Arene–Molybdenum Chemistry: Nucleophilic Addition to the Cations $[C_6H_6Mo(\pi-C_3H_5)L_2]^+$ Giving Cyclohexadienyl Derivatives

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The dimer $[C_6H_6Mo(\pi-C_3H_5)Cl]_2$ is cleaved by chelate ligands L_2 giving the cations $[C_6H_6Mo(\pi-C_3H_5)L_2]^+$ [$L_2 = Ph_2PCH_2CH_2PPh_2$ (dppe), $Me_2PCH_2CH_2PMe_2$ (dmpe), or $(MeSCH_2)_2$]. The cations react with nucleophiles ($R^- = H^-$, Bu^n, and, when L_2 = dppe, CN^-) giving the neutral cyclohexadienyl derivatives $[(C_6H_6R)Mo(\pi-C_3H_5)L_2]$. An asymmetric structure for the latter is suggested by ^1H n.m.r. spectra at 270 MHz and double-resonance experiments. The cations $[(C_6H_6R')Mo(\pi-C_3H_5)L_2']^+$, ($R'$ = H or Me, L_2' = en, bipy, and *o*-phenylenediamine) are also described.

It has been shown that the dimer $[(C_6H_6)Mo(\pi-C_3H_5)Cl]_2$ readily gives neutral complexes of the type $[(C_6H_6)Mo(\pi-C_3H_5)LX]$, where LX is a 3-electron ligand and that, in the presence of dichloroethylaluminium, the dimer will catalyse a number of hydrocarbon reactions.[1] In a continuing exploration of this arene–molybdenum–π-allyl system we have investigated the preparation and properties of cationic systems of the type $[(C_6H_5R)Mo(\pi-C_3H_5)L_2]^+$, where L_2 is a chelate 4-electron ligand. Part of this work has been briefly communicated.[2]

RESULTS

Treatment of the dimer $[(C_6H_6)Mo(\pi-C_3H_5)Cl]_2$ (ref. 3) in ethanol with chelate ligands [L_2 = 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(dimethylphosphino)ethane (dmpe), ethylenediamine (en), 2,5-dithiahexane (dth), 2,2′-bipyridine (dipy), or *o*-phenylenediamine] causes smooth cleavage of the chloro-bridge system together with displacement of the chloro-ligand giving the cations $[(C_6H_6)Mo(\pi-C_3H_5)L_2]^+$, (I). The crystalline air-stable complexes were isolated as salts with counter-anions such as chloride, hexafluorophosphate, or tetrafluoroborate. The solubilities of the salts depended markedly on the counter-anion, the chloride salts being soluble in water, ethanol, and dichloromethane, whereas the tetrafluoroborate and hexafluorophosphate salts were only very slightly soluble in water but dissolved in acetone, dichloromethane, and dimethyl sulphoxide.

The structures of the cations (I) shown in the Scheme are proposed on the basis of the data and assignments given in Table 1 and the Experimental section. I.r. spectra of all the complexes (I) showed bands assignable to benzene and the π-allyl ligands. The ^1H n.m.r. spectra all showed a sharp singlet assignable to the benzene hydrogen atoms in the region τ 4—5 and coupling with the ^{31}P nuclei was not observed. This band was at rather lower fields than for neutral complexes of the type $[(C_6H_6)Mo(\pi-C_3H_5)LX]$,[4] presumably due to the positive charge on the cations (I). Also the resonances assigned to the hydrogen atoms H_{syn} and H_{anti} of the π-allyl group occurred as close overlapping doublets and were less well separated than in the neutral analogues.[3,4]

It has been previously shown that cationic arene complexes may undergo nucleophilic attack on the arene ring forming cyclohexadienyl derivatives.[5] The complexes (I) behave in a similar manner and treatment with lithium tetrahydroaluminate or butyl-lithium gave yellow, crystalline solids. Elemental analyses of these were consistent with the stoicheiometry $[(C_6H_6R)Mo(\pi-C_3H_5)L_2]$ (II; L_2 = dmpe, dppe, or dth; R = H or Bu^n). The mass spectrum of the complex (II; L_2 = dmpe, R = Bu^n) showed a peak corresponding to the parent ion $[(C_6H_6Bu^n)^{98}Mo(\pi-C_3H_5)(dmpe)]^+$. Since the spectral data on all the complexes (II) showed strong similarities, it seems reasonable that they have related structures. Treatment of the complex (II; L_2 = dppe, R = H) with triphenylmethylium tetrafluoroborate reformed the parent complex (I; L_2 = dppe) in high yield. This shows that no major change, such as ligand loss, occurs on hydride addition to complex (I). Incidentally, treatment of the parent cation (I; L_2 = dth) with sodium tetrahydroborate at low temperatures gave a red complex which the analytical and spectroscopic data suggest to be the unchanged cation as a salt with the anion BH_4^-.

I.r. spectra of the cyclohexadienyl complexes (II; R = H) all show an intense band near 2 740 cm^{-1} which is absent in the spectrum of the complex (II; L_2 = dppe, R = D), prepared by lithium tetradeuterioaluminate reduction of the appropriate cation (II). The latter deuteride derivative, however, showed a new band at 2 400 cm^{-1}. The complexes (II; R = Bu^n) also did not show a strong band near 2 740 cm^{-1}. These observations suggest that in the complexes (II; R = H) there is a C–H_{exo} group of the type previously found in cyclohexadienyl and cyclopentadiene complexes.[5] Many of the known complexes containing the grouping $[(C_6H_6)Mo(\pi-C_3H_5)]$ show a weak band in the i.r. spectrum near 1 530 cm^{-1} assignable to the C–C stretch of the π-allyl group. Such a band was observed in some, but not all, of the complexes (II). Therefore, the i.r. evidence is generally consistent with the formulation given for complexes (II).

^1H N.m.r. spectra of the complexes (II) were complex and warrant detailed discussion. They were determined at 60 MHz, and in some cases at 100 or 270 MHz, together with spin-decoupling experiments. The relevant data are given in Table 2 and the Experimental section. The 270 MHz spectra of the complexes (II; L_2 = dmpe, R = H or Bu^n) and the spin-decoupling experiments are described first. Assignments given in Table 2 have been made on the following basis (for the labelling of the hydrogen atoms see the Scheme). The triplet assigned to H_a collapsed to a 1 : 1 doublet (*J* 5·2 Hz) when bands assigned to H_b of H_c were irradiated. Also the chemical-shift position of the triplet

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[1] M. L. H. Green, J. Knight, L. C. Mitchard, G. G. Roberts, and W. E. Silverthorn, *J.C.S. Chem. Comm.*, 1972, 987.

[2] M. L. H. Green, J. Knight, L. C. Mitchard, G. C. Roberts, and W. E. Silverthorn, *Chem. Comm.*, 1971, 1619.

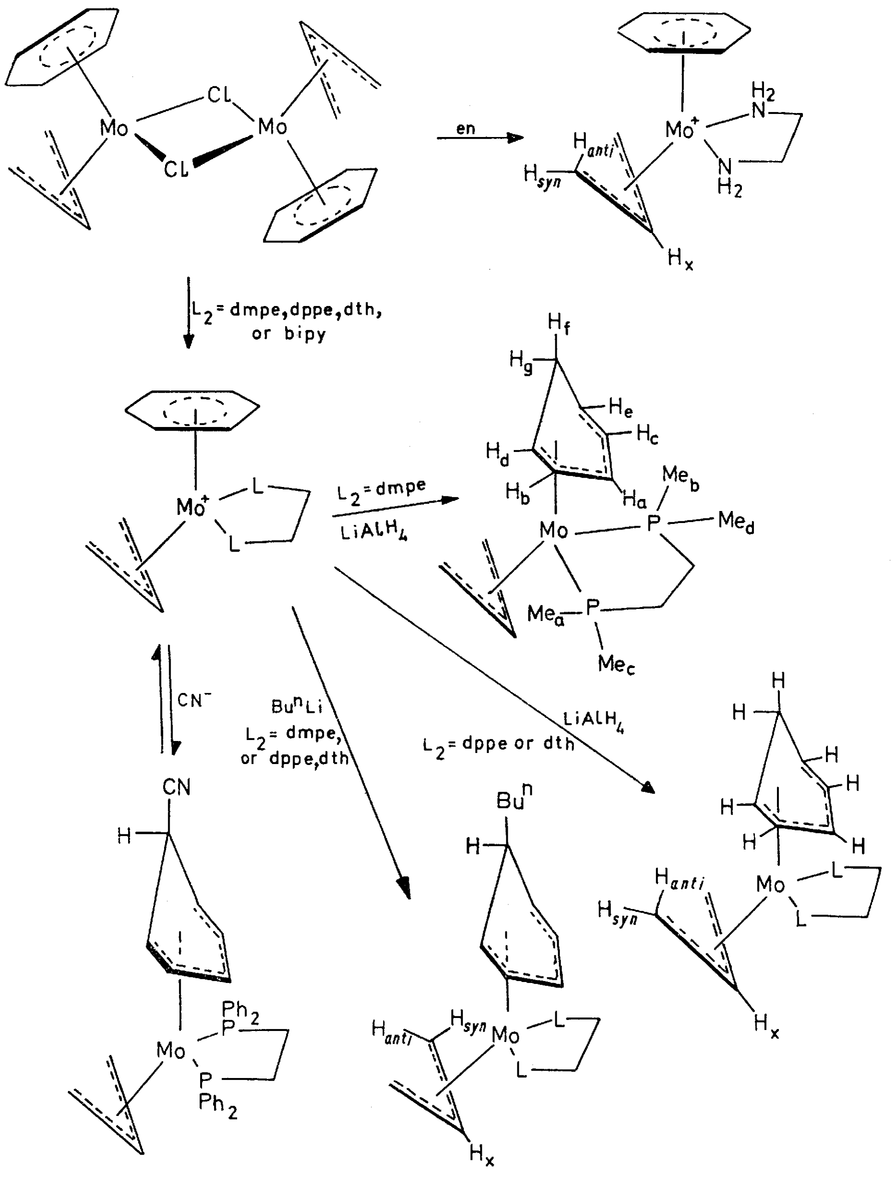
[3] M. L. H. Green and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 301.

[4] M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 1403.

[5] D. A. White, *Organometallic Chem. Rev.* (*A*), 1968, **3**, 497.

was similar to the equivalent hydrogen atom in previously described cyclohexadienyl complexes, such as $[(C_6H_7)Mn(CO)_3]$. Irradiation of H_c also caused the band assigned to H_e to sharpen markedly and irradiation of H_e caused H_c to collapse to a 1 : 1 doublet. It may be noted that irradiation of H_c caused H_b to change slightly and *vice versa,* so that it seems there may be slight interaction between these two hydrogen atoms. The band assigned to H_b appeared as four lines of an apparently regular 1 : 3 : 3 : 1 quartet. Irradiation of H_a or H_d caused this to collapse to a triplet (1 : 2 : 1), but irradiation of other bands caused no major change. An explanation of the quartet appearance of H_b may be that, apart from coupling to H_a and H_d, there may be further coupling with a ^{31}P nucleus of the dmpe ligand. Double-resonance experiments also showed that in the complexes (II; L_2 = dmpe, R = Bu^n) there is coupling between the bands assigned to H_e and H_g and when R = H there is coupling between H_f (or H_g) (τ 7·25) and H_g (or H_f) (τ 7·71).

A band assigned to the allyl H_x hydrogen atom was most clearly seen in the spectrum of the complex where R = Bu^n, at τ 7·08, and its appearance closely resembled the equivalent band in other neutral (arene)Mo(π-allyl) derivatives. Irradiation experiments showed that this band is coupled to the band at τ 8·4 and that irradiation of the latter collapsed the former to a simpler (four-line) band. Given the validity of these assignments, then a marked feature of the spectra is the occurrence of the resonances assigned to H_b,H_c and to H_d,H_e at different chemical shifts. This contrasts with spectra of other cyclohexadienyl derivatives where, as expected, these pairs of hydrogen atoms are equivalent. The non-equivalence in complexes (II) suggests that they are *asymmetric.*



SCHEME

TABLE 1

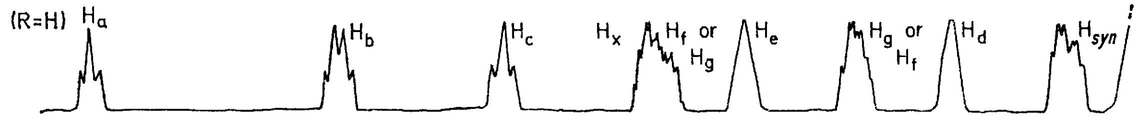
Analytical and i.r. data

	Complex	Colour	Analytical data (%) Found (Calc.) C	H	Selected i.r. data (cm^{-1})[a]
(1)	$[(C_6H_6)Mo(\pi\text{-}C_3H_5)(Me_2PCH_2)_2]^+PF_6^-$	Orange	35·4(35·3)	5·4(5·3)	3 080m,[b] 1 530m,[c] 1 430m,[d] 1 005m,[e] 850vs,[f] 565s[f]
(2)	$[(C_6H_6)Mo(\pi\text{-}C_3H_5)(Ph_2PCH_2)_2]^+BF_4^-$	Red	59·8(60·0)	4·9(5·0)	3 040w,[b] 1 530w,[c] 1 040s[g]
(3)	$[(C_6H_6)Mo(\pi\text{-}C_3H_5)(NH_2CH_2)_2]^+PF_6^-$	Dark red	31·1(31·4)	4·8(4·6)[h]	3 370s,[i,j] 3 330s,[i,j], 3 080w,[i,j] 1 600s,[k] 1 535w,[c] 850vs[f]
(4)	$[(C_6H_6)Mo(\pi\text{-}C_3H_5)(MeSCH_2)_2]^+Cl^-$	Red-brown	41·5(41·9)	5·6(5·6)	3 040w,[b] 1 530w[c]
(5)	$[(C_6H_6)Mo(\pi\text{-}C_3H_5)(MeSCH_2)_2]^+PF_6^-$	Red-brown	32·2(32·3)	4·3(4·3)	
(6)	$[(C_6H_7)Mo(\pi\text{-}C_3H_5)(Me_2PCH_2)_2]$	Orange-yellow	48·5(49·0)	7·5(7·7)	2 740s[l]
(7)	$[(C_6H_7)Mo(\pi\text{-}C_3H_5)(Ph_2PCH_2)_2]$	Yellow	68·3(68·3)	5·9(5·9)	2 740s[l]
(8)	$[(C_6H_7)Mo(\pi\text{-}C_3H_5)(MeSCH_2)_2]$	Yellow	45·8(46·1)	6·4(6·5)	2 750s[l]
(9)	$[(C_6H_6\text{-}n\text{-}C_4H_9)Mo(\pi\text{-}C_3H_5)(Ph_2PCH_2)_2]$	Yellow	70·1(69·8)	6·8(6·6)	
(10)	$[(C_6H_6\text{-}n\text{-}C_4H_9)Mo(\pi\text{-}C_3H_5)(Me_2PCH_2)_2]$	Yellow	54·6(54·1)	8·7(8·6)[m]	1 535w[e]
(11)	$[(C_6H_6\text{-}n\text{-}C_4H_9)Mo(\pi\text{-}C_3H_5)(MeSCH_2)_2]$	Primrose yellow	39·4(51·3)[n]	6·3(7·6)	1 530w[e]
(12)	$[(C_6H_6CN)Mo(\pi\text{-}C_3H_5)(Ph_2PCH_2)_2]$	Yellow	66·7(67·6)	5·6(5·5)[o]	2 220m,[p] 1 535vw[e]
(13)	$[(C_6H_6)Mo(\pi\text{-}C_3H_5)(bipy)]^+PF_6^-$	Deep red	44·1(44·2)	3·6(3·7)[q]	
(14)	$[(C_6H_5Me)Mo(\pi\text{-}C_3H_5)(NH_2CH_2)_2]^+PF_6^-$	Orange	33·1(33·2)	5·1(4·85)[r]	3 335s,[i] 3 310s,[i] 3 270m,[i] 1 595s,[k] 1 535m,[e] 830vs[f]
(15)	$[(C_6H_5Me)Mo(\pi\text{-}C_3H_5)\{o\text{-}(NH_2)_2\text{-}C_6H_4\}]^+PF_6^-$	Red	39·9(39·9)	4·7(4·4)[s]	3 320s,[i] 3 270m,[i] 3 235m,[i] 1 630,[k] 1 540m, 835s[f]

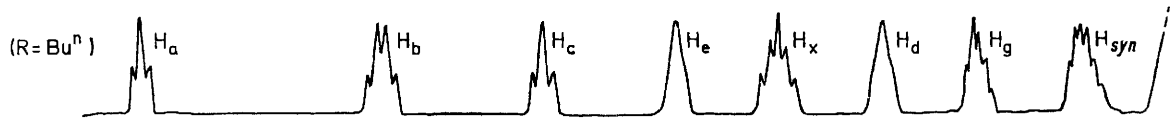
[a] Measured on mulls in Nujol. [b] Antisymmetric stretch of C–H in benzene. [c] C–C Stretch of π-C_3H_5. [d] C–C Asymmetric stretch of C_6H_6. [e] C–H In-plane bend of C_6H_6. [f] PF_6 Stretch. [g] BF_4 Stretch. [h] N, 6·5(6·6%). [i] N–H Stretch. [j] For the chloride salt. [k] N–H Deformation. [l] C–H *exo*-Stretch. [m] Parent ion, *m/e* 424 (^{98}Mo). [n] Decomposes rapidly at room temperature, S, 17·1(16·1%). [o] N, 5·6(5·5%). [p] C≡N Stretch. [q] N, 5·3(5·4%). [r] N, 6·4(6·5%). [s] N, 5·9(5·8%).

TABLE 2

Spin-decoupling data for the complexes $[(C_6H_6R)Mo(\pi\text{-}C_3H_5)(dmpe)]$ (R = H or Bu^n)



τ 4·30	5·70	6·60	7·25	7·42	7·71	8·30	8·60
↑	t($J_{H_d{}^{31}P}$ 4·00)	d($J_{H_cH_e}$ 5·25)					
d($J_{H_aH_c}$ 5·20)	↑	*b*					
d($J_{H_aH_b}$ 5·20)	*b*	↑	*c*	*c*			
		c	↑		*c*		*c*
		d($J_{H_aH_c}$ 5·20)	*b*	↑	*c*	*d*	*d*
			f	*b*		*b*	
	t($J_{H_b{}^{31}P}$ 4·00)		*f*	*b*	*e*	↑	
			f				↑

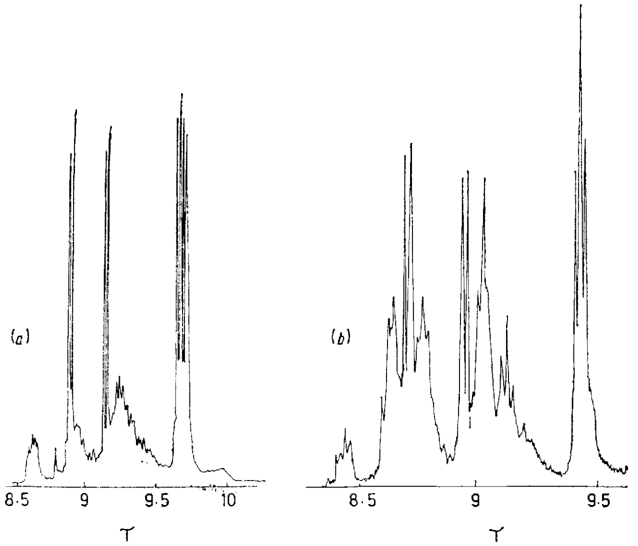


τ 4·40	5·82	6·70	6·95	7·08	7·75	8·05	8·40
↑	t($J_{H_d{}^{31}P}$ 4·00)	d($J_{H_bH_c}$ 5·25)	*a*				
d($J_{H_aH_c}$ 5·20)	↑	*b*	*b*		*e*		
d($J_{H_aH_b}$ 5·20)	*b*	↑	*e*				
		d($J_{H_aH_c}$ 5·20)	↑	*f*		*e*	
			b	↑			*e*
	t($J_{H_b{}^{31}P}$ 4·00)		*b*		↑		
			b			↑	
			b	*f*			↑

↑ Indicates position of irradiation; see Scheme for labelling of hydrogen atoms. [a] Essentially no change from original appearance shown in spectrum. [b] Reduced in intensity. [c] Slight change in appearance. [d] Poor resolution, inconclusive. [e] Sharpening observed. [f] Appeared simpler.

For the complexes (II; L_2 = dmpe, R = H or Bu^n) the region τ 8—10 was complex (Figure). When R = H, two sharp doublets were seen, at τ 8·90 and 9·15, which may be assigned by analogy with other dmpe systems to the $(CH_2)_2$ group. Also, there were two close sharp doublets, at τ 9·70 and 9·75. These integrated for six hydrogen atoms and may be assigned to two of the methyl groups of the dmpe ligand each coupling to a ^{31}P nucleus. The other two methyl groups, together with the remaining allyl hydrogen atoms, appeared as a broad complex band between τ 8·95 and 9·60. It is, of course, to be expected that the two methyl groups on each phosphorus atom will be non-equivalent since they differ in their relation to the rest of the molecule. The appearance of the two doublets near τ 9·70 shows that either Me_a,Me_b or Me_c,Me_d are non-equivalent. Similarly, for the complex (II; L_2 = dmpe, R = Bu^n) the symmetrical triplet at τ 9·45, which presumably arises from the corresponding two P-methyl groups, may be understood as overlapping doublets.

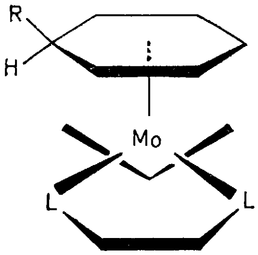
The i.r. and ^1H n.m.r. data presented above suggest that the complexes (II; L_2 = dmpe, R = H or Bu^n) have a CHR group with the R group in the *exo*-position. It appears that the C_6H_6 system of the C_6H_6R group is asymmetric with respect to the rest of the molecule and a possible structure is shown below.



^1H N.m.r. spectra at 270 MHz in the region τ 8—10 of the complexes $[(C_6H_7)Mo(\pi\text{-}C_3H_5)(dmpe)]$ (*a*) and $[C_6H_6Bu^n)Mo(\pi\text{-}C_3H_5)(dmpe)]$ (*b*)

The thermal instability of the complexes [II; L_2 = $(MeSCH_2)_2$, R = H or Bu^n] precluded detailed time-consuming n.m.r. studies. For example, benzene solutions darkened considerably after 15 min at room temperature, although the solid could be kept at −20 °C for several days without observable change. However, consistent ^1H n.m.r. spectra could be obtained by rapid determination at reduced temperature (0 °C). These showed very similar features to the above spectra, except that the bands assigned to H_b now appeared as triplets rather than as quartets. The spectra still indicated that there is asymmetry in these complexes, especially the bands assigned to the two Me–S hydrogen atoms which occurred at widely separated chemical shifts.

In conclusion, the spectroscopic data strongly suggest an asymmetric structure of the type shown below. This in turn would be consistent with a rigid system where the C_6 ring does not rotate about the ring–Mo axis.



The arene derivatives $[(C_6H_6)Mn(CO)_3]^+$ and $[(C_6H_6)RuCl_2]^n$ were found to react under mild conditions with several nucleophiles such as CN^- or OMe^- giving cyclohexadienyl derivatives.[6] However, they were too unstable to be isolated. We found that treatment of the complex (I; L_2 = dppe, X^- = Cl^-) with sodium cyanide gave yellow crystals which the data given in Table 1 suggest is the complex $[(C_6H_6CN)Mo(\pi\text{-}C_3H_5)(dppe)]$. It is stable under an atmosphere of nitrogen but decomposes when exposed to air for several hours. The complex dissolves only slightly in light petroleum or benzene and is decomposed in chloroform, dimethyl sulphoxide, or acetone. ^1H N.m.r. spectra in the latter three solvents were identical to that of the parent cation (II; L_2 = dppe) showing that the CN group reversibly dissociates.

DISCUSSION

Structures proposed for complexes (I) and (II) and their reactions are shown in the Scheme. The reactions of the cations (I) show that nucleophilic attack occurs on the arene ring rather than on the π-allyl group. The product from the latter reaction would be the propene derivative $[(arene)Mo(CH_2{=}CHCH_2X)L_2]$. There is presently no definitive rule for predicting the course of such nucleophilic addition reactions. However, it seems that there is a tendency for reactions of this type to prefer the product which does not involve the reduction of the valency state of the metal. It is in these cases to be expected that a metal such as molybdenum will nearly always give a product which obeys the 18-electron rule.

EXPERIMENTAL

All preparations, reactions, and purifications were carried out in the absence of oxygen. Tetrahydrofuran, diethyl ether, benzene, and dichloromethane were dried by heating under reflux over finely ground calcium hydride followed by distillation. Light petroleum refers to hydrocarbon mixtures (b.p. 30—40 °C). I.r. spectra were determined using a Perkin-Elmer 457 spectrometer and were calibrated with a polystyrene film. ^1H N.m.r. spectra were recorded using JEOL C-60-HL, Perkin-Elmer 100 MHz, or Brucker 270 MHz instruments. Mass spectra were determined using an A.E.I. M.S.9 instrument. The dimers $[(C_6H_5R)Mo(\pi\text{-}C_3H_5)Cl]_2$ were prepared as previously described.[3]

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[6] M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, 1969, **8**, 1950; R. A. Zelonka and M. C. Baird, *J. Organometallic Chem.*, 1972, **35**, C43.

π-Allyl(benzene)[1,2-bis(diphenylphosphino)ethane]molybdenum Tetrafluoroborate.—The dimer $[(C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·25 g, 0·5 mmol) in ethanol (95%, 15 cm^3) was treated with 1,2-bis(diphenylphosphino)ethane (0·4 g, 1·0 mmol) and the mixture was heated under reflux for 6 h. The resulting deep red solution was cooled and filtered. The solvent was removed from the filtrate under reduced pressure giving a light orange solid. This is the crude chloride salt $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(Ph_2PCH_2)_2]Cl$. It was extracted with water (20 cm^3), the extract was filtered, and the orange filtrate was treated with a few drops of a saturated aqueous solution of sodium tetrafluoroborate until no further precipitation was observed. The pink precipitate was collected, washed with water (2 × 5 cm^3), and dried *in vacuo*. The product was then extracted with dichloromethane (10 cm^3), the extract was filtered, and ethanol (95%, 5 cm^3) was added to the brick-red filtrate. Concentration of the solution under reduced pressure gave red *crystals* which were washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo, ca.* 65%.

π-Allyl(benzene)[1,2-bis(dimethylphosphino)ethane]molybdenum Hexafluorophosphate.—The dimer $[(C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·25 g, 0·5 mmol) in ethanol (95%, 15 cm^3) was treated with 1,2-bis(dimethylphosphino)ethane (0·22 cm^3, 1·5 mmol) and the mixture was heated under reflux for 2 h. The solvent was removed from the resulting deep red solution under reduced pressure and the residue was washed with light petroleum to remove excess of tertiary phosphine, giving the crude product as the chloride salt. The residue was then extracted with ethanol (95%, 15 cm^3) and the solution was filtered. The filtrate was treated with a slight excess of saturated aqueous ammonium hexafluorophosphate and the orange precipitate was collected and washed with water and then dried *in vacuo*. The product was extracted with acetone (15 cm^3) and filtered. Ethanol (10 cm^3) was added to the filtrate. Reduction of the volume of the solution under reduced pressure gave orange *crystals* which were recrystallised twice from acetone–ethanol and finally dried *in vacuo, ca.* 90%.

π-Allyl(benzene)(2,5-dithiahexane)molybdenum Salts.—The dimer $[(C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·5 g, 1·0 mmol) in 25% ethanol (95%, 15 cm^3) was treated with 2,5-dithiahexane (0·28 cm^3, 2·0 mmol) and the mixture was heated under reflux for 45 min. The resulting deep red solution was filtered, the solvent was removed under reduced pressure, and the residue was washed with light petroleum. The residue was then extracted with ethanol (10 cm^3) and filtered. Petroleum ether (b.p. 100—120 °C, 5 cm^3) was added to the filtrate and the solution was concentrated under reduced pressure giving red-brown crystals which were recrystallised a second time from ethanol–petroleum ether and then dried giving the pure chloride salt $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(MeSCH_2)_2]^+Cl^-$. The analogous hexafluorophosphate salt was prepared by addition of aqueous ammonium hexafluorophosphate to an ethanol extract of the *chloride*. It was recrystallised from ethanol–petroleum ether, *ca.* 90%. The ethylenediamine derivative $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(en)]^+PF_6^-$ was prepared in a similar manner to the 2,5-dithiahexane analogue except that the chloride salt was not isolated. Recrystallisation was from acetone–water giving dark red *needles, ca.* 90%. The toluene derivative $[(C_6H_5Me)Mo(\pi\text{-}C_3H_5)(NH_2CH_2)_2]^+PF_6^-$ was similarly prepared starting from the dimer $[(C_6H_5Me)Mo(\pi\text{-}C_3H_5)Cl]_2$. Recrystallisation was from acetone–water, *ca.* 72%.

π-Allyl(benzene)(o-phenylenediamino)toluenemolybdenum Hexafluorophosphate.—The toluene dimer $[(C_6H_5Me)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·15 g) in toluene (50 cm^3) was treated with an excess of *o*-phenylenediamine (1·0 g) and the mixture was heated under reflux for 1 h. The solvent was removed under reduced pressure and the residue was extracted with warm water (15 cm^3) giving a red solution. Excess of aqueous ammonium hexafluorophosphate was added giving a red precipitate which was separated, washed with water, dried, and then recrystallised from acetone–water giving red *crystals*. These were dried *in vacuo, ca.* 66%. The 2,2′-bipyridine analogue $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(bipy)]^+PF_6^-$ was similarly prepared, *ca.* 60%.

π-Allyl[1,2-bis(dimethylphosphino)ethane]cyclohexadienylmolybdenum.—The crude complex $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(Me_2PCH_2)_2]^+Cl^-$ (0·40 g, 1·0 mmol) in tetrahydrofuran (20 cm^3) at −60 °C was treated with lithium tetrahydroaluminate (0·2 g) and the mixture was stirred at −20 °C for 1 h. The resulting yellow solution at −78 °C was treated with water (0·2 cm^3) and, after warming to room temperature, benzene (15 cm^3) was added to the mixture. The benzene layer was separated, filtered, and the orange-yellow filtrate was concentrated under reduced pressure giving a yellow solid. This was extracted with light petroleum (20 cm^3) and the extract was filtered. The filtrate was concentrated (10 cm^3) and then slowly cooled to −78 °C. Yellow *crystals* appeared which were separated and dried *in vacuo, ca.* 60%. The analogue $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(Ph_2PCH_2)_2]$ was similarly prepared from the salt $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(Ph_2PCH_2)_2]^+Cl^-$ at −50 °C. Hydrolysis gave a yellow solid which was recrystallised from ethanol at −50 °C giving the pure product, *ca.* 50%. The 2,5-dithiahexane analogue $[(C_6H_7)Mo(\pi\text{-}C_3H_5)(MeSCH_2)_2]$ was also prepared in the same way as the 1,2-bis(dimethylphosphino)ethane analogue. Recrystallisation was from benzene–petroleum ether (b.p. 100—120 °C) giving yellow *crystals* which were dried *in vacuo* and stored at −10 °C, *ca.* 45%.

π-Allyl(2,5-dithiahexane)(exo-n-butylcyclohexadienyl)molybdenum.—A suspension of the complex $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(MeSCH_2)_2]^+Cl^-$ (0·37 g, 1·0 mmol) in light petroleum (20 cm^3) at −20 °C was treated with n-butyl-lithium (5 cm^3, 1·5M), and the solution was stirred for 3 h. Some effervescence was observed and the mixture became yellow. The solution was cooled to −78 °C and a few drops of water were added. The mixture was allowed to warm slowly to room temperature before the solvent was removed under reduced pressure. The light brown residue was extracted with light petroleum (40 cm^3), the extract was filtered, and the volume of the filtrate was reduced *in vacuo* giving primrose-yellow *crystals*. These decompose steadily at room temperature, *ca.* 40%.

π-Allyl[1,2-bis(dimethylphosphino)ethane](exo-n-butylcyclohexadienyl)molybdenum.—The crude complex $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(Me_2PCH_2)_2]^+Cl^-$ (0·40 g, 1·0 cm^3) in tetrahydrofuran (20 cm^3) at −60 °C was treated with an excess of n-butyl-lithium in hexane (5 cm^3, 1·5M). The mixture was allowed to warm to room temperature and the resulting orange solution was then cooled again to −78 °C and treated with water (3 cm^3). After warming the mixture slowly to room temperature the solvent was removed under reduced pressure and the residue was then extracted with light petroleum (15 cm^3). The extract was filtered and the filtrate was cooled slowly to −78 °C giving yellow *crystals* which were finally dried *in vacuo, ca.* 55%. The analogue $[(C_6H_6Bu^n)Mo(\pi\text{-}C_3H_5)(Ph_2PCH_2)_2]$ was similarly prepared except that the product was extracted with ethanol and recrystallised from ethanol at −40 °C, *ca.* 40%.

π-Allyl[1,2-*bis*(*diphenylphosphino*)*ethane*](exo-*cyanocyclohexadienyl*)*molybdenum*.—The complex $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(Ph_2PCH_2)_2]^+Cl^-$ (0·61 g, 1·0 mmol) in ethanol (95%, 20 cm^3) was treated with an excess of sodium cyanide (0·1 g) in water (5 cm^3) and the mixture was heated under reflux for 2 h. After this time a slight lightening of the initially orange-red solution was observed and then the solvent was removed under reduced pressure giving an orange-yellow solid which was extracted with benzene (10 cm^3). The extract was filtered and petroleum ether (b.p. 100—120 °C, 5 cm^3) was added to the yellow filtrate and the solution was slowly concentrated under reduced pressure giving a microcrystalline yellow solid. The *crystals* were collected and washed with light petroleum (3 × 5 cm^3) and finally dried *in vacuo*, *ca.* 35%.

Reaction between π-Allyl[1,2-*Bis*(*diphenylphosphino*)*ethane*](*cyclohexadienyl*)*molybdenum and Triphenylmethylium Tetrafluoroborate*.—The complex $[(C_6H_7)Mo(\pi\text{-}C_3H_5)(PhPCH_2)_2]$ (0·30 g, 0·5 mmol) in dichloromethane (15 cm^3) was treated with an excess of $Ph_3C^+BF_4^-$ (0·5 g) and the mixture was stirred at room temperature for 1 h. The solution changed from yellow to red and was filtered. The filtrate was concentrated under reduced pressure and diethyl ether was added dropwise giving *crystals* of the complex $[(C_6H_6)Mo(\pi\text{-}C_3H_5)(PhPCH_2)_2]^+BF_4^-$ which were identified by comparison of the i.r. spectrum with an authentic sample, *ca.* 90%.

^{1}H *N.m.r. Data*.—The data are presented as follows. The complex is numbered as in Table 1 followed by chemical shift, *relative intensity*, **multiplicity** (J Hz), assignment, *etc.*

(1) 4·25;[a] 6·30;[b] 7·95, *4*,;[c,d] 8·20, *4*, **c**;[e] 8·45, *12*, **c**, Me_4. At 60 MHz.

(2) 2·10, *20*, **c**, Ph_4; 4·55;[a] 6·15;[b] 6·71—7·90, *8*, **c** $(CH_2)_2$.[c] At 60 MHz.

(3) 4·75;[a] 5·0—5·2, *4*, **br**, NH_2; 6·40;[b] 7·25, *4*, **c**;[e] 7·82, *2*, **d** (J 6·75);[c] 8·30, *2*, **d** (J 7·50).[d] At 60[f] and 100 MHz.[g]

(4) 4·30;[a] 6·40;[b] 6.90, 4, **s**;[c] 7·30, *6*, **s**, Me_2; 7·65, *4*, **c**.[c,d] At 60 MHz.[h]

(6) 4.35, *1*, **t** (J 5·20) H_a; 5·70, *1*, four lines, H_b; 6·60, *1*, **t** (5·25) H_c; 7·25, *2*, **c**, H_x, H_f; 7·42, *1*, **s**, br, H_e; 7·71, *1*, **c**, H_g; 8·30, *1*, **br**, H_d; 8·60, *1*, **c**, H_{anti}; 8·90, *2*, **d** (sepn. 5·50) CH_2P; 8·95, 9·10, *3*, **c**, H_{syn}; 9·15, *2*, **d** (sepn. 5·50), CH_2P, 9·2—9·6, *6*, **c**, Me_a,Me_b, or Me_c,Me_d; 9·70, *3*, **d** (J 5·5) Me_c or Me_d (or Me_a or Me_b); 9·75, *3*, **d** (J 5·5) Me_a or Me_b (or Me_c or Me_d). At 270 MHz.[i]

(7) 3·00, *20*, **c**, Ph; 4·90, *1*, **br**, H_a; 6·10, *1*, **br**, H_b; 6·50, *2*, **br**, H_d and H_x; 7·9—9·5, *12*, **c**, H_d, H_e, H_f, H_g.[c,d] At 60 MHz.[i]

(8) 4.70, *1*, **t** (J 5·20), H_a; 5·85, *1*, **t** (J 5·25) H_b; 6·87, *1*, **t** (J 5·25), H_c; 7·0—9·5, *19*, **c**, containing sharp singlets at 8·40, *3*, Me_a or Me_b, and at 9·10, *3*, Me_b or Me_a superimposed on H_d, H_e, H_f, H_g, $\pi\text{-}C_3H_5$.[e] At 60 MHz.[i]

(9) 2·90, *20*, **c**, Ph_4; 4·50, *1*, **c**, H_a; 5·80, *1*, **c**, H_b; 7·4—9·5, *22*, **c**, H_c, H_d, H_e, H_g, H_x, Bu^n.[c–e] At 60 MHz.[j]

(10) 4·40, *1*, **t** (J 5·20) H_a; 5·81, *1*, four lines, H_b [6·70, *1*, **t** (sepn. 5·25), H_c]; 6·95, *1*, H_e; 7·08, *1*, **c**, H_x; 7·75, *1*, **br**, H_d; 8·05, *1*, **c**, H_g; 8·4, *1*, **c**, H_{anti}; 8·6—8·9, a broad band containing doublet [8·70, 2, (sepn. 5·50), CH_2P] and the remainder due to H_{syn},H_{anti}, and/or part of n-butyl group; 8·95—9·3, *9*, broad band containing doublet [8·95, *2* (sepn. 5·50), CH_2P] and remainder due to Me_c, Me_d, or Me_a,Me_a and H_{syn},H_{anti} and/or n-butyl not in previous band; 9·25, *3*, overlapping doublets [triplet (J 5·50)], Me_a or Me_b (or Me_c or Me_d); 9·75, *3*, (sepn. 5·50), Me_b or Me_a (or Me_d or Me_c). At 270 MHz.[i]

(11) 4·70, *1*, **t br**, H_a; 5·91, *1*, **t** (J 5·20) H_b; 7·0—9·5, 28, complex band containing sharp singlets at 8·2, *3*, Me_a or Me_b and at 8·80,*3*, Me_b or Me_a, superimposed on H_a, H_e, $\pi\text{-}C_3H_5$, Bu^n. At 60 MHz.[f–h]

(14) 4·8—5·6, *5*, **c**, Ph, 5·9, *1*, **c**, H_x; 6·8, *4*, **c**,[c,d] 7·4, *4*, **br**, $(NH_2)_2$; 8·2, *2*, **d** (J 7·0); 8.4, *3*, **s**, Me; 8, 6, *2*, **d** (J 21·6). At 60 MHz.[h]

(15) 2·9, *4*, **c**, C_6H_4; 5·1, *5*, **c**, Ph; 5·59, *1*, **br**, H_x, 6·85 *4*, **br** $(NH_2)_2$; 8·05, *2*, **d** (J 7·0); 8·3, *3*, **s**, Me; 8·45, *2*, **d** (J 21·0). At 60 MHz.[h]

[a] As *6*, **s**, C_6H_6.
[b] As *1*, **c**, H_x of $\pi\text{-}C_3H_5$.
[c] H_{anti} of $\pi\text{-}C_3H_5$.
[d] H_{syn} of $\pi\text{-}C_3H_5$.
[e] $(CH_2)_2$.
[f] In $[^2H_6]Me_2SO$.
[g] In $[^2H_6]Me_2CO$.
[h] In $[^2H_2]H_2O$.
[i] In $[^2H_6]C_6H_6$.
[j] In $[^2H]CHCl_3$.

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