

The Synthesis and Metal Coordination Chemistry of a Novel Phosphine- and Thiolate-Substituted Ferrocenediyl Ligand

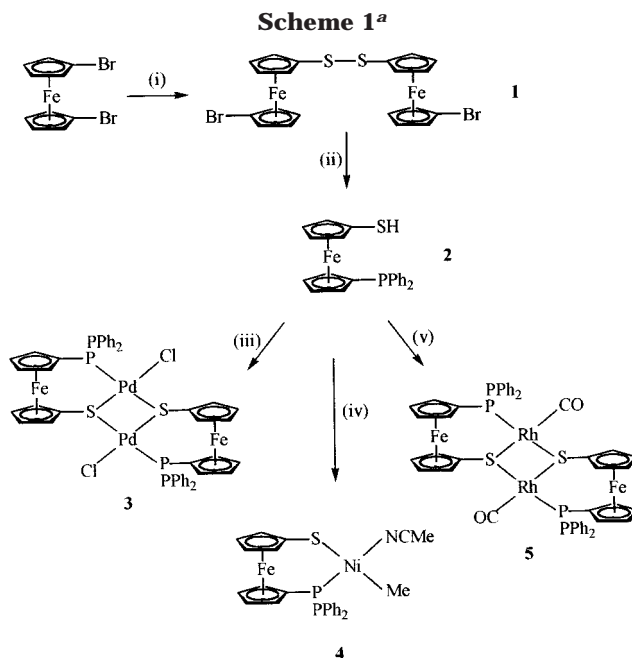
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Summary: A novel, asymmetric 1,1'-disubstituted ferrocenediyl ligand featuring phosphine and thiolate substituents has been conveniently synthesized and structurally characterized, and its coordination chemistry was probed by reaction with late transition metal reagents. Bridged dimeric species, with the thiolate S adopting a binucleating role, are observed for Pd(II) and Rh(I) metal centers, while a mononuclear, square planar Ni(II) complex is formed on reaction of the ligand with [Ni(TMEDA)Me₂].

The formation of asymmetric, multidentate ligands, focusing on aspects of hemilability,¹ has been of great interest. In particular, ferrocenyl and ferrocenediyl ligands are sought after due to their extensive coordination chemistry and applications within catalysis.^{2,3} While hemilabile P/S,⁴ P/S,⁵ P/O,^{6,7} and N/O⁸ ligand systems are well-known and important in catalysis, examples of analogous asymmetric 1,1'-substituted ferrocenes^{9–14} are rare and those that are known are



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^a Reagents and conditions: (i) *n*-BuLi, THF, –25 °C, 30 min; 0.5 S₂Cl₂, THF, rt, 16 h. (ii) 2 LiEt₃BH, THF, rt, 30 min; 2 KPPH₂, THF, rt, 20 h; H⁺. (iii) *n*-BuLi, toluene, rt, 2 h; trans-[Pd(PhCN)₂Cl₂], toluene, 60 °C, 20 h. (iv) Ni(TMEDA)Me₂, MeCN, rt, 2 h. (v) *n*-BuLi, THF, rt, 0.5 h; [Rh(CO)₂Cl]₂, MeOH, rt, 2 h.

neutral in character. For asymmetric substitution around ferrocenes, laborious, inefficient and nonfacile synthetic routes are largely employed, but here, we describe the first and convenient synthesis of a unique phosphine- and thiolate- (P/S⁻) substituted ferrocenediyl ligand and a preliminary study into its coordination chemistry.

The new, versatile precursor compound di[1'-bromoferrocene]disulfide **1** was synthesized (see Experimental Section) from 1,1'-dibromoferrocene,¹⁵ using 1 equiv of *n*-butyllithium in a cooled THF solution, followed by addition of freshly distilled sulfur dichloride (0.5 equiv). After aqueous workup and column chromatography (neutral grade II alumina, 20:80 CH₂Cl₂–hexane) and washing with hexane the product was obtained in 30% yield (Scheme 1). Although this sterically hindered ligand probably has in its own right interesting but yet to be explored coordination properties, it has here been

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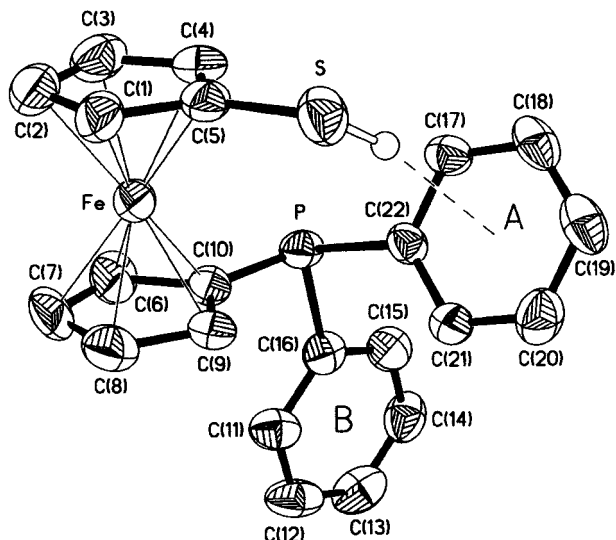


Figure 1. Molecular structure of **2** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): C(5)–S 1.761(7), P–C(10) 1.814(8), P–C(16) 1.850(4), P–C(22) 1.852(3), C(10)–P–C(16) 101.0(2), C(10)–P–C(22) 102.7(3), C(16)–P–C(22) 99.7(2).

utilized to form **2**, the first neutral-anionic P/S⁻ ferrocene ligand. The S–S linkage in **1** was cleaved by treatment with lithium triethylborohydride (2 equiv) in THF. After 2 h, potassium diphenylphosphide (2 equiv) was added, and the resulting suspension was stirred for 20 h at room temperature. Acidification was effected by concentrated HCl (dropwise addition), and after extraction (diethyl ether), evaporation to dryness, and washing (cold pentane), **2** was isolated in 53% yield. ¹H NMR spectroscopy showed the asymmetrical substitution of the cyclopentadienyl rings with the presence of signals due to S–H, phenyl groups, and four pseudo triplets for the C₅H₄ ring protons. Single-crystal X-ray analysis (see Experimental Section) confirmed the structure of **2** to be that shown in Figure 1. The two cyclopentadienyl rings are almost perfectly eclipsed and are inclined by less than 1° to each other. The C–S distance of 1.761(7) Å is noticeably longer than that seen in other π-complexed C₅ and C₆ S–H substituted ring systems (ca. 1.72 Å),^{16,17} there being no other structurally characterized examples of ferrocenyl S–H compounds; the only slightly similar structure to have been reported is a diphenylphosphinyl benzenethiol species [2-(Ph₂PO)-6-(Me₃-Si)C₆H₃SH].¹⁸ The angles at phosphorus are all significantly reduced from tetrahedral, ranging between 99.7(2) and 102.7(3) Å, the most “acute” angle being that subtended by the two phenyl rings. The conformation is stabilized by an intramolecular S–H⋯π interaction [H⋯π 2.77 Å] to one (A) of the two phenyl rings. Interestingly, this interaction is mirrored by an intermolecular C–H⋯π contact from C(1)–H [H⋯π 2.88 Å], which approaches into the opposite face of ring A (the two H⋯π vectors are inclined by 177°). Ring B is involved in an aromatic edge-to-face interaction with ring A of a symmetry-related molecule (ring centroid⋯ring centroid 5.00 Å).

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As an investigation into its coordination chemistry, **2** was deprotonated (using *n*-butyllithium), treated with *trans*-[Pd(PhCN)₂Cl₂] in toluene, and stirred at room temperature for 20 h. Following workup and crystallization in CH₂Cl₂–hexane (1:1), **3** was isolated as a brown microcrystalline powder in 64% yield, which analyzes as a bridged dimer species, with a structure seemingly analogous to the product formed with the previously reported 1-thiolate, 1′-(mesitylthio)ferrocene ligand;^{12b} that is, for each ligand in the Pd dimer, the thiolate S adopts a binucleating role. This role of bridging thiolate has also been observed in other palladium complexes of P/S⁻ ligands.¹⁹

To further probe its chemistry, **2** was treated with dimethyl[tetramethylethylenediamine]nickel(II) in acetonitrile (Scheme 1). After stirring at room temperature for 2 h, an orange-pink precipitate was obtained, washed (3 × 10 mL, acetonitrile), and dried in vacuo to give **4** in 46% yield. The microanalytical and NMR spectroscopic data indicate formation of a mononuclear Ni complex in this case. We suggest that the complex has a square planar structure due to its characteristic color (tetrahedral Ni(II) complexes are usually blue or green) and the lack of broadening in the NMR spectra (i.e., diamagnetic metal center). The ³¹P{¹H} NMR shows one peak at 29.92 ppm (shifted significantly downfield with respect to **2** (–17.42 ppm)), and this is in the range for nickel-chelating phosphines. ¹H NMR shows that only one isomer is formed, that with the acetonitrile ligand *trans* to the phosphine. The spectrum shows the methyl groups shifted upfield to –0.05 ppm (in the region for nickel methyl complexes), and this signal is a doublet due to phosphorus coupling. The C₅H₄ ring protons show four pseudo triplets, and the acetonitrile methyl group exhibits a singlet at 4.25 ppm (shifted downfield compared to the resonance of free acetonitrile).

Rhodium(I) complexes with phosphorus-sulfur donor ligands have shown excellent activities and stability as methanol carbonylation catalysts.²⁰ This was a motivation for the reaction of the lithium salt of **2** with tetracarbonyldichlororhodium(I) in methanol, which resulted in the formation of a yellow, sulfide-bridged dimeric species (**5**), analogous to **3**, in excellent yield. The ¹H NMR spectrum shows two pseudo triplets in the ferrocenyl region (3.89 and 4.37 ppm) along with a multiplet at 4.43 ppm, due to two pairs of overlapping pseudo triplets, and in the phenyl region, there are downfield shifted (from the ligand) multiplets at 7.43 and 8.04 ppm. The ³¹P{¹H} NMR spectrum shows a doublet at 36.60 ppm due to coupling of the phosphorus with rhodium. The coupling constant is 165 Hz, which is in good agreement with other ferrocenyl phosphine rhodium(I) complexes.²¹ The IR spectrum shows a single strong band at 1972 cm⁻¹ in the CO-stretching region, indicating terminal ²¹ (and no bridging) CO ligands in **5** and further reinforces the assignment of bridging thiolates in both **5** and **3**.

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From the results described above, we expect this novel ferrocenediyl ligand system, and its subsequent analogues (i.e., O/S^- , N/S^-), to display diverse coordination chemistry and to support metal environments relevant to a number of homogeneous catalytic processes.

Experimental Section

General Procedures. All preparations were carried out using standard Schlenk techniques.²² All solvents were distilled over standard drying agents under nitrogen directly before use, and all reactions were carried out under an atmosphere of nitrogen. Deactivated alumina gel (neutral grade II, 3% H_2O) was used for chromatographic separations. All NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 270.1 MHz (1H), 67.9 MHz ($^{13}C\{^1H\}$), and 101.3 MHz ($^{31}P\{^1H\}$). Chemical shifts (δ) are reported in ppm using $CDCl_3$ (1H , 7.25 ppm, $^{13}C\{^1H\}$ 77.0 ppm) as the reference, while $^{31}P\{^1H\}$ spectra were referenced to H_3PO_4 . Infrared spectra were recorded using NaCl solution cells (CH_2Cl_2) using a Mattson Polaris Fourier Transform IR spectrometer. Mass spectra were recorded using positive FAB methods, on an Autospec Q mass spectrometer. Microanalyses were carried out at SACS, University of North London.

Syntheses: **1.** 1,1'-Dibromoferrocene (2.00 g, 5.74 mmol) was dissolved in dry, oxygen-free THF (35 mL) and cooled to $-25^\circ C$. *n*-Butyllithium (3.40 mL, 5.44 mmol) was added and the solution maintained at $-25^\circ C$ for 30 min. Freshly distilled sulfur dichloride (0.22 mL, 2.72 mmol) was then added at $-25^\circ C$, and the solution was allowed to warm to room temperature and stirred for 16 h. The solvent was removed and the residue suspended in CH_2Cl_2 . Water was added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 , and the combined organic fractions were dried ($MgSO_4$) and evaporated to an orange oil. Column chromatography (neutral grade II alumina, 20:80 CH_2Cl_2 -hexane) enabled separation of the product in the second fraction. This fraction was evaporated to dryness and washed several times with hexane (100 mL) until no traces of impurity were seen in the 1H NMR of the compound, and **1** was isolated as a yellow solid (0.50 g, 0.85 mmol, 30%). Anal. Calcd for $C_{20}H_{16}S_2Br_2Fe_2$: C 40.58, H 2.72. Found: C 40.72, H 2.70. 1H NMR δ ($CDCl_3$): 4.08 (2H, t, C_5H_4), 4.32 (4H, m, C_5H_4), 4.39 (2H, t, C_5H_4). MS: m/z 592 (M^+), 295 ($C_{10}H_8SBrFe^+$).

2. **1** (2.00 g, 4.16 mmol) was dissolved in THF (40 mL), lithium triethylborohydride (9.61 mL, 9 mmol) was added, and the solution was stirred at room temperature for 2 h. The solvent was removed and the residue redissolved in THF (40 mL). Potassium diphenylphosphide (21.0 mL, 10.4 mmol) was added, and the solution immediately became cloudy. The reaction was stirred for 20 h at room temperature, and the solvent was then removed. The residue was extracted with diethyl ether (3×100 mL), and 1% aqueous KOH solution (200 mL) was added to the diethyl ether solution by cannula. The solution was vigorously stirred, and the aqueous layer was removed and acidified by dropwise addition of concentrated hydrochloric acid. Once the thiol had formed, it precipitated as a yellow solid. The solid was extracted with diethyl ether (3×50 mL), dried (Na_2SO_4), and evaporated to give an orange solid. The crude product was washed with pentane at $0^\circ C$ (3×20 mL), enabling isolation of **2** as a yellow solid (1.70 g, 4.24 mmol, 51%). Cooling a pentane solution of the ligand grew crystals suitable for X-ray diffraction. Anal. Calcd for $C_{22}H_{19}SPFe$: C 65.69, H 4.76. Found: C 65.74, H 4.75. $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): -17.42 . 1H NMR δ ($CDCl_3$) 2.76 (1H, s, *SH*), 4.04

(2H, t, C_5H_4), 4.08 (2H, t, C_5H_4), 4.22 (2H, t, C_5H_4), 4.38 (2H, t, C_5H_4), 7.31 (10H, m, C_6H_5). MS: m/z 402 (M^+), 218 ($M - PPh_2^+$).

3. **2** (0.15 g, 0.37 mmol) was dissolved in toluene (30 mL), *n*-butyllithium (0.15 mL of a 2.5 M solution in hexane, 0.37 mmol) was added, and the solution was stirred for 2 h. After this time, the solution had turned dark red and was cloudy. THF (10 mL) was added to aid dissolution, and the solution was added to bis(benzonitrile)palladium(II) dichloride (0.14 g, 0.37 mmol) dissolved in toluene (40 mL) at $60^\circ C$. The solution was stirred at this temperature for 20 h. The solvent was removed, and the residue washed with hexane (3×50 mL) and precipitated from a CH_2Cl_2 solution by layering with hexane. **3** was isolated as a brown microcrystalline powder (0.26 g, 0.24 mmol, 64%). Anal. Calcd for $C_{44}H_{36}S_2P_2Fe_2Pd_2Cl_2$: C 48.65, H 3.34. Found: C 48.51, H 3.20. $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 27.31. 1H NMR δ ($CDCl_3$): 3.94 (2H, t, C_5H_4), 4.25 (2H, t, C_5H_4), 4.33 (2H, t, C_5H_4), 4.42 (2H, t, C_5H_4), 7.41 (6H, m, C_6H_5), 7.88 (4H, m, C_6H_5). MS: m/z 1051 ($M - Cl^+$), 1015 ($M - 2Cl^+$), 909 ($M - 2Cl - Pd^+$).

4. **2** (0.15 g, 0.37 mmol) in acetonitrile (20 mL) was added to a solution of dimethyl[tetramethylethylenediamine]nickel(II) (0.08 g, 0.37 mmol) in acetonitrile (20 mL). The solution darkened and an orange solid precipitated. The reaction was stirred for 2 h, and the pink-orange product was filtered, washed with acetonitrile (3×10 mL), and dried in vacuo (0.09 g, 0.17 mmol, 46%). Anal. Calcd for $C_{25}H_{24}FeNNiPS$: C 58.14, H 4.65. Found: C 58.28, H 4.64. $^{31}P\{^1H\}$ NMR δ (C_6D_6): 29.92. 1H NMR δ_H (C_6D_6): -0.05 (3H, d, CH_3 , $^3J_{PH}$ 8 Hz), 3.78 (2H, t, C_5H_4), 3.92 (2H, t, C_5H_4), 4.11 (2H, t, C_5H_4), 4.25 (3H, s, $CNCH_3$), 4.63 (2H, t, C_5H_4), 7.06 (6H, m, C_6H_5), 8.22 (4H, m, C_6H_5). MS: m/z 475 ($M - MeCN^+$), 460 ($M - MeCN - Me^+$), 401 ($M - MeCN - Me - Ni - H^+$).

5. **2** (0.16 g, 0.39 mmol) was dissolved in THF (10 mL) and *n*-butyllithium (0.24 mL, 0.39 mmol, 1.6 M solution in hexanes) added. The solution was stirred for 30 min at room temperature and the solvent removed in vacuo. The residue was redissolved in THF (10 mL) and added to a solution of $[Rh(CO)_2Cl]_2$ (0.08 g, 0.193 mmol) dissolved in methanol (30 mL). There was an immediate precipitation of a yellow powder, and the suspension was stirred at room temperature for 2 h. The supernatant liquid was removed by filtration and **5** washed with hexane (3×20 mL) and dried in vacuo (0.18 g, 88%). Anal. Calcd for $C_{46}H_{36}Fe_2O_2P_2S_2Rh_2$: C 51.91, H 3.41. Found: C 51.56, H 2.94. $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 36.60 (d, $^1J_{Rh-P}$ 165 Hz). 1H NMR δ ($CDCl_3$): 3.89 (4H, t, C_5H_4), 4.37 (4H, t, C_5H_4), 4.43 (8H, m, C_5H_4), 7.43 (12H, m, C_6H_5), 8.04 (8H, m, C_6H_5). MS: m/z (THF) 604 ($RhL(CO)THF^+$), 575 ($M - CO^+$), 523 ($M - THF^+$). IR (CH_2Cl_2): ν_{CO} 1972 cm^{-1} .

Crystal Data for 2: $C_{22}H_{19}PSFe$, $M = 402.3$, monoclinic, $P2_1/c$ (no. 14), $a = 8.708(4)$ Å, $b = 17.125(5)$ Å, $c = 13.134(4)$ Å, $\beta = 107.53(5)^\circ$, $V = 1867.5(11)$ Å³, $Z = 4$, $D_c = 1.431$ g cm^{-3} , $\mu(Mo K\alpha) = 10.1$ cm^{-1} , $T = 193$ K, yellow plates; 3070 independent measured reflections, F^2 refinement, $R_1 = 0.066$, $wR_2 = 0.148$, 1857 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50^\circ$], 206 parameters. CCDC 177081.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams, tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and isotropic and anisotropic displacement parameters for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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