Dinuclear Allyl and μ-Vinyl Complexes from the Reactions of a μ-Hydrido Dimanganese and a μ-Hydrido Manganese–Molybdenum Complex with Alkynes containing α-Methyl or α-Methylene Substituents

Andrew D. Horton, Alan C. Kemball, and Martin J. Mays*
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

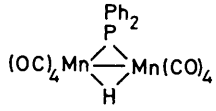
The photolytic reactions of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ and of $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_4]$ with alkynes containing α-methyl or α-methylene substituents have been studied. The dimanganese complex reacts with MeC≡CH to give, in comparable yields, the η^3-allyl complex $[Mn_2(\mu\text{-}PPh_2)(\eta^3\text{-}C_3H_5)(CO)_7]$ and an inseparable mixture of the two μ-vinyl complexes $[Mn(\mu\text{-}PPh_2)_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Me)=CH_2\}(CO)_7]$ and $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(H)=C(H)Me\}(\mu\text{-}PPh_2)(CO)_7]$. With MeC≡CMe, $[Mn_2(\mu\text{-}PPh_2)(\eta^3\text{-}syn\text{-}MeCHCHCH_2)(CO)_7]$ and $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Me)=C(H)Me\}(\mu\text{-}PPh_2)(CO)_7]$ are obtained, again in comparable yields. Reactions of the dimanganese complex with EtC≡CH and PhC≡CMe proceed analogously. The molybdenum–manganese complex does not give μ-vinyl complexes on reaction with MeC≡CH, MeC≡CMe, or EtC≡CH. Instead MeC≡CH gives $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}PPh_2)Mn(\eta^3\text{-}C_3H_5)(CO)_3]$ as the sole product whereas MeC≡CMe and EtC≡CH both give the same inseparable isomeric mixture of $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}PPh_2)Mn(\eta^3\text{-}syn\text{-}MeCHCHCH_2)(CO)_3]$ and $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}PPh_2)Mn(\eta^3\text{-}anti\text{-}MeCHCHCH_2)(CO)_3]$. Deuteriation studies show that the formation of the allyl complexes from the alkynes involves a 1,2 hydrogen shift within the ligand; a mechanistic scheme for the reactions of the dimanganese and molybdenum–manganese complexes with α-methyl- and α-methylene-substituted alkynes consistent with such a shift is proposed.

The reactions of alkynes with dinuclear and polynuclear complexes containing μ-hydrido ligands generally give, in the first instance, insertion products containing μ-vinyl ligands.[1-5] In a previous paper we reported that the dimanganese complex $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ (**1**) reacts in this way with RC≡CR′ under photolysis to give the μ-vinyl complexes $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(R)=C(H)R'\}(\mu\text{-}PPh_2)(CO)_7]$.[6] The range of alkynes studied was, however, restricted to PhC≡CPh, PhC≡CH, and HC≡CH and we have now extended our investigations to alkynes containing α-methyl or α-methylene substituents. In addition to giving μ-vinyl complexes such alkynes also give η^3-allyl complexes by a process which must involve hydrogen transfer within the ligands. In order to explore the generality of these hydrogen-transfer reactions we have also studied the reactions of alkynes containing α-methyl or α-methylene substituents with the μ-hydrido heterodimetallic complex $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_4]$ (**2**).[7,8] Complexes (**1**) and (**2**) react differently with acetylene itself, the former giving a simple μ-vinyl complex[6] whereas the latter gives, as the major product, the complex $[(\eta\text{-}C_5H_5)(CO)Mo\{\mu\text{-}\sigma\text{:}\eta^4\text{-}C(H)=CHCH_2C(H)PPh_2\}Mn(CO)_3]$, in which the bridging $C_4H_5PPh_2$ ligand is formally derived by coupling of the $\mu\text{-}PPh_2$ and μ-H ligands in (**2**) with two molecules of C_2H_2.[7]

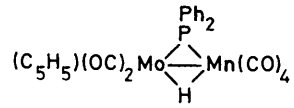
Results and Discussion

(*a*) *Reactions of* (**1**) *with Alkynes.*—Photolysis of MeC≡CH with a solution of (**1**) in hexane gives a red product and an orange complex in addition to unreacted starting material. The red product was identified by its spectroscopic properties and by microanalysis as an isomeric mixture of the two μ-vinyl complexes $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(R)=CHR'\}(\mu\text{-}PPh_2)(CO)_7]$ [R = Me, R′ = H, (**3a**); R = H, R′ = Me (**3b**)], with the ratio (**3a**):(**3b**) being estimated from the ^{1}H n.m.r. spectrum of the mixture as *ca.* 11:7. The coupling between the α- and β-CH protons in (**3b**) is 13.6 Hz, which indicates that these protons are *trans* to each other[6] and that an apparent *cis* insertion of the alkyne has occurred. Such *cis* insertion has been confirmed by *X*-ray crystallography for the related isonitrile-substituted complex $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Ph)=C(H)Ph\}(\mu\text{-}PPh_2)(CO)_6(CNBu^t)]$.[9]

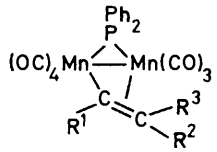
The orange product from the reaction of MeC≡CH with (**1**) was obtained in a yield comparable to that of (**3a**) and (**3b**) combined. It gives the same molecular ion peak in its mass spectrum (*m/e* 532) as the mixture of (**3a**) and (**3b**) and, on the basis of its ^{1}H n.m.r. spectrum, it was identified as the η^3-allyl complex $[Mn_2(\mu\text{-}PPh_2)(\eta^3\text{-}C_3H_5)(CO)_7]$ (**4a**). Five ^{1}H n.m.r. signals, each corresponding to one proton, were observed at 298 K in addition to a multiplet due to the phenyl groups. The signal at δ 5.03 p.p.m. shows coupling to the other four signals and is assigned to H^3 (see numbering scheme). The remaining four protons can be assigned as *syn* (δ 3.82 and 3.40) or *anti* (δ 2.56 and 2.02) on the basis of the magnitude of their coupling to the central proton (6.1 Hz for the *syn* protons and 11.6 Hz for the *anti*). The observation of five proton signals for (**4a**) suggests that the two terminal carbon atoms of the allyl ligand are in non-equivalent environments and this was confirmed by ^{13}C n.m.r. spectroscopy. In addition to seven ^{13}CO resonances the undecoupled spectrum at 298 K showed one doublet at δ 89.60 [*J*(CH) 157.8 Hz] and two triplets at δ 50.1 [*J*(CH) 153.6 Hz] and δ 49.2 [*J*(CH) 156.2 Hz] due respectively to the central and two terminal carbon atoms of the allyl ligand. In the structure of the related molybdenum–manganese complex $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}PPh_2)Mn(\eta^3\text{-}C_3H_5)(CO)_3]$ (**5a**) (see below), which has been determined by *X*-ray crystallography,[10] the allyl–manganese bond axis is in the $Mo(\mu\text{-}PPh_2)Mn$ plane and *cis* to the bridging ligand. On this basis (**4a**) is tentatively assigned the structure shown. Rotation of the allyl ligand about the allyl–manganese axis as shown in Scheme 1 would exchange the environments of the two *syn* hydrogen atoms as well as those of the two *anti* hydrogen atoms and, at 363 K in [$^2H_8$]toluene, the ^{1}H n.m.r. signals due to H^1, H^2, H^4, and H^5 do collapse to give two broad signals which are the average of H^1/H^2 and H^4/H^5. These changes are reversible although, on cooling, weak signals due to low concentrations of (**3a**)/(**3b**) are also observed.



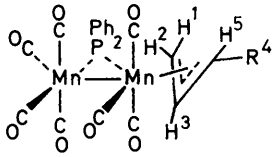
(1)



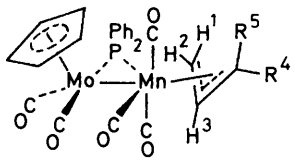
(2)



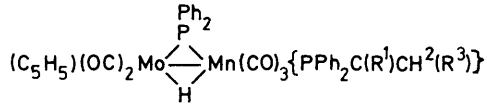
(3a) R^1 = Me, R^2 = H^2, R^3 = H^3
(3b) R^1 = H^1, R^2 = Me, R^3 = H^3
(3c) R^1 = Me, R^2 = Me, R^3 = H^3
(3d) R^1 = Et, R^2 = H^2, R^3 = H^3
(3e) R^1 = H^1, R^2 = Et, R^3 = H^3
(3f) R^1 = Ph, R^2 = Me, R^3 = H^3
(3g) R^1 = Me, R^2 = Ph, R^3 = H^3



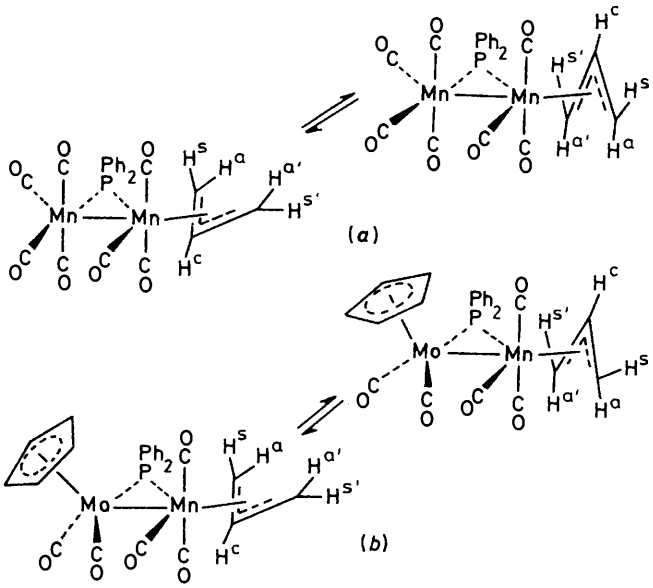
(4a) R^4 = H^4
(4b) R^4 = Me
(4c) R^4 = Ph



(5a) R^4 = H^4, R^5 = H^5
(5b) R^4 = Me, R^5 = H^5
(5c) R^4 = H^4, R^5 = Me



(6a) R^1 = Me^1, R^3 = Me
(6b) R^1 = H^1, R^3 = H^3



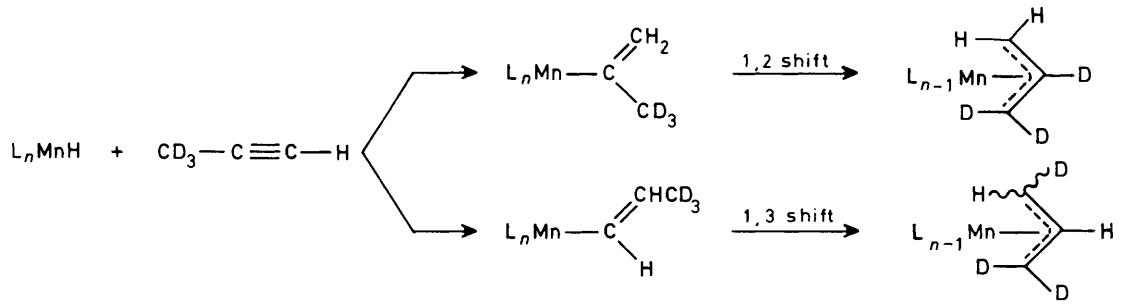
Scheme 1. Isomer interconversion in the dinuclear allyl complexes

In addition to the reaction with MeC≡CH the reactions of (**1**) with MeC≡CMe, EtC≡CH, and PhC≡CMe were also investigated and, in each case, μ-vinyl [(**3c**)—(**3g**)] and η^3-allyl [(**4b**) or (**4c**)] products were obtained, the proposed structures of which are shown. Reaction with the symmetrical alkyne, MeC≡CMe, gave only the one μ-vinyl species, (**3c**), but the unsymmetrical alkynes each gave rise to inseparable mixtures of two isomeric μ-vinyl complexes just as in the reaction with propyne.

It can be deduced from the magnitude of the ^1H–^1H coupling of the vinylic hydrogen atoms in the ^1H n.m.r. spectrum of (**3e**) (13.8 Hz) that the ethyl group is *trans* to the manganese atom, but the stereochemistry of (**3c**), (**3f**), or (**3g**) cannot be assigned in this way. It is likely, however, that these complexes have analogous structures to those of (**3b**) and (**3e**). The ^1H n.m.r. spectra of the orange η^3-allyl complexes $[Mn_2(\mu\text{-}PPh_2)(\eta^3\text{-}RCHCHCH_2)(CO)_7]$ [R = Me, (**4b**); R = Ph, (**4c**)] reveal that the R groups are in *syn* positions, since the central allyl proton shows ^1H–^1H couplings in each case of *ca.* 11 Hz to two (*anti*) protons and of *ca.* 7 Hz to one (*syn*) proton.

(*b*) *Reactions of* (**2**) *with Alkynes.*—U.v. irradiation of a solution of (**2**) in hexane–benzene (3:1) in the presence of MeC≡CH gives the η^3-allyl complex $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}PPh_2)Mn(\eta^3\text{-}C_3H_5)(CO)_3]$ (**5a**). In contrast to the reaction of (**1**) with MeC≡CH no evidence was obtained for the formation of μ-vinyl complexes. Complex (**5a**) can also be obtained from the reaction of (**2**) with allene[10] and an *X*-ray diffraction study[10] confirms that the structure in the solid state is as shown here. In solution the ^1H n.m.r. spectrum of (**5a**) at room temperature shows, in addition to resonances assigned to phenyl and two cyclopentadienyl groups, resonances due to ten η^3-allyl hydrogen atoms. This spectrum is consistent with the presence in solution of two isomers, their concentration ratio being estimated from the relative intensities of the C_5H_5 and η^3-allyl signals due to each species as *ca.* 4:1. The assignment of the hydrogen resonances for (**5a**), given in the Experimental section, has been made on the basis of their distinctive chemical shifts and ^1H–^1H coupling constants. Selective irradiation of each of the η^3-allyl resonances results in the collapse of a resonance due to a corresponding hydrogen in the other isomer. Thus, for example, irradiation of an *anti* allyl hydrogen in the major isomer results in the collapse of one of the *anti* allyl hydrogens in the minor isomer and *vice versa*. These results are consistent with the operation of a fluxional process which interconverts the two isomers of (**5a**) at a rate which is too slow at room temperature to result in broadening of the resonances but sufficiently rapid to result in spin saturation transfer.[11]

The interconversion of the two isomers of (**5a**) presumably takes place *via* a 180° rotation of the allyl ligand round the manganese–allyl bond axis as proposed for (**4a**) and shown in Scheme 1. In (**4a**) such a rotation exchanges the environments of the two *anti* and two *syn* protons so that the two rotamers give



Scheme 2. Effect of 1,2- and 1,3-hydrogen-atom shifts on deuterium atom distribution in the allyl products from reaction of $CD_3C{\equiv}CH$ with (**1**) and (**2**)

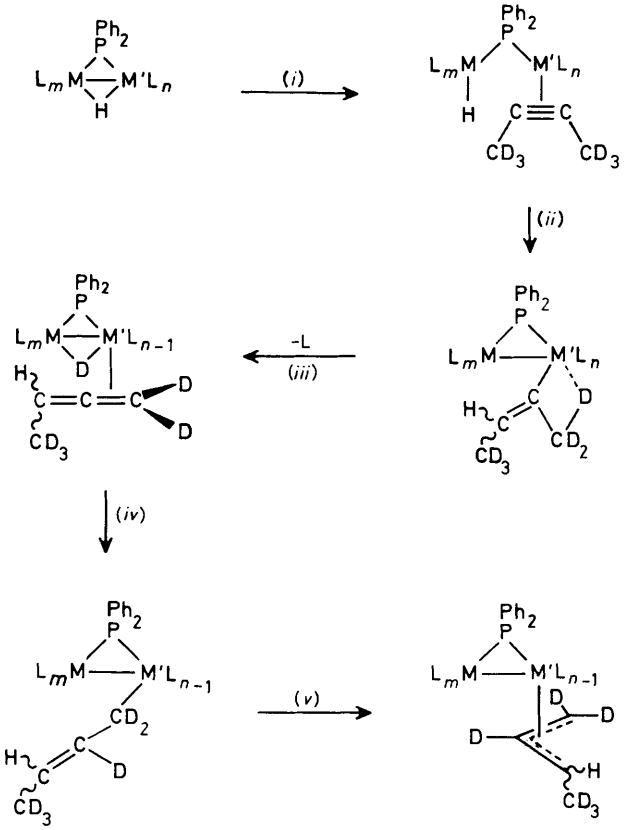
rise to only five allyl signals in the slow-exchange limit. In (**5a**), on the other hand, the lower symmetry of the complex results in the five allyl protons in each of the rotamers occupying non-equivalent sites and hence to the observation of ^1H n.m.r. signals corresponding to the presence of two isomers.

Reaction of (**2**) with MeC≡CMe and with EtC≡CH leads, in each case, to an inseparable mixture of $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}PPh_2)Mn(\eta^3\text{-}syn\text{-}MeCHCHCH_2)(CO)_3]$ (**5b**) and the corresponding η^3-*anti*-1-methylallyl complex (**5c**). In addition to this mixture the reaction with MeC≡CMe gave rise to an orange-yellow complex which was identified as $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_3\{PPh_2C(Me){=}C(H)Me\}]$ (**6a**) on the basis of its spectroscopic properties. In particular the ν(CO) i.r. spectrum of (**6**) is almost identical to that of $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_3(PPh_2CH{=}CH_2)]$, (**6b**), which was synthesised directly from (**2**) and $Ph_2PCH{=}CH_2$ for comparative purposes. Substitution by organophosphines of CO groups on the manganese rather than the molybdenum atom in (**2**) has been confirmed by an *X*-ray diffraction study of a related complex, $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_2(dppm\text{-}PP')]$ (dppm = $Ph_2PCH_2PPh_2$) and by n.m.r. studies on a range of other monosubstituted organophosphine derivatives analogous to (**6**).[8]

The reactions of (**2**) with MeC≡CMe and with EtC≡CH differ from the reactions of (**1**) with these ligands in that, with (**1**), only the η^3-*syn*-allyl complex is obtained as opposed to the *ca.* 1:1 mixture of *syn* and *anti* complexes which is obtained with (**2**). A further difference is that the reactions with (**2**) do not give μ-vinyl complexes of the type obtained in reactions of these alkynes with (**1**). These differences are discussed below in the light of the proposed mechanism for the hydrogen shift reaction.

(*c*) *Mechanism of the Hydrogen Shift Reaction.*—The formation of η^3-allyl ligands from reactions of (**1**) and (**2**) with alkynes must involve either a 1,2- or a 1,3-hydrogen shift within the ligand. These alternatives can, in principle, be distinguished by appropriately chosen experiments using deuteriated alkynes, as shown for $CD_3C{\equiv}CH$ in Scheme 2.

Reaction of (**1**) with $CD_3C{\equiv}CH$ gave $[^2H_3]$(**4a**), the ^1H n.m.r. spectrum of which showed four peaks at δ 3.82, 3.40, 2.56, and 2.02 corresponding to the four non-equivalent H atoms on the terminal carbon atoms of the allyl ligand. These peaks were of equal intensity but half that, relative to the μ-PPh_2 phenyl resonance, of the corresponding allyl signals of undeuteriated (**4a**). No resonance was observed for $[^2H_3]$(**4a**) at δ 5.03, showing that the hydrogen atom position on the central carbon atom was fully deuteriated. Similar results were obtained using $CD_3C{\equiv}CPh$. In this instance the ^1H n.m.r. spectrum of the $[^2H_3]$phenylallyl product, $[Mn_2(\mu\text{-}PPh_2)(\eta^3\text{-}C_3HD_3Ph)(CO)_7]$ $[^2H_3]$(**4c**), showed, in addition to the phenyl group resonances, the signal at δ 4.07 which was assigned in undeuteriated (**4c**) to the allyl proton on the same carbon atom

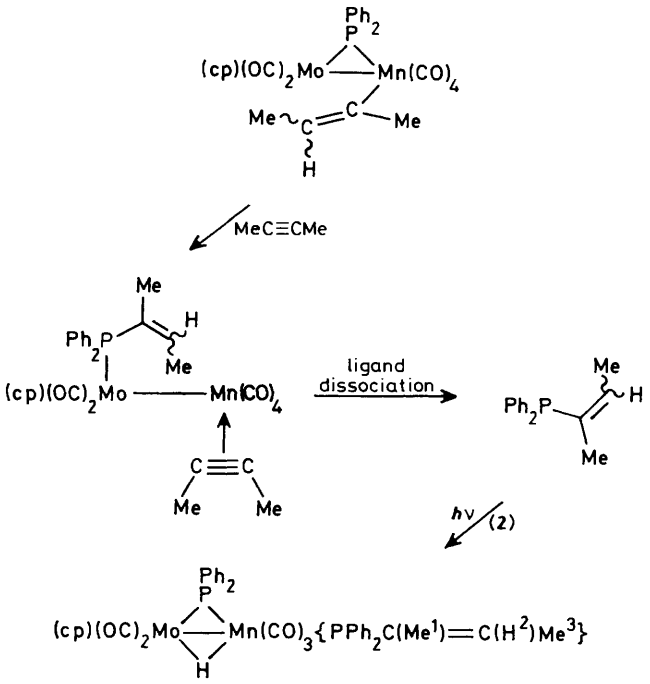


Scheme 3. A possible mechanism for the formation of allyl complexes from the reaction of (**1**) and (**2**) with alkynes; M = Mo or Mn, M′ = Mn

as the phenyl group. None of the remaining allyl resonances in (**4c**) was present in the ^1H n.m.r. spectrum of the deuteriated complex. Again this is only consistent with a 1,2 H-atom shift.

Finally, the reaction of $CD_3C{\equiv}CH$ with (**2**) was studied. The ^1H n.m.r. spectrum of the product $[^2H_3]$(**5a**) showed the eight resonances due to the *syn* and *anti* protons of each of the two isomers of undeuteriated (**5a**) but again at half the intensity, relative to the μ-PPh_2 phenyl resonance, of the corresponding allyl signals of the undeuteriated complex. The resonances at δ 4.79 and 4.40 due to the central allyl proton, H^3, of each rotamer were absent, as expected for a 1,2- rather than a 1,3-hydrogen-atom shift.

A possible mechanism, consistent with a 1,2 hydrogen-atom shift, for the isomerisation involved in the reactions of (**1**) and (**2**) with alkynes to give allyl complexes is shown in Scheme 3,



Scheme 4. Proposed mechanism for the formation of (**6a**) (cp = η-C_5H_5)

using $CD_3C{\equiv}CCD_3$ as an illustrative example. Steps (*i*) and (*ii*), involving co-ordination of the alkyne and insertion into an M–H bond to give a σ-vinyl ligand bonded to one metal atom, parallel those which have been previously discussed for reactions of (**1**) with alkynes not possessing α-methyl or α-methylene substituents.[9] If such substituents are present, as in the case of $CD_3C{\equiv}CCD_3$, then oxidative addition of a C–D bond of the α-substituent to one of the metal centres is possible [step (*iii*)], giving an η^2-allene ligand. Transfer of the metal-bound deuterium atom to the central carbon atom of the η^2-allene ligand would then lead to the observed allyl product.

There are precedents in the chemistry of mononuclear species for the transformations of σ-vinyl complexes to allyl complexes, and for the proposal that an allene intermediate is involved. Thus, Green and co-workers[12] have proposed that the first step in the reaction of H^- with a variety of cationic molybdenum alkyne complexes, *e.g.* $[(\eta\text{-}C_5H_5)Mo(MeC{\equiv}CMe)(CO)(PEt_3)]^+$ is the formation of a neutral σ-vinyl species which then isomerises *via* an η^2-allene intermediate to give the observed η^3-*anti*-1-methylallyl product. Similarly Schwartz *et al.*[13] have shown that thermolysis of $[M\{\sigma\text{-}C(Me){=}CHMe\}(CO)(PPh_3)_2]$ gives $[M(\eta^3\text{-}syn\text{-}MeCHCH\text{-}CH_2)(CO)(PPh_3)_2]$ (M = Rh or Ir) and again an intermediate η^2-allene species was invoked.

The intermediacy of a σ-vinyl complex in the above mechanistic scheme is supported, in the case of reaction of MeC≡CMe with (**2**), by the isolation of (**6a**) from the product mixture. A possible mechanism of formation of (**6a**) is shown in Scheme 4. Attack of a second molecule of alkyne on the σ-vinyl intermediate leads to reductive P–C coupling,[9] giving the tertiary phosphine ligand which may then dissociate from the complex and rapidly substitute for a CO ligand in (**2**).

The formation of μ-vinyl complexes, in addition to allyl complexes, in the reactions of (**1**) with alkynes can also be rationalised in terms of a σ-vinyl intermediate, with loss of CO and co-ordination of the σ-vinyl ligand to the second metal centre representing an alternative and competing pathway to that involving the hydrogen-atom shift. Neither of these steps is readily reversible under thermolytic or photolytic conditions. Thus the μ-vinyl complexes (**3a**) and (**3b**) were recovered in quantitative yield after being refluxed in hexane solution for several hours. Similarly, the allyl complex (**4a**) was recovered quantitatively after being refluxed under the same conditions. Photolysis of the solutions was similarly ineffective in bringing about isomerisation although some decomposition occurred. In [$^2H_8$]toluene solution, however, as already indicated, low concentrations of (**3a**)/(**3b**) were detected by ^1H n.m.r. spectroscopy after heating a sample of (**4a**) to 363 K for *ca.* 2 h.

The fact that reactions of (**2**) with alkynes do not give μ-σ:η^2-vinyl complexes can be rationalised in terms of the greater lability of the CO ligands on manganese in the heteronuclear complex as compared to those on the molybdenum atom.[8] This presumably favours the pathway involving oxidative addition to the manganese centre (which leads to the allyl complexes) over that involving co-ordination of the vinyl ligand to the molybdenum centre.

The other main difference between the reactions of (**1**) and of (**2**) with α-methyl or α-methylene substituted alkynes, namely the exclusive formation of *syn*-allyl complexes in the case of (**1**) and of *syn*/*anti* mixtures in the case of (**2**) is less easy to rationalise. Since the *syn*-allyl complex (**5b**), which can be prepared free of the *anti*-allyl complex (**5c**) by reacting (**2**) with butadiene, does not isomerise to (**5c**) under the reaction conditions,[10] it seems likely that both isomers are formed in the initial reaction of (**2**) with MeC≡CMe. The reaction of (**1**) with PhC≡CPh gives $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Ph){=}CHPh\}(\mu\text{-}PPh_2)(CO)_7]$ in which the phenyl substituents on the vinyl ligand adopt a *cis* configuration.[9] On the other hand, the methyl substituents on the vinyl ligand in $[\{(\eta\text{-}C_5H_5)(CO)_2Mo\}_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Me){=}C(H)Me\}(\mu\text{-}PMe_2)]$, obtained from reaction of $[\{(\eta\text{-}C_5H_5)(CO)_2Mo\}_2(\mu\text{-}H)(\mu\text{-}PMe_2)]$ with MeC≡CMe have been shown by an *X*-ray diffraction study to adopt a *trans* configuration.[14] It is accordingly possible that the configuration of the allyl ligands in the complexes obtained in this study depends on the configuration of the σ-vinyl intermediates involved in their formation. An exclusively *cis* configuration for the substituents on the σ-vinyl ligand in the dimanganese system and a *cis*–*trans* mixture in the molybdenum–manganese system could account for the observed product distribution. Unfortunately, we were not able to determine from the spectroscopic data the relative orientation of the methyl groups in (**6a**) which, by extension, would have indicated the relative orientation of these groups in the corresponding σ-vinyl intermediate.

Experimental

All reactions were carried out with magnetic stirring under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. U.v. irradiation was carried out in a glass photolysis vessel using a Hanovia 125 W medium-pressure immersion lamp in a water- or ethanol-cooled quartz inner tube.

Work-up procedures were generally performed in air. Preparative thin-layer chromatography (t.l.c.) was carried out on commercial Merck plates coated with a 0.25-mm layer of silica, or on 1-mm silica plates prepared in the Department; products are presented in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously.[15] The ^{13}C spectra are ^1H-gated decoupled unless otherwise stated. Proton and ^{13}C chemical shifts are given in δ on the p.p.m. scale relative to $\delta(SiMe_4) = 0.0$ p.p.m; *J* in Hz. All n.m.r. spectra were recorded at 293 K unless otherwise stated. The complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$

(**1**)[6] and $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_4]$ (**2**)[8] were prepared by the literature methods. All other reagents were obtained from the usual commercial suppliers and used without further purification.

1. *Reactions of* (**1**) *with Alkynes.*—(*a*) *With propyne.* Excess propyne was added to a solution of (**1**) (0.052 g, 0.1 mmol) in hexane (50 cm^3) in a glass photolysis vessel by bubbling the gas through the solution for 1 min. A quartz inner tube containing the u.v. filament was placed into the vessel and the solution was irradiated with u.v. light for 5 h at 223 K. After removal of the solvent on a rotary evaporator, the residue was redissolved in the minimum of CH_2Cl_2 and separated by preparative t.l.c. using hexane–dichloromethane (3:1) as eluant. Unreacted (**1**) eluted first as a bright yellow band (0.016 g, 30%), followed by a red band containing the inseparable isomers $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Me)\text{=}CH_2\}(\mu\text{-}PPh_2)(CO)_7]$ (**3a**) and $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(H)\text{=}C(H)Me\}(\mu\text{-}PPh_2)(CO)_7]$ (**3b**) (combined yield 0.016 g, 28%), and an orange band containing $[Mn_2(\mu\text{-}PPh_2)(\eta^3\text{-}C_3H_5)(CO)_7]$ (**4a**) (0.011 g, 21%). These complexes were isolated in microcrystalline form after removal of solvent under reduced pressure.

Isomeric mixture of (**3a**) and (**3b**) (Found: C, 50.1; H, 3.2. $C_{22}H_{15}Mn_2O_7P$ requires C, 49.6; H, 2.8%). Mass spectrum: *m/e* 532 (M^+), $M^+ - n$(CO) (n = 2—5, 7). $\nu_{max.}$(CO) at 2 064m, 2 018m, 2 003s, 1 978s, 1 964m, 1 956m, 1 942m cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$) [ratio (**3a**):(**3b**), 11:7]; (**3a**), δ 7.83—7.01 (m, 10 H, Ph), 4.06 [d, ^3J(PH) 9.6, 1 H, H^2/H^3], 3.45 [d, ^3J(PH) 8.2, 1 H, H^3/H^2], 3.00 (s, 3 H, Me); (**3b**), δ 8.32 [dd, $^3J(H^1H^3)$ 13.6, J(PH) 8.5, 1 H, H^1], 7.83—7.01 (m, 10 H, Ph), 4.85 [ddq, $^3J(H^2H^3)$ 5.8, ^3J(PH) 5.0, 1 H, H^3], 1.66 (d, 3 H, Me).

(**4a**). Mass spectrum: *m/e* 532 (M^+). $\nu_{max.}$(CO) at 2 070s, 2 021m, 1 996s, 1 984s, 1 957s, 1 949(sh) cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$), δ 7.7—7.3 (m, 10 H, Ph), 5.03 [dddd, $J(H^1H^3) = J(H^3H^5)$ 11.6, $J(H^2H^3) = J(H^3H^4)$ 6.1, 1 H, H^3], 3.82 (d, 1 H, H^2/H^4), 3.40 (d, 1 H, H^4/H^2), 2.56 (d, 1 H, H^1/H^5), 2.02 (d, 1 H, H^5/H^1); ^{13}C ($CDCl_3$, ^1H undecoupled), δ 233.0 (s, 1 CO), 223.1 (s, 1 CO), 219.0 (s, 1 CO), 214.9 [d, ^2J(PC) 10.8, 1 CO], 214.4 [d, ^2J(PC) 13.2, 1 CO], 213.7 [d, ^2J(PC) 13.8, 1 CO], 212.9 [d, ^2J(PC) 15.4, 1 CO], 142—126 (m, Ph), 89.6 [d, J(HC) 157.8, CH_2CHCH_2], 50.1 [t, J(HC) 153.6, CH_2CHCH_2], 49.2 [t, J(HC) 156.2, CH_2CHCH_2].

(*b*) *With but-2-yne.* But-2-yne (60 μl, 1.5 mmol) was added to a solution of (**1**) (0.050 g, 0.09 mmol) in hexane (50 cm^3) and the solution photolysed as in (*a*) at room temperature for 1 h. The residue was then separated by preparative t.l.c. as in (*a*) using hexane–CH_2Cl_2 (9:1) as eluant. Removal of solvent gave unreacted (**1**) (0.035 g, 70%), red $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Me)\text{=}C(H)Me\}(\mu\text{-}PPh_2)(CO)_7]$ (**3c**) (0.006 g, 12%) and orange $[Mn_2(\mu\text{-}PPh_2)(\eta^3\text{-}syn\text{-}MeCHCHCH_2)(CO)_7]$ (**4b**) (0.005 g, 10%).

(**3c**). Mass spectrum: *m/e* 546 (M^+), $M^+ - n$CO (n = 2—5, 7). $\nu_{max.}$(CO) at 2 061m, 2 016vs, 2 000s, 1 976s, 1 961m, 1 955m, 1 936 cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$), δ 7.91—6.93 (m, 10 H, Ph), 4.56 [dq, ^3J(PH) 6.0, $J(H^2H^3)$ 6.0, 1 H, H^3], 2.83 (s, 3 H, Me^1), 1.57 (d, 3 H, Me^2).

(**4b**). Mass spectrum: *m/e* 546 (M^+), $M^+ - n$CO (n = 2—5, 7). $\nu_{max.}$(CO) at 2 067m, 2 017m, 1 992s, 1 981s, 1 953s, 1 941s cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$), δ 8.0—7.3 (m, 10 H, Ph), 4.78 [ddd, $J(H^1H^2) = J(H^3H^5)$ 10.7, $J(H^3H^2)$ 6.6, 1 H, H^3], 3.66 [ddd, $J(H^1H^2)$ 2.4, J(PH) 4.4, 1 H, H^2], 3.29 [dq, $J(H^4H^5)$ 6.1, 1 H, H^5], 2.01 (d, 3 H, Me), 1.74 (dd, 1 H, H^1).

(*c*) *With but-1-yne.* But-1-yne (60 μl, 1.5 mmol) and (**1**) (0.104 g, 0.2 mmol) were photolysed in hexane solution (50 cm^3) at room temperature for 5 h using an analogous procedure to that in (*a*). Separation of the reaction products by t.l.c. as in (*a*) using hexane–CH_2Cl_2 (9:1) as eluant gave unreacted (**1**) (0.007 g, 6.5%), then an inseparable mixture of the isomeric red complexes $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Et)\text{=}CH_2\}(\mu\text{-}PPh_2)(CO)_7]$ (**3d**) and $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(H)\text{=}C(H)Et\}(\mu\text{-}PPh_2)(CO)_7]$ (**3e**) (combined yield 0.018 g, 18%) and finally (**4b**) (0.032 g, 31%).

Isomeric mixture of (**3d**) and (**3e**). Mass spectrum: *m/e* 546 (M^+), $M^+ - n$(CO) (n = 2—5, 7). $\nu_{max.}$(CO) at 2 064m, 2 018s, 2 003s, 1 978m, 1 962m, 1 956m, 1 937m cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$) [ratio (**3d**):(**3e**), 9:8]; (**3d**), δ 7.9—7.0 (m, 10 H, Ph), 4.03 [dd, ^3J(PH) 10.4, $J(H^2H^3)$ 1.4, 1 H, H^2/H^3], 3.49 [dd, ^3J(PH) 9.8, 1 H, H^3/H^2], 3.29 (m, 1 H, CH_AH_BMe), 2.98 (m, 1 H, CH_AH_BMe), 1.25 [dd, $J(HH_A) = J(HH_B)$ = 7.3, 3 H, CH_2Me]; (**3e**), δ 8.40 [dd, $J(H^1H^3)$ 13.8, ^3J(PH) 8.5, 1 H, H^1], 7.9—7.0 (m, 10 H, Ph), 4.87 [ddt, ^3J(HH) 5.7, ^3J(PH) 5.7, 1 H, H^3], 1.84 [dq, ^3J(HH) 7.45, 2 H, CH_2CH_3], 0.98 (t, 3 H, Me).

(*d*) *With phenylpropyne.* Phenylpropyne (100 μl, 0.8 mmol) and (**1**) (0.052 g, 0.1 mmol) were photolysed in hexane solution (50 cm^3) at room temperature for 5 h as in (*a*). Separation of the reaction products by t.l.c. as in (*a*) using hexane–CH_2Cl_2 (9:1) as eluant gave unreacted (**1**) (0.034 g, 65%), then an inseparable mixture of the red isomeric complexes $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Ph)\text{=}C(H)Me\}(\mu\text{-}PPh_2)(CO)_7]$ (**3f**) and $[Mn_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}C(Me)\text{=}C(H)Ph\}(\mu\text{-}PPh_2)(CO)_7]$ (**3g**) (combined yield 0.013 g, 21%), and finally the orange complex $[Mn_2(\mu\text{-}PPh_2)(\eta^3\text{-}syn\text{-}PhCHCHCH_2)(CO)_7]$ (**4c**) (0.006 g, 10%).

Isomeric mixture of (**3f**) and (**3g**) (Found: C, 55.9; H, 3.8; P, 5.7. $C_{28}H_{19}Mn_2O_7P$ requires C, 55.3; H, 3.1; P, 5.1%). Mass spectrum: *m/e* 608 (M^+), $M^+ - n$(CO) (n = 2—7). $\nu_{max.}$(CO) at 2 061m, 2 016vs, 2 000s, 1 976s, 1 964m, 1 952m, 1 942m cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$) [ratio (**3f**):(**3g**), 5:9]; (**3f**), δ 8.0—6.9 (m, 15 H, Ph), 5.34 [d, ^3J(PH) 8.6, 1 H, H^3], 3.06 [d, ^4J(PH) 0.9, 3 H, Me]; (**3g**), δ 8.0—6.9 (m, 15 H, Ph), 4.70 [dq, ^3J(PH) 7.7, $J(H^1H^3)$ 6.1, 1 H, H^3], 1.66 (d, 3 H, Me).

(**4c**) (Found: C, 54.4; H, 3.3. $C_{28}H_{19}Mn_2O_7P$ requires C, 55.2; H, 3.1%). Mass spectrum: *m/e* 608 (M^+), $M^+ - n$(CO) (n = 2, 3, 5, 7). $\nu_{max.}$(CO) at 2 068s, 2 017m, 1 995s, 1 983s, 1 957s, and 1 944m cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$), δ 8.1—7.0 (m, 15 H, Ph), 5.67 [dddd, $J(H^1H^3) = J(H^3H^5)$ 11.1, $J(H^2H^3)$ 6.9, ^3J(PH) 0.6, 1 H, H^3], 4.07 (d, 1 H, H^5), 3.83 [ddd, ^3J(PH) 4.2, $J(H^1H^2)$ 1.7, 1 H, H^2], 2.03 (dd, 1 H, H^1).

2. *Reactions of* (**2**) *with Alkynes.*—(*a*) *With propyne.* Excess propyne was added to a solution of (**2**) (0.114 g, 0.2 mmol) in hexane–benzene (3:1, 40 cm^3) which was then photolysed for 2 h at 258 K as in 1(*a*) to give a dark red solution. After evaporation of the solvent on a rotary evaporator the residue was dissolved in the minimum of CH_2Cl_2 and separated by t.l.c. using hexane–CH_2Cl_2 (9:1) as eluant. Unreacted (**2**) (0.018 g, 16%) and a dark red crystalline complex, identified spectroscopically as $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}PPh_2)Mn(\eta^3\text{-}C_3H_5)(CO)_3]$ (**5a**) (0.072 g, 62%), were obtained on evaporation of the solvent. N.m.r. (^1H, $CDCl_3$): rotamer 1 (80%), δ 7.6—7.0 (m, 10 H, Ph), 5.05 (s, 5 H, C_5H_5), 4.95 (obscured, H^3), 3.60 [m, 1 H, H^2], 3.41 [m, $J(H^3H^4)$ 6.3, 1 H, H^4], 2.27 [d, $J(H^3H^5)$ 11.2, 1 H, H^5], 1.06 [d, $J(H^1H^3)$ 12.7, 1 H, H^1]; rotamer 2 (20%), δ 5.14 (s, 5 H, C_5H_5), 4.60 [m, $J(H^3H^5)$ 11.9, $J(H^1H^3)$ 11.9, 1 H, H^3], 3.60 (m, 1 H, H^2), 2.90 (m, 1 H, H^4), 2.56 (d, 1 H, H^1), 2.51 (d, 1 H, H^5).

(*b*) *With but-2-yne.* Complex (**2**) (0.114 g, 0.2 mmol) and C_2Me_2 (200 μl, large excess) in hexane–benzene (3:1, 40 cm^3) were photolysed as in 1(*a*) for 2 h at room temperature. Separation by t.l.c. using hexane–CH_2Cl_2 (9:1) as eluant gave unreacted (**2**) (0.055 g, 48%), an inseparable mixture of dark red $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}PPh_2)Mn(\eta^3\text{-}syn\text{-}MeCHCHCH_2)(CO)_3]$ (**5b**) and the corresponding *anti* isomer (**5c**) [combined yield of (**5b**) and (**5c**) 0.024 g, 20%] and orange-yellow $[(\eta\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Mn(CO)_3\{PPh_2C(Me)\text{=}C(H)Me\}]$ (**6a**) (0.010 g, 8%) together with several other unidentified products in low yield.

Isomeric mixture of (**5b**) and (**5c**). $\nu_{max.}$(CO) at 2 029, 1 951 (sh), 1 946s, 1 923m, and 1 876m cm^{-1} (n-hexane). N.m.r.: ^1H (CD_2Cl_2, 278 K) [ratio (**5b**):(**5c**), *ca.* 1:1]; (**5b**), rotamer 1

(74%), δ 7.8—7.0 (m, 10 H, Ph), 5.00 (s, 5 H, C_5H_5), 4.79 [ddd, $J(H^1H^3)$ 11.8, $J(H^3H^5)$ 10.7, $J(H^2H^3)$ 7.1, 1 H, H^3], 3.46 [ddd, $^3J(PH)$ 3, $J(H^1H^2)$ 1, 1 H, H^2], 3.05 [dq, $J(H^4H^5)$ 6.2, 1 H, H^5], 1.96 (d, 3 H, Me^4), 0.77 (dd, 1 H, H^1); rotamer 2 (26%), δ 5.13 (s, 5 H, C_5H_5), 4.40 [ddd, $J(H^1H^3)$ 11.1, $J(H^3H^5)$ 10.0, $J(H^2H^3)$ 5.9, 1 H, H^3], 3.27 [dq, $J(H^4H^5)$ 6.2, 1 H, H^5], 2.68 [m, $^4J(PH)$ 3.1, 1 H, H^2], 2.23 (d, 1 H, H^1), 1.97 (d, 3 H, Me^4); (**5c**), rotamer 1 (50%), δ 7.8—7.0 (m, 10 H, Ph), 5.02 (s, 5 H, C_5H_5), 4.81 (obscured, H^3), 4.68 (obscured, H^4), 3.51 [ddd, $J(H^2H^3)$ 6.7, $J(H^1H^2)$ 1.7, $^3J(PH)$ 1, 1 H, H^2], 2.67 [dd, $J(H^1H^3)$ 11.7, 1 H, H^1], 0.12 [d, $J(H^4H^5)$ 6.9, 3 H, Me^5]; rotamer 2 (50%), δ 5.01 (s, 5 H, C_5H_5), 4.81 (obscured, H^3), 4.39 [dq, $J(H^3H^4)$ 8.0, $J(H^4H^5)$ 6.9, 1 H, H^4], 3.82 [m, $J(H^2H^3)$ 8.0, $^3J(PH)$ 3, $J(H^1H^2)$ 2.6, 1 H, H^2], 1.58 [dd, $J(H^1H^3)$ 12.7, 1 H, H^1], 1.35 (d, 3 H, Me^5).

(**6a**). Mass spectrum: *m/e* 782 (M^+), $M^+ - n$(CO) (n = 1—5). $\nu_{max.}$(CO) at 2 024w, 1 953s, 1 938s, 1 915m, 1 883m cm^{-1} (n-hexane). N.m.r.: ^1H ($CDCl_3$), δ 8.0—7.0 (m, 20 H, Ph), 6.1 (m, 1 H, H^2), 4.50 (s, 5 H, C_5H_5), 1.91 [d, $J(H^2H^3)$ 6.3, 3 H, Me^3], 1.67 [d, $^3J(PH)$ 9.9, 3 H, Me^1], −14.25 [dd, $^2J(PH)$ 32.5, 20.4, 1 H, Mo(μ-H)Mn].

(*c*) *With but-1-yne.* Complex (**2**) (0.114 g, 0.2 mmol) and EtC≡CH (excess bubbled into solution) were photolysed for 2 h at 275 K as in 1(*a*). Separation by t.l.c. as in 2(*b*) gave unreacted (**2**) (0.042 g, 37%) and an inseparable mixture of (**5b**) and (**5c**) (0.045 g, 38%), together with several other products in very low yield which were not identified. ^1H N.m.r. spectroscopy showed that the ratio of (**5b**):(**5c**) obtained was, within experimental error, the same (*ca.* 1:1) as that from the reaction of (**2**) with MeC≡CMe.

3. *Deuteriation Studies.*—(*a*) *Reaction of* $CD_3C{\equiv}CH$ *with* (**1**). $CD_3C{\equiv}CH$ was generated by reaction of equimolar amounts of CD_3I and NaC≡CH in refluxing toluene.[16] The $CD_3C{\equiv}CH$ generated was passed through a cold trap at 248 K and bubbled directly into a solution of (**1**) (0.156 g, 0.3 mmol) in hexane (75 cm^3) which was then photolysed for 1.5 h at 283 K. [Mn_2(μ-σ:η^2-$C_3D_3H_2$)(μ-PPh_2)$(CO)_7$] [$^2H_3$](**3a**)/(**3b**) (0.028 g, 18%) and [Mn_2(μ-PPh_2)(η^3-$C_3D_3H_2$)$(CO)_7$] [$^2H_3$](**4a**) (0.016 g, 13%), were separated from unreacted (**1**) (0.033 g, 21%) as in 1(*a*).

(*b*) *Reaction of* $CD_3C{\equiv}CH$ *with* (**2**). This experiment was carried out in an analogous manner to that with the undeuteriated alkyne using 0.114 g (0.2 mmol) of (**2**). Complex [$^2H_3$](**3a**) (0.02 g, 17%) and unreacted (**2**) (0.035 g, 31%) were obtained in addition to low yields of several uncharacterised new complexes which are presumably formed as a result of impurities in the alkyne.

(*c*) *Reaction of* $CD_3C{\equiv}CPh$ *with* (**1**). Sodium (0.2 g, 12 mmol) and phenylethylene (1.3 cm^3, 12 mmol) were dissolved in tetrahydrofuran (100 cm^3) and refluxed for 24 h until no sodium remained. The solution was cooled and, after addition of CD_3I (1.8 g, 12 mmol), was then warmed gently to *ca.* 313 K for 0.5 h. The [$^2H_3$]phenylpropyne was isolated by addition of water (100 cm^3) and extraction into diethyl ether (3 × 100 cm^3 aliquots). The combined ether extracts were washed with aliquots (50 cm^3) of dilute HCl (3), dilute $NaHCO_3$ solution (3), and water (3). After drying over anhydrous magnesium sulphate the ether was removed leaving an oil containing both [$^2H_3$]-phenylpropyne and phenylethyne in a ratio, estimated from ^1H n.m.r. spectroscopy, of *ca.* 9:1. This mixture (0.2 cm^3, excess) was reacted with (**1**) (0.156 g, 0.3 mmol) without further purification using an analogous procedure to that for the undeuteriated alkyne. Separation of the products by t.l.c. gave [$^2H_3$](**3f**)/(**3g**) (0.51 g, 28%) and [$^2H_3$](**4c**) (0.012 g, 6%) together with unreacted (**1**) (0.081 g, 52%).

4. *Reaction of* $Ph_2PCH{=}CH_2$ *with* (**2**).—Complex (**2**) (0.12 g, 0.21 mmol) and $Ph_2PCH{=}CH_2$ (0.06 cm^3, excess) in hexane–benzene (9:1 50 cm^3) were irradiated with u.v. light at room temperature for 1.5 h. The solvent was removed on a rotary evaporator and the residue redissolved in the minimum of CH_2Cl_2 and applied to the base of t.l.c. plates. Elution with hexane–CH_2Cl_2 (3:1) gave unreacted (**2**) (0.011 g, 34%), orange-yellow [(η-C_5H_5)$(CO)_2$Mo(μ-H)(μ-PPh_2)Mn$(CO)_3$-($PPh_2CH{=}CH_2$)] (**6b**) (0.013 g, 31%), and an uncharacterised red complex (0.015 g).

(**6b**). Mass spectrum: *m/e* 698 ($M^+ - 2CO$), $M^+ - n$(CO) (n = 3—5). $\nu_{max.}$(CO) at 2 025m, 1 954s, 1 939s, 1 917m, 1 883m cm^{-1}. N.m.r. (^1H, $CDCl_3$): δ 8.0—7.2 (m, 20 H, Ph), 6.99 [ddd, $J(H^1H^3)$ 18.2, $J(H^1H^2)$ 12.0, $^2J(PH)$ 7.7, 1 H, H^1], 6.04 [dd, $^3J(PH)$ 36.3, 1 H, H^2], 5.47 [dd, $^3J(PH)$ 18.2, 1 H, H^3], 4.63 (s, 5 H, C_5H_5), −14.08 [dd, $^2J(PH)$ 32.1, 23.0, 1 H, Mo(μ-H)Mn].

Acknowledgements

We thank Dr. A. G. Kent for valuable discussion, and the S.E.R.C. BP Chemicals Limited (Hull Division) and the British Petroleum Company p.l.c. for financial support.

References

1 A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1614.
2 K. Burgess, *Polyhedron*, 1984, **3**, 1175.
3 J. Lewis and B. F. G. Johnson, *Gazz. Chim. Ital.*, 1979, **109**, 271.
4 J. B. Keister and J. R. Shapley, *J. Organomet. Chem.*, 1975, **85**, C29.
5 J. L. Graff and M. S. Wrighton, *J. Am. Chem. Soc.*, 1980, **102**, 2123.
6 J. A. Iggo, M. J. Mays, P. R. Raithby, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1983, 205.
7 A. D. Horton, M. J. Mays, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1985, 247.
8 A. D. Horton, M. J. Mays, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1987, 1557.
9 K. Henrick, J. A. Iggo, A. C. Kemball, M. J. Mays, M. McPartlin, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1987, 2669.
10 A. D. Horton, Ph.D. Thesis, University of Cambridge, 1986; A. D. Horton, M. J. Mays, and P. R. Raithby, *Polyhedron*, 1988, **7**, 987.
11 S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, 1963, **39**, 2892.
12 S. R. Allen, P. K. Baker, S. G. Barnes, M. Bottrill, M. Green, A. G. Orpen, I. D. Williams, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1983, 927.
13 J. Schwartz, D. W. Hart, and B. McGiffert, *J. Am. Chem. Soc.*, 1974, **96**, 5613.
14 A. D. Horton, M. J. Mays, and M. McPartlin, unpublished work.
15 J. A. Iggo, M. J. Mays, P. R. Raithby, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 633.
16 T. F. Rutledge, *J. Org. Chem.*, 1959, **24**, 840.

Received 24*th February* 1988; *Paper* 8/00729B