

# 1,1'-Bis(trimethylsilylseleno)ferrocene in cluster synthesis: a redox active surface on a copper–selenide core†‡

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1,1'-Bis(trimethylsilylseleno)ferrocene **1** has been prepared from the reaction of  $[1,1'\text{-Fe}(\eta^5\text{-C}_5\text{H}_4\text{SeLi})_2(\text{TMEDA})]$  and  $\text{ClSiMe}_3$  in good yield. The reactive silyl groups on **1** are used as a driving force for the synthesis of  $[\text{Cu}_8\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\}_4(\text{PPh}_2\text{Et})_4]$  **2**, a cluster possessing four peripheral ferrocenyl moieties.

Owing to the inherent redox active metal centre, the functionalisation of the cyclopentadienyl rings in ferrocene and subsequent ligation to metal centres are currently of great research interest in cluster, materials and inorganic synthesis.<sup>1</sup> Many of these ferrocene-containing molecules display interesting charge transport, non-linear optical and magnetic properties related to the metal–metal interactions between the ferrocene units and other metal centres in the structure.<sup>2</sup> It has been demonstrated that nanoparticle (Au) surfaces can be functionalised with ferrocenyl units, although these redox centres are spatially removed from the metallic core due to the micellar type of stabilisation provided by the thiolate ligands.<sup>3</sup> Bidentate 1,1'-bis(diphenylphosphino)ferrocene<sup>4</sup> (dppf) has been shown to be an excellent ligand in carbonyl cluster chemistry due to the flexibility of the ferrocene unit, through a combination of ring twisting and tilting. 1,1'-Ferrocenyldichalcogenolates have many similar characteristics and have been shown to bridge metal centres<sup>5</sup> and bind in a chelating fashion to one metal.<sup>6</sup> These dichalcogenolates are synthesized either *via* insertion of chalcogens into the C–Li bond of dilithioferrocene<sup>7</sup> or *via* deprotonation of the corresponding dichalcogenols.<sup>8</sup>

The use of silylated selenium reagents offers a powerful entry into the formation of metal–selenium bonds in both coordination and polynuclear chemistry.<sup>9</sup> Their utility in the latter exploits the bridging capacity of the selenium centre in alkyl- and aryl-selenolate ligands and has been used to effectively stabilise metal–selenide cores. Herein we describe the unprecedented complexation of 1,1'-diselenolatoferrocene units onto a polymeric core.

We reasoned that the synthesis of the bis-silylated reagent  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SeSiMe}_3)_2]$  **1** and its use in the synthesis of metal–chalcogen clusters would permit facile introduction of redox active iron centres onto metal–chalcogen cluster surfaces, which may be intimately coupled (*via* the C<sub>5</sub>–Se rings) to the cluster core. Owing to the large variety of bonding modes for selenium and the success of the use of silylselenoethers in cluster synthesis,<sup>9</sup>  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SeSiMe}_3)_2]$  **1** was targeted and prepared from the corresponding dilithiodiselenolate.<sup>§</sup> When chlorotrimethylsilane is added to a suspension of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SeLi})_2(\text{TMEDA})]$ <sup>10</sup> in pentane at 0 °C, **1** is isolated as a golden yellow powder in 65% yield. Compound **1** is susceptible to rapid air decomposition both in solution and the solid state. Even under an inert atmosphere, **1** must be stored cold and in the absence of light in order to avoid decomposition. The molecular structure of **1** (Fig. 1) shows that the selenolate groups are held

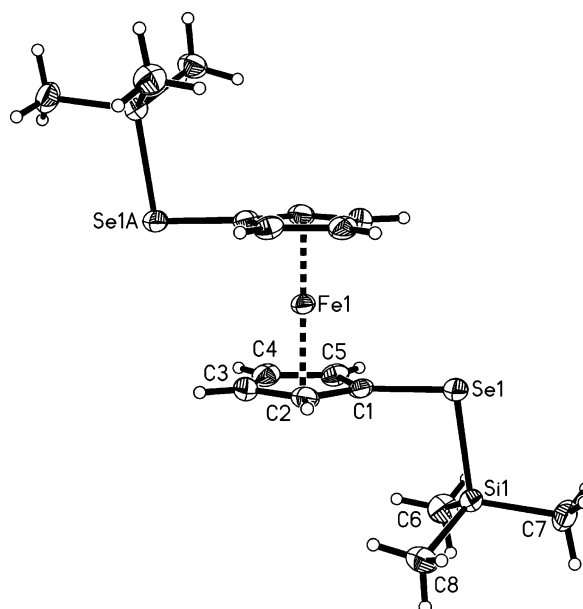


Fig. 1 Molecular structure of  $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SeSiMe}_3)_2$  **1**. Selected bond lengths (Å) and angles (°): Fe1–C 2.041(3)–2.048(3), C1–Se1 1.916(3), Se1–Si1 2.2930(8); C1–Se1–Si1 95.32(8).

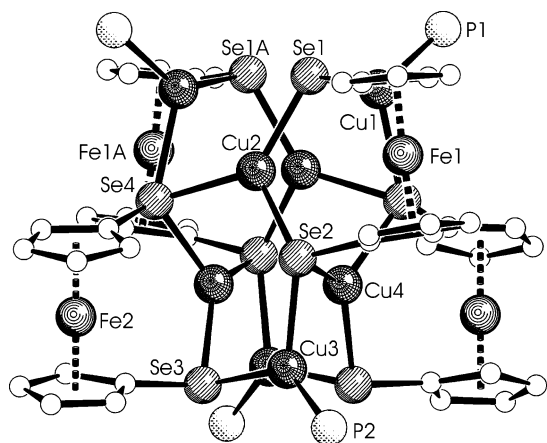
in a *trans* configuration in the solid state with the two Cp rings adopting a staggered conformation. The iron atom sits on a crystallographic inversion centre with the planes of the cyclopentadienyl rings parallel and the selenium atoms lie slightly above (0.02 Å) the C<sub>5</sub> rings.<sup>¶</sup>

The reaction of **1** with 2 equivalents of  $\text{CuOAc} \cdot 3\text{PPh}_2\text{Et}$  in THF affords  $[\text{Cu}_8\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\}_4(\text{PPh}_2\text{Et})_4] \cdot (\text{OC}_4\text{H}_8)_2$  **2**·THF in good yield, the reaction driven by the formation and elimination of  $\text{Me}_3\text{SiOAc}$ .<sup>||</sup> The molecular structure of **2** is shown in Fig. 2. There are two crystallographically independent and chemically equivalent molecules in the unit cell, both of which reside on a two-fold rotation axis.<sup>\*\*</sup> Bond lengths and angles discussed in the text for **2** refer to molecule 1.

Cluster **2** contains a copper–selenium core shielded by four ferrocenyl and four phosphine ligands. All of the copper centres exhibit a trigonal planar geometry either through a combination of two selenium and one phosphorus bonds (Cu1, Cu3, Cu1A, Cu3A) or three Cu–Se interactions (Cu2, Cu2A, Cu4, Cu4A). The Cu–Se [2.356(1)–2.463(1) Å] and Cu–P distances [2.214(2)–2.226(2) Å] are similar to those found in other copper–selenium clusters.<sup>11</sup> Both of the crystallographically independent ferrocenyl moieties display moderate deviations from co-planarity of the two C<sub>5</sub> rings (2.0 and 5.3° for Fe2 and Fe1, respectively). Whilst the two Cp rings about Fe1 deviate 15.7° from being eclipsed, the two about Fe2 are better described as adopting a staggered (29.5°) conformation. The selenium atoms in **2** are slightly displaced (0.07–0.28 Å) from the planes defined by their respective C<sub>5</sub> rings. Overall, the eight Se centres define a non-bonded [3.352(1)–4.411(1) Å] dodecahedral framework bridging either two (Se1, Se1A, Se3,

† Electronic supplementary information (ESI) available: cyclic voltammograms for **1** and **2**, <sup>1</sup>H NMR spectrum for **1**. See <http://www.rsc.org/suppdata/cc/b0/b010023o/>

‡ Dedicated to Dr Arthur J. Carty on the occasion of his 60th birthday.



**Fig. 2** Molecular structure of  $[\text{Cu}_8\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\}_4(\text{PPh}_2\text{Et})_4]$  **2** (molecule **1**; phosphine carbon atoms omitted). Selected bond lengths (Å): Se(1)–Cu(2) 2.355(1), Se(1)–Cu(1) 2.411(1), Se(2)–Cu(2) 2.362(1), Se(2)–Cu(4) 2.397(1), Se(2)–Cu(3) 2.434(1), Se(3)–Cu(4A) 2.354(1), Se(3)–Cu(3) 2.399(1), Se(4)–Cu(4A) 2.380(1), Se(4)–Cu(2) 2.431(1), Se(4)–Cu(1A)–Cu(1A) 2.463(1).

Se3A) or three (Se2, Se2A, Se4, Se4A) metals. It is interesting to note that the observed  $\text{Cu}_8\text{Se}_8$  core geometry in **2** has been predicted to be unstable for related  $[(\text{FeCl})_{4-x}\text{Cu}_{4+x}(\text{SePr}^i)_8]$  complexes.<sup>11b</sup>

The cyclic voltammogram of **1** (ESI<sup>†</sup>) displays one irreversible wave at +1.33 V (*versus*  $\text{CoCp}_2/\text{CoCp}_2^+$ ), complicated by the deposition of the material onto the electrode surface. In **2**, two irreversible oxidation waves of equal current are observed at +1.11 and +1.35 V,<sup>††</sup> although the first wave may be due to oxidation of Cu(I) centres. Unlike surface modified Au particles with ferrocenylalkanethiolate ligands where the Fe centres are spatially ‘removed’ from the cluster,<sup>3</sup> in **2** the Fe centres are intimately associated with the polymetallic core. Oxidation of **2** to higher potential results in cluster decomposition only. Any electronic communication between the iron and copper centres in the molecular complex **2** suggests similar effects in related *nanoscale*  $[\text{Cu}_{2m}\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\}_m - n\text{Se}_n(\text{PR}_3)_x]$  complexes and we are actively pursuing their synthesis.

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## Notes and references

§ *Synthesis of 1*:  $\text{ClSiMe}_3$  (0.13 mL, 3.26 mmol) was added dropwise to a suspension of  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SeLi})_2(\text{TMEDA})]$  (0.16 mmol) in pentane (40 mL) at 0 °C. The orange suspension gradually became yellow in colour and after two hours the suspension was filtered to remove LiCl and the filtrate was concentrated slowly to afford X-ray quality golden orange crystals of **1**. Yield 65%. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ): δ 4.30 vt (CH,  $J_{\text{HH}}$  1.8 Hz, 4), 4.05 vt (CH,  $J_{\text{HH}}$  1.8 Hz, 4), 0.225 (Si–CH<sub>3</sub>, s, 18). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 77.3 (CH, s), 71.5

(CH, s), 69.3 (C–Se, s), 1.6 (CH<sub>3</sub>, s). <sup>77</sup>Se: δ 9.7 (s); <sup>29</sup>Si: δ 13.7 (s) ppm. Exact mass: Calcd. 489.925276. Found 489.924389.

¶ *Crystal data for 1*:  $\text{C}_{16}\text{H}_{26}\text{FeSe}_2\text{Si}_2$ ,  $M = 488.3$ , triclinic, space group  $P\bar{1}$ ,  $a = 6.1366(2)$ ,  $b = 9.1532(5)$ ,  $c = 10.1063(6)$  Å,  $\alpha = 65.321(2)$ ,  $\beta = 81.568(3)$ ,  $\gamma = 79.697(3)^\circ$ ,  $V = 505.85(4)$  Å<sup>3</sup>,  $T = 200$  K,  $Z = 1$ ,  $\mu = 4.454$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 54.9$ , 7283 measured, 2282 independent reflections ( $R_{\text{int}} = 0.069$ ) on an Enraf-Nonius Kappa-CCD diffractometer. All non-hydrogen atoms were refined anisotropically to yield  $R = 0.0432$ ,  $wR_2 = 0.1020$ ,  $\text{GoF} = 1.043$ .

|| *Synthesis of 2*:  $\text{CuOAc}$  (0.07 g, 0.57 mmol) was dissolved with  $\text{PPh}_2\text{Et}$  (0.35 mL, 1.72 mmol) in THF (5 mL). After stirring for 30 min, a solution of **1** (0.14 g, 0.28 mmol) in THF (0.5 mL) was added dropwise. After stirring for a further hour, the orange solution was layered with pentane (20 mL). Pale orange crystals of **2**·THF formed within a few days. Yield 60% (based on Cu). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ): δ 7.74 (br s,  $\text{H}_{\text{phenyl}}$ , 8 H), 7.64 (br s,  $\text{H}_{\text{phenyl}}$ , 8 H); 7.07–7.02 (mult.,  $\text{H}_{\text{phenyl}}$ , 24H), 5.25 (br s,  $\text{H}_{\text{Cp}}$ , 4H,  $\Delta\nu_{\frac{1}{2}}$  11.1 Hz), 4.60 (br s,  $\text{H}_{\text{Cp}}$ , 4H,  $\Delta\nu_{\frac{1}{2}}$  11.1 Hz), 4.30 (br s,  $\text{H}_{\text{Cp}}$ , 4H,  $\Delta\nu_{\frac{1}{2}}$  11.1 Hz), 4.03 (s,  $\text{H}_{\text{Cp}}$ , 4H,  $\Delta\nu_{\frac{1}{2}}$  11.1 Hz), 3.90 (s,  $\text{H}_{\text{Cp}}$ , 8H,  $\Delta\nu_{\frac{1}{2}}$  12.8 Hz), 3.87 (s,  $\text{H}_{\text{Cp}}$ , 4H,  $\Delta\nu_{\frac{1}{2}}$  12.8 Hz), 3.81 (s,  $\text{H}_{\text{Cp}}$ , 4H); 2.13 (mult., –CH<sub>2</sub>–, 8H), 1.28 (mult., –CH<sub>3</sub>, 12H). <sup>31</sup>P{<sup>1</sup>H} NMR: δ –4.1 ( $\Delta\nu_{\frac{1}{2}}$  19.2 Hz, due to  $J_{\text{PCu}^{12}}$ ) ppm. Anal. Calcd. for  $\text{C}_{96}\text{H}_{92}\text{Cu}_8\text{P}_4\text{Se}_8\text{Fe}_4(\text{OC}_4\text{H}_8)$ : C, 42.8; H, 3.59%. Found: C, 42.6; H, 3.46%.

\*\* *Crystal data for 2*:  $\text{C}_{96}\text{H}_{92}\text{Fe}_4\text{Cu}_8\text{Se}_8\text{P}_4\cdot\text{THF}$ ,  $M = 2805.1$ , monoclinic, space group  $P2_1/n$ ,  $a = 24.051(1)$ ,  $b = 15.5641(8)$ ,  $c = 28.042(6)$  Å,  $\beta = 108.202(1)^\circ$ ,  $V = 9971.8(9)$  Å<sup>3</sup>,  $T = 223$  K,  $Z = 4$ ,  $\mu = 5.261$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 56.6$ , 59974 measured, 23541 independent reflections ( $R_{\text{int}} = 0.072$ ) on a Siemens SMART CCD diffractometer. All non-hydrogen atoms (with the exception of solvent atoms) were refined anisotropically to yield  $R = 0.0553$ ,  $wR_2 = 0.1154$ ,  $\text{GoF} = 0.973$ .

CCDC reference number 182/1890. See <http://www.rsc.org/suppdata/cc/b0/b0100230/> for crystallographic files in .cif format.

†† Electrochemical experiments were performed under an argon atmosphere in glass distilled THF with a platinum working, platinum flag counter and silver wire in THF/electrolyte reference electrode using a Princeton Applied Research (PAR) 263 potentiostat. Potentials are referenced to cobaltocene as an internal reference, added at the end of the experiments.

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