

SYNTHESIS AND POLYMERISATION OF BIS(η -STYRENE)MOLYBDENUM AND RELATED STUDIES: CRYSTAL STRUCTURES OF $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2)_2$ AND $[\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{H})_2]\text{BF}_4$

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Summary

The synthesis of the compounds $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{R})_2$, where $\text{R} = \text{CH}=\text{CH}_2$, $4\text{-C}_6\text{H}_4\text{CH}=\text{CH}_2$ and $\text{CH}_2\text{CH}=\text{CH}_2$ is described. The crystal structure of $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2)_2$ has been determined. These vinyl monomers are polymerised by free radical initiation using AIBN. Di- η -benzenemolybdenum is lithiated by $\text{Bu}^n\text{Li}/\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ to give a bis(η -lithiobenzene)molybdenum derivative, which reacts with D_2O , MeI , or SiMe_3Cl to give $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{R})_2$, where $\text{R} = \text{D}$, Me or SiMe_3 respectively. The dilithio system reacts with SiMe_2Cl_2 to give a polymeric mixture containing $\text{Cl}\{\text{SiMe}_2\text{-}\eta\text{-C}_6\text{H}_5\text{Mo-}\eta\text{-C}_6\text{H}_5\}_n\text{SiMe}_2\text{Cl}$, and hydrolysis of this yields the disiloxane $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{OSiMe}_2\text{-}\eta\text{-C}_6\text{H}_5)$, whose crystal structure has been determined. Co-condensation of molybdenum atoms with dimethylphenylsilane gives $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{H})_2$, which is oxidised by aqueous HBF_4 to give the compound $[\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{H})_2]\text{BF}_4$, whose crystal structure has been determined.

Organotransition metal polymers based on vinyl derivatives of ferrocene or of $\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_4$ are well known [1–4]. In these compounds and their polymers the metal centres are relatively unreactive, and for example do not readily undergo ligand substitution. We decided to attempt to prepare and explore the properties of homopolymers of organotransition metal compounds in which the metal centre was highly electron-rich and, accordingly, reactive. Bis- η -arene-molybdenum compounds have high energy centres, and have been shown to be precursors towards many η -arenemolybdenum derivatives [5]. We describe here the synthesis and polymerisation of bis- η -arene-molybdenum compounds containing unsaturated $\text{C}=\text{C}$ groups attached to the η -arene rings.

Results and discussion

In a typical experiment molybdenum metal was co-condensed with an excess of chlorobenzene to give green, air-sensitive crystals of the previously described [6] bis(η -chlorobenzene)molybdenum (**1**). Optimum yields of **1** (ca. 25%) were obtained in experiments lasting approximately 3 h. Yields (%) decreased when the reaction time was increased to 5 or 6 h. The longer, lower yield, reactions were accompanied by formation of a dark reddish-brown material, which was not characterised.

In order to find whether the chloro group of **1** would undergo nucleophilic substitution with Grignard reagents the reaction between **1** and methylmagnesium chloride was studied. The expected coupling product, namely, di- η -toluenemolybdenum (**2**) was formed in good yield. However, subsequent reactions involving a series of other Grignard reagents resulted in the formation of both the coupling products and substantial yields of other products.

Typically, bis(η -chlorobenzene)molybdenum (**1**) in tetrahydrofuran was treated with an excess of the Grignard reagent (molar ratio 1/7) at room temperature. The reaction did not occur immediately, and slow colour changes were observed. In some cases several attempts were made to improve yields. Where yields of the desired coupling products were low, the residual reaction mixtures were hydrolysed giving additional products.

Treatment of bis(η -chlorobenzene)molybdenum with allylmagnesium chloride formed very air-sensitive green needles of the desired Mo(η -C₆H₅CH₂CH=CH₂)₂ (**3**). The analytical and spectroscopic data which characterises **3**, and all the other new compounds described in this work, are given in Table 1. These data are not further discussed unless the interpretation is not obvious. The X-ray crystal structure of **3** has been determined, and is discussed below.

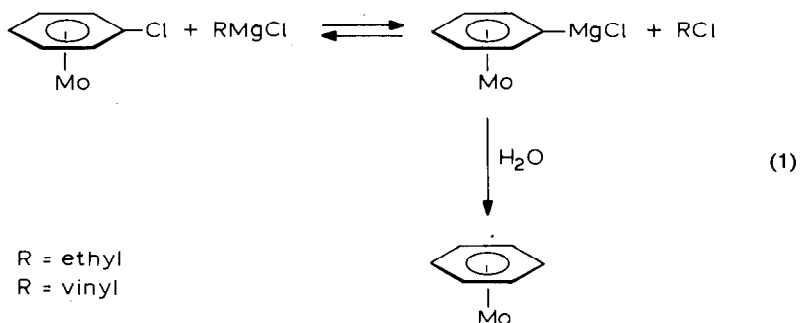
Bis(η -chlorobenzene)molybdenum reacts with ethylmagnesium chloride giving bright green, very air-sensitive crystals of (η -benzene)(η -ethylbenzene)molybdenum (**4**). Both the NMR and mass spectra showed the presence of Mo(η -C₆H₆)₂ as a contaminant in the product.

The yield of the mono- η -ethylbenzene compound **4** was promoted by use of a large excess of Grignard reagent. However, dibenzenemolybdenum was always present in the products. Compound **4** was extracted from the reaction mixture with petroleum ether. Addition of ethanol to the insoluble residues gave a further amount of Mo(η -C₆H₆)₂.

Qualitative comparison of the rates of reactions at ambient temperature of bis(η -chlorobenzene)molybdenum with ethylmagnesium chloride and allylmagnesium chloride showed that conversion into **4** occurs more rapidly than the formation of **3**. For example, after 24 h with EtMgCl there was no evidence for bis(η -chlorobenzene)molybdenum, whilst in the related allylbenzene coupling reaction, starting material was still isolated after three days.

The generation of di- η -benzenemolybdenum during the formation of **4** by hydrolysis of insoluble residues could arise from the presence of Mo(η -C₆H₅MgCl)₂ formed by the exchange reaction (eq. 1).

The exchange reaction could also account for the change of colour of the reaction mixture from green to red. The change of colour of the residue from red back to green after hydrolysis supports this view. We note that bis-arene-molybdenum compounds are normally green, whilst those which have unsaturated hydrocarbon

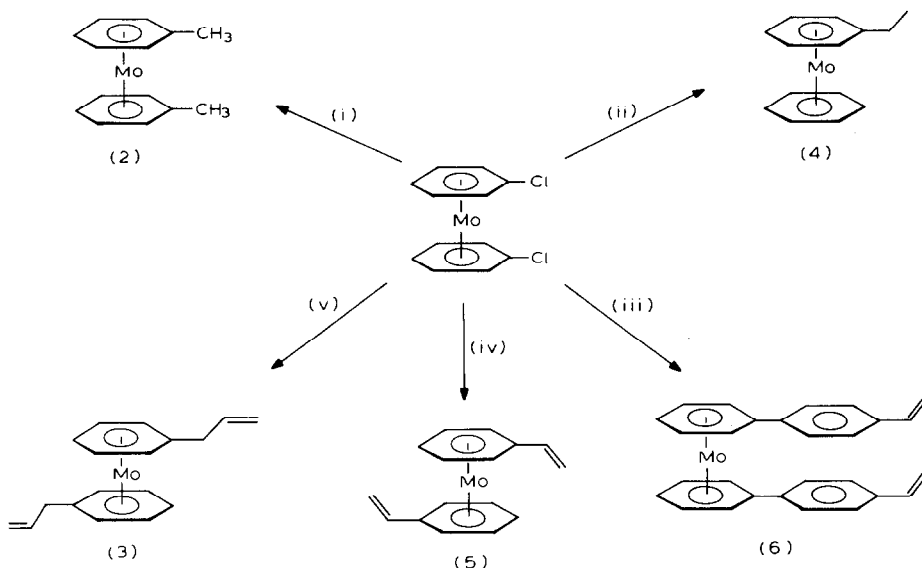


substituents in the η -arene ring are red-yellow (see Table 1). We attribute this green-to-red shift to conjugation of unsaturated substituents with the η -arene ring.

The absence of any of the expected $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{Et})_2$ is not fully accounted for in terms of the metal-halogen exchange equilibrium alone. Hydrogen abstraction from solvent during the exchange process could account for the formation of coordinated benzene prior to the addition of water, i.e. in the product derived from the petroleum ether extracts.

Treatment of bis(η -chlorobenzene)molybdenum (Scheme 1) with vinylmagnesium bromide at room temperature for a week gave a deep red solution, from which were isolated bright copper-orange, very air-sensitive crystals of $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{CH}=\text{CH}_2)_2$ (5) in yields of about 35%. Hydrolysis of the petroleum-insoluble portion of the product gave a small yield of a green solid. The NMR spectrum showed this to be a

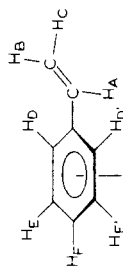
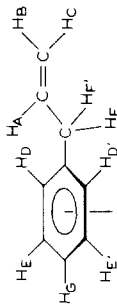
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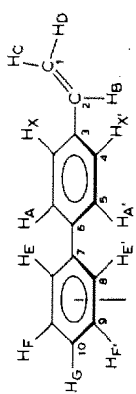


SCHEME 1. (i) MeMgCl in THF/ Et_2O at r.t. for 5 d, 41%; (ii) EtMgCl in Et_2O at r.t. for 5 d, 38%; (iii) $4\text{-(CH}_2=\text{CH)C}_6\text{H}_4\text{MgCl}$ in THF at r.t. for 7 d, 78%; (iv) vinylmagnesium bromide in THF at r.t. for 7 d, 34.6%; (v) allylmagnesium chloride in THF at r.t. for 5 d, 38%.

TABLE I
ANALYTICAL AND SPECTROSCOPIC DATA

Compound	Colour	Analysis (Found (calcd.)(%))		NMR data ^a
		C	H	
(3) $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2)_2$	Green	65.06 (64.78)	6.07 ^c (5.85)	5.85 [ddt, 2H, $J(\text{A-C}(\text{trans}))$ 17.0, H_A], 4.99 [m, 4H, $J(\text{A-B}(\text{cis}))$ 10.2, H_B and H_C], 4.64 [d, 4H, $J(\text{A-F})$ 6.7, H_D and H_D'], 4.57 [t, 4H, $J(\text{B-C})$ 1.3, H_E and H_E'], 4.51 [t, 2H, $J(\text{B-F})$ and $J(\text{C-F})$ 1.2, H_G], 2.86 [dt, 4H, $J(\text{ring})$ 4.8, H_F and H_F'] ^b
(4) $\text{Mo}(\eta\text{-C}_6\text{H}_6)(\eta\text{-C}_6\text{H}_5\text{Et})$	Green ^d			4.6 [m, 11H, Ph and C_6H_6], 2.1 [q, 2H, J 7.5, $\text{C}_6\text{H}_5\text{Me}$], 1.0 [t, 3H, J 7.5, $\text{CH}_2\text{-CH}_3$] ^b
(5) $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{CH}=\text{CH}_2)_2$	Red-orange	63.16 (62.88)	5.26 ^e (5.09)	6.11 [dd, 2H, $J(\text{A-B}(\text{trans}))$ 17.5, H_A], 5.22 [dd, 2H, $J(\text{A-C}(\text{cis}))$ 10.7, H_B], 4.92 [dd, 2H, $J(\text{B-C})$ 1.1, H_C], 4.79 [d, 4H, $J(\text{ring})$ 5.2, H_D and H_D'], 4.65 [t, 4H, H_E and H_E'], 4.55 [t, 2H, H_F] ^b



<p>(6) $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{-4-C}_6\text{H}_4\text{CH}=\text{CH}_2)_2$</p> 	Red	73.68 (73.47)	5.30 ^f (5.34)	<p>7.10 [m, dd, 8 H, $J(\text{A-X})$ 8.4, H_A, H_X, H_X and H_Y], 6.58 [dd, 2H, $J(\text{B-C})$ <i>trans</i> 17.6, H_B], 5.61 [dd, 2H, $J(\text{B-D})$ <i>cis</i> 10.9, H_C], 5.08 [dd, 2H, $J(\text{C-D})$ 1.0, H_D], 5.03 [d, 4H, $J(\text{ring})$ 4.9, H_E and H_E], 4.67 [t, 4H, H_F and H_F], 4.51 [t, 2H, H_G]^b</p> <p>¹³C {¹H} NMR: 113.34, C(1); 137.49, C(2); 136.34, C(3); 126.54, C(4); 127.81, C(5); 143.02, C(6); 93.24, C(7); 77.74, C(8); 79.31, C(9); 77.74, C(10)^g</p> <p>4.89 [qn, 2H, J 2.8, <i>p</i>-H of Ph], 4.69 [d, 4H, J 0.7, <i>m</i>-H of Ph], 4.68 [s, 4H, <i>o</i>-H of Ph], 0.29 [s, 12H, SiMe]^b</p> <p>4.70 [t, 2H, J 4.78, <i>p</i>-H of Ph], 4.61–4.54 [c, 6H, Si-H and <i>m</i>-H of Ph], 4.51 [d, 4H, J 5.15, <i>o</i>-H of Ph], 0.18 [d, 12H, J 3.68, SiMe]^b</p>
<p>(12) $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{OSiMe}_2\eta\text{-C}_6\text{H}_5)_2$</p>	Green ^h			
<p>(13) $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{H})_2$</p>	Green	52.15 (52.02)	6.57 ⁱ (6.43)	
<p>(14) $[\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{H})_2]\text{BF}_4$</p>	Yellow	42.21 (41.92)	5.31 (5.31)	

^a ¹H NMR unless otherwise stated. Data given as: chemical shift (δ , ppm) (multiplicity, relative intensity, J (Hz), assignment), etc. ^b 300 MHz in benzene-*d*₆. ^c *m/e* ⁹⁸Mo: 334 [*P*⁺], $\nu(\text{C}=\text{C})$ 1625 cm⁻¹. ^d *m/e*, ⁹⁸Mo: 282 [*P*⁺]. ^e *m/e*, ⁹⁸Mo: 306 [*P*⁺]. ^f *m/e*, ⁹⁸Mo: 458 [*P*⁺]. ^g 250 MHz in C₆D₆. ^h *m/e*, ⁹⁸Mo: 384 [*P*⁺]. ⁱ *m/e*, ⁹⁸Mo: 370, [*P*⁺], Si: 15.24 (15.12)%.

3/1 mixture of di- η -benzenemolybdenum and (η -benzene)(η -ethylbenzene)molybdenum (**4**).

When the above reaction of bis(η -chlorobenzene)molybdenum and vinylmagnesium bromide was interrupted after 48 h, mostly starting material was isolated. In an attempt to limit the side reactions the reaction mixture was kept at 0°C for 16 days. However, only a small amount of coupling product had formed, and more than 80% of the bis(η -chlorobenzene)molybdenum could be recovered. The yield of di- η -styrenemolybdenum improved as the excess of Grignard reagent was increased.

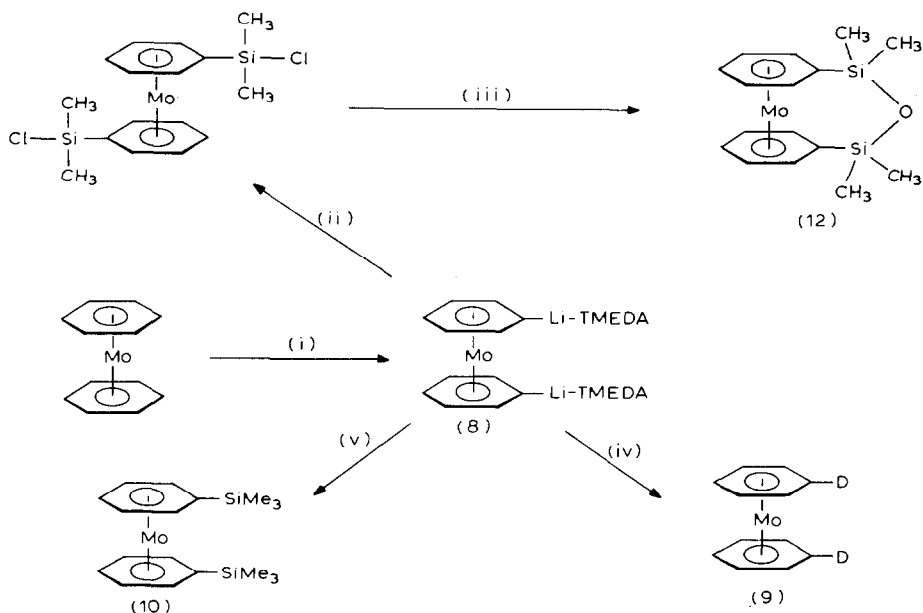
The reaction between bis(η -chlorobenzene)molybdenum and *p*-styrylmagnesium chloride (1/5) proceeded very smoothly, and the reaction mixture gradually changed to a brilliant red. After one week red crystals of $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{-4-C}_6\text{H}_4\text{CH=CH}_2)_2$ (**6**) were isolated in 80% yield.

The high yield in which bis(η -*p*-styrylbenzene)molybdenum (**6**) is isolated, compared with the failure to form $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{Et})_2$ in the EtMgCl reaction can be ascribed to the reduction in the degree of metal-halogen exchange for the η -styrylmagnesium chloride reaction. The η -benzenemagnesium chloride system and the Grignard reagent, *p*-styrylmagnesium chloride would be expected to have similar C-Mg bond energies, so that there will be little driving force for exchange.

Treatment of $\text{Mo}(\eta\text{-C}_6\text{H}_6)_2$ (**7**) with excess *N,N,N',N'*-tetramethylethylenediamine (TMEDA) *n*-butyllithium mixture gave a brown suspension, which reacted in the manner expected for bis(η -lithiobenzene)molybdenum (**8**). For example, addition of deuterium oxide to the brown precipitate gives bis(η -monodeuteriobenzene)molybdenum (**9**), which was characterised by NMR and mass spectra. Further, addition of trimethylchlorosilane to the brown precipitate gave the compound $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_3)_2$ (**10**). The green, air-sensitive compound **10** has also been prepared by co-condensation of molybdenum atoms with phenyltrimethylsilane [7]. There is no reaction between **7** and hexane solutions of η -butyllithium, in the absence of tetramethylethylenediamine.

Treatment of the dilithio compound **8** with dichlorodimethylsilane gives a highly sensitive green solid (**11**), which did not sublime in vacuo at 150°C. Further, the NMR spectrum showed two broad bands of relative intensity 10/6 at δ 4.6 and 0.15 ppm. The involatility and broad nature of the NMR spectrum suggest the compound **11** to be a polymer of general formula $\text{Cl}\{\text{SiMe}_2\text{-}\eta\text{-C}_6\text{H}_5\text{Mo-}\eta\text{-C}_6\text{H}_5\}_n\text{-SiMe}_2\text{Cl}$. Related dimethylsilyl-ferrocenylene polymers ($n = 1400\text{--}7000$) have been described, and were prepared by reaction between 1,1'-dilithioferrocene and SiMe_2Cl_2 [8]. Further, extraction of the more soluble fraction of the initial reaction mixture containing **11** followed by hydrolysis gave a small quantity of green crystals and a green oil. The characterising data show the green crystals to be the compound $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{OSiMe}_2\text{-}\eta\text{-C}_6\text{H}_5)$ (**12**). An attempt was made to determine the crystal structure of **12**, but persistent mirror effects though the plane of symmetry precluded satisfactory refinement. The values R 7.73% (R_w 9.28%) were obtained and the data strongly supported the structure shown in Scheme 2. The related compound $\text{Fe}(\eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{OSiMe}_2\text{-}\eta\text{-C}_5\text{H}_4)$ has been described [9]. The air-sensitive oil from which **12** was obtained was stable up to 180°C and the IR and NMR spectra showed strong similarities to those of **12**. We assume that the green oil contains oligomers analogous to **12** but with intermolecular Si-O-Si linkages.

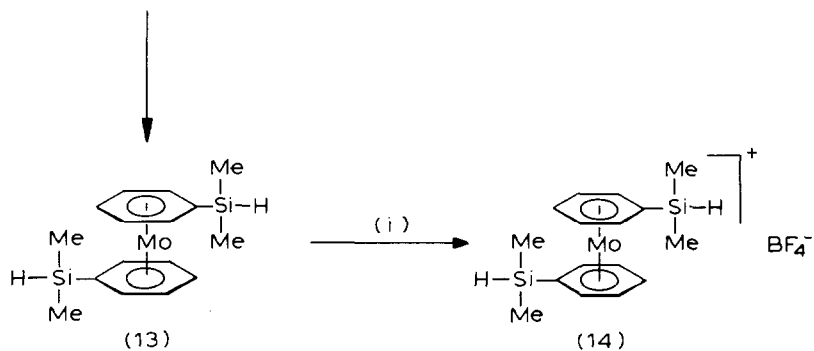
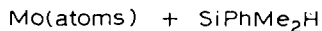
The reactions between **8** and SiMe_2ClR , $\text{R} = \text{CH=CH}_2$, and $\text{CH}_2\text{CH=CH}_2$ gave



SCHEME 2. (i) BuⁿLi·TMEDA in cyclohexane at 50°C for 2.5 h, > 90%; (ii) SiMe₂Cl₂ in cyclohexane at r.t. for 1 h, 22%; (iii) H₂O at 0°C, ca. 5%; (iv) D₂O, > 90%; (v) SiMe₃Cl in cyclohexane at r.t. for 1 h, 29%.

only small quantities of viscous green oils, which appeared (NMR and IR) to be polymeric and were not further characterised.

Co-condensation of molybdenum atoms with dimethylphenylsilane gave air-sensitive green crystals of Mo(η -C₆H₅SiMe₂H)₂ (**13**) (Scheme 3). The photo-electron spectrum of **13** [10] showed a first ionisation energy at 5.53 eV, assignable to ionisation from the metal based ²A_{1g} orbital, essentially of *d*-character. Treatment of **13** with tetrafluoroboric acid gave the paramagnetic (NMR) compound [Mo(η -C₆H₅SiMe₂H)₂]⁺BF₄⁻ (**14**). The crystal structure of **14** has been determined.



SCHEME 3. (i) HBF₄·Et₂O in toluene/diethyl ether (3/1) at r.t., > 90%.

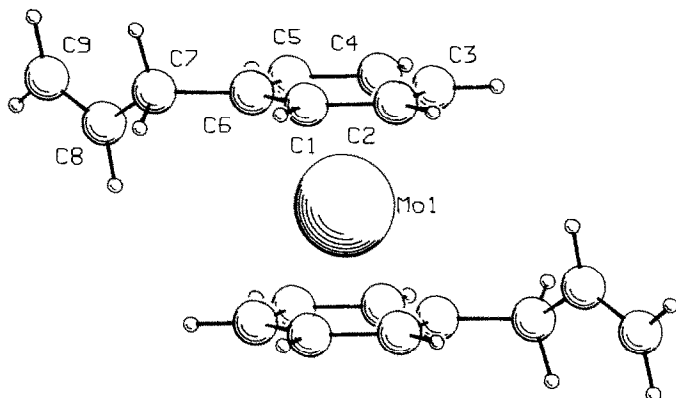


Fig. 1. Molecular structure of **3**.

The molecular structures of **3** and **14** are shown in Fig. 1 and 2 [11] with selected bond lengths and angles given in Table 2. Both molecules contain a Mo(η -arene)₂ sandwich; in **3** the central molybdenum lies on a centre of symmetry, which therefore relates the two η -allylbenzene ligands such that the allyl substituents lie *trans* to each other; in **14** the molecules are found in a crystallographic term with the silyl substituents almost *trans*, as expected from steric considerations, and the phenyl rings are slightly staggered. Molecules in both complexes are separated by Van der Waals' distances and no unusually close intermolecular contacts are observed. In **14** the closest distance between anion and cation is 2.357 Å for F(1)–H(16). In both **3** and **14** the η -C₆ rings are planar within experimental error, with C–C distances in the ranges 1.401(10)–1.419(9) Å (mean 1.411 Å) for **3**, and 1.378(14)–1.435(13) Å (mean 1.41 Å), and 1.358(16)–1.433(13) Å (mean 1.40 Å) for **14**. The mean Mo–C(ring) distances are 2.277 and 2.273 Å for **3** and **14**, respectively, and the perpendicular distances of the Mo from the mean planes defined by the benzene rings are 1.787 Å for **3**, and 1.784 and 1.789 Å for **14**, close to the values found for other bis(arene)molybdenum complexes [12,13]. The angle between the

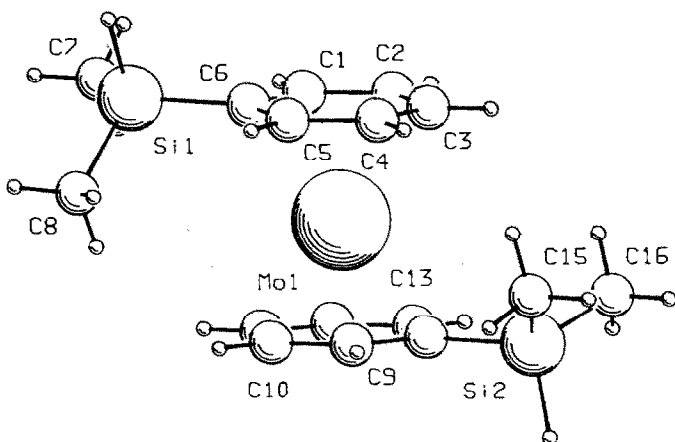


Fig. 2. Molecular structure of the cation of **14**.

TABLE 2
SELECTED BOND LENGTHS (Å) AND ANGLES (°)

For 3:			
Mo(1)–C(1)	2.271(6)		
Mo(1)–C(2)	2.264(6)		
Mo(1)–C(3)	2.279(6)		
Mo(1)–C(4)	2.275(6)		
Mo(1)–C(5)	2.280(6)		
Mo(1)–C(6)	2.290(6)		
C(1)–C(2)	1.401(10)	C(6)–C(1)–C(2)	121.1(7)
C(1)–C(6)	1.411(10)	C(1)–C(2)–C(3)	120.6(7)
C(2)–C(3)	1.409(11)	C(2)–C(3)–C(4)	118.8(7)
C(3)–C(4)	1.419(9)	C(3)–C(4)–C(5)	120.4(6)
C(4)–C(5)	1.410(9)	C(4)–C(5)–C(6)	120.5(6)
C(5)–C(6)	1.416(9)	C(5)–C(6)–C(1)	118.6(6)
C(6)–C(7)	1.521(9)	C(1)–C(6)–C(7)	120.4(6)
C(7)–C(8)	1.482(10)	C(5)–C(6)–C(7)	121.0(6)
C(8)–C(9)	1.303(11)	C(6)–C(7)–C(8)	115.2(6)
		C(7)–C(8)–C(9)	125.3(9)
For 14:			
Mo(1)–C(1)	2.272(8)	Mo(1)–C(9)	2.248(9)
Mo(1)–C(2)	2.268(9)	Mo(1)–C(10)	2.268(8)
Mo(1)–C(3)	2.268(8)	Mo(1)–C(11)	2.290(9)
Mo(1)–C(4)	2.266(8)	Mo(1)–C(12)	2.277(8)
Mo(1)–C(5)	2.270(8)	Mo(1)–C(13)	2.274(8)
Mo(1)–C(6)	2.299(8)	Mo(1)–C(14)	2.281(8)
Si(1)–C(6)	1.871(10)	Si(2)–C(14)	1.866(11)
Si(1)–C(7)	1.856(12)	Si(2)–C(15)	1.847(13)
Si(1)–C(8)	1.858(12)	Si(2)–C(16)	1.849(12)
Si(1)–H(23)	1.50(2)	Si(2)–H(24)	1.50(2)
C(1)–C(2)	1.419(14)	C(9)–C(10)	1.397(15)
C(1)–C(6)	1.435(13)	C(9)–C(14)	1.419(14)
C(2)–C(3)	1.384(15)	C(10)–C(11)	1.399(15)
C(3)–C(4)	1.378(14)	C(11)–C(12)	1.358(16)
C(4)–C(5)	1.422(14)	C(12)–C(13)	1.405(15)
C(5)–C(6)	1.420(13)	C(13)–C(14)	1.433(13)
B(1)–F(1)	1.373(8)		
B(1)–F(2)	1.384(7)		
B(1)–F(3)	1.382(8)		
B(1)–F(4)	1.378(7)		
C(6)–Si(1)–C(7)	110.0(6)	C(14)–Si(2)–C(15)	110.3(6)
C(6)–Si(1)–C(8)	111.6(6)	C(14)–Si(2)–C(16)	109.4(6)
C(7)–Si(1)–C(8)	113.0(8)	C(15)–Si(2)–C(16)	113.9(8)
C(6)–Si(1)–H(23)	103.9(5)	C(14)–Si(2)–H(24)	104.4(5)
C(7)–Si(1)–H(23)	109.0(5)	C(15)–Si(2)–H(24)	109.2(5)
C(8)–Si(1)–H(23)	108.9(5)	C(16)–Si(2)–H(24)	109.2(5)
C(6)–C(1)–C(2)	120.7(9)	C(14)–C(9)–C(10)	121.5(10)
C(1)–C(2)–C(3)	120.3(10)	C(9)–C(10)–C(11)	120.5(10)
C(2)–C(3)–C(4)	120.5(10)	C(10)–C(11)–C(12)	119.4(10)
C(3)–C(4)–C(5)	120.9(9)	C(11)–C(12)–C(13)	121.8(10)
C(4)–C(5)–C(6)	120.5(9)	C(12)–C(13)–C(14)	120.4(9)
C(1)–C(6)–Si(1)	123.1(7)	C(9)–C(14)–Si(2)	120.9(8)
C(5)–C(6)–Si(1)	119.6(8)	C(13)–C(14)–Si(2)	122.7(7)
C(5)–C(6)–C(1)	117.2(9)	C(13)–C(14)–C(9)	116.3(9)

TABLE 2 (continued)

F(2)–B(1)–F(1)	109.3(4)
F(3)–B(1)–F(1)	109.8(4)
F(3)–B(1)–F(2)	109.7(4)
F(4)–B(1)–F(1)	108.9(4)
F(4)–B(1)–F(2)	109.4(4)
F(4)–B(1)–F(3)	109.7(4)

two phenyl rings in **14** is 176.8° . In both compounds the substituent atom attached to the phenyl ring is found to be out of the plane defined by the ring and away from the molybdenum atom by 0.06 Å for C(7) in **3**, and 0.11 and 0.05 Å for Si(1) and Si(2), respectively, in **14**. Such distortions appear to be common for other substituted benzenes bonded to molybdenum, and have been attributed to changes in the molecular orbitals caused by ligand–metal bonding [14,15]. The allyl groups of **3** point away from the molybdenum, with the torsion angle C(6)–C(7)–C(8)–C(9) of 120.5° .

Attempts to add the Si–H bond of **13** across acetylene using hexachloroplatinic acid as a catalyst led to extensive decomposition, and yielded only a very small yield of a green solid, for which the mass spectrum gave a highest set of bands corresponding to the expected product, namely, $\text{Mo}(\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{CH}=\text{CH}_2)_2$ (**15**). Despite the large excess of acetylene present in the reaction mixture, the major product is an oligomer resulting from further reaction of **15** with **13** to give a polymer with repeat unit $\{\text{SiMe}_2\eta\text{-C}_6\text{H}_5\text{-Mo-}\eta\text{-C}_6\text{H}_5\text{SiMe}_2\text{CH}_2\text{CH}_2\}$ - (**16**) and presumably (and as supported by a weak band at 970 cm^{-1} in the infrared spectrum) vinylic end groups. The NMR spectrum of **16** shows three broad resonances at δ 4.75, 4.64 and 4.57 ppm (2/4/4), for the *para*, *meta* and *ortho* protons of the η -arene rings respectively. The Si-methylene protons appear as a four proton signal at δ 0.81 ppm, while the twelve Si-methyl protons resonate at δ 0.21 ppm. Very small yields of **15** could also be isolated from the reaction between **8** and $\text{ClSiMe}_2(\text{CH}=\text{CH}_2)$.

Polymerisation studies

The polymerisation of some organometallic monomers is impeded by their tendency to react with the initiators employed. Examples of this problem are found in the oxidation of vinylferrocene by peroxides, and the instability of (η -styrene)tricarboxylchromium in the presence of acids [16]. The initiation modes available for the homopolymerisation of the new organomolybdenum monomers, di- η -styrenemolybdenum (**5**), bis(η -allylbenzene)molybdenum (**3**) and bis(η -styrylbenzene)molybdenum (**6**), are likely to be severely restricted as a result of the electron richness and ease of oxidation of the compounds. Thus, cationic initiation was ruled out owing to the instantaneous oxidation of the bis- η -arene-molybdenum moiety by acids. Anionic initiation in the presence of alkyllithium reagents was not attempted in view of poor results obtained in the related ferrocene systems.

Since vinylferrocene was successfully polymerised in the presence of halogenated solvents, the same reactions were tried on di- η -styrenemolybdenum, bis(η -allylbenzene)molybdenum and bis(η -styrylbenzene)molybdenum. However, the organomolybdenum compounds decomposed rapidly in chloroform.

Polymerisation by photolysis in benzene was also investigated. Bis(η -styrylbenzene)molybdenum proved stable to prolonged irradiation. Di- η -styrenemolybdenum liberated a small amount of free styrene, and formed a trace of ethylbenzene. There was photochemical reaction analogous to that observed by Nesmeyanov for η -styrenetricarbonylchromium [17].

The photolysis of bis(η -allylbenzene)molybdenum led to a slow reaction and liberation of allylbenzene and 1-propenylbenzene (cq. 1/1, NMR). However, di- η -styrenemolybdenum could be polymerised at 60°C in benzene, using azobisisobutyronitrile (AIBN) as initiator. The monomer, solvent and azo compound were extensively purified prior to polymerisation. Conversion of 76% to polymer was attained in a 36 h reaction and with a relatively high initiator concentration. Some decomposition of the monomer was observed under these conditions.

The polymer was purified by repeated precipitation from a small volume of benzene by addition to a large volume of rapidly stirring petroleum ether. A dull green solid was isolated. This colour change supports the proposal that the orange colour of the monomer results from the conjugation effect of the arene ring and the vinylic bond. Once the unsaturated functionality is removed, the colour commonly observed for bis- η -arene-molybdenum(0) compounds, green, returns.

Poly{di- η -styrenemolybdenum} is readily soluble in benzene, and the ^1H NMR spectrum shows the absence of the three vinylic proton resonances, observed at δ 6.11, 5.22 and 4.92 ppm in the spectrum of the monomer. There is also a broadening of the aromatic resonances (δ 4.2-5.2 ppm), and the appearance of a new broad signal at δ 1-2 ppm. A further weak broad band is observed at δ 7.0 ppm, consistent with the presence of phenyl groups which are not bonded to molybdenum in the polymer chains. We assume that this results from some decomposition of the monomer under the polymerisation conditions. The infrared spectrum shows no bands assignable to C=C double bonds of the monomer.

Two conformations can be envisaged for poly{di- η -styrenemolybdenum}. The first involves polymerisation through one functional group, with unreacted vinyl groups remaining pendant to the polymer chain. These vinyl groups may be consumed partly by crosslinking reactions, but this would be expected to be accompanied by a sharp decrease in solubility.

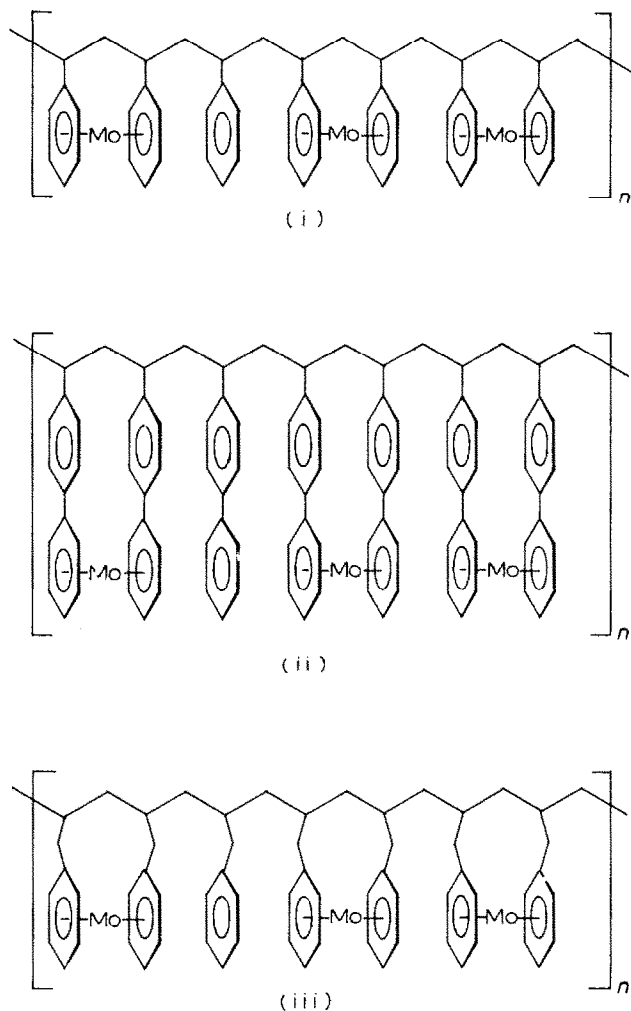
The second conformation results from an alternating intramolecular-intermolecular propagation step, to give a structure similar to that obtained in the free radical polymerisation of 1,1'-divinylferrocene [18].

The absence of unreacted vinyl groups in the NMR spectrum, and the high solubility of poly{bis- η -styrenemolybdenum} strongly support the structure for poly(bis- η -styrene)molybdenum shown in Scheme 4.

The presence of a small amount of styrene means that this macromolecule is not a true homopolymer but a copolymer of styrene and di- η -styrenemolybdenum.

Bis(η -styrylbenzene)molybdenum (**6**) was also polymerised by AIBN at 60°C giving 81% conversion after 36 h. A yellow-brown polymeric powder precipitated during the reaction. Purification was carried out by repeated precipitation from tetrahydrofuran extracts of the product by addition of petroleum ether.

The ^1H NMR spectrum of the polymer showed the absence of the sharp vinyl resonances present in the spectrum of **6**. There was a broad band at δ 1-2 ppm. A broad signal at δ -7 ppm may be assigned to the presence in the polymer of incorporated uncoordinated 4-vinylbiphenyl groups. Relative intensity data suggest



SCHEME 4. Representations of the structures proposed for the polymers formed: (i) from **5**, (ii) from **6**, and (iii) from **3**; it is presumed that the metal-free groups are randomly distributed along the polymer chain.

the ratio of units of **6** to 4-vinyldiphenyl in the polymer to be ca. 5/1, respectively. We presume free 4-vinyldiphenyl is formed from decomposition of **6** during the polymerisation reaction. The absence of substantial amounts of C=C groups in the polymer is supported by the infrared spectrum. Thus the data for the polymer formed from bis(η -styrylbenzene)molybdenum are consistent with a cyclic ladder structure in which is incorporated 4-styrylbenzene (Scheme 4).

Bis(η -allylbenzene)molybdenum (**3**) in benzene undergoes polymerisation in the presence of AIBN, but at a slower rate than for **5** giving a 58% yield after 60 h at 70°C. The poly{bis(η -allylbenzene)molybdenum} is green-brown and soluble in benzene. The proton NMR and infrared spectra again provide evidence for both cyclopolymerisation and the presence of uncoordinated allylbenzene in the polymer chain.

A molecular weight determination of poly{bis(η -allylbenzene)molybdenum} was carried out by vapour phase osmometry. A value of \bar{M}_n 11000 g/mole was obtained, which corresponds to a number average degree of polymerisation of \bar{X}_n 33 ± 10 .

In conclusion, we have described new routes to the synthesis of 1,1'-disubstituted bis- η -arene-molybdenum compounds via bis(η -chlorobenzene)molybdenum or a 1,1'-dilithiobenzenemolybdenum system as precursors. The bis- η -arene-vinyl monomers undergo radical induced polymerisation together with loss of the organic ligand and partial inclusion on the resulting polymers. In view of the inhomogeneous nature of the polymers detailed physical properties were not investigated.

Experimental

All manipulations were carried out in an inert atmosphere box, or on a conventional vacuum line, using standard Schlenk tube techniques under an atmosphere of argon. Argon was purified by scrubbing on a drying column containing activated molecular sieves and BTS catalyst.

Solvents were dried and purified by prolonged reflux over suitable drying agents, followed by distillation under an atmosphere of dinitrogen. Benzene, tetrahydrofuran, petroleum ether (66–80°C) and cyclohexane were dried over potassium; toluene and petroleum ether (100–120°C) were dried over molten sodium; diethyl ether and petroleum ether (30–40°C) were dried over Na/K alloy. NMR solvents were kept over the same drying agents or activated molecular sieves, and freshly distilled before use. Elemental analyses were obtained from the microanalytical laboratory of this laboratory, or from Alfred Bernhardt Ltd., Germany.

Infrared spectra were recorded on Pye–Umicam SP2000 and Perkin–Elmer 983 spectrophotometers as mulls. NMR spectra were recorded on the following instruments: ^1H NMR, 60 MHz JNM PMX-60, 300 MHz Bruker WH-300, ^{13}C NMR, 62.8 MHz AM 250. Visible and UV spectra were recorded on a Perkin–Elmer 552 spectrophotometer, and mass spectra on an AEI 902 mass spectrometer. Molecular weight determinations were carried out on a Knauer Vapour Pressure Osmometer Model No. 11.00.

Bis(η -chlorobenzene)molybdenum (I)

The synthesis of bis(η -chlorobenzene)molybdenum was carried out using the published method described elsewhere [19,20]. The reaction chamber was a glass belljar. In a typical experiment molybdenum atoms (5.30 g), vaporized from a pre-melted ingot (28.54 g), were co-condensed with a large excess of chlorobenzene (180 cm³) over 4 h. The power used to generate the metal atoms was ca. 3.0 kW. The co-condensate of molybdenum atoms with chlorobenzene, initially orange, gradually became dark red. After warming to roomtemperature the reaction mixture was a dull green. The reaction mixture was washed out of the machine with tetrahydrofuran (600 cm³) and filtered through Celite. The solvent and excess ligand were then removed under reduced pressure leaving a dark green solid. Extraction of the product with hot toluene (450 cm³) gave a dark green turquoise solution which was filtered on a Celite bed, concentrated (to 200 cm³) and cooled to –78°C. Dark green plates separated which were washed with cold petroleum ether (40–60°C: 3 \times 20 cm³) and dried in vacuo. Further concentration of the supernatant resulted in more product. The combined yield was 4.2 g, 23.7% (calculated on the metal leaving the furnace).

A second, red-brown material was observed during the preparation but this was not investigated. The yields of **1** varied, for unknown reasons, between 9–24%, and the lower yields were accompanied by an increased yield of the red material.

Bis(η -toluene)molybdenum (2)

A dark green solution of bis(η -chlorobenzene)molybdenum (250 mg, 0.78 mmol) in tetrahydrofuran (70 cm³) was treated with methylmagnesium chloride (6.0 cm³ of 1.0 M, 6.0 mmol) in diethyl ether at room temperature. The reaction mixture was protected from light and left for 5 d. The solution gradually lightened to yellow-green. The volatile components were removed under reduced pressure, leaving a sticky brownish solid behind. The product was extracted with petroleum ether (40–60°C, 150 cm³). The green extract was filtered, concentrated and cooled to –78°C giving green crystals. These were collected and dried in vacuo. Yield: ca. 90 mg, 41%.

Bis(η -allylbenzene)molybdenum (3)

Bis(η -chlorobenzene)molybdenum (1.0 g, 3.12 mmol) in tetrahydrofuran (200 cm³) was added at room temperature to allylmagnesium chloride (40 cm³ of 0.6 M solution, 24.0 mmol) in tetrahydrofuran. The reaction vessel was covered in aluminium foil and kept at room temperature for 5 d during which time the solution lightened to yellow-green. The solvent was removed under reduced pressure and a brownish oily solid was obtained. After drying in vacuo, the product was extracted with petroleum ether (200 cm³, 40–60°C). The mixture was filtered and the solvent was removed under reduced pressure. The product was then redissolved in petroleum ether (30–40°C), the solution filtered and concentrated to ca. 50 cm³. On cooling to –78°C, fine green needle crystals separated, which were collected and dried in vacuo. A second crop of crystals was obtained from the mother liquor. Yield of **3**: 396 mg, 38%.

(η -Benzene)(η -ethylbenzene)molybdenum (4)

Bis(η -chlorobenzene)molybdenum (980 mg, 3.05 mmol) in tetrahydrofuran (200 cm³) was added to a freshly prepared 1 M solution of ethylmagnesium chloride in diethyl ether (20 cm³, 20 mmol) at –30°C. The reaction mixture was protected from light and kept at room temperature for 5 d. The solution changed rapidly from green to dark red. After removal of the volatile components under reduced pressure, the residual red sticky solid was thoroughly dried in vacuo. The product was then extracted with vigorously stirred petroleum ether (40–60°C, 250 cm³). The extract was filtered and the yellow-green filtrate was concentrated to dryness giving a bright green solid containing a trace of red material. A second similar extraction was carried out giving a lighter coloured filtrate which was combined with the first product. The red material did not redissolve. The green solution was filtered and concentrated to about 20 cm³, then cooled to –78°C. Green crystals formed within a few hours. The supernatant was decanted at –78°C and the crystals dried in vacuo. Alternatively, the product was purified by sublimation onto a liquid dinitrogen cooled probe, and subsequently crystallized from petroleum ether. Yield: 260 mg (30.4%). After extracting the original residue twice with petroleum ether, the excess Grignard reagent was destroyed by slow addition of about 80 cm³ of absolute alcohol. This was then removed in vacuo and addition of toluene (200 cm³) yielded a yellow-red solution. This was filtered and taken down to dryness. A pale yellow

solid was obtained, and this was washed twice with 100 cm³ distilled water and extracted with toluene (150 cm³). The green solution was dried over MgSO₄, and after cooling to -30°C gave green crystals. These were recrystallized from toluene, washed with cold petroleum ether (40-60°C) and dried in vacuo. Yield: 300 mg.

Bis(η-styrene)molybdenum (5)

Bis(η-chlorobenzene)molybdenum (1.7 g, 5.30 mmol) in tetrahydrofuran (340 cm³) was added to vinylmagnesium bromide (12.1 cm³ of a 1.3 M solution, 15.90 mmol) in tetrahydrofuran at -30°C. The mixture was allowed to warm to room temperature and was kept in the dark for 7 d. During this period the solution gradually changed to dark red. The volatile components were removed under reduced pressure, leaving a reddish oily residue. This was heated to about 60°C under vacuum for 2 h, and dried into a sticky solid. The product was then extracted with petroleum ether (30 cm³, 40-60°C). The bright orange extract was filtered and reduced to dryness under vacuum. The product was redissolved in petroleum ether (150 cm³, 40-60°C) and filtered free of the residual white material. The filtrate was concentrated to about 30 cm³ and cooled to -80°C. Orange platelet crystals deposited. The supernatant was decanted and more product was obtained from this after concentration and further cooling. The crystals were dried in vacuo. Yield: 557 mg, 34.6%. After the orange material had been extracted with petroleum ether, the vinylmagnesium bromide in the brown residue was destroyed by dropwise addition of water. The mixture was left to settle and the supernatant liquor was decanted. The residue was further washed with distilled water (2 × 200 cm³). After decantation, the residue was dried at 60°C in vacuo.

Addition of toluene (200 cm³) afforded a yellow-red solution which was dried over magnesium sulfate. The solvent was removed under reduced pressure giving a dark red oil. This was distilled in vacuo at 60°C onto a probe (at 77 K) giving a green sublimate. The sublimate was crystallized from toluene at -30°C giving green crystals which were washed with cold petroleum ether and dried in vacuo. The ¹H NMR data showed the product to be a mixture of Mo(η-C₆H₆)₂ and 4. Yield: 300 mg.

Bis(η-(4-vinylphenyl)benzene)molybdenum (6)

4-Chlorostyrene (22.0 g, 0.16 mol) was added slowly to magnesium turnings (4.82 g, 0.2 mol) in tetrahydrofuran (250 cm³) giving the Grignard reagent, 4-vinylphenylmagnesium chloride. Bis(η-chlorobenzene)molybdenum (1.0 g, 3.12 mmol) in tetrahydrofuran (200 cm³) at -20°C was treated with 4-vinylphenylmagnesium chloride in tetrahydrofuran (27.4 cm³, 15.58 mmol). After warming to room temperature, the dull green reaction mixture was carefully sealed, protected from light and left for one week. The solution gradually became orange-red and showed a small amount of flocculant white precipitate. The volatile components were removed under reduced pressure, leaving an oily reddish solid. After drying for several hours in vacuo, petroleum ether (250 cm³, 60-80°C) was added. The pale orange extract was filtered and the residue was further extracted with toluene (250 cm³), giving a deep orange-red solution. After filtration and cooling to -80°C dark red crystals separated. These were washed with petroleum ether (40-60°C) (3 × 20 cm³) and dried in vacuo. Yield: 1.11 g, 78%.

Bis(η-lithiobenzene)molybdenum system (8)

Reaction of di-η-benzenemolybdenum with n-butyllithium / N,N,N',N'-tetramethylethylenediamine. In a typical reaction an equimolar mixture of BuⁿLi and TMEDA was prepared as follows: BuⁿLi (9.0 mmol; 5.6 cm³ of a 1.6 M stock solution in hexane) in cyclohexane (30 cm³) was treated with dried and freshly distilled TMEDA (1.3 cm³), causing the solution to change from colourless to pale yellow. A suspension of di-η-benzenemolybdenum (454 mg, 1.8 mmol) in cyclohexane (100 cm³) was added to the pale yellow solution. No immediate reaction was observed and the mixture was warmed to 50°C and stirred for 2.5 h. During this period the solution changed from green to dark red, with the formation of a brown precipitate of **8** during later stages of the reaction.

For all subsequent preparations of the brown precipitate **8** a molar ratio of di-η-benzenemolybdenum/BuⁿLi · TMEDA of 1/5 was used.

Bis(η-monodeuteriobenzene)molybdenum (9)

The brown suspension **8** was treated with a dropwise addition of D₂O (3 cm³) at room temperature. An immediate colour change to green was observed and some heat was generated. The volatile components were removed under reduced pressure. After removal of the last traces of TMEDA at 60°C under vacuum, the product was sublimed at 70°C and 10⁻³ torr giving a green sublimate which the infrared and mass spectra showed to be Mo(η-C₆H₅D)₂. Yield: > 90% (*m/e*, ⁹⁸Mo: 256 [MoC₁₂H₁₀D₂]⁺).

Bis(η-trimethylsilylbenzene)molybdenum (10)

The brown suspension of bis(η-lithiobenzene)molybdenum (1.8 mmol) in cyclohexane (100 cm³) at 0°C was added to a solution of dried and freshly distilled chlorotrimethylsilane (2.3 cm³, 18 mmol) in cyclohexane (30 cm³) at 0°C. The mixture was warmed to room temperature and stirred for 1 h, during which it changed to yellow-green. Water (60 cm³) was added to wash out the TMEDA and lithium salts. The resulting green cyclohexane layer was decanted and solvent was removed under reduced pressure. The residue was washed with water (2 × 10 cm³), dried in vacuo and the product was extracted with petroleum ether (100 cm³, 60–80°C). After filtration through Celite, the solution was concentrated and cooled to –78°C for 12 h giving green crystals. These were collected and dried in vacuo. Yield: 210 mg, 29%. Comparison of the NMR, infrared and mass spectral data with that of an authentic sample showed the product to be bis(η-trimethylsilylbenzene)molybdenum.

Bis(η-chlorodimethylsilylbenzene)molybdenum (11) and cyclo-bis(dimethyl-η-phenylsilyl ether) molybdenum (12)

A suspension of bis(η-lithiobenzene)molybdenum (2.62 mmol) in cyclohexane (100 cm³), prepared as described above, was added during 1 h to an excess (26.2 mmol) of dried and freshly distilled dichlorodimethylsilane, with stirring, at 0°C. The reaction mixture was warmed to room temperature and left for 1 h. During this time the solution turned green and insoluble material separated. The volatile components of the reaction mixture were removed under reduced pressure and the oily residue was thoroughly dried in vacuo. The residue was extracted with petroleum ether (150 cm³, 40–60°C) and the green extract was filtered, concentrated to

about 20 cm³ and cooled to -30°C. A green, very air-sensitive solid precipitated which was collected and dried in vacuo. Yield 22%. The remaining green supernatant was then carefully hydrolysed by addition of water (3 cm³) at 0°C. After 1 h at room temperature the volatile components of the hydrolysed reaction mixture were removed under reduced pressure and the residue was washed with water (10 cm³). After drying in vacuo, the green viscous oil was redissolved in petroleum ether (40–60°C), filtered, concentrated and cooled to -30°C. After ca. 5 d several large crystals appeared. These were washed with cold (-100°C) petroleum ether (40–60°C) and dried in vacuo. Yield of **12**: ca. 5%.

Bis(η-phenyldimethylsilane)molybdenum (13)

Molybdenum atoms (1.42 g) generated from a 5.32 g premelted ingot, were co-condensed with dimethylphenylsilane (50 cm³, b.p. 158°C) over a period of 4.5 h. The matrix changed from yellow through orange to dark red. After warming to room temperature the reaction mixture was washed from the reaction chamber with toluene (300 cm³) and the extract was filtered from colloidal metal on a Celite bed. The solvent was removed from the filtrate under reduced pressure. Purification was achieved by sublimation of the product followed by recrystallisation of the sublimate from petroleum ether (40–60°C) at -78°C. Yield: 1.81 g, 33.2% (based on metal evaporated from the furnace).

Bis(η-dimethylsilylbenzene)molybdenum tetrafluoroborate (14)

Bis(η-dimethylsilylbenzene)molybdenum (1.0 g, 2.86 mmol) in a 3/1 mixture toluene/diethyl ether (150 cm³) was treated with HBF₄·Et₂O (2 cm³) resulting in immediate formation of an orange precipitate. The colourless solution was decanted and the residue washed with cold diethyl ether (3 × 10 cm³). The product was purified by crystallization from diethyl ether at 0°C. The yellow, air-sensitive crystals included single crystals suitable for X-ray diffraction studies. Yield: > 90%.

Homopolymerisation of di-η-styrenemolybdenum

Di-η-styrenemolybdenum (242 mg, 0.80 mmol) and AIBN (12.1 mg), (twice recrystallized from absolute methanol) were dissolved in benzene (10 cm³), and the solution was heated in a constant-temperature bath at 60°C for 48 h. Some decomposition leading to solid material was observed. After cooling to room temperature the filtered benzene solution was added dropwise to 250 cm³ petroleum ether (40–60°C) with vigorous stirring. The precipitated polymer was isolated and then reprecipitated two more times from benzene (10 cm³) into petroleum ether (40–60°C, 250 cm³). The solution was decanted and the pale green solid dried in vacuo for 24 h at 10⁻³ torr. Yield: 184 mg, 76%.

Infrared spectrum (Nujol mull on KBr plates, cm⁻¹): 718 m, 795 s b, 812 m sh, 865 w s, 885 m, 1015 s, 1045 m b, 1090 m b, 1150 w, 1260 m, 1300 w, 3040 m sh. ¹H NMR (300 MHz in benzene^{-d₆}, (ppm)): 7.05 (b, C₆H₅), 5.1–4.2 (b, C₆H₅), 2.0–1.0 (b, CH₂ and CH).

Homopolymerisation of bis(η-4-styrylbenzene)molybdenum

The polymerisation of bis(η-4-styrylbenzene)molybdenum was carried out in the same way as described for di-η-styrenemolybdenum. Bis(η-4-styrylbenzene)-molybdenum (210 mg, 0.46 mmol) and AIBN (10.5 mg) was dissolved in benzene

(15 cm³) and heated to 60°C for 48 h. The polymer precipitated as a yellow/brown solid during the reaction. The product was purified by precipitation (2 ×) from tetrahydrofuran (10 cm³) into petroleum ether (40–60°C, 250 cm³). Yield: 170 mg, 81%.

Infrared spectrum (Nujol mull on KBr plates, cm⁻¹): 520 m, 725 m, 785 m, 825 s b, 895 m, 1040 m b, 1080 m b, 1120 m, 1150 m, 1260 m, 1300 w, 3040 m sh. ¹H NMR (300 MHz in tetrahydrofuran-*d*₈, (ppm)): 7.2 (b, C₆H₅), 5.0–4.5 (b, C₆H₅), 2.0–1.0 (b, CH₂ and CH).

Homopolymerisation of bis(η-allylbenzene)molybdenum

The homopolymerisation of bis(η-allylbenzene)molybdenum was carried out as for di-η-styrenemolybdenum. A 15% conversion to polymer was obtained after heating the reaction mixture to 60°C for 48 h (2% AIBN). The conversion increased to 58% after 60 h at 70°C (5% AIBN).

VPO molecular weight determination. \bar{M}_n 1100 g/mole (2% AIBN), \bar{X}_n 33. Infrared spectrum (Nujol mull on KBr plates, cm⁻¹): 522 m, 782 s, 810 s b, 890 m, 1005 m b, 1035 m b, 1100 w, 1210 w, 1260 m, 1405 w, 3040 m. ¹H NMR (300 MHz in benzene-*d*₆, (ppm)): 7.05 (b, C₆H₅), 5.0–4.2 (b, C₆H₅), 2.0–1.0 (b, CH₂ and CH).

Crystal data for 3. C₁₈H₂₀Mo, *M* = 332.3, monoclinic, *a* 14.853(2), *b* 6.113(3), *c* 16.019(2) Å, β 90.629(10)°, *U* 1454.3 Å³, (by least squares refinement on diffractometer angles for 25 automatically centred reflections, 38 < θ < 40°, λ 1.5418 Å), space group *C2/c*, *Z* = 4, *D*_c = 1.52 Mg m⁻³, green air-sensitive plate, crystal dimensions 0.875 × 0.30 × 0.05 mm, μ(Cu-Kα) 75.53 cm⁻¹, *F*(000) = 680.

Crystal data for 14. C₁₆H₂₄BF₄MoSi₂, *M* = 455.3, monoclinic, *a* 7.152(5), *b* 17.106(4), *c* 16.751(4) Å, β 99.68(6)°, *U* 2020.2 Å³, (by least squares refinement on diffractometer angles for 25 automatically centred reflections, 18 < θ < 28°, λ 1.5418 Å), space group *P2₁/n* (alt. *P2₁/c*, no. 14), *Z* = 4, *D*_c 1.50 Mg m⁻³, yellow needle, crystal dimensions 0.25 × 0.175 × 1.0 mm, μ(Cu-Kα) 69.39 cm⁻¹, *F*(000) = 924.

Data collection and processing: Crystals sealed under nitrogen in Lindemann glass capillaries mounted on an Enraf–Nonius CAD4 diffractometer. **3**: scan mode ω–2θ with ω scan width (0.9 + 0.14 tan θ)° and ω scan speed range 0.87–6.71° min⁻¹. 5173 reflections measured (1.0 < θ < 75.0°, ±*h*, *k*, ±*l*, two quadrants), 1496 unique (merging *R* = 0.042 after absorption correction [21] (max., min. correction 4.77, 1.01)) giving 1070 observed (*I* > 3σ(*I*)). Approx. 11% decay in intensity corrected during processing. **14** scan mode ω–2θ with ω scan width (1.05 + 0.14 tan θ)° and ω scan speed range 0.91–6.71° min⁻¹. 6093 reflections were measured (1.0 < θ < 75°, +*h*, *k*, ±*l*), 4122 unique (merging *R* = 0.029 after absorption correction (max., min. correction 1.38, 1.0)) giving 2663 observed (*I* > 3σ(*I*)). Approx. 7% decay in intensity corrected during processing

Structure analysis and refinement

The solution was by the heavy atom method. Full matrix refinement with all non-hydrogen atoms anisotropic for **3** and for **14**. Hydrogen atoms were included in calculated positions, riding on their attached carbons (overall H *U*_{iso} refined to 0.072(8) Å² for **3**; phenyl hydrogen *U*_{iso} refined to 0.09 Å², methyl hydrogen *U*_{iso} fixed at 0.12 Å² for **14**). The BF₄⁻ anion of **14** exhibited high thermal motion, but as

TABLE 3

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC/EQUIVALENT ISOTROPIC VIBRATION PARAMETERS FOR 3

Atom	x	y	z	$U_{\text{iso}}/U_{\text{equiv}}$
Mo(1)	0.0000	0.0000	0.0000	0.0338
C(1)	0.1491(4)	0.082(1)	-0.0016(5)	0.0436
C(2)	0.1172(4)	0.120(1)	0.0791(4)	0.0473
C(3)	0.0741(5)	-0.047(1)	0.1240(4)	0.0451
C(4)	0.0631(4)	-0.255(1)	0.0860(4)	0.0456
C(5)	0.0950(4)	-0.293(1)	0.0047(4)	0.0401
C(6)	0.1384(4)	-0.124(1)	-0.0401(4)	0.0405
C(7)	0.1766(5)	-0.166(1)	-0.1264(5)	0.0550
C(8)	0.1261(5)	-0.327(1)	-0.1780(5)	0.0591
C(9)	0.1590(9)	-0.508(1)	-0.2079(6)	0.0772
H(1)	0.1799	0.2024	-0.0323	0.072(8)
H(2)	0.1250	0.2681	0.1050	0.072(8)
H(3)	0.0517	-0.0196	0.1818	0.072(8)
H(4)	0.0325	-0.3753	0.1170	0.072(8)
H(5)	0.0868	-0.4402	-0.0215	0.072(8)
H(6)	0.2397	-0.2202	-0.1193	0.072(8)
H(7)	0.1771	-0.0236	-0.1573	0.072(8)
H(8)	0.0614	-0.2937	-0.1907	0.072(8)
H(9)	0.2234	-0.5471	-0.1967	0.072(8)
H(10)	0.1199	-0.6069	-0.2420	0.072(8)

no satisfactory disordered model was found, the ion was refined anisotropically subject to soft geometrical restraints [22], as were the SiMe_2H groups. The hydrogens attached to silicon were refined with individual isotropic vibration parameters; the resulting low values suggest there may be some rotational disorder of the methyl groups and these hydrogens, but difference Fourier syntheses did not reveal positions for any partially occupied carbons. Corrections were made for anomalous dispersion [23] and isotropic extinction [24]. Chebyshev weighting schemes [25] were applied where $w = 1/\sum_{r=1}^n A_r T_r(X)$ with coefficients, A_r , for **3** 103.1 and 102.8; for **14** 414.3, 607.4, 237.8 and 42.4 to give satisfactory agreement analyses. Final R and R_w values* are 5.06 and 6.49% for **3** and 6.60 and 8.82% for **14**. Solution and refinement used the Oxford CRYSTALS package [26] on the VAX 11/750 computer in the Chemical Crystallography Laboratory, Oxford University. Scattering factors were taken from International Tables for X-ray Crystallography [27]. Fractional atomic coordinates and isotropic/equivalent isotropic vibration parameters for **3** and **14** are given in Tables 3 and 4 respectively**.

$$* R = \frac{\sum \|F_0\| - \|F_c\|}{\sum \|F_0\|}, R_w = \sqrt{\frac{\sum w(\|F_0\| - \|F_c\|)^2}{\sum w(\|F_0\|)^2}}$$

** Full tables of bond lengths and angles, thermal vibration parameters, least squares planes and observed and calculated structure factors are available from the authors.

TABLE 4

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC/EQUIVALENT ISOTROPIC VIBRATION PARAMETERS FOR **14**

Atom	x/a	y/b	z/c	$U_{\text{iso}}/U_{\text{equiv}}$
Mo(1)	0.00066(8)	0.13242(4)	0.36228(4)	0.0474
Si(1)	-0.1721(5)	0.2979(2)	0.4843(2)	0.0827
Si(2)	0.1082(5)	0.0127(2)	0.1871(2)	0.0902
C(1)	-0.175(1)	0.1288(6)	0.4632(6)	0.0622
C(2)	-0.212(1)	0.0596(6)	0.4163(7)	0.0701
C(3)	-0.274(1)	0.0642(7)	0.3337(7)	0.0627
C(4)	-0.303(1)	0.1358(7)	0.2960(6)	0.0625
C(5)	-0.267(1)	0.2064(6)	0.3408(6)	0.0619
C(6)	-0.203(1)	0.2043(6)	0.4257(6)	0.0594
C(7)	-0.087(2)	0.2771(9)	0.5932(7)	0.1074
C(8)	-0.018(2)	0.3676(7)	0.441(1)	0.1263
C(9)	0.169(1)	0.1623(6)	0.2644(6)	0.0671
C(10)	0.227(1)	0.2132(6)	0.3290(7)	0.0666
C(11)	0.295(1)	0.1841(7)	0.4065(7)	0.0668
C(12)	0.306(1)	0.1056(7)	0.4183(7)	0.0645
C(13)	0.251(1)	0.0524(6)	0.3548(6)	0.0625
C(14)	0.179(1)	0.0800(6)	0.2748(6)	0.0605
C(15)	-0.091(2)	0.055(1)	0.1157(8)	0.1305
C(16)	0.059(2)	-0.0854(6)	0.225(1)	0.1150
B(1)	0.5999(9)	-0.1539(4)	0.3575(4)	0.0872
F(1)	0.465(1)	-0.1144(5)	0.3911(6)	0.1425
F(2)	0.596(1)	-0.2322(4)	0.3780(6)	0.1409
F(3)	0.563(1)	-0.1458(6)	0.2743(5)	0.1624
F(4)	0.776(1)	-0.1232(4)	0.3875(5)	0.1225
H(1)	-0.1307	0.1245	0.5229	0.09(1)
H(2)	-0.1936	0.0074	0.4434	0.09(1)
H(3)	-0.2990	0.0152	0.3012	0.09(1)
H(4)	-0.3494	0.1379	0.2363	0.09(1)
H(5)	-0.2856	0.2577	0.3120	0.09(1)
H(6)	-0.1821	0.2439	0.6149	0.1200
H(7)	0.0374	0.2492	0.6000	0.1200
H(8)	-0.0714	0.3278	0.6234	0.1200
H(9)	0.1105	0.3440	0.4411	0.1200
H(10)	-0.0767	0.3801	0.3837	0.1200
H(11)	-0.0043	0.4167	0.4736	0.1200
H(12)	0.1197	0.1842	0.2096	0.09(1)
H(13)	0.2195	0.2710	0.3198	0.09(1)
H(14)	0.3346	0.2208	0.4527	0.09(1)
H(15)	0.3564	0.0851	0.4737	0.09(1)
H(16)	0.2629	-0.0051	0.3653	0.09(1)
H(17)	-0.1278	0.0180	0.0694	0.1200
H(18)	-0.2022	0.0636	0.1437	0.1200
H(19)	-0.0506	0.1059	0.0948	0.1200
H(20)	0.0211	-0.1211	0.1776	0.1200
H(21)	0.1776	-0.1053	0.2589	0.1200
H(22)	-0.0450	-0.0836	0.2581	0.1200
H(23)	-0.369(3)	0.3310(9)	0.4746(9)	0.030(9)
H(24)	0.280(3)	0.0086(9)	0.147(1)	0.06(1)

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