New unsymmetrical thioether- and thiolate-substituted ferrocenediyl ligands and their metal complexes

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A series of new unsymmetrical 1,1′-disubstituted ferrocenediyl ligands featuring thioether or thiolate substituents have been conveniently synthesised. The chelating nature of the ligands is shown by coordination with a range of transition metal centres and bridged metal dimeric species are observed with platinum and palladium. Electrochemical studies show that the diferrocene species is a partially delocalised Robin–Day Class II system, whilst on coordination of metal centres to the monoferrocene ligands, the oxidation potential of the ferrocene subunit is greatly increased ranging from 0.25 to 0.60 V upon passing from platinum(II) to palladium(II) ions. Interestingly, the outer ferrocenediyl subunits of the dimeric complexes indicate electronic interaction through the diplatinum or dipalladium backbones. The chromium- and vanadium-containing species act as low activity, pre-catalysts for ethylene polymerisation.

Introduction

In coordination chemistry, the ferrocenyl moiety has played a significant role as a backbone or a substituent in ancillary ligands due to (i) the specific and unique geometries that the ferrocene provides and (ii) its electronic (redox) properties, whereby the possibility of switching the redox active state of the ferrocene backbone gives access to potential control of reactivity at a metal centre.[1,2] Ferrocene species with donor heteroatoms (e.g. P, N, S, O) substituted onto the cyclopentadienyl rings are well-known especially those featuring homo-substitution (i.e. the same donor atom along with the same alkyl or aryl substituents) but much less well-known are unsymmetrical 1,1′-disubstituted ferrocenes featuring hetero-combinations of N, P or S atoms[3] and as far as we are aware our communication in 2000[4] featured the first examples of unsymmetrical purely S-substituted neutral and neutral-anionic ferrocenediyl ligands. Complete syntheses of the new 'neutral–neutral' 1-(methylthio)-1′-(mesitylthio)ferrocene and the 'neutral–anionic' 1′-(mesitylthio)ferrocene-1-thiol ligands is detailed here, along with their Pt(II), Pd(II), Cr(III) and V(III) coordination chemistry, and potential to polymerise olefins.

Results and discussion

(i) Synthesis of ligands

The new disulfide, di[1′-(mesitylthio)ferrocene]disulfide (1) was formed via a modification of the synthetic methods developed by Herberhold et al. (Scheme 1).[5] A THF solution of 1,2,3-trithia-[3]ferrocenophane was treated with two equivalents of mesityllithium and the mixture stirred at room temperature for 20 h. Purification via column chromatography (neutral grade II alumina, CH2Cl2–hexane (1 : 9)) enabled separation of 1 in ca. 30% yield (other products isolated were dimesityl disulfide and a small amount of the original ferrocenophane). The proposed mechanism is shown in Scheme 2, where the S–S bonds are cleaved by mesityl ion leading to mesityl thiolate and 1′-(mesitylthio)ferrocene-1-thiolate, which are both oxidised and S–S bonds reformed on aerobic work-up of the reaction mixture.

From 1, both 1-(methylthio)-1′-(mesitylthio)ferrocene 2 and 1′-(mesitylthio)ferrocene-1-thiol 3 can be formed in good yield (Scheme 1). For 2, a THF solution of 1 was treated with 2 equivalents of methyllithium and the reaction mixture stirred

at room temperature for 20 h. After aqueous work-up, followed by column chromatography (neutral grade II alumina, CH2Cl2:hexane 1:4) 2 was isolated in ca. 50% yield. This is the maximum yield possible, as cleavage of the disulfide bond by methyllithium generates one molecule of 2 and one of 1′-mesitylthio)ferrocene-1-thiolate (which is oxidised during work-up to regenerate the starting material). It should be noted that we have recently developed[6] a higher yielding route to a range of unsymmetrical thioethers, by utilising lithium triethylborohydride to break the disulfide bond followed by reaction with RX (X = halide). The ¹H NMR spectrum of 2 shows three methyl signals in increasing δ values due to para-mesityl methyl, sulfur methyl and ortho-mesityl methyls, respectively, and in the cyclopentadienyl proton region there are four pseudo-triplets emphasising the asymmetry of the substitution.

1′-(Mesitylthio)ferrocene-1-thiol (3) was also synthesised in high yield via the treatment of a THF solution of 1 at −78 °C, with two equivalents of lithium triethylborohydride. After stirring at room temperature for 2 h, the solvent was removed in vacuo and the crude residue dissolved in dry, oxygen-free diethyl ether. Under anaerobic conditions and utilising nitrogen-saturated reagents, the air-sensitive orange 3 was isolated in 88% yield. In the ¹H NMR spectrum of 3, the thiolate proton is observed at 2.98 ppm along with four pseudo-triplets in the cyclopentadienyl region, along with characteristic mesityl methyl and mesityl proton signals at 2.21, 2.48 and 6.86 ppm, respectively.

Reaction of 1 with lithium triethylborohydride results in the near quantitative yield of the lithium thiolate salt, which can be used in situ in reaction with transition metal reagents (see later).

(ii) Metal complexes of 2

The reactivity of 2 was investigated with platinum(II) and palladium(II) precursors and compared to analogous reactions involving 1,1′-(bismethylthio)ferrocene[7] and 1,1′-bis(mesityl-thio)ferrocene.[8]

A slight excess of the ligand was added to a toluene solution of bis(benzonitrile)dichlorometal(II) (where metal is PtII or PdII) and the mixture heated to 60 °C. The yellow (for 4) and purple (for 5) solutions were heated at 60 °C for 20 h and hot filtered to remove any unreacted metal complex. Complexes 4 and 5 were isolated in 91 and 85% yields, respectively, via
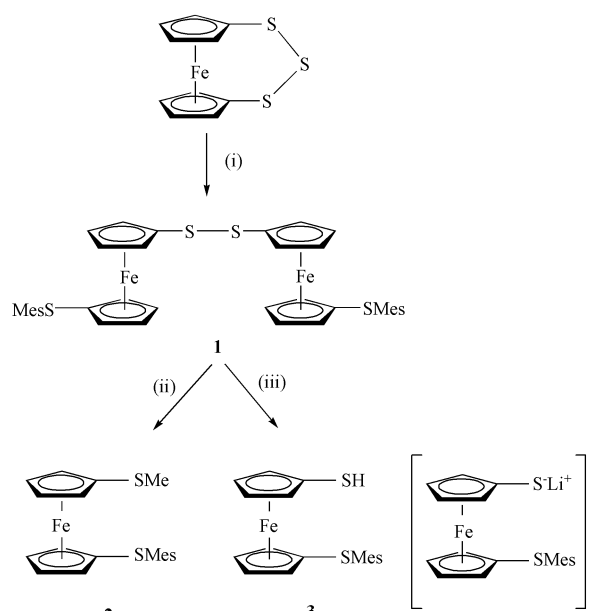
Scheme 1 Formation of ligands **1**–**3** and complexes **4**–**9**. Reagents and conditions: (i) MesLi, THF, −78 °C, then stirring at 25 °C, 16 h; (ii) MeLi (1.6 M), THF, stirring, 16 h; (iii) LiEt₃BH, THF, stirring, 1.5 h (stop here for lithio salt and use *in situ*) then for thiol formation KOH/diethyl ether, HCl until pH 2; (iv) MCl₂(PhCN)₂ (M = Pt or Pd), toluene, 60 °C, 20 h; (v) (from lithio salt) MCl₂(PhCN)₂ (M = Pt or Pd), toluene, 60 °C, 16 h; (vi) (from lithio salt) MCl₃(THF)₃ (M = Cr or V), THF, −78 °C, then stirring at 25 °C, 16 h.

washing and reprecipitation. In the positive ion FAB mass spectra, neither complex showed a molecular ion but did show peaks indicating loss of chlorine groups. In the room-temperature ¹H NMR spectra, both complexes gave signals characteristically shifted to lower field compared to the free ligand. Most of the signals in the spectra were broadened, especially in the ferrocenyl region due to the fluxional nature of the molecule *via* bridge reversal of the ferrocenophane linkage and sulfur inversion of the R groups.[7] Variable-temperature spectra were not taken as it was assumed that the fluxional processes would follow those observed previously and this is not the focus of the present research.

(iii) Metal complexes of 3

1′-(Mesitylthio)ferrocene-1-thiol or its thiolate anion (generated *in situ* by reaction of **3** with two equivalents of lithium triethylborohydride) were treated with a range of transition metal centres. For example, reaction with bis(benzonitrile)-
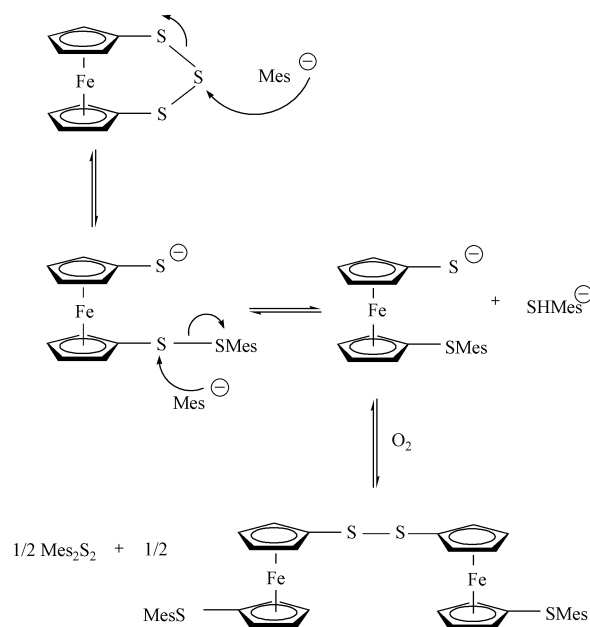
Scheme 2 Suggested mechanism for the formation of **1**.

dichlorometal(ɪɪ) (M = Pt or Pd) in toluene at 60 °C gave an initial precipitate of lithium chloride which was filtered off and after evaporation of the filtrate to dryness and washing with hexane, enabled isolation of **6** and **7** as yellow (93%) and purple (81%) powders, respectively. The bridging, dinuclear nature of the complexes is unusual, especially in ferrocenyl systems and only limited analogous examples are known.[9]

Due to excessive broadening of the signals, the ¹H NMR spectra were run at low temperatures (*ca.* −65 °C) and showed striking similarities. For **6**, the methyl groups on the mesityl ring show separate peaks (rather than the 2:1 ratio normally observed), with one resonance for a methyl group at 3.32 ppm – this deshielding is presumably due to significant interaction with the platinum metal centre. As expected for asymmetry resulting from a slowing of the fluxional processes, the ferrocenyl region shows eight separate resonances with similar sized ³J_{H-H} couplings, although due to slight broadening these could not be accurately measured. Once again, all the signals are shifted downfield with respect to the free ligand, due to the effect of the platinum centres. The spectrum of **7** (at 65 °C) is very similar to **6** in the shape, number and shift of the signals. For **6**, mass spectrometry indicates the presence of the molecular ion (196 amu) and fragmentation peaks corresponding to loss of chloride groups (1160 and 1125 amu). For **7**, a molecular ion is not observed, but instead peaks due to loss of mesityl (897 amu) and mesitylthio (870 amu) groups are apparent. The X-ray structure of **7** confirms the bridging dinuclear structure and this has been published previously in our initial communication.[4]

It should be noted that all attempts to synthesise a nickel(ɪɪ) complex with this new ligand failed to produce any tractable product. We propose that this is due to steric factors, as to date reactions with mesityl-containing neutral–neutral ferrocenediyl thioether ligands have also failed.

Complexes **8** and **9** were formed using 1-(lithiumthiolato)-1′-(mesitylthio)ferrocene which was syringed into a solution of M(thf)₃Cl₃ (M = Cr, V) at −78 °C. Colour changes were immediately observed, purple to yellow for chromium and salmon-pink to dark red for vanadium. On stirring at room temperature, both solutions became deep red and following evaporation to dryness, washing, extraction and filtration, dark purple solids were obtained in 48% yield for **8** and 43% yield for **9**. The paramagnetic **8** and **9** are highly air-sensitive materials but reasonable microanalysis results were obtained, and though mass spectrometry was inconclusive, the magnetic susceptibility

measurements obtained *via* Evans' method NMR spectroscopy[10] (with the samples being made up in a N_2-filled glove box) gave good results. The magnetic moments were calculated to be 3.79 and 2.40 μ_B for chromium and vanadium, respectively, and are in reasonable agreement with the spin-only values (3.87 and 2.87 μ_B, respectively). The method of calculation used is an adaption of the one described by Evans[10] and enables calculation of the magnetic susceptibility (χ_{exp}) in cgs units. The values are slightly lower than calculated by spin-only methods. This is due to spin–orbit coupling which tends to reduce the value of the magnetic moment for complexes with d^1 and d^2 electronic configurations. The magnetic susceptibility measurements by Evans' method NMR and microanalysis support a simple chelating structure but a dimeric structure (as seen for **6** and **7**) cannot be conclusively ruled out.

Electrochemistry

Complexes **2** and **3** in CH_2Cl_2 solution exhibit common one-electron oxidation with features of chemical reversibility in cyclic voltammetry, which is typical of monoferrocene molecules. However, notably different is the behaviour of the two complexes as far as their exhaustive oxidation is concerned. In fact, the solution resulting from controlled potential electrolysis of **2** ($E_w = +0.8$ V) displays a cyclic voltammetric profile quite complementary to the original one, which indicates complete chemical stability of the redox couple **2**/[**2**]$^+$. It is noted that as a consequence of the exhaustive one electron removal, the original yellow solution ($\lambda_{max} = 443$ nm) does not appreciably change colour, thus suggesting that the sulfur-based substituents significantly contribute to the HOMO level (iron-centred ferrocenium species are blue to green coloured). In contrast, as illustrated in Fig. 1b, the solution resulting from controlled potential electrolysis of **3** displays a cyclic voltammetric profile characterised by two reversible reductions.
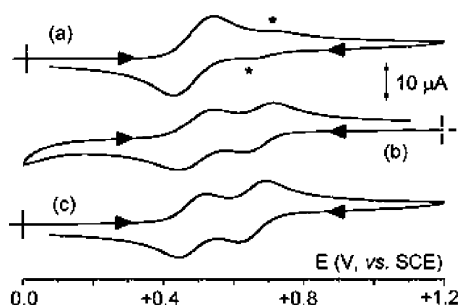

Fig. 1 Cyclic voltammograms recorded at a platinum electrode in CH_2Cl_2 solutions containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) and: (a) **3** (1.1 × 10^{-3} mol dm^{-3}), initial; (b) **3** after exhaustive oxidation; (c) **1** (0.7 × 10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

In fact, as shown in Fig. 1a, the main anodic process exhibited by **3** is followed by a minor oxidation (starred peak-system), which tends to disappear with increased scan rate (at 2.0 V s^{-1} no more traces are detected). This means that [**3**]$^+$ undergoes a slow chemical reaction to the by-product responsible for the second anodic process. Exhaustive oxidation ($E_w = +0.8$ V) consumes about 1.7/1.8 electrons per molecule and the original yellow solution ($\lambda_{max} = 443$ nm) turns red–brown, displaying a main absorption at 453 nm together with two further broad absorptions at 670 and 845 nm, respectively.

As deduced from Fig. 1c, the voltammetric profile of the diferrocene complex **1** is quite complementary to that of the product resulting from exhaustive two-electron oxidation of **3**. This suggests that oxidation of **3** is accompanied by heterolytic cleavage of the –S–H function of the monocation [**3**]$^+$ and the subsequent dimerisation of the thio radical leads to [**1**]$^+$. Within the cyclic voltammetric time scale, this is proved by the appear-

ance of the above cited minor starred peak system, which corresponds to the second oxidation of the diferrocene **1**. During the long periods of controlled potential electrolysis complete conversion to [**1**]$^{2+}$ occurs. In confirmation, an authentic sample of electrogenerated [**1**]$^{2+}$ affords a voltammetric profile identical to that shown in Fig. 1b and exhibits a red–brown colour and a visible spectrum quite coincident with that illustrated for the species resulting from exhaustive oxidation of **3**.

The appearance of two separate one-electron oxidations for **1** ($\Delta E°' = 0.17$ V) suggests that the two ferrocenediyl units are mutually interacting. Assuming that the value of the relative comproportionation constant ($K_{com} = 7 × 10^2$) might for the most part reflect the degree of electronic communication in the mixed-valent complex [**3**]$^+$,[11] it suggests that the biferrocenium ion [**1**]$^+$ belongs to the partially delocalised Robin–Day Class II.[12]

Considering the metallaferrocenes studied here, Figs. 2a and b compare the cyclic voltammetric profile of the platinum complex **4** with that of the corresponding free ligand **2**. As seen, the one electron oxidation of the ferrocene subunit in **4** occurs at potential values about 0.25 V higher than that of **2**. Controlled potential coulometry ($E_w = +1.0$ V) shows the consumption of one electron per molecule of **4**, but cyclic voltammetric tests on the exhaustively oxidised solution prove that [**4**]$^+$ partially undergoes decomposition releasing the free ligand **2** (in its oxidised form [**2**]$^+$).
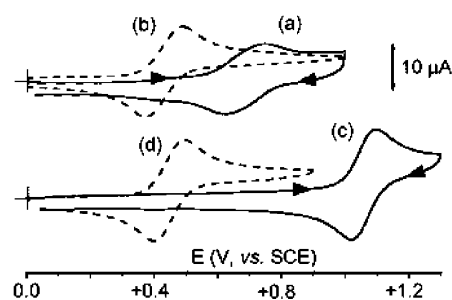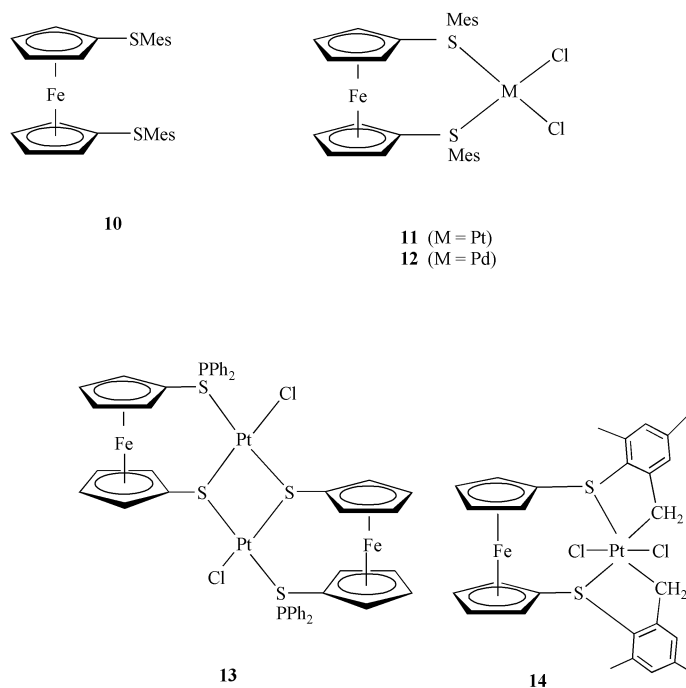

Fig. 2 Cyclic voltammograms recorded at a platinum electrode in CH_2Cl_2 solutions containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) and: (a) **4** (0.8 × 10^{-3} mol dm^{-3}); (b) **2** (0.7 × 10^{-3} mol dm^{-3}); (c) **11** (1.1 × 10^{-3} mol dm^{-3}); (d) **10** (1.0 × 10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

It is interesting to compare the redox behaviour of the couple **2**/**4** with that of the related symmetric ligand 1,1′-bis(mesityl-thio)ferrocene, **10**, and its platinum complex **11** (Scheme 3).[8] As illustrated in Figs. 2c and d, in this case the separation between the one-electron oxidation of the platinum complex and that of the free ligand is about 0.6 V. This means that the symmetric ligand **10** exhibits a higher coordinating ability towards the $PtCl_2$ fragment than that of the asymmetric ligand **2**. Also in this case, despite the features of chemical reversibility of the one-electron oxidation of **11**, exhaustive oxidation is again accompanied by partial release of the free ligand **10** (in its oxidised form [**10**]$^+$).

Notably different is the behaviour of the "hang-glider like" cyclometalated platinum complex **14**.[8] The corresponding monocation [**14**]$^+$ is quite long-lived indicating that hexa-coordination renders the platinum complex stable in its oxidised form. The one-electron removal causes the original light yellow solution to turn light green, suggesting that the HOMO level is essentially iron centred. In contrast to the platinum complexes **4** and **11**, the corresponding palladium complexes **5** and **12** afford an oxidation process which shows fast release of the corresponding free ferrocene ligands (*i.e.* in the backscan, a new peak coincident with that of the ferrocenium/ferrocene couple arises). To illustrate this, Fig. 3 shows the voltammetric response of **12**. Finally, Figs. 4a and b show the cyclic voltammetric behaviour of the dinuclear platinum and palladium complexes **6** and **7**, respectively. Apart from the presence of

10

11 (M = Pt)
12 (M = Pd)

13

14

Scheme 3 Related compounds **10**–**14** used in electrochemical studies.

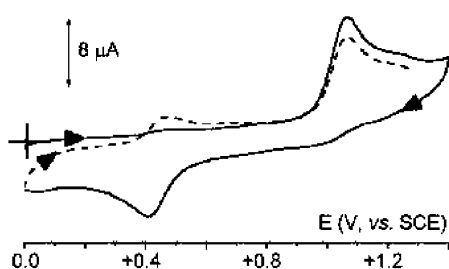**Fig. 3** Cyclic voltammogram recorded at a platinum electrode in CH_2Cl_2 solution of **12** (0.8×10^{-3} mol dm^{-3}). [NBu$_4$][PF$_6$] (0.2 mol dm^{-3}) supporting electrolyte. Scan rate 0.2 V s^{-1}.
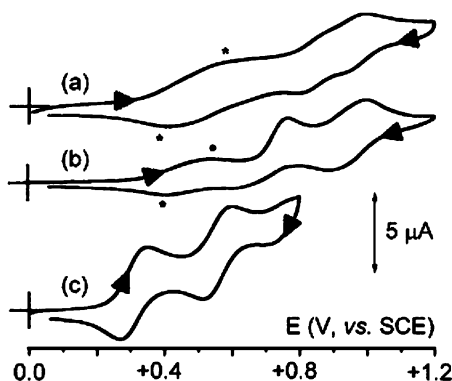
Fig. 4 Cyclic voltammograms recorded at a platinum electrode in CH_2Cl_2 solution of: (a) **6** (0.9×0^{-3} mol dm^{-3}); (b) **7** (1.0×10^{-3} mol dm^{-3}); **13** (1.1×10^{-3} mol dm^{-3}). [NBu$_4$][PF$_6$] (0.2 mol dm^{-3}) supporting electrolyte. Scan rate 0.02 V s^{-1}.

Table 1 Formal electrode potentials (V, *vs.* SCE) and peak-to-peak separations (mV) for the ferrocene-centred processes exhibited by complexes under study in CH_2Cl_2 solution

Complex	$E°'_{0/+}$	$\Delta E_p{}^a$	$E°'_{+/2+}$	$\Delta E_p{}^a$
3	+0.48	97		
2	+0.43	103		
10	+0.45	94		
1	+0.49	76	+0.66	76
4	+0.69	107		
5	+1.01^b	–		
11	+1.06	65		
12	+1.07^b	–		
14	+0.83	67		
6	+0.83^c	^{d}	+0.94^c	^{d}
7	+0.75^c	^{d}	+0.97^c	^{d}
13	+0.31	73	+0.57	65
FcH	+0.39	60		

^{a} Measured at 0.1 V s^{-1}. ^{b} Peak potential value for irreversible processes. ^{c} Measured from DPV technique. ^{d} Difficult to measure.

small amounts of free ligand (starred peaks) two more or less separated anodic processes are present, which we assign to the two ferrocene ligands. It is quite evident that the palladium centres allow a greater mutual interaction of the ferrocene ligands than platinum centres ($\Delta E°' = 0.22$ V *vs.* $\Delta E°' = 0.11$ V). Despite the features of chemical reversibility within the cyclic voltammetric time scale, decomposition occurs upon exhaustive electrolysis even at the potentials of the first process.

It is interesting to compare the behaviour of the platinum complex **6** with that of the similar complex **13**,[13] where in the ferrocene substituents a diphenylphosphino group replaces the mesitylthio group. As illustrated in Fig. 4c, in this case two well separated ferrocene oxidations are present ($\Delta E°' = 0.26$ V), thus illustrating the delicate electronic effects played by partial replacement of functional groups in complex molecules and their unpredictable role on the intramolecular electronic mobility. In addition, the red–brown mixed-valent monocation [**13**]$^+$, which can be tentatively assigned as partially delocalised ($K_{com} = 2 \times 10^4$), is quite stable.

The formal electrode potentials of the ferrocene centred processes for all the derivatives studied are compiled in Table 1.

Finally, we note that all the complexes display an irreversible anodic process in the range from +1.5 to +1.6 V, which is likely centred on the sulfur substituents, and in addition, all the platinum and palladium complexes display irreversible reduction processes in the range from −1.2 to −1.6 V, which are attributed to the corresponding M(II)/M(0) process.

Ethylene polymerisation

The results of the Schlenk tests for the chromium and vanadium complexes **8** and **9** are shown in Table 2. It may be noted that the catalyst structure has been assumed to be a

Table 2 The pre-catalysts and their activities for ethylene polymerisation (L = 1′-(mesitylthio)ferrocene-1-thiolate)

Pre-catalyst (mg, mmol)	Solvent/mL	Activating agent (eq.)	Pressure ethylene/bar	Time of run/h	Yield of polymer/g	Procatalyst activity/ g mmol^{-1} h^{-1} bar^{-1}
CrL(THF)$_2$Cl$_2$ (25, 0.04)	Toluene (200)	MAO (100)	1	1	0.345	8.6
CrL(THF)$_2$Cl$_2$ (25, 0.04)	Toluene (200)	Et$_2$AlCl (100)	1	1	0.315	7.9
CrL(THF)$_2$Cl$_2$ (25, 0.04)	Toluene (200)	MeAlCl$_2$ (100)	1	1	0.010	0.3
CrL(THF)$_2$Cl$_2$ (25, 0.04)	Toluene (200)	AlMe$_3$ (100)	1	1	0.115	2.9
VL(THF)$_2$Cl$_2$ (25, 0.04)	Toluene (200)	MAO (100)	1	1	0.100	2.5
VL(THF)$_2$Cl$_2$ (25, 0.04)	Toluene (200)	Et$_2$AlCl (100)	1	1	0.156	3.9
VL(THF)$_2$Cl$_2$ (25, 0.04)	Toluene (200)	MeAlCl$_2$(100)	1	1	1.120	28.0
VL(THF)$_2$Cl$_2$ (25, 0.04)	Toluene (200)	AlMe$_3$ (100)	1	1	0.185	4.6

mononuclear octahedral complex; if it were to exist in a dimeric form under polymerisation conditions, the activities would be almost exactly the same.

There were no oligomers detected in any of the polymerisations runs. The analysis of the polyethylene was carried out at BP (Sunbury) and showed that it was all HDPE (high density polyethylene), giving M_w in the range 330,000–990,000 with polydispersities in the range 2–4. This is consistent with other research into Cr^{III} pre-catalysts and indicative of a single site catalyst.[14] The catalysts do not polymerise ethylene in the absence of an initiator, but when activated show moderate to low activity for ethylene polymerisation. The most active catalyst was the vanadium complex, when activated with MeAlCl$_2$, which shows an activity of 28 g mmol^{-1} h^{-1} bar^{-1}. Some caution must be taken when analysing the results as previous work in the Gibson group has shown that when vanadium procatalysts are activated with aluminium alkyl initiators, the ligand is displaced and a vanadium–aluminium species forms.[14]

Experimental

All preparations were carried out using standard Schlenk techniques.[15] All solvents were distilled over standard drying agents under nitrogen directly before use and all reactions were carried out under an atmosphere of nitrogen. Alumina gel (neutral – grade II) was used for chromatographic separations unless specified otherwise.

All NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 250.1 MHz (^{1}H) and 101.3 MHz (^{31}P{^{1}H}), respectively. Chemical shifts are reported in δ using CDCl$_3$ (^{1}H, δ 7.25 ppm) as the reference for ^{1}H spectra, while the ^{31}P{^{1}H} spectra were referenced to H$_3$PO$_4$. Infrared spectra were recorded using NaCl solution cells (CH$_2$Cl$_2$ or THF) on a Mattson Polaris Fourier Transform IR spectrometer. Mass spectra were recorded using positive FAB methods, on an Autospec Q mass spectrometer. Microanalyses were carried out by SACS, University of North London. Material and apparatus for electrochemistry have been described elsewhere.[16]

Di[1′-mesitylthioferrocene]disulfide (1)

1,2,3-Trithia-[3]ferrocenophane (1 g, 3.6 mmol, 1 eq.) was dissolved in THF (20 mL) and cooled to −78 °C. Mesityl-lithium (2 eq.), generated *in situ* and dissolved in THF (20 mL), was added to this by cannula. The reaction was stirred at room temperature overnight. Water (20 mL) was added and the layers separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (2 × 20 mL) and the combined organics were dried (MgSO$_4$) and evaporated to dryness. Column chromatography (neutral grade II alumina, CH$_2$Cl$_2$–hexane (2 : 8)) enabled separation of the product (0.40 g, 0.54 mmol, 30%).

Anal. Calc. for C$_{38}$H$_{38}$S$_4$Fe$_2$: C 62.13, H 5.21%. Found: C 62.14, H 5.32%; δ_H (CDCl$_3$): 2.21 (s, 6H, CH$_3$), 2.47 (s, 12H, CH$_3$), 4.07 (s, 4H, C$_5$H$_4$), 4.21 (s, 4H, C$_5$H$_4$), 4.32 (d, 8H, C$_5$H$_4$),

6.85 (s, 4H, C$_6$H$_2$); *m/z*: 734 (M)$^+$, 423 (M − 2SMes)$^+$, 367 (M − S − SMes)$^+$, 334 (M − 2S − SMes)$^+$, 304 (M − 4S − Mes)$^+$.

1-(Methylthio)-1′-(mesitylthio)ferrocene (2)

Compound **1** (0.58 g, 0.79 mmol, 1 eq.) was dissolved in dry, deoxygenated THF (40 mL). To this solution was added methyl-lithium (1.6 M solution in diethyl ether, 1.1 mL, 1.74 mmol, 2 eq.) and the reaction stirred for 16 h. The solvent was removed, the residue dissolved in diethyl ether and water added. The layers were separated and the aqueous layer extracted (3 × 20 mL, diethyl ether). The combined organic layers were dried (MgSO$_4$) and evaporated to dryness. Separation of the product was achieved by column chromatography (neutral grade II alumina, CH$_2$Cl$_2$–hexane (1 : 4)). The product was eluted as the first fraction and formed an orange oil on removal of the solvent (0.15 g, 0.4 mmol, 50%). The only other product was the starting disulfide, which was recovered in 25% yield.

Anal. Calc. for C$_{20}$H$_{22}$S$_2$Fe: C 62.83, H 5.8%. Found: C 62.75, H 5.82%; δ_H (CDCl$_3$): 2.24 (s, 3H, CH$_3$), 2.34 (s, 3H, SCH$_3$), 2.51 (s, 6H, CH$_3$), 4.13 (t, 2H, C$_5$H$_4$), 4.26 (m, 4H, C$_5$H$_4$), 4.34 (t, 2H, C$_5$H$_4$), 6.88 (s, 2H, C$_6$H$_2$); *m/z*: 382 (M)$^+$, 367 (M − Me)$^+$, 334 (M − SMe)$^+$, 271 (M − CpSMe)$^+$, 232 (M − SMe − Mes)$^+$.

1′-(Mesitylthio)ferrocene-1-thiol (3)

Compound **1** (0.20 g, 0.27 mmol, 1 eq.) was dissolved in dry, deoxygenated THF (20 mL). To this solution was added lithium triethylborohydride (1 M solution in THF, 0.54 mL, 0.54 mmol, 2 eq.) and the reaction stirred for 1.5 h. The solvent was removed *in vacuo* and the residue dissolved in diethyl ether (20 mL). To this solution was added, by cannula, nitrogen saturated 1% KOH solution (20 mL) and the solution was stirred vigorously. The aqueous layer was removed by cannula to a dry Schlenk tube under nitrogen and acidified with nitrogen-saturated concentrated HCl added dropwise until the pH reached 2 and at this point a precipitate formed. This was extracted with diethyl ether (3 × 20 mL) and dried (Na$_2$SO$_4$). The solvent was removed to give an orange solid. This was recrystallised from pentane at −25 °C to give the pure thiol (0.13 g, 0.47 mmol, 88%).

Anal. Calc. for C$_{19}$H$_{20}$S$_2$Fe: C 61.80, H 5.47%. Found: C 61.73, H 5.46%; δ_H (CDCl$_3$): 2.21 (s, 3H, CH$_3$), 2.48 (s, 6H, 2 CH$_3$), 2.98 (s, 1H, SH) 4.11 (t, 2H, C$_5$H$_4$), 4.21 (m, 4H, C$_5$H$_4$), 4.33 (t, 2H, C$_5$H$_4$), 6.86 (s, 2H, C$_6$H$_2$); *m/z*: 368 (M)$^+$, 367 (M − H)$^+$, 334 (M − SH)$^+$.

Lithium 1′-(mesitylthio)ferrocene-1-thiolate

Di[1′-(mesitylthio)ferrocene]disulfide (0.10 g, 0.135 mmol, 1 eq.) was dissolved in dry, deoxygenated THF. To this solution was added lithium triethylborohydride (1 M solution in THF, 0.3 mL, 0.3 mmol, 2.2 eq.) and the reaction stirred for 1.5 h. The volatile by-products were removed *in vacuo* and the residue redissolved in THF (10 mL). The solution was reacted *in situ* with a range of metal centres.

Dichloro[1-(methylthio)-1′-(mesitylthio)ferrocene]platinum(II) (4)

A solution of **2** (0.15 mmol, 17 mL of a 9 mM stock solution in toluene, 1.2 eq.) in toluene was injected into a solution of bis(benzonitrile)dichloroplatinum(II) (0.06 g, 0.13 mmol, 1 eq.) dissolved in toluene (20 mL) at 60 °C. The solution was stirred for 20 h at this temperature and the solvent removed *in vacuo*. The residue was washed with hexane (30 mL), dissolved in CH_2Cl_2 (5 mL) and reprecipitated using hexane (40 mL), enabling isolation of the product as a yellow powder (0.10 g, 0.12 mmol, 91%).

Anal. Calc. for $C_{20}H_{22}S_2FePtCl_2$: C 37.05, H 3.42%. Found: C 37.46, H 3.62%; δ_H (CDCl$_3$): 2.22 (s, 3H, CH$_3$), 2.46 (s, 6H, CH$_3$), 2.67 (s, 3H, SCH$_3$), 4.34 (br m, C$_5$H$_4$), 4.37 (br m, C$_5$H$_4$), 4.44 (br m, C$_5$H$_4$), 5.00 (br m, C$_5$H$_4$) 6.87 (s, 2H, C$_6$H$_2$); *m/z*: 611 (M − Cl)$^+$, 577 (M − 2Cl)$^+$, 382 (L)$^+$.

Dichloro[1-(methylthio)-1′-(mesitylthio)ferrocene]palladium (5)

A solution of **2** (0.15 mmol, 17 mL of a 9 mM stock solution in toluene, 1.2 eq.) in toluene was injected into a solution of bis(benzonitrile)dichloropalladium(II) (0.05 g, 0.13 mmol, 1 eq.) dissolved in toluene (20 mL) at 60 °C. The solution was stirred for 20 h at this temperature and the solvent removed *in vacuo*. The residue was washed with hexane (30 mL), dissolved in CH_2Cl_2 (5 mL) and reprecipitated using hexane (40 mL), enabling isolation of the product as a purple powder (0.06 g, 0.11 mmol, 85%).

Anal. Calc. for $C_{20}H_{22}S_2FePdCl_2$: C 42.92, H 3.96%. Found: C 43.02, H 3.85%; δ_H (CDCl$_3$): 2.22 (s, 3H, CH$_3$), 2.44 (s, 6H, CH$_3$), 2.65 (s, 3H, SCH$_3$), 4.28 (t, 2H, C$_5$H$_4$), 4.33 (t, 2H, C$_5$H$_4$), 4.39 (t, 2H, C$_5$H$_4$), 4.67 (br m, C$_5$H$_4$), 6.87 (s, 2H, C$_6$H$_2$); *m/z*: 525 (M − Cl)$^+$, 487 (M − 2Cl)$^+$, 382 (L)$^+$.

Bis[1′-(mesitylthio)ferrocene-1-(μ-thiolato)]bisplatinum(II)-dichloride (6)

Lithium 1′-(mesitylthio)ferrocene-1-thiolate (0.27 mmol) was dissolved in toluene (30 mL). Bis(benzonitrile)dichloroplatinum(II) (0.13 g, 0.27 mmol, 1 eq.) was also dissolved in toluene at 60 °C, giving a pale yellow solution. To this solution was added the toluene solution of lithium 1′-(mesitylthio)ferrocene-1-thiolate, resulting in an immediate darkening of the solution to deep red–orange. The solution was stirred at 60 °C for 16 h. An off-white precipitate was deposited, which was filtered off and washed with hot toluene (2 × 20 mL) and the filtrate evaporated to a brown oil. The oil was suspended in hot hexane (2 × 40 mL) enabling precipitation of the product as a pale brown yellow powder (0.15 g, 0.13 mmol, 93%). Recrystallisation from CH_2Cl_2–hexane (1:1) resulted in yellow crystals suitable for spectroscopy and microanalysis.

Anal. Calc. for $C_{38}H_{38}S_4Fe_2Pt_2Cl_2$: C 38.17, H 3.2%. Found: C 38.18, H 3.1%; δ_H (CDCl$_3$), −30 °C: 2.19 (s, 6H, CH$_3$), 2.45 (s, 6H, CH$_3$), 3.32 (s, 6H, CH$_3$), 4.11 (m, 2H, C$_5$H$_4$), 4.25 (m, 2H, C$_5$H$_4$), 4.42 (m, 2H, C$_5$H$_4$), 4.46 (m, 2H, C$_5$H$_4$), 4.55 (m, 2H, C$_5$H$_4$), 4.60 (m, 2H, C$_5$H$_4$), 4.67 (m, 2H, C$_5$H$_4$), 5.20 (m, 2H, C$_5$H$_4$), 6.80 (s, 2H, C$_6$H$_2$), 6.93 (s, 2H, C$_6$H$_2$); *m/z*: 1196 (M)$^+$, 1160 (M − Cl)$^+$, 1125 (M − 2Cl)$^+$, 1061 (M − Mes − Me)$^+$, 821 (M − 2SMes − 2Cl)$^+$.

Bis[1′-(mesitylthio)ferrocene-1-(μ-thiolato)]bispalladium(II) dichloride (7)

Lithium 1′-(mesitylthio)ferrocene-1-thiolate (0.27 mmol) was dissolved in toluene (30 mL). Bis(benzonitrile)dichloropalladium(II) (0.10 g, 0.27 mmol, 1 eq.) was dissolved in toluene at 60 °C, giving a deep red solution. To this solution was added the toluene solution of lithium 1′-(mesitylthio)ferrocene-1-thiolate, resulting in immediate darkening of the solution to dark purple. The solution was stirred at 60 °C for 16 h. A black precipitate was deposited, which was filtered off and washed

with hot toluene (2 × 20 mL) and the filtrate was evaporated to a black oil. The oil was suspended in hot hexane (2 × 40 mL) causing precipitation of the product as a purple–black powder (0.11 g, 0.11 mmol, 81%). Recrystallisation from CH_2Cl_2–hexane (1:1) resulted in purple crystals suitable for spectroscopy and microanalysis.

Anal. Calc. for $C_{38}H_{38}S_4Fe_2Pd_2Cl_2$: C 44.82, H 3.76%. Found: C 44.66, H 3.77%; δ_H (CDCl$_3$), −40 °C: 2.16 (s, 6H, CH$_3$), 2.41 (s, 6H, CH$_3$), 3.29 (s, 6H, CH$_3$), 4.07 (m, 2H, C$_5$H$_4$), 4.28 (m, 2H, C$_5$H$_4$), 4.44 (m, 4H, C$_5$H$_4$), 4.57 (m, 2H, C$_5$H$_4$), 4.60 (m, 2H, C$_5$H$_4$), 4.66 (m, 2H, C$_5$H$_4$), 5.07 (m, 2H, C$_5$H$_4$), 6.80 (s, 2H, C$_6$H$_2$), 6.93 (s, 2H, C$_6$H$_2$); *m/z*: 982 (M − Cl)$^+$, 937 (M − Cl − 3Me)$^+$, 897 (M − Mes)$^+$, 870 (M − SMes)$^+$, 754 (M − SMes − Mes)$^+$, 647 (M − 2SMes − 2Cl)$^+$.

Bis(tetrahydrofuran)dichloro[1′-(mesitylthio)ferrocene-1-(thiolato)]chromium(III) (8)

Trichlorotris(tetrahydrofuran)chromium(III) (0.24 g, 0.65 mmol, 1 eq.) was dissolved in THF (30 mL) and cooled to −78 °C. To this solution was added the solution of lithium 1′-(mesitylthio)-ferrocene-1-thiolate (0.65 mmol), resulting in immediate colour change from purple to yellow. As the solution warmed to room temperature the colour darkened to a deep red, this colour was maintained over 16 h stirring at room temperature. The solvent was removed and the extracts washed with heptane (100 mL) and extracted with toluene (3 × 30 mL), leaving the precipitated lithium chloride behind as an off-white solid. The toluene was removed yielding a deep purple solid (0.20 g, 0.32 mmol, 48%).

Anal. Calc. for $C_{27}H_{35}S_2O_2FeCrCl_2$: C 50.9, H 5.56%. Found: C 48.4, H 5.67%; *m/z*: 456 (M − Cl − 2THF)$^+$, 419 (M − 2Cl − 2THF)$^+$, 368 (L)$^+$; Magnetic moment by Evans' method NMR spectroscopy (CDCl$_3$, cyclohexane): 3.79 μ_B (theoretical value: 3.88 μ_B).

Bis(tetrahydrofuran)dichloro[1′-(mesitylthio)ferrocene-1-(thiolato)]vanadium(III) (9)

Trichlorotris(tetrahydrofuran)vanadium(III) (0.24 g, 0.65 mmol, 1 eq.) was dissolved in THF (30 mL) and cooled to −78 °C. To this solution was added the solution of lithium 1′-(mesitylthio)-ferrocene-1-thiolate (0.65 mmol), resulting in immediate colour change form pink to red. As the solution warmed to room temperature the colour darkened to purple, this colour was maintained over 16 h stirring at room temperature. The solvent was removed and the extracts washed with heptane (3 × 30 mL) and extracted into toluene (3 × 30 mL), leaving the precipitated lithium chloride behind as an off white solid. The toluene was removed yielding a deep purple–black solid (0.18 g, 0.28 mmol, 43%).

Anal. Calc. for $C_{27}H_{35}S_2O_2FeVCl_2$: C 51.26, H 5.58%. Found: C 50.89, H 5.86%; Magnetic moment by Evans' method NMR spectroscopy (CDCl$_3$, cyclohexane): 2.40 μ_B (theoretical value: 2.82 μ_B).

Ethylene polymerisations

All polymerisations were carried out according to the following procedure. The pre-catalyst (0.04 mmol) was thoroughly dried (drying piston overnight or in a Schlenk tube on a vacuum line if the compound is air sensitive) and added to a clean, dry Schlenk tube, charged with a stirrer bar, under nitrogen. The pre-catalyst was suspended in dry, deoxygenated toluene (200 mL) and to this suspension was added methylaluminoxane (10% solution in toluene, 0.4 mmol, 2.66 mL). The addition of methylaluminoxane caused complete dissolution of all species and often a colour change. The Schlenk tube was then transferred to the ethylene line (p = 1 bar), where it was flushed through with ethylene several times and then stirred at the fastest rate for 1 h. After this time acidified methanol (200 mL) was added and effervescence was observed. The layers were

separated and the organic layer dried (MgSO$_4$) and a small sample submitted for GC-MS. The remaining solvent was removed and the sample analysed by ^{1}H, ^{31}P{^{1}H} NMR and FAB mass spectrometry.

Acknowledgements

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