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New ferrocene based dithiolate ligands

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ABSTRACT

The preparation and characterization of the three ferrocene based dithiolane complexes $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)NHC(O)(CH_2)_4\overline{CHS_2CH_2CH_2}]$**1**, $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2OC(O)(CH_2)_4\overline{CHS_2CH_2CH_2}]$ **2** and $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)NHC(O)(CH_2)\overline{CHS_2CH_2CH_2}]$ **3**, with different spacer groups between the ferrocenyl moiety and the dithiolane unit, are reported. The complexation of **1** and **2**, using the oxidative addition of the S–S bonds to Pt(0), is also described, leading to the square planar Pt(II) complexes $[Pt(PPh_3)_2(S_2CH_2CH_2CH\text{-}\kappa^2\text{-}S,S)(CH_2)_4C(O)NH(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ **4** and $[Pt(PPh_3)_2(S_2CH_2CH_2CH\text{-}\kappa^2\text{-}S,S)(CH_2)_4C(O)OCH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ **5**, respectively. The reduction of the S–S bond in **1** and **2** yields the corresponding dithiols; these can be deprotonated and treated with $ClSiMe_3$ to prepare $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)NHC(O)(CH_2)_4CH(SSiMe_3)CH_2CH_2(SSiMe_3)]$ **7** and $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2OC(O)(CH_2)_4CH(SSiMe_3)CH_2CH_2(SSiMe_3)]$ **9**, respectively. The complexes were characterized via NMR and UV–Vis absorption spectroscopy, cyclic voltammetry and single crystal X-ray diffraction for **1** and **4**.

1. Introduction

The synthesis of substituted bis(η^5-cyclopentadienyl)iron(II) (ferrocene) complexes continues to play an important role in organometallic chemistry due in part to the ease of handling of ferrocene complexes, the ease of functionalization and flexibility of the cyclopentadienyl rings together with the accessible Fe(II)/Fe(III) redox couple [1]. Because ferrocene displays greatly adaptable synthetic chemistry, numerous functionalizations have been incorporated for applications in different areas including catalysis, sensing and biology [2]. For example, several successful functionalizations of ferrocene have been reported by Beer and co-workers for the selective sensing of both ionic and neutral species [3]. Two factors are responsible for the recognition of anion or neutral analytes by ferrocenyl compounds: H-bonding interactions between the functional group (usually amide) on the ferrocene based receptor and the analyte and, secondly, the electrostatic attraction of the analyte to the oxidized form of ferrocene (ferrocenium) [4]. In this vein, Beer, Davis and co-workers have illustrated that the bis(amido) ferrocene $[Fe\{(\eta^5\text{-}C_5H_4)NHC(O)(CH_2)_4\overline{CHS_2CH_2CH_2}\}_2]$ can be prepared from 1,1′-diaminoferrocene and two equivalents of lipoic acid [5]. The disulfide linkages can then be used to anchor the ferrocenylamido units directly onto gold surfaces via oxidation of the S–S bond, or from the corresponding tetrathiol after reduction of the two S_2 units. More recently, Kraatz and co-workers have coupled lipoic acid to the amine unit in $[Fe(C_5H_4CO_2Me)(C_5H_4NH_2)]$, and oxidatively added the S–S bond onto Au nanoparticles for the electrochemical detection of HIV-1 reverse transcriptase [6]. It is possible to model such metal/sulfur surface chemistry processes with molecular coordination chemistry by the reactions of dithiolanes with a zero-valent platinum complex [7]. One of the significant features of disulfide redox chemistry is the oxidative addition of the S–S bond to low-valent metal centers, which can play an important role in different areas such as medicinal chemistry and transition metal catalysis [8–10]. In this work, we describe the synthesis and characterization of ferrocene based dithiolanes containing an alkyl spacer between the ferrocenyl unit and the chalcogen center and their reaction chemistry with Pt(0).

2. Experimental

All syntheses were performed under a dinitrogen atmosphere using standard Schlenk line and glove box techniques unless otherwise stated. All chemicals were used as received from Strem Chemicals and/or Aldrich. Tetrahydrofuran, diethyl ether, hexanes and pentane purchased from Caledon were dried by passing through packed columns of activated alumina using a commercially available MBraun MB-SP Series solvent purification system. Dichloromethane, chloroform and chloroform-d were purchased

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from Caledon, and distilled over P_2O_5. Ferrocenyl amine, ferrocenyl methanol and 2-(1,2-dithiolan-3-yl)acetic acid were prepared following literature procedures [11–13]. Lipoic acid chloride was prepared by modification of a published procedure using lipoic acid and oxalyl chloride in toluene with DMF as a catalyst [14].

^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a Varian Mercury 400 MHz spectrometer and are reported in ppm. These spectra were referenced internally to solvent peaks relative to $SiMe_4$ (δ = 0 ppm). ^{31}P{^{1}H} NMR spectra were recorded on the same spectrometer and are referenced to 85% H_3PO_4 (δ = 0 ppm). An Autolab30 electrochemical workstation equipped with GPES 4.9 software was used for cyclic voltammetry (CV) experiments. A homemade glassy carbon (GC, Tokai GC-20) working-electrode 3 mm in diameter was prepared by polishing over silicon carbide papers (500, 1200, 2400 and 4000) followed by diamond paste (Struers, 1 and 0.25 μm). The GC electrodes were stored in ethanol and polished before each set of experiments with the 0.25 mm diamond paste (Struers), rinsed with dry ethanol (Commercial Alcohols) and sonicated in dry ethanol for 5 min. An Ag wire and a platinum wire served as the reference and counter electrodes, respectively. Electrochemical experiments were carried out in dry DCM (Caledon) containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) or tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Prior to each electrochemical experiment, the solutions were saturated with 99.999% Ar gas for 15 min and the inert atmosphere was maintained during the measurements.

Infrared (IR) absorption spectra were obtained on a Bruker Vector 33 IR spectrophotometer in the solid state. A film of solid was formed on the surface of a NaCl crystal cell by evaporating the solvent of a concentrated solution of the compound of interest. High-resolution mass spectra were recorded on a MAT8400 mass spectrometer.

All reactions have been completed in subdued light due to the sensitivity of S–S bonds in these compounds [15].

2.1. N-Ferrocenyl-rac-5-(1,2-dithiolan-3-yl)pentanamide (**1**)

Ferrocenyl amine (0.16 g, 0.77 mmol) was dissolved in 10 ml of dichloromethane. Triethylamine (0.14 ml, 0.97 mmol) was added and the yellow solution was cooled to 0 °C. Freshly prepared lipoic acid chloride (0.97 mmol) in toluene was added. The solution was stirred at 0 °C for 30 min and at room temperature for 20 h. It was then diluted with 20 ml of dichloromethane and washed with 1 M NaOH, saturated NaCl, 1 M HCl and NaCl aqueous solutions. The organic layer was separated and dried over $MgSO_4$. The solvent was removed *in vacuo* yielding 0.20 g (66%) of compound **1** as an orange-brown solid.

^{1}H NMR (400 MHz, $CDCl_3$, 5 mM, 23 °C) δ = 6.47 (br s, 1H), 4.57 (vt, J_{HH} = 2.0 Hz, 2H), 4.14 (s, 5H), 3.98 (vt, J_{HH} = 2.0 Hz, 2H), 3.58 (m, 1H), 3.12 (m, 2H), 2.47 (m, 1H), 2.24 (td, $^3J_{HH}$ = 7.4, $^2J_{HH}$ = 1.6 Hz, 2H), 1.92 (m, 1H), 1.71 (m, 4H), 1.49 (m, 2H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ = 170.9 (C(O)), 94.4 (CN), 69.1 (Cp), 64.5 (CH), 61.4 (CH), 56.4 (CHS), 40.2 (CH_2), 38.5 (CH_2S), 37.0 (CH_2), 34.6 (CH_2), 28.8 (CH_2), 25.3 (CH_2). HRMS: Calcd for $C_{18}H_{23}ONS_2Fe$ (*m*/*z*): 389.0570 Found: 389.0571. Anal. Calc. (%) for $C_{18}H_{23}ONS_2Fe$: C 55.53, H 5.96, N 3.60, S 16.44. Found: C 55.65, H 5.90, N 3.56, S 16.41.

2.2. Ferrocenemethyl rac-5-(1,2-dithiolane-3-yl)pentanoate (**2**) [16]

Ferrocenyl methanol (0.17 g, 0.77 mmol) was dissolved in 10 ml of dichloromethane. Triethylamine (0.14 ml, 0.97 mmol) was added and the yellow solution was cooled to 0 °C. Freshly prepared lipoic acid chloride (0.97 mmol) in toluene was added. The solution was stirred at 0 °C for 30 min and at room temperature for 20 h. It was then diluted with 20 ml of dichloromethane and washed with 1 M NaOH, saturated NaCl, 1 M HCl and NaCl aqueous solutions. The organic layer was separated and dried over $MgSO_4$. The solvent was removed *in vacuo* yielding 0.27 g (86%) of compound **2** as an air-stable orange oil.

^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) δ = 4.87 (s, 2H), 4.24 (vt, J_{HH} = 1.8 Hz, 2H), 4.15 (vt, J_{HH} = 1.8 Hz, 2H), 4.13 (s, 5H), 3.51 (m, 1H), 3.10 (m, 2H), 2.41 (m, 1H), 2.27 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 1.86 (m, 1H), 1.64 (m, 4H), 1.41 (m, 2H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ = 172.8 (C(O)), 80.8 (CH_2), 69.1 (CH), 68.4 (CH), 68.1 (Cp), 62.3 (C) 55.8 (CHS), 39.7 (CH_2), 38.0 (CH_2S), 34.1 (CH_2), 33.6 (CH_2), 28.2 (CH_2), 24.2 (CH_2). HRMS: Calcd for $C_{19}H_{24}O_2S_2Fe$ (*m*/*z*): 404.0567 Found: 404.0562. Anal. Calc. (%) for $C_{19}H_{24}O_2S_2Fe$: C 56.38, H 5.94, S 15.83. Found: C 55.83, H 5.97, S 16.30.

2.3. N-Ferrocenyl-rac-2-(1,2-dithiolane-3yl)ethylamide (**3**)

2-(1,2-Dithiolan-3-yl)acetic acid (0.14 g, 0.85 mmol) was dissolved in 10 ml of toluene to which DMF (0.01 ml, 20 mol %) was added as a catalyst. Oxalyl chloride (0.09 ml, 1.02 mmol) in 3 ml of toluene was added drop wise to the solution. It was stirred for 5–10 min (until no further gas was observed). This solution was added to a mixture of ferrocenyl amine (0.14 g, 0.68 mmol) and Et_3N (0.12 ml, 0.85 mmol) in 10 ml of CH_2Cl_2 at 0 °C. It was stirred at 0 °C for 10 min and at room temperature for 25 h. After that the solution was diluted with 15 ml of CH_2Cl_2, washed with 1 M NaOH, saturated NaCl, 1 M HCl and NaCl aqueous solutions. The organic layer was separated and the solvent was removed under vacuum. The product was purified over a glass plate covered with silica gel in 2 steps, first with 1:4 ethylacetate/hexane solvent and then with 1:2.5 ethylacetate/hexane solvent for a better separation. Recrystallization from CH_2Cl_2:heptane at −5 °C yielded **3** as a microcrystalline orange solid (0.25 CH_2Cl_2 solvate from ^{1}H NMR). Yield: 65%.

^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) δ = 6.73 (br s, 1H), 4.69 (br s, 1H), 4.53 (br s, 1H), 4.18 (s, 5H), 4.14 (m, 1H), 4.02 (br s, 2H), 3.18 (m, 2H), 2.59 (m, 2H), 2.55 (m, 1H), 2.00 (m, 1H). HRMS: Calcd for $C_{15}H_{17}S_2FeON$ (*m*/*z*): 347.0101 Found: 347.0101. Anal. Calc. (%) for $C_{15}H_{17}ONS_2Fe\cdot(CH_2Cl_2)_{0.25}$: C 49.70, H 4.79, N 3.80, S 17.40. Found: C 50.71, H 4.63, N 3.89, S 17.97.

2.4. cis-(N-Ferrocenyl-rac-6,8-dithiolatooctaneamide) bis(triphenylphosphine)platinum(II) (**4**)

0.20 g of [$Pt(PPh_3)_4$] (0.16 mmol) was dissolved in 15 ml of benzene. 0.066 g of **1** (0.16 mmol) was added to the solution. Compound **1** was completely dissolved after about 10 min of stirring. The progress of the reaction was monitored by NMR spectroscopy. ^{1}H and ^{31}P NMR spectra indicated that the reaction was complete after 20 h. The product was isolated by adding ~15 ml of pentane and removing the mother liquor from the purified product. The dark orange solid was dissolved in a mixture of $CHCl_3$ and pentane (2:2.5) and cooled to −25 °C to yield single crystals suitable for X-ray diffraction analysis. Yield = 47%.

^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) δ = 7.47 (t, $^3J_{HH}$ = 7.6 Hz, 6H), 7.41 (t, $^3J_{HH}$ = 7.6 Hz, 6H), 7.24 (m, 6H), 7.14 (t, $^3J_{HH}$ = 7.6 Hz, 6H), 7.09 (t, $^3J_{HH}$ = 7.6 Hz, 6H), 6.55 (s, 1H), 4.61 (s, 1H), 4.57 (s, 1H), 4.14 (s, 5H), 3.97 (s, 2H), 3.34 (m, 2H), 2.89 (m, 1H), 2.14 (m, 1H), 2.10 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 1.68 (m, 1H), 1.56 (m, 2H), 1.34 (m, 4H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$) δ = 171.6 (C(O)), 134.8 (CH), 130.0 (CH), 127.5 (CH), 94.8 (CN), 69.1 (Cp), 64.2 (CH), 61.3 (CH), 39.6 (CHS), 38.7 (CH_2), 37.4 (CH_2S), 27.5 (CH_2), 26.0 (CH_2), 25.3 (CH_2), 24.5 (CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 23 °C) δ = 24.8 (dd, $^2J_{PP}$ = 21.0 Hz, $^1J_{PPt}$ = 2865 Hz), 22.8 (dd, $^2J_{PP}$ = 21.0 Hz, $^1J_{PPt}$ = 2804 Hz). HRMS: Calcd for $C_{54}H_{53}FeNOP_2PtS_2$ (*m*/*z*): 1108.2041 Found: 1108.2038.

Anal. Calc. (%) for $C_{54}H_{53}FeNOP_2PtS_2$: C 58.47, H 4.82, N 1.26, S 5.77. Found: C 57.30, H 4.51, N 1.11, S 4.89.

2.5. *cis*-(Ferrocenemethyl *rac*-6,8-dithiolatooctanoate) bis(triphenylphosphine)platinum(II) (**5**)

$[Pt(PPh_3)_4]$ (0.20 g, 0.16 mmol) was dissolved in 15 ml of benzene. Compound **2** (0.65 g, 0.16 mmol) was added to the solution. It was stirred at room temperature for 20 h and NMR spectroscopy confirmed the completion of the reaction. The product was purified by washing with pentane several times to yield **5** as a dark brown oil, which invariably contained traces of Ph_3P/Ph_3PO (as determined by $^{31}P\{^1H\}$ NMR spectroscopy) which could not be separated chromatographically due to the instability of **5** on silica/alumina. Yield = 51%.

^1H NMR (400 MHz, $CDCl_3$, 23 °C) δ = 7.52–7.08 (m), 4.88 (s, 2H), 4.27 (vt, J_{HH} = 1.8 Hz, 2H), 4.17 (vt, J_{HH} = 1.9 Hz, 2H), 4.16 (s, 5H), 3.30 (m, 2H), 2.88 (m, 1H), 2.18 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 2.11 (m, 1H), 1.64 (m, 1H), 1.49 (m, 2H), 1.30 (m, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ = 24.9 (dd, $^2J_{PP}$ = 21.0 Hz, $^1J_{PPt}$ = 2860 Hz), 22.8 (dd, $^2J_{PP}$ = 21.0 Hz, $^1J_{PPt}$ = 2801 Hz).

2.6. *N*-Ferrocenyl-*rac*-6,8-dithioloctaneamide (**6**)

The orange-brown solid $C_{18}H_{23}FeNOS_2$ (**1**) (0.15 g, 0.38 mmol) was dissolved in 10 ml of THF and a degassed solution of $NaBH_4$ (0.029 g, 0.77 mmol) in 4 ml of water was added. The solution was stirred at room temperature for 2 h. 1 M HCl (0.77 ml, 0.77 mmol) was then added and the solution was stirred for 15 min. The solution was diluted with 20 ml of degassed water and extracted with dichloromethane (2 × 20 ml). The organic layers were combined, dried over $MgSO_4$ and the solvent was evaporated *in vacuo* to yield **6** as an orange oil. Yield = 81%.

^1H NMR (400 MHz, $CDCl_3$, 23 °C) δ = 6.46 (br s, 1H), 4.61 (br s, 2H), 4.16 (s, 5H), 4.02 (vt, J_{HH} = 1.8 Hz, 2H), 2.94 (m, 1H), 2.75–2.65 (m, 2H), 2.24 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 1.88 (m, 1H), 1.76–1.65 (m, 4H), 1.60–1.48 (m, 3H), 1.34 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 1.30 (d, $^3J_{HH}$ = 8.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$) δ = 170.8 (C(O)), 94.5 (CN), 69.2 (Cp), 64.5 (CH), 61.4 (CH), 42.8 (CHS), 41.8 (CH_2), 39.3 (CH_2S), 38.8 (CH_2), 37.1 (CH_2), 26.6 (CH_2), 25.22 (CH_2). HRMS: Calcd for $C_{18}H_{25}ONS_2Fe$ (*m*/*z*): 391.0727 Found: 391.0716.

2.7. *N*-Ferrocenyl-*rac*-6,8-trimethylsilylsulfooctanamide (**7**)

$ClSiMe_3$ (0.15 ml, 1.15 mmol) was added to a stirred solution of $C_{18}H_{25}FeNOS_2$ (**6**) (0.11 g, 0.30 mmol) which was dissolved in 15 ml of CH_2Cl_2 with NEt_3 (0.16 ml, 1.15 mmol) at 0 °C. The solution was stirred at 0 °C for 15 min and at room temperature for 3 h. 20 ml of heptane was added and the CH_2Cl_2 was removed under vacuum. The heptane solution was filtered and the solvent was evaporated *in vacuo* to yield compound **7** as an orange oil. Yield = 90%.

^1H NMR (400 MHz, $CDCl_3$, 23 °C) δ = 6.53 (br s, 1H), 4.57 (m, 2H), 4.14 (s, 5H), 3.98 (vt, J_{HH} = 2.0 Hz, 2H), 3.55 (m, 1H), 2.86 (m, 2H), 2.61 (m, 3H), 2.23 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 1.86 (m, 1H), 1.68 (m, 2H), 1.52 (m, 2H), 0.31(s, 9H), 0.30(s, 9H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$) δ = 111.0 (CN), 69.1 (Cp), 64.5 (CH), 62.6 (CH), 61.4 (CHS), 41.4 (CH_2), 38.2 (CH_2S), 37.2 (CH_2), 32.7 (CH_2), 26.4 (CH_2), 25.6 (CH_2), 1.7 (CH_3), 1.0 (CH_3). HRMS: Calcd for $C_{24}H_{41}FeNOS_2Si_2$ (*m*/*z*): 535.1517 Found: 535.1525.

2.8. Ferrocenemethyl *rac*-6,8-dithioloctanoate (**8**)

The orange oil $C_{19}H_{24}FeO_2S_2$ (**2**) (0.15 g, 0.38 mmol) was dissolved in 10 ml of THF and a degassed solution of $NaBH_4$ (0.029 g, 0.77 mmol) in 4 ml of water was added. The solution was stirred at room temperature for 2 h. 1 M HCl (0.77 ml, 0.77 mmol) was then added and the solution was stirred for 15 min. The solution was diluted with 20 ml of degassed water and extracted with dichloromethane (2 × 20 ml). The organic layers were combined, dried over $MgSO_4$ and the solvent was evaporated *in vacuo* to yield **8** as an orange oil. Yield = 64%.

^1H NMR (400 MHz, $CDCl_3$, 23 °C) δ = 4.89 (s, 2H), 4.26 (vt, J_{HH} = 2.0 Hz, 2H), 4.17 (vt, J_{HH} = 1.8 Hz, 2H), 4.15 (s, 5H), 2.89 (m, 1H), 2.74–2.64 (m, 2H), 2.29 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 1.88 (m, 1H), 1.61–1.73 (m, 4H), 1.55–1.45 (m, 3H), 1.33 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 1.27 (d, $^3J_{HH}$ = 7.6 Hz, 1H). HRMS: Calcd for $C_{19}H_{26}O_2S_2Fe$ (*m*/*z*): 406.0724 Found: 406.0735.

2.9. Ferrocenemethyl *rac*-6,8-trimethylsilylsulfooctanoate (**9**)

$ClSiMe_3$ (0.15 ml, 1.15 mmol) was added to a stirred solution of $C_{19}H_{26}FeO_2S_2$ (**8**) (0.12 g, 0.30 mmol) dissolved in 15 ml of CH_2Cl_2 with NEt_3 (0.16 ml, 1.15 mmol) at 0 °C. The solution was stirred at 0 °C for 15 min and at room temperature for 3 h. 20 ml of heptane was added and the CH_2Cl_2 was removed under vacuum. The heptane solution was filtered and the solvent was evaporated *in vacuo* to yield compound **9** as an orange oil. Yield = 82%.

^1H NMR ($CDCl_3$, 23 °C) δ = 4.88 (s, 2H), 4.25 (vt, J_{HH} = 1.8 Hz, 2H), 4.16 (vt, J_{HH} = 1.8 Hz, 2H), 4.15 (s, 5H), 2.82 (m, 1H), 2.60 (m, 2H), 2.28 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 1.78 (m, 2H), 1.60 (m, 4H), 1.41 (m, 2H), 0.31 (s, 9H), 0.30 (s, 9H). HRMS: Calcd for $C_{25}H_{42}FeO_2S_2Si_2$ (*m*/*z*): 550.1514 Found: 550.1520.

2.10. Crystallography

Single crystal X-ray diffraction measurements were performed on a Bruker APEXII diffractometer, with the molecular structures determined via direct methods using the SHELX suite of crystallographic programs [17]. Single crystals of the complexes were selected, immersed in paraffin oil and mounted on a nylon loop. Crystals were placed in a cold stream of N_2. Multiple data sets for **1** were collected but all crystals weakly diffracting, a consequence of their plate-like morphology. With the exception of disordered carbon atoms of the alkyl chain (beginning at C151) and C_3S_2 rings in both independent molecules in **1**, all non-hydrogen atoms were refined anisotropically, while hydrogen atoms were kept at their calculated distances and refined using a riding model. Disordered atoms were refined with occupancy 0.66667:0.33333 and common C–C and C–S bond distances were restrained with the SADI command in SHELXTL. Satisfactory refinement of the data for **1** was completed with the use of a TWIN command and resultant BASF value of 0.12315. A summary of the crystallographic data is presented in Table 1.

3. Results and discussion

3.1. Synthesis

Under exposure to light or with heat, the five-membered ring in lipoic acid opens at the S–S junction and undergoes a polymerization reaction [15]. Thus all reactions involving five-membered dithiolane ring in the starting reagents and products were carried out under subdued lighting conditions, and high reaction temperatures have been avoided. Ligands were synthesized via a coupling reaction between a ferrocenyl unit and an acid chloride. Lipoic acid chloride was synthesized using oxalyl chloride and DMF as a catalyst. It has been shown previously that DMF can act as a catalyst in the synthesis of acid chlorides using oxalyl chloride [18].

The ferrocenyl complex **1** was obtained as an air stable orange solid in 66% yield, starting from ferrocenyl amine [11] and lipoic acid chloride (Scheme 1) and fully characterized.

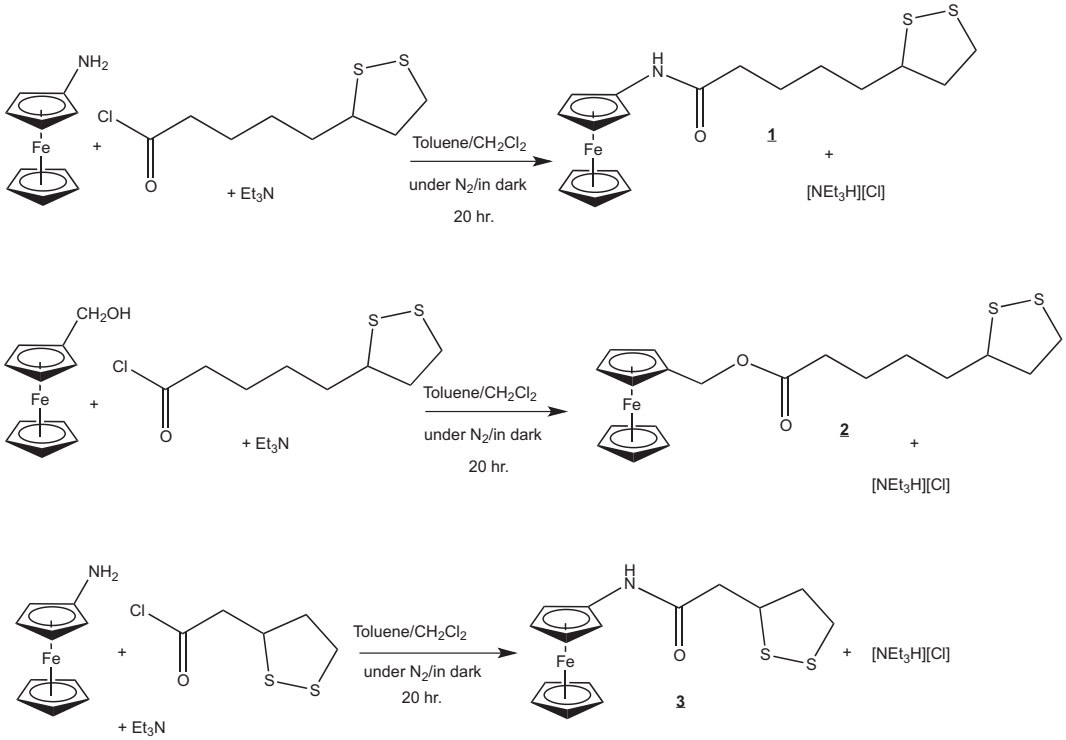
Table 1
Selected crystal data, data collection and refinement parameters for **1** and **4**.

	1	**4**. 3.5 $CHCl_3$
Formula	$C_{18}H_{23}FeNOS_2$	$C_{57.5}H_{56.5}Cl_{10.5}FeNOP_2PtS_2$
M_r	389.34	1526.76
T [K]	150(2)	150(2)
λ ($Mo_{K\alpha}$) [Å]	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	Pca2(1)	P − 1
A [Å]	10.0366(10)	16.910(3)
B [Å]	11.1816(11)	20.310(4)
C [Å]	31.259(3)	20.370(4)
α [°]	90	90.122(9)
β [°]	90	103.733(6)
γ [°]	90	111.205(5)
V [Å^3]	3508.1(6)	6306(2)
Z	8	4
ρ_{caled} (g cm^{-3})	1.474	1.608
μ [mm^{-1}]	1.101	3.047
F (000)	1632	3044
Crystal size mm^3	0.09 × 0.08 × 0.03	0.10 × 0.06 × 0.05
2 θ range [°]	1.82–28.72	1.03–31.70
Index ranges	$-13\leq h\leq 13$, $-15\leq k\leq 15$, $-42\leq l\leq 42$	$-24\leq h\leq 24$, $-29\leq k\leq 29$, $-30\leq l\leq 29$
Collected reflections	80,156	353,324
Unique reflections	9059	42,107
R_{int}	0.0548	0.1624
Restraints	63	0
Parameters	424	1369
GOF	1.086	1.007
$R1$ [$I > 2\sigma(I)$]	$R1 = 0.0608$, $wR2 = 0.1442$	$R1 = 0.0550$, $wR2 = 0.1094$
$wR2$ all	$R1 = 0.0764$, $wR2 = 0.1519$	$R1 = 0.1275$, $wR2 = 0.1393$
Max/min electron density (e Å^{-3})	1.057 and −1.194	2.805 and −1.791

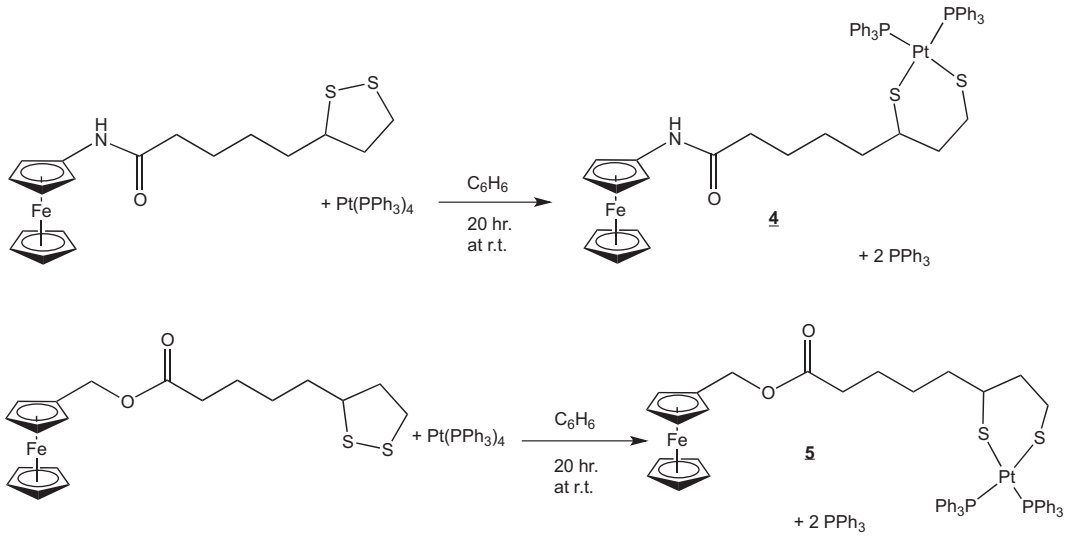
Compound **2** was synthesized following a similar procedure using freshly prepared lipoic acid chloride, ferrocenyl methanol [12] and triethylamine. The ferrocenyl ester has previously been reported using a *N,N′*-dicylcohexylcarbodiimide coupling procedure, although yields were not reported [16]. Here, the product was obtained as an air-stable, orange oil in 86% yield. For the synthesis of **3**, 2-(1,2-dithiolan-3-yl)acetic acid [13] was converted to the related acid chloride and a coupling reaction was completed with ferrocenyl amine yield the shorter chain ferrocenyl amide in 66% yield.

The first example of the oxidative addition of a disulfide linkage to Pt(0) was reported in 1964 by Davison et al. [19] and this is now a well developed strategy for the complexation of thiolate ligands onto electron rich platinum metal centers [7,20–22]. Recently, Weigand and co-workers published the reaction of a 1,2-dithiolane derivative with a Pt(0) source leading to the *cis* mononuclear complex of platinum [$(Ph_3P)_2Pt(-S-CH_2-CHPh-CH_2-S-)$] [21] and we successfully targeted reactions of the disulfide complexes **1** and **2** with Pt(0). The oxidative addition of **1** and **2** (Scheme 2) was carried out by dissolving [$Pt(PPh_3)_4$] in benzene followed by the addition of the disulfide reagents. The progress of these reactions was easily followed by ^{31}P NMR spectroscopy, which indicated the reactions were complete after ~20 h of stirring at room temperature.

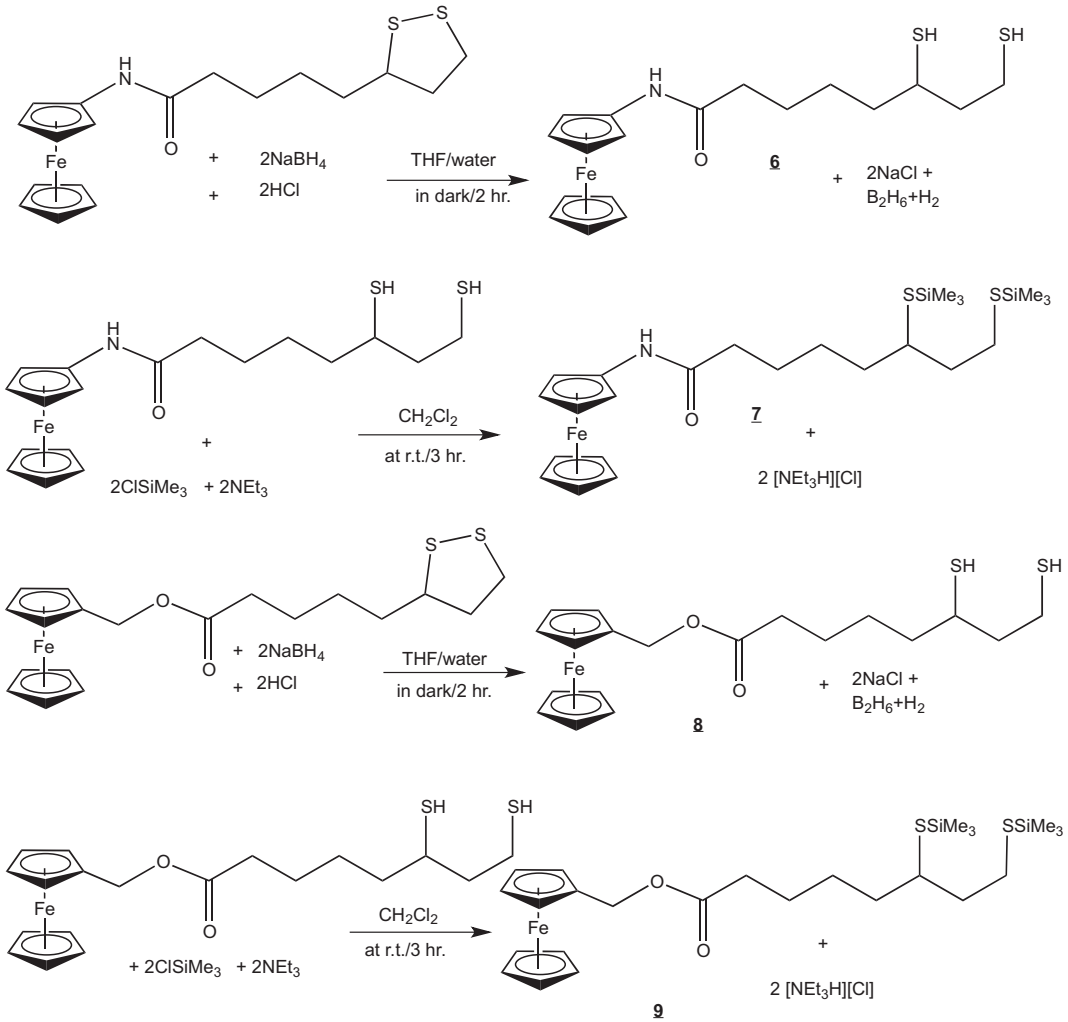
As reported by Beer et al. for [$Fe\{(\eta^5\text{-}C_5H_4)NHC(O)(CH_2)_4\overline{CHS_2CH_2CH_2}\}_2$] [5], reduction of the disulfide linkages in **1** and **2** can be carried out with $NaBH_4$ to yield the corresponding dithiols after acidic work-up (Scheme 3). The formation of dithiols [$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)NHC(O)(CH_2)_4CH(SH)CH_2CH_2(SH)$] **6** and [$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2OC(O)(CH_2)_4CH(SH)CH_2CH_2(SH)$] **8** was indicated by the appearance of peaks assigned to −SH at ~1.30 ppm in their ^1H NMR spectra (see discussion below). The dithiols could also be reacted with $ClSiMe_3$ in the presence of base to yield the corresponding silylated reagents [$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)NHC(O)(CH_2)_4CH(SSiMe_3)CH_2CH_2(SSiMe_3)$] **7** and [$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2OC(O)(CH_2)_4CH(SSiMe_3)CH_2CH_2(SSiMe_3)$] **9**, respectively (Scheme 3).



Scheme 1. Synthesis of **1**–**3**.



Scheme 2. Oxidative addition of **1** and **2** to [$Pt(PPh_3)_4$].



Scheme 3. Synthesis of **6**–**9**.

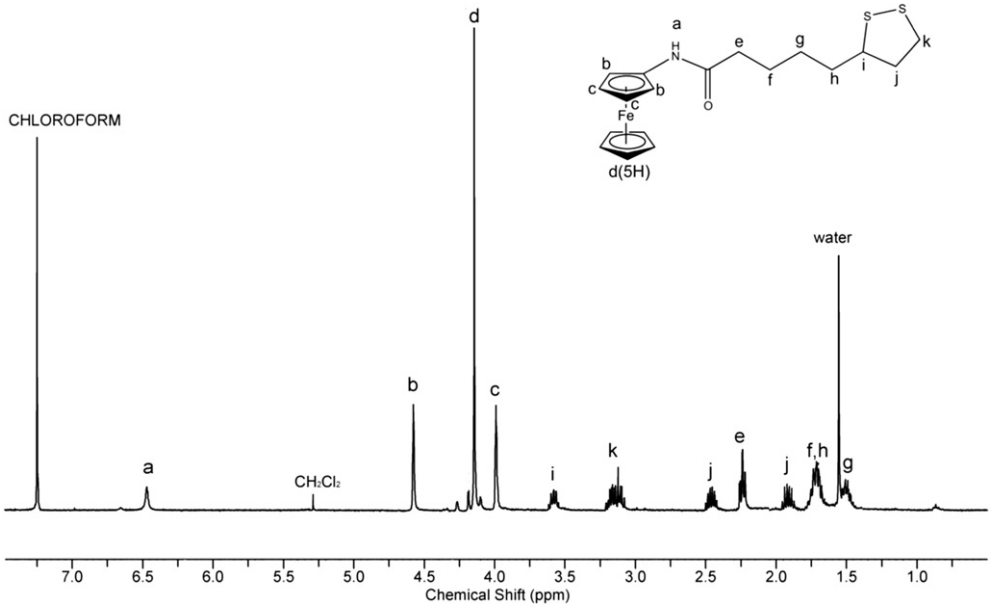


Fig. 1. ^{1}H NMR spectrum of 5 mM of **1** in $CDCl_3$.

3.2. Characterization

All complexes were characterized by NMR spectroscopy and chemical shift data were obtained at room temperature in $CDCl_3$. Due to the complex aliphatic region in their ^{1}H NMR spectra, 2D NMR spectroscopic methods were used for the assignment of the signals. All peaks in the ^{1}H NMR spectra were assigned completely using gcosy and gHSQC techniques. The ^{1}H NMR spectrum of **1** (Fig. 1) shows a slight downfield shift of the proton peaks of the substituted cyclopentadienyl ring versus those of ferrocenyl amine [11]. The peak for the amino group in $FcNH_2$ at 2.60 ppm has disappeared and a signal at 6.47 ppm is readily assigned to the presence of the amide. All assigned peaks are illustrated in Fig. 1.

The ^{1}H NMR spectrum of **2** displays similar pattern in the aliphatic region to those reported for **1**, with a very slight shift in the chemical shifts due to the presence of an ester linkage versus the amide functional group. The two hydrogen atoms in the CH_2 spacer bonded to the cyclopentadienyl ring and −C(O)O− group are assigned to the signal at 4.87 ppm (singlet). The peaks for the hydrogen atoms in the ferrocenyl group are assigned in Fig. S1. The ^{1}H NMR spectrum of **3** was analyzed using gcosy techniques and assigned via comparison with values reported for similar compounds [13]. The assigned ^{1}H NMR spectrum of **3** is shown in Fig. S2.

^{31}P NMR spectroscopy was particularly useful for confirming the formation of **4** and **5**. ^{1}H and ^{13}C{^{1}H} NMR spectra of **4** and **5** show similar patterns to the spectra of **1** and **2** with slight shift in the

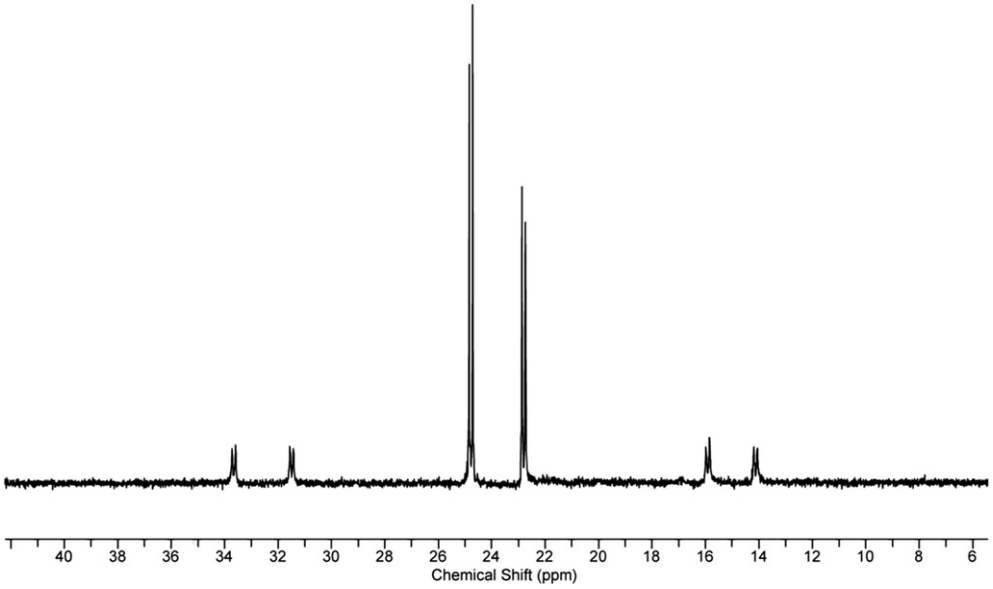


Fig. 2. ^{31}P{^{1}H} NMR spectrum of **4** in $CDCl_3$.

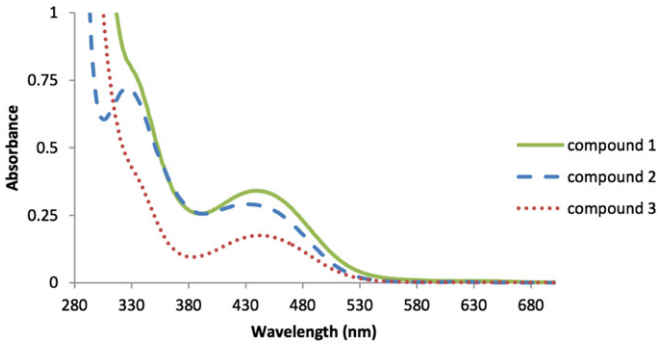


Fig. 3. Absorption spectra of **1**, **2** and **3** in CH_2Cl_2.

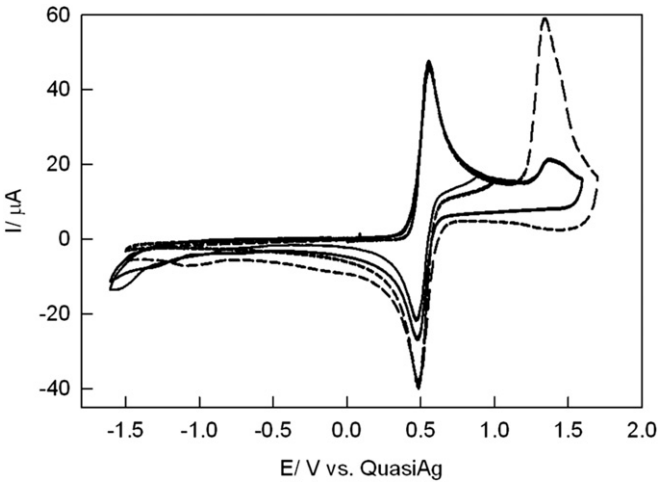


Fig. 4. Cyclic voltammograms for 2.25 mM solutions of **1** (dashed lines) and **4** (solid lines) in 0.1 M TBAP/dichloromethane. The potential is referenced relative to ferrocene oxidation at 0.68 V under the same conditions.

position of the peaks of the ferrocenyl unit in addition to the presence of signals for PPh_3. The peak assigned to the lone CH in the C_3S_2 ring is shifted from 3.58 ppm in the ^{1}H NMR spectrum of **1** to 3.32 ppm for **4**. A similar shift in the corresponding CH resonance (3.52 ppm) was observed in the ^{1}H NMR spectrum of **2** versus **5** (3.30 ppm). In the $^{31}P\{^1H\}$ NMR spectra of **4** and **5** two peaks are present at ~25 and 23 ppm. These peaks display ^{195}Pt satellites with $^1J_{PtP}$ values in the range of 2801 and 2865 Hz and $^2J_{PP}$ values of 21 Hz for the two inequivalent phosphorus nuclei. The $^{31}P\{^1H\}$ NMR spectrum of **4** is shown in Fig. 2. The observed coupling constant values are in close agreement with those reported for related square planar Pt(II) complexes with two *cis*-phosphine ligands *trans* to two ligands with different *trans* influences [7,21,23,24].

The formation of **6**–**9** was also followed by NMR spectroscopy. Formation of the dithiols was confirmed by the appearance of signals assigned to −SH groups. These were observed at 1.34 (t, $^3J_{HH}$ = 7.9 Hz, 1H) and 1.30 (d, $^3J_{HH}$ = 8.2 Hz, 1H) ppm for **6** and at 1.33 (t, $^3J_{HH}$ = 8.2 Hz, 1H) and 1.27 (d, $^3J_{HH}$ = 7.6 Hz, 1H) ppm for **8**. The proton signals for those H centers closest to the thiols shifted ~0.5 ppm to the lower chemical shifts relative to their position in the ^{1}H NMR spectra of **1** and **2** upon opening of the C_3S_2 ring. The position of −CH signal in the C_3S_2 ring was the most shifted, from 3.58 ppm for **1** to 2.94 ppm for **6** and, similarly, from 3.52 ppm in **2** to 2.89 ppm for **8**. Deprotonation of the dithiols with Et_3N and treatment with $ClSiMe_3$ results in the signals for the thiol peaks replaced with 2 peaks centered around ~0.3 ppm and assigned to $-SSiMe_3$. The ^{1}H NMR spectra of **6** and **7** are shown in supporting information, respectively (Figs. S3 and S4).

The absorption spectra of compounds **1**–**3** are presented in Fig. 3. They all display a maximum between 440 and 450 nm with molar absorption coefficients (ε) of 184, 102 and 37 M^{-1} cm^{-1} respectively, the absorption assigned to the symmetry forbidden d−d transition and consistent with spectra of related ferrocenyl amides [11]. Compound **2** shows a well-resolved maximum at 330 nm with ε = 255 M^{-1} cm^{-1} which is assigned to the transition from the highest π-orbital to the antibonding σ-orbital in the S–S bond [25]. This transition is not resolved for **1** and **3** and is not present for the Pt complexes **4** and **5**.

IR spectroscopy identified the amide and ester functional groups in the synthesized ferrocenyl complexes. Three characteristic amide peaks are present in the IR spectra of **1** and **3**. These peaks are at 3294 cm^{-1} (N–H stretching), 1654 cm^{-1} (C=O stretching + N–H bending + C–N stretching), 1560 cm^{-1} (N–H bending + C–N stretching) for **1** and at 3277 cm^{-1} (N–H stretching), 1675 cm^{-1} (C=O stretching + N–H bending + C–N stretching), 1573 cm^{-1} (N–H bending + C–N stretching) for **3**. These assignments were completed according to values reported for other ferrocenyl amides [11]. The IR spectrum of **2** displays 3 characteristic peaks for the ester functional group at 1734 cm^{-1} (C=O stretching), 1176 and 1243 cm^{-1} (C–O stretching).

3.2.1. Cyclic voltammetry

The electrochemistry of **1** and **4** were investigated by cyclic voltammetry as 2.25 mM solutions in 0.1 M TBAP/dichloromethane at room temperature using a glassy carbon working-electrode (Fig. 4).

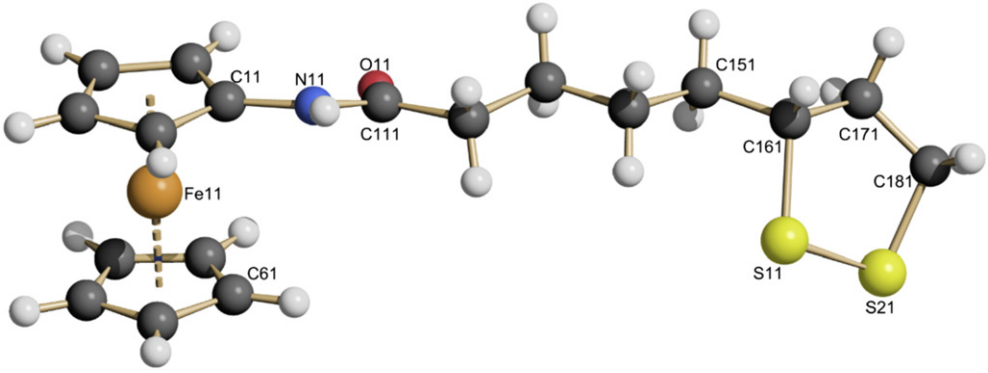


Fig. 5. The molecular structure of **1** (molecule 1). Selected bond lengths (Å) and angles (degrees): N11–C111 1.333(7), N11–C11 1.428(7), O11–C111 1.228(6), S11–C161 1.881(9), S11–S21 2.005(7), S21–C181 1.8051(4), C161–C171 1.5351(2), C171–C181 1.4821(4), C161–S11–S21 98.8(4); C181–S21–S11 95.6(7), C151–C161–C171 112.0(8), C151–C161–S11 107.4(7), C171–C161–S11 107.4(7), C181–C171–C161 113.61(2), C171–C181–S21 110.01(1).

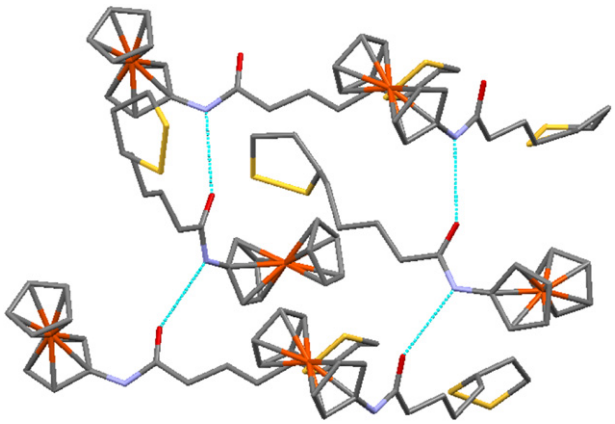


Fig. 6. Molecular structure of **1** with hydrogen bonding interactions.

As expected each show a quasi-reversible wave at 0.52 V (ΔE_p at 50 mV/s is 68 mV) that can be assigned to the oxidation of the ferrocene moiety (oxidation of ferrocene is at 0.65 V under the same conditions; $\Delta E_p = 73$ mV, $I_a/I_c = 1.0$). The ratio of anodic and cathodic currents (I_a/I_c), one measure of the chemical reversibility of the oxidation, is one for **1** but slightly larger for **4** (ranges from 1.1 to 1.3 for scan rates 500 mV/s and 50 mV/s, respectively) suggesting that the latter is slightly unstable to oxidation. Unlike in the cyclic voltammetry of ferrocene, for **1** there is an additional single electron oxidation peak at 1.35 V that can be assigned to the oxidation of the disulfide moiety [26]. The shape of the anodic peak arising from the oxidation is indicative of an absorption process, suggesting that upon oxidation the resulting intermediate is reacting with the electrode. A similar, yet smaller the anodic peak caused by the oxidative process is also observed in the CV of **4**. This additional oxidative process in **4** is not due impurities in the sample, as the purity was established by NMR spectroscopy prior to the electrochemical experiment both in the absence and presence of the supporting electrolyte. As mentioned above the complex **4** is slightly reactive under oxidative conditions leading to what appears to be some disulfide (or Pt–S oxidative products) formation that is responsible for the higher I_a/I_c.

3.2.2. X-ray crystallography

Orange crystals of **1** were obtained by recrystallization from CH_2Cl_2/heptane, and the structure determined using single crystal X-ray diffraction techniques. Complex **1** crystallizes in the non-centrosymmetric, orthorhombic space group Pca2(1) with 8 molecules in the unit cell. There are two independent molecules in the asymmetric unit, reflecting the presence of the enantiomeric pair. Each of the C_3S_2 rings exhibited some site disorder which was satisfactorily refined with 0.66667:0.33333 occupancy and a figure representing the refined model is provided in the Supporting information (Fig. S5). A summary of the pertinent bond lengths and angles for molecule 1 is listed in the caption of Fig. 5. Within the experimental deviation, the S–S bond length in **1** is similar to that found in lipoic acid (2.053(4)) [27]. The Cp rings are almost perfectly parallel. The molecular structure of **1** is shown in Fig. 5 (molecule 1).

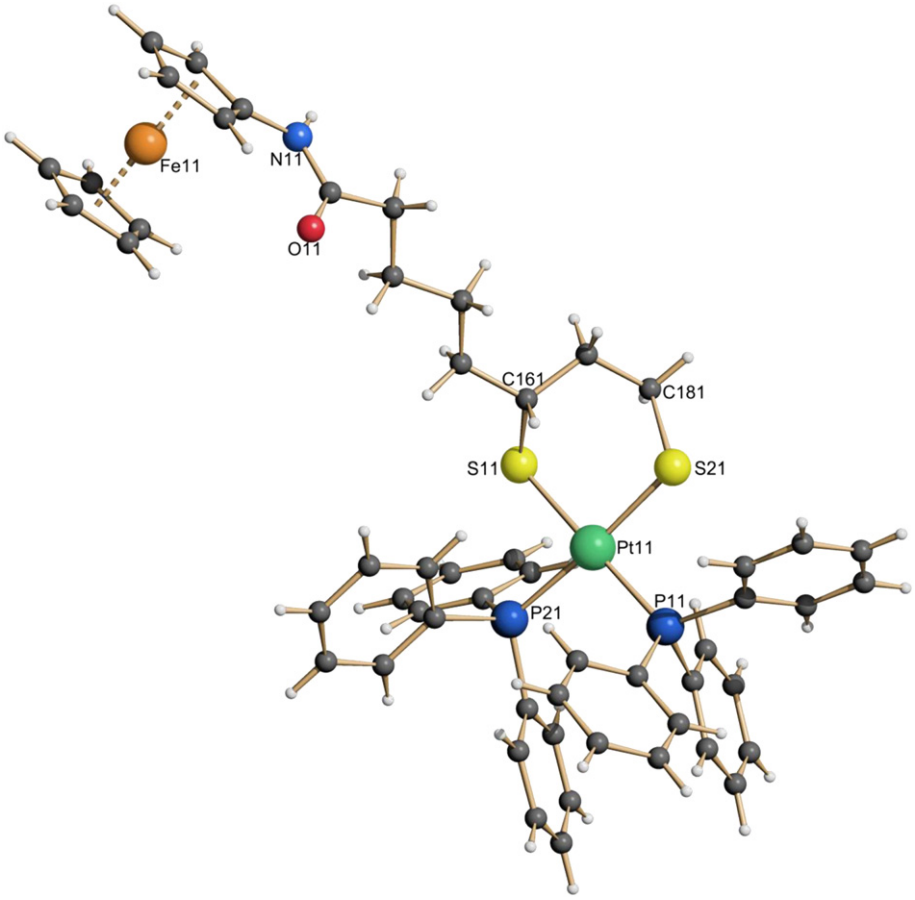


Fig. 7. Molecular structure of **4** (molecule 1). Selected bond lengths [Å] and angles [°] for **4**: Pt11–S11 2.360(1), Pt11–S21 2.339(1), Pt11–P11 2.287(1), Pt11–P21 2.306(1), S11–C161 1.842(6); S11–Pt11–S21 91.73(5), S11–Pt11–P11 179.10(5), P11–Pt11–P21 97.50(5), S21–Pt11–P11 87.41(5), S21–Pt11–P21 174.92(5), C171–C161–S11 109.4(4).

As illustrated in Fig. 6, compound **1** displays H-bonding interactions in the crystal. Each molecule of **1** displays two hydrogen bonding interactions with two neighboring molecules via the amide protons (N···O = 3.026 Å).

Dark orange crystals of [Pt(PPh_3)$_2$($S_2CH_2CH_2CH$-κ^2-*S*,*S*)$(CH_2)_4$C(O)NH(η^5-C_5H_4)Fe(η^5-C_5H_5)] **4** were obtained by recrystallization from $CHCl_3$/pentane. The ligated complex **4** crystallizes in the triclinic space group P $\bar{1}$ ($Z = 4$) and the molecular structure of one of the two independent (chiral) molecules present in the asymmetric unit is shown in Fig. 7. As for **1**, both enantiomers are found in the asymmetric unit although unlike **1**, complex **4** crystallizes in a centrosymmetric space group. Bond lengths and angles discussed in the text refer to molecule 1. The coordination geometry of platinum center is a slightly distorted square planar with two phosphines and one dithiolate ligand that coordinates in a bidentate fashion to yield a six-membered ring. The Pt–S (2.339(1)–2.3603(1) Å) and Pt–P bond lengths (2.287(1)–2.306(1)) and S–Pt–S (average of 91.73(5)°) and P–Pt–P angles (97.50(5)°) compare well with those reported for related complexes [7,21]. Notably, the –S–CH–CH_2– bond angle is markedly increased in **4** (112.6(4)°) compared to that in **1** (107.4(7)°), a consequence of the ring opening and consistent with the change in ^{1}H NMR chemical shifts. The Cp rings defined by C11–C51 and C61–C101 are almost perfectly parallel. Selected bond lengths and angles are summarized in the caption of Fig. 7. Unlike for the crystal packing observed in **1** there is no H-bonding observed in **4** and can perhaps be attributed to the sterics of the PPh_3 ligands and the large number of $CHCl_3$ present in the lattice.

4. Conclusion

The preparation and characterization of three new ferrocene based dithiolane compounds are reported. These were designed to contain an amide or ester functional group in their structure. The synthesis and purification of these materials was a challenging one because of the sensitivity of the S–S bond in these compounds and the formation of insoluble polymers when compounds are exposed to light or heat. Their cyclic voltammograms display a reversible oxidation assigned to the ferrocenyl unit and one quasi-reversible oxidation related to the dithiolane ring. Complexation of these ligands was studied using oxidative addition of their S–S bonds to platinum(0) centers, resulting in *cis* mononuclear platinum(II) complexes.

Acknowledgments

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Appendix A. Supplementary material

CCDC 848844 and 848845 contain the supplementary crystallographic data for **1** and **4** respectively in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.12.003.

References

[1] P. Stepnicka, Ferrocenes: Ligands, Materials And Biomolecules, J. Wiley, Chichester, England, Hoboken, NJ, 2008.
[2] (a) P.D. Beer, Acc. Chem. Res. 31 (1998) 71–80;
(b) D.J. Evans, Inorg. Chim. Acta 363 (2010) 1070–1107;
M. Salmain, G. Jaouen, C. R. Chimie 6 (2003) 249–325;
L. Dai, T. Tu, S. You, W. Deng, X. Hou, Acc. Chem. Res. 36 (2003) 659–666;
A.R. Gomez, A. Javier, C.J. Carlos, Angew. Chem. Int. Ed. 45 (2006) 7674–7771.
[3] P.D. Beer, E.J. Hayes, Coord. Chem. Rev. 240 (2003) 167–189.
[4] D. Astruc, M.C. Daniel, J. Ruiz, Chem. Commun. (2004) 2637–2649.
[5] P.D. Beer, J.J. Davis, D.A. Drillsma-Migrom, F. Szemes, Chem. Commun. (2002) 1716–1717.
[6] (a) M. Labib, S. Martic, P.O. Shipman, H.-B. Kraatz, Talanta 85 (2011) 770–778;
(b) M. Labib, P.O. Shipman, S. Martic, H.-B. Kraatz, Electrochim. Acta 56 (2011) 5122–5128.
[7] T. Weidner, F. Bretthauer, N. Ballav, H. Motschmann, H. Orendi, C. Bruhn, U. Siemeling, M. Zharnikov, Langmuir 24 (2008) 11691–11700.
[8] K.J. Bonnington, M.C. Jennings, R.J. Puddephatt, Organometallics 27 (2008) 6521–6530.
[9] T. Jacob, M. Blanco, W.A. Goddard, J. Phys. Chem. C 111 (2007) 2749–2758.
[10] U. Siemeling, F. Bretthauer, C. Bruhn, J. Organomet. Chem. 695 (2010) 626–629.
[11] K. Heinze, M. Schlenker, Eur. J. Inorg. Chem. (2004) 2974–2988.
[12] W.L. Davis, R.F. Shago, E.H.G. Langner, J.C. Swarts, Polyhedron 24 (2005) 1611–1616.
[13] Y.S. Chen, R.G. Lawton, Tetrahedron Lett. 38 (1997) 5785–5788.
[14] A.F. Wagner, E. Walton, G.E. Boxer, M.P. Pruss, K. Folkers, J. Am. Chem. Soc. 78 (1956) 5079–5081.
[15] J.A. Barltrop, P.M. Hayes, M. Calvin, J. Am. Chem. Soc. 76 (1954) 4348–4367.
[16] H. Tsutsumi, S. Furumoto, M. Morita, Y. Matsuda, J. Electrochem. Soc. 139 (1992) 1522–1525.
[17] (a) G.M. Sheldrick, SHELXTL PC Version 6.1 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data, Bruker Analytical X-ray Systems, 2000;
(b) G.M. Sheldrick, Acta Crystallogr. 64A (2008) 112–122.
[18] J. Clayden, N. Greeves, S. Warren, P. Wothers, Organic Chemistry, Oxford University Press, Oxford, 2001;
R.S. Rogers, Tetrahedron Lett. 33 (1992) 7473–7474.
[19] A. Davison, N. Edelstein, R.H. Holm, A.H. Maki, Inorg. Chem. 3 (1964) 814–817.
[20] G.C. Fortman, T. Kegl, C.D. Hoff, Curr. Org. Chem. 12 (2008) pp. 1279-1297;
V.G. Albano, M. Monari, I. Orabona, A. Panunzi, F. Ruffo, J. Am. Chem. Soc. 123 (2001) 4352–4435;
V.P. Ananikov, I.P. Beletskaya, G.G. Aleksandrov, I.L. Eremenk, Organometallics 22 (2003) 1414–1421;
S.M. Aucott, H.L. Milton, S.D. Robertson, A.M.Z. Slawin, G.D. Walker, J.D. Woollins, Chem. Eur. J. 10 (2004) 1666–1676;
A. Ishii, S. Kashiura, Y. Hayashi, W. Weigand, Chem. Eur. J. 13 (2007) 4326–4333 and references therein.
[21] W. Weigand, G. Bosl, B. Vondielingen, K. Gollnick, Z. Naturforsch., B: Chem. Sci. 49 (1994) 513–518.
[22] U. Siemeling, F. Bretthauer, C. Bruhn, T. Fellinger, W. Tong, M.C.W. Chan, Z. Naturforsch., B: Chem. Sci. 65 (2010) 1089–1096.
[23] W.P. Power, R.E. Wasylishen, Inorg. Chem. 31 (1992) 2176–2183.
[24] W. Weigand, R. Wunsch, K. Polborn, Inorg. Chim. Acta 273 (1998) 106–110.
[25] G. Bergson, L. Schotte, G. Claeson, Acta Chem. Scand. 16 (1962) 1159–1174.
[26] O. Corduneanu, M. Garnett, A.M.O. Brett, Anal. Lett. 40 (2007) 1763–1768.
[27] R.M. Stroud, C.H. Carlisle, Acta Crystallogr., Sect. B: Struct. Sci., B 28 (1972) 304–306.