Some Studies of η-Cycloheptatrienylmolybdenum Compounds

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The cation $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_6H_5R)]^+$ readily undergoes displacement of the arene ligand allowing the following compounds to be prepared: $[Mo(\eta\text{-}C_7H_7)L_3][PF_6]$ [L_3 = $(MeCN)_3$, $(MeCN)_2(PPh_3)$, $(MeCN)(Ph_2PCH_2CH_2PPh_2)$, $(PMe_2Ph)_3$, $(PMePh_2)_3$, or $(CO)(PMe_2Ph)_2$]; $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}X)_3Mo(\eta\text{-}C_7H_7)]A$ (X = Cl, Br, OMe, or OEt; A = PF_6 or BF_4); and $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}X)_3Mo(\eta\text{-}C_7H_7)]$ (X = Cl, Br, I, or OMe). The last neutral compounds are paramagnetic, and electronic, e.s.r., i.r., and photolectron spectral studies have been made. The new compounds $K_2[Mo(\eta\text{-}C_7H_7)(CN)_3]$, $[Mo(\eta^5\text{-}C_6H_7)(\eta\text{-}C_7H_7)]$, $[Mo(\eta\text{-}C_7H_7)(PPh_3)(pd)]$ (pd = pentane-2,4-dionate), and $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_7H_7)(PPh_3)]$ are also described.

DURING an exploration of the chemistry of arene-molybdenum derivatives it was found that the mixed sandwich compounds $[Mo(\eta\text{-arene})(\eta\text{-}C_7H_7)][PF_6]$ could be readily prepared. These compounds provide a versatile route to mono(η-cycloheptatrienyl)molybdenum derivatives and these studies, which have been briefly communicated in part,[1] are described here. A somewhat related study on $Mo(\eta\text{-}C_7H_7)$ derivatives has recently appeared.[2]

RESULTS AND DISCUSSION

Chemical Studies.—The mixed sandwich compounds $[Mo(\eta\text{-}C_6H_5R)(\eta\text{-}C_7H_7)][PF_6]$ (1; R = H or Me) reacted readily with donor ligands (L = MeCN, PMe_2Ph, or $PMePh_2$) causing smooth displacement of the arene ligand and $[Mo(\eta\text{-}C_7H_7)L_3][PF_6]$ were formed in excellent yield. The reactions may be carried out in excess of the pure ligand as solvent (L = MeCN) (2) or in ethanol solutions [L = PMe_2Ph (3) or $PMePh_2$ (4)]. Compound (2) is air-sensitive, and reacts with common solvents such as ethanol or chloroform so that recrystallisation was only possible from acetonitrile. Treatment of (1; R = Me) in ethanol with excess of 1,2-bis(diphenylphosphino)ethane (dppe) gave a pink compound whose stoicheiometry corresponds to $[Mo(\eta\text{-}C_7H_7)(dppe)_2][PF_6]$ (5). This formulation is supported by the ^1H and proton-decoupled ^{31}P n.m.r. spectra (Table 1). For example, the ^{31}P n.m.r. spectrum shows two bands of intensity ratio 3 : 1 and the chemical shift of the less-intense band occurs near that of phosphorus in unco-ordinated dppe. These data strongly suggest that of the four phosphorus atoms in the two dppe ligands only three co-ordinate to the molybdenum.

Many of the complexes $[Mo(\eta^7\text{-}C_7H_7)L_3][PF_6]$ undergo ready exchange of one or more of the ligands L. For example, treatment of (3) in acetone with carbon monoxide gave $[Mo(\eta\text{-}C_7H_7)(CO)(PMe_2Ph)_2][PF_6]$ (6) in high yield. The ^1H n.m.r. spectrum of (3) in acetone shows only a 1 : 2 : 1 triplet for the $\eta\text{-}C_7H_7$ hydrogens. However on addition of an excess of PMe_2Ph a quartet assignable to the $\eta\text{-}C_7H_7$ hydrogens was seen. It thus appears that in acetone solutions of (3) there is the equilibrium (1). The acetonitrile ligands in (2) are also labile and (2) reacted with triphenylphosphine giving brown crystals of the compound $[Mo(\eta\text{-}C_7H_7)(NCMe)_2(PPh_3)][PF_6]$ (7). Treatment of (2) with dppe gave $[Mo(\eta\text{-}C_7H_7)(NCMe)(dppe)][PF_6]$ (8).

$$[Mo(\eta\text{-}C_7H_7)(PMe_2Ph)_3][PF_6] + Me_2CO \rightleftharpoons [Mo(\eta\text{-}C_7H_7)(OCMe_2)(PMe_2Ph)_2][PF_6] + PMe_2Ph \quad (1)$$

With tetrahydroborate the cation $[Mo(\eta\text{-}C_7H_7)(CO)_3]^+$ undergoes addition of hydride to the $\eta\text{-}C_7H_7$ ring giving the neutral cycloheptatriene compound $[Mo(C_7H_8)(CO)_3]$. We found that (1; R = H) also reacts with $[BH_4]^-$ but that hydride addition occurs at the benzene ring giving the red cyclohexadienyl derivative $[Mo(\eta^5\text{-}C_6H_7)(\eta\text{-}C_7H_7)]$ (9). Solutions of (9) in light petroleum are rapidly oxidised by oxygen. The data relevant to the authentication of the compounds (2)—(9) are given in Table 1.

Compounds (1) reacted readily with sodium methoxide in methanol giving sea-green-black air-sensitive crystals which the data given below suggest to be binuclear $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OMe)_3Mo(\eta\text{-}C_7H_7)]$ (10). This is moderately soluble in methanol, benzene, and dichloromethane and solutions are rapidly decomposed on exposure to air. Preliminary *X*-ray studies of crystals of (10) from toluene showed disordering to be present. The mass spectrum of (10) shows a highest group of bands at *m/e* 459—475 which have the correct pattern for a binuclear Mo_2 compound and which correspond to the parent ion of the stoicheiometry (10).

Oxidation of (10) in methanol gave a green diamagnetic cation isolated as the salt $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OMe)_3Mo(\eta\text{-}C_7H_7)][PF_6]$ (11). Compound (1; R = Me) in hot aqueous ethanol (95%) gave a red solution from which green crystals were precipitated. These were recrystallised from hot ethanol giving green crystals which the data in Table 1 show to be the salt $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OEt)_3Mo(\eta\text{-}C_7H_7)][PF_6]$ (17). The ^1H n.m.r. spectrum of (17) in wet acetone shows that slow reaction occurs with release into the solvent of free ethanol and a new band appears at τ 2.827 which may be assigned to hydrogen of a μ-hydroxo-group. Further evidence for the lability of the bridging ethoxo-groups arises from the observation that refluxing (17) in excess of methanol gave the tri-μ-methoxo-analogue (11) and this reaction is reversible, *viz.* (2). Also, the ^1H n.m.r. spectrum of (11) in wet acetone shows a slow change, which indicates

$$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OEt)_3Mo(\eta\text{-}C_7H_7)][PF_6] \underset{\text{excess of EtOH}}{\overset{\text{excess of MeOH}}{\rightleftharpoons}} [(\eta\text{-}C_7H_7)Mo(\mu\text{-}OMe)_3Mo(\eta\text{-}C_7H_7)][PF_6] \quad (2)$$

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[1] E. F. Ashworth, M. L. H. Green, and J. Knight, *J. Less-Common Metals*, 1974, **36**, 213; *J.C.S. Chem. Comm.*, 1974, 5.

[2] M. Bochmann, M. Cooke, M. Green, H. P. Kirsch, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1976, 381.

there are only two μ-(OMe) groups, and a band assignable to a μ-OH group. This ^1H n.m.r. sample was recovered and the i.r. spectrum showed changes from that of (11) including new strong absorptions at *ca.* 3 550 and *ca.* 1 650 cm^{-1} assignable to O–H vibrations. Treatment of (10) in toluene with hydrogen chloride caused smooth replacement of the bridging methoxo-ligands by chloro-ligands and dark green crystals of the neutral trichloride $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)]$ (12) were isolated. A more convenient route to (12) is by treatment of (1; R = Me) in methanol with lithium chloride. Compound (12) is sparingly soluble in dichloromethane and benzene and insoluble in tetrahydrofuran (thf); its solutions decompose rapidly on exposure to air and it reacts with ethanol and acetone. The compound may be sublimed slowly, with some decomposition, at 200 °C and 10^{-5} mmHg.* The mass spectrum of (12) shows a highest group of bands at *m/e* 471—489. These have the intensity distribution expected for the parent ion of (12).

TABLE 1

Analytical and ^1H n.m.r. data

Compound	Colour	Analysis [a] (%)			^1H n.m.r. data [c]
		C	H	N or halogen [b]	
$[Mo(\eta\text{-}C_7H_7)(NCMe)_3][PF_6]$ (2)	Deep red	33.9 (34.3)	3.7 (3.5)	9.1 (9.2)	7.9, MeCN [d,e]
$[Mo(\eta\text{-}C_7H_7)(NCMe)_2(PPh_3)][PF_6]$ (7)	Brown	50.4 (51.5)	4.2 (4.2)	4.0 (4.2)	2.63, **15**, *c*, Ph_3; 5.06, **7**, *br*, C_7H_7; 7.92, **6**, *c*, Me_2; in $[^2H_6]Me_2CO$ [f]
$[Mo(\eta\text{-}C_7H_7)(NCMe)(dppe)][PF_6]$ (8)	Pink-red	55.1 (54.5)	4.5 (4.5)	2.0 (1.8)	2.2, 2.5, **20**, *c*, Ph_4; 4.95, **7**, *t* (2), C_7H_7; **4**, *d*(9), CH_2CH_2; in $[^2H_6]Me_2CO$ [e]
$[Mo(\eta\text{-}C_7H_7)(PMe_2Ph)_3][PF_6]$ (3)	Purple	50.0 (49.9)	5.8 (5.4)		2.48, **15**, *c*, Ph_3; 5.17, **7**, *q* (2.5), C_7H_7; 8.2, **18**, *c*, Me_6; in $[^2H_6]Me_2CO$
$[Mo(\eta\text{-}C_7H_7)(PMePh_2)_3][PF_6]$ (4)	Purple	59.2 (59.2)	5.2 (5.4)		2.64, **30**, *c*, *br*, Ph_6; 4.87, **7**, *t* (2), C_7H_7; 8.4, **9**, *c*, Me_3; in $[^2H_6]Me_2CO$
$[Mo(\eta\text{-}C_7H_7)(CO)(PMePh_2)_2][PF_6]$ (6)	Light green	53.3 (53.7)	4.5 (4.3)		
$[Mo(\eta\text{-}C_7H_7)(dppe)_2][PF_6]$ (5)	Pink	62.3 (62.8)	4.9 (4.9) [g]		2.4, 20, *c*, *br*, Ph_4; 4.55, **7**, *t* (2.5), C_7H_7; 8.31, **6**, *c*, Me_2; in $[^2H_6]Me_2CO$
$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OMe)_3Mo(\eta\text{-}C_7H_7)]$ (10)	Black-green	43.3 (43.7)	4.9 (4.9)		
$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OMe)_3Mo(\eta\text{-}C_7H_7)][PF_6]$ (11)	Green	33.5 (33.4)	3.4 (3.8) [h]		3.75, **14**, *s*, *br*, C_7H_7; 6.03, **9**, *s*, OMe; in $[^2H_6]Me_2SO$
$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OEt)_3Mo(\eta\text{-}C_7H_7)][PF_6]$ (17)	Green	36.2 (36.7)	4.5 (4.4)		3.95, **14**, *s*, *br*, C_7H_7; 5.63, **6**, *q* (6.5), OCH_2; 8.85, **9**, *t* (6.5), Me; in $[^2H_6]Me_2CO$
$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)]$ (12)	Dark green	35.0 (34.9)	3.0 (2.9)	21.5 (22.1) [i]	
$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ (15)	Lime-green	28.8 (29.7)	2.6 (2.5)	18.7 (18.8) [j]	
$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Br)_3Mo(\eta\text{-}C_7H_7)]$ (13)	Dark green	27.6 (27.4)	2.6 (2.3)	40.1 (39.0)	
$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Br)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ (16)	Lemon	23.9 (24.2)	2.1 (2.2)	34.1 (34.2)	
$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}I)_3Mo(\eta\text{-}C_7H_7)]$ (14)	Black	22.5 (22.3)	2.1 (2.0)		
$[\{Mo(\eta\text{-}C_7H_7)Cl_2\}_n]$ (18)	Orange	32.0 (32.6)	2.8 (2.7)	27.6 (27.5)	
$[\{MoBr_2(\eta\text{-}C_7H_7)\}_n]$ (19)	Orange	23.6 (24.2)	2.2 (2.0)	46.3 (46.2)	
$[\{Mo(\eta\text{-}C_7H_7)I_2\}_n]$ (20)	Black	19.0 (19.0)	1.8 (1.6)		
$[Mo(\eta^5\text{-}C_6H_7)(\eta\text{-}C_7H_7)]$ (9)	Red	59.3 (58.7)	5.1 (5.3)		4.97, **1**, *t* (4.5); H_a; 5.12, **7**, *s*, C_7H_7; 5.45, **2**, *c*, H_b; 6.97 , **2**, *t* (6.2) H_c; 7.50, **1**, *d* (12.5), H_e; 7.5, **1**, *c*, H_d; in C_6D_6
$K_2[Mo(\eta\text{-}C_7H_7)(CN)_3]$ (21)	Purple	34.5 (34.8)	2.6 (2.6)	12.0 (12.2) [k]	5.46, *s*, C_7H_7; in D_2O
$[Mo(\eta\text{-}C_7H_7)(pd)(PPh_3)]$ (22)	Red	65.9 (65.7)	5.5 (5.3)		2.8, **15**, *c*, Ph_3; 5.13, **7**, *s*, C_7H_7; 5.53, **1**, *s*, CH; 8.61, **6**, *s*, Me_2; in C_6D_6
$[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_7H_7)(PPh_3)]$ (23)	Orange-red	68.8 (68.6)	5.3 (5.5)		3.0, **15**, *c*, Ph_3; 5.35, **7**, *d* (2.5), C_7H_7; 8.06, **2**, *d* (7.5), CH_2; 9.0, **2**, *d* (9), CH_2; in C_6D_6

[a] Calculated values are given in parentheses.
[b] Except F.
[c] Given as chemical shift (τ), **relative intensity**, *multiplicity* (*J*/Hz), and assignment.
[d] Displacement of MeCN occurs; C_7H_7 resonance not observed because of rapid exchange equilibria.
[e] ν(CN) at 2 269 cm^{-1}.
[f] ν(CN) at 2 270 cm^{-1}.
[g] F, 10.1 (11.1); Mo, 8.5 (8.1); P, 13.7 (13.0)%; ^{31}P n.m.r. in $[^2H_6]Me_2CO$ relative to trimethyl phosphate, −76.5(3) and −2.3(1) p.p.m.
[h] F, 18.6 (18.6); Mo, 31.8 (31.3); P, 5.1 (5.1)%.
[i] Mo, 38.4 (39.9)%; i.r. spectrum (mull) (50—400) 360s, 225s, and 72m cm^{-1}.
[j] I.r. spectrum (mull) (50—400): 295s, 278 (sh), and 100m cm^{-1}.
[k] K, 22.4 (23.2), Mo, 27.6 (27.8)%; ν(CN) at 2 050 cm^{-1}.

Treatment of (1; R = Me) in thf or 1,2-dimethoxyethane with lithium bromide gave dark green crystals which the data show to be the compound $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Br)_3Mo(\eta\text{-}C_7H_7)]$ (13). The mass spectrum of (13) shows a group of bands in the range *m/e* 603—626 of intensity distribution expected for the parent ion of (13). Compound (13) may also be prepared by treat-

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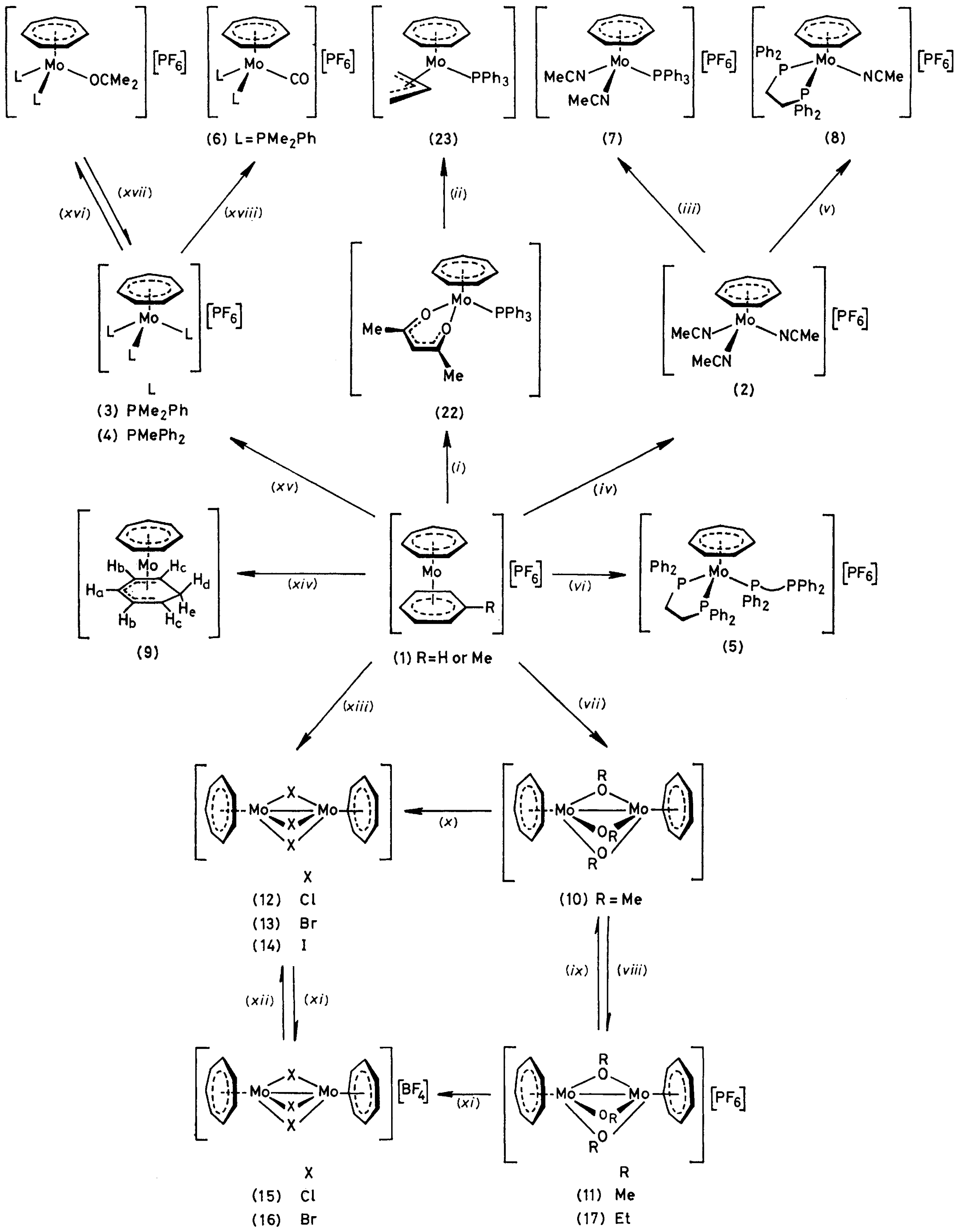
* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 eV ≈ 1.60×10^{-19} J; 1 atm = 101 325 Pa; 1 G = 10^{-4} T.



SCHEME (*i*) Na[pd] (1 mol) + PPh_3 (1 mol) in MeOH, 50 °C, 1 h; (*ii*) $MgBr(C_3H_5)$ in thf–OEt_2, −70 °C, 5 min followed by water, 20 °C, 1 h; (*iii*) PPh_3 in MeCN, reflux, 1 h; (*iv*) MeCN, 80 °C, 1 h; (*v*) dppe (1 mol) in MeCN, reflux, 3 h; (*vi*) excess of dppe in EtOH, reflux, 12 h; (*vii*) NaOMe in MeOH, 65 °C, 1 h; (*viii*) R = Me, O_2 + $[NH_4][PF_6]$ in MeOH, 20 °C, 1 h; (*ix*) Na–Hg in toluene, 20 °C, 30 min; (*x*) X = Cl, R = Me, HCl in toluene, 20 °C, 30 s; (*xi*) X = Cl, aqueous HCl, reflux, 10 min, then HBF_4, 20 °C; (*xii*) X = Cl, $[Co(\eta\text{-}C_5H_5)_2]$ in toluene, 20 °C, 2 h; (*xiii*) LiX in MeOH (X = Cl), thf (X = Br), glyme (X = I), 65 °C, 30 min; (*xiv*) $Na[BH_4]$ in thf, 20 °C, 3 h; (*xv*) excess of phosphine in EtOH, reflux, 10 h; (*xvi*) L = PMe_2Ph, (3) dissolved in acetone, 20 °C; (*xvii*) L = PMe_2Ph, excess of PMe_2Ph in acetone, 20 °C; and (*xviii*) 1 atm of CO in acetone, 20 °C, 12 h, L = PMe_2Ph

ment of (10) with hydrogen bromide. It is generally similar in solubility and stability to the trichloride (12). Black crystals of the compound $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}I)_3Mo(\eta\text{-}C_7H_7)]$ (14) were prepared by treatment of (1; R = Me) in 1,2-dimethoxyethane with lithium iodide. This compound is insoluble in all the solvents studied. The mass spectrum shows a highest group of bands whose *m/e* values and relative intensity correspond to the parent ion of (14).

Compounds (12) and (13) are readily oxidised to the corresponding diamagnetic cations $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}X)_3Mo(\eta\text{-}C_7H_7)]^+$ [X = Cl (15) or Br (16)]. These cations are light green and they may be isolated as the tetrafluoroborate or hexafluorophosphate salts. The most convenient route to the compound $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ (15) is by reaction of (1; R = Me) with boiling concentrated hydrochloric acid followed by addition of tetrafluoroboric acid in the presence of air. The salt (15) is readily reduced using $[Co(\eta\text{-}C_5H_5)_2]$ to the neutral compound (12). Sodium amalgam will similarly reduce (15) to (12) but excess of the reducing agent causes further reaction to an unidentified yellow species. Cyclic-voltammetric studies of (15) in dichloromethane with tetrabutylammonium perchlorate as the electrolyte show that there are two reversible redox processes at −0.96 and 0.00 V relative to the calomel electrode. Preliminary crystal-structure studies on $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ show the structure given in the Scheme. The Mo–Mo distance is 3.076 Å which is not inconsistent with a Mo–Mo bond.[3] A metal–metal bond would account for the observed diamagnetism of (15) and also allow both molybdenum atoms to obey the 18-electron rule.

A further example of the ease of exchange of the bridging ligands in the compounds $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}X)_3Mo(\eta\text{-}C_7H_7)]$ arises from the observation that recrystallisation of (13) from ethanol–dichloromethane gave green crystals which the mass spectrum shows to contain impurities of $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)(\mu\text{-}Br)_2Mo(\eta\text{-}C_7H_7)]$ {*m/e* 559 for $[Mo_2Br_2Cl(C_7H_7)_2]^+$}. In this context we note that $[Mo(\eta\text{-}C_7H_7)(OCMe_2)(dppe)]^+$ readily and quantitatively abstracts chlorine from dichloromethane.[4]

Treatment of (11) in acetone with hydrogen chloride precipitated orange-red microcrystals. Analysis shows the stoicheiometry $[\{Mo(C_7H_7)Cl_2\}_n]$ (18). The mass spectrum shows a parent ion corresponding to $[Mo_2(C_7H_7)_2Cl_3]^+$ and the rest of the spectrum is very similar to that of the neutral compound (12). Compound (18) dissolves slightly in concentrated hydrochloric acid and may be recovered by evaporation of the solution. It appeared to be stable in air. Similarly, treatment of (11) with concentrated hydrobromic acid in air gave an orange solid which analysis showed to have the stoicheiometry $[\{MoBr_2(C_7H_7)\}_n]$ (19). The mass spectrum showed bands at *m/e* 603—623 characteristic of $[Mo_2Br_3(C_7H_7)_2]^+$. Compound (19) dissolves in tetrafluoroboric acid and on concentration the compound $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Br)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ crystallised. With concentrated hydriodic acid compound (11) gave a black solid which analysed according to the formulation $[\{Mo(C_7H_7)I_2\}_n]$ (20). The mass spectrum showed a highest peak corresponding to $[Mo(C_7H_7)I_2]^+$. The compound is insoluble in most solvents. The i.r. spectra of compounds (17)—(20) all showed bands assignable to the $Mo(\eta\text{-}C_7H_7)$ group.

Treatment of (1; R = Me) in methanol with sodium cyanide did not give a binuclear product, instead the compound $K_2[Mo(\eta\text{-}C_7H_7)(CN)_3]$ (21) was formed in high yield. Treatment of (1; R = Me) in methanol with PPh_3 and sodium pentane-2,4-dionate, Na[pd], gave deep red crystals which the data in Table 1 show to be the compound $[Mo(\eta\text{-}C_7H_7)(pd)(PPh_3)]$ (22). This reacted with allylmagnesium bromide to give the η^3-allyl compound $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_7H_7)(PPh_3)]$ (23) as orange-red air-sensitive crystals. Compounds (22) and (23) are characterised by the data in Table 1.

Physical Studies.—The binuclear structure of the cation (15) is firmly established by the crystallographic studies.[3] The data in Table 1 and the chemical similarities discussed above strongly suggest that the cations (11), (16), (17), and (19) have the same basic structure with bridging halogeno- or alkoxo-groups. On the basis of the Mo–Mo distance in (15) of 3.076 Å we propose that there is a Mo–Mo bond in these cations which enables the general requirement for an 18-electron environment to be satisfied.

The reversibility of the reduction of these cations to the neutral compounds (10), (12), and (13) together with the data in Table 1 suggests that the neutral compounds have the related dimeric structure shown in the Scheme. In particular, the i.r. spectra of (12) and (15) are entirely consistent with this proposal. The i.r. spectra of other species containing the system $Mo(\mu\text{-}Cl)_3Mo$, *e.g.* $K_3[Mo_2Cl_9]$, show bands assignable to the $(\mu\text{-}Cl)_3$ groups in the 200—350 cm^{-1} region.[5] Mass-spectral studies indicate a binuclear compound. Bulk magnetic-susceptibility data for (12) at 293 K give $\chi = 2.26 \times 10^{-8}$ $m^3\ kg^{-1}$ which corresponds to a value of $\mu_{eff.} = 1.424$ B.M., assuming Curie's law and that the correction for diamagnetic susceptibility is small. This value for $\mu_{eff.}$ is consistent with there being one unpaired electron in (12).

Given that the paramagnetic neutral compounds (10) and (12)—(14) are in fact dimers, they may be described as mixed-oxidation-state compounds. Since they are both volatile and soluble and may be oxidised to stable cations, their electronic structure could be studied by a wide variety of physical methods. The aim of these studies was to try to establish the degree of localisation of the unpaired electron. In principle, the e.s.r. spectra should indicate whether the unpaired electron is equally localised on both molybdenum atoms on an e.s.r. time

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[3] N. W. Alcock, personal communication.

[4] M. L. H. Green and R. B. A. Pardy, *J. Organometallic Chem.*, 1976, **117**, C13.

[5] I. E. Grey and P. W. Smith, *Austral. J. Chem.*, 1969, **22**, 1627; C. Miniscloux, G. Martino, and L. Sajus, *Bull. Soc. chim. France*, 1973, 2179; W. E. Delphin, R. A. D. Wentworth, and M. S. Matson, *Inorg. Chem.*, 1974, **13**, 2552.

scale. This is possible because the nuclei ^{95}Mo and ^{97}Mo have spin $\frac{5}{2}$ and have a combined abundance of 25.18%, whilst the remaining naturally occurring isotopes of molybdenum have spin 0. The separated multiplicities and relative intensities of expected contributions to the e.s.r. spectrum of a binuclear delocalised molybdenum system are given in Table 2. As a result of the combination of low isotropic abundance and splitting into many lines, each line of the undecet is considerably (99 times) less intense than the central singlet. Further splitting of all the lines is possible in (12) and (13) where coupling to the bridging chlorine or bromine nuclei can occur.

TABLE 2

Predicted multiplicity and relative intensity for a binuclear delocalised molybdenum system with one unpaired electron

I_T	Relative total intensity	Multiplicity
0	9 $P(0,0)$	Singlet
$\frac{5}{2}$	6 $P(0,\frac{5}{2})$	Sextet
5	1 $P(\frac{5}{2},\frac{5}{2})$	Undecet

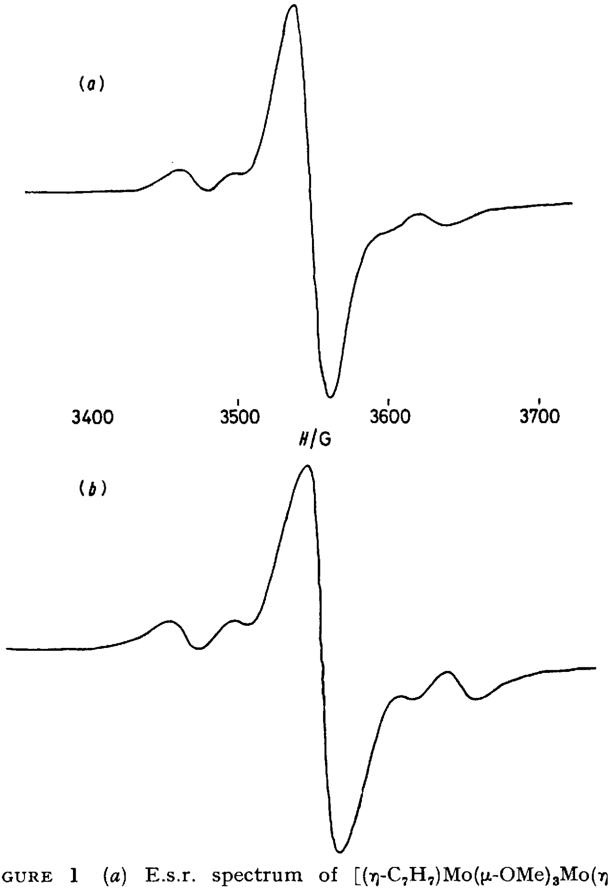

FIGURE 1 (a) E.s.r. spectrum of $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OMe)_3Mo(\eta\text{-}C_7H_7)]$. (b) Calculated e.s.r. spectrum of an Mo_2 system

The linewidth of the spectra prevented the observation of halogen splitting and difficulties in the purification and solubility of the compounds rendered observation of weak satellite lines dubious. Nevertheless, the relative intensities of the central singlet to components of the sextet clearly indicate that the electron is coupling with two molybdenum atoms and the spectra fit best the calculated spectrum for a delocalised bi- rather than mono- or tri-nuclear systems. A typical spectrum for (10) together with the calculated spectrum is given in Figure 1. The spectra were calculated assuming that the linewidths were constant for all the peaks and that the curves were Lorentzian.

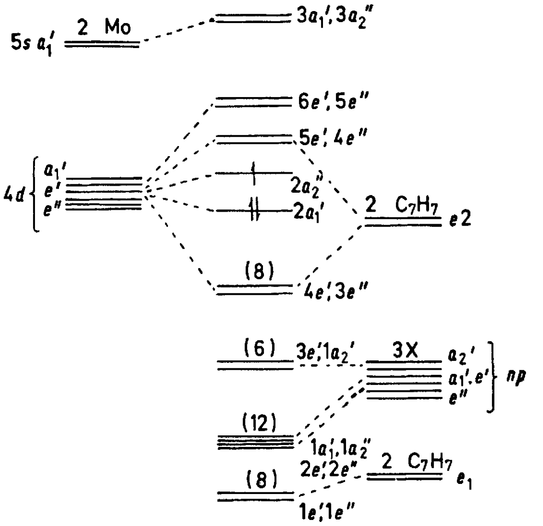

FIGURE 2 Molecular-orbital diagram for the compounds $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}X)_3Mo(\eta\text{-}C_7H_7)]$ (X = Cl, Br, or I) assuming D_{3h} symmetry

Clearly the weight of the evidence is that on an e.s.r. time scale the unpaired electron is equally localised on both molybdenums. The fact that hyperfine coupling to the molybdenum nuclei occurs at all indicates that the orbital occupied by the unpaired electron has molybdenum *s* character. The e.s.r. spectral data are shown in Table 3.

TABLE 3

E.s.r. data for the compounds $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}X)_3Mo(\eta\text{-}C_7H_7)]$

X	$\langle g \rangle$	$A_{iso.}$/G	Linewidth/G
Cl	1.92 ± 0.01	29	25
Br	1.93 ± 0.01	28	40
OMe	1.91 ± 0.01	32	23

In order to assign the photoelectron (p.e.) spectra we have drawn up the molecular orbital (m.o.) diagrams shown in Figure 2 for a halogeno-bridged dimer. One assumption used in the construction of this diagram is that the two molybdenum atoms are equivalent. For simplicity it is assumed that the η-C_7H_7 rings have an infinite rotational axis so that the neutral compounds (12)—(14) have D_{3h} symmetry. The metal and ligand valence orbitals considered for this scheme are the metal 4*d* and 5*s*, the ring e_1 π and e_2 π, and the halogen *p* orbitals, which give us 37 electrons to assign to the m.o.s. The order of the symmetry-allowed combinations is tentatively proposed on the basis of chemical experience. For example, the metal $4d$ and $5s$ orbitals will lie at higher energies than the halogen p orbitals. The relative positions of the ring e_1 and the halogen p orbitals are difficult to decide. For clarity we have placed the p above the e_1 orbitals. When the 37 electrons are placed in the m.o.s the unpaired electron occupies an antibonding orbital, $2a_2''$. This is in satisfactory accord with the e.s.r. data which give a symmetry a_1' or a_2'' for the unpaired electron. An m.o. scheme for the lower-symmetry methoxo-bridged compound will resemble that of the halogeno-bridged compounds except in those levels largely concerned with the bridging ligand.

The assignments of the p.e. spectra based on the m.o. diagram are given in Table 4. Of particular interest are the two lowest overlapping bands. These fit with a simple picture of ionisation from the configuration $2a_1'^2\,2a_2''^1$, the band area being roughly proportional to occupancy, the lower ionisation-energy band [5.1 (10) and 5.8 eV (12)] being due to ionisation of the $2a_2''$ electron and the higher band [5.4 (10) and 6.2 eV (12)] being due to ionisation of the $2a_1'$ electrons. This picture assumes that any exchange splitting of the accessible ion states remains unresolved. The metal orbitals largely concerned in the formation of these m.o.s would be the molybdenum $4d_{z^2}$ orbitals. Other studies suggest that these will be non-bonding with respect to the cycloheptatrienyl rings.[6] The third band [6.7 (10) and 7.2 eV (12)] may be assigned by analogy with published data [6] to ionisations largely localised on the Mo(η-C_7H_7) orbitals $4e'$ and $3e''$. The first ionisation for (12) is at higher energy than for (10) suggesting a higher effective nuclear charge for the molybdenum atoms in (12).

TABLE 4

Photoelectron spectra: vertical ionisation energies (eV)

[(η-C_7H_7)Mo(μ-OMe)$_3$-Mo(η-C_7H_7)]	[(η-C_7H_7)Mo(μ-Cl)$_3$-Mo(η-C_7H_7)]	Assignment
5.1	5.8	$2a_2''$
5.4	6.2	$2a_1'$
6.7	7.3	$4e',3e''$
8.2 (sh)		
8.7	8.7	
9.9	9.9	$1e',1e''$
	10.8	
11.3		
12.5	11.6	C–C and C–H ionisations
14.3	12.7	
16.0	14.7	
	16.6	

Interpretation of the p.e. spectrum on the basis of inequivalent molybdenums involves prediction of the ionisation pattern from a configuration $(Mo_A)^2(Mo_B)^1$. This will depend on the exchange coupling between the two atoms. In the absence of exchange interaction two signals are expected of relative intensity 2 : 1 corresponding to ionisation from the two separate atoms, A and B, respectively. The band of relative intensity 2 should occur at the lower ionisation energy as the electrons on atom A would be expected to be less strongly bound than that on atom B. If exchange interaction is sufficient the band of intensity 2 will split into two components corresponding to the triplet- and singlet-ion states from the configuration $(Mo_A)^1(Mo_B)^1$ of relative intensity 3 : 1. The three bands would then have the intensity pattern 3 : 1 : 2, the most-intense band occurring at the lowest ionisation energy. Neither of the patterns correspond to the shape found for the lowest two bands nor with the diamagnetism of compounds of the cations. However, if exchange interaction was sufficiently large the singlet state from $(Mo_A)^1(Mo_B)^1$ could mix with that from $(Mo_A)^2$ and one of the resulting singlet states may well then become the ground state of the ion. In this case the observed intensity distribution would be explained. However, in allowing the mixing of these two states we have abandoned the simple valence-bond model with which we started. This modification is equivalent to allowing configuration interaction to adjust the simple m.o. model. Insofar as the delocalised model leads directly to an explanation of the p.e. spectrum we prefer it to the localised model as a description of the electronic structure of these molecules.

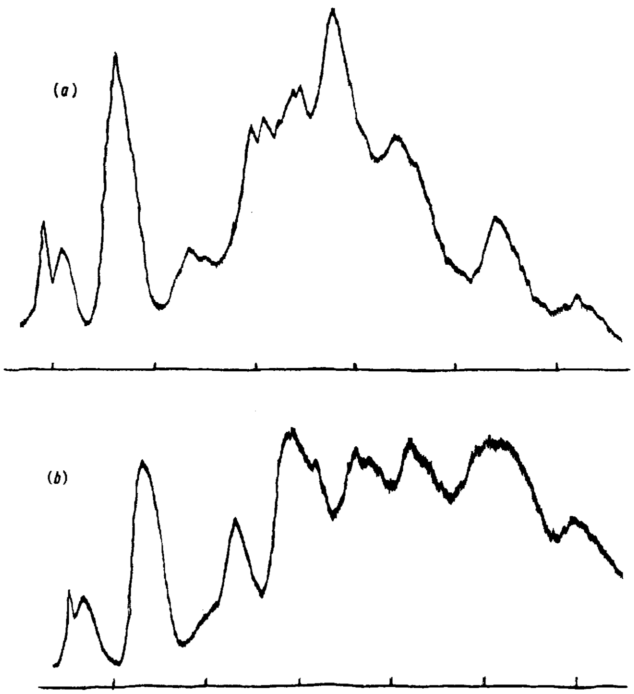

FIGURE 3 Photoelectron spectra of (a) [(η-C_7H_7)Mo(μ-Cl)$_3$Mo(η-C_7H_7)], (b) [(η-C_7H_7)Mo(μ-OMe)$_3$Mo(η-C_7H_7)]

Comparison of the electronic spectra of (12) with (15) shows that only the former has a strong intense band at 1 040 nm. Transitions in this region in some mixed-valence compounds have been discussed in terms of resonances between two equivalent valence structures $M_1^{n+}M_2^{(n+1)+}$ and $M_1^{(n+1)+}M_2^{n+}$. Therefore the possibility may not be ruled out that neutral compounds such

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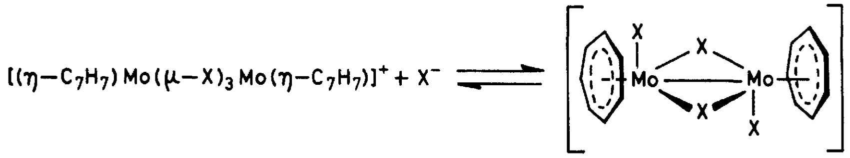
[6] S. Evans, J. C. Green, S. E. Jackson, and B. Higginson, *J.C.S. Dalton*, 1974, 304; C. J. Groenenboom, H. J. de Liefde-Meiyer, and F. Jellinek, *J. Organometallic Chem.*, 1975, **97**, 73.

as (10) behave similarly, *i.e.* are classifiable as class II.[7] However, the band at 1 040 nm may well be due to transitions such as from the $2a_2''$ orbital to a low-lying state. This would permit description of the electronic structure of (12) in terms of a symmetrical electron distribution. Our preferred description of the bonding, bearing in mind the presence of a metal–metal bond in the cation (15), is that given in Figure 2, where the unpaired electron is located in the antibonding $2a_2''$ orbital which is of largely metal *d* character. This description predicts the Mo–Mo distance in (12) to be greater than in (15), and attempts to determine the crystal structure of (12) are in progress.

The structures of compounds (23)—(25) are unknown. However, it has been shown that the compound $[Ru_2Cl_3(arene)_2][PF_6]$ adds a chloride ion giving $[Ru_2Cl_4(arene)_2]$.[8] By analogy, we propose structure (A; X = Cl, Br, or I) for compounds (23)—(25). We have noted that the exchange of bridging ligands in compounds (11) and (14)—(16) occurs very readily. The mechanism for this exchange may proceed *via* equilibrium (3).



(3)

(A)

EXPERIMENTAL

All the manipulations were carried out in an inert atmosphere or *in vacuo*. Infrared spectra were determined using a Perkin-Elmer 457 spectrometer and calibrated with a polystyrene film. Far-i.r. spectra were recorded on a Beckmann IR 11 spectrometer. Hydrogen-1 n.m.r. spectra were obtained using JEOL C-60-HL or Perkin-Elmer 100-MHz instruments, ^{31}P n.m.r. spectra on a Bruker 90-MHz instrument. E.s.r. spectra were recorded using a JEOL JES-PE, electronic spectra on a Cary 17, p.e. spectra on a Perkin-Elmer PS16/18, and mass spectra on an A.E.I. M.S.9 instrument. Bulk magnetic moments were measured using the Evans modification of the Gouy method.[9]

Mass-spectral Studies.—The compounds $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}X)_3Mo(\eta\text{-}C_7H_7)]$ (X = Cl, Br, OMe, or I) are sufficiently volatile for mass spectra to be obtained. In each case the highest group of peaks had a characteristic intensity pattern corresponding to that calculated from the relative abundance of the isotopes of Mo, Cl, and Br expected for a binuclear compound. Only the more intense lines were recorded. The data are presented as compound, probe temperature (θ_c/°C), *m/e* for stated isotopes (relative intensity), and assignment: $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OMe)_3Mo(\eta\text{-}C_7H_7)]$, 150 (for ^{92}Mo only), 459 (13.5), $[Mo_2(C_7H_7)_2(OMe)_3]^+$, 429 (2), $[Mo_2(C_7H_7)_2H(OMe)_2]^+$, 214 (3), $[Mo(C_7H_7)(OMe)]^+$, 199 (100), $[Mo(C_7H_7)O]^+$, 173 (3), $[Mo(C_5H_5)O]^+$; $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)]$, 130 (for ^{92}Mo and ^{35}Cl only), 471 (3), $[Mo_2(C_7H_7)_2Cl_3]^+$, 253 (3), $[Mo(C_7H_7)Cl_2]^+$, 218 (36), $[Mo(C_7H_7)Cl]^+$, 197 (9), $[Mo(C_5H_5)Cl]^+$, 91 (100), $[C_7H_7]^+$; $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Br)_3Mo(\eta\text{-}C_7H_7)]$, 190 (for ^{92}Mo and ^{79}Br), 605 (2), $[Mo_2{}^{79}Br_2{}^{81}Br(C_7H_7)_2]^+$ and $[{}^{94}Mo{}^{92}MoBr_3(C_7H_7)_2]^+$, 341 (<1), $[MoBr_2(C_7H_7)]^+$, 262 (36), $[MoBr(C_7H_7)]^+$, 91 (100), $[C_7H_7]^+$; $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}I)_3Mo(\eta\text{-}C_7H_7)]$, 345 (for ^{92}Mo only), 747 (12), $[Mo_2(C_7H_7)_2I_3]^+$, 656 (3), $[Mo_2(C_7H_7)_2I_3]^+$, 620 (6), $[Mo_2(C_7H_7)_2I_2]^+$, 529 (2), $[Mo_2(C_7H_7)I_2]^+$, 437 (25), $[Mo(C_7H_7)I_2]^+$, 310 (100), $[Mo(C_7H_7)I]^+$, 254 (14), $[Mo(C_5H_5)I]^+$; $[\{Mo(C_7H_7)Cl_2\}_n]$, 200 (for ^{92}Mo and ^{35}Cl), 471 (6), $[Mo_2(C_7H_7)_2Cl_3]^+$, 253 (23), $[Mo(C_7H_7)Cl_2]^+$, 218 (38), $[Mo(C_7H_7)Cl]^+$, 192 (13), $[Mo(C_5H_5)Cl]^+$, 91 (100), $[C_7H_7]^+$; and $[\{Mo(\eta\text{-}C_7H_7)I_2\}_n]$, 250 (for ^{92}Mo), 437 (40), $[Mo(C_7H_7)I_2]^+$, 310 (88), $[Mo(C_7H_7)I]^+$.

Electronic Spectra.—Data (in CH_2Cl_2 at room temperature) given as λ/nm (ε/dm^3 mol^{-1} m^{-1}): $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)]$, 1 040 ($4.6 \times 10^6$), 660 ($1.1 \times 10^5$), 412 ($1.4 \times 10^6$), and 284 ($3.7 \times 10^6$); $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)][BF_4]$, 410 (*ca.* 10^6), 315 (*ca.* 10^6), and 280 (*ca.* 10^6).

Tris(acetonitrile)(η-cycloheptatrienyl)molybdenum Hexafluorophosphate (2).—The compound $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ (1; R = Me) (0.2 g, 0.47 mmol) in redistilled acetonitrile (20 cm^3) was stirred at 80 °C for 1 h. The solvent was removed under reduced pressure giving deep red crystals (0.2 g, *ca.* 93%). Recrystallisation from cold acetonitrile gave a low yield of the pure compound owing to its great solubility.

Bis(acetonitrile)(η-cycloheptatrienyl)(triphenylphosphine)molybdenum Hexafluorophosphate (7).—Compound (1; R = Me) (0.1 g, 0.24 mmol) in acetonitrile (5 cm^3) was treated with triphenylphosphine (0.14 g) and the solution was heated under reflux for 1 h. The solvent was removed under reduced pressure giving a brown residue which was washed with light petroleum (2×20 cm^3) and then recrystallised from acetonitrile–ethanol giving brown crystals. These were collected, washed with diethyl ether, and dried *in vacuo*, *ca.* 55%. The same product could be obtained by treatment of a solution of compound (2) in acetonitrile with stoicheiometric PPh_3 for 1 h at 80 °C.

Acetonitrile[1,2-bis(diphenylphosphino)ethane](η-cycloheptatrienyl)molybdenum Hexafluorophosphate (8).—Compound (2) (3.0 g, 7.07 mmol) in acetonitrile (50 cm^3) was treated with 1,2-bis(diphenylphosphino)ethane (2.73 g, 6.86 mmol) and the solution was heated under reflux for 3 h and then filtered. The solution was concentrated under reduced pressure and then heated. The product crystallised out on cooling, and was recrystallised from acetonitrile and washed with toluene (10 cm^3), *ca.* 72%. The compound may also be recrystallised from dichloromethane–light petroleum.

(η-Cycloheptatrienyl)tris(dimethylphenylphosphine)molybdenum Hexafluorophosphate (3).—Compound (1; R = Me) (0.2 g, 0.47 mmol) in ethanol (15 cm^3) was treated with an

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[7] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[8] M. A. Bennett and A. K. Smith, *J.C.S. Dalton*, 1974, 233.

[9] D. F. Evans, G. V. Phizackerley, and R. F. Phillips, *J. Chem. Soc.* (*A*), 1971, 1931.

excess of dimethylphenylphosphine (1.0 cm^3) and the solution was stirred under reflux for 10 h. Purple crystals separated and the reaction mixture was cooled in ice. The supernatant liquor was removed and the purple crystals were washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo*, *ca.* 50%. All attempts to recrystallise the product from acetone–ethanol led to decomposition to yellow species.

Carbonyl(η-*cycloheptatrienyl*)*bis*(*methyldiphenylphosphine*)-*molybdenum Hexafluorophosphate* (6).—The compound $[\mathrm{Mo}(\eta\text{-}C_7H_7)(\mathrm{PMePh_2})_3][\mathrm{PF_6}]$ (4) (0.1 g, 0.18 mmol) in acetone (3 cm^3) was treated with carbon monoxide (1 atm) at room temperature (r.t.) for 12 h. Ethanol (5 cm^3) was added giving a dense green precipitate which was separated. The residue was washed with cold ethanol and then with diethyl ether. The green residue was finally recrystallised from acetone–ethanol giving green crystals which were collected, washed with diethyl ether, and dried *in vacuo*, *ca.* 70%.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*](η-*cycloheptatrienyl*)-*molybdenum Hexafluorophosphate* (5).—Compound (1; R = Me) (0.2 g, 0.47 mmol) in ethanol (80 cm^3) was treated with dppe (0.5 g, 1.26 mmol) and the mixture was heated under reflux for 12 h. The resulting mixture was filtered whilst hot and then cooled to r.t. giving pink crystals. These were collected, washed with benzene and diethyl ether, and finally recrystallised from acetone–ethanol. The resulting pink crystals were washed, and dried *in vacuo*, *ca.* 18%.

(η-*Cycloheptatrienyl*)(*pentane*-2,4-*dionato*)(*triphenylphosphine*)*molybdenum* (22).—Compound (1; R = Me) (0.85 g, 2.0 mmol), $\mathrm{PPh_3}$ (0.53 g, 2.0 mmol), and sodium pentane-2,4-dionate (0.27 g, 2.1 mmol) in pure methanol (25 cm^3) were warmed to 50 °C for 1 h. The initially pale green mixture turned deep red giving red crystals after 35 min. The mixture was then allowed to cool to 0 °C over 3 h and the resulting red crystals were separated from the green-brown liquor, washed with methanol, and dried *in vacuo*, 0.93 g (85%).

(η-*Allyl*)(η-*cycloheptatrienyl*)(*triphenylphosphine*)*molybdenum* (23).—Compound (22) (0.35 g, 0.64 mmol) in dry tetrahydrofuran (15 cm^3) was cooled (−70 °C) and treated with allylmagnesium bromide in diethyl ether (2 cm^3, 1 mol dm^{-3}). The initial red colour changed to orange-red after 5 min and then the solvent was removed under reduced pressure. The residue was extracted with light petroleum (60 cm^3, b.p. 30—40 °C) and water was added (0.5 cm^3) to destroy the excess of the Grignard reagent. The hydrolysed mixture was stirred for 1 h at r.t., the petroleum layer was separated, and the solvent was removed under reduced pressure. Well formed orange-red crystals separated which were collected and recrystallised from light petroleum at r.t., yield 0.15 g (*ca.* 50%).

Dipotassium Tricyano(η-*cycloheptatrienyl*)*molybdate* (21).—The compound $[\mathrm{Mo}(\eta\text{-}C_6H_6)(\eta\text{-}C_7H_7)][\mathrm{PF_6}]$ (1; R = H) (1.0 g, 2.4 mmol) was added to potassium cyanide (0.8 g, 12 mmol) in methanol (200 cm^3) at 20 °C giving a pale green solution. This was heated at 45 °C for 30 min giving a pink-purple solution which was filtered and concentrated. After 1 d at −20 °C purple needles separated. These were collected, washed with cold methanol and diethyl ether, and finally dried *in vacuo*, *ca.* 0.7 g (82%).

(η-*Cycloheptatrienyl*)(1—5-η-*cyclohexadienyl*)*molybdenum* (9).—Compound (1; R = H) (0.64 g, 1.51 mmol) in dry thf (40 cm^3) was treated with $\mathrm{Na[BH_4]}$ (0.7 g, 18.4 mmol) and the mixture was stirred for 3 h. The initially green solution became orange-red. The solvent was removed under reduced pressure and the residue was extracted with light petroleum (100 cm^3). The extract was filtered and cooled slowly to −100 °C. Red crystals separated which were recrystallised from light petroleum (20 cm^3). The brick-red crystals were dried under reduced pressure, *ca.* 0.16 g (40%).

Tri-μ-*chloro-bis*[(η-*cycloheptatrienyl*)*molybdenum*] (12).—*Method* (*a*). Dry lithium chloride (3.5 g, 82.5 mmol) in methanol (30 cm^3) was added to (1; R = Me) (2.0 g, 4.7 mmol) in methanol (50 cm^3) and the mixture was heated with stirring at 65 °C. The initially green solution quickly darkened and a dark green powder was deposited. After 30 min the mixture was cooled and the supernatant liquor was separated. The residue was washed with methanol (2 × 20 cm^3) and dried under reduced pressure, 0.9 g (89%). The product is sufficiently pure for further use but may be recrystallised with difficulty from dichloromethane or by slowly cooling saturated solutions in chlorobenzene from 90 to 40 °C during 1 week.

Method (*b*). The compound $[(\eta\text{-}C_7H_7)\mathrm{Mo}(\mu\text{-OMe})_3\mathrm{Mo}(\eta\text{-}C_7H_7)]$ (10) (0.38 g, 0.814 mmol) in toluene (30 cm^3) was treated with hydrogen chloride gas for 30 s. A dark green precipitate separated which was collected and recrystallised from dichloromethane–ethanol, giving dark green crystals which were washed with acetone (2 × 10 cm^3) then diethyl ether (10 cm^3) and dried under reduced pressure, *ca.* 0.18 g (21%).

Method (*c*). The compound $[(\eta\text{-}C_7H_7)\mathrm{Mo}(\mu\text{-Cl})_3\mathrm{Mo}(\eta\text{-}C_7H_7)][\mathrm{BF_4}]$ (15) (0.5 g, 0.88 mmol) in toluene (100 cm^3) was treated with a solution of resublimed $[\mathrm{Co}(\eta\text{-}C_5H_5)_2]$ (0.136 g, 0.72 mmol) in toluene (200 cm^3) and the mixture was stirred at r.t. for 2 h. The initially red mixture became green, was then filtered and the filtrate was concentrated under reduced pressure. Dark green microcrystals separated which were collected, washed with light petroleum (2 × 20 cm^3), and dried under reduced pressure, 0.1 g (35%).

Tri-μ-*bromo-bis*[(η-*cycloheptatrienyl*)*molybdenum*] (13).—*Method* (*a*). The reaction was carried out essentially as described for the compound (12) except the solvent was thf and lithium bromide replaced the chloride, yield *ca.* 70%.

Method (*b*). The reaction was carried out as described for (12) except that hydrogen bromide was used, yield *ca.* 30%.

Tri-μ-*iodo-bis*[(η-*cycloheptatrienyl*)*molybdenum*] (14) was prepared as described for the bromo-analogue except that lithium iodide was used and the solvent was 1,2-dimethoxyethane, yield *ca.* 40%.

Tri-μ-*methoxo-bis*[(η-*cycloheptatrienyl*)*molybdenum*] (10).—Sodium methoxide (10 cm^3, 1 mol dm^{-3}) in methanol (30 cm^3) was added to (1; R = Me) (2.0 g, 47 mmol) in methanol (60 cm^3) and the mixture was heated with stirring at 65 °C for 1 h. On cooling, dark green crystals separated and the mixture was left at −10 °C for 12 h. The crystals were separated, washed with water (2 × 20 cm^3), and dried *in vacuo*, 0.52 g (50%). The product could be recrystallised from toluene at −20 °C.

Tri-μ-*methoxo-bis*[(η-*cycloheptatrienyl*)*molybdenum*] *Hexafluorophosphate* (11).—*Method* (*a*). Compound (1; R = Me) (2.0 g, 4.7 mmol) in methanol was heated under reflux for 40 min. The initially green solution darkened to brown and green crystals separated. The mixture was cooled at

0 °C for 12 h and the supernatant liquor was separated. The residue was washed with cold methanol (2 × 15 cm^3) then diethyl ether (10 cm^3), and dried *in vacuo*, 1.3 g (90%). The product could be recrystallised from methanol.

Method (*b*). Compound (10) (0.5 g, 1.07 mmol) in methanol (50 cm^3) was treated with ammonium hexafluorophosphate (2.0 g, 12.3 mmol) in methanol and the mixture was exposed to air for 1 h. The product was isolated as described in (*a*), *ca.* 90%.

Tri-μ-ethoxo-bis[(η*-cycloheptatrienyl*)*molybdenum*] *Hexafluorophosphate* (17).—Compound (1; R = Me) (0.8 g, 1.89 mmol) in pure ethanol (20 cm^3) was heated under reflux for 30 min during which time pale green crystals separated from a red solution. The mixture was cooled to 0 °C and the crystals were separated, washed with cold ethanol (2 × 5 cm^3) then diethyl ether (5 cm^3), and finally dried *in vacuo*, 0.43 g (69%).

Tri-μ-chloro-bis[(η*-cycloheptatrienyl*)*molybdenum*] *Hexafluorophosphate* (15).—*Method* (*a*). Compound (1; R = Me) (1.0 g, 2.36 mmol) was treated with hydrochloric acid (40 cm^3, 36%) and heated under reflux for 1 h. Tetrafluoroboric acid (7.5 cm^3, 48%) was added and the orange solution was concentrated under reduced pressure (45 °C). Light green crystals separated and these were collected, washed with water (2 × 5 cm^3), and dried *in vacuo*, 0.6 g (72%).

Method (*b*). Compound (11) (1.4 g, 3.3 mmol) was treated with HCl (5 cm^3, 36%) and HBF_4 (5 cm^3, 40%). The solution was filtered and the filtrate was warmed to 65 °C. After 1 h the solution was concentrated under reduced pressure until light green crystals separated. The product was isolated as described in (*a*), 0.8 g (61%).

The Compound $[\{Mo(\eta\text{-}C_7H_7)Cl_2\}_n]$ (18).—*Method* (*a*). Compound (1; R = Me) (1.0 g, 2.36 mmol) in hydrochloric acid (10 cm^3, 36%) was heated to boiling and the solution was filtered. Air was drawn through the filtrate for 1 h and the resulting orange solution was concentrated under reduced pressure giving orange crystals which were collected, washed with cold concentrated HCl, and dried *in vacuo*, 0.2 g (32%).

Method (*b*). The compound $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ (1.5 g, 2.65 mmol) in acetone (70 cm^3) was treated with hydrogen chloride gas for 1 h. Bright red-orange crystals separated which were isolated as described in (*a*), 0.2 g (*ca.* 14%).

The Compound $[\{MoBr_2(\eta\text{-}C_7H_7)\}_2]$ (19).—Compound (11) (0.25 g, 0.53 mmol) was shaken with hydrobromic acid (AnalaR 48%, 10 cm^3) and a yellow solid formed. The mixture was left for 14 h whilst the solid and the solution became orange. The solid was separated, washed with HBr (5 cm^3) then acetone (10 cm^3), and finally diethyl ether (10 cm^3). It was dried *in vacuo*, *ca.* 0.1 g. The compound $[\{Mo(\eta\text{-}C_7H_7)I_2\}_2]$ (20) was similarly prepared from (11) and freshly distilled hydriodic acid, yield *ca.* 50%.

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