Arene–Molybdenum Chemistry: Reactions of Di-μ-chloro-bis[(η-allyl)-(η-arene)molybdenum] with Cyclic Olefins

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The violet solutions formed from $(AlEtCl_2)_2$ and the compounds $[\{Mo(\eta\text{-}C_3H_5)(\eta\text{-arene})Cl\}_2]$ (arene = C_6H_6, C_6H_5Me, or $C_6H_3Me_3$-1,3,5) react with norbornadiene (nbd), cyclo-octa-1,3,5,7-tetraene(cot), or cyclohepta-1,3,5-triene (cht), and the corresponding cations $[Mo(\eta\text{-}C_3H_5)(\eta\text{-arene})(\eta\text{-olefin})]^+$ have been isolated from the hydrolysed reaction mixtures. Prolonged reaction with cht yields the cycloheptatrienyl sandwich compounds $[Mo(\eta\text{-}C_7H_7)(\eta\text{-arene})][PF_6]$. The compound $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_6H_6)(cht)][PF_6]$ undergoes deprotonation on an alumina column to the neutral compound $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_6H_6)(\eta^3\text{-}C_7H_7)]$. The violet solution reacts with cyclopentene and hydrolysis of the product in the presence of lithium chloride or alkaline sodium dithionite gives $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Cl]$ or paramagnetic $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]$ respectively; with cyclohexene the 17-electron cation $[Mo(\eta\text{-}C_6H_6)_2]^+$ is formed in high yield.

PREVIOUSLY we described reactions between the dimers $[(\eta\text{-arene})(\eta\text{-}H_5C_3)Mo(\mu\text{-}Cl)_2Mo(\eta\text{-}C_3H_5)(\eta\text{-arene})]$,(I), and simple straight-chain mono- or di-olefins at 20 °C in the presence of bis(dichloroethylaluminium).[1] In all cases cationic diene compounds were formed of stoicheiometry $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_6H_6)(\eta\text{-diene})]\ [PF_6]$.[1] Here we describe the reactions of (I) with some cyclic olefins under similar conditions. Aspects of this work have been briefly reported elsewhere.[2,3]

RESULTS

The Compounds $[Mo(\eta\text{-}C_3H_5)(\eta\text{-arene})(\eta\text{-diene})][PF_6]$ *formed from Cyclic Polyolefins*.—All the reactions described below were carried out in three stages. First, the dimers (I) were treated with ethylaluminium dichloride in toluene giving a violet solution which the evidence suggests to be a solution of the compound $[Mo(AlEtCl_2)(\eta\text{-}C_3H_5)(\eta\text{-}C_6H_6)]$.[1] The violet solution was then treated with the cyclic olefin and finally the mixture was carefully hydrolysed at low temperatures and the products were isolated. The cyclic olefins cyclohepta-1,3,5-triene (cht), cyclo-octa-1,3,5,7-tetraene (cot), and bicyclo[2.2.1]hepta-2,5-diene (nbd) all reacted rapidly with the violet solution and following hydrolysis the corresponding olefin compounds $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_6H_6)(\eta\text{-olefin})][PF_6]$ [olefin = nbd (II), cot (III), or cht (IV)] respectively were isolated. Compounds (II)—(IV) are all red crystalline solids soluble in acetone giving air-stable solutions. They are sparingly soluble in ethanol and insoluble in diethyl ether. The ^1H n.m.r. spectrum of (II) shows that the bridgehead hydrogens of the nbd ligand have different chemical shifts whilst the CH_2 hydrogens have the same chemical shift. These data suggest structure (IIa) rather than (IIb). The ^1H n.m.r. spectrum of (III) shows that the cot ligand is fluxional at the probe temperature. Compound (IV) decomposes slowly at 20 °C in acetone, methanol, or dichloromethane with evolution of propene (g.l.c.). This precluded determination of a good quality ^1H n.m.r. spectrum and only broad resonances were observed. These generally supported a structure analogous to those proposed for compounds (II) and (III).

When an acetone solution of (IV) was slowly eluted through an alumina column with acetone a deprotonation reaction occurred and a deep-red crystalline compound of stoicheiometry $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_6H_6)(\eta^3\text{-}C_7H_7)]$, (V), was formed. This is soluble in benzene and light petroleum and is moderately air sensitive. It may be sublimed at 100°C with marked decomposition. The mass spectrum showed the highest peak at m/e 302 and this may be assigned to the ion $[^{92}Mo(C_{16}H_{18})]^+$. The ^1H n.m.r. spectrum showed bands assignable to $\eta\text{-}C_6H_6$, $\eta\text{-}C_3H_5$, and $\eta^3\text{-}C_7H_7$ groups. The latter group has been identified in the compounds $[Mo(\eta\text{-}C_5H_5)(\eta^3\text{-}C_7H_7)(CO)_2]$.[4]

The Cationic Sandwich Compounds (*η-Arene*)(*η-cycloheptatrienyl*)*molybdenum Hexafluorophosphate*.—Treatment of the dimers (I; arene = benzene, toluene, or mesitylene) with $AlEtCl_2$ and cht for a prolonged period (*ca.* 2 d), followed by hydrolysis, gave high yields of the 18-electron mixed sandwich compounds $[Mo(\eta\text{-arene})(\eta\text{-}C_7H_7)][PF_6]$ [arene = benzene (VI), toluene (VII), or mesitylene (VIII)]. Little of the initially formed products, *e.g.* (IV), was isolated under these conditions. The reaction rate and yield of the products (VI)—(VIII) increased in the order benzene < toluene < mesitylene. For example, when the reaction mixture was hydrolysed after only 3 h the yield of compound (VII) was 69% whilst (VI) was formed in only 38% yield after 22 h. Compounds (VI)—(VIII) in dry dichloromethane show little evidence of decomposition in air after 1 d. However, they react in acetone and alcohol so that recrystallisation from these solvents must be rapid and at reduced temperatures. Some reactions of compounds (VI)—(VIII) have been briefly noted [2,3] and will be described in detail later.

The Mixed Sandwich Compounds $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Cl]$ and $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]$.—Treatment of the violet solution of the dimers (I) with cyclopentene for 2 h at room temperature gave a red-brown oil. Hydrolysis of the oil with excess of sodium dithionite at −50 °C gave the neutral paramagnetic compound $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]$, (IX), in high yield (*ca.* 85%). This compound has been described previously but could be prepared in only small quantities.[5] The method described here enabled 50 g quantities of (IX) to be conveniently prepared in *ca.* 1 week. Compound (IX) was identified from its mass spectrum and other data given in the Table. It is very air sensitive and sublimes *in vacuo* at 80 °C giving large red crystals.

When the brown-red oil formed from cyclopentene was

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[1] M. L. H. Green and J. Knight, *J.C.S. Dalton*, 1974, 311.

[2] E. F. Ashworth, M. L. H. Green, and J. Knight, *J.C.S. Chem. Comm.*, 1974, 5; M. L. H. Green, J. Knight, and J. A. Segal, *ibid.*, 1975, 283.

[3] E. F. Ashworth, M. L. H. Green, and J. Knight, *J. Less-Common Metals*, 1974, **36**, 213.

[4] R. B. King, *J. Organometallic Chem.*, 1967, **8**, 129.

[5] E. O. Fischer and F. J. Kohl, *Chem. Ber.*, 1965, **98**, 3134; W. H. Werner, E. O. Fischer, and J. Muller, *ibid.*, 1970, **103**, 2258.

hydrolysed with a methanol solution of lithium chloride a compound of stoicheiometry [Mo(η-C_5H_5)(η-C_6H_6)Cl], (X), was isolated in high yield. The compound (X) is purple-black and dissolves in tetrahydrofuran and benzene giving deep maroon-red solutions which are only slowly decomposed in air. Compound (X) was characterised by the data in the Table and the proposed structure is shown in the Scheme.

The Salt [Mo(η-C_6H_6)$_2$][PF_6].—The violet solution of the dimers (I) reacted slowly with cyclohexene at 20 °C and from the hydrolysed reaction products the salt [Mo(η-C_6H_6)$_2$][PF_6], (XI), was isolated in 50% yield. This salt has been described previously[6] and our product was identified by analysis and reduction with sodium dithionite to neutral bis(η-benzene)molybdenum, which was, in turn, identified by its mass spectrum.

Compound	Colour	Analysis[a](%)		¹H n.m.r. data[b]
		C	H	
[Mo(η-C_3H_5)(η-C_6H_6)(cot)][PF_6], (III)	Dark red	44.4(44.0)	4.3(4.1)	4.44,*6*,*s*,η-C_6H_6; 4.75,*8*,*s*,C_8H_8; *ca.* 4.7,*1*,*c*,CH; 6.14,*2*,*d*(9),H_{syn}; 6.93,*2*,*d*(14),2 H_{anti} in [$^2H_6$]Me_2CO
[Mo(η-C_3H_5)(η-C_6H_6)(nbd)][PF_6], (II)	Red	42.0(42.5)	4.0(4.2)	3.80,*1*,*c*,CH; 4.52,*6*,*s*,C_6H_6; 5.03,*2*,*t*(3) $H^{2,6}$ or $H^{3,5}$; 5.75,*2*,*t*(4),$H^{3,5}$ or $H^{2,6}$; 6.32,*1*,*c*,H^1 or H^4; 6.80,*1*,*c*,H^4 or H^1; 7.03,*2*,*d*(7), 2 H_{syn}; 8.15.*2*,*d*(11),2 H_{anti}; 9.05,*2*,*c*,H^7 in [$^2H_6$]Me_2CO
[Mo(η-C_3H_5)(η-C_6H_6)(cht)][PF_6], (IV)	Red	42.3(42.5)	4.0(4.2)	
[Mo(η-C_3H_5)(η-C_6H_6)(η^3-C_7H_7)], (V)	Dark red	62.9(62.7)	5.9(5.9)	3.88,*2*,*c*[c]; 4.83,*2*,*c*[c]; 6.06,*6*,*s*,η-C_6H_6; 6.23,*1*,*c*,CH; 6.90,*2*,*c*[c]; 7.92,*2*,*d*(8), 2 H_{syn}; 8.53,*2*,*d*(12), 2 H_{anti}; 9.07,*2*,*c* in η-C_6D_6
[Mo(η-C_6H_6)(η-C_7H_7)][PF_6], (VI)	Bright green	37.9(38.1)	3.3(3.2)	3.58,*6*,*s*, η-C_6H_6; 4.23,*7*,*s*,η-C_7H_7 in [$^2H_6$]Me_2CO
[Mo(η-C_6H_5Me)(η-C_7H_7)][PF_6], (VII)	Bright green	39.6(39.7)	3.8(3.6)	3.65,*5*,*c*,Ph; 4.34,*7*,*s*,η-C_7H_7; 7.70, *3*,*s*,Me in [$^2H_6$]Me_2CO
[Mo(η-$C_6H_3Me_3$)(η-C_7H_7)][PF_6], (VIII)	Green	42.4(42.5)	4.0(4.2)	3.50,*3*,*s*,C_6H_3; 4.40,*7*,*s*,η-C_7H_7; 7.71, *9*,*s*,Me_3 in [$^2H_6$]Me_2CO
[Mo(η-C_5H_5)(η-C_6H_6)Cl], (X)[d]	Red-black	48.4(48.1)	4.1(4.0)	5.41,*5*,*s*,η-C_5H_5; 5.97,*6*,*s*,η-C_6H_6 in C_6D_6
[Mo(η-C_6H_6)$_2$][PF_6]	Yellow	36.6(36.3)	3.3(3.1)	

[a] Calculated values are given in parentheses. [b] Given as chemical shift (τ), *relative intensity*, *multiplicity* (*J* in Hz), and assignment. [c] See ref. 4 for analogy with C_7H_7 hydrogens in [Mo(η-C_5H_5)(η^3-C_7H_7)(CO)$_2$]. [d] Cl, 13.0(12.9%).

DISCUSSION

The structures and reactions of the compounds (II)—(X) are shown in the Scheme. It appears that the violet solutions formed from the dimers (I) and $AlEtCl_2$ react with different olefins in several different ways. (*i*) Some dienes, such as buta-1,3-diene or nbd, co-ordinate directly as the unchanged ligand. (*ii*) Certain monoenes such as *cis*-pent-2-ene and oct-1-ene undergo complex reactions on the metal and eventually give rise to both η-allylic and diene ligands and these reactions involve dehydrogenation of the monoene.[1] (*iii*) The cyclic olefins cyclopentene and cyclohexene also undergo dehydrogenation giving η-C_nH_n ligands. Finally, (*iv*), propene and butenes undergo dimerisation as well as dehydrogenation giving η-allylic and diene ligands.[1]

EXPERIMENTAL

All operations were made under dry nitrogen. ¹H n.m.r. spectra were recorded using JEOL (60 MHz) or Varian (100 MHz) spectrometers. The dimers (I) were prepared as described previously.[7] Ethylaluminium dichloride was used as a solution in pure benzene or toluene which had been previously dried using calcium hydride. All olefins and solvents were carefully dried and distilled before use. The reaction vessels were Schlenk tubes which were rigorously dried before use.

(η-*Allyl*)(η-*benzene*)(η-*bicyclo*[2.2.1]*hepta*-2,5-*diene*)*molybdenum Hexafluorophosphate*, (II).—The dimer [{Mo(η-C_3H_5)(η-C_6H_6)Cl}$_2$] (0.9 g, 1.8 mmol) was treated at 0 °C with $AlEtCl_2$ (0.9 g, 7.2 mmol) in benzene (10 cm³). The resulting deep violet solution was treated with bicyclo-[2.2.1]hepta-2,5-diene (nbd) (1.0 cm³, 8.0 mmol). After 15 min red crystals and a pale-red mother liquor were seen and after a further 1 h the supernatant liquor was decanted and discarded. The red residue was washed with light petroleum (b.p. 30—40 °C, 50 cm³) and dried under reduced pressure. Ethanol (4 cm³, 95%) at −78 °C was (slowly) added to the cooled (−78 °C) residue and the mixture was allowed to warm slowly to room temperature. Reaction with gas evolution occurred and after 30 min, water (20 cm³) was added giving a red solution. This was filtered into aqueous ammonium hexafluorophosphate giving a thick orange precipitate which was filtered and washed with water (2 × 10 cm³) and then dried *in vacuo*. The solid was dissolved in acetone (50 cm³) and the solution was filtered into an equal volume of ethanol. The mixture was then concentrated slowly under reduced pressure giving small scarlet *crystals* which were collected and washed with ethanol then dried *in vacuo*, *ca.* 1.0 g (62%).

(η-*Allyl*)(η-*benzene*)(η-*cyclo-octa*-1,3,5,7-*tetraene*)*molybdenum Hexafluorophosphate*, (III).—The violet solution at

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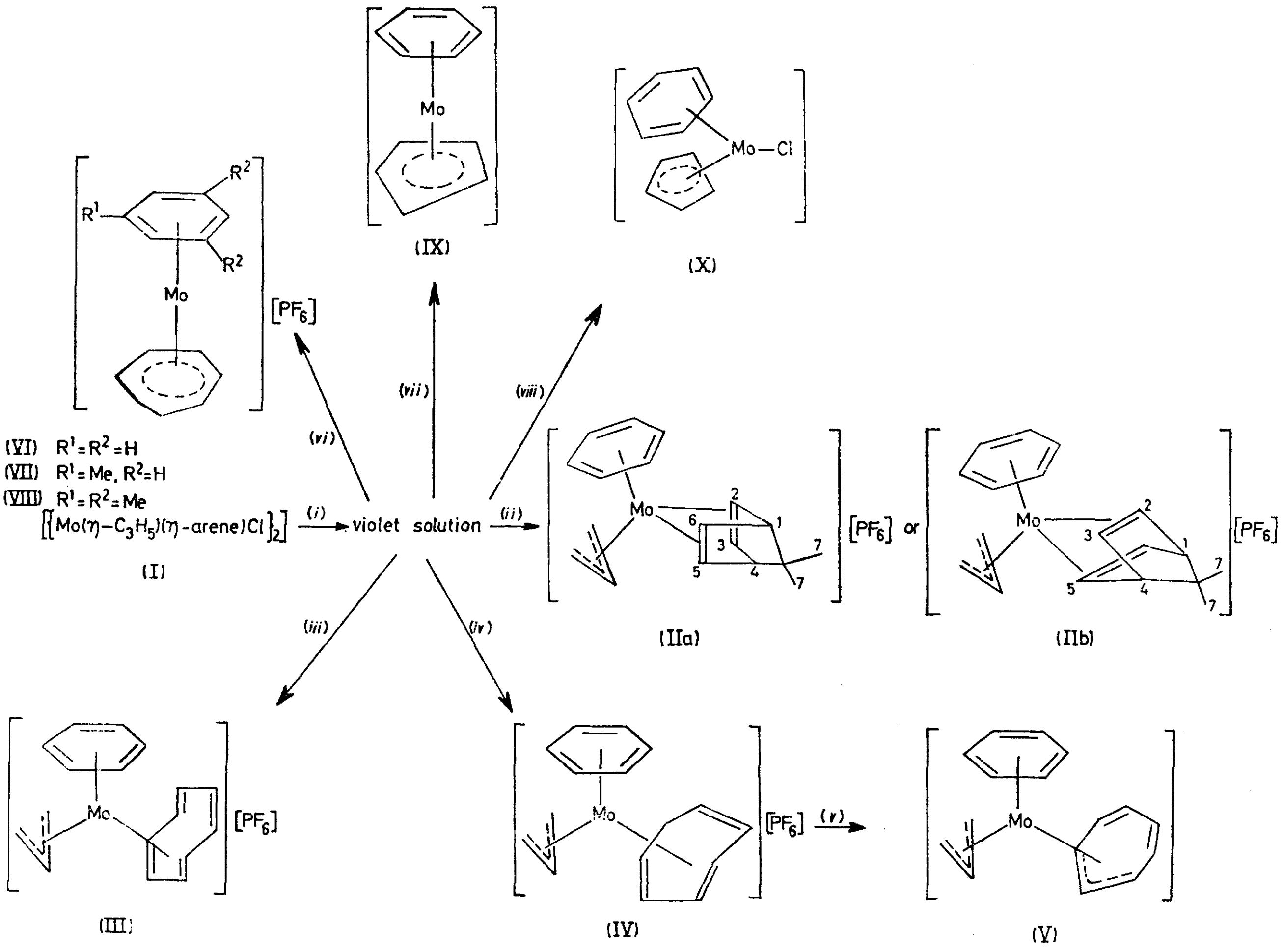
[6] E. O. Fischer, F. Scherer, and H. O. Stahl, *Chem. Ber.*, 1960, **93**, 2056.

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

0 °C prepared as above from dimer (I; arene = benzene) (2 g), was treated dropwise with cylco-octa-1,3,5,7-tetraene (1.5 cm^3, 12 mmol) with stirring. A rapid reaction occurred giving a red oil. After 5 min the supernatant mother liquor was discarded and the residual red oil was washed with dry light petroleum (b.p. 30—40 °C, 2 × 30 cm^3) and the residue was dried under reduced pressure. The foamy residue was cooled to -100 °C and ethanol (15 cm^3, 95%) was added. The mixture was allowed to react at low temperature with vigorous shaking until gas evolution had effectively ceased. It was then allowed to warm to room temperature and water (50 cm^3) was added to give a red solution which was filtered into aqueous ammonium hexafluorophosphate giving a deep-red precipitate. This was filtered off, washed with water, dried, and then recrystallised from acetone–ethanol as described above. The resulting dark-red *crystals* were recrystallised from dichloromethane–tetrahydrofuran, collected, washed with diethyl ether, and dried *in vacuo*, 2.04 g (50%).



SCHEME (*i*), $(AlEtCl_2)_2$ in benzene or toluene; (*ii*), nbd (20 °C) then EtOH and $[NH_4][PF_6]$; (*iii*) cot (20 °C) then EtOH, and $[NH_4]$-$[PF_6]$; (*iv*), cht (20 °C, 2 min) then EtOH and $[NH_4][PF_6]$; (*v*) Al_2O_3 (20 °C); (*vi*), cht (2 d), then EtOH and $[NH_4][PF_6]$. arene = C_6H_6, C_6H_5Me, or $C_6H_3Me_3$ -1, 3, 5; (*vii*), cyclopentene then KOH and $Na_2[S_2O_4]$ (-50 °C); (*viii*), cyclopentene, then LiCl in MeOH (-50 °C).

(*η-Allyl*)(*η-benzene*)(*η-cyclohepta-*1,3,5-*triene*)*molybdenum Hexafluorophosphate*, (IV).—The cooled purple solution from dimer (I; arene = benzene) (2 g) was treated with freshly distilled cyclohepta-1,3,5-triene (1.25 g, 14 mmol) in benzene (5 cm^3) and the mixture was allowed to react for 2 min. The supernatant liquor was separated from the resulting red oil which was washed, dried, and then hydrolysed with ethanol at -100 °C as described above. Following isolation of the hexafluorophosphate salt, as described above, the red-brown crystals from acetone–ethanol were washed with successive portions of acetone (5 cm^3) and again recrystallised from acetone–ethanol. This extra purification step was required to remove some of the compound $[Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_7H_7)][PF_6]$ present as impurity. The pure compound was isolated as scarlet *crystals*, 0.95 g (26%).

(*η-Toluene*)(*η-cycloheptatrienyl*)*molybdenum Hexafluorophosphate*, (VII).—The violet solution at 0 °C, prepared from dimer (I; arene = tolene) (88 g, 0.17 mol) in a three-necked flask (1l) was treated with cyclohepta-1,3,5-triene (45 g, 0.49 mol) at 0 °C in benzene (150 cm^3). A red-brown oil formed within minutes and the mixture was allowed to stand at 20 °C for 17 h during which time there was slow evolution of a gas and the mixture became green-brown. The supernatant mother liquor was removed from the green-brown oil which was then washed with light petroleum (b.p. 30—40 °C, 3 × 300 cm^3) with vigorous shaking. The resulting semi-solid mass was dried under reduced pressure (15 min) and then cooled to −100 °C. The frozen mass was treated with cold ethanol (200 cm^3, 95%, −78 °C) and the mixture was shaken vigorously and allowed to warm slowly to room temperature. When gas evolution was no longer observed ice-cold water (800 cm^3) was added in portions and the resulting solution was immediately filtered into excess of aqueous ammonium hexfluorophosphate {$[H_4N][PF_6]$ (56 g) in water (200 cm^3)}. The resulting green precipitate was filtered off as quickly as possible, washed with cold water, and dried under reduced pressure. The product was dissolved in acetone (300 cm^3) and filtered into ethanol (150 cm^3). Some green crystals separated almost immediately and rapid concentration of the volume of the solution under reduced pressure (to 160 cm^3) gave further green crystals. The dark coloured filtrate was separated and discarded and the green crystals were washed with ethanol until the washing was pale green. A further recrystallisation under the same conditions as above gave the pure compound as grass-green *crystals*. These were collected, washed with diethyl ether, and dried *in vacuo*, 65 g (65%). The analogues (VI) and (VIII) were prepared similarly; the benzene compound, (VI), was also prepared in 65% yield with the minor modification that after addition of the cycloheptatriene the mixture was warmed to 70 °C with stirring for 1 h. After allowing the products to cool to room temperature, hydrolysis isolation was carried out exactly as described above for (VII).

(η-Allyl)(η-benzene)(1—3-η-cycloheptatrienyl)molybdenum, (V).—The compound $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_6H_6)(C_7H_8)][PF_6]$ (0.13 g, 0.3 mmol) in acetone (20 cm^3) was slowly passed through an alumina column under nitrogen. Elution with acetone gave a dark red solution from which the solvent was removed under reduced pressure. The residue was extracted with light petroleum (b.p. 30—40 °C, 20 cm^3) and the filtered solution was cooled slowly to −80 °C. Red-black *crystals* separated which were recrystallised again from cold light petroleum giving the pure compound, 0.03 g (35%).

Bis(η-benzene)molybdenum Hexafluorophosphate.—The violet solution from dimer (I; arene = benzene) (1.0 g) was treated with pure cyclohexene (3 cm^3, 30 mmol) and the mixture was allowed to stand for 12 h at 20 °C. A yellow-brown oil separated during this period and this was washed, dried, hydrolysed, and extracted with water as described in the other preparations above. The bright-yellow hexafluorophosphate was filtered off, washed, dried, and finally recrystallised twice from acetone–ethanol as described above giving yellow crystals, 0.91 g (58%).

(η-Benzene)chloro(η-cyclopentadienyl)molybdenum, (X).—The violet solution from dimer (I; arene = benzene) (10.0 g, 20 mmol) and $AlEtCl_2$ (10.4 g, 80 mmol) in toluene (150 cm^3) was treated dropwise with pure dry cyclopentene at −50 °C. The mixture was warmed to 20 °C with stirring and a red-brown oil precipitated. The mixture was allowed to stand for 2 h at 20 °C and the supernatant liquor was separated. The residual oil was washed with light petroleum (2 × 100 cm^3) and dried under reduced pressure giving a red-brown tarry mass. Lithium chloride (15 g) in methanol (100 cm^3) was cooled to −50 °C and then added to the tar at −50 °C. The mixture was shaken vigorously and allowed to warm slowly. When effervescence became somewhat vigorous the mixture was cooled again. Eventually the reaction subsided and the mixture was allowed to warm to room temperature. The black precipitate was filtered off, washed with water (40 cm^3), and dried under reduced pressure, giving the crude product (9.43 g, 86%). Recrystallisation was readily effected from benzene–light petroleum (b.p. 100—120 °C) and the pure compound appeared as small black *crystals*.

(η-Benzene)(η-cyclopentadienyl)molybdenum, (IX).—The red-brown tar, prepared as described in the previous preparation, was cooled to −50 °C and treated with aqueous potassium hydroxide (600 cm^3, 30%) containing sodium dithionite (60 g) at −50 °C. The mixture was stirred vigorously until room temperature was reached and the deep red microcrystalline precipitate was separated, washed with water, and dried under reduced pressure. The residue was extracted with benzene, the solution was filtered, and light petroleum (b.p. 100—120 °C) was added. The resulting solution was concentrated under reduced pressure giving a red crystalline solid, 7.6 g (80%). Further purification was carried out by sublimation *in vacuo* (10^{-2} mmHg) * at 80—90 °C.

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* 1 mm Hg ≈ 13.6 × 9.8 Pa.