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Hang-gliding with Ferrocenes: Unusual Coordination Chemistry of 1,1′-Bis(mesitylthio)ferrocene

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Summary: A rare C,S-cyclometalated Pt^{IV} complex is one of a series of transition metal complexes formed by the new redox-active and sterically hindered ligand 1,1′-bis(mesitylthio)ferrocene. Simple Pd^{II} and Pt^{II} chelate species can be synthesized by less forcing reaction conditions, in addition to a $Re_2(CO)_6Br_2$ dinuclear species featuring the ferrocene ligand adopting a binucleating role and forming an unusual "quasi-closed" bridged structure.

Ferrocene-containing materials are currently undergoing something of a renaissance due to their increasing role in the rapidly growing area of materials science.[1] The substitution of ferrocenes by various donor heteroatoms has led to a series of chelating ligands that have found wide application, e.g., incorporation of phosphines for homogeneous catalysis in organic synthesis, chiral phosphines for enantiomeric synthesis, and amino alcohols for asymmetric catalysis.[1,2] Another currently very topical area is the search for well-defined, single-site organotransition metal olefin polymerization catalysts, with some of the most significant recent developments occurring with late transition metal systems.[3] We decided to couple these areas and target ligands so as to (i) create redox-active centers, either within the backbone or as pendant groups, which would offer an opportunity to change quite dramatically the electronic environment of the active site, and (ii) introduce bulky, sterically hindered substituents, which can strongly influence the productivity and microstructure of polyolefins.

Initial results on the ability of titanium and zirconium complexes bearing the chelating dianionic 1,1′-ferrocenedithiolate ligand to polymerize ethylene have recently been communicated.[4] In the course of this research program, we have observed some remarkable coordination chemistry and herein report the formation of a new, sterically hindered ferrocene ligand system and the unexpected chemistry and the unusual modes of coordination that it undergoes with late transition metal centers.

The new 1,1′-bis(mesitylthio)ferrocene ligand **1** was formed by the addition of a toluene solution of dimesityl disulfide[5] to a suspension of 1,1′-dilithioferrocene in hexane under a N_2 atmosphere. The mixture was stirred at room temperature for 16 h, then after an aqueous workup and column chromatography (neutral grade II alumina, 9:1 hexane/CH_2Cl_2 eluent), a yellow microcrystalline solid was obtained in 65% yield. This synthesis follows an approach similar to that used in the formation of other 1,1′-disubstituted ferrocenediyl sulfides,[6] although it had been suggested that bulky substituents such as *tert*-butylthio could not be incorporated due to the steric crowding and subsequent lack of reactivity (nucleophilic cleavage) of the disulfide starting reagents. We believe that 1,1′-ferrocene-derived sulfur ligands have great potential in coordination chemistry.[7] The ligand shows a fully reversible redox couple ($E_{1/2} = 0.68$ V vs Ag/AgCl), but to date, electrochemistry on the complexes has proved inconclusive due to the large positive shift in redox potentials.

Ligand **1** was then reacted with labile transition metal centers so as to explore its coordination chemistry (Scheme 1). First, a slight excess of **1** and $Re(CO)_5Br$ were stirred in refluxing THF. The reaction was monitored by infrared spectroscopy and shown to be complete after 20 h with the appearance of three strong bands at 2022, 1923, and 1908 cm^{-1} in the CO stretching region, consistent with a *fac*-$LRe(CO)_3Br$ structure. However, rather than the simple bidentate, chelate $(L-L)Re(CO)_3Br$ species, mass spectrometry, and an X-ray crystal structure determination indicated that an unusual $Re_2(CO)_6Br_2$ dinuclear species **2** had been formed, the first to involve a ferrocenediyl sulfur ligand. The only other "quasi-closed bridged" dirhenium structure, namely, $Re_2(\mu\text{-}OMe)_2(CO)_6(\mu\text{-}dppf)$,[8] features bridging dppf and methoxo ligands but is formed from the dinuclear starting reagent $Re_2(CO)_{10}$. Our system utilizes the mononuclear starting species, $Re(CO)_5Br$, and thus illustrates that due to the steric bulk of the ligand, the simple mononuclear chelate species cannot form, a

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(1) For a detailed literature review see: Togni, A., Hayashi, T., Eds. *Ferrocenes: Homogeneous Catalysis−Organic Synthesis−Materials Science*; VCH: Weinheim, Germany, 1995. Togni, A., Halterman, R. L., Eds. *Metallocenes*; Wiley-VCH: Weinheim, Germany, 1998.

(2) For a comprehensive overview of ferrocene and other metallocene chemistry see: Long, N. J. In *Metallocenes: An Introduction to Sandwich Complexes*; Blackwell Science: Oxford, U.K., 1998.

(3) For a recent review article see: Britsovek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem.* **1999**, *111*, 448; *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

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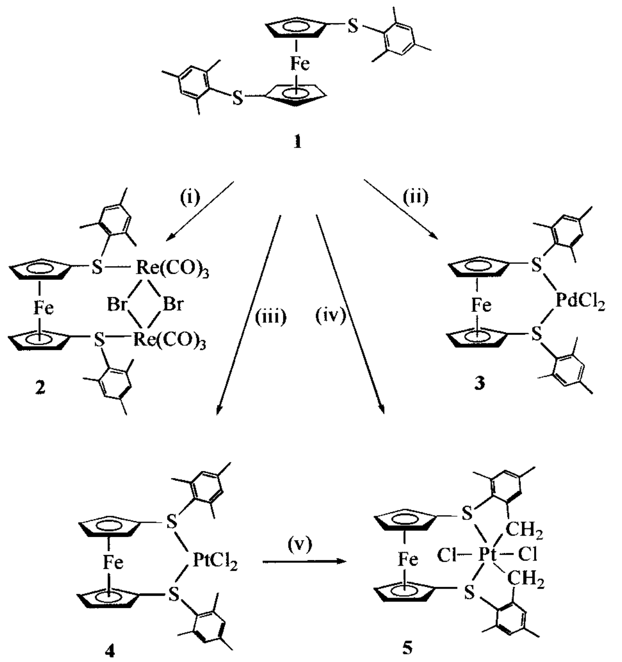
10.1021/om0004388 CCC: $19.00

Scheme 1[a]



[a] (i) $Re(CO)_5Br$, THF, reflux, 20 h. (ii) $Pd(PhCN)_2Cl_2$, toluene, reflux, 20 h. (iii) $Pt(PhCN)_2Cl_2$, toluene, 60 °C, 16 h. (iv) $Pt(PhCN)_2Cl_2$, toluene, reflux, 20 h. (v) toluene, reflux, 10 h.

rearrangement must occur, and the unusual dinuclear structure is the result.

The X-ray analysis of **2**[9] shows the bis(mesitylthio)ferrocene ligand to adopt a binucleating coordination mode, bridging between the rhenium centers of a $Re_2(CO)_6(\mu\text{-}Br)_2$ unit to form the C_s symmetric complex illustrated in Figure 1. The geometry at rhenium is distorted octahedral with cis angles in the range 83.25(8)−98.9(4)°. The rhenium coordination distances are generally unexceptional, although the Re−S bond distance of 2.541(3) Å lies toward the high end of those reported in the literature; the two Re−Br distances are the same. The two mesityl ring systems (and the sulfur lone pairs) are oriented syn, a geometry that is almost certainly enforced by the steric bulk of the methyl substituents. The only intramolecular interactions of note are a pair of weak $C-H\cdots\pi$ hydrogen bonds between C_s-related methyl hydrogen atoms and their adjacent substituted Cp rings ($H\cdots\pi$ 2.75 Å). The adoption by the bis(mesitylthio)ferrocene ligand of a binucleating rather than a bidentate coordination mode could be either a consequence of the initial formation of the $Re_2(CO)_8Br_2$ dinuclear species followed by displacement of a pair of axial carbonyls and bis(mesitylthio)ferrocene ligand coordination or that the THF complex $[\{Re(CO)_3(THF)(\mu\text{-}Br)\}_2]$[10] is formed with subsequent displacement of the THF molecules. Indeed, no reaction was observed on heating **1** and $Re(CO)_5Br$ in *toluene* at 60 °C for 16 h. Alternatively, the steric bulk of the mesityl groups could inhibit the ligand from adopting a chelating geometry, as mononuclear rhenium carbonyl species with ligands such as dppf and 1,1′-bis(methylthio)ferrocene are well-known.[1]

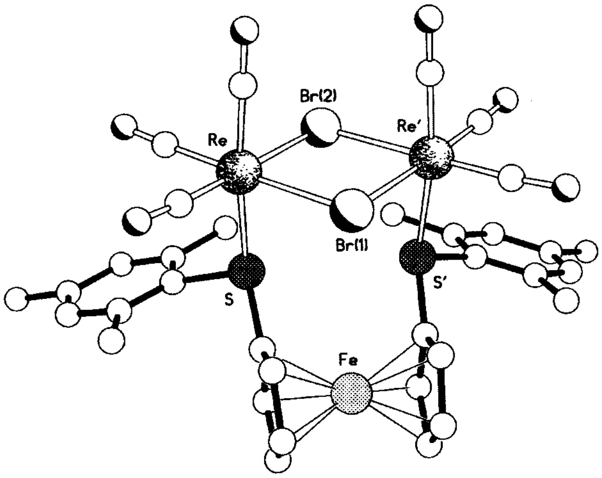


Figure 1. Molecular structure of the C_s symmetric complex **2**. Selected bond lengths (Å) and angles (deg): Re−S 2.541(3), Re−Br(1) 2.6542(12), Re−Br(2) 2.6607(12), Re−C(15) 1.920(14), Re−C(16) 1.91(2), Re−C(17) 1.85(2), S−Re−Br(1) 89.35(8), S−Re−Br(2) 83.25(8), C(15)−Re−S 171.3(4), C(16)−Re−S 90.0(4), C(17)−Re−S 98.9(4), C(15)−Re−Br(1) 89.7(5), C(16)−Re−Br(1) 177.0(5), C(17)−Re−Br(1) 94.6(5), C(17)−Re−Br(2) 177.1(5), C(16)−Re−Br(2) 93.5(5), C(15)−Re−Br(2) 88.0(4), Br(1)−Re−Br(2) 83.47(4), C(15)−Re−C(16) 90.5(6), C(15)−Re−C(17) 89.8(6), C(16)−Re−C(17) 88.5(7), Re−Br(1)−Re′ 96.62(6), Re−Br(2)−Re′ 96.31(6).

In contrast to the unexpected reaction with Re, a bidentate coordination mode to a single metal center was obtained by treatment of **1** with *trans*-$Pd(PhCN)_2Cl_2$ and *trans*-$Pt(PhCN)_2Cl_2$ but under different conditions (Scheme 1). The Pd complex **3** was formed after 20 h from refluxing toluene and isolated as a black powder in ca. 40% yield. Its ^1H NMR spectrum showed the expected two "pseudo triplet" signals at 4.41 and 4.78 ppm for the cyclopentadienyl ring proton resonances with slight downfield shifts of all the ligand resonances due to coordination to the metal. The analogous Pt complex **4**, a yellow microcrystalline solid, was synthesized in ca. 50% yield but under more mild conditions (toluene, 60 °C, 16 h). However, employing the conditions used to form the Pd species **3** (i.e., prolonged reflux in toluene) from either **4** or directly from **1** and $Pt(PhCN)_2Cl_2$ gave, after column chromatography (neutral grade II alumina, 2:3 CH_2Cl_2/hexane eluent), an orange product in 41% yield. Observation of a complicated ^1H NMR spectrum suggested that the ligand had adopted a different coordination mode, and this was confirmed via the growth of small pale orange crystals, which were shown by single-crystal X-ray analysis to be the unusual cis-coordinated "hang-glider-like" complex **5** (Figure 2).[11] In contrast to **2**, the bis(mesitylthio)ferrocene ligand is chelating rather than binucleating, adopting a unique

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[9] Crystal data for **2**: $C_{34}H_{30}O_6S_2Br_2Re_2Fe$, $M = 1186.8$, orthorhombic, space group *Pnma* (no. 62), $a = 15.518(2)$, $b = 23.182(4)$, $c = 10.227(2)$ Å, $V = 3679.2(9)$ Å^3, $Z = 4$ (the complex has crystallographic C_s symmetry), $\rho_c = 2.143$ g cm^{-3}, μ(Mo Kα) $= 92.8$ cm^{-1}, $F(000) = 2240$, $T = 293$ K; yellow blocky needles, 0.27 × 0.14 × 0.09 mm, Siemens P4/PC diffractometer, graphite-monochromated Mo Kα radiation, ω-scans, 3322 independent reflections. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.049$, $wR_2 = 0.072$ for 1952 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$] and 218 parameters: CCDC 139099.

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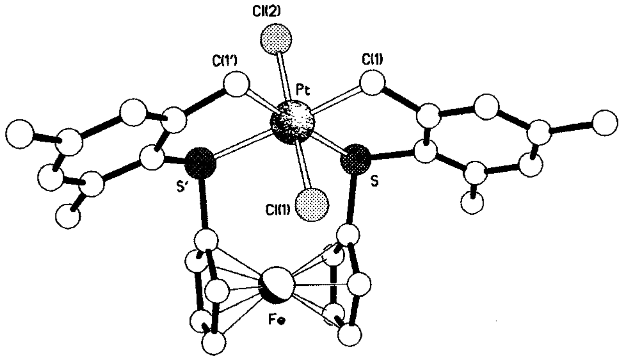

Figure 2. Molecular structure of the C_s symmetric “hang-glider-like” complex **5**. Selected bond lengths (Å) and angles (deg): Pt−Cl(1) 2.308(2), Pt−Cl(2) 2.340(2), Pt−S 2.4249(13), Pt−C(1) 2.058(6), C(1)−Pt−C(1′) 92.6(4), C(1)−Pt−Cl(1) 85.4(2), C(1)−Pt−Cl(2) 91.2(2), Cl(1)−Pt−Cl(2) 175.14(7), C(1′)−Pt−S 177.3(2), C(1)−Pt−S 84.8(2), Cl(1)−Pt−S 95.13(4), Cl(2)−Pt−S 88.06(5), S−Pt−S′ 97.75(6), Pt−C(1)−Ar 112.8(4).

tetradentate coordination mode through deprotonation of two of the methyl substituents to form a pair of CH_2-CCSPt chelate rings. The complex has crystallographic C_s symmetry, and the ferrocene unit adopts an eclipsed conformation, which is also observed in **2**. The geometry at platinum is distorted octahedral with cis angles in the range 84.8(2)−97.75(6)°. The Pt−S [2.425(1) Å] and Pt−C [2.058(6) Å] distances are typical of octahedral Pt^{IV} species. Both of the five-membered chelate rings are folded, the platinum atom lying 0.62 Å out of the C_3S plane. The combined effect of these two folds is to create a 141° dihedral angle between the two mesityl “wings” of the complex. In common with **1**, there is a weak intramolecular C−H⋯π interaction between one of the hydrogen atoms of each of a pair of methyl groups and their proximal C_5H_4 rings (H⋯π 2.92 Å). The only intermolecular packing interaction of note is a π-stacking of adjacent mesityl ring systems to form a continuous sinusoidal motif (centroid⋯centroid and mean interplanar separations of 3.71, 3.53 Å).

This cyclometalation reaction, featuring sulfur (and also ferrocene ligands) on Pt is, so far as we are aware, unique. The only other similar example is a C,P-cyclometalated compound of Pt^{II} formed from *trans*-Pt-$(PhCN)_2Cl_2$ and tri-*o*-tolylphosphine, which on oxidative addition of halogens gives neutral C,P-cyclometalated Pt^{IV} species.[12] The driving force for our reaction comes from the conversion of Pt^{II} to Pt^{IV} and, perhaps, a disproportionation reaction to also generate Pt^0, in addition to the steric bulk of the mesityl substituents; it is interesting to note that there is no evidence for any cyclometalated products from the reactions with Pd.

This important reaction highlights a novel platinum C−H activation system carrying a redox-tunable ligand which may be exploited to optimize the catalytic potential of the system. These and other catalytic applications will be the subject of future studies.

Experimental Section

General Procedures. All preparations were carried out using standard Schlenk techniques.[13] All solvents were distilled over standard drying agents under nitrogen directly before use, and all reactions were carried out under an atmosphere of nitrogen. Alumina gel (neutral-grade II) was used for chromatographic separations. All NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 250.1 MHz (^1H). Chemical shifts are reported in δ using $CDCl_3$ (^1H, δ 7.25 ppm) as the reference for the spectra. 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 in the Department of Chemistry, University of North London.

Synthesis of 1. 1,1′-Dilithioferrocene (0.64 g, 3.23 mmol) was suspended in hexane (50 mL), and dimesityl disulfide (2.10 g, 7.00 mmol) in toluene (20 mL) was added to the suspension and the mixture stirred for 16 h. Water (20 mL) was added, the aqueous layer was extracted with dichloromethane (2 × 10 mL), and the combined organic layers were dried ($MgSO_4$) and evaporated to dryness. The crude product was subjected to column chromatography (activated neutral grade II alumina, 1:9 CH_2Cl_2/hexane), which enabled the separation of **1** (1.03 g, 65%). Recrystallization of the yellow solid was carried out by slow evaporation of a solution of hot hexane. Anal. Calcd for $C_{28}H_{30}S_2Fe$: C, 69.13, H, 6.22. Found: C, 69.15, H, 6.39. ^1H NMR (270 MHz, $CDCl_3$): δ 2.24 (s, 6H; CH_3), 2.52 (s, 12H; CH_3), 4.17 (t, 4H; C_5H_4), 4.30 (t, 4H; C_5H_4), 6.88 (s, 4H; C_6H_2); FAB (+ve) MS (CH_2Cl_2) *m*/*z* 486 $(M)^+$, 336 $(M - SMes)^+$.

Synthesis of 2. A solution of **1** (0.12 g, 0.25 mmol) in THF (5 mL) was added to a solution of $Re(CO)_5Br$ (0.09 g, 0.23 mmol) also in THF (15 mL) and the mixture heated to reflux for 20 h. The solvent was removed in vacuo and the crude solid washed with hot hexane (2 × 20 mL) to remove any unreacted starting materials. Two-layer recrystallization from hexane/CH_2Cl_2 resulted in the formation of an orange crystalline solid (0.14 g, 46%). Anal. Calcd for $C_{34}H_{30}O_6S_2Br_2Re_2Fe$: C, 34.41, H, 2.55. Found: C, 34.73, H, 2.60. ^1H NMR (270 MHz, $CDCl_3$): δ 2.26 (s, 6H; CH_3), 2.44 (s, 12H; CH_3), 4.41 (t, 4H; C_5H_4), 4.59 (t, 4H; C_5H_4), 6.86 (s, 4H; C_6H_2); IR (CH_2Cl_2) ν 2022, 1923, 1908 cm^{-1} (C═O); FAB (+ve) MS (CH_2Cl_2) *m*/*z* 1169 $(M - O)^+$.

Synthesis of 3. A solution of **1** (0.2 g, 0.40 mmol) in toluene (60 mL) was added to dichlorobis(benzonitrile)palladium(II) (0.15 g, 0.40 mmol) also in toluene (60 mL). The solution darkened immediately and was stirred at room temperature for 20 h. A black precipitate was filtered off and the filtrate evaporated to dryness and washed with hot hexane (5 × 10 mL). Two-layer recrystallization (CH_2Cl_2/hexane) of the crude solid gave a dark brown microcrystalline solid (0.11 g, 40%). Anal. Calcd for $C_{30}H_{34}S_2FePdCl_6$: C, 43.22, H, 4.08. Found: C, 42.93, H, 3.95. ^1H NMR (270 MHz, $CDCl_3$): δ 2.21 (s, 6H; CH_3), 2.84 (s, 12H; CH_3), 4.41 (t, 4H; C_5H_4), 4.78 (t, 4H; C_5H_4), 6.88 (s, 4H; C_6H_2); FAB (+ve) MS (CH_2Cl_2) *m*/*z* 663 $(M)^+$, 627 $(M - Cl)^+$, 592 $(M - 2Cl)^+$.

Synthesis of 4. A solution of **1** (0.12 g, 0.25 mmol) in toluene (30 mL) was added to dichlorobis(benzonitrile)platinum(II) (0.11 g, 0.23 mmol) also in toluene (30 mL). The solution was heated to 60 °C and stirred for 16 h. The yellow precipitate formed was filtered off, washed with hot hexane

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[11] Crystal data for **5**: $C_{28}H_{28}S_2Cl_2FePt$, $M = 750.5$, orthorhombic, space group *Pnma* (no. 62), $a = 12.492(1)$, $b = 20.637(1)$, $c = 10.089(1)$ Å, $V = 2600.9(4)$ Å^3, $Z = 4$ (the complex has crystallographic C_s symmetry), $\rho_c = 1.916$ g cm^{-3}, μ(Cu Kα) = 178.9 cm^{-1}, $F(000) = 1464$, $T = 293$ K; pale orange rhombs, 0.11 × 0.10 × 0.07 mm, Siemens P4/RA diffractometer, graphite-monochromated Cu Kα radiation, ω-scans, 2235 independent reflections. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.033$, $wR_2 = 0.073$ for 1942 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 128°$] and 161 parameters: CCDC 139100.

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[13] Errington, R. J. In *Advanced Practical Inorganic and Metalorganic Chemistry*; Blackie: London, 1997.

(4 × 10 mL), and recrystallized (CH_2Cl_2/hexane) (0.09 g, 50%). Anal. Calcd for $C_{28}H_{30}S_2FePtCl_2$: C, 44.69, H, 4.02. Found: C, 44.79, H, 3.97. ^1H NMR (270 MHz, $CDCl_3$): δ 2.22 (s, 6H; CH_3), 2.83 (s, 12H; CH_3), 4.40 (t, 4H; C_5H_4), 4.79 (t, 4H; C_5H_4), 6.86 (s, 4H; C_6H_2); FAB (+ve) MS (CH_2Cl_2) *m*/*z* 753 $(M)^+$, 715 $(M - Cl)^+$, 680 $(M - 2Cl)^+$.

Synthesis of 5. (Method iv) **1** (0.12 g, 0.25 mmol) was added to a toluene (30 mL) solution of dichlorobis(benzonitrile)-platinum(II) (0.11 g, 0.23 mmol). The reaction mixture was stirred, heated to reflux for 20 h, and then filtered to remove a black precipitate. The resulting dark brown solution was evaporated to dryness and the crude brown solid washed with hot hexane (4 × 10 mL). Further purification was achieved by column chromatography (neutral grade II alumina, 2:3 CH_2Cl_2/hexane eluent), which resulted in the isolation of an orange microcrystalline solid (0.07 g, 41%). Anal. Calcd for $C_{28}H_{28}S_2Cl_2FePt{\cdot}0.5CH_2Cl_2$: C, 42.43, H, 3.56. Found: C, 42.27, H, 3.52. ^1H NMR (270 MHz, $CDCl_3$): δ 1.84 (s, 6H; CH_3), 2.28 (s, 6H; CH_3), 3.98 (d, 2H; CH_2), 4.14 (m, 2H; C_5H_4), 4.30 (m, 2H; C_5H_4), 4.58 (d, 2H; CH_2), 4.91 (m, 2H; C_5H_4), 5.13 (m, 2H; C_5H_4), 6.70 (s, 2H; C_6H_2), 6.99 (s, 2H; C_6H_2); FAB (+ve) MS (CH_2Cl_2) *m*/*z* 750 $(M)^+$.

Acknowledgment. This research was supported by the EPSRC, and Johnson Matthey plc is thanked for the loan of platinum salts.

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** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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