New S/O-substituted ferrocenediyl ligands and their metal complexes[†]

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New unsymmetrical S/O 1,1'-disubstituted ferrocenediyl ethers and hydroxides have been synthesised. The coordination chemistry of 1-(methylsulfanyl)-1'-(methoxy)ferrocene **6** has been investigated with palladium(II) and platinum(II) precursors. With palladium(II), a bis- μ -chloro-bridged dimeric complex **10** was obtained with the ligand bound solely through the thioether donor group. With platinum(II), a bis-ligand *trans*-sulfur ligated complex **11** was obtained and structurally characterised.

Introduction

The synthesis of ferrocenyl ligands featuring one or more donor heteroatoms has received a great deal of attention in recent years and extensive studies into their coordination chemistry and applications within catalysis have been undertaken.^{1,2} As well as providing a rigid ligand framework with a wide bite angle, the electronic (redox) properties of the ferrocene unit provide the possibility of electrochemically controlling the reactivity and binding at a metal centre.3 Planar chiral unsymmetrically 1,2-disubstituted ferrocenes have found wide applications in asymmetric catalysis and symmetrical 1,1'-disubstituted ferrocenes are common bidentate ligands in coordination chemistry (1,1'-bis{diphenylphosphino}ferrocene being employed most prevalently).^{2,4} Unsymmetrically 1,1'-disubstituted ferrocenes featuring hetero-combinations of N, P, S, Se or O atoms, usually formed via bromo, 5,6 lithio7,8 or stannyl9 intermediates, are less well known but have received increasing attention in recent yearsfor instance, we have recently published the synthesis of novel 1,1'-P/O ferrocenyl ethers (1, see Fig. 1)¹⁰ and hydroxyferrocenes (2, 3).¹¹



Fig. 1 1,1'-Ferrocenediyl ethers and hydroxides.

Ferrocene compounds containing hydroxyl-substituents and their application in coordination chemistry are rare: their tendency to decompose in air to cyclopentenone species makes their synthesis and handling a challenge.¹² Favourable intermolecular hydrogen-bonding interactions were thought to stabilise these hydroxyferrocenes allowing their structural characterisation and coordination chemistry to be investigated. Recently, new synthetic routes to ferrocenyl ethers have been developed.¹³ Ferrocenecontaining crown ethers and cryptands have been synthesised and their use as alkali and transition metal complexing agents investigated.¹⁴ Although more stable than hydroxyferrocenes, their application as ligands in coordination chemistry is still relatively scarce and warrants further study.^{15,16} Herein, we report the synthesis of new S/O-substituted ferrocenediyl ligands and their coordination chemistry with palladium and platinum precursors. Thioether- and thiolate-substituted ferrocenyl ligands are considerably less well studied than the corresponding phosphine derivatives but have been shown to stabilise unusual metal complexes.^{7,16-20} In addition, the application of ligands containing hard oxygen and soft sulfur donor groups in catalysis is also a growing area of importance and the beneficial effect of soft sulfur donors on the activity of harder transition metal polymerisation catalysts, such as titanium and zirconium, has been noted.²¹

Results and discussion

Ligand synthesis

The use of bis(trimethylsilyl)peroxide in the preparation of metallocenyl hydroxides^{11,22} and trimethylsilylethers²³ prompted its application in the synthesis of 1-(bromo)-1'-(methoxy)ferrocene **4**.¹⁰ From this starting material, a variety of sulfur heteroatomsubstituted ferrocenyl ethers have been synthesised as shown in Scheme 1.

4 was reacted with one equiv. of *n*-butyllithium in a cooled THF solution and the lithio-intermediate 5 quenched in situ with different sulfur-containing electrophiles. 1-(Methylsulfanyl)-1'-(methoxy)ferrocene 6 was obtained using dimethyl disulfide as the quenching agent as an orange oil in 82% yield following purification via column chromatography. The ¹H NMR spectrum of 6 shows two singlets at 2.28 and 3.66 ppm corresponding to the SMe and OMe protons respectively. The cyclopentadienyl protons show the expected four pseudo-triplets, indicating unsymmetrical substitution of the cyclopentadienyl rings. Reaction of 5 with diphenyl disulfide gave 7 as an orange crystalline solid in 59% yield following purification via column chromatography. Again, the ¹H NMR spectrum confirmed the unsymmetrical substitution of the cyclopentadienyl rings together with signals for the methoxy and phenyl protons. We have recently reported the synthesis of sterically hindered bis-sulfido-bridged dithioferrocenes18 and have also investigated cleavage of the disulfide bridge in the synthesis of unsymmetrical thioether-, thiol- and thioether-, thioether-substituted ferrocenes.¹⁹ A novel ether-substituted

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Scheme 1 Reagents and conditions: (i) *n*-BuLi, THF, -78 °C, 10 min; (ii) RSSR, THF, rt, 20 h; (iii) S₂Cl₂, THF, rt, 20 h; (iv) *n*-BuLi, THF, -78 °C, 10 min; (v) TMSOOTMS, -78 °C, 1 h; (vi) hydrolysis.

bis-sulfido-bridged ferrocene was synthesised *via* reaction of **5** with freshly distilled sulfur chloride to give **8** as a brown oil in 44% yield following purification *via* column chromatography. The ¹H NMR spectrum of **8** shows a singlet at 3.59 ppm corresponding to the OMe protons. The cyclopentadienyl protons show two pseudo-triplets at 3.82 and 4.07 ppm and a multiplet at 4.32 ppm. The positive FAB mass spectrum shows the molecular ion (494 amu) and peaks corresponding to cleavage of the disulfide bond (247 amu).

The hydroxyferrocenes 2 and 3 were found to be unexpectedly stable which was thought to be due to intermolecular hydrogen bonding interactions. It was therefore decided to investigate the synthesis of a thioether-substituted hydroxyferrocene 9 to probe this stabilising hydrogen bonding interaction further. 1-(Phenylsulfanyl)-1'-(bromo)ferrocene was synthesised as described by Dong and co-workers.5 It was then dissolved in THF and cooled to -78 °C. One equivalent of n-butyllithium was added followed by bis(trimethylsilyl)peroxide and the reaction mixture was stirred at -78 °C for one hour before being warmed to room temperature. Several attempts were required to isolate pure 1'-(hydroxy)ferrocenediylphenylsulfide 9 as it was found to decompose more readily in air than 2 or 3 and purification via column chromatography was not possible. The best method was found to be to dissolve the crude product in a 1 : 1 mixture of 5% potassium hydroxide solution and methanol under nitrogen atmosphere to give an orange solution containing an orange precipitate. The solution containing the product was isolated via filtration and neutralised by adding solid CO₂ until a yellow precipitate was visible. The precipitate was extracted into diethyl ether solution and the solvent removed *in vacuo* to leave 9 as a yellow solid. 9 was obtained pure after washing with hexane at -78 °C. Unfortunately it was not possible to grow a crystal of 9 suitable for X-ray diffraction, and it is proposed that the reason 9 was observed to decompose more readily than either 2 or 3 lies in the fact that the $S \cdots H$ -O hydrogen bonding interaction would be expected to be weaker than the corresponding hydrogen bonding interactions in 2 or 3. The P=O···H-O hydrogen bonding interaction in particular would be expected to be considerably stronger and indeed 3 was found to be air stable in the solid state for at least one month.

The ¹H NMR spectrum of **9** showed two broad pseudo-triplets due to the cyclopentadienyl protons at 3.71 and 4.04 ppm together with a multiplet at 4.33 ppm. The five phenyl protons showed a triplet at 6.84 ppm corresponding to the *para* proton, a doublet of doublets (observed as a triplet) at 6.97 ppm corresponding to the *meta* protons and a doublet at 7.24 ppm corresponding to the *ortho* protons. It was not possible to obtain a ¹³C{¹H} NMR spectrum as the sample decomposed in solution during collection of the data. The positive ion FAB mass spectrum showed the molecular ion (310 amu) but no fragmentation pattern was observed.

Coordination chemistry

The coordination chemistry of ligands 6, 7 and 8 was attempted with palladium(II) and copper(I) precursors. A stable metal complex could only be isolated and characterised successfully using 6 and palladium(II) precursors however, and despite repeated attempts, no metal complexes were obtained with 7 and 8. Reaction of 7 and 8 with (1,5-cyclooctadiene)palladium dichloride, bis(acetonitrile)palladium dichloride or bis(benzonitrile)palladium dichloride led to decomposition and recovery of unreacted ligand. Attempts to form copper(I) complexes by reaction with tetrakis(acetonitrile)copper(I) hexafluorophosphate led to similar results. The failure of 7 or 8 to form stable coordination compounds with late transition metal precursors, all of which had given stable compounds with the analogous diphenylphosphino ligand 1, is attributed to the relatively poorer donor ability of thioether donor groups compared to phosphines. It should be noted that thioether complexes of Pd(II) and Cu(I) are also abundant in the literature, but in the case of 7 and 8, the combination of the hard methoxy donor group and arylsulfanyl or disulfide donor atoms makes the ligand unsuitable for stabilising palladium(II) and copper(I) centres.

A palladium(II) complex of 6 was successfully synthesised by adding a toluene solution of 6 to a CH₂Cl₂ solution of bis(benzonitrile)palladium dichoride. The reaction mixture was stirred at room temperature overnight and solvent was then removed in vacuo to give a green solid which was washed with hexane and dried under vacuum. The complex, 10, exhibited an interesting dichroic nature: solutions in acetonitrile, chloroform, toluene or benzene are purple whereas solutions in dichloromethane are green in colour as is the dried solid. The ¹H NMR spectrum of 10 shows two singlets at 2.33 and 3.22 ppm corresponding to the SMe and OMe protons respectively. This indicates that on coordination a downfield shift is observed for the thioether protons, suggesting coordination of the sulfur heteroatom to the palladium centre, whereas a slight upfield shift is observed for the methoxy protons suggesting that they are not interacting with the palladium centre. Interestingly, the cyclopentadienyl protons show three well-resolved pseudo-triplets at 3.81, 3.98 and 4.05 ppm and a very broad peak at 4.70 ppm. The positive FAB mass spectrum shows a peak at 403 amu corresponding to 6.PdCl⁺ and a peak corresponding to the ligand (262 amu). Elemental analysis indicates a 1 : 1 complex of formula $6 \cdot PdCl_2$. The data suggest a 1:1 complex bound solely through the sulfur heteroatom suggesting a three-coordinate palladium dichloride complex. A three-coordinate palladium(II) complex is unlikely (especially with a relatively sterically unencumbered ligand such as **6**) as palladium(II) complexes commonly adopt a square planar geometry due to their d^8 electronic configuration. For this reason, together with the fact that the colour of the complex is solvent-dependent (suggesting the potential for solvent coordination) the structure shown in Scheme 2 is proposed.



Scheme 2 Reagents and conditions: (i) (PhCN)₂PdCl₂, CH₂Cl₂/toluene, rt, 20 h; (ii) (PhCN)₂PtCl₂, toluene, 60 °C, 20 h.

Complex 10 is green in colour in CH₂Cl₂ solution and in the solid state but purple in colour in toluene, benzene, acetonitrile and chloroform solution. It is likely that these solvents are able to coordinate to the palladium centre breaking up the dimeric structure and causing a change in colour of the complex. Unfortunately, despite repeated attempts, it was not possible to grow a crystal of 10 suitable for X-ray analysis. Such a chloride-bridged dimeric complex has previously been structurally characterised containing the osmocene ligand $[Os(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4P\{O\}Ph_2)]$ bound solely through the phosphine donor group.²⁴ Cationic Pd(BF₄)₂ complexes of 1,1'-bis[(alkyl)chalcogeno]ferrocenes have been reported by Sato and co-workers.¹⁶ It is worth noting that both the bis(methylthio)ferrocene and bis(methoxy)ferroene palladium complexes were thought to bind in a chelating fashion (although the methoxy version could not be characterised by NMR spectroscopy or X-ray crystallography due to its sensitivity). It might be expected, therefore, that the mixed SMe/OMe ligand 6 should form a chelating complex in reactions with bis(benzonitrile)palladium dichloride rather than the observed complex 10, although no such chelating complex was detected.

The coordination chemistry of **6** was also investigated with platinum precursors. A toluene solution of **6** was added to a toluene suspension of bis(benzonitrile)platinum dichloride. The reaction mixture was stirred at 60 °C overnight and some precipitate observed was removed by filtration, the filtrate being evaporated to dryness. The resulting orange powder was washed with hexane and dried under vacuum. Analysis by ¹H NMR spectroscopy showed that the product consisted of a mixture of unreacted bis(benzonitrile)platinum dichloride and a bis ligand *trans*-sulfur ligated platinum complex bis[1-(methylsulfanyl- κ S)-1'-(methoxy)ferrocene]platinum dichloride **11**. The mixture was purified by dissolving in CH₂Cl₂ and layering with hexane causing

the product to crystallise in 35% yield. The yield of the reaction could be improved by reacting two equivalents of ligand per platinum centre. In contrast, a chelating platinum dichloride complex was formed with 1,1'-bis(methylthio)ferrocene²⁰ and it is thought that the presence of the harder methoxy donor group in 6 causes the preferential formation of 11 rather than a chelated complex. The ¹H NMR spectrum in CDCl₃ showed two singlets at 2.67 and 3.65 ppm corresponding to the SMe and OMe protons respectively together with signals corresponding to the cyclopentadienyl protons. The ligand displays signals at 2.28 and 3.66 ppm in CDCl₃ corresponding to the SMe and OMe protons indicating that on coordination a downfield shift is observed for the thioether protons, suggesting coordination of the sulfur heteroatom to the platinum centre, whereas no shift is observed for the methoxy protons suggesting that they are not interacting with the platinum centre. The positive FAB mass spectrum showed the molecular ion (790 amu) and a peak due to the ligand (262 amu).

Crystals of **11** suitable for X-ray diffraction analysis were grown from a saturated CH_2Cl_2 solution which was layered with hexane under a nitrogen atmosphere and the structure is shown in Fig. 2.



Fig. 2 The molecular structure of the centrosymmetric complex 11. Selected bond lengths (Å) and angles (°): Pt–Cl 2.2995(8), Pt–S 2.3088(7); Cl–Pt–Cl' 180, Cl–Pt–S 95.70(3), Cl–Pt–S' 84.30(3), S–Pt–S' 180.

The coordination geometry at platinum is only slightly distorted square planar, the {PtCl₂S₂} plane being completely flat, a consequence of the metal atom being positioned on a centre of symmetry. With the Pt–Cl and Pt–S bond lengths being very similar [2.2995(8) and 2.3088(7) Å respectively] the main distortion is in the Cl–Pt–S angles which are 84.30(3) and 95.70(3)°; the platinum coordination distances themselves are unexceptional.²⁵ The S–Me carbon atom is near coplanar with the coordination plane, the Cl–Pt–S–Me torsion angle being *ca.* 15°. The S-substituted Cp ring, therefore, is steeply inclined (*ca.* 99°) to the PtCl₂S₂ plane.

Conclusions

The coordination chemistry of unsymmetrical 1,1'-disubstituted ferrocenediyl ligands that lack a phosphine donor moiety is underdeveloped, mainly due to the many applications of phosphine ligands in homogeneous catalysis driving research into coordination chemistry with phosphine ligands. Ferrocenyl ether ligands in particular and, to a lesser extent, ferrocenyl thioethers have been little studied as ligands in coordination chemistry but have excellent scope for the stabilisation of new and interesting coordination complexes. Despite the low steric demands of 6, the coordination chemistry with palladium(II) and platinum(II) is still dominated by the thioether donor group and even when carefully controlling the reaction stoichiometry, complexes with pendant methoxy groups were obtained. The observation that the methoxy donor group interacts at best only weakly with the metal centre suggests potential applications for ligands derived from 6 in hemilabile catalysis.²⁶ The coordination chemistry of other 1,1'-unsymmetrical N/O ferrocenediyl ligands has also been investigated and will be reported in a separate publication.

Experimental

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General procedures

All preparations were carried out using standard Schlenk techniques.²⁷ All solvents were distilled over standard drying agents under nitrogen directly before use, and all reactions were carried out under an atmosphere of nitrogen. Chromatographic separations were carried out on alumina (neutral grade II, 3% H₂O). ¹H NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 270.1 MHz (¹H). ¹³C{¹H} NMR spectra were obtained on either a Bruker DRX-400 or AM-500 spectrometer. Chemical shifts (δ) are reported in ppm using the residual proton impurities in the NMR solvent as an internal reference. Mass spectra were recorded using positive FAB methods, on an Autospec Q mass spectrometer. Microanalyses were carried out at Department of Health and Human Sciences, London Metropolitan University.

Syntheses

Synthesis of 1-(methylsulfanyl)-1'-(methoxy)ferrocene (6). 4 (0.800 g, 2.71 mmol, 1 eq.) was dissolved in dry THF (30 cm³) and cooled to -78 °C. To this solution was added *n*-butyllithium (1.6 M in hexanes, 1.69 cm³, 2.71 mmol, 1 eq.) and the solution stirred at -78 °C for 10 minutes. Dimethyl disulfide (0.29 cm³, 3.3 mmol, 1.2 eq.) was added and the mixture allowed to warm to room temperature. The solution was stirred at room temperature for 20 h and the solvent was removed in vacuo and the residue redissolved in CH₂Cl₂ (50 cm³). Water was added (3 \times 25 cm³) and the layers separated. The organic layer was dried $(MgSO_4)$ and the solvent removed in vacuo to yield an orange oil. The crude mixture was purified by column chromatography (neutral grade II alumina, petroleum spirit bp 40–60 °C) to give pure 6 as an orange oil (0.59 g, 2.2 mmol, 82%). Anal. Calc. for C₁₂H₁₄FeOS: C 54.98, H 5.38%, Found: C 54.92, H 5.34%; ¹H NMR δ (CDCl₃) ppm: 2.28 (s, 3H, SCH₃) 3.66 (s, 3H, OCH₃) 3.85 (t, 2H, C₅H₄), 4.08 (t, 2H, C_5H_4), 4.20 (t, 2H, C_5H_4), 4.32 (t, 2H, C_5H_4); ${}^{13}C{}^{1}H{}$

NMR δ(CDCl₃) ppm: 20.6 (SCH₃), 57.5 (OCH₃), 56.2, 63.3, 69.0, 72.1, 83.5, 127.9 (*C*₅H₄); *m/z*: 262 (M⁺), 216 (M⁺ – SMe).

Synthesis of 1-(phenylsulfanyl)-1'-(methoxy)ferrocene (7). 4 (0.540 g, 1.83 mmol, 1 eq.) was dissolved in dry THF (30 cm³) and cooled to -78 °C. To this solution was added *n*-butyllithium (1.6 M in hexanes, 1.14 cm³, 1.83 mmol, 1 eq.) and the solution stirred at -78 °C for 10 minutes. Diphenyl disulfide (0.710 g, 2.19 mmol, 1.2 eq.) dissolved in THF (5 cm³) was added and the mixture allowed to warm to room temperature. The solution was stirred at room temperature for 20 h and the solvent was removed *in vacuo* and the residue redissolved in CH_2Cl_2 (50 cm³). Water was added $(3 \times 25 \text{ cm}^3)$ and the layers separated. The organic layer was dried (MgSO₄) and the solvent removed *in vacuo* to yield a brown oil. The crude mixture was purified by column chromatography (neutral grade II alumina, petroleum spirit bp 40-60 °C/toluene, 4 : 1) to give pure 7 as an orange solid (0.35 g, 1.1 mmol, 59%). Anal. Calc. for C₁₇H₁₆FeOS: C 62.98, H 4.97%, Found: C 63.11, H 4.84%; ¹H NMR δ (CDCl₃) ppm: 3.70 (s, 3H, OCH₃) 3.94 (t, 2H, C_5H_4), 4.18 (t, 2H, C_5H_4), 4.39 (t, 2H, C_5H_4), 4.43 (t, 2H, C_5H_4), 7.05 (m, 3H, C₆ H_5), 7.17 (m, 2H, C₆ H_5); ¹³C{¹H} NMR δ (CDCl₃) ppm: 57.6 (OCH₃), 56.3, 63.5, 70.6, 75.3, 75.7, 128.3 (C₅H₄), 124.8, 125.7, 128.6, 140.8 (C_6H_5); m/z: 324 (M⁺), 216 (M⁺ – SPh).

Synthesis of di[1'-(methoxy)ferrocene]disulfide (8). 4 (0.800 g, 2.71 mmol, 1 eq.) was dissolved in dry THF (30 cm³) and cooled to -78 °C. To this solution was added *n*-butyllithium (1.6 M in hexanes, 1.69 cm³, 2.71 mmol, 1 eq.) and the solution stirred at -78 °C for 10 minutes. Freshly distilled sulfur chloride (0.10 cm³, 1.3 mmol, 0.48 eq.) was added and the mixture allowed to warm to room temperature. The solution was stirred at room temperature for 20 h and the solvent was removed in vacuo and the residue redissolved in CH₂Cl₂ (50 cm³). Water was added (3×25 cm³) and the layers separated. The organic layer was dried (MgSO₄) and the solvent removed in vacuo to yield an orange oil. The crude mixture was purified by column chromatography (neutral grade II alumina, hexane/toluene, 1:5) to give pure 8 as a brown oil (0.29 g, 0.60 mmol, 44%). Anal. Calc. for C₂₂H₂₂Fe₂O₂S₂: C 53.46, H 4.49%, Found: C 53.64, H 4.58%; ¹H NMR δ(CDCl₃) ppm: 3.59 (s, 3H, OCH₃) 3.82 (t, 2H, C₅H₄), 4.07 (t, 2H, C₅H₄), 4.32 (m, 4H, C_5H_4); ¹³C{¹H} NMR δ (CDCl₃) ppm: 57.5 (OCH₃), 56.1, 63.3, 70.7, 74.2, 82.3, 128.2 (C_5H_4); m/z: 494 (M⁺), 247 (M⁺ – Fc(S)(OMe)).

Synthesis of 1'-(hydroxy)ferrocenediylphenylsulfide (9). 1-(Phenylsulfanyl)-1'-(bromo)ferrocene (0.30 g, 0.80 mmol, 1 eq.) was dissolved in dry THF (20 cm³) and cooled to -78 °C. To this solution was added *n*-butyllithium (1.6 M solution in hexane, 0.50 cm^3 , 0.80 mmol, 1 eq.) and the solution stirred at $-78 \text{ }^\circ\text{C}$ for 10 min. Bis(trimethylsilyl)peroxide (0.13 cm³, 1.2 mmol, 1.5 eq.) was added and the solution stirred at -78 °C for 1 h before being allowed to warm to room temperature and stirred for 1 h. The solvent was removed *in vacuo* and the residue redissolved in 5% KOH/methanol, 1:1, and stirred vigorously for 10 minutes. The mixture was filtered and solid CO₂ added to the filtrate piece by piece until a light yellow precipitate was observed to form. The reaction mixture was extracted with diethyl ether $(2 \times 25 \text{ cm}^3)$ and the organic layer dried (Na₂SO₄) and evaporated to dryness. The resulting precipitate was washed with cold hexane (5 cm^3) to yield 9 as a yellow powder (0.048 g, 0.15 mmol, 19%). Anal. Calc.

for C₁₆H₁₄FeOS: C 61.95, H 4.55%, Found: C 61.87, H 4.34%; ¹H NMR δ (C₆D₆) ppm: 3.71 (t, 2H, C₅H₄), 4.04 (m, 4H, C₅H₄), 4.33 (t, 2H, C₅H₄), 6.84 (t, 1H, SC₆H₅), 6.97 (t, 2H, SC₆H₅), 7.84 (d, 2H, SC₆H₅); *m/z*: 310 (M⁺).

Synthesis of [{1-(methylsulfanyl- κ S)-1'-(methoxy)ferrocene}palladium chloride(μ -chloride)]₂ (10). 6 (0.075 g, 0.29 mmol, 1.1 eq.) was dissolved in dry toluene (3 cm³) and added *via* cannula to a solution of bis(benzonitrile)palladium dichloride (0.100 g, 0.260 mmol, 1 eq.) dissolved in dry CH₂Cl₂ (7 cm³) and the reaction mixture was stirred at room temperature for 20 h. The solvent was removed *in vacuo* and the residue washed with dry hexane (2 × 10 cm³) and dried under vacuum to yield 10 as a green solid (0.062 g, 0.071 mmol, 49%). Anal. Calc. for C₂₄H₂₈Cl₄Fe₂O₂Pd₂S₂: C 32.80, H 3.21%, Found: C 32.69, H 3.26%; ¹H NMR δ (C₆D₆) ppm: 2.32 (s, 3H, SCH₃), 3.22 (s, 3H, OCH₃), 3.81 (t, 2H, C₅H₄), 3.98 (t, 2H, C₅H₄), 4.05 (t, 2H, C₅H₄), 4.70 (br, 2H, C₅H₄); ¹³C{¹H} NMR δ (C₆D₆) ppm: 22.8 (SCH₃), 57.3 (OCH₃), 57.1, 64.4, 70.4, 70.6, 81.3, 128.0 (obscured by solvent) (C₅H₄); *m*/*z*: 403 (LPdCl⁺), 262 (L⁺).

Synthesis of bis[1-(methylsulfanyl-kS)-1'-(methoxy)ferrocene]platinum dichloride (11). 6 (0.134 g, 0.510 mmol, 1.1 eq.) was dissolved in dry toluene (10 cm³) and added via cannula to a suspension of bis(benzonitrile)platinum dichloride (0.220 g, 0.460 mmol, 1 eq.) in dry toluene (10 cm³) at 60 °C. The reaction mixture was stirred at 60 °C for 20 h before being filtered and the filtrate evaporated to dryness. The resulting orange powder was washed with hexane (10 cm³) and dried under vacuum. Further purification was achieved by redissolving the product in CH₂Cl₂ and layering with hexane causing the product to crystallise out. The crystals were isolated via filtration and dried under vacuum to yield **11** as an orange crystalline solid (0.064 g, 0.081 mmol, 35%). Anal. Calc. for C24H28Cl2Fe2O2PtS2: C 36.48, H 3.57%, Found: C 36.49, H 3.51%; ¹H NMR δ(CDCl₃) ppm: 2.67 (s, 3H, SCH₃), 3.65 (s, 3H, OCH₃), 4.11 (br t, 2H, C₅H₄), 4.31 (br t, 2H, C₅H₄), 4.39 (br, 4H, C_5H_4); ${}^{13}C{}^{1}H$ NMR δ (CDCl₃) ppm: 23.7 (SCH₃), 57.8 (OCH_3) , 56.9, 64.4, 70.4, 72.1, 79.8, 128.2 (C_5H_4) ; m/z: 790 (M^+) , 262 (L⁺).

Crystal data for 11. $C_{24}H_{28}Cl_2Fe_2O_2PtS_2$, M = 790.27, monoclinic, $P2_1/c$ (no. 14), a = 10.1812(5), b = 7.9632(3), c = 15.9154(7)Å, $\beta = 95.796(4)^\circ$, V = 1283.74(10) Å³, Z = 2 (C_i symmetry), $D_c = 2.044$ g cm⁻³, μ (Mo-K α) = 6.942 mm⁻¹, T = 173 K, orange blocks, Oxford Diffraction Xcalibur 3 diffractometer; 4371 independent measured reflections, F^2 refinement, $R_1 = 0.030$, $wR_2 = 0.058$, 4271 independent observed absorption-corrected reflections $[|F_o| > 4\sigma(|F_o|), 2\theta_{max} = 65^\circ]$, 152 parameters.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602576e

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