Bis(η-cyclopentadienyl)molybdenum Chemistry: Synthesis and Reactions of Ring-functionalised Compounds

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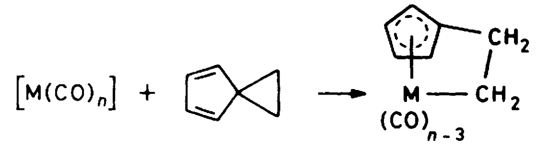
Co-condensation of molybdenum atoms with spiro[2.4]hepta-4,6-diene gives the compound $[Mo(\eta\text{-}C_5H_4CH_2CH_2)_2]$. Treatment of $[Mo(\eta\text{-}C_5H_4CH_2CH_2)_2]$ with iodine gives the tetraiodo-derivative $[Mo(\eta\text{-}C_5H_4CH_2CH_2I)_2I_2]$ (2). The tetrabromo- and tetrachloro-analogues of (2) are similarly prepared. The iodo-groups of (2) can be exchanged with the SPh radical to give $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)_2(SPh)_2]$ which reacts with hydrogen chloride to form the compound $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)_2Cl_2]$ (4). Abstraction of a halide ion from (4) gives $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)(\eta\text{-}C_5H_4CH_2CH_2SPh)Cl]PF_6$. Complex (2) reacts with dimethylamine to give $[Mo(\eta\text{-}C_5H_4CH_2CH_2NMe_2)(\eta\text{-}C_5H_4CH_2CH_2NMe_2H)H][PF_6]_2$.

Although there is an extensive and interesting chemistry of bent bis(η-cyclopentadienyl) derivatives of the transition metals there have been relatively few studies of compounds in this class where there are reactive functionalities attached to the η-cyclopentadienyl rings. The main reason for this lies in the choice of a suitable synthetic route since the common methods of synthesis of bis(η-cyclopentadienyl) derivatives require conditions where the presence of a reactive functional group, for example one attached to a substituted cyclopentadienide anion, would interfere with the reaction. We wished to synthesise ring-functionalised cyclopentadienyl derivatives since many applications for such compounds can be envisaged.[1,2]

Eilbracht has shown the reaction (1) to be quite general for the synthesis of η-cyclopentadienyl transition-metal carbonyl compounds in which there is a hydrocarbon chain bridging the metal and η-cyclopentadienyl group.



(1)

η-Cyclopentadienyl transition-metal compounds which have a bridging hydrocarbon system of this type, *i.e.* $M\{\eta\text{-}C_5H_4(CH_2)_xCH_2\}$, have been dubbed 'tucked-in' compounds[3] and for convenience we will use this phrase.

In this paper we have utilised the ability of spiro[2.4]hepta-4,6-diene to form the tucked-in group $M(\eta^5\text{-}C_5H_4CH_2CH_2)$ as a route to ring-functionalised derivatives of bis(η-cyclopentadienyl)molybdenum compounds. Part of this work has been briefly communicated.[4]

Results

Spiro[2.4]hepta-4,6-diene was synthesised using a modification of the previously described reaction procedure[5] and typically up to 500 g were synthesised in a single one-step reaction.

Using the metal-vapour synthesis apparatus described elsewhere,[6,7] molybdenum atoms were co-condensed with spiro[2.4]hepta-4,6-diene and the compound $[Mo(\eta\text{-}C_5H_4CH_2CH_2)_2]$ (1) could be isolated from the reaction mixture in 50—60% yield. In a typical run 6.0 g of molybdenum atoms were added to 150 cm^3 of spiro[2.4]hepta-4,6-diene to give 10—12 g of (1). There is a certain amount of oligomerisation of the spiro[2.4]hepta-4,6-diene during the reaction but about 40% can be recovered from the reaction mixture.

Compound (1) is moderately air sensitive and solutions in light petroleum show evidence of decomposition after a few minutes. It sublimes *in vacuo* at *ca.* 100 °C. Treatment of (1) with iodine causes a rapid reaction and black-green crystals of the tetraiodo-derivative $[Mo(\eta\text{-}C_5H_4CH_2CH_2I)_2I_2]$ (2) separate within a few minutes.

Compound (2) is slightly soluble in tetrahydrofuran and the deep green solutions show evidence for decomposition within days. Solutions in dimethyl sulphoxide decompose within hours. Both (1) and (2) may be stored for prolonged periods under dinitrogen at room temperature.

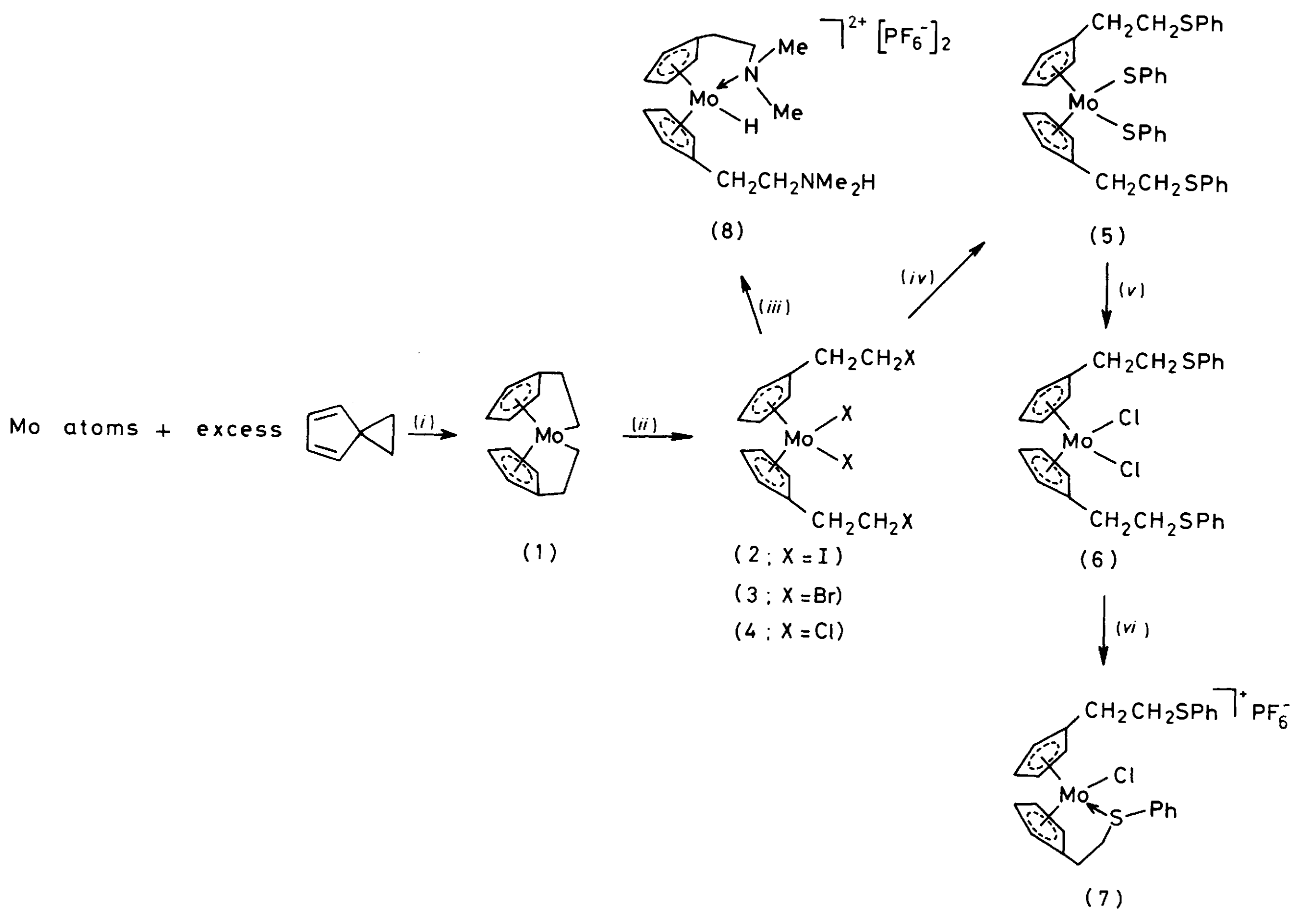
The tetrabromo-analogue of (2), namely $[Mo(\eta\text{-}C_5H_4CH_2CH_2Br)_2Br_2]$ (3), and the tetrachloro-analogue $[Mo(\eta\text{-}C_5H_4CH_2CH_2Cl)_2Cl_2]$ (4) are similarly prepared from (1) and bromine or chlorine respectively. However, (4) is obtained in higher yield from the reaction between (1) and the reagent $PhICl_2$.

When (2) is treated with NaSPh the red tetra(thiophenyl) derivative $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)_2(SPh)_2]$ (5) is formed in high yield. We have previously shown that the metal-sulphur bond in compounds of the type $[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$ (R = alkyl) readily undergo cleavage of the Mo–S bond with hydrogen chloride.[8] In accord with this, treatment of (5) with hydrogen chloride cleaves the two Mo–SPh bonds giving the dichloro-derivative $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)_2Cl_2]$ (6).

In an attempt to ascertain whether compound (6) would readily act as a ligand it was reacted with a solution of anhydrous iron(II) chloride in thf. An immediate reaction occurred giving the tucked-in compound $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)(\eta\text{-}C_5H_4CH_2CH_2SPh)Cl]PF_6$ (7).

Treatment of (2) with dimethylamine and subsequently with ammonium hexafluorophosphate gave the pink compound $[Mo(\eta\text{-}C_5H_4CH_2CH_2NMe_2)(\eta\text{-}C_5H_4CH_2CH_2NMe_2H)H][PF_6]_2$ (8).

The data characterising the compounds (1)—(8) are given in the Table. The ^{1}H n.m.r. spectra are especially diagnostic for the proposed structures and show several features of



Scheme. (*i*) −196 °C (50—60%); (*ii*) X = Cl: Cl_2 in light petroleum (b.p. 60—80 °C) for 15 min (30%) or $PhICl_2$ in thf (90%); X = Br: Br_2 in light petroleum (b.p. 60—80 °C) (60%); X = I: I_2 in thf (95%); (*iii*) $NHMe_2$ in thf at 56 °C then NH_4PF_6, (76%); (*iv*) NaSPh in ethanol, reflux for 5 h (87%); (*v*) HCl gas in CH_2Cl_2 for 1 h (83%); (*vi*) $FeCl_2$ in thf at 50 °C for 1 h (37%)

interest. The four non-equivalent ring hydrogens of the tucked-in $\overline{\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)}$ group occur as separate complex bands in all compounds. The four hydrogens of the bridging CH_2CH_2 group are also non-equivalent and each hydrogen occurs as a well-resolved multiplet analysable as a doublet of doublets of doublets. For the compounds (7) and (8) the two η-C_5H_4 groups are non-equivalent and each ring gives rise to four separately resolved multiplets.

Discussion

The yields from metal atom co-condensation reactions are rather unpredictable; however, the formation of (1) certainly proceeds very smoothly so that we were able to prepare (1) in a routine manner and on a useful laboratory scale.

The tetraiodo-compound (2) has reactive functionalities on both the metal and the η-cyclopentadienyl ligands and thus provides a useful starting point for the synthesis of other ring-functionalised derivatives.

The tetra(thiophenyl) derivatives were prepared since it was anticipated that the synthesis would proceed readily, as found. The compound (5) can be regarded as a potential tetradentate ligand *via* the sulphur atoms, as will be described elsewhere. It was anticipated that the molybdenum–sulphur bonds of (5) would be readily and selectively cleaved with hydrochloric acid enabling the generation of molybdenum–halogen bonds in (6) which can be seen to be a precursor for further metal substituted derivatives.

We were interested to discover whether (6) would be isolable and would act as a bidentate sulphur donor ligand, for example to iron(II) chloride. However, as noted there is a preferential substitution by donor sulphur onto the molybdenum centre giving (7). This reaction suggests that the tucked-in $\overline{\text{M}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{L})}$ system is not sterically demanding, indeed it is probably favoured both for reasons of entropy and enthalpy.

It seems likely that the formation of tucked-in systems such as $\overline{\text{M}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{L})}$ will give rise to substantial limitations on possible variations of reactive functionalities L on the one hand and of substituents on the metal centre on the other.

The formation of (8) clearly involves the quaternisation of the CH_2I groups and the formation of the Mo–H can be envisaged to proceed *via* hydrogen abstraction from a Mo–$NHMe_2$ moiety giving an intermediate $MoH(CH_2{=}NHMe)$ system, as shown previously in the formation of molybdenum amine hydride derivatives from the reaction between $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ and primary amines.[9] In support of this mechanism we have shown that treatment of $[Mo(\eta\text{-}C_5H_5)_2I_2]$ with dimethylamine gives hydrido-molybdenum derivatives.[10]

In conclusion, the compounds (2)—(6) clearly indicate synthetic strategies for the isolation of many ring-functionalised bis(η-cyclopentadienyl)molybdenum compounds.

Experimental

All operations were performed *in vacuo* or in an inert atmosphere. All solvents were rigorously dried before use by

Table. Analytical and spectroscopic data

		Analysis[a] (%)		
Compound	Colour	C	H	N.m.r. data[b]
(1) $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CH_2CH_2})_2]$	Red	60.3 (60.0)	5.9 (5.7)	4.71, **2**, *m* (6 lines), 4.41, **2**, *m* (6 lines), 4.07, **2**, *m* (6 lines), 3.88, **2**, *m* (6 lines), 2(η-C_5H_4); 2.81, **2**, *ddd* (*J* 3.6, 11.0, 12.6), 2.52, **2**, *ddd* (*J* 6.9, 10.7, 12.6), 2(C–CH_2); −0.37, **2**, *ddd* (*J* 5.6, 6.9, 11.0), −1.42, **2**, *ddd* (*J* 3.6, 5.6, 10.7), 2(CH_2–Mo)[c]
(2) $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CH_2CH_2I})_2\mathrm{I}_2]$	Dark green	21.3 (21.3)	2.0 (2.0)	5.49, **8**, *s,br*, 2(η-C_5H_4); 3.48, **4**, *t* (*J* 7), 2(C–CH_2); 2.91, **4**, *t* (*J* 7), 2(CH_2I)[d]
(3) $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CH_2CH_2Br})_2\mathrm{Br}_2]$	Green	28.3 (27.95)	2.65 (2.7)	5.40, **8**, *s,br*, 2(η-C_5H_4); 3.30, **4**, *t* (*J* 6.5), 2(C–CH_2); 2.79, **4**, *t* (*J* 6.5), 2(CH_2Br)[e]
(4) $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CH_2CH_2Cl})_2\mathrm{Cl}_2]$	Green	39.9 (39.8)	3.9 (3.8)	5.35, **4**, *s,br*, 5.27, **4**, *s,br*, 2(η-C_5H_4); 3.56, **4**, *t* (*J* 7), 2(C–CH_2); 2.92, **4**, *t* (*J* 7), 2(CH_2Cl)[e]
(5) $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CH_2CH_2SPh})_2(\mathrm{SPh})_2]$	Brick-red	63.5 (63.7)	5.3 (5.0)	7.5—7.0, **20**, *c*, 4(SPh); 5.32, **4**, *t* (*J* 2.5), 5.05, **4**, *t* (*J* 2.5), 2(η-C_5H_4); 3.09, **4**, *t* (*J* 6.6), 2(C–CH_2); 2.71, **4**, *t* (*J* 6.6), 2(SCH_2)[c]
(6) $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CH_2CH_2SPh})_2\mathrm{Cl}_2]$	Dark green	54.85 (54.85)	4.8 (4.6)	7.5—7.2, **10**, *c*, 2(SPh); 5.33, **4**, *t* (*J* 2.8), 5.27, **4**, *t* (*J* 2.8), 2(η-C_5H_4); 3.15, **4**, *t* (*J* 7), 2(C–CH_2); 2.71, **4**, *t* (*J* 7), 2(CH_2S)[e]
(7) $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CH_2CH_2SPh})(\eta\text{-}\mathrm{C_5H_4CH_2CH_2SPh})\mathrm{Cl}]\mathrm{PF_6}$	Bright green	46.0 (46.0)	3.7 (3.8)	7.6—7.15, **10**, *c*, 2(SPh); 6.38, **1**, *m* (2 lines), 6.27, **1**, *s,br*, 5.88, **1**, *s,br*, 5.75, **1**, *s,br*, 5.69, **1**, *m* (2 lines), 5.65, **1**, *s,vbr*, 5.48, **1**, *s,br*, 5.35, **1**, *s,br*, 2(η-C_5H_4); 4.55, **1**, *br*, 3.95, **1**, *br*, 3.25, **2**, *s,br*, 3.14, **2**, *c*, 2.64, **2**, *s,br*, 2(CH_2CH_2)[f]
(8) $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CH_2CH_2NMe_2})(\eta\text{-}\mathrm{C_5H_4CH_2CH_2NMe_2H})\mathrm{H}][\mathrm{PF_6}]_2$[g,h]	Orange-pink	32.95 (32.75)	4.5 (4.5)	6.47, **1**, *m* (5 lines), 6.24, **1**, *m* (2 lines), 5.91, **1**, *m* (4 lines), 5.69, **1**, *m* (4 lines), 4.86, **1**, *m* (4 lines), 4.67, **1**, *m* (4 lines), 4.35, **1**, *m* (3 lines), 2(η-C_5H_4); 3.66, **3**, *c*, 2.8, **1**, *c*, 2(C–CH_2); 3.16, **6**, *s*, $NHMe_2$; 2.93, **2**, *m* (6 lines) CH_2–$NHMe_2$; 2.58, **1**, *m* (4 lines), 2.54, **1**, *m* (4 lines) CH_2–NMe_2; 2.63, **3**, *s*, 2.61, **3**, *s*, Mo–NMe_2; −8.95, **1**, *s*, Mo–H[f]

[a] Calculated values are given in parentheses. [b] Given as chemical shift (δ), **relative intensity**, *multiplicity* (*J* in Hz), assignment; *m* = symmetrical multiplet, *c* = unsymmetrical multiplet, *s* = singlet, *t* = triplet, *d* = doublet. [c] In C_6D_6. [d] In C_4D_8O. [e] In $CDCl_3$. [f] In $(CD_3)_2CO$. [g] ν(Mo–H) = 1 850 cm^{-1}, ν(N–H) = 3 210 cm^{-1}. [h] N, 4.1 (4.2)%.

standard procedures. Infrared spectra were determined on Nujol mulls using a Pye Unicam SP 2000 spectrophotometer, and were calibrated with polystyrene. Proton and ^{13}C n.m.r. spectra were determined on a Bruker 300MHz instrument. Microanalyses were performed by the microanalytical laboratory of this department.

Spiro[2.4]*hepta*-4,6-*diene*.—A modification of the published method was employed.[5] A 5 l three-necked flask equipped with addition funnel, mechanical stirrer, and a dry-ice condenser was charged with sodium hydride (350 g of a 60% dispersion in mineral oil, 8.7 mol). The sodium hydride was washed with light petroleum (2 × 500 cm^3, b.p. 30—40 °C) and tetrahydrofuran (thf) (1 500 cm^3) was added. A mixture of freshly cracked and distilled cyclopentadiene (330 cm^3, 4 mol) and 1,2-dibromoethane (330 cm^3, 3.85 mol) was added dropwise (**CARE**) over 5 h. An exothermic reaction occurs with vigorous evolution of dihydrogen. After the addition was complete the reaction mixture was treated with methanol in a dropwise manner and, when the excess sodium hydride was decomposed, water (1 000 cm^3) was added. The organic layer was separated. The remaining aqueous layer was washed with light petroleum (2 × 100 cm^3, b.p. 30—40 °C). The combined organic extracts were dried over magnesium sulphate. Distillation separated the pure compound (b.p. 117 °C). The yield was 270 cm^3, 76%.

Bis[2-(1′—5′-η-*cyclopentadienediyl*)*ethyl*]*molybdenum* (1).—Molybdenum atoms (6.0 g, 62.5 mmol), generated from a molten ingot (*ca.* 25 g), were co-condensed with spiro[2.4]-hepta-4,6-diene (150 cm^3) onto the reactor wall for 4 h. The wall was cooled by liquid dinitrogen and the apparatus is described in detail elsewhere.[6,7] The mixture was allowed to warm to room temperature and was then washed from the reaction vessel with thf (1 000 cm^3). The extract was filtered through a Celite bed and then the solvent and excess of spiro-[2.4]hepta-4,6-diene were removed under reduced pressure. The residue was extracted with light petroleum (4 × 500 cm^3, b.p. 60—80 °C) giving a dark red solution which was filtered and the filtrate was concentrated to *ca.* 50 cm^3 under reduced pressure. Cooling to −20 °C and then to −78 °C gave large red crystals which were collected, washed with cold light petroleum (2 × 30 cm^3, b.p. 30—40 °C) and dried *in vacuo*. The yield was 10—12 g, 35—43 mmol, 50—60%.

Di-iodobis[η^5-(2-*iodoethyl*)*cyclopentadienyl*]*molybdenum* (2).—Iodine (5.4 g, 21.3 mmol) in thf (50 cm^3) was added to (1) (3.0 g, 10.7 mmol) in thf (50 cm^3). Immediately a purple precipitate appeared which redissolved when addition of the iodine was complete. After 5 min lustrous green-black crystals separated and after 2 h they were collected, washed with ethanol, and dried under reduced pressure (6.5 g). The mother-liquor was concentrated under reduced pressure and cooled to −78 °C giving a further 1.5 g of the crystals. The combined yield was 95%.

Dibromobis[η^5-(2-*bromoethyl*)*cyclopentadienyl*]*molybdenum* (3).—Compound (1) (0.5 g, 1.43 mmol) in light petroleum (b.p. 60—80 °C) was treated with bromine (1 cm^3, 20 mmol). A green powder immediately separated which was collected and recrystallised from acetone–toluene as green crystals, 0.64 g, 1.06 mmol, 60%.

Dichlorobis[η^5-(2-*chloroethyl*)*cyclopentadienyl*]*molybdenum* (4).—*Method A.* Compound (1) (0.5 g, 1.8 mmol) in light petroleum (b.p. 60—80 °C) was treated with chlorine gas for 15 min. A green oily solid separated. The supernatant liquor was decanted and the residue was extracted with dichloromethane (25 cm^3). The extract was chromatographed on a Florisil column made up in light petroleum (b.p. 60—80 °C). Elution with diethyl ether gave a green-brown solution which was concentrated under reduced pressure and light petroleum (b.p. 60—80 °C) was added. The resulting green powder was collected, washed with light petroleum (b.p. 30—40 °C) and dried *in vacuo*, 0.23 g, 0.55 mmol, 30%.

Method B. Compound (1) (0.4 g, 1.43 mmol) in thf (50 cm^3) was treated with $PhICl_2$ (0.8 g, 2.9 mmol) in thf (30 cm^3). The mixture was warmed to 50 °C for 1 h and the initially red solution became dark green. The solvent was removed under reduced pressure and the green residue was recrystallised from toluene–thf, 0.55 g, 1.30 mmol, 90%.

Bis[η^5-(2-*phenylthioethyl*)*cyclopentadienyl*]*bis*(*phenylthio*)*molybdenum* (5).—A solution of NaSPh was prepared by addition of sodium (1.5 g, 65.2 mmol) to thiophenol (10 g, 90 mmol) in ethanol (100 cm^3). This was added to a slurry of (2) (3.3 g, 4.2 mmol) in ethanol (100 cm^3). Refluxing for 5 h gave a red solution and then the solvent was removed under reduced pressure. The red residue was chromatographed on a Florisil column made up in light petroleum (b.p. 60—80 °C). Elution with toluene separated a broad red band which was collected and concentrated (to 50 cm^3). Light petroleum (50% cm^3, 60—80 °C) was added and the mixture was cooled to −20 °C and then to −78 °C giving dark red crystals which were collected, washed with light petroleum (b.p. 60—80 °C) and dried *in vacuo*, 2.6 g, 3.6 mmol, 87%. The compound is slightly soluble in toluene and moderately soluble in dichloromethane and thf.

Dichlorobis[η^5-(2-*phenylthioethyl*)*cyclopentadienyl*]*molybdenum* (6).—Compound (5) (1.8 g, 2.5 mmol) in dichloromethane (150 cm^3) was treated with a stream of hydrogen chloride gas for 1 h. The initially red solution slowly turned dark green. The solvent was removed under reduced pressure and the dark green residue was crystallised from dichloromethane–light petroleum (b.p. 60—80 °C) giving dark green cubic crystals, 1.2 g, 2.1 mmol, 83%.

Chloro[η^5-(2-*phenylthioethyl*)*cyclopentadienyl*][η^5-(2-*phenylthioethyl*)*cyclopentadienyl*-S)*molybdenum Hexafluorophosphate* (7).—The compound $FeCl_2{\cdot}1.5thf$[11] (0.52 g, 2.1 mmol) in thf (50 cm^3) was added to (6) (0.5 g, 0.88 mmol) in thf and the mixture was heated to 50 °C for 1 h. The solvent was removed under reduced pressure and the green residue was extracted with water (20 cm^3). The extract was filtered though Celite and excess aqueous ammonium hexafluorophosphate was added giving a flocculent green precipitate. This was collected, washed with water (2 × 10 cm^3) and dried *in vacuo*. It was then recrystallised from acetone–water as emerald green needles, 0.23 g, 0.34 mmol, 37%.

[η^5-(2-*Dimethylaminoethyl*)*cyclopentadienyl*][η^5-(2-*dimethylammonioethyl*)*cyclopentadienyl*]*hydridomolybdenum Bis*(*hexafluorophosphate*) (8).—Dimethylamine (4.5 g, 100 mmol) in thf (10 cm^3) was added to a slurry of (2) (0.6 g, 0.76 mmol) in ethanol–thf (200 cm^3 of a 1 : 1 mixture). The mixture was refluxed for 5 h giving a clear orange solution. The solvent was removed under reduced pressure and the residue was extracted with hot water (3 × 50 cm^3). The pale orange aqueous extract was filtered and an aqueous solution of potassium hexafluorophosphate was added giving a pale orange precipitate. This was collected and washed with water. Recrystallisation from acetone–light petroleum (b.p. 60—80 °C) gave orange-pink needles, 0.38 g, 0.58 mmol, 76%.

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