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# SYNTHESIS OF HETERO-BINUCLEAR DERIVATIVES OF THE TETRATHIOLATO COMPLEXES [$Mo(\eta$-$C_5H_4CH_2CH_2SR)_2(SR)_2)$], R = $Pr^n$ AND Ph, WITH PLATINUM, PALLADIUM, AND RHODIUM

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## Summary

The compound $Mo(\eta$-$C_5H_4(CH_2)_2SPr^n)_2(SPr^n)_2$ acts as a bidentate ligand giving the heteronuclear bi-metallic compounds [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2(PtCl_2)$], [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2(PdCl_2)_2$], [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2(RhCl_3)_2$], [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(\mu$-$SPr^n)_2Rh(dppe)$]$BF_4$, [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(\mu$-$SPr^n)_2(COD)Rh$]Cl, [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(\mu$-$SPr^n)_2Pt(PPh_3)_2$]$(PF_6)_2$, and the compound [$Mo(\eta$-$C_5H_4(CH_2)_2SPh)_2Cl_2$] bonds via the ring-sulphur substituents giving [$Mo(\eta$-$C_5H_4(CH_2)_2$-$\mu$-$SPh)_2Cl_2Rh(COD)$]Cl.

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Previously we described the compound [$Mo(\eta$-$C_5H_4CH_2CH_2SPh)_2(SPh)_2$] [1] which was designed as a potentially tetradentate sulphur ligand. However, due to low solubility it was not possible to fully characterise the adducts which the compound formed with platinum group metal compounds. It was decided to synthesise the analogous compound [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2$] in the hope of obtained more soluble systems.

## Results and discussion

Treatment of the compound [$Mo(\eta$-$C_5H_4CH_2CH_2I)_2I_2$] with sodium n-propylthiolate gave red crystals of the tetrathiolato derivative [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2$] (**1**).

The compound **1** readily forms adducts of stoichiometry [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2(PtCl_2)$ and [$Mo(\eta$-$C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2(PdCl_2)_2$)] when treated with [$(PhCN)_2PtCl_2$] and [$(PhCN)_2PdCl_2$] respectively. However, low solu-

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TABLE 1. ANALYTICAL AND SPECTROSCOPIC DATA

| Compound | Colour | Analysis (Found (calcd.) (%)) | | NMR data[a] |
|---|---|---|---|---|
| | | C | H | |
| Mo($\eta$-$C_5H_4CH_2CH_2SPr^n)_2$-$(SPr^n)_2$<br>(**1**) | Red | 53.7<br>(53.5) | 7.6<br>(7.4) | $^1$H: 4.7 [4H, m, 3 lines, $\eta$-$C_5H_4$], 4.2 [4H, m, 3 lines, $\eta$-$C_5H_4$], 2.7 [8H, m, 10 lines, $C_5(CH_2)_2$], 2.6 [4H, t, $J$ 7.3, $SCH_2$], 2.3 [4H, t, $J$ 7.3, $SCH_2$], 1.7 [4H, sextet, $J$ 7.3, $SCH_2CH_2CH_3$], 1.5 [4H, sextet, $J$ 7.3, $SCH_2CH_2CH_3$], 1.1 [6H, t, $J$ 7.3, $SCH_2CH_2CH_3$], 0.8 [6H, t, $J$ 7.3, $SCH_2CH_2CH_3$] [b] |
| [Mo($\eta$-$C_5H_4CH_2CH_2SPr^n)_2$-($\mu$-$SPr^n)_2$Rh(dppe)]$PF_6$<br>(**2**) | Red | 53.3<br>(53.3) | 5.8<br>(5.9) | $^1$H: 8.0 [8H, c, part of 4PPh], 7.5 [12H, c, part of 4PPh], 5.6 [4H, m, 3 lines, $\eta$-$C_5H_4$], 5.5 [4H, m, 3 lines, $\eta$-$C_5H_4$], 2.8 [4H, t, $J$ 7.5, $2CH_2Cp$], 2.7 [4H, t, $H$ 7.5, $2CH_2CH_2Cp$], 2.5 [4H, t, $J$ 7.0, $2SCH_2$], 2.4 [4H, d, $J$ 17.1, $P(CH_2)_2$], 1.6 [4H, sextet, $J$ 7.0, $2SCH_2CH_2CH_3$], 1.4 [4H, c, br, $2SCH_2$], 1.0 [6H, t, $J$ 7.0, $2CH_3$], 1.0 [4H, sextet, $J$ 7.0, $2SCH_2CH_2CH_3$], 0.9 [6H, t, $J$ 4.2, $2CH_3$] [c] |
| [Mo($\eta$-$C_5H_4CH_2CH_2SPr^n)_2$-($\mu$-$SPr^n)_2$(COD)Rh]Cl<br>(**3**) | Red | 46.3<br>(46.2) | 6.8<br>(6.6) | $^1$H: 5.9 [4H, m, 3 lines, $\eta$-$C_5H_4$], 5.7 [4H, m, 3 lines, $\eta$-$C_5H_4$], 4.1 [4H, s, br, CH of $C_8H_{12}$], 2.8 [4H, t, $J$ 7.6, $2SCH_2$], 2.6 [4H, t, $J$ 7.1, $2CpCH_2$], 2.5 [4H, t, $J$ 7.1, $2CH_2$], 2.4 [4H, s, br, $2SCH_2$], 1.9 [8H, s, br, $CH_2$ of $C_8H_{12}$], 1.6 [4H, sextet, $J$ 7.6, $2CH_2$], 1.3 [4H, sextet, $J$ 7.6, $2CH_2$], 0.9 [6H, t, $J$ 7.6, $2CH_3$], 0.8 [6H, t, $J$ 7.6, $2CH_3$] [c]<br>$^{13}$C: 111.6 [s, C(Cp)], 103.0 [d, CH(Cp)] 96.1, [d, CH(Cp)], 82.5, [d, $J(^{103}Rh–C)$ 11.3, Rh–CH], 38.1, [t, $CH_2$], 34.8 [t, $CH_2$], 34.2 [t-$CH_2$], 31.2 [t, $CH_2$], 30.2 [t, $CH_2$], 25.8 [t, $CH_2$], 23.4 [t, $CH_2$], 13.7 [q, $CH_3$], 13.6, [q, $CH_3$] [c] |
| [Mo($\eta$-$C_5H_4CH_2CH_2SPr^n)_2$-($\mu$-$SPr^n)_2Pt(PPh_3)_2](PF_6)_2$<br>(**4**) | Red | 46.8<br>(47.8) | 4.6<br>(4.5) | $^1$H: 7.7 [12H, c, part of 6Ph], 7.55 [6H, c, part of 6Ph], 7.43, [12H, c, part of 6Ph], 5.8 [4H, m, 3 lines, $\eta$-$C_5H_4$], 5.7 [4H, m, 3 lines, $\eta$-$C_5H_4$], 2.9 [4H, t, $J$ 7.1, $2CH_2$], 2.5 [4H, t, $J$ 7.1, $2CH_2$], 2.4 [4H, t, $J$ 7.6, $2SCH_2$], 1.9 [4H, br, $2SCH_2$], 1.8 [4H, sextet, $J$ 7.1, $2SCH_2CH_2CH_3$], 1.0 [6H, t, $J$ 7.1, $2CH_3$], 0.57 [4H, br, $2SCH_2CH_2$], 0.48 [6H, t, $J$ 6.9, $2CH_3$] [c]<br>$^{13}$C: [135.4, d, 132.9, d, 129.7, d, $J$ 95, 129.7, s, 128.4, d, 6-Ph], 103.7 [d, $\eta$-$C_5H_4$], 97.3 [d, $\eta$-$C_5H_4$], 39.4 [t, $CH_2$], 34.5 [t, $CH_2$]. 33.4 [t, $CH_2$], 23.4 [t, $CH_2$], 13.4 [q, $CH_3$], 12.6 [q, $CH_3$] [c] |
| [Mo($\eta$-$C_5H_4CH_2CH_2$-$\mu$-$SPh)_2$-$Cl_2Rh(COD)$]Cl<br>(**6**) | Green | 46.5<br>(44.0) | 4.1<br>(4.3) | $^1$H: 7.67 [2H, c, 4 lines, SPh], 7.56 [2H, c, br, SPh], 7.40 [2H, c, 4 lines, SPh], 7.32 [2H, c, 5 lines, SPh], 7.2 [2H, c, 6 lines, SPh], 5.9 [2H, m, br, $\eta$-$C_5H_4$], 5.7 [2H, c, 3 lines, $\eta$-$C_5H_4$], 5.4 [4H, c, 6 lines, $\eta$-$C_5H_4$], 4.33 [4H, s, br, 4-CH of $C_8H_{12}$], 3.3 [4H, t, $J$ 7.0, $2CH_2$], 2.7 [4H, t, $J$ 7.0, $2CH_2$], 2.45 [4H, s, br, $2CH_2$ of $C_8H_{12}$], 1.7 [4H, br. d, $J$ 7, $2CH_2$ of $C_8H_{12}$] [c] |

[a] Given as: Chemical shift ($\delta$) [rel. intensity, multiplicity, $J$ in Hz, assignment]. [b] In $C_6D_6$. [c] In $(CD_3)_2CO$. Mo: 8.2 (8.2)%.

bility prevented full characterisation. Similarly, the reaction between **1** and $RhCl_3 \cdot 3H_2O$ produced an insoluble red compound with a stoichiometry corresponding to $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2(RhCl_3)_2]$.

The reactive cation $[(dppe)Rh(acetone)_2]BF_4$, prepared by hydrogenation of $[(nbd)Rh(dppe)]BF_4$ [2], was treated with **1** giving red crystals of $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPr^n)_2(\mu\text{-}SPr^n)_2Rh(dppe)]BF_4$, (**2**).

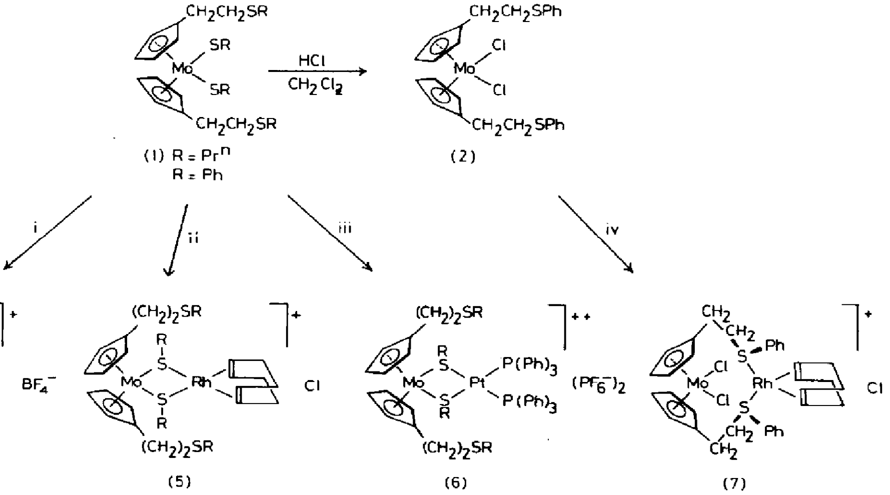
The compound **2** was readily soluble in polar solvents. The $^1H$ NMR spectrum of **2**, and of all the new compounds described in this work are given in Table 1 and these data are only discussed when assignments are not self-evident.

The $^1H$ NMR spectrum of **2** showed that one proton resonance was unusually broad, and this is assignable to the protons of the α-methylene group bound to the sulphur atom which is coordinated to the rhodium centre. The broadening can then be attributed to the occurrence of fluxional inversion of the $\mu\text{-}SPr^n$ group. There is considerable evidence that similar sulphur-bridged bimetallic complexes have puckered $M(SR)_2M'$ rings in which the sulphur atoms undergo rapid inversion [3,4].

If the sulphur atoms attached to the ethyl side chains were coordinated to the rhodium, then it would be expected that two resonances arising from the hydrogens bound to the α-carbons on either side of the sulphur atom would be broadened, but since only one broad band is observed it is proposed that it is the sulphur atoms attached to the molybdenum which are coordinating to the rhodium (see Scheme 1).

Addition of **1** to the cycloocta-1,5-diene (COD) compound $[(COD)RhCl]_2$ gave red crystals of $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPr^n)_2(\mu\text{-}SPr^n)_2(COD)Rh]Cl$ (**3**).

The $^1H$ 300 MHz NMR spectrum shows, in addition to signals assignable to the parent ligand, bands assignable to one 1,5-cyclooctadiene group as two broad singlets at 4.2 and 1.9 ppm in the ratio 4/8. The resonance at 4.2 ppm is assigned to the olefinic protons and the other signal at 1.9 ppm to the methylene protons. The resonance at 2.8 ppm assigned to the $CH_2$ groups attached to the bridging sulphur atoms is broadened. This indicates that the rhodium centre is coordinated by the sulphur of the $Mo(SPr^n)_2$ grouping. The symmetry of the compound requires that the apparent equivalence of the hydrogens both of the four $CH_2$ and of the four CH



SCHEME 1. (i) $[(dppe)Rh(acetone)_2]BF_4$ in acetone at room temperature, 79%. (ii) $[(COD)RhCl]_2$ in $CH_2Cl_2$ at room temperature, 86%. (iii) $[(PPh_3)_2Pt][PF_6]_2$ in acetone at room temperature, 81%. (iv) $[(COD)RhCl]_2$ in acetone at 50°C, 51%.

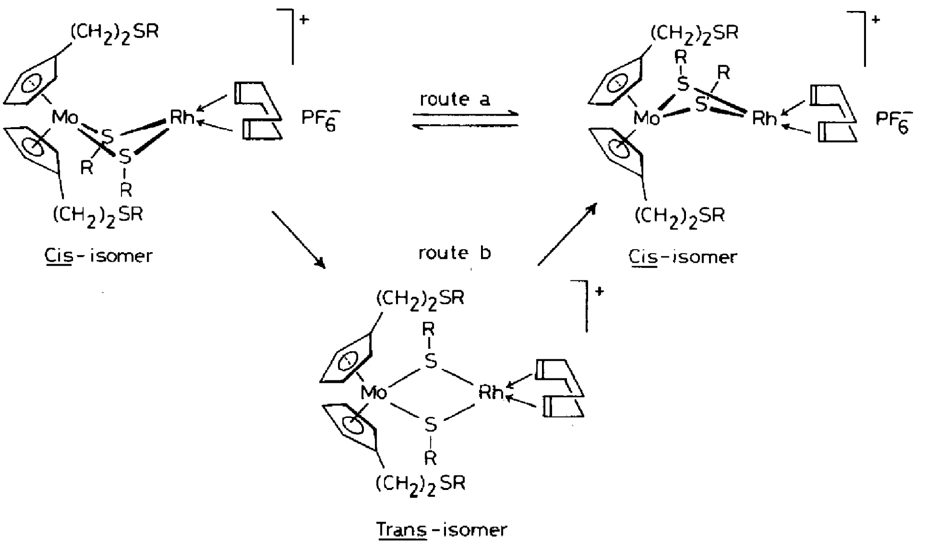
groups of the cycloocta-1,5-diene group must reflect the occurrence of a dynamic process.

Variable temperature $^1H$ 300 MHz spectra of **3** between −70 and 25°C show that at the lower temperature there is a complex set of broad multiplets assignable to non-equivalent $\eta$-cyclopentadienyl hydrogens, and two broad singlets due to two sets of non-equivalent olefinic protons at 4.2 and 3.8 ppm of relative intensities 2/2 are observed. This is consistent with a single *cis*- or *trans*-configuration of the *S*-propyl groups. The apparent higher symmetry of **3** at higher temperatures can be explained by an overall *cis*-up to *cis*-down equilibrium. This equilibrium may occur either by a symmetrical, concerted inversion (Scheme 2) (route A) or via sequential steps involving an intermediate *trans*-propyl isomer (route B). If route B is correct then it is required that the equilibrium concentration of the *trans* isomer is small, since only one isomer is observed in the NMR spectrum. Further, there is no change in chemical shift of the propyl hydrogens with temperature as might be expected for a change from *cis*- and *trans*-isomers.

Thus the *cis*-isomer appears to be more stable and this is supported by the fact that of six X-ray structure determinations for compounds containing the $[(\eta\text{-}C_5H_5)_2M(SR)_2]$ moiety, five have been found to adopt this geometry. That an equilibrium of some type occurs is not at all surprising since *cis–trans* isomerisation has been postulated to account for the $^1H$ NMR spectra of similar complexes, for example, $[(MeSCH_2CH_2SMe)PtCl_2]$ [5], and $[(RR'S)_2PtCl_2]$ [6].

Addition of **1** to $[(PPh_3)_2Pt](PF_6)_2$ gave red crystals of $[Mo(\eta\text{-}C_5H_4CH_2CH_2\text{-}SPr^n)_2(\mu\text{-}SPr^n)_2Pt(PPh_3)_2](PF_6)_2$ (**4**). It appears from the NMR data that the sulphur atoms of the $Mo(SPr^n)$ groups are donating to the platinum.

Treatment of $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)_2(SPh)_2]$ with hydrogen chloride gas gave green microcrystals of $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)_2Cl_2]$ (**5**) [1]. Addition of **5** to $[(COD)RhCl]_2$ gave red crystals of $[Mo(\eta\text{-}C_5H_4CH_2CH_2\text{-}\mu\text{-}SPh)_2Cl_2Rh(COD)]Cl$ (**6**). The infrared spectrum showed bands at 280 and 260 cm$^{-1}$ assignable to *cis*-Mo–Cl stretches [7]. The $^1H$ NMR spectrum is consistent with an essentially



SCHEME 2. Possible mechanisms for fluxional inversion.

rigid structure, in which the SPh groups are coordinated to the rhodium atom in a "skew" manner (Scheme 1). This causes the methylene hydrogens of the cyclooct-1,5-adiene to be non-equivalent and consequently two multiplets would be expected, as observed. The $\eta$-cyclopentadienyl hydrogens would also be expected to be more complex, as observed, since the molecule no-longer has a plane of symmetry.

Most of the heteronuclear, bimetallic compounds described above are comparable to those which contain the ligand $M(\eta\text{-}C_5H_5)_2(SR)_2$ (M = Mo or W) [8]. It is interesting that of the possible combinations the tetrathiolato derivative prefers to coordinate using the $Mo(SR)_2$ group rather than using one or two of the sulphur atoms of the $\eta\text{-}C_5H_4(CH_2)_2SPr^n$ groups.

## Experimental

All reactions and manipulations were carried out in an inert atmosphere or in vacuo. Petroleum ether (b.p. > 80°C), toluene, and tetrahydrofuran were dried by refluxing over potassium metal under dinitrogen. The petroleum ethers (30–40 and 40–60°C) were dried over sodium–potassium alloy. Solvents were distilled immediately prior to use. Dichloromethane was dried by refluxing over $CaH_2$ and stored over molecular sieves (type 4A).

Celite 545 Filter Aid was used as supplied by Koch–Light Laboratories Ltd. Alumina 100–120 mesh supplied by East Anglia Chemicals was deactivated before use by the addition of 6% by weight of distilled water.

Infrared spectra were recorded on a Pye Unicam SP2000 spectrometer as mulls in either Nujol or hexachlorobutadiene (HCBD) between CsI or KBr plates and were calibrated using HCBD. NMR spectra were obtained on either 60 MHz, JNM-PMX; 90 MHz, Bruker WH90; 300 MHz, Bruker WH300; or 400 MHz, Bruker WH400 instruments and were calibrated using solvent peaks as internal standards. All chemical shifts are given in ppm relative to tetramethylsilane $\delta$ 0 ppm. Coupling constants ($J$) are in hertz (Hz). Mass spectra were obtained on an AEI MS 902 mass spectrometer. Parent ions given as $m/e$ assignments, for $^{98}Mo$.

### *Bis(3-thiahexyl-η-cyclopentadienyl)bis(η-propanethiolato)molybdenum (1)*

Sodium metal (0.5 g; 21.4 mmol) was dissolved in a mixture of ethanol (50 $cm^3$) and 1-propanethiol (1.6 g; 26.2 mmol). The resulting solution was added to a suspension of $[Mo(\eta\text{-}C_5H_4CH_2CH_2I)_2I_2]$ (2.06 g; 2.6 mmol) in ethanol (100 $cm^3$). After refluxing for 5 h the solution was taken to dryness under reduced pressure. The red solid was extracted with petroleum ether (40–60°C, 2 × 100 $cm^3$) to give a red solution. This was concentrated to approx. 50 $cm^3$ under reduced pressure and cooled to −20°C initially and then to −78°C giving brick-red needles. These were collected by filtration and dried in vacuo. Yield 1.03 g; 67%.

### *Reaction between $[Mo(\eta\text{-}C_5H_4CH_2CH_2SC_3H_7)_2(SC_3H_7)_2]$ and $[(C_6H_5CN)_2PtCl_2]$*

The compound $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2]$ (0.6 g; 1.10 mmol) in tetrahydrofuran (50 $cm^3$) was added to $[(C_6H_5CN)_2PtCl_2]$ (1.1 g; 2.3 mmol) in the same solvent. A green powder immediately precipitated. The supernatant liquid was decanted off and the green solid was washed with tetrahydrofuran (2 × 50 $cm^3$) and dried in vacuo. Yield, 0.8 g; 80%. The solid was insoluble in all the common solvents, except liquid $SO_2$ and dimethylsulphoxide. Found: C, 38.1; H, 5.2. {Bis($\eta$-

(3-thiahexyl)cyclopentadienyl)bis($\mu$-propylthiolato)molybdenum}dichloroplatinum, $MoC_{26}H_{44}Cl_2S_4Pt$, calcd.: C, 38.4; H, 5.4%.

*Reaction between* $[Mo(\eta\text{-}C_5H_4CH_2CH_2SC_3H_7)_2(SC_3H_7)_2]$ *and* $[(C_6H_5CN)_2PdCl_2]$

A solution of $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2]$ (0.6 g; 1.04 mmol) in tetrahydrofuran was added to a solution of $[(C_6H_5CN)_2PdCl_2]$ (0.8 g; 2.18 mmol) in the same solvent. A green powder was immediately precipitated, and the supernatant liquid decanted. The green solid was washed with tetrahydrofuran (2 × 50 $cm^3$) and dried in vacuo. Yield 0.5 g; 85%. As with the Pt analogue, the product proved to be insoluble in all the common solvents, except $SO_2$ and dimethylsulphoxide. Found: C, 33.3; H, 4.6. {Bis($\eta$-(3-thiahexyl)cyclopentadienyl)di($\mu$-propylthiolato)molybdenum}dichloropalladium, $MoC_{26}H_{44}S_4(PdCl_2)_2$ calcd.: C, 33.4; H, 4.7%.

*Reaction between* $[Mo(\eta\text{-}C_5H_4CH_2CH_2I)_2I_2]$ *and* $RhCl_3 \cdot 3H_2O$

A solution of $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2]$ (0.2 g; 0.36 mmol) in tetrahydrofuran (50 $cm^3$) was added dropwise to a solution of $RhCl_3 \cdot 3H_2O$ (0.15 g; 0.87 mmol) in tetrahydrofuran/methanol (1/1) (20 $cm^3$). An immediate red precipitate was formed. The precipitate was allowed to settle, and the supernatant liquid removed. The red powder was washed with tetrahydrofuran (2 × 20 $cm^3$), and dried in vacuo. Yield 0.3 g; 80%. Again this compound was found to be soluble only in $SO_2$(liq) and dimethylsulphoxide. Found: C, 31.5; H, 4.3. $MoC_{26}H_{44}S_4(RhCl_3)_2$ calcd.: C, 31.2; H, 4.4%.

*{Bis($\eta$-3-thiahexyl)cyclopentadienyl)di($\mu$-propylthiolato)molybdenum}(bis-1,2-(diphenylphosphino)ethanerhodium tetrafluoroborate (2)*

A solution of $[(nbd)Rh(dppe)]BF_4$ (0.23 g; 0.34 mmol) was hydrogenated as described [2], and cooled to −78°C. The resulting orange solution was added dropwise to a solution of $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2]$ (0.2 g; 0.34 mmol) in acetone at −78°C. The solution was slowly allowed to warm to room temperature and the solvent removed under reduced pressure. The red oily residue was washed with petroleum ether (40–60°C, 2 × 20 $cm^3$) and toluene (1 × 20 $cm^3$), then dissolved in a minimum of acetone (20 $cm^3$). The solution was concentrated under reduced pressure, then 1–2 $cm^3$ of diethyl ether was added, the solution filtered, and then cooled to −78°C. Red microcrystals were obtained, which were filtered and washed with petroleum ether (40–60°C) (2 × 10 cm) and dried in vacuo. Yield: 0.35 g, 79%.

*{Bis($\eta$-(3-thiahexyl)cyclopentadienyl)di($\mu$-propylthiolato)molybdenum}($\eta$-cyclo-octa-1,5-diene)rhodium hexafluorophosphate (3)*

To a solution of $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2]$ (0.75 g; 1.3 mmol) in dichloromethane (50 $cm^3$) was added $[(COD)RhCl]_2$ (0.6 g; 1.21 mmol) in the same solvent (30 $cm^3$). The solution was stirred for 2 d, after which the solvent was removed under reduced pressure. The resulting red oily residue was first washed with petroleum ether (40–60°C, 2 × 30 $cm^3$) and then toluene (2 × 30 $cm^3$) to remove any residual molybdenum starting material. The oil was then redissolved in dichloromethane (30 $cm^3$), and the resulting solution was concentrated under reduced pressure. A few drops of toluene were added, the solution was filtered, and then cooled to −78°C. After several days red-orange microcrystals were obtained. Yield, 1.0 g; 77%.

This complex was converted into the hexafluorophosphate salt by the addition of a saturated solution of $NH_4PF_6$ in acetone to a stirred solution (0.5 g; 0.46 mmol) of the chloride salt. A white gelatinous precipitate slowly formed. The solution was filtered, and the filtrate taken to dryness under reduced pressure. The red residue was washed with distilled water ($2 \times 20$ $cm^3$), and recrystallised from an acetone/diethyl ether mixture. Yield, 0.4 g; 86%.

*{Bis(η-(3-thiahexyl)cyclopentadienyl)di(μ-propylthiolato)molybdenum} bis(triphenylphosphine)platinum bishexafluorophosphate (4)*

A suspension of $[(PPh_3)_2PtCl_2]$ (0.5 g; 0.63 mmol) in acetone (20 $cm^3$) was stirred with a solution of $AgPF_6$ (0.31 g; 1.26 mmol) in acetone (10 $cm^3$). A gelatinous precipitation of AgCl formed. The solution was filtered, and the filtrate was treated in a dropwise manner with a suspension of $[Mo\text{-}\eta\text{-}C_5H_4CH_2CH_2SPr^n)_2(SPr^n)_2]$ (0.36 g; 0.69 mmol) in acetone (30 $cm^3$). The red solution darkened, and after 15 min the solvent was removed under reduced pressure to give a dark red residue which was washed with toluene ($2 \times 30$ $cm^3$) to remove any unreacted Mo starting material. The remaining solid was extracted with acetone (50 $cm^3$), the solution was concentrated under reduced pressure. Ethanol (5 $cm^3$) was added and the solution was cooled to −78°C. After 24 h red crystals separated. They were collected, washed with petroleum ether (40–60°C, $2 \times 10$ $cm^3$) and finally dried in vacuo. Yield, 0.7 g; 81%.

*{$\mu_2$-(SR)$_2$[bis[η-(3-phenyl-3-thiapropyl)cyclopentadienyl]dichloromolybdenum}-(cycloocta-1,5-diene)rhodium hexafluorophosphate (6)*

A suspension of $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)_2Cl_2]$ (0.15 g; 0.26 mmol) in acetone (25 $cm^3$) was added to a solution of $[(COD)RhCl]_2$ (0.14 g; 0.29 mmol) in acetone (25 $cm^3$). The mixture was stirred at 40°C for 4 h after which time the $[Mo(\eta\text{-}C_5H_4CH_2CH_2SPh)_2Cl_2]$ had completely dissolved. The solution was allowed to cool, and the solvent removed under reduced pressure. The green residue was extracted with acetone (30 $cm^3$), and the solution concentrated. After cooling to −78°C for 24 h, a green powder was deposited which washed with diethyl ether and dried in vacuo. Yield, 0.11 g; 51%.

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