



## New ferrocene based dithiolate ligands

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### ABSTRACT

The preparation and characterization of the three ferrocene based dithiolane complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{NHC}(\text{O})(\text{CH}_2)_4\text{CHS}_2\text{CH}_2\text{CH}_2]$  **1**,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2\text{OC}(\text{O})(\text{CH}_2)_4\text{CHS}_2\text{CH}_2\text{CH}_2]$  **2** and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{NHC}(\text{O})(\text{CH}_2)\text{CHS}_2\text{CH}_2\text{CH}_2]$  **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  $[\text{Pt}(\text{PPh}_3)_2(\text{S}_2\text{CH}_2\text{CH}_2\text{CH}-\kappa^2\text{-S,S})(\text{CH}_2)_4\text{C}(\text{O})\text{NH}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$  **4** and  $[\text{Pt}(\text{PPh}_3)_2(\text{S}_2\text{CH}_2\text{CH}_2\text{CH}-\kappa^2\text{-S,S})(\text{CH}_2)_4\text{C}(\text{O})\text{OCH}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$  **5**, respectively. The reduction of the S–S bond in **1** and **2** yields the corresponding dithiols; these can be deprotonated and treated with  $\text{ClSiMe}_3$  to prepare  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{NHC}(\text{O})(\text{CH}_2)_4\text{CH}(\text{SSiMe}_3)\text{CH}_2\text{CH}_2(\text{SSiMe}_3)]$  **7** and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2\text{OC}(\text{O})(\text{CH}_2)_4\text{CH}(\text{SSiMe}_3)\text{CH}_2\text{CH}_2(\text{SSiMe}_3)]$  **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**.

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## 1. Introduction

The synthesis of substituted bis( $\eta^5$ -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  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{NHC}(\text{O})(\text{CH}_2)_4\text{CHS}_2\text{CH}_2\text{CH}_2]_2$  can be prepared from 1,1'-diaminoferrrocene 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  $\text{S}_2$  units. More recently, Kraatz and co-workers have coupled lipoic acid to the amine unit in  $[\text{Fe}(\text{C}_5\text{H}_4\text{CO}_2\text{Me})(\text{C}_5\text{H}_4\text{NH}_2)]$ , 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<sub>2</sub>O<sub>5</sub>. 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].

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>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<sub>4</sub> ( $\delta = 0$  ppm). <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on the same spectrometer and are referenced to 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta = 0$  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  $\mu$ m). 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<sub>6</sub>) 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<sub>4</sub>. The solvent was removed *in vacuo* yielding 0.20 g (66%) of compound **1** as an orange-brown solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 5 mM, 23 °C)  $\delta = 6.47$  (br s, 1H), 4.57 (vt,  $J_{\text{HH}} = 2.0$  Hz, 2H), 4.14 (s, 5H), 3.98 (vt,  $J_{\text{HH}} = 2.0$  Hz, 2H), 3.58 (m, 1H), 3.12 (m, 2H), 2.47 (m, 1H), 2.24 (td,  $^3J_{\text{HH}} = 7.4$ ,  $^2J_{\text{HH}} = 1.6$  Hz, 2H), 1.92 (m, 1H), 1.71 (m, 4H), 1.49 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CDCl<sub>3</sub>)  $\delta = 170.9$  (C(O)), 94.4 (CN), 69.1 (Cp), 64.5 (CH), 61.4 (CH), 56.4 (CHS), 40.2 (CH<sub>2</sub>), 38.5 (CH<sub>2</sub>S), 37.0 (CH<sub>2</sub>), 34.6 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>). HRMS: Calcd for C<sub>18</sub>H<sub>23</sub>ONS<sub>2</sub>Fe ( $m/z$ ): 389.0570 Found: 389.0571. Anal. Calc. (%) for C<sub>18</sub>H<sub>23</sub>ONS<sub>2</sub>Fe: 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<sub>4</sub>. The solvent was removed *in vacuo* yielding 0.27 g (86%) of compound **2** as an air-stable orange oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23 °C)  $\delta = 4.87$  (s, 2H), 4.24 (vt,  $J_{\text{HH}} = 1.8$  Hz, 2H), 4.15 (vt,  $J_{\text{HH}} = 1.8$  Hz, 2H), 4.13 (s, 5H), 3.51 (m, 1H), 3.10 (m, 2H), 2.41 (m, 1H), 2.27 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 2H), 1.86 (m, 1H), 1.64 (m, 4H), 1.41 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CDCl<sub>3</sub>)  $\delta = 172.8$  (C(O)), 80.8 (CH<sub>2</sub>), 69.1 (CH), 68.4 (CH), 68.1 (Cp), 62.3 (C) 55.8 (CHS), 39.7 (CH<sub>2</sub>), 38.0 (CH<sub>2</sub>S), 34.1 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 24.2 (CH<sub>2</sub>). HRMS: Calcd for C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub>Fe ( $m/z$ ): 404.0567 Found: 404.0562. Anal. Calc. (%) for C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub>Fe: 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-3-yl)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<sub>3</sub>N (0.12 ml, 0.85 mmol) in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub>, 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<sub>2</sub>Cl<sub>2</sub>:heptane at –5 °C yielded **3** as a microcrystalline orange solid (0.25 CH<sub>2</sub>Cl<sub>2</sub> solvate from <sup>1</sup>H NMR). Yield: 65%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23 °C)  $\delta = 6.73$  (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<sub>15</sub>H<sub>17</sub>S<sub>2</sub>FeON ( $m/z$ ): 347.0101 Found: 347.0101. Anal. Calc. (%) for C<sub>15</sub>H<sub>17</sub>ONS<sub>2</sub>Fe·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.25</sub>: 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-dithiolato)octaneamide bis(triphenylphosphine)platinum(II) (**4**)

0.20 g of [Pt(PPh<sub>3</sub>)<sub>4</sub>] (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. <sup>1</sup>H and <sup>31</sup>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<sub>3</sub> and pentane (2:2.5) and cooled to –25 °C to yield single crystals suitable for X-ray diffraction analysis. Yield = 47%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23 °C)  $\delta = 7.47$  (t,  $^3J_{\text{HH}} = 7.6$  Hz, 6H), 7.41 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 6H), 7.24 (m, 6H), 7.14 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 6H), 7.09 (t,  $^3J_{\text{HH}} = 7.6$  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,  $^3J_{\text{HH}} = 7.8$  Hz, 2H), 1.68 (m, 1H), 1.56 (m, 2H), 1.34 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CDCl<sub>3</sub>)  $\delta = 171.6$  (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<sub>2</sub>), 37.4 (CH<sub>2</sub>S), 27.5 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 24.5 (CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 23 °C)  $\delta = 24.8$  (dd,  $^2J_{\text{PP}} = 21.0$  Hz,  $^1J_{\text{PPt}} = 2865$  Hz), 22.8 (dd,  $^2J_{\text{PP}} = 21.0$  Hz,  $^1J_{\text{PPt}} = 2804$  Hz). HRMS: Calcd for C<sub>54</sub>H<sub>53</sub>FeNOP<sub>2</sub>PtS<sub>2</sub> ( $m/z$ ): 1108.2041 Found: 1108.2038.

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