ChemComm

# New unsymmetrical thioether- and thiolate-substituted ferrocene ligands and an unusual bridged-Pd dimer complex

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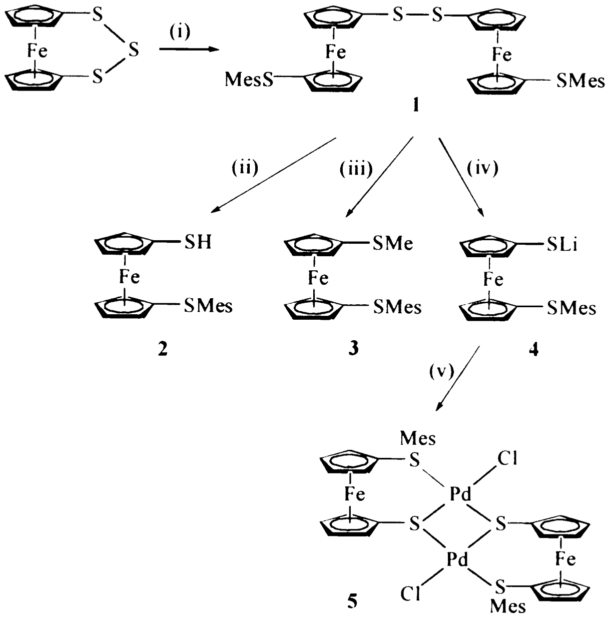
*Received (in Cambridge, UK) 18th September 2000, Accepted 18th October 2000*
*First published as an Advance Article on the web*

**A series of new unsymmetrical 1, 1'-disubstituted ferrocenediyl ligands featuring thioether or thiolate substituents have been conveniently synthesised and, as an example of their coordinating ability, a bridged palladium dimer has been formed and structurally characterised.**

Although ferrocene was discovered nearly fifty years ago, the search for new ferrocene derivatives and chemistry continues apace. In particular, versatile, stable and synthetically undemanding ferrocenyl and ferrocenediyl ligands are sought after due to their extensive coordination chemistry and applications within catalysis.[1,2] Ferrocene species with donor heteroatoms (*e.g.* P, N, S, O) substituted onto the cyclopentadienyl rings are well known, especially those featuring homo-substitution (*i.e.* the same donor atom along with the same alkyl or aryl substituents). Much less well-known are unsymmetrical 1,1′-disubstituted ferrocenes featuring hetero-combinations of N, P or S atoms, formed *via* bromo,[3,4] lithio[5,6] or stannyl[7,8] intermediates. These ligands are neutral in character and their preparations are often non-trivial. So far as we are aware, examples of unsymmetrical purely S-substituted neutral and neutral–anionic ferrocenediyl ligands (*i.e.* analogous to the hemilabile P/S$^-$,[9] P/O$^-$,[10,11] and N/O$^-$[12] ('SHOP') based-catalysts) are hitherto unknown. Here, we report the new and convenient syntheses of the first examples of these types of ligands and a preliminary study of their coordination chemistry which has led to the isolation and structural characterisation of a novel palladium dimer complex.

The new ligands **1–4** can be synthesised from the well known 1, 2, 3-trithia[3]ferrocenophane[13] (Scheme 1). By utilising an elegant method first described by Herberhold *et al*,[14] the trisulfur bridge can be cleaved by organolithium reagents to form (after air oxidation) bis(1′-organylthiolatoferrocenyl)disulfanes. Herberhold *et al.* have prepared the species RS–Fc–SS–Fc–SR (R = *n*-butyl, phenyl; Fc = 1,1′-ferrocenediyl), but during our research into the formation of redox-active and sterically hindered ligands for homogeneous catalysis, we reacted the ferrocenophane (1 equiv.) with mesityllithium (2 equiv.) and formed RS–Fc–SS–Fc–SR **1** (where R = mesityl). This species may be an interesting, sterically hindered ligand in its own right, but at present, we have concentrated on the formation of the monoferrocenediyl species **2–4**.† On reaction of **1** (1 equiv.) with lithium triethylborohydride (2.2 equiv.) in THF and after acid/base work-up, the air-sensitive orange solid **2** was isolated in 88% yield. $^1$H NMR spectroscopy showed the unsymmetrical substitution of the cyclopentadienyl rings with the presence of signals due to S-mesityl, S–H and *four* pseudo triplets for the $C_5H_4$ ring protons.

A solution of **1** was also treated with methyllithium (2.2 equiv.) and the reaction mixture stirred for 16 h. Cleavage of the disulfide linkage was effected and the crude orange mixture obtained was washed, extracted and purified *via* column chromatography [neutral grade II alumina, $CH_2Cl_2$–hexane (1:4)] and **3** was isolated as an air- and moisture-stable orange oil (50%) (*N.B.* 25% of **1** was also isolated). The use at this stage of various organolithium reagents can of course, lead to derivatisation and a possible 'fine-tuning' of the steric and redox properties of the ligands. Finally, a solution of **1** (1 equiv.) in THF was treated with lithium triethylborohydride (2.2 equiv.) and stirred for 1.5 h. On evaporation to dryness, a dark red oily product **4** was formed in quantitative yield but was not isolated due to its unstable nature. As confirmation of its formation and as a preliminary investigation into its coordination chemistry, **4** was treated with *trans*-[Pd(PhCN)$_2$Cl$_2$] (2 equiv.) in toluene and heated to 60 °C for 16 h. Following work-up and crystallisation in $CH_2Cl_2$–hexane (1:1), the purple–black product **5** was isolated in 81% yield as a crystalline solid. The X-ray analysis of **5**‡ shows that the desired bidentate coordination of the ferrocenediyl species has been achieved. Surprisingly, however, a bridged dimer has been formed where, for each ligand, one of the sulfur atoms is binucleating and carries a formal negative charge whereas the other links to a single palladium ion and is formally neutral (Fig. 1). The complex has non-crystallographic $C_2$ symmetry about an axis passing through the centre of, and normal to the plane of, the $Pd_2S_2$ ring, *i.e.* both ferrocenediyl units lie on the same side of the two linked coordination planes. Each ferrocenediyl unit adopts a staggered conformation, their S–$C_5H_4$ bonds 'subtending' angles of 45 and 46° for Fe(1) and Fe(2), respectively. The two palladium coordination planes are folded by *ca.* 30° out of plane with respect to each other about the S(3)···S(4) vector. The transannular Pd···Pd and S···S distances in the central four-membered ring are 3.394 and 2.998 Å, respectively. The geometry at each palladium centre is distorted square planar with *cis* angles in the ranges 81.1(2)–101.9(2) and 81.0(2)–102.5(2)° at Pd(1) and Pd(2), respectively. The Pd–S distances fall into two distinct groups with those to the negatively charged bridging sulfurs sig-



**Scheme 1** *Reagents and conditions*: (i) 2 MesLi, THF, 20 h; (ii) 2.2 LiEt$_3$BH, THF, 1.5 h, H$^+$; (iii) 2.2 MeLi, THF, 16 h; (iv) 2.2 LiEt$_3$BH, THF, 1.5 h; (v) *trans*-[Pd(PhCN)$_2$Cl$_2$], toluene, 60 °C, 16 h.

DOI: 10.1039/b007511f

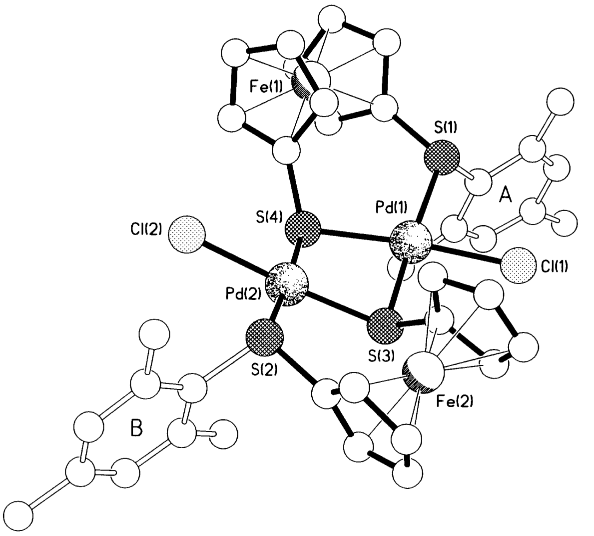


**Fig. 1** The molecular structure of **5**. Selected bond lengths (Å) and angles (°); Pd(1)–Cl(1) 2.332(5), Pd(1)–S(1) 2.365(4), Pd(1)–S(3) 2.305(4), Pd(1)–S(4) 2.303(5), Pd(2)–Cl(2) 2.334(5), Pd(2)–S(2) 2.354(4), Pd(2)–S(3) 2.305(5), Pd(2)–S(4) 2.309(4); S(4)–Pd(1)–S(3) 81.1(2), S(4)–Pd(1)–S(1) 101.9(2), S(3)–Pd(1)–S(1) 176.1(2), S(3)–Pd(2)–S(4) 81.0(2), S(3)–Pd(2)–S(2) 102.5(2), S(4)–Pd(2)–S(2) 176.2(2), Pd(2)–S(3)–Pd(1) 94.8(2), Pd(1)–S(4)–Pd(2) 94.7(2).

nificantly shorter than those to the others. Surprisingly, the Pd–S bridge distances are symmetric, *i.e.* there is no *trans* influence of the chloride ligands. The complexes are linked by a combination of C–H···π and π–π interactions to form sheets that extend in the *ab* plane (Fig. 2). The space between adjacent parallel sheets is occupied by disordered dichloromethane molecules. This type of bridged system featuring a thioether/thiolate ligand appears to be unique, the only other similar species being a palladium dimer featuring bridging *di*thiolate ligands.[15]

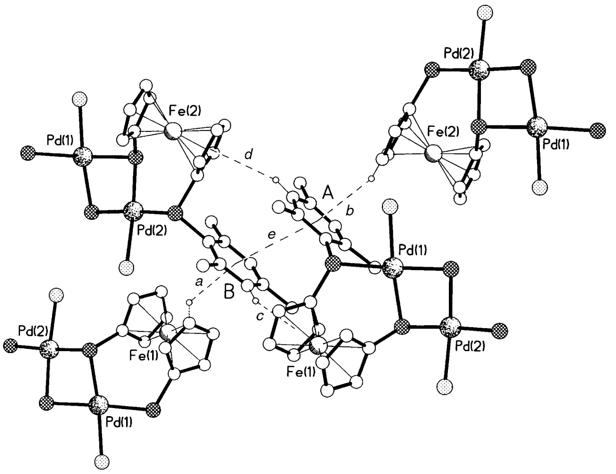


**Fig. 2** Part of one of the C–H··π and π–π linked sheets of molecules present in the structure of **5**. The H··π distances (Å) and C–H··π angles (°) are (*a*) 2.76, 136; (*b*) 2.72, 141; (*c*) 2.79, 161; (*d*) 2.87, 159. The centroid··centroid and mean interplanar separations between rings **A** and **B** are (*e*) 3.98, 3.73 Å.

Work is in progress to explore the diverse coordination chemistry expected for these ligands and their role in homogeneous catalysis.

We acknowledge financial support from the EPSRC and Johnson Matthey plc are thanked for the loan of platinum salts.

## Notes and references

† *Syntheses*: **2**: compound **1** (0.50 g, 0.65 mmol) was dissolved in dry, deoxygenated THF (30 cm$^3$) and to this lithium triethylborohydride (1 M solution in THF, 1.40 cm$^3$, 1.40 mmol) was added and the reaction mixture stirred for 1.5 h. The solvent was removed *in vacuo* and the residue then re-dissolved in diethyl ether. The dark red solution was poured onto dilute base (1% KOH) (20 cm$^3$), followed by dropwise addition of conc. HCl. The layers were separated and the aqueous layer extracted with diethyl ether (3 × 20 cm$^3$). The combined organic layers were dried ($MgSO_4$) and evaporated to dryness to leave an air-sensitive orange solid **2** (0.42 g, 88%); $\delta_H$($CDCl_3$) 2.21 (3H, s, $CH_3$), 2.47 (6H, s, $CH_3$), 2.98 (1H, s, SH), 4.10 (2H, t, $C_5H_4$), 4.21 (4H, t, $C_5H_4$), 4.33 (2H, t, $C_5H_4$), 6.86 (2H, s, $C_6H_2$); *m/z* 367 ($M - H^+$), 334 ($M - SH^+$).

**3:** a solution of **1** (0.58 g, 0.79 mmol) in THF (40 cm$^3$) was treated with methyllithium (1.6 M solution in diethyl ether, 1.1 cm$^3$, 1.74 mmol) and the reaction mixture stirred for 16 h. The solvent was evaporated *in vacuo*, the residue was dissolved in diethyl ether (50 cm$^3$) and water (10 cm$^3$) was added. The layers were separated and the aqueous layer extracted with diethyl ether (3 × 20 cm$^3$). The combined organic layers were dried ($MgSO_4$), then evaporated to dryness. The product was purified by column chromatography [neutral grade II alumina, $CH_2Cl_2$–hexane (20:80)] and after removal of the solvent, isolated as an orange oil (0.15 g, 50%); $\delta_H$($CDCl_3$) 2.24 (3H, s, $CH_3$), 2.34 (3H, s, $SCH_3$), 2.51 (6H, s, $CH_3$), 4.13 (2H, t, $C_5H_4$), 4.26 (4H, m, $C_5H_4$), 4.34 (2H, t, $C_5H_4$), 6.88 (2H, s, $C_6H_2$); *m/z* 382 ($M^+$), 367 ($M - CH_3^+$), 271 ($M - C_5H_4SCH_3^+$).

**4** and **5**: a solution of **1** (0.10 g, 0.135 mmol) in THF (30 cm$^3$) was treated with lithium triethylborohydride (1 M solution in THF, 0.3 cm$^3$, 0.30 mmol) and the reaction stirred for 1.5 h. The air-sensitive dark red solution of **4** was formed in quantitative yield and due to its instability was reacted *in situ* without work-up. Thus, a toluene (30 cm$^3$) solution of **4** was treated with bis(benzonitrile)palladium(II) dichloride (0.103 g, 0.27 mmol) also in toluene (30 cm$^3$). There was an immediate darkening of the solution to deep purple and stirring at 60 °C was continued for 16 h. A black ppt. was filtered off and the filtrate washed with water (2 × 10 cm$^3$), dried ($MgSO_4$) and evaporated to dryness. The crude residue was washed with hot hexane (2 × 40 cm$^3$) and recrystallised from $CH_2Cl_2$–hexane (1:1) to leave a purple crystalline powder **5** (0.11 g, 81%); $\delta_H$($CDCl_3$) 2.16 (6H, s, $CH_3$), 2.41 (6H, s, $CH_3$), 3.29 (6H, s, $CH_3$), 4.07 (2H, m, $C_5H_4$), 4.28 (2H, m, $C_5H_4$), 4.44 (2H, m, $C_5H_4$), 4.57 (2H, m, $C_5H_4$), 4.60 (2H, m, $C_5H_4$), 4.66 (2H, m, $C_5H_4$), 5.07 (2H, m, $C_5H_4$), 6.80 (2H, m, $C_6H_2$), 6.93 (2H, s, $C_6H_2$); *m/z* 982 ($M - Cl^+$), 897 ($M -$ mes$^+$).

‡ *Crystal data* for **5**: $C_{38}H_{38}S_4Cl_2Fe_2Pd_2\cdot3.5CH_2Cl_2$, $M$ = 1315.6, monoclinic, space group $P2_1/c$ (no. 14), $a$ = 16.411(4), $b$ = 14.897(3), $c$ = 22.093(4) Å, $\beta$ = 95.06(1)°, $V$ = 5380(2) Å$^3$, $Z$ = 4, $D_c$ = 1.624 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 18.2 cm$^{-1}$, $F$(000) = 2620, $T$ = 293 K; deep red plates, 6985 independent reflections, $F^2$ refinement to give $R_1$ = 0.078, $wR_2$ = 0.161 for 3473 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 45°$], 560 parameters (the high $R_1$ is a consequence of crystal decomposition and disorder in the $CH_2Cl_2$ groups). The platinum analogue is isomorphous [$a$ = 16.383(3), $b$ = 14.875(2), $c$ = 22.167(3) Å, $\beta$ = 94.95(1)°, $V$ = 5382(2) Å$^3$].[16]

CCDC 182/1826. See http://www.rsc.org/suppdata/cc/b0/b007511f/ for crystallographic files in .cif format.

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