Chemistry of Molybdenum Complexes with (Triphenylmethyl)allene†

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The cationic allene complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]BF_4$ **1**, was converted into the dihydronaphthyl complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$ in the presence of KSCN as the major product. When the reaction was carried out at high concentration, the allylic complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{\eta^3\text{-}CH_2C(COC_{10}H_7Ph_2)CHCPh_3\}]$ was isolated as a minor product. Reaction of allene with the dihydronaphthyl complex also induced insertion of CO followed by C–C coupling to give the allylic complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{\eta^3\text{-}CH_2C(COC_{10}H_7Ph_2)CH_2\}]$. In $CHCl_3$ migration of the organic moiety on Mo in the dihydronaphthyl to the C_5H_5 ligand occurred giving $[MoCl\{\eta^5\text{-}C_5H_4(C_{10}H_7Ph_2)\}(CO)_3]$. In tetrahydrofuran and MeCN, similar reactions gave $[MoH\{\eta^5\text{-}C_5H_4(C_{10}H_7Ph_2)\}(CO)_3]$ and $C_5H_5(C_{10}H_7Ph_2)$ respectively. Under thermolytic conditions $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)\{C(O)\text{-}C_{10}H_7Ph_2\}]$ was also converted into $[MoCl\{\eta^5\text{-}C_5H_4(C_{10}H_7Ph_2)\}(CO)_2(PPh_3)]$. The latter complex and $[W(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$ have been characterized by X-ray diffraction analysis.

Organic prop-2-ynyl, allenyl and allene compounds[1] as well as their transition-metal derivatives[2] have attracted a great deal of attention in recent years. We have reported the preparation of various cationic complexes containing (triphenylmethyl)allene (abbreviated as tritylallene)[3] from the reactions of $MCH_2C{\equiv}CH$ with Ph_3C^+.[4] Even though Ph_3C^+ is used mostly for the purpose of hydride abstraction,[5] electrophilic addition of the trityl cation to the metal-co-ordinated prop-2-ynyl ligand resulting in carbon–carbon bond formation was observed in our system and analogous examples have been reported.[6] The preparation of tritylallene complexes is thus comparable to the reaction of a metal prop-2-ynyl complex with a protic acid, *i.e.* electrophilic additions at the terminal carbon atom generate a π-allene ligand.[7] The co-ordinated tritylallene undergoes cyclization on the tungsten metal centre to form 1,4-dihydro- and 1,2-dihydro-1,1-diphenylnaphthalene. Transformation of an iron σ-but-2-ynyl complex to metallated *p*-xylene in the presence of acid is one of a few examples where a six-membered ring is formed from complexes with a C≡C containing ligand.[8] The addition of thiol groups to allenic intermediates gives five- and six-membered sulfur rings[9] possibly through nucleophilic attack.

It is well known that complexes of the second-period transition metals show different reactivity from that of the corresponding first and the third ones. In order to elaborate the cyclization chemistry mentioned above, a study was thus undertaken to explore the reactivities of the molybdenum analogue. Ample reactivities of the molybdenum complex indeed provide various entries to many polyaromatic compounds.[10] Herein, we report chemistry of the cationic molybdenum complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]BF_4$ **1** containing a tritylallene ligand and its reactions which lead efficiently to a variety of polyaromatic compounds.

Results and Discussion

Cyclization of the η^2*-(Triphenylmethyl)allene Ligand on the Metal.*—We previously reported cyclization of co-ordinated tritylallene on the cationic tungsten complex $[W(\eta^5\text{-}C_5H_5)(CO)_3(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]BF_4$, producing 1,4-dihydro- and 1,2-dihydro-1,1-diphenylnaphthalene.[4] When this cyclization was carried out in the presence of PPh_3 it yielded $[W(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$, which was characterized by X-ray crystallography. An ORTEP[11] drawing is shown in Fig. 1. Selected interatomic distances and angles are listed in Table 1. The double bond C(4)–C(5) [1.327(8) Å] is localized and within the expected range (*cf.* 1.33 Å for buta-1,3-diene). The plane defined by C(5)–C(4)–C(13) at the C_α atom approximately parallels the M–C(2) vector [C(5)–C(4)–W–C(2) 176(1)°].

The tritylallene ligand of complex **1** underwent cyclization in acetonitrile producing only 1,4-dihydro-1,1-diphenylnaphthalene after decomplexation. The absence of the 1,2-dihydro isomer in this system is attributed to the relatively weaker Mo–C bond which inhibits formation of the carbene intermediate. In the presence of PPh_3, complex **1** was converted into $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)\{C(O)C_{10}H_7Ph_2\}]$ **2**. A PPh_3-promoted insertion of CO after the deprotonation step suitably accounts for this product. The insertion of CO into $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Me]$ also readily takes place at room temperature.[12] The formation of $[W(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$ with no CO insertion, as compared to the facile formation of **2**, parallels the

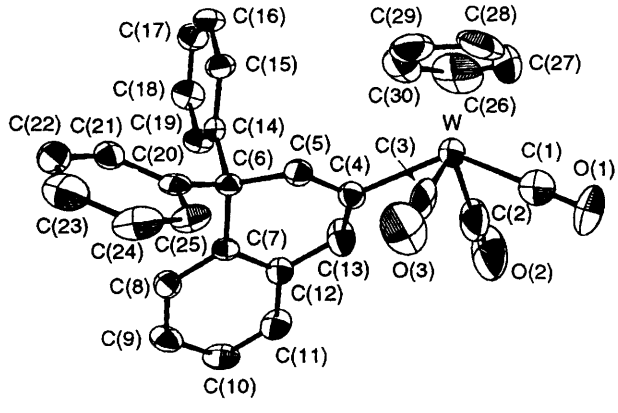


Fig. 1 Structure of $[W(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$ showing the atom numbering scheme

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Selected bond distances (Å) and angles (°) of $[W(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$

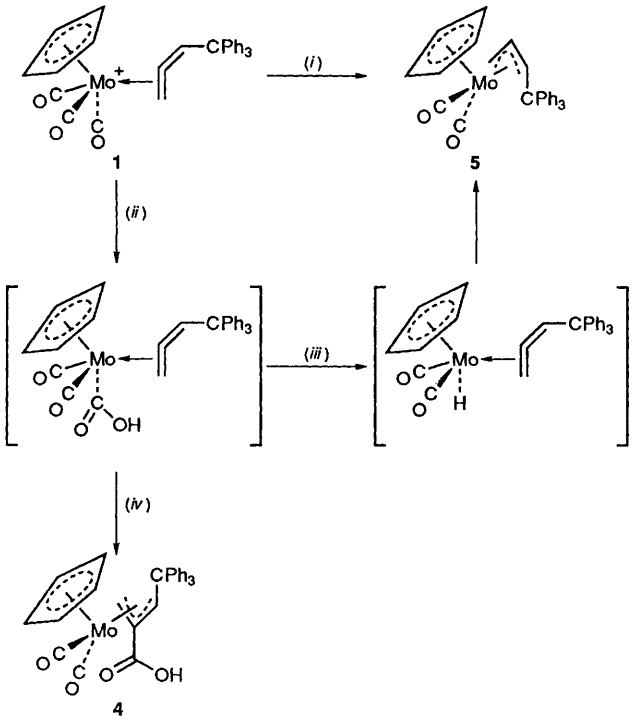
W–C(1)	1.964(8)	C(6)–C(7)	1.538(7)
W–C(2)	1.982(8)	C(6)–C(14)	1.551(7)
W–C(3)	1.972(7)	C(6)–C(20)	1.551(7)
W–C(4)	2.280(5)	C(7)–C(8)	1.384(7)
W–C(26)	2.352(7)	C(7)–C(12)	1.387(7)
W–C(27)	2.302(7)	C(8)–C(9)	1.383(8)
W–C(28)	2.317(7)	C(9)–C(10)	1.363(9)
W–C(29)	2.316(7)	C(10)–C(11)	1.375(9)
W–C(30)	2.340(6)	C(11)–C(12)	1.382(8)
C(1)–O(1)	1.165(9)	C(12)–C(13)	1.490(8)
C(2)–O(2)	1.132(9)	C(26)–C(27)	1.364(14)
C(3)–O(3)	1.153(8)	C(26)–C(30)	1.356(12)
C(4)–C(5)	1.327(8)	C(27)–C(28)	1.397(14)
C(4)–C(13)	1.498(8)	C(28)–C(29)	1.401(12)
C(5)–C(6)	1.517(8)	C(29)–C(30)	1.356(12)
C(1)–W–C(2)	76.8(3)	C(7)–C(6)–C(14)	110.9(4)
C(1)–W–C(3)	76.8(3)	C(7)–C(6)–C(20)	109.5(4)
C(1)–W–C(4)	134.5(2)	C(14)–C(6)–C(20)	110.1(4)
C(2)–W–C(3)	106.4(3)	C(6)–C(7)–C(8)	122.2(4)
C(2)–W–C(4)	81.3(3)	C(6)–C(7)–C(12)	119.0(4)
C(3)–W–C(4)	71.9(2)	C(8)–C(7)–C(12)	118.8(5)
W–C(1)–O(1)	179.2(7)	C(7)–C(12)–C(11)	119.1(5)
W–C(2)–O(2)	174.7(7)	C(7)–C(12)–C(13)	120.9(5)
W–C(3)–O(3)	178.7(6)	C(11)–C(12)–C(13)	120.0(5)
W–C(4)–C(5)	119.4(4)	C(4)–C(13)–C(12)	115.9(5)
W–C(4)–C(13)	122.6(4)	C(27)–C(26)–C(30)	109.2(8)
C(5)–C(4)–C(13)	117.3(5)	C(26)–C(27)–C(28)	106.9(7)
C(4)–C(5)–C(6)	125.5(5)	C(27)–C(28)–C(29)	107.3(7)
C(5)–C(6)–C(7)	110.0(4)	C(28)–C(29)–C(30)	107.1(7)
C(5)–C(6)–C(14)	106.9(4)	C(26)–C(30)–C(29)	109.3(7)
C(5)–C(6)–C(20)	109.4(4)		

sluggish tendencies of many tungsten compounds to undergo alkyl to carbonyl migrations relative to those of molybdenum.[13]

In the molybdenum system the carbonylation could be suppressed when the cyclization was carried out in the presence of KSCN dissolved in MeCN (containing the minimum volume of water) for deprotonation. In order to prevent nucleophilic addition of OH^- (described below) onto the terminal CO, complex **1** was suspended in the solvent mixture. The reaction at 0 °C yielded a neutral dihydronaphthyl complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$ **3** as the major product in 52% yield. Complexes **2** and **3** were thermally stable and were characterized by microanalytical data and spectroscopic methods. In their ^1H NMR spectra, while the resonances of the CH_2 of the six-membered ring appeared in the same region (δ 3.41 and 3.27), the CH resonance of **2** shifts downfield (δ 6.68 *vs.* 5.88) due to the conjugation effect. In the presence of PPh_3, insertion of CO into **3** readily gave **2**. This is different from the molybdenum–allyl system[13b] where a carbonylation product was observed only when the initial preparation step was carried out in the presence of PPh_3, *i.e.* thermolysis of (η^1-allyl)-molybdenum with PPh_3 gave a (η^3-allyl)molybdenum product with no carbonylation.

The annulation process was suppressed at temperatures lower than 0 °C and in the presence of large amount of water. The reaction of complex **1** with water in MeCN was carried out by *slowly* warming the reaction mixture from −78 °C to room temperature in the presence of KSCN. Thoroughly dissolved in the mixed solvent, complex **1** afforded $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{\eta^3\text{-}CH_2C(CO_2H)CHCPh_3\}]$ **4** in low yield, see Scheme 1. This product was derived from nucleophilic attack of OH^- at one of the terminal CO ligands followed by coupling of the resulting carboxylate with the π-tritylallene ligand.

Reaction of Complex **1** *with* NMe_3–*Water*.—The reaction of complex **1** with water could be further modified by carrying it out in the presence of NMe_3 in MeCN at −20 °C. The yellow



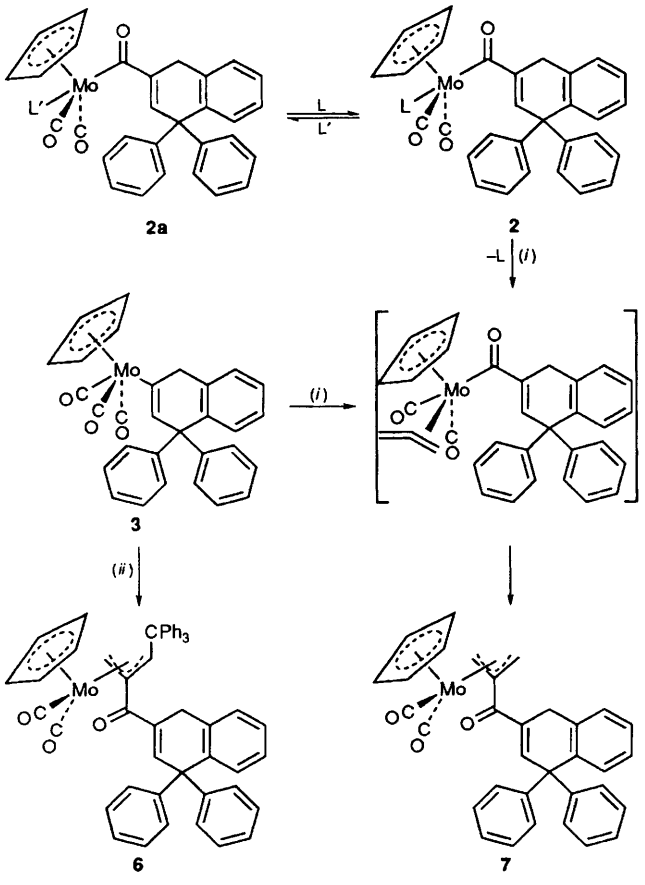
Scheme 1 (*i*) NMe_3–water; (*ii*) OH^-; (*iii*) NMe_3; (*iv*) KSCN–water

crystalline product $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(\eta^3\text{-}anti\text{-}CH_2CHCHCPh_3)]$ **5** was isolated in 74% yield. Its ^1H NMR spectrum in CD_3CN exhibits four allylic protons at δ 4.94, 4.26, 2.62 and −0.28. The relatively upfield shift (−0.28) of the *anti*-proton is attributed to the isotropic deshielding effect of the trityl group as has been found in many similar complexes and verified by X-ray diffraction.[14] The *anti* configuration of the trityl group is also confirmed by the relatively smaller coupling constant J_{HH} of 9.5 Hz between the central proton and the proton next to the trityl group. It is well known that α-substituted allylic cyclopentadienyl complexes generally adopt an *exo* conformation in order to minimize the steric interaction between the C_5H_5 and the substituent. We believe complex **5** should also adopt this conformation.

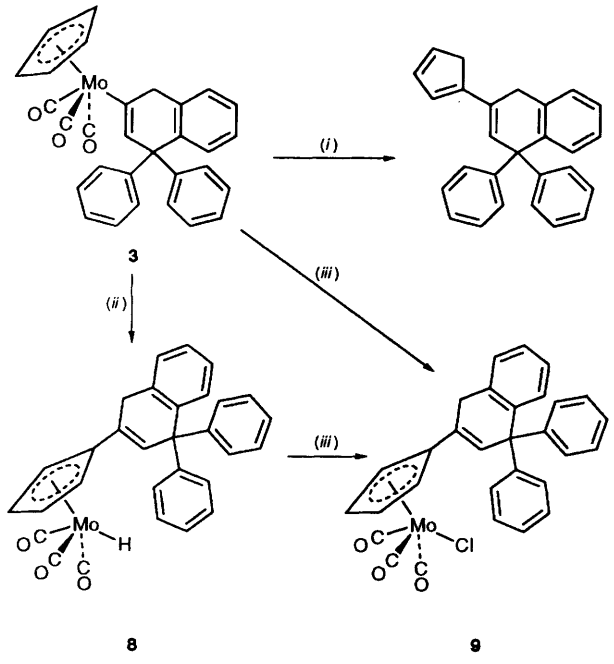
Nucleophilic attack of OH^- at the terminal CO with subsequent extrusion of CO_2 (which may be assisted by NMe_3 to give the metal hydride) followed by coupling of the hydride with allene satisfactorily accounts for the formation of complex **5** in Scheme 1. The NMe_3 serves as a base for deprotonation of the carboxylate for the extrusion of CO_2, while SCN^- is probably not suitable for deprotonation of the metal carboxylate group.

Reaction of Allene with Complex **3**.—When the annulation reaction of complex **1** (followed by deprotonation using KSCN) was carried out at higher concentration, the allylic complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{\eta^3\text{-}CH_2C(COC_{10}H_7Ph_2)CHCPh_3\}]$ **6**, in addition to **3**, was also isolated as a minor product in *ca.* 5% yield. The allylic ligand consists of two C_{22} units, derived originally from the tritylallene ligands, coupled through a CO molecule, see Scheme 2. Since carbonylation readily occurs for **4**, formation of **6** could be rationalized as follows. The free tritylallene, released from **1**, promotes insertion of CO and simultaneously co-ordinates to the metal centre of **3**. Coupling of the resulting acyl ligand with the centre carbon of the co-ordinated allene suitably accounts for formation of the product.[15]

In order to verify the proposed pathway we carried out the reaction of complex **3** with unsubstituted allene. Gaseous allene was passed through a solution of the complex dissolved in



Scheme 2 (*i*) Allene; (*ii*) $H_2C{=}C{=}CHPh_3$; L = PPh_3, L′ = $P(OPh)_3$



Scheme 3 (*i*) Heat, MeCN; (*ii*) thf; (*iii*) $CHCl_3$

MeCN or CH_2Cl_2 at room temperature. Complex **3** underwent carbonylation and co-ordination of allene, then the coupling reaction gave the allylic product, $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{\eta^3\text{-}CH_2C(COC_{10}H_7Ph_2)CH_2\}]$ **7**. Complex **6** was similarly prepared from the reaction of **3** with free tritylallene in 71% yield.

The mass spectrum and microanalytical data for complex **7** are consistent with the formulation. In the IR spectrum the ν(CO) stretching, all below 2000 cm^{-1}, indicates the neutral character of the complex. In the ^1H NMR spectrum the resonances attributed to the CH_2 and CH protons of the dihydronaphthalene moiety appear at δ 3.47 and 7.22, respectively. These are accompanied by allylic resonances at δ 3.27 and 1.78. For **6**, other than the CH_2 and CH resonances, the broad resonances of the three inequivalent allylic protons appear at δ 5.93, 2.80 and −0.09. These data establish the π-allylic co-ordination of the tritylallene.

Interestingly, the reaction of allene with complex **2** also afforded **7**. The first possible pathway for this reaction may involve replacement of the PPh_3 ligand by allene followed by the same coupling reaction, Scheme 2. An alternative, *i.e.* direct insertion of allene into the acyl group followed by decomplexation of PPh_3 with concomitant η^3 co-ordination of the allylic group, is less likely. The phosphine ligand of **2** was replaced readily by an excess of $P(OPh)_3$, giving only the *trans* isomer, at room temperature *via* formation of a possible intermediate $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$ **3** and the exchange process is reversible. The decarbonylation of **2** giving $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)(C_{10}H_7Ph_2)]$ occurred only at 78 °C, but replacement of the phosphine ligand took place at room temperature. Therefore the phosphine ligand should be kinetically more labile than CO in the molybdenum complex. This provides indirect evidence that the allene substitution, not the direct insertion of allene, is the first step for the formation of **7**.

In the literature there are a few examples of similar coupling reactions. In the presence of $[Fe(CO)_5]$, allenes and aldehydes give substituted trimethylenemethane complexes; this is proposed to proceed *via* coupling of the carbonyl carbon of the aldehyde with the centre carbon of the allene followed by elimination of CO_2.[16] Recently, migratory insertion of allene into alkyl- and acyl-palladium complexes leading to stable η^3-allylic compounds has been reported.[17] The acetyl group gives a rapid allene insertion, but alkyl ligands require a poorly co-ordinating ligand such as BF_4 to give the same insertion. The allene insertion proceeds considerably faster than the insertion of alkenes.

Thermolysis of Complexes **2** *and* **3**.—Intramolecular migration of the dihydronaphthalene ligand to the C_5H_5 ligand of complex **3** was observed *at room temperature* when **3** was dissolved in various solvents. In tetrahydrofuran (thf), the reaction was conveniently monitored by IR spectroscopy. The two terminal CO absorptions of **3** at 1967 and 1883 cm^{-1} were shifted to 2016 and 1923 cm^{-1} cleanly in 30 min. However, when isolated by hexane-induced precipitation from the thf solution, the product was contaminated with some unidentified material. Spectroscopic data for the product indicated the formation of $[MoH\{\eta^5\text{-}C_5H_4(C_{10}H_7Ph_2)\}(CO)_3]$ **8**. No attempt was made to further purify **8**. Notably the C_5H_4 resonance in the ^1H NMR spectrum is no longer a singlet but shows two multiplets at δ 5.73 and 5.36 and the hydride at δ −5.34. In $CDCl_3$ the ^1H NMR resonances slowly decreased in intensity and a new set of resonances attributed to $[MoCl\{\eta^5\text{-}C_5H_4(C_{10}H_7Ph_2)\}(CO)_3]$ **9** appeared, see Scheme 3. When the migration reaction was carried out in $CDCl_3$, **9** was obtained directly. The characteristic feature (multiplets at δ 5.82 and 5.50) of the substituted C_5H_4 resonance is also seen in the ^1H NMR spectrum of **9**.

When the reaction was carried out in refluxing MeCN (**3** is not soluble in MeCN at room temperature), a better donor, migration was followed by decomplexation of the substituted C_5H_4 moiety giving the organic product $C_5H_5(C_{10}H_7Ph_2)$ and $[Mo(CO)_3(MeCN)_3]$. In the ^1H NMR spectrum of the organic product the H–H coupling of the proton resonances on the C_5H_5 ring reveals the patterns corresponding to a 1-substituted structure.[18] The tris(acetonitrile) complex was identified by comparing its spectroscopic data with those of an authentic sample.

For complex **2**, migration of the dihydronaphthalene group to the C_5H_5 ligand in thf requires a higher temperature and

takes 3 d, yielding a mixture of *cis* and *trans* isomers of $[MoH\{\eta^5\text{-}C_5H_4(C_{10}H_7Ph_2)\}(CO)_2(PPh_3)]$ **10**. Under thermolytic conditions, decarbonylation should precede the migration reaction. The decarbonylation of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)(COMe)]$ also takes 48 h in refluxing thf.[19] Even though PPh_3 is kinetically labile, the equilibrium of the decarbonylation is not shifted toward the formation of **3**. This reaction is solvent dependent. When the thermolysis was carried out in benzene the decarbonylation product $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)(C_{10}H_7Ph_2)]$ **12** was obtained and no migration of the organic ligand to the C_5H_5 ligand was observed.

In the ^1H NMR spectrum of complex **10** the protons of the substituted C_5H_4 ligand give several multiplets and the hydride resonance appears as a doublet at δ −4.96 (J_{HP} = 49.7 Hz). Both *cis* and *trans* isomers with a ratio of 2:1 were observed at −60 °C.[20] The *trans* isomer displays two sets of resonances for the monosubstituted C_5H_4 ligand and a smaller J_{HP} for the hydride resonance in its ^1H NMR spectrum. Intramolecular exchange of the *trans* and *cis* isomers may proceed *via* an intermediate with apical hydrogen.[21] In $CDCl_3$ the ^1H resonances of **10** slowly decreased in intensity and a new set of resonances attributed to $[MoCl\{\eta^5\text{-}C_5H_4(C_{10}H_7Ph_2)\}(CO)_2(PPh_3)]$ **11** appeared. Thermolysis of **2** directly in $CHCl_3$ also yielded the migration product **11**. Only the *cis* isomer was obtained in both reactions. The *cis* and *trans* isomers of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)_2X]$ have been reported,[22] the *cis* was found as the major isomer from the thermal substitution reaction of Mo–X (X = Br or I) and PPh_3, but the *trans* was the major one from the reaction of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(PPh_3)(\eta\text{-}COMe)]$ with X_2. Complex **11** has been confirmed by spectroscopic as well as X-ray diffraction analysis. The ^1H NMR spectrum shows four multiplet resonances at δ 6.10, 5.66, 5.40 and 4.96 assignable to the four protons of the C_5H_4 unit and two broad resonances at δ 6.59 and 3.37 assignable to CH and CH_2, respectively. Single crystals of the complex were grown from a saturated MeCN solution slowly cooled to 0 °C. An ORTEP diagram of the structure is shown in Fig. 2, and Table 2 contains selected bond lengths and angles. It is clear that the 1,4-dihydronaphthalene group, originally bound to the Mo, has migrated to the C_5H_5 ring and the two CO ligands are in a cisoid configuration. The organic group on the C_5H_4 and the phosphine ligand lie mutually opposite with respect to the Mo, thus minimizing unfavourable steric interactions between them. The fact that C(6)–C(15) is found to be a double bond [1.34(1) Å] demonstrates that the migration would not induce isomerization.

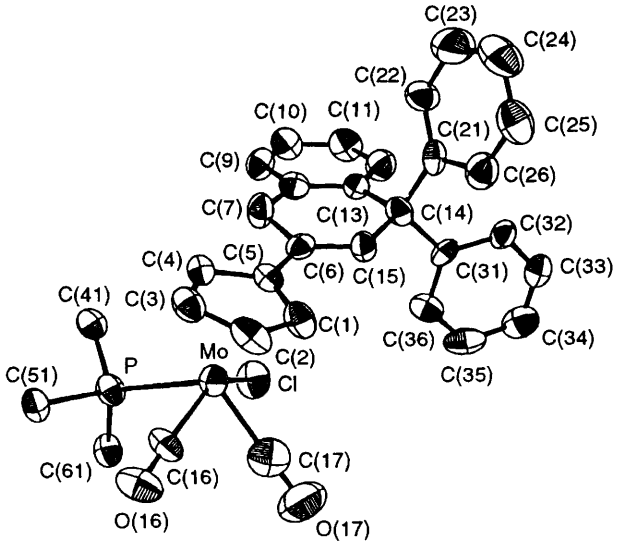


Fig. 2 Structure of compound **11** showing the atom numbering scheme; the phenyl groups of the phosphine ligand are omitted for clarity

Preparation of monosubstituted cyclopentadienyl half-sandwich transition-metal complexes by migration of a ligand on the metal to the C_5H_5 ring generally requires drastic reaction conditions, *i.e.* deprotonation with strong base or irradiation.[23] Thermal decarbonylation of benzoyl derivatives $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(COPh)]$ yielding the dimer $[\{Mo(\eta^5\text{-}C_5H_4Ph)(CO)_3\}_2]$ is one of few examples of thermally induced migration.[24] Metal-to-ring migration of the acyl group occurred on deprotonation with strong base.[25] Irradiation of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2Ph)]$ in alkane solvent at 298 K under CO led to transfer of the benzyl group to the C_5H_5 ring to form $[Fe(\eta^4\text{-}C_5H_5CH_2Ph)(CO)_3]$. Subsequent irradiation resulted in the transfer of a hydrogen from the cyclopentadienyl ring to iron to form $[FeH(\eta^5\text{-}C_5H_4CH_2Ph)(CO)_2]$.[26] Reaction between the acetylide $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(C_2Ph)]$ and the alkyne $C_2(CO_2Me)_2$ gave the ring-substituted product $[RuCl(\eta^5\text{-}C_5H_4C_2Ph)(PPh_3)_2]$.[27] When **2** was dissolved in CD_3CN we obtained the organic product $C_5H_5(C_{10}H_7Ph_2)$ at room temperature. The replacement of the kinetically labile phosphine ligand by the solvent was followed by decarbonylation and coupling reaction leading to the observed product. The migration of the dihydronaphthalene group should be related to both the steric and electronic properties of the ligand. In a recent paper,[12b] a molybdenum complex with a η^1-allylic ligand did not show similar reactivity and a simple molybdenum vinyl complex prepared from the reaction of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^-$ and $MeO_2CC{\equiv}CCO_2Me$ would not undergo such a migration reaction.[28]

Conclusion

The tritylallene ligand on the cationic molybdenum carbonyl complex **1** displays rich reactivities. Cyclization of the ligand

Table 2 Selected bond distances (Å) and angles (°) of $[MoCl\{\eta^5\text{-}C_5H_4(C_{10}H_7Ph_2)\}(CO)_2(PPh_3)]$ **11**

Mo–P	2.530(3)	C(7)–C(8)	1.507(13)
Mo–Cl	2.504(3)	C(5)–C(6)	1.479(12)
Mo–C(1)	2.336(7)	C(5)–C(4)	1.420(13)
Mo–C(2)	2.249(9)	C(6)–C(15)	1.338(13)
Mo–C(3)	2.289(9)	C(8)–C(9)	1.389(12)
Mo–C(4)	2.387(8)	C(8)–C(13)	1.388(13)
Mo–C(5)	2.454(7)	C(9)–C(10)	1.389(13)
Mo–C(16)	1.937(9)	C(10)–C(11)	1.389(14)
Mo–C(17)	1.962(11)	C(11)–C(12)	1.382(14)
P–C(41)	1.835(10)	C(12)–C(13)	1.417(13)
P–C(51)	1.817(9)	C(13)–C(14)	1.541(12)
P–C(61)	1.837(9)	C(14)–C(15)	1.503(12)
C(1)–C(2)	1.416(13)	C(14)–C(21)	1.556(12)
C(1)–C(5)	1.428(13)	C(14)–C(31)	1.536(12)
C(2)–C(3)	1.413(14)	C(16)–O(16)	1.142(11)
C(3)–C(4)	1.417(12)	C(17)–O(17)	1.158(13)
C(7)–C(6)	1.509(13)		
P–Mo–Cl	80.24(9)	C(6)–C(7)–C(8)	115.0(8)
P–Mo–C(16)	79.1(3)	C(7)–C(8)–C(9)	117.8(8)
P–Mo–C(17)	115.7(3)	C(7)–C(8)–C(13)	122.3(8)
Cl–Mo–C(16)	134.5(3)	C(9)–C(8)–C(13)	119.8(8)
Cl–Mo–C(17)	78.7(3)	C(8)–C(13)–C(12)	119.2(8)
C(16)–Mo–C(17)	74.6(4)	C(8)–C(13)–C(14)	122.0(8)
Mo–P–C(41)	115.0(3)	C(12)–C(13)–C(14)	118.8(8)
Mo–P–C(51)	116.0(3)	C(13)–C(14)–C(15)	111.3(7)
Mo–P–C(61)	116.7(3)	C(13)–C(14)–C(21)	110.1(7)
C(41)–P–C(51)	102.5(4)	C(13)–C(14)–C(31)	109.4(7)
C(41)–P–C(61)	103.4(4)	C(15)–C(14)–C(21)	104.7(7)
C(51)–P–C(61)	101.1(4)	C(15)–C(14)–C(31)	109.4(7)
C(1)–C(5)–C(6)	125.2(8)	C(21)–C(14)–C(31)	111.8(7)
C(6)–C(5)–C(4)	126.3(8)	C(6)–C(15)–C(14)	126.8(8)
C(7)–C(6)–C(5)	117.7(8)	Mo–C(16)–O(16)	177.1(9)
C(7)–C(6)–C(15)	120.7(8)	Mo–C(17)–O(17)	178.6(9)
C(5)–C(6)–C(15)	121.4(8)		

requires temperatures above 0 °C while nucleophilic attack of OH^- at the terminal CO occurs at lower temperature. Carbonylation of the molybdenum complex containing the dihydronaphthalene ligand readily takes place in the presence of two-electron donor ligands, *i.e.* PPh_3 or allene. In the case of allene, coupling of allene with the resulting acyl moiety gives η^3-allylic complexes. Migration of the σ-bonded organic fragment to the co-ordinated C_5H_5 produces a substituted cyclopentadiene ligand.

Experimental

General Procedures.—All manipulations were performed under nitrogen using vacuum-line, dry-box and standard Schlenk techniques. The NMR spectra were recorded on Bruker AM-300WB and AC-200 spectrometers, with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93). The IR spectra were measured on a Perkin-Elmer 983 instrument and wavenumbers (cm^{-1}) were assigned relative to a polystyrene standard. Fast atom bombardment and electron-impact mass spectra were obtained with a JEOL SX-102A spectrometer. Diethyl ether and CH_2Cl_2 were distilled from CaH_2 and stored over molecular sieves prior to use. Benzene and thf were distilled from sodium–benzophenone. All other solvents and reagents were reagent grade used without further purification. The compound $[Mo(CO)_6]$ was obtained from Strem Chemical, and Ph_3CPF_6, PPh_3 and KSCN from Janssen Chimica. Prop-2-ynyl bromide (Merck) was distilled in small quantity before use. The complexes $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$[29] and $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_2C{\equiv}CH)]$,[30] $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(\eta^2\text{-}CH_2{=}C{=}CHCPh_3)]BF_4$ **1**,[4] $[W(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$,[4] $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{C(O)C_{10}H_7Ph_2\}]$ **2**,[4] and $CH_2{=}C{=}CHCPh_3$[4] were prepared according to the literature methods.

Reaction of Complex **1** *with* KSCN–*Water.*—(*a*) *In the presence of the minimum amount of water.* Acetonitrile–water (10:1, 15 cm^3) saturated with KSCN was added to a flask containing solid complex **1** (0.247 g, 0.40 mmol) at 0 °C to give a suspension of **1**. This was stirred for 1 h at 0 °C then warmed to room temperature to give a light yellow suspension. The solid was filtered off then washed with cold acetonitrile (3 × 5 cm^3) to give yellow crystals, identified as $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$ **3** (0.11 g, 52%). IR (KBr): 2016m, 1967s, 1883vs cm^{-1} ν(CO). NMR ($CDCl_3$): ^1H, δ 7.50–6.82 (m, Ph), 5.88 (s, 1 H, HC=), 5.11 (s, 5 H, C_5H_5) and 3.41 (s, 2 H, CH_2); ^{13}C, δ 227.5, 227.4 (CO), 147 (CH=), 140, 135, 129–126 (Ph), 92.7 (C_5H_5), 56.8 (CPh_2) and 41.6 (CH_2). FAB mass spectrum: *m/z* 529 (M^+), 500 ($M^+ - CO$) and 444 ($M^+ - 3\,CO$) (Found: C, 68.6; H, 5.00. Calc. for $C_{30}H_{22}MoO_3$: C, 68.45; H, 4.20%). When the reaction was carried out at higher concentration the cold MeCN filtrate, obtained from washing the final product, contained another product $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{\eta^3\text{-}CH_2C(COC_{10}H_7Ph_2)CHCPh_3\}]$ **6** in *ca.* 5% yield. The preparation of **6** is described below.

(*b*) *In the presence of a large amount of water.* A KSCN saturated aqueous solution (7 cm^3) was added to a flask containing solid complex **1** (0.50 g, 0.81 mmol) at −78 °C. Acetonitrile (*ca.* 15 cm^3) was added slowly until all the suspension had completely dissolved. The solution was warmed slowly to −20 °C during a 2 h period then to room temperature and stirred at room temperature for 30 min. The solvent was removed under vacuum to give a brown precipitate. Water (40 cm^3) was added to give an aqueous solution with precipitates. These precipitates were filtered off then washed with diethyl ether (3 × 20 cm^3) to give light yellow crystals identified as $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{\eta^3\text{-}CH_2C(CO_2H)CHCPh_3\}]$ **4** (0.08 g, 18%). IR (KBr): 1946vs, 1867vs (terminal CO) and 1657s cm^{-1} (CO_2H). NMR [$(CD_3)_2SO$]: ^1H, δ 7.51–6.84 (m, Ph), 5.72 (s, 1 H, H_{syn}, HC=), 5.27 (s, 5 H, C_5H_5), 3.27 (s, Ph_3CHC=) and −0.32 (s, 1 H, H_{anti}, HC=); ^{13}C, δ 235.6, 235.5 (terminal CO), 175.2 (CO_2H), 147, 130, 127, 126 (Ph), 95.8 (C_5H_5), 70.9 (central C), 70.0 (Ph_3CHC=), 60.4 (Ph_3C) and 50.3 (=CH_2). FAB mass spectrum: *m/z* 546 (M^+), 518 ($M^+ - CO$) and 490 ($M^+ - 2\,CO$) (Found: C, 66.3; H, 4.65. Calc. for $C_{30}H_{24}MoO_4$: C, 66.2; H, 4.45%).

Reaction of Complex **1** *with* NMe_3.—Acetonitrile–NMe_3 (40% aqueous solution) (1:1, 10 cm^3) containing complex **1** (0.280 g, 0.46 mmol) was stirred at −20 °C for 1 h. Then the solvent was removed under vacuum; diethyl ether (3 × 5 cm^3) was added and the resulting yellow solution was filtered. The crude product was obtained after removal of solvent and washed with cold ether (2 × 2 cm^3) to give yellow crystals of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(\eta^3\text{-}CH_2CHCHCPh_3)]$ **5** (0.169 g, 74%). IR (KBr): 1930vs, 1847vs and 1837 (sh) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.28–7.16 (m, 15 H, Ph), 5.25 (s, 5 H, C_5H_5); 4.94 (d, J_{HH} = 9.5, 1 H, CH), 4.26 (ddd, J_{HH} = 12.6, 9.5, 9.0, 1 H, CH), 2.62 (d, J_{HH} = 9.0, 1 H, C*H*H) and −0.28 (d, J_{HH} = 12.6 Hz, 1 H, CH*H*). FAB mass spectrum: *m/z* 502 (M^+), 474 ($M^+ - CO$) and 446 ($M^+ - 2\,CO$) (Found: C, 70.05; H, 4.65. Calc. for $C_{29}H_{24}MoO_2$: C, 69.6; H, 4.85%).

Reaction of Complex **2** *with* $P(OPh)_3$.—A $CDCl_3$ solution (2.0 cm^3) containing complex **2** (0.108 g, 0.137 mmol) and $P(OPh)_3$ (0.32 g, 1.03 mmol) was stored at room temperature and the reaction monitored by ^{31}P NMR spectra; it was found to be 90% complete after 2 h. The solution was subjected to chromatography on a silica gel plate. Elution by $CHCl_3$–hexane (5:1) gave two bands: the first was a colourless product, PPh_3, and the second gave the desired product. The pure product was obtained after removal of solvent, the residue was washed with hexane (2 × 2 cm^3) to give yellow crystals identified as $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{P(OPh)_3\}\{C(O)C_{10}H_7Ph_2\}]$ **2a** (0.097 g, 85%). IR (KBr): 1945s, 1860vs and 1583s cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.80–6.53 (m, Ph), 4.76 (d, J_{PH} = 0.7 Hz, 5 H, C_5H_5) and 3.35 (br, 2 H, CH_2); ^{13}C, δ 256.1 (d, J_{PC} = 11.3, C=O), 235.0 (d, J_{PC} = 36.2 Hz, 2 CO), 152.1–120.6 (Ph), 95.9 (C_5H_5), 56.5 (CPh_2) and 29.5 (CH_2); ^{31}P, δ 191.7 [$P(OPh)_3$]. FAB mass spectrum: *m/z* 839 ($M^+ + 1$), 810 ($M^+ - CO$) and 782 ($M^+ - 2\,CO$) (Found: C, 69.2; H, 4.65. Calc. for $C_{48}H_{37}MoO_6P$: C, 68.9; H, 4.45%).

Reactions of Complex **3** *with Allenes.*—(*a*) *With unsubstituted allene.* This experiment was carried out in a NMR tube. A sample of complex **3** (0.054 g, 0.103 mmol) was dissolved in nitrogen-purged CD_3CN (0.5 cm^3) and allene gas was passed through it. The solution was stored at room temperature for 1 d. Monitoring of the experiment by NMR spectroscopy indicated the formation of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{\eta^3\text{-}CH_2C(COC_{10}H_7Ph_2)CH_2\}]$ **7**. The solvent was removed under vacuum to give a yellow precipitate. The desired product was separated from the crude mixture by recrystallization from hexane at −20 °C, 0.045 g (78%). IR (KBr): 1964vs, 1898vs and 1617m cm^{-1}. NMR ($CDCl_3$, 0 °C): ^1H, δ 7.56–6.71 (m, Ph), 7.22 (br, 1 H, CH=), 5.20 (s, 5 H, C_5H_5), 3.47 (br, 2 H, CH_2), 3.27 (br, 2 H, H_{syn}) and 1.78 (br, 2 H, H_{anti}); ^{13}C, δ 233.7 (CO), 195.0 (C=O), 147.3–125.2 (Ph), 134.9 (C=), 89.6 (C_5H_5), 55.4 (CPh_2), 36.0 (allylic C) and 29.8 (CH_2). FAB mass spectrum: *m/z* 568 (M^+) and 512 ($M^+ - 2\,CO$) (Found: C, 69.4; H, 5.0. Calc. for $C_{33}H_{26}MoO_3$: C, 69.95; H, 4.65%). In a few instances, $C_5H_5(C_{10}H_7Ph_2)$ was obtained in *ca.* 10% yield (see below) as a minor product.

(*b*) *With tritylallene.* To acetonitrile–water (1:4, 5 cm^3) containing tritylallene (0.076 g, 0.269 mmol) was added complex **3** (0.059 g, 0.112 mmol). The suspension was stirred at room temperature for 1 h, then the solvent was removed under vacuum. The crude product was first extracted with diethyl ether then placed on a silica gel column and eluted with CH_2Cl_2–hexane (1:4). The first fraction gave a yellow solid after removal of solvent. This was identified as $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{\eta^3\text{-}CH_2C(COC_{10}H_7Ph_2)CHCPh_3\}]$ **6** (0.064 g,

71%). IR (KBr): 1948vs, 1879s and 1634m cm^{-1}. NMR: ^1H (CD_2Cl_2, −10 °C), δ 7.54–6.78 (m, Ph), 5.93 (br, 1 H, CH_{syn}), 5.24 (s, 5 H, C_5H_5), 4.80 (br, 1 H, =CH), 3.84, 3.43 (AB, J_{HH} = 20.0 Hz, 2 H, CH_2), 2.80 (br, 1 H, H_{syn}) and −0.09 (br, 1 H, H_{anti}); ^{13}C ($CDCl_3$), δ 232.4, 232.1 (CO), 149.8–125.9 (Ph), 94.6 (C_5H_5), 74.1 (allylic C), 60.6 (CPh_3), 55.2 (CPh_2), 48.7 (allylic CH_2) and 30.6 (CH_2). FAB mass spectrum: *m/z* 810 (M^+), 782 (M^+ − CO) and 754 (M^+ − 2 CO) (Found: C, 77.25; H, 4.80. Calc. for $C_{52}H_{40}MoO_3$: C, 77.2; H, 5.00%).

Thermal Reactions of Complex **3**.—(*a*) *In thf*. Complex **3** (0.147 g, 0.279 mmol) was dissolved in thf (20 cm^3). The solution was stirred at room temperature for 30 min. The solvent was removed under vacuum to give a brown precipitate which was redissolved in CH_2Cl_2. Addition of hexane caused precipitation of the product. This powder included an unstable major product (>85%) identified as [MoH($C_5H_4C_{10}H_7Ph_2$)$(CO)_3$] **8** (0.024 g, *ca.* 50% based on **3**). Complex **8** is unstable and no attempt was made further to purify it. IR ($CHCl_3$): 2016s and 1923vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.47–6.58 (m, Ph), 5.73 (dd, J_{HH} = 2.2, 2 H, C_5H_4), 5.36 (dd, J_{HH} = 2.2 Hz, 2 H, C_5H_4), 3.43 (br, 2 H, CH_2) and −5.34 (s, MoH).

(*b*) *In* $CHCl_3$. This experiment was carried out in a NMR tube and monitored by NMR spectroscopy. Complex **3** (0.040 g, 0.076 mmol) was dissolved in $CDCl_3$ (0.5 cm^3) in a NMR tube at room temperature. After 3 d the colour had changed from yellow to orange. This solution was subjected to chromatography on silica gel. The third band, eluted by ethyl acetate–hexane (1:6), gave [MoCl{$C_5H_4(C_{10}H_7Ph_2)$}$(CO)_3$] **9** (0.031 g, 73%). IR (CH_2Cl_2): 2049s and 1968vs cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.75–6.79 (m, Ph), 6.61 (t, 1 H, =CH), 5.82 (dd, J_{HH} = 2.2, 2 H, C_5H_4), 5.50 (dd, J_{HH} = 2.2 Hz, 2 H, C_5H_4) and 3.46 (d, 2 H, CH_2); ^{13}C, δ 241.7 (CO), 223.6 (CO), 146.8–125.5 (Ph), 139.8 (CH=), 119.6, 93.1, 91.3 (C_5H_5), 55.2 (CPh_3) and 31.7 (CH_2). FAB mass spectrum: *m/z* 534 (M^+ − CO), 532 (M^+ − Cl), 478 (M^+ − 3 CO) and 441 (M^+ − 3 CO − Cl) (Found: C, 65.0; H, 3.20. Calc. for $C_{30}H_{21}ClMoO_3$: C, 64.25; H, 3.75%). Compound **9** can also be prepared by dissolution of **8** in chloroform; 3 h were required for the complete consumption of **8**, NMR yield >80%.

(*c*) *In* CD_3CN. This experiment was carried out in a NMR tube and monitored by NMR spectroscopy. Complex **3** (0.040 g, 0.076 mmol) was suspended in CD_3CN (0.5 cm^3) in a NMR tube at room temperature. The suspension dissolved after heating to 80 °C and changed from yellow to orange. This solution was filtered. The ^1H NMR spectrum indicated the formation of an organic compound $C_5H_5(C_{10}H_7Ph_2)$ (NMR yield: 95%) and [$Mo(CO)_3(CD_3CN)_3$] which was identified by its IR spectrum. Attempted purification of the organic product by column chromatography on silica gel led to its decomposition. NMR (CD_3CN): ^1H, δ 7.45–6.77 (m, Ph), 6.60 (ddt, 1 H, J_{HH} = 2.2, 1.1, 0.6, =CH), 6.52 (ddt, J_{HH} = 5.3, 2.2, 1.6, 1 H, =CH), 6.48 (br, 1 H, =CH), 6.32 (ddt, J_{HH} = 5.3, 1.6, 1.1, 1 H, =CH), 3.57 (br, 2 H, CH_2) and 3.24 (ddd, J_{HH} = 1.6, 1.6, 0.6, 2 H, CH_2); ^{13}C, δ 149.0, 148.3, 141.8, 136.2, 133.6, 133.0, 128.9, 131.9, 129.4, 129.2, 127.6, 127.5, 127.1 (Ph and C_5H_5), 56.8 (CPh_3), 41.7 (CH_2) and 32.0 (CH_2). FAB mass spectrum: *m/z* 346 (M^+).

Thermal Reactions of Complex **2**.—(*a*) *In thf*. Complex **2** (1.00 g, 1.27 mmol) was dissolved in nitrogen-purged thf (30 cm^3). The solution was heated to reflux for 3.5 h, then the solvent was removed under vacuum to give a red precipitate which was recrystallized to afford an orange-red powder identified as [MoH{$C_5H_4(C_{10}H_7Ph_2)$}$(CO)_2(PPh_3)$] **10** (0.583 g, *ca.* 60%). IR (KBr): 1927s and 1851s cm^{-1}. NMR (C_6D_6, 25 °C): ^1H, δ 7.71–6.67 (m, Ph), 6.60 (br, 1 H, CH=), 5.01 (dd, J_{HH} = 2.1, 2 H, C_5H_4), 4.67 (dd, J_{HH} = 2.1, 2 H, C_5H_4), 3.43 (br, 2 H, CH_2) and −4.96 (d, J_{HP} = 49.7 Hz, MoH); ^{31}P, δ 71.5 (PPh_3). Two isomers (*cis* and *trans* in a 2:1 ratio) were observed at −60 °C. NMR ($CDCl_3$): *cis*, ^1H, δ 7.61–6.56 (m, Ph), 5.75, 5.67, 5.10, 5.00 (br, 4 H, C_5H_4), 3.54 (br, 2 H, CH_2) and −5.12 (d, J_{HP} = 64.1 Hz, MoH); ^{31}P, δ 71.4; *trans*, ^1H, δ 7.61–6.56 (m, Ph), 5.39, 4.86 (br, 4 H, C_5H_4), 3.54 (br, 2 H, CH_2) and −5.62 (d, J_{HP} = 21.4 Hz, MoH); ^{31}P, δ 69.5; ^{13}C, δ 232.1 (CO), 148.2 (=C), 141.6–135.3 (Ph), 131.6 (=CH), 110.0, 90.2, 87.2 (C_5H_4), 55.5 (CPh_3) and 33.3 (CH_2). FAB mass spectrum: *m/z* 764 (M^+) and 707 (M^+ − H − 2 CO).

(*b*) *In* $CHCl_3$. This experiment was carried out in a NMR tube and monitored by NMR spectroscopy. Complex **2** (0.040 g, 0.051 mmol) was dissolved in $CDCl_3$ (0.5 cm^3) in a NMR tube at room temperature. After 3 d it had changed from yellow to orange. It was then subjected to column chromatography on silica gel eluted by ethyl acetate–hexane (1:6). The third band gave [MoCl{$C_5H_4(C_{10}H_7Ph_2)$}$(CO)_2(PPh_3)$] **11** (0.028 g, 70%). IR ($CHCl_3$): 1962vs and 1876s cm^{-1}. NMR (C_6D_6): ^1H, δ 7.42–6.59 (m, Ph), 6.59 (br, 1 H, =CH), 6.10, 5.66, 5.40, 4.96 (m, 4 H, C_5H_4) and 3.37 (br, 2 H, CH_2); ^{13}C, δ 256.6 (J_{PC} = 27.9 Hz, CO), 148.1 (=C), 141.8–126.5 (Ph), 131.6 (CH=), 115.0, 99.3, 97.5, 90.3, 83.1 (C_5H_4), 55.3 (CPh_3) and 31.8 (CH_2); ^{31}P, δ 50.0 (PPh_3). FAB mass spectrum: *m/z* 770 (M^+ − CO), 742 (M^+ − 2 CO) and 707 (M^+ − 2 CO − Cl) (Found: C, 71.55; H, 4.30. Calc. for $C_{47}H_{36}ClMoO_2P$: C, 71.0; H, 4.55%). Compound **11** can also be produced by dissolution of **10** in chloroform; 3 h were required for the complete consumption of **10**, NMR yield >80%.

(*c*) *In benzene*. Complex **2** (0.053 g, 0.067 mmol) was dissolved in benzene (20 cm^3) and heated to reflux for 4 h resulting in a red solution. The solvent was removed under vacuum to give a red precipitate which was recrystallized from hexane to afford a purple powder, identified as [Mo(η^5-C_5H_5)$(CO)_2(PPh_3)$-($C_{10}H_7Ph_2$)] **12** (0.023 g, 46%). IR (KBr): 1933m and 1847vs cm^{-1}. NMR (C_6D_6, 25 °C): ^1H, δ 7.55–6.89 (m, Ph), 6.88 (br, 1 H, CH=), 4.48 (d, J_{PH} = 1.2 Hz, 5 H, C_5H_5) and 4.08 (d, 2 H, CH_2); ^{31}P, δ 70.8 (PPh_3). FAB mass spectrum: *m/z* 762 (M^+); 734 (M^+ − CO) and 706 (M^+ − 2 CO) (Found: C, 74.1; H, 5.00. Calc. for $C_{47}H_{37}MoO_2P$: C, 74.2; H, 4.90%).

X-Ray Analysis.—Single crystals suitable for an X-ray diffraction study of [W(η^5-C_5H_5)$(CO)_3(C_{10}H_7Ph_2)$] were grown from cold hexane solution. A suitable crystal was glued to a glass fibre and mounted on an Enraf-Nonius CAD4 diffractometer. Initial lattice parameters were determined from a least-squares fit to 25 accurately centred reflections having 10.0 < 2θ < 25°. Cell constants and other pertinent data are collected in Table 3. Data were collected using the θ–2θ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 7° min^{-1}. The scan angle was determined for

Table 3 Crystal and intensity collection data* for [W(η^5-C_5H_5)-$(CO)_3(C_{10}H_7Ph_2)$] and [MoCl{η^5-$C_5H_4(C_{10}H_7Ph_2)$}$(CO)_2(PPh_3)$] **11**

Molecular formula	$C_{30}H_{22}O_3W$	$C_{47}H_{36}ClMoO_2P$
Space group	$P\bar{1}$	$P2_1/n$
a/Å	8.076(2)	13.184(5)
b/Å	9.043(4)	17.946(7)
c/Å	18.116(4)	19.147(11)
α/°	91.31(3)	—
β/°	91.66(2)	106.10(3)
γ/°	113.13(3)	—
U/Å^3	1213.3(7)	4353(3)
Z	2	4
F(000)	600	1784
Crystal dimensions/mm	0.13 × 0.5 × 0.5	0.2 × 0.3 × 0.25
Total number of reflections	3187	5665
Unique reflections [$I > 2\sigma(I)$]	2889	3079
R	0.028	0.053
R'	0.029	0.044

* Details in common: Mo-Kα radiation, λ = 0.7107 Å; 2θ range 2–45°.

each reflection according to the equation 0.8 + 0.35 tan θ. Three check reflections were measured every 30 min throughout the data collection period and showed no apparent decay.

The raw intensity data were converted into structure-factor amplitudes and their estimated standard deviations (e.s.d.s) by correction for scan speed, background and Lorentz polarization effects. An empirical absorption based on the azimuthal scan data was applied to the intensities. Crystallographic computations were carried out on a Microvax III computer using the NRCC structure determination package.[31] Merging of equivalent and duplicate reflections gave a total of 3187 unique measured data for which 2889 were considered observed, $I > 2.0\sigma(I)$; an absorption correction was applied to give maximum and minimum transmission factors of 1.00 and 0.44. The structure was first solved by using the heavy-atom method (Patterson synthesis) which revealed the position of the metal, then refined *via* standard least-squares and Fourier-difference techniques. The quantity minimized by the least-squares program was $\Sigma w(F_o - F_c)^2$, where $w = 1/[\sigma(F_o)]^2$. Electron-density Fourier-difference synthesis allocated the maximum and minimum residual peaks at 1.420 and −0.790 e Å^{-3}. The analytical forms of the scattering factor tables for the neutral atoms were used.[32] All other non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were included in the structure-factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined. Final refinement using full-matrix, least squares converged smoothly to $R = 0.028$ and $R' = 0.029$. Final values of refined atomic positional parameters (with e.s.d.s) are listed in Table 4.

The procedures for the structure determination of complex **11** were similar. The final residuals were $R = 0.053$ and $R' = 0.044$ for 3079 reflections, $I > 2.0\ \sigma(I)$, 489 parameters refined. Largest difference peak and hole 0.670 and −0.600 e Å^{-3}. Final values of all refined atomic positional parameters (with e.s.d.s) are listed in Table 5.

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

Table 4 Atomic parameters of $[W(\eta^5\text{-}C_5H_5)(CO)_3(C_{10}H_7Ph_2)]$ with estimated standard deviations in the last digit

Atom	*x*	*y*	*z*
W	0.339 52(3)	0.228 11(3)	0.099 80(2)
C(1)	0.344 8(10)	0.220 0(10)	−0.008 5(4)
C(2)	0.294 0(11)	0.000 0(9)	0.076 0(5)
C(3)	0.595 2(9)	0.354 0(9)	0.080 9(3)
C(4)	0.510 4(7)	0.188 4(7)	0.193 6(3)
C(5)	0.608 1(7)	0.311 1(6)	0.238 9(3)
C(6)	0.694 3(6)	0.298 1(6)	0.312 6(3)
C(7)	0.742 6(6)	0.149 7(6)	0.310 8(3)
C(8)	0.880 9(7)	0.141 0(6)	0.355 0(3)
C(9)	0.919 4(7)	0.004 8(7)	0.354 8(4)
C(10)	0.818 8(8)	−0.122 9(7)	0.309 1(4)
C(11)	0.682 6(8)	−0.116 0(6)	0.263 9(3)
C(12)	0.642 6(7)	0.019 2(6)	0.264 2(3)
C(13)	0.495 4(8)	0.024 2(7)	0.214 1(4)
C(14)	0.554 8(6)	0.283 6(6)	0.372 0(3)
C(15)	0.482 4(7)	0.400 2(6)	0.377 6(3)
C(16)	0.356 0(7)	0.388 6(7)	0.429 6(4)
C(17)	0.299 8(7)	0.263 8(7)	0.476 7(3)
C(18)	0.369 7(8)	0.150 3(7)	0.471 3(3)
C(19)	0.495 7(7)	0.157 9(7)	0.419 2(3)
C(20)	0.867 6(6)	0.451 8(6)	0.328 5(3)
C(21)	0.918 0(7)	0.524 0(6)	0.398 1(3)
C(22)	1.077 4(7)	0.657 9(7)	0.410 3(4)
C(23)	1.187 6(8)	0.719 4(7)	0.353 0(4)
C(24)	1.138 6(8)	0.649 8(7)	0.283 2(4)
C(25)	0.980 6(7)	0.516 4(6)	0.271 3(3)
C(26)	0.060 1(9)	0.172 2(11)	0.153 2(6)
C(27)	0.063 9(11)	0.247 0(12)	0.088 3(5)
C(28)	0.194 0(12)	0.403 7(11)	0.098 3(4)
C(29)	0.275 2(9)	0.416 2(9)	0.168 8(5)
C(30)	0.189 6(9)	0.273 4(10)	0.201 0(4)
O(1)	0.348 8(9)	0.213 7(9)	−0.072 7(3)
O(2)	0.254 8(10)	−0.131 8(7)	0.060 7(4)
O(3)	0.744 7(6)	0.429 9(7)	0.070 8(3)

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Table 5 Atomic parameters of $[MoCl\{\eta^5\text{-}C_5H_4(C_{10}H_7Ph_2)\}(CO)_2(PPh_3)]$ **11**

Atom	*x*	*y*	*z*
Mo	0.242 44(7)	0.066 47(5)	0.113 25(5)
P	0.299 18(19)	−0.061 29(16)	0.165 55(13)
Cl	0.388 89(21)	0.102 70(15)	0.222 23(14)
C(1)	0.253 6(7)	0.167 5(5)	0.038 8(5)
C(2)	0.174 0(7)	0.116 8(6)	0.002 6(5)
C(3)	0.221 5(7)	0.048 9(5)	−0.008 3(5)
C(7)	0.553 2(7)	0.116 7(5)	0.086 0(5)
C(5)	0.352 4(7)	0.130 7(5)	0.047 6(5)
C(6)	0.457 3(7)	0.165 9(5)	0.075 2(4)
C(4)	0.332 1(7)	0.056 7(5)	0.021 1(5)
C(8)	0.657 4(7)	0.155 1(5)	0.118 1(5)
C(9)	0.747 0(7)	0.110 9(5)	0.141 0(5)
C(10)	0.845 4(7)	0.142 0(5)	0.172 6(5)
C(11)	0.853 7(7)	0.218 7(6)	0.182 3(5)
C(12)	0.765 6(7)	0.263 7(6)	0.160 4(5)
C(13)	0.665 6(7)	0.231 8(5)	0.127 1(5)
C(14)	0.568 7(7)	0.283 4(5)	0.103 2(5)
C(15)	0.467 6(7)	0.239 6(5)	0.085 1(5)
C(16)	0.106 8(7)	0.018 3(5)	0.099 1(5)
O(16)	0.024 8(5)	−0.007 2(4)	0.089 9(4)
C(17)	0.166 3(8)	0.127 3 6)	0.167 4(6)
O(17)	0.119 9(6)	0.163 7(5)	0.197 9(4)
C(21)	0.568 1(7)	0.324 1(5)	0.031 4(5)
C(22)	0.639 7(8)	0.311 8(6)	−0.005 9(5)
C(23)	0.631 2(9)	0.346 5(6)	−0.072 0(6)
C(24)	0.551 4(9)	0.395 3(7)	−0.101 1(6)
C(25)	0.476 8(8)	0.409 5(6)	−0.064 3(5)
C(26)	0.486 8(8)	0.375 2(5)	0.001 5(5)
C(31)	0.569 5(6)	0.338 6(5)	0.164 7(5)
C(32)	0.606 9(7)	0.410 9(5)	0.165 8(5)
C(33)	0.609 1(7)	0.456 6(5)	0.222 6(5)
C(34)	0.577 0(7)	0.435 8(6)	0.279 9(5)
C(35)	0.539 6(8)	0.364 6(6)	0.281 0(5)
C(36)	0.534 2(7)	0.316 2(6)	0.223 6(5)
C(41)	0.430 7(7)	−0.090 7(5)	0.161 4(5)
C(42)	0.520 4(8)	−0.054 6(6)	0.202 1(7)
C(43)	0.619 7(8)	−0.073 9(7)	0.199 8(8)
C(44)	0.633 4(8)	−0.130 9(7)	0.157 0(6)
C(45)	0.548 0(9)	−0.168 0(8)	0.116 3(6)
C(46)	0.446 7(8)	−0.147 8(7)	0.119 4(5)
C(51)	0.216 4(7)	−0.138 7(5)	0.122 5(5)
C(52)	0.176 9(8)	−0.141 1(5)	0.046 9(5)
C(53)	0.114 4(8)	−0.198 6(6)	0.010 8(5)
C(54)	0.088 7(8)	−0.256 2(6)	0.050 1(6)
C(55)	0.124 9(9)	−0.255 5(6)	0.123 7(6)
C(56)	0.188 2(8)	−0.198 6(6)	0.159 7(5)
C(61)	0.303 7(7)	−0.076 0(5)	0.261 3(5)
C(62)	0.369 0(9)	−0.128 1(6)	0.303 4(5)
C(63)	0.362 0(9)	−0.144 8(6)	0.373 0(6)
C(64)	0.292 1(10)	−0.109 7(7)	0.399 2(6)
C(65)	0.226 8(9)	−0.055 8(7)	0.359 8(6)
C(66)	0.232 7(8)	−0.040 0(6)	0.290 2(5)
O(1)	0.835 4(10)	0.483 8(8)	0.088 4(7)
O(2)	0.972 4(12)	0.524 4(9)	0.086 9(8)

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