 1.93 (obscured, H^4), 1.83 (dd, 1 H, H^1), −0.50 [dd, ^{3}*J*(PH) 9.6, 1 H, H^5] Minor (11%): 5.04 (s, 5 H cp), 4.89 (s, 5 H, cp)[f]
(3b) [Mo$_2$(η^5-C$_5$H$_5$)$_2$(μ-PMe$_2$)(η^3-C$_4$H$_7$)(CO)$_3$]	1 914s, 1 832s, 1 776m	Major (93%): 5.23 (s, 5 H, cp), 4.92 (s, 5 H, cp), 3.76 [ddd, *J*(H^{3}H^5) 10.1, *J*(H^{1}H^3) 9.6, *J*(H^{3}H^4) 7.5, 1 H, H^3], 2.24 [dq, *J*(H^{1}H^2) 6.4 1 H H^1], 1.98 [d, ^{2}*J*(PH) 11.0, 3 H, P*Me*$^{\rm A}$Me$^{\rm B}$], 1.94 [d, ^{2}*J*(PH) 8.8, 3 H, PMe$^{\rm A}$*Me*$^{\rm B}$], 1.74 (d, 3 H, Me^2), 1.74 (obscured, H^4), −0.98 [dd, ^{3}*J*(PH) 10.9, 1 H, H^5] Minor (7%): 5.02 (s, 5 H, cp), 4.87 (s, 5 H, cp)[g]
(3c) [Mo$_2$(η^5-C$_5$H$_5$)$_2$(μ-PMe$_2$)(η^3-C$_5$H$_9$)(CO)$_3$]	1 932s, 1 870 (sh), 1 860s, 1 785m	Major (87%): 5.17 (s, 5 H, cp), 4.77 (s, 5 H, cp), 1.96—1.87 (m, 6 H, PMe$_2$), 1.87 (obscured, H^1), 1.68 (s, 3 H, Me^3), 1.67 [d, *J*(H^{1}H^2) 6.4, 3 H, Me^2], 1.65 (obscured, H^4), −1.21 [dd, ^{3}*J*(PH) 12.3, *J*(H^{4}H^5) 0.8, 1 H, H^5] Minor (13%): 4.99 (s, 5 H, cp), 4.70 (s, 5 H, cp)[h]
(3d) [Mo$_2$(η^5-C$_5$H$_5$)$_2$(μ-PMe$_2$)(η^3-C$_6$H$_9$)(CO)$_3$]	1 930s, 1 867 (sh), 1 859s, 1 796m	Major (94%): 5.88 [m, *J*(H^{1}H^9) 14.8, *J*(H^{7}H^9) 6.7, *J*(H^{8}H^9) 6.7, 1 H H^9], 5.59 [m, *J*(H^{1}H^2) 10.4, *J*(H^{1}H^7) 2, 1 H, H^1], 5.23 (s, 5 H, cp), 4.90 (s, 5 H, cp), 3.84 [ddd, *J*(H^{2}H^3) 9.9 *J*(H^{3}H^4) 9.8, *J*(H^{3}H^6) 7.8, 1 H, H^3], 2.72 (dd, 1 H, H^2), 2.00 [d, ^{2}*J*(PH) 9.5, 3 H, P*Me*$^{\rm A}$Me$^{\rm B}$], 1.92 [d, ^{2}*J*(PH) 8.3, 3 H, PMe$^{\rm A}$*Me*$^{\rm B}$], 1.85—1.79 (m, 4 H, H^5, H^6, H^7, H^8), −0.83 [dd, ^{3}*J*(PH) 10.9, 1 H, H^4] Minor (6%): 5.02 (s, 5 H, cp), 4.84 (s, 5 H, cp)[g]
(4a) [Mo$_2$(η^5-C$_5$H$_5$)$_2$O{μ-σ:η^2-C(Me)=CHMe}(μ-PPh$_2$)(CO)]	1 861	8.0—7.2 (m, 10 H, Ph), 5.09 (s, 5 H, cp), 4.72 [d, ^{3}*J*(PH) 1.4, 5 H, cp], 3.19 [d, ^{4}*J*(PH) 0.7, 3 H, Me^1], 2.75 [q, *J*(H^{2}H^3) 6.3, 1 H, H^2], 1.83 (d, 3 H, Me^3)
(4b) [Mo$_2$(η^5-C$_5$H$_5$)$_2$O{μ-σ:η^2-C(Et)=CH$_2$}(μ-PPh$_2$)(CO)]	1 867	8.1—7.1 (m, 10 H, Ph), 5.11 (s, 5 H, cp), 4.78 [d, ^{3}*J*(PH) 1.3, 5 H, cp], 3.38 (s, 1 H, H^2), 3.15 [dq, *J*(H^{a}H^b) 11.5, *J*(H^{a}H^c) 7.3, 1 H, H^a], 2.48 [dq, *J*(H^{b}H^c) 7.3, 1 H, H^b], 2.01 (s, 1 H, H^3), 1.88 (t, 3 H, Me^c)
(5a) [Mo$_2$(η^5-C$_5$H$_5$)$_2$O{μ-σ:η^2-C(Me)=CHMe}(μ-PMe$_2$)(CO)]	1 859	5.17 [d, ^{3}*J*(PH) 0.6, 5 H, cp], 4.92 [d, ^{3}*J*(PH) 1.4, 5 H, cp], 3.20 [d, ^{4}*J*(PH) 0.9, 3 H, Me^1], 2.10 [d, ^{2}*J*(PH) 10.1, 1, 3 H, P*Me*$^{\rm A}$Me$^{\rm B}$], 2.01 [d, ^{2}*J*(PH) 10.8, 3 H, PMe$^{\rm A}$*Me*$^{\rm B}$], 1.84 (obscured, H^2), 1.74 [d, *J*(H^{2}H^3) 6.3, 3 H, Me^3]
(5b) [Mo$_2$(η^5-C$_5$H$_5$)$_2$O{μ-σ:η^2-C(Et)=CH$_2$}(μ-PMe$_2$)(CO)]	1 862	5.21 [d, ^{3}*J*(PH) 0.7, 5 H, cp], 4.94 [d, ^{3}*J*(PH) 1.6, 5 H, cp], 3.20 [dq, *J*(H^{a}H^b) 18.9, *J*(H^{a}H^c) 7.4, 1 H, H^a], 3.15 (s, 1 H, H^2), 2.53 [dq, *J*(H^{b}H^c) 7.4 1 H, H^b], 2.14 [d, ^{2}*J*(PH) 10.1, 3 H, P*Me*$^{\rm A}$Me$^{\rm B}$], 2.06 [d, ^{2}*J*(PH) 10.5, 3 H, PMe$^{\rm A}$*Me*$^{\rm B}$], 2.0 (s, 1 H, H^3), 1.90 (t, 3 H, Me)

Table (*continued*)

Compound	ν(CO) cm^{-1} (hexane)	^{1}H N.m.r.^{a}
(**5c**) [$Mo_2(\eta^5\text{-}C_5H_5)_2O\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)$]	1 863	5.17 (s, 5 H, cp), 5.11 (s, 5 H, cp), 3.05 (s, 3 H, Me^{1}), 2.92 (s, 1 H, H^{2}), 1.98 [d, ^{2}J(PH) 9.1, 3 H, $\mathrm{P}Me^{A}\mathrm{Me}^{B}$], 1.80 [d, ^{2}J(PH) 9.7, 3 H, $\mathrm{PMe}^{A}Me^{B}$], 0.40 (s, 1 H, H^{3})
(**6**) [$Mo_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)_3$]	1 934s, 1 861s, 1 803m	5.63 [d, ^{3}J(PH) 0.7, 5 H, cp], 4.85 [d, ^{3}J(PH) 1.1, 5 H, cp], 2.96 (s, 1 H, H^{2}), 2.71 (s, 3 H, Me^{1}), 2.24 (s, 1 H, H^{3}), 2.05 [d, ^{2}J(PH) 10.8, 3 H, $\mathrm{P}Me^{A}\mathrm{Me}^{B}$], 1.80 [d, ^{2}J(PH) 9.7, 3 H, $\mathrm{PMe}^{A}Me^{B}$]

[a] Recorded at 298 K in $CDCl_3$ solution unless otherwise stated (*J* in Hz); s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet; cp = η^5-C_5H_5. [b] Recorded in CD_2Cl_2 at 203 K. [c] Recorded at 248 K. [d] Recorded in [$^{2}H_8$]toluene at 263 K. [e] Recorded in CD_3COCD_3 at 238 K. [f] Recorded at 233 K. [g] Recorded at 215 K. [h] Recorded at 238 K.

(μ-PPh$_2$)(CO)], the structure of which has been determined by *X*-ray diffraction.[9] It is not, however, possible to determine from the ^{1}H n.m.r. data whether R^{3} in (**4a**) and (**5a**) is *cis* or *trans* to the Mo–C σ bond. Complexes (**4a**), (**4b**), (**5a**), and (**5b**) most probably arise from oxidation of the corresponding μ-vinyl complexes [$Mo_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(R^1){=}CHR^3\}(\mu\text{-}PR_2)(CO)_3$] which, together with the allyl complexes, are presumably the initial insertion products in the reaction of (**1a**) and (**1b**) with 1,3-butadiene. Indeed in the reaction of (**1b**) with allene such a μ-vinyl complex [$Mo_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)_3$], (**6**) is formed in higher yield than the allyl complex (**3a**). Complex (**6**), the proposed structure of which is shown in Figure 2, is also obtained as one component of an inseparable mixture (the other component is the isomeric complex [$Mo_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(H){=}CHMe\}(\mu\text{-}PMe_2)(CO)_3$]) in the reaction of (**1b**) with propyne.[7] Photolysis of (**6**) under a dinitrogen atomosphere does give the corresponding oxo complex [$Mo_2(\eta^5\text{-}C_5H_5)_2O\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)$] (**5c**), albeit in low yield.

Experimental

Details of the experimental procedures and of the instrumentation used to obtain spectroscopic data have been given in Part 1 of this series.[6] The complexes [$Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_4$] [R = Ph (**1a**) or Me (**1b**)] were prepared by the literature methods.[6,10] All other reagents were obtained from the usual commercial suppliers and used without further purification.

Reactions of [$Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4$] (**1a**) *with Dienes.*—(*i*) *Allene.* Complex (**1a**) (0.62 g, 1.0 mmol) was dissolved in hexane–benzene (30:1) (150 cm^{3}) in a glass photolysis vessel. A water-cooled quartz inner tube containing the u.v. filament (Hanovia 125-W medium-pressure immersion lamp) was placed in the vessel and the solution was then treated with an excess (*ca.* two-fold) of allene. After irradiation for 4 h the solvent was removed on a rotary evaporator and the residue, having been dissolved in the minimum quantity of CH_2Cl_2, was adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column (silica, Merck Kieselgel 60 mesh). Elution with hexane–CH_2Cl_2 (1:1) gave unreacted (**1a**) (0.31 g, 50%). Further elution with light petroleum (b.p. 40—60 °C)–ethyl acetate (9:1) gave a green band, which, on evaporation of the solvent, yielded green, crystalline [$Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PPh_2)(\eta^3\text{-}C_3H_5)(CO)_3$] (**2a**) (0.22 g, 35%) (Found: C, 52.8; H, 4.4; P, 4.9. $C_{28}H_{25}Mo_2O_3P$ requires C, 53.2; H, 4.0; P, 4.9%); mass spectrum *m*/*z* 632 (M^+) and M^+ − CO.

(*ii*) 1,3-*Butadiene.* Complex (**1a**) (0.62 g, 1.0 mmol) and 1,3-butadiene (large excess bubbled into solution) were used in an analogous procedure to (*i*) above to give unreacted (**1a**) (0.02 g, 3%) and green crystalline [$Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PPh_2)(\eta^3\text{-}syn\text{-}MeCHCHCH_2)(CO)_3$] (**2b**) (0.55 g, 85%). Complex (**2b**) was followed on the column by two minor red products identified from spectroscopic data (Table) as [$Mo_2(\eta^5\text{-}C_5H_5)_2O\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CHMe\}(\mu\text{-}PPh_2)(CO)$] (**4a**) (0.005 g) and [$Mo_2(\eta^5\text{-}C_5H_5)_2O\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Et){=}CH_2\}(\mu\text{-}PPh_2)(CO)$] (**4b**) (0.008 g). Complex (**2b**) (Found: C, 52.1; H, 4.0; P, 4.2. $C_{29}H_{27}Mo_2O_3P$ requires C, 53.9; H, 4.2; P, 4.8%); *m*/*z* 646 (M^+) and M^+ − *n*CO (*n* = 1—3). Complex (**4a**): *m*/*z* 606 (M^+) and M^+ − CO. Complex (**4b**): *m*/*z* 606 (M^+) and M^+ − CO.

(*iii*) 2-*Methyl*-1,3-*butadiene.* Complex (**1a**) (0.62 g, 1.0 mmol) and 2-methyl-1,3-butadiene (2 cm^{3}, large excess) were used in an analogous procedure to (*i*) above to give unreacted (**1a**) (0.35 g, 55%) and green crystalline [$Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PPh_2)\{\eta^3\text{-}syn\text{-}MeCHC(Me)CH_2\}(CO)_3$] (**2c**) (0.14 g, 21%) (Found: C, 52.9; H, 4.3; P, 3.7. $C_{30}H_{29}Mo_2O_3P$ requires C, 54.6; H, 4.4; P, 4.7%); *m*/*z* 660 (M^+) and M^+ − *n*CO (*n* = 1 or 2).

(*iv*) 1,3-*Cyclohexadiene.* Complex (**1a**) (0.62 g, 1.0 mmol) and 1,3-cyclohexadiene (2 cm^{3}, large excess) were used in an analogous procedure to (*i*) above to give unreacted (**1a**) (0.585 g, 94%) and green [$Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PPh_2)(\eta^3\text{-}C_6H_9)(CO)_3$] (**2d**) (0.015 g, 2%); *m*/*z* 672 (M^+) and M^+ − *n*CO (*n* = 1—3).

Reactions of [$Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_4$] (**1b**) *with Dienes.*—(*i*) *Allene.* Complex (**1b**) (0.2 g, 0.4 mmol) was dissolved in hexane–benzene (1:1) (60 cm^{3}) and a small excess (*ca.* two-fold) of allene was bubbled into the solution. After u.v. irradiation for 4 h unreacted (**1b**) (0.12 g, 60%) was separated from the other products by column chromatography as in the reaction of allene with (**1a**). The remaining products were separated by t.l.c. using light petroleum (b.p. 40—60 °C)–ethyl acetate (9:1) as eluant to give (in order of decreasing R_F values) [$Mo_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)_3$] (**6**) (0.045 g, 22%), red [$Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PMe_2)(\eta^3\text{-}C_3H_5)(CO)_3$] (**3a**) (0.025 g, 12%), and 0.005 g (combined yield) of at least three other products. Complex (**3a**) (Found: C, 42.0; H, 4.2. $C_{18}H_{21}Mo_2O_3P$ requires C, 42.5; H, 4.1%), *m*/*z* 508 (M^+) and M^+ − *n*CO (*n* = 1—3). N.m.r.: ^{13}C ($CDCl_3$, ^{1}H noise decoupled, 233 K) δ 248.0 [d, ^{2}J(PC) 20.0, 1CO (*cis*)], 240.5 [s, 1CO (*trans*)], 239.0 [d, ^{2}J(PC) 7.7, 1CO], 92.8 (s, C_5H_5), 73.3 (s, $CH_2\mathit{C}HCH_2$), 45.5 [d, ^{2}J(PC) 5.6, $\mathit{C}H_2CHCH_2$], 41.8 (s, $CH_2CH\mathit{C}H_2$), 30.2 [d, ^{1}J(PC) 15.3, $\mathrm{P}Me^{A}\mathrm{Me}^{B}$], and 23.0 p.p.m. [d, ^{1}J(PC) 30.0 Hz, $\mathrm{PMe}^{A}Me^{B}$]. Complex (**6**) (Found: C, 42.1; H, 4.4. $C_{18}H_{21}Mo_2O_3P$ requires C, 42.5; H, 4.1%); *m*/*z* 508 (M^+) and M^+ − *n*CO (*n* = 1—3). N.m.r.: ^{13}C($CDCl_3$, ^{1}H noise decoupled, 243 K) δ 239.5 [s, 1CO (*trans*)], 238.6 [d, ^{2}J(PC) 24.2, 1CO (*cis*)], 236.8 [d, ^{2}J(PC) 23.3, 1CO (*cis*)], 169.9 [d, ^{2}J(PC) 8.9, $\mathit{C}(Me)CH_2$], 92.8 (s, C_5H_5), 92.4 (s, C_5H_5), 51.6 [s, $C(Me)\mathit{C}H_2$], 42.6 [s, $C(\mathit{Me})CH_2$], 30.9 [d, ^{1}J(PC) 15.2, $\mathrm{P}Me^{A}\mathrm{Me}^{B}$], and 24.6 [d, ^{1}J(PC) 30.6, $\mathrm{PMe}^{A}Me^{B}$]; ^{13}C($CDCl_3$, ^{1}H gated decoupled, 243 K) δ 51.6 [ddd, *J*(CH) 169.3, 150.5, ^{2}J(PC) 4.8, $C(Me)\mathit{C}H_2$], 42.6 [q, *J*(CH) 126.8, $C(\mathit{Me})CH_2$], 30.9 [qd, *J*(CH) 129.7, ^{1}J(PC) 15.2, $\mathrm{P}Me^{A}\mathrm{Me}^{B}$], and 24.6 p.p.m. [qd, *J*(CH) 130.3, ^{1}J(PC) 30.6 Hz, $\mathrm{PMe}^{A}Me^{B}$].

(*ii*) 1,3-*Butadiene.* Complex (**1b**) (0.2 g, 0.4 mmol) and 1,3-butadiene (large excess bubbled into solution) in hexane–benzene (1:1) (60 cm^{3}) were irradiated with u.v. light for 5 h.

Chromatographic separation of the products as in the reaction of (**1b**) with allene gave unreacted (**1b**) (0.11 g, 55%), red [$\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PMe_2)(\eta^3}$-*syn*-$\mathrm{MeCHCHCH_2)(CO)_3}$] (**3b**) (0.056 g, 27%), and two minor red products identified spectroscopically[7] as [$\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2O\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Et){=}CH_2\}(\mu\text{-}PMe_2)(CO)}$] (**5b**) (0.002 g) and [$\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2O\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CHMe\}(\mu\text{-}PMe_2)(CO)}$] (**5a**) (0.002 g). Complex (**3b**) (Found: C, 42.7; H, 4.3; P, 6.8. $\mathrm{C_{19}H_{23}Mo_2O_3P}$ requires C, 43.7; H, 4.4; P, 5.9%); *m*/*z* 622 (M^+) and $M^+ - n\mathrm{CO}$ (n = 1—3). N.m.r.: ^{13}C(CDCl$_3$, ^{1}H noise decoupled, 233 K) δ 92.8 (s, $\mathrm{C_5H_5}$), 91.2 (s, $\mathrm{C_5H_5}$), 73.6 (s, $\mathrm{CH_2}$*C*HCHMe), 63.5 (s, $\mathrm{CH_2CH}$*C*HMe), 39.7 [d, ^2J(PC) 6.2, *C*$\mathrm{H_2CHCHMe}$], 30.8 [d, ^1J(PC) 13.3, P*Me*$^\mathrm{A}$Me$^\mathrm{B}$], 22.6 [d, ^1J(PC) 28.4 Hz, PMe$^\mathrm{A}$*Me*$^\mathrm{B}$], and 18.6 p.p.m. (s, $\mathrm{CH_2CHCH}$*Me*); the spectrum was not of sufficient quality to allow observation of the ^{13}CO signals. Complex (**5b**): *m*/*z* 482 (M^+) and $M^+ - \mathrm{CO}$. Complex (**5a**): *m*/*z* 482 (M^+) and $M^+ - \mathrm{CO}$.

(*iii*) 2-*Methyl*-1,3-*butadiene*. Complex (**1b**) (0.2 g, 0.4 mmol) and 2-methyl-1,3-butadiene (0.3 cm^3, large excess) were used in an analogous procedure to that in (*ii*) above to give unreacted (**1b**) (0.16 g, 80%) and red [$\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PMe_2)\{\eta^3}$-*syn*-$\mathrm{MeCHC(Me)CH_2\}(CO)_3}$] (**3c**) (0.025 g, 11%) (Found: C, 45.1; H, 4.8. $\mathrm{C_{20}H_{25}Mo_2O_3P}$ requires C, 44.8; H, 4.7%); *m*/*z* 536 (M^+) and $M^+ - n\mathrm{CO}$ (n = 1—3).

(*iv*) 1,3-*Cyclohexadiene*. Complex (**1b**) (0.2 g, 0.4 mmol) and 1,3-cyclohexadiene (0.4 cm^3, large excess) were used in an analogous procedure to (*ii*) above to give unreacted (**1b**) (0.8 g, 40%) and red [$\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PMe_2)(\eta^3\text{-}C_6H_9)(CO)_3}$] (**3d**) (0.06 g, 27%) (Found: C, 45.6; H, 4.4; P, 5.2. $\mathrm{C_{21}H_{25}Mo_2O_3P}$ requires C, 46.0; H, 4.6; P, 5.7%); *m*/*z* 548 (M^+) and $M^+ - n\mathrm{CO}$ (n = 1—3).

Photolysis of Complex (**6**) *under a Dinitrogen Atmosphere*.—Complex (**6**) (0.01 g, 0.02 g, mmol) was dissolved in hexane (15 cm^3) and irradiated with u.v. light for 1.5 h under $\mathrm{N_2}$ to give an orange-green solution. Evaporation of the solvent and t.l.c. separation as in the reaction of (**1b**) with allene gave the red complex [$\mathrm{Mo_2(\eta^5\text{-}C_5H_5)_2O\{\mu\text{-}\sigma{:}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}PMe_2)(CO)}$] (**5c**)[7] (0.001 g) as the only isolable product; *m*/*z* 468 (M^+) and $M^+ - \mathrm{CO}$.

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References

1 Part 3, T. Adatia, M. McPartlin, M. J. Mays, M. J. Morris, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1989, 1555.
2 A. Davison and W. C. Rode, *Inorg. Chem.*, 1967, **6**, 2124.
3 J. W. Faller, C-C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organomet. Chem.*, 1973, **52**, 361.
4 J. W. Faller, H. H. Murray, D. L. White, and K. H. Chao, *Organometallics*, 1983, **2**, 400.
5 J. W. Faller and B. C. Whitmore, *Organometallics*, 1986, **5**, 752.
6 K. Henrick, A. D. Horton, M. McPartlin, and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1988, 1083.
7 G. Conole, K. Henrick, A. D. Horton, M. McPartlin, and M. J. Mays, *New J. Chem.*, 1988, **12**, 559.
8 A. D. Horton, Ph.D. Thesis, Cambridge University, 1985.
9 K. Endrich, R. Korswagen, T. Zahn, and M. L. Ziegler, *Angew Chem., Int. Ed. Engl.*, 1982, **21**, 919.
10 R. G. Hayter, *Inorg. Chem.*, 1963, **2**, 1031.

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