Thiolato-bridged η-Cycloheptatrienyl Molybdenum Complexes

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A new series of binuclear thiolato-bridged molybdenum complexes $[(\eta\text{-}C_7H_3R^1_4)Mo(\mu\text{-}SR^2)_3Mo(\eta\text{-}C_7H_3R^1_4)][BF_4]$ (R^1 = H or Me; R^2 = Et, Pr, Bu, Ph or CH_2Ph) have been prepared by treating the mixed-sandwich compounds $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_3R^1_4)][BF_4]$ (R^1 = H or Me) or $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)][BF_4]$ with the corresponding thiols R^2SH. Dynamic NMR studies reveal that all of these complexes (except for R^2 = Ph) are fluxional due to the inversion at the pyramidal sulfur centre. The activation free energy of this intramolecular process has been estimated by the coalescence temperature method. The values range from $\Delta G^\ddagger$ = 52.9 to 58.1 kJ mol^{-1} and increase in the order: $R^2 = CH_2Ph < Bu < Pr < Et$. Cyclic voltammetric studies of the binuclear compounds show that they undergo two reversible one-electron reductions and the ease of reduction is dependent on the electron-donating ability of the R^1 and R^2 groups.

There is an extensive chemistry of molybdenum compounds with sulfur ligands. Apart from their intrinsic interest, the chemistry has been developed with a view to providing insight into the mechanism of the important industrial process of hydrodesulfurisation[1] and the active site of molybdenum nitrogenase which catalyses the reduction of dinitrogen to ammonia.[2]

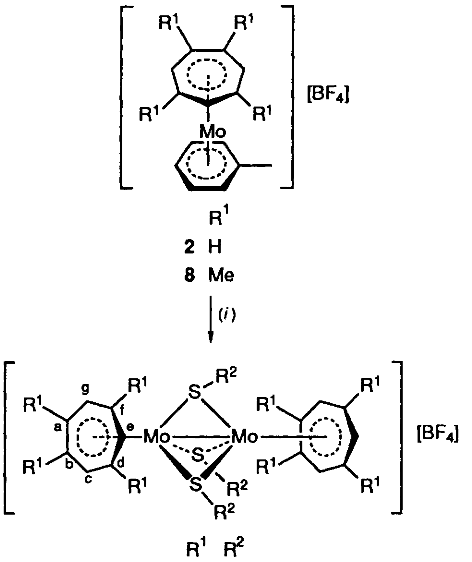
Although many thiolato-bridged complexes with a variety of co-ligands have been reported, the use of the cycloheptatrienyl moiety as supporting ligand remains relatively unexploited.[3] The relative paucity of these compounds is due primarily to the lack of synthetic routes to suitable starting materials. We have demonstrated that the compounds $[Mo(\eta\text{-}C_6H_5R)(\eta\text{-}C_7H_7)][PF_6]$ (R = H or Me) and $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** are excellent precursors to half-sandwich derivatives of the $Mo(\eta\text{-}C_7H_7)$ moiety.[4,5] Here we report the use of these compounds to prepare a new series of binuclear thiolato-bridged molybdenum compounds with cycloheptatrienyl rings.

Results and Discussion

Synthetic Studies.—Treatment of the complex $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][BF_4]$ **2** with thiols R^2SH at 80–100 °C gave the corresponding thiolato-bridged molybdenum complexes $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}SR^2)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ (R^2 = Pr^n **3**, Bu^n **4**, Ph **5**, or CH_2Ph **6**) in moderate to excellent yields (Scheme 1). When compound **2** was treated with butane-1-thiol, the reaction mixture changed from light- to dark-green over a period of 4 h. The reaction was clean giving only a small amount of side-products as monitored by ^1H NMR spectroscopy. However, the reaction of **2** with propane-1-thiol took longer (20 h) to consume all of the starting compound **2** and significant amounts of unidentified side-products were also formed. For the reaction between **2** and benzenethiol or phenylmethanethiol, the colour changed to dark green immediately.

The 1,2,4,6-tetramethylcycloheptatrienyl analogue of **5**, namely $[(\eta\text{-}C_7H_3Me_4\text{-}1,2,4,6)Mo(\mu\text{-}SPh)_3Mo(\eta\text{-}C_7H_3Me_4\text{-}1,2,4,6)][BF_4]$ **7** was prepared in excellent yield by treating the corresponding mixed-sandwich compound $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_3Me_4\text{-}1,2,4,6)][BF_4]$ **8**[6] with benzenethiol.

It was anticipated that the complex **2**, upon treatment with thiolate ions (SR^-), might give the neutral complexes $[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}SR)_3Mo(\eta^7\text{-}C_7H_7)]$. However the reaction between **2** and 1.5 equivalents of lithium thioethoxide in tetrahydrofuran (thf) gave a mixture of products from which only the salt $[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}SEt)_3Mo(\eta^7\text{-}C_7H_7)][BF_4]$ **9** was isolated, in low yield.



	R^1
2	H
8	Me

	R^1	R^2
3	H	Pr
4	H	Bu
5	H	Ph
6	H	CH_2Ph
7	Me	Ph
9	H	Et

Scheme 1 *Reagents and conditions:* (*i*) for **3**, in propane-1-thiol at 75 °C for 20 h (30%); for **4**, in butane-1-thiol at 80 °C for 4 h (70%); for **5**, in benzenethiol at 100 °C for 6 h (87%); for **6**, in phenylmethanethiol at 100 °C for 5 h (88%); for **7**, in benzenethiol at 100 °C for 5 h (91%); for **9**, LiSEt in thf at 60 °C for 3 h (26%)

An alternative route to these binuclear compounds is through the paramagnetic salt $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)][BF_4]$ **10** which is prepared by treating $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** with $HBF_4\cdot Et_2O$ in diethyl ether.[5] Treatment of **10** with benzenethiol or phenylmethanethiol gave the dimers **5** or **6** in good yields (Scheme 2).

The new compounds **3**–**9** have been characterised by various spectroscopic methods (^1H and ^{13}C NMR, and IR), elemental analysis and mass measurement [fast atom bombardment

Table 1 Analytical and mass spectrometric data

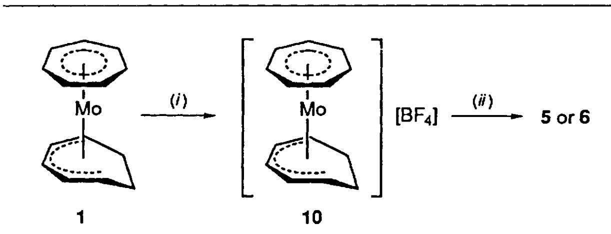
Compound	Colour	$M^{+\,a,b}$	Analysis[b] (%) C	H	S
3	Dark green	599 (599)	39.9 (40.3)	5.1 (5.1)	14.0 (14.0)
4	Dark green	642 (641)	42.7 (42.9)	5.7 (5.7)	12.9 (13.2)
5	Dark green	701 (701)	49.0 (48.8)	3.6 (3.7)	12.2 (12.2)
6	Brown	743 (743)	49.9 (50.6)	4.4 (4.3)	11.6 (11.6)
7	Green	814 (814)	53.0 (53.3)	5.1 (5.0)	10.5 (10.7)
9	Dark green	557 (557)	37.5 (37.3)	4.6 (4.5)	14.2 (14.9)

[a] By fast atom bombardment, M^+ = molecular ion peak for the cation. [b] Calculated values given in parentheses.

Table 2 NMR data

Compound	NMR data[a]
3	^{1}H:[b] 5.53 (s, 14 H, η-C_7H_7), 2.56 (br s, 6 H, SCH_2), 1.72 (br s, 6 H, SCH_2CH_2), 1.10 [t, *J*(H–H), 7.2, 9 H, CH_3] ^{13}C-{^{1}H}:[c] 94.2 (η-C_7H_7), 49.4 (SCH_2), 26.5 (SCH_2CH_2), 13.9 (CH_3)
4	^{1}H:[b] 5.53 (s, 14 H, η-C_7H_7), 2.58 (br s, 6 H, SCH_2), 1.68 (br s, 6 H, SCH_2CH_2), 1.58–1.42 (m, 6 H, CH_2CH_3), 1.00 [t, *J*(H–H) 7.2, 9 H, CH_3] ^{13}C-{^{1}H}:[c] 94.2 (η-C_7H_7), 47.5 (SCH_2), 35.2 (SCH_2CH_2), 22.8 (CH_2CH_3), 14.4 (CH_3)
5[d]	^{1}H: 7.59–7.55 (m, 6 H, H_o), 7.49–7.41 (m, 9 H, H_m and H_p), 5.54 (s, 14 H, η-C_7H_7) ^{13}C-{^{1}H}: 143.2 (C_i), 131.9 (C_o or C_m), 130.5 (C_o or C_m), 129.3 (C_p), 96.6 (η-C_7H_7)
6[d]	^{1}H: 7.57–7.40 (m, 15 H, Ph), 5.55 (s, 14 H, η-C_7H_7), 3.98 (br s, 6 H, SCH_2) ^{13}C-{^{1}H}: 140.2 (C_i), 129.9 (C_o or C_m), 129.8 (C_o or C_m), 128.9 (C_p), 93.6 (η-C_7H_7), 50.8 (SCH_2)
7[d]	^{1}H: 7.43 (br s, 15 H, Ph), 5.14 (s, 2 H, H_c, H_e or H_g), 4.85 (s, 2 H, H_c, H_e, or H_g), 4.73 (s, 2 H, H_c, H_e or H_g), 2.58 (s, 6 H, Me_a, Me_b, Me_d or Me_f), 2.40 (s, 6 H, Me_a, Me_b, Me_d or Me_f), 2.13 (s, 6 H, Me_a, Me_b, Me_d or Me_f), 1.61 (s, 6 H, Me_a, Me_b, Me_d or Me_f) ^{13}C-{^{1}H}: 143.3 (C_i), 132.7 (C_o or C_m), 130.2 (C_o or C_m), 129.2 (C_p), 109.6 (C_a, C_b, C_d or C_f), 106.2 (C_a, C_b, C_d or C_f), 103.4 (C_a, C_b, C_d or C_f), 99.4 (C_c, C_c or C_g), 98.8 (C_a, C_b, C_d or C_f), 96.6 (C_c, C_e or C_g), 94.8 (C_c, C_e or C_g), 27.8 (Me_a, Me_b, Me_d or Me_f), 27.1 (Me_a, Me_b, Me_d or Me_f), 26.1 (Me_a, Me_b, Me_d or Me_f), 23.0 (Me_a, Me_b, Me_d or Me_f)
9[d]	^{1}H: 5.79 (s, 14 H, η-C_7H_7), 2.76 (br s, 6 H, SCH_2), 1.35 (br s, 9 H, CH_3) ^{13}C-{^{1}H}: 94.1 (η-C_7H_7), 41.0 (SCH_2), 17.9 (CH_3)

[a] Given as: chemical shift (δ) [multiplicity (*J* in Hz), relative intensity, and assignment] where s = singlet, t = triplet, m = multiplet, br s = broad signal. [b] In [$^2H_1$]chloroform. [c] In [$^2H_6$]acetone at 243 K. [d] In [$^2H_6$]acetone.



Scheme 2 *Reagents and conditions*: (*i*) $HBF_4{\cdot}Et_2O$ in Et_2O, (*ii*) for **5**, in benzenethiol at 80 °C for 3 h (71% based on **1**); for **6**, phenylmethanethiol at 90 °C for 3 h (64% based on **1**)

(FAB)]. The spectral data and assignments are given in Table 1 and 2. These data will not be further discussed except where interpretation is not straightforward. The structures proposed for the new compounds are shown in Schemes 1 and 2.

Variable-temperature NMR Studies.—The room-temperature ^{1}H NMR spectra of complexes **3**, **4**, **6** and **9** each show the band assignable to the SCH_2 protons is broad. For compounds **3** and **4**, the bands assigned to the other methylene protons also occur as broad signals. These observations suggested that the molecules are fluxional and variable-temperature NMR studies were performed. A typical variable-temperature ^{1}H NMR spectrum is given in Fig. 1 for compound **9** in [$^2H_6$]acetone. This shows a sharp singlet at δ 5.78 assignable to the η-C_7H_7 protons, a poorly resolved quartet at δ 2.78 assignable to the SCH_2 protons and a triplet at δ 1.38 assignable to the methyl groups at 318 K. On cooling to 283 K line broadening occurs to give two broad signals for the SCH_2 and CH_3 protons. Further lowering the temperature to 243 K sharpens these bands and gives the low-temperature limit spectrum. The spectrum shows that the triplet and quartet reappear but are shifted upfield while the η-C_7H_7 singlet exhibits a small downfield shift. The lower temperature spectra also develop new bands but in much lower intensity. These occur as a singlet at δ 5.80, two overlapping quartets at δ 2.96 and 2.91, a quartet at δ 2.38 and two overlapping triplets at δ 1.47 and 1.45. The *J*(H–H) coupling constants are 7.4 Hz for all of these triplets and quartets. These spectra of **9** are attributed to the presence of two isomers **A** and **B** of compound **9** which interconvert through inversion at the sulfur (Fig. 2).[7] At low temperature, the rate of interconversion is so slow that the lifetime of each isomer is long relative to the NMR time-scale. Thus the ^{1}H NMR spectrum of **9** at 243 K exhibits resonances at δ 5.82 (η-C_7H_7), 2.71 (SCH_2) and 1.25 (CH_3) due to the isomer **A** (R = Et) and at δ 5.80 (η-C_7H_7), 2.96, 2.91 and 2.38 (S_aCH_2, S_bCH_2 or S_cCH_2), and 1.47 and 1.45 ($S_aCH_2CH_3$, $S_bCH_2CH_3$ or $S_cCH_2CH_3$) due to the isomer **B** (R = Et). We assume the absorption of the remaining SCH_2CH_3 is obscured by the triplet at δ 1.25. Integrations of the two η-C_7H_7 signals show the ratio of the isomers **A**:**B** (R = Et) is *ca*. 4:1 at the slow-exchange limit. This observation is in contrast to the results reported by Knox and co-workers[3b] who found that for the compounds [(OC)$_3$Mo(μ-SR)$_3$Mo(η-C_7H_7)] (R = Me, Et, Pr^i or Bu^t) the isomer of type **B** was the major isomer.

The compounds **3** and **4** have similar temperature-dependent ^{1}H NMR spectra but band overlap precludes unambiguous assignment. For compound **6**, ^{1}H NMR also reveals the presence of two isomers at low temperature but the relative position of the two η-C_7H_7 absorptions are inverted. A variable-temperature ^{1}H NMR study was also carried out on the compound **5**. Although line broadening occurs for the phenyl absorptions at low temperature, the η-C_7H_7 absorption remains as a sharp singlet. It seems that inversion at the sulfur does not occur in this compound. Presumably, the bulkiness of the phenyl groups precludes the formation of the less symmetrical isomer **B**.

The activation parameters for the dynamic processes were estimated by the coalescence temperature method described by Sandström.[8] By considering the two cycloheptatrienyl absorptions, the sulfur inversion process may be approximated to a two-site exchange process with unequal equilibrium site populations and no coupling between sites. The results are in Table 3 and the estimated $\Delta G^{\ddagger}$ values are in good agreement

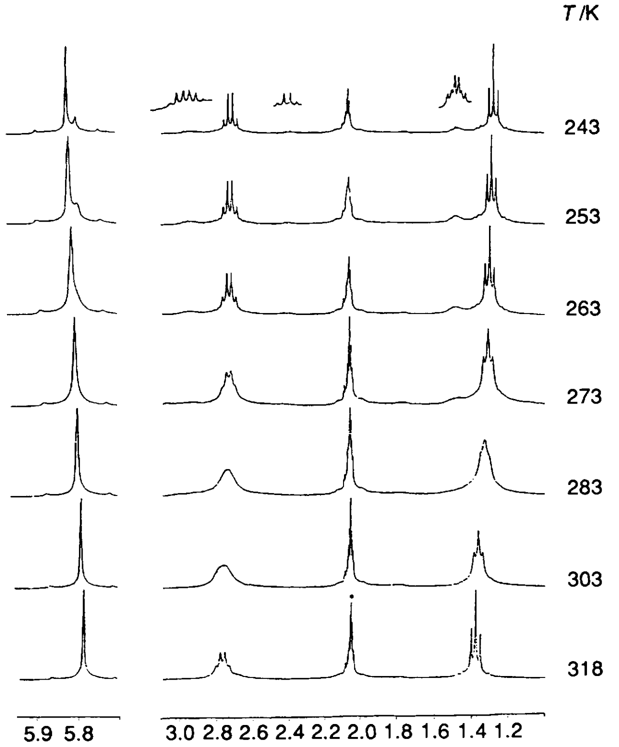


Fig. 1 Variable-temperature ^1H NMR spectra of **9** in [$^2H_6$]acetone: * indicates solvent

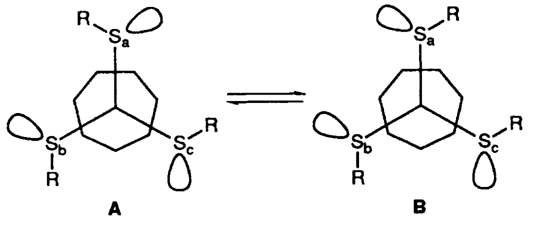


Fig. 2 View of the proposed molecular geometry of compounds **3**–**7** and **9** down the Mo–Mo bond axis

Table 3 Data from NMR coalescence-temperature studies

Compound	ΔP^a	$\delta\nu^b$/Hz	k^c/s^{-1}	$T_c{}^d$/K	$\Delta G^‡$/kJ mol^{-1}
3	0.54	7.4	19.8	263 ± 5	57.6 ± 1.0
4	0.54	8.8	23.6	263 ± 5	57.2 ± 1.0
6	0.64	24.3	62.0	253 ± 5	53.0 ± 1.0
9	0.55	5.4	14.4	263 ± 5	58.3 ± 1.0

[a] Difference in fractional proportion of the sites. The total population is taken as unity. [b] Difference in chemical shift of the sites. [c] Rate constant. [d] Coalescence temperature.

with the values reported for related compounds [3b,9] and occur in the order R^2 = Et > Pr > Bu > CH_2Ph.

The ^{13}C NMR spectra of **3** and **4** are also worthy mentioning. At room temperature, the ^{13}C NMR spectrum of **4** in [$^2H_6$]acetone shows only three signals assignable to aliphatic carbons. Lowering the temperature to 243 K causes a small upfield shift for the three signals and gives one more signal at δ 47.5 together with some weak peaks (Fig. 3). It is obvious that the signals with higher intensity at δ 94.2, 47.5, 35.2, 22.8 and 14.4 at 243 K are due to the major isomer **A** (R = Bu), whilst the weak peaks are due to the minor isomer **B** (R = Bu). Because of the low abundance and the inequivalence of the three bridges of the minor isomer not all of the signals appear in the spectrum.

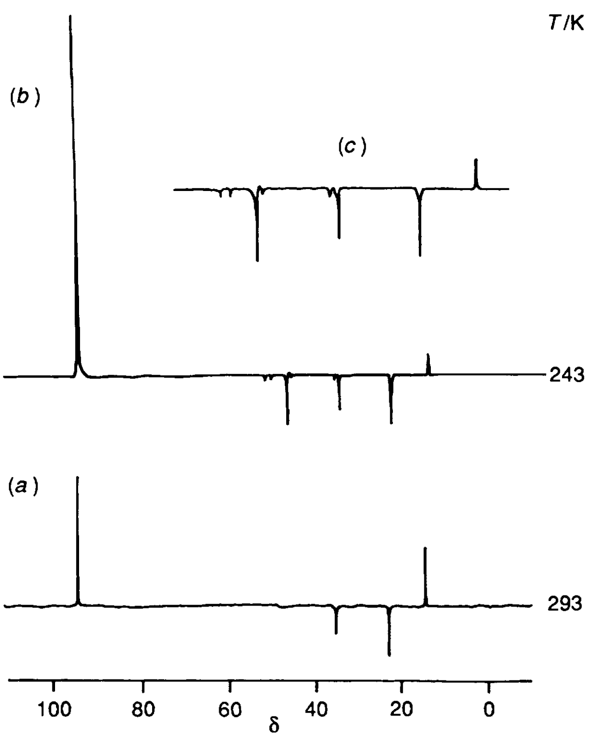


Fig. 3 Distortionless enhancement by polarization transfer (DEPT) ($\theta = \frac{3}{4}\pi$) ^{13}C-{^1H} NMR spectra of **4** in [$^2H_6$]acetone: (*a*) at 293 K, (*b*) at 243 K, (*c*) expansion of (*b*) in the region δ 10–60 showing peaks due to the minor isomer **B** (R = Bu)

Table 4 Electrochemical data[a]

Compound	$E_{\frac{1}{2}}$(red. 1)^b/ V	$\Delta E_p(1)^c$/ mV	$E_{\frac{1}{2}}$(red. 2)^b/ V	$\Delta E_p(2)^c$/ mV
3	−1.02	60	−1.60	65
4	−1.01	55	−1.59	60
5	−0.79	60	−1.30	60
6	−0.95	60	−1.52	65
7	−0.99	50	−1.54	60
9	−0.98	50	−1.57	60

[a] Recorded with NBu_4PF_6 as electrolyte in MeCN (0.1 mol dm^{-3}) at ambient temperature. Scan rate = 100 mV s^{-1}. [b] Relative to saturated calomel electrode. [c] Separation between the anodic and cathodic potentials.

Nevertheless, the three weak peaks at δ 52.8, 51.2 and 46.6 may be assigned to the three carbons next to S_a, S_b and S_c. The absence of the SCH_2 signal at room temperature may result from the fast averaging sulfur inversion process which broadens the signal to the baseline. The room-temperature ^{13}C NMR spectrum of **3** in [$^2H_6$]acetone exhibits a very small broad signal for the SCH_2 groups which sharpens at 243 K.

The ^1H NMR spectrum of **7** in [$^2H_6$]acetone shows three different bands assignable to cycloheptatrienyl protons and four different bands assignable to methyl protons whilst the ^{13}C NMR spectrum exhibits seven peaks for the cycloheptatrienyl ring carbons and four peaks for the methyl carbons. This clearly indicates that the two cycloheptatrienyl rings are symmetry related but there is no plane of symmetry through the Mo–Mo bond in the molecule. This result is consistent with the structure proposed in Scheme 1.

Electrochemical Studies.—The electrochemistry of the new series of complexes has been studied by cyclic voltammetry. All of these complexes exhibit two reversible reduction waves (Red. 1 and Red. 2). Fig. 4 shows the cyclic voltammogram for the compound **4** which is typical. The electrochemical data are

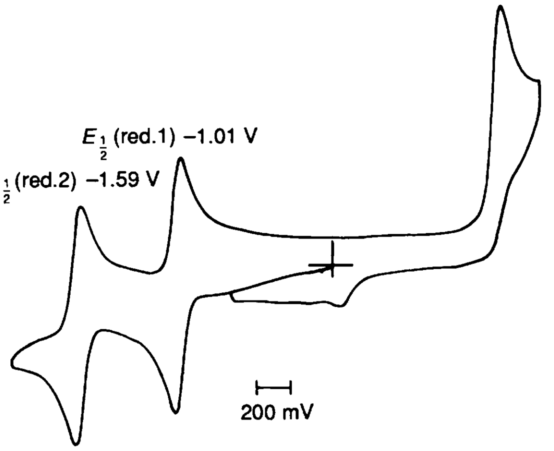


Fig. 4 Cyclic voltammogram of **4** recorded in acetonitrile at a scan rate of 100 mV s^{-1} with NBu_4PF_6 as electrolyte

summarised in Table 4. The potentials were referenced to the ferrocenium-ferrocene couple at +0.355 V relative to the saturated calomel electrode (SCE) and the reversibility judged by comparison of ΔE_p at various scan rates with that of the ferrocenium–ferrocene internal standard.[10] The reduction potentials ($E_{\frac{1}{2}}$) depend on the substituent on the sulfur atoms and increase in the order R^2 = Pr < Bu < Et < CH_2Ph < Ph which reflects the electron donating nature of the alkyl group and the electron withdrawing property of the phenyl group. A similar trend was also observed for the complexes $[\{Mo(\eta\text{-}C_5H_5)(NO)(\mu\text{-}SR)\}_2]$,[11] $[NEt_4][(OC)_3Mn(\mu\text{-}SR)_3Mn(CO)_3]$[12] and $[(\eta\text{-}C_5H_4Pr^i)Mo(\mu\text{-}SR)_4Mo(\eta\text{-}C_5H_4Pr^i)]$.[13] The presence of four methyl groups of the cycloheptatrienyl rings in **7** lowers the $E_{\frac{1}{2}}$ values substantially as expected.

We propose that the two one-electron reductions are accompanied by cleavage of the Mo–Mo bond giving the anions $[(\eta\text{-}C_7H_3R^1{}_4)Mo(\mu\text{-}SR^2)_3Mo(\eta\text{-}C_7H_3R^1{}_4)]^-$ in which both molybdenum atoms retain 18 electrons. A similar proposal has been made for the two one-electron oxidations of the compound $[NEt_4][(OC)_3Mn(\mu\text{-}SR)_3Mn(CO)_3]$.[12] It was suggested that the oxidation is accompanied by an increase in bond order between the manganese atoms.

In conclusion, the new compounds and proposed structures are shown in Schemes 1 and 2. The ready accessibility of the starting materials $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_3R^1{}_4)][BF_4]$ (R^1 = H or Me) and $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ and high yield of the reactions provide an effective pathway to the binuclear bridging sulfur compounds. The thiolato-bridged complexes exhibit inversion at the sulfur with low energy barriers and undergo two one-electron reversible reductions.

Experimental

General.—All manipulations and reactions were carried out using either standard Schlenk-line techniques under an atmosphere of dinitrogen or in an inert-atmosphere dry-box containing dinitrogen. Dinitrogen was purified by passage over a BTS catalyst and 5 Å molecular sieves. Solvents were pre-dried by standing over 5 Å molecular sieves and then distilled under an atmosphere of dinitrogen from potassium (tetrahydrofuran), sodium (toluene), phosphorus pentaoxide (dichloromethane), or sodium–potassium alloy [light petroleum (b.p. 40–60 °C) and diethyl ether]. Acetonitrile was distilled from calcium hydride. Deuteriated solvents for NMR studies were stored in Young's ampoules and transferred by pipette in the dry-box.

Proton and ^{13}C NMR spectra were recorded on a Brüker AM 300 spectrometer (^1H, 300; ^{13}C, 75.43 MHz). Spectra were referenced internally using the residue solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane (δ = 0). All chemical shifts are quoted in δ and coupling constants in Hz. Infrared spectra were recorded on a Perkin Elmer 1510 FT interferometer or a Perkin Elmer 457 grating spectrometer, on which spectra below 400 cm^{-1} were obtained. Mass spectra (FAB) were obtained by the SERC mass spectrometry service, University College, Swansea. Microanalyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory. Cyclic voltammetry measurements were carried out using an Oxford Instruments potentiostat and recorded on a Rikadenki x-y chart recorder. The cell used comprised a vacuum-tight chamber fitted with inlets for a platinum disc working electrode, a platinum gauze auxiliary electrode, and a silver wire pseudo-reference electrode. Typically, experiments were carried out using *ca.* 15 cm^3 of *ca.* 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate in acetonitrile solution containing *ca.* 2 mg of sample under dinitrogen at ambient temperature.

The compounds $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1**,[5] $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][BF_4]$ **2**[14] and $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_3Me_4\text{-}1,2,4,6)][BF_4]$ **8**[6] were prepared as described.

Preparations.—$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}SPr)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ **3**. A suspension of green $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][BF_4]$ **2** (1 g, 2.7 mmol) in propane-1-thiol (30 cm^3) was heated at 75 °C for 20 h. The mixture turned dark greenish red during the course of the reaction. All the volatiles were removed *in vacuo*, then the residue was extracted with thf (2 × 40 cm^3) followed by acetone (2 × 30 cm^3). The combined extracts were concentrated to *ca.* 80 cm^3 and then cooled at −20 °C affording dark green microcrystals. After collecting the crystals by filtration, the filtrate was further concentrated and cooled to give a second crop of product. Combined yield, 0.28 g (30%).

$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}SBu)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ **4**. A mixture of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][BF_4]$ **2** (1 g, 2.7 mmol) and butane-1-thiol (20 cm^3) was heated at 80 °C for 4 h. The volatiles were removed from the resulting dark green suspension under reduced pressure and the resulting residue was extracted with thf (2 × 50 cm^3). The thf solution was concentrated to *ca.* 50 cm^3, then diethyl ether (20 cm^3) was added. Cooling to −20 °C gave dark green microcrystals. These were collected by filtration. The filtrate was further concentrated and cooled to give a second crop of product. This step was repeated several times to give more product. Combined yield, 0.7 g (70%).

$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}SPh)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ **5**. (*a*) A mixture of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][BF_4]$ **2** (4 g, 10.9 mmol) and benzenethiol (50 cm^3) was heated at 100 °C for 6 h. After cooling to room temperature, light petroleum (b.p. 40–60 °C) (150 cm^3) was added. A green solid precipitated and was collected by filtration and then washed with light petroleum (b.p. 40–60 °C) (3 × 50 cm^3) to remove trace amounts of benzenethiol. The solid obtained after drying was essentially pure but it was recrystallised from an acetone–thf (1:2) at −20 °C. Yield, 3.7 g (87%).

(*b*) A solution of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** (0.2 g, 0.71 mmol) in diethyl ether (50 cm^3) was treated with an excess of $HBF_4 \cdot Et_2O$ (*ca.* 1 cm^3). There was immediate precipitation of a light material and loss of colour of the solution. The solid was allowed to settle and the supernatant liquor was filtered off. The solid was washed with diethyl ether (30 cm^3) and dried *in vacuo*. Benzenethiol (5 cm^3) was then added and the mixture was heated at 80 °C for 3 h. After cooling to room temperature, light petroleum (b.p. 40–60 °C) (80 cm^3) was added. A dark green solid precipitated and was collected by filtration and washed with light petroleum (b.p. 40–60 °C) (2 × 40 cm^3). The crude product was recrystallised from an acetone–thf mixture at −20 °C. Yield, 0.2 g (71%).

$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}SCH_2Ph)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ **6**. A mixture of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][BF_4]$ **2** (1 g, 2.7 mmol) and phenylmethanethiol (15 cm^3) was heated at 100 °C for 5 h. After cooling to room temperature, light petroleum (b.p. 40–60 °C) (200 cm^3) was added to precipitate the product. The resulting greenish brown solid obtained after filtration was washed with light petroleum (b.p. 40–60 °C) (2 × 50 cm^3) and dried *in vacuo*. The product was essentially pure, but it was recrystallised from acetone–thf (1:2) at −20 °C. Yield, 1.0 g (88%).

(*b*) The compound $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** (0.1 g, 0.36 mmol) was dissolved in diethyl ether (30 cm^3). The solution was treated with an excess of $HBF_4 \cdot Et_2O$ (*ca.* 0.5 cm^3). There was immediate precipitation of a light material and loss of colour to the solution. The solid was allowed to settle and the supernatant liquor was filtered off. The solid was washed with diethyl ether (20 cm^3) and dried *in vacuo*. Phenylmethanethiol (3 cm^3) was then added and the mixture was heated at 90 °C for 3 h. After cooling to room temperature, light petroleum (b.p. 40–60 °C) (100 cm^3) was added. The brown solid precipitated was collected by filtration and then washed with light petroleum (b.p. 40–60 °C) (2 × 30 cm^3). The crude product was recrystallised from acetone–thf mixture at −20 °C. Yield, 95 mg (64%).

$[(\eta\text{-}C_7H_3Me_4\text{-}1,2,4,6)Mo(\mu\text{-}SPh)_3Mo(\eta\text{-}C_7H_3Me_4\text{-}1,2,4,6)][BF_4]$ **7**. A mixture of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_3Me_4\text{-}1,2,4,6)][BF_4]$ **8** (0.1 g, 0.24 mmol) and benzenethiol (10 cm^3) was heated at 100 °C for 5 h. After cooling to room temperature, light petroleum (b.p. 40–60 °C) (200 cm^3) was added. The pale greenish yellow solution was decanted with some oily substance left which was extracted with thf (3 × 20 cm^3). The thf solution was concentrated to *ca.* 40 cm^3 and then cooled at −80 °C to give some green microcrystals which were collected by filtration, washed with light petroleum (b.p. 40–60 °C) (10 cm^3) and dried *in vacuo*. The filtrate was concentrated and cooled again to give a second crop of product. Combined yield, 97 mg (91%).

$[(\eta\text{-}C_7H_7)Mo(\mu\text{-}SEt)_3Mo(\eta\text{-}C_7H_7)][BF_4]$ **9**. A stirred suspension of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][BF_4]$ **2** (1 g, 2.7 mmol) and lithium thioethoxide (0.28 g, 4.1 mmol) in thf (40 cm^3) was heated at 60 °C for 3 h. The initially green suspension slowly darkened. After removing the volatiles *in vacuo*, the residue was extracted with toluene (2 × 50 cm^3). The insoluble oily material was extracted with thf (2 × 50 cm^3) followed by acetone (2 × 30 cm^3). The combined acetone–thf solution was concentrated to *ca.* 60 cm^3 and then cooled at −20 °C. Some green solid was obtained which was recrystallised with acetone–thf again to give the product as dark green microcrystals. Yield, 0.23 g (26%).

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