



# Dinuclear platinum(II) complexes containing ferrocenylalkyl–thiolate and –selenolate ligands



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## ABSTRACT

Alkylation reactions of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with haloalkylferrocenes  $\text{FcCH}_2\text{Cl}$ ,  $\text{Fc}(\text{CH}_2)_6\text{Br}$  and  $\text{Fc}(\text{CH}_2)_{11}\text{Br}$  [ $\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$ ] gave the cationic  $\mu$ -thiolate complexes  $[\text{Pt}_2(\mu\text{-S})\{\mu\text{-S}(\text{CH}_2)_n\text{Fc}\}(\text{PPh}_3)_4]^+$  ( $n = 1, 6, 11$ ), isolated as  $\text{PF}_6^-$  and/or  $\text{BPh}_4^-$  salts, and characterised by ESI mass spectrometry, NMR spectroscopy, microelemental analysis, and by an X-ray structure determination on  $[\text{Pt}_2(\mu\text{-S})\{\mu\text{-SCH}_2\text{Fc}\}(\text{PPh}_3)_4]\text{PF}_6$ . The complex contains the typical folded  $\{\text{Pt}_2(\mu\text{-S})_2\}$  core with an axial ferrocenylmethylthiolate ligand. The corresponding selenolate complex  $[\text{Pt}_2(\mu\text{-Se})\{\mu\text{-SeCH}_2\text{Fc}\}(\text{PPh}_3)_4]^+$  was similarly obtained by alkylation of  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$  with  $\text{FcCH}_2\text{Cl}$ , and isolated as  $\text{PF}_6^-$  and  $\text{BPh}_4^-$  salts. The attempted liberation of  $\text{FcCH}_2\text{SH}$  from  $[\text{Pt}_2(\mu\text{-S})\{\mu\text{-SCH}_2\text{Fc}\}(\text{PPh}_3)_4]^+$  using  $\text{Na}_2\text{S}$  was not successful.

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## 1. Introduction

The ferrocenylalkyl [ $\text{Fc}(\text{CH}_2)_n$ ;  $\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$ ] substituent is able to provide a remarkable stabilisation of primary phosphanes and arsanes [such as in the air-stable compounds  $\text{Fc}(\text{CH}_2)_n\text{PH}_2$  ( $n = 1, 2$ ) and  $\text{Fc}(\text{CH}_2)_2\text{AsH}_2$ ] [1,2] and recent theoretical studies have investigated the electronic basis for this [3,4]. We subsequently wished to investigate whether the ferrocenylalkyl group could also stabilise other reactive main group element hydrides such as thiols, selenols and tellurols.

While the chemistry of deprotonated ferrocene-thiols (thiolates) and corresponding selenolates with the chalcogen atom directly bonded to a cyclopentadienyl ring is well-established [5], less is known about ferrocenylalkyl–thiolates and –selenolates. As an example, the long chain thiols  $\text{Fc}(\text{CH}_2)_n\text{SH}$  ( $n = 6, 8, 11$ ) are used in forming self-assembled monolayers on gold surfaces [6], and have been prepared by reaction of the bromides  $\text{Fc}(\text{CH}_2)_n\text{Br}$  with thiourea, forming intermediate thiuronium salts  $[\text{Fc}(\text{CH}_2)_n\text{SC}(\text{NH}_2)_2]^+\text{Br}^-$ , which can be converted to the free thiols [7]. The silylated reagents  $\text{FcCH}_2\text{SeSiMe}_3$  and  $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SeSiMe}_3)_2$  have recently been developed as selenolate transfer agents, for example for synthesis of the aggregate  $[\text{Ag}_8(\text{SeCH}_2\text{Fc})_8(\text{PPh}_3)_4]$  [8]. Analogous compounds with carboxylate spacers, viz.  $\text{FcC}(\text{O})\text{OCH}_2\text{CH}_2\text{ESiMe}_3$  ( $\text{E} = \text{S}, \text{Se}$ ) have also been developed [9].

As an initial route into the chemistry, we chose to investigate the potential liberation of the thiol or selenol from dinuclear

platinum(II) complexes  $[\text{Pt}_2(\mu\text{-E})\{\mu\text{-E}(\text{CH}_2)_n\text{Fc}\}(\text{PPh}_3)_4]^+$  ( $\text{E} = \text{S}, \text{Se}$ ), generated by alkylation of the parent complexes  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** [10] and  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$  **2** [11]. The alkylation chemistry of these and closely-related complexes is now a facile and well-understood reaction [12], and the availability of suitable ferrocene-based alkylating agents  $\text{Fc}(\text{CH}_2)_n\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) suggested that these derivatives should be readily obtainable. We have previously reported a screening survey using ESI mass spectrometry of the alkylation chemistry of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  towards  $\text{FcCH}_2\text{NMe}_3^+\text{I}^-$  which identified the ion  $[\text{Pt}_2(\mu\text{-S})\{\mu\text{-SCH}_2\text{Fc}\}(\text{PPh}_3)_4]^+$  [13], but the complex has not to date been isolated and characterised. Independently of investigations into potential routes to ferrocenyl chalcogenol species, the chemistry of ferrocene-appended platinum complexes has attracted some interest [14], in particular platinum complexes of ferrocene–thiolate ligands [15].

## 2. Results and discussion

### 2.1. Synthesis of ferrocenylalkyl–thiolate and –selenolate platinum(II) complexes

A number of derivatives of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  that contain ancillary ferrocene groups are already known, but none containing the desired ferrocenylalkylthiolate groups. Thus, there is an extensive chemistry of the related phosphine system  $[\text{Pt}_2(\mu\text{-S})_2(\text{dppf})_2]$  [ $\text{dppf} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2$ ] [16–20] and derivatives where a ferrocene is attached via the sulfide centres, which include a number of organomercury derivatives [13,21] and the ferrocene-1,1'-dithiolate derivative  $[\text{Pt}_2\{\mu\text{-}(\text{SC}_5\text{H}_4)_2\text{Fc}\}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^{2+}$

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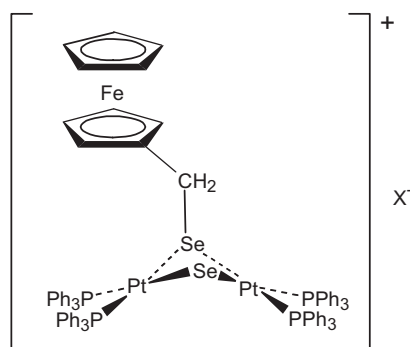
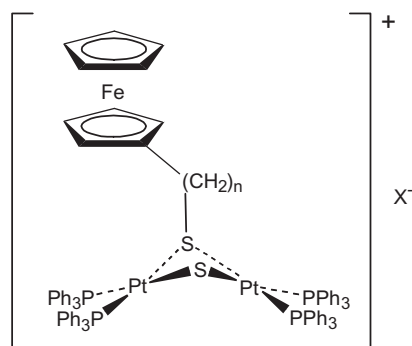
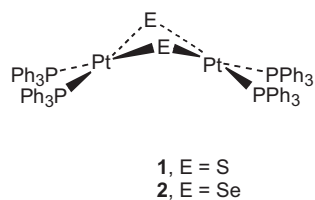
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[22]. However, the only isolated derivative of  $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$  containing a selenium-appended ferrocene is  $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeHgFc})(\text{PPh}_3)_4]^+$  [23].

Ferrocenylmethyl compounds  $\text{FcCH}_2\text{X}$  are well known to have alkylating characteristics, dependent on the nature of the leaving group X [24]. Reaction of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  with readily available  $\text{FcCH}_2\text{OH}$  in refluxing methanol proceeded very slowly giving  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{Fc})(\text{PPh}_3)_4]^+$  together with a significant number of other species, as shown by positive-ion ESI mass spectrometry.  $[\text{FcCH}_2\text{NMe}_3]\text{I}$  has been used in a number of ferrocenylmethylation reactions, mainly because of its availability and higher reactivity [24,25]. Repeated attempts to produce the pure monoalkylated derivative  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{Fc})(\text{PPh}_3)_4]^+$  **3** by refluxing  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  **1** with 1 mol equivalent of  $[\text{FcCH}_2\text{NMe}_3]\text{I}$  for 24 h were unsuccessful, with the solid product always contaminated by the presence of  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-I})(\text{PPh}_3)_4]^+$ , identified by a peak at  $m/z$  1599 in the ESI mass spectrum. This species is prevalent in systems containing  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  and  $\text{I}^-$ , and has been characterised independently [26]. Substitution of the  $\text{I}^-$  anion for  $\text{BPh}_4^-$  via metathesis gave the previously uncharacterised salt  $[\text{FcCH}_2\text{NMe}_3]\text{-BPh}_4$ , which was then refluxed for 4 days with  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  in a 1:1 mol ratio. The isolated solid of  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{Fc})(\text{PPh}_3)_4]\text{-BPh}_4$  from the reaction mixture contained a significant amount of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  starting material. More potent ferrocenylalkylating agents were therefore investigated.

The use of halomethylferrocene derivatives as alkylating agents has not been as extensively applied as  $\text{FcCH}_2\text{NMe}_3^+$ , due to their relative instability at room temperature, which requires them to

be used as soon as possible after synthesis in order to avoid decomposition.  $\text{FcCH}_2\text{Cl}$  (which can be readily generated from  $\text{FcCH}_2\text{OH}$  by reaction with oxalyl chloride, a non-oxidising chlorinating agent [27]) proved to be much more reactive towards  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ . The reaction was carried out in methanol and it was found that the addition of a mild, insoluble base ( $\text{CaCO}_3$ ) served to eliminate traces of acidic by-products from the chlorination process, which were manifested in the formation of a green initial reaction solution which turned to the expected yellow-orange colour on addition of  $\text{CaCO}_3$ . After filtration of the reaction mixture, the product was isolated from the filtrate as either its  $\text{PF}_6^-$  or  $\text{BPh}_4^-$  salts, **3a** and **3b** respectively. The ESI mass spectrum of **3a** showed a single ion due to the parent cation  $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{Fc})(\text{PPh}_3)_4]^+$  at  $m/z$  1702.282 (calculated  $m/z$  1702.261). Crystallisation of **3a** from  $\text{CH}_2\text{Cl}_2$ -diethyl ether gave orange crystals that were suitable for an X-ray structure determination, and were found to be the bis-dichloromethane solvate, in agreement with microanalytical data. The  $^1\text{H}$  NMR spectra of **3a** and **3b** showed the expected  $\text{PPh}_3$  (and  $\text{BPh}_4^-$ ) resonances as a complex multiplet, three resonances for the cyclopentadienyl protons as expected, together with an  $\text{SCH}_2$  resonance that appeared as a broad singlet, with a broadened base. Although coupling constants could not be measured, its appearance is characteristic for the  $\text{SCH}_2$  protons of other mono-alkylated derivatives of  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ , arising from  $^{31}\text{P}$  and  $^{195}\text{Pt}$  coupling. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra showed a complex central resonance centred around  $\delta$  24, with two sets of satellites due to coupling to  $^{195}\text{Pt}$  clearly visible, and  $^1\text{J}(\text{PtP})$  coupling constants of 3264 and 2627 Hz for phosphines *trans* to thiolate and sulfide



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