Ferrocenylamine Complexes of Platinum(II) Including Cycloplatinated Derivatives

P. Ramani R. Ranatunge-Bandarage, Brian H. Robinson,* and Jim Simpson*

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

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Ferrocenylamines, $[(\eta^5\text{-}C_5H_4CH(R)NMe_2)Fe(\eta^5\text{-}C_5H_5)]$ (R = H, Me), $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_2)Fe(\eta^5\text{-}C_5H_5)]$ and $[(\eta^5\text{-}C_5H_4CH_2NHPh)Fe(\eta^5\text{-}C_5H_5)]$, L, react with *cis*-$PtCl_2(DMSO)_2$ to give, initially, *trans*-$PtCl_2(DMSO)L$ and eventually, with *tertiary* amines, the novel mononuclear platinocycles σ-$Pt[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CHRNMe_2)](DMSO)Cl$ (R = H, Me). Metathesis gave the bromo and iodo platinocycle analogues. These complexes represent a new class of Pt(II) compound with potential cytotoxic activity. All compounds were characterized by ^1H, ^{13}C, and ^{195}Pt NMR and IR, and assignments were assisted by the synthesis of DMSO-d_6 analogues. X-ray crystal structures of *trans*-$PtCl_2(DMSO)[(\eta^5\text{-}C_5H_4CH_2NMe_2)Fe(\eta^5\text{-}C_5H_5)]$ ($P\bar{1}$ with a = 10.395(2) Å, b = 13.402(4) Å, c = 14.481(5) Å, α = 67.75(3)°, β = 77.02(2)°, γ = 89.00(2)°, Z = 4) and σ-$Pt[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CH_2NMe_2)](DMSO)Cl$ ($P2_1/c$, a = 14.239(12) Å, b = 10.990(17) Å, c = 11.067(6) Å, β = 105.33(6)°, Z = 4) were determined. The coordination sphere for the platinocycle has the σ-PtC bond *trans* to the chloride. Monodentate π-acceptor ligands replaced DMSO in the platinocycles to give σ-$Pt[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CHRNMe_2)]L'Cl$, L' = Ph_3P, $(PhO)_3P$, CO, but cleaved the Pt–N bond of the *trans* intermediates. Cycloplatination of $[(\eta^5\text{-}C_5H_4CH(Me)NMe_2)Fe(\eta^5\text{-}C_5H_5)]$ is stereoselective. ^{195}Pt and ^1H NMR studies of the reaction mechanism for *cis*-$PtCl_2(DMSO)_2$ with $[(\eta^5\text{-}C_5H_4CH_2NMe_2)Fe(\eta^5\text{-}C_5H_5)]$ and the subsequent cycloplatination are described. Other labile Pt(II) complexes (e.g. $Pt(COD)Cl_2$) do not undergo these cycloplatination reactions.

Introduction

During investigations into the synthesis of Pt(II) complexes of ferrocenylamines with potential antiproliferative activity, difficulties arose because the basicity of the ferrocenylamines in the medium appropriate for the reaction with $PtCl_4^{2-}$ allowed a proton to effectively compete with the Pt(II) ion,[1] leading to the formation of ferrocenylamine salts. The search for alternative Pt(II) sources led to the surprising discovery that ferrocenylamines underwent facile cycloplatination reactions when $Pt(DMSO)_2Cl_2$ was the precursor.[2] While orthometalation is pervasive in Pd(II) chemistry,[3,4] there are few[5] examples of intramolecular cycloplatination with an amine as the metalation site, unless the reaction involves oxidative addition of aryl–halogen bonds or substituted pyridines,[3,6] and no data to indicate whether fusion to an aromatic ring of an amine alters the cytotoxicity of Pt(II)–amine complexes.

Cyclopalladation of tertiary benzylic amines involves coordination of the N-donor ligand to the Pd(II) substrate followed by intramolecular electrophilic attack of the coordinated species on a carbon atom of the aromatic ring and nucleophilically-assisted proton removal by the free or coordinated base. Most of the resulting complexes have a five-membered palladocyclic ring, but several six-membered systems are known.[3] A number of factors, including the nature of the groups on the ring and the degree of substitution of the amine, influence the rate and efficacy of cyclopalladation reactions.[3,4] Electrophilic attack at a metallocycle ring is expected to be more facile than at a phenyl ring,[7] and cyclopalladation has been extended to N-donor ligands containing a ferrocenyl moiety where the fusion takes place to the five-membered cyclopentadienyl ring. It has been established that cyclopalladation of [(*N*,*N*-dimethylamino)methyl]ferrocene and ferrocenylimines results in cleavage of the Pd–N bond, or formation of dimeric halogen-bridged structures which can be split by phosphines to give mononuclear palladocycles.[4,8-10] *Endo* stereochemistry is favored with bicyclic derivatives from which it was concluded[9] that the strain associated with the formation of two fused five-membered rings is not large. However, the direction of metalation reactions with ferrocenylamines is influenced by the metal ion, and conclusions reached from Pd(II) chemistry will not necessarily hold for other metals such as Pt(II); for example, with $RMn(CO)_5$, metalation of an

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N-methyl group of the ferrocenylamine occurs[11] in preference to attack at the aromatic ring. Because Pt(II)–ligand interactions are particularly strong, it seems that intramolecular electrophilic attack involving a Pt(II)–amine entity only occurs in very specific circumstances. Cycloplatination of the aromatic ring of benzylamine and phenylethylamine Pt(II) derivatives was discovered[5a] in reactions which involved the prior hydrolysis of the Pt–Cl bond. Interestingly, the kinetically preferred ring conformation was six-membered, not the thermodynamically directed five-membered system. A similar hydrolysis mechanism can be invoked for the only example of cycloplatination of a primary amine.[5b]

Pt(II) derivatives of ferrocenylamines[1,2,12] and conjugates of carboxato- or phosphine–ferrocene moieties and Pt(II)–amine complexes[13,14] have previously been prepared, and their biodistribution and antiproliferative activity assessed, but intramolecular ring fusion has not been observed in conditions where Pt–Cl hydrolysis could occur. Recently, we embarked on a wide-ranging investigation of ferrocenylamine–Pt(II) compounds. The strategy was to study the influence of leaving group, nitrogen functionality, chirality, oxidation state, and number of Pt(II) moieties per ferrocenyl group on the biological activity of these compounds. New ferrocenylamine complexes prepared from $Pt(DMSO)_2Cl_2$ have, in many instances, unusual reactivity and stereochemistry, and they provide an entry into a new series of platinum-based ferrocenyl drug precursors with cytotoxic activity.[15] Furthermore, access to ferrocenium analogues offered the possibility that they would be effective as radiation sensitizers with target organ specificity.[16,17] In this paper we describe the chemistry of complexes with one Pt(II) center per ferrocenyl unit; the following paper[18] deals with those complexes with two Pt(II) centers. Redox properties,[19] biodistribution, toxicity, and tumour activity[15] will be described in subsequent papers.

Experimental Section

Preparations of ferrocenylamine–platinum(II) complexes were carried out under an atmosphere of dry nitrogen in a fumehood, as most of the ferrocenylamine compounds have acrid odors. Most complexes decomposed to ferrocenium compounds on heating in methanol, acetone, or any other solvents in air after 1 h, so reactions were carried out under nitrogen. All solvents were dried by standard methods. The compounds *cis*-$Pt(DMSO)_2Cl_2$,[20] $[(\eta^5\text{-}C_5H_4CH(R)NMe_2)Fe(\eta^5\text{-}C_5H_5)]$ (R = H, Me),[21] $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_2)Fe(\eta^5\text{-}C_5H_5)]$,[21,22] and $[(\eta^5\text{-}C_5H_4CH_2NHPh)Fe(\eta^5\text{-}C_5H_5)]$[22] were prepared by literature procedures. NMR and IR spectra were recorded on Varian 300VXR (5-mm probe) and Digilab FTIR spectrometers, respectively; ^{195}Pt NMR spectra are referenced to Na_2PtCl_6. Analyses were carried out by the Campbell Microanalytical laboratory, University of Otago.

***trans*-$PtCl_2(DMSO)[(\eta^5\text{-}C_5H_4CH_2NMe_2)Fe(\eta^5\text{-}C_5H_5)]$, 1.** $[(\eta^5\text{-}C_5H_4CH_2NMe_2)Fe(\eta^5\text{-}C_5H_5)]$ (24.3 mg, 0.1 mmol) in acetone (40 cm^3) was added to *cis*-$PtCl_2(DMSO)_2$ (21.1 mg; 0.05 mmol) and the mixture refluxed for 30 min under nitrogen in the absence of light. The mixture was cooled to room temperature and the solvent evaporated *in vacuo*. The crude solid product was taken up in CH_2Cl_2, a few drops of hexane were added, and the yellow solid was filtered, washed with hexane, and dried *in vacuo*. Recrystallization of the product from CH_2Cl_2/hexane gave pure **1**; yield 91%. Mp: 162 °C with dc. Anal. Calcd for $C_{15}H_{23}NOSCl_2FePt$: C, 30.68; H, 3.95; N, 2.39; S, 5.46; Cl, 12.07. Found: C, 30.38; H, 3.91; N, 2.34; S, 5.95; Cl, 12.66. IR (KBr, cm^{-1}): 1149 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}): 339 ν_{Pt-Cl}, 379 ν_{Pt-S}. ^1H NMR ($CDCl_3$): δ 2.66 (s, 6H, $^3J_{Pt-H}$ = 26 Hz, CH_3N), 3.35 (s, 6H, $^3J_{Pt-H}$ = 17 Hz, CH_3S), 4.03 (s, 2H, $^3J_{Pt-H}$ = 19.8 Hz, CH_2N), 4.15 (s, 5H, η^5-C_5H_5Fe), 4.24 (m, 2H, two β-H of η^5-C_5H_4Fe), 4.52 (m, 2H, two α-H of η^5-C_5H_4Fe). ^{13}C NMR ($CDCl_3$): δ 44.42 (CH_3S), 51.79 (CH_3N), 64.18 (CH_2N), 69.07 (CH, two of η^5-C_5H_4Fe), 72.00 (CH, two of η^5-C_5H_4Fe), 68.84 (CH, five of η^5-C_5H_5Fe), 78.06 (quaternary C). ^{195}Pt NMR ($CDCl_3$, 25 °C): δ −3049. UV–visible (CH_2Cl_2; λ_{max}, nm): 325 (ε = 563), 444 (ε = 153).

trans-$PtCl_2(DMSO\text{-}d_6)[(\eta^5\text{-}C_5H_4CH_2NMe_2)Fe(\eta^5\text{-}C_5H_5)]$ was prepared from *cis*-$PtCl_2(DMSO\text{-}d_6)_2$; yield 80%. IR (KBr, cm^{-1}): 1145 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}): 339 ν_{Pt-Cl}, 380 ν_{Pt-S}. ^1H NMR ($CDCl_3$): δ 2.67 (s, 6H, $^3J_{Pt-H}$ = 25.4 Hz, CH_3N), 4.04 (s, 2H, $^3J_{Pt-H}$ = 20.9 Hz, CH_2N), 4.16 (s, 5H, η^5-C_5H_5Fe), 4.25 (m, 2H, two β-H of η^5-C_5H_4Fe), 4.53 (m, 2H, two α-H of η^5-C_5H_4Fe). ^{13}C NMR ($CDCl_3$): 51.80 (CH_3N), 64.20 (CH_2N), 69.10 (CH, two of η^5-C_5H_4Fe), 72.03 (CH, two of η^5-C_5H_4Fe), 68.87 (CH, five of η^5-C_5H_5Fe), 78.05 (quaternary C).

***trans*-$PtCl_2(DMSO)[(\eta^5\text{-}C_5H_4CH(CH_3)NMe_2)Fe(\eta^5\text{-}C_5H_5)]$, 2.** To *cis*-$PtCl_2(DMSO)_2$ (10.6 mg; 0.025 mmol) in dry, nitrogen flushed acetone (20 cm^3) was added $[(\eta^5\text{-}C_5H_4CH(CH_3)NMe_2)Fe(\eta^5\text{-}C_5H_5)]$ (12.9 mg; 0.05 mmol). The mixture was refluxed at 60–70 °C for 30 min and then rapidly cooled to room temperature. The solvent was evaporated and a yellow solid was obtained by adding hexane to the mixture, filtering, and drying *in vacuo*. The crude yellow solid was dissolved in CH_2Cl_2, the solution was filtered through a Celite pad, the solvent was evaporated, and the pale yellow solid was recrystallized from CH_2Cl_2/hexane; yield 42%. Mp: 200 °C with dec. Anal. Calcd for $C_{16}H_{25}NOSCl_2FePt$: C, 31.96; H, 4.19; N, 2.33. Found: C, 31.80; H, 3.97; N, 2.23. IR (KBr, cm^{-1}): 1146 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}): 335 ν_{Pt-Cl}, 380 ν_{Pt-S}. ^1H NMR ($CDCl_3$): δ 2.11 (d, 3H, *J* = 6.9 Hz, CH_3CH), 2.29 (s, 3H, $^3J_{Pt-H}$ = 30 Hz, CH_3N), 2.67 (s, 3H, $^3J_{Pt-H}$ = 26 Hz, CH_3N), 3.41 (s, 6H, $^3J_{Pt-H}$ = 21.6 Hz, CH_3S), 4.22 (m, 4H, η^5-C_5H_4Fe), 4.17 (s, 5H, η^5-C_5H_5Fe), 4.76 (q, 1H, *J* = 7 Hz, CH_3CH). ^{13}C NMR ($CDCl_3$): δ 19.58 (CH_3CH), 44.50 and 44.97 (CH_3S), 50.60 (CH_3N), 64.15 ($CHCH_3$), 69.56 (CH, four of η^5-C_5H_4Fe), 69.22 (CH, five of η^5-C_5H_5Fe), 78.20 (quaternary C). UV–visible (CH_2Cl_2; λ_{max}, nm): 326 (ε = 638); 450 (ε = 81).

***trans*-$PtCl_2(DMSO)[(\eta^5\text{-}C_5H_4(CH_2)_2NH_2)Fe(\eta^5\text{-}C_5H_5)]$, 3.** A solution of *cis*-$PtCl_2(DMSO)_2$ (21.1 mg; 0.05 mmol) and ligand $[(\eta^5\text{-}C_5H_4(CH_2)_2NH_2)Fe(\eta^5\text{-}C_5H_5)]$ (22.9 mg; 0.1 mmol) in acetone (40 cm^3) was refluxed at 70 °C for 30 min. The solvent was evaporated and the solid washed with hexane. The crude product was purified by preparative tlc (acetone/hexane, 2:3) to give **3** (R_f = 0.4). Recrystallization from CH_2Cl_2/ether gave the pure pale yellow **3**; yield 49%. Mp: 166 °C with dec. Anal. Calcd for $C_{14}H_{21}NOSCl_2FePt$: C, 29.33; H, 3.69; N, 2.44; S, 5.59. Found: C, 31.15; H, 3.86; N, 2.40; S, 5.69. IR (KBr, cm^{-1}): 1142 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}) 343 ν_{Pt-Cl}, 374 ν_{Pt-S}. ^1H NMR ($CDCl_3$): δ 2.67 (t, 2H, CH_2CH_2N, *J* = 14 Hz), 3.06 (t, 2H, $^3J_{Pt-H}$ = 28.0 Hz, *J* = 14.2 Hz, CH_2CH_2N), 3.41 (s, 6H, CH_3S), 4.15 (s, 5H, η^5-C_5H_5-Fe), 4.12 (m, 4H, η^5-C_5H_4Fe), 5.68 (bs, 2H, NH_2). ^{13}C NMR

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($CDCl_3$): δ 43.88 (CH_3S), 31.08 (CH_2CH_2N), 46.64 (CH_2CH_2N), 68.86 (*C*H, η^5-C_5H_5Fe), 68.42 (*C*H, two of α-C of η^5-C_5H_4Fe), 68.05 (*C*H, two β-C of η^5-C_5H_4Fe), 83.89 (quaternary C). ^{195}Pt NMR ($CDCl_3$, 25 °C): δ −3075. UV–visible (CH_2Cl_2; λ_{max}, nm): 308 (ε = 234), 433 (ε = 87).

***trans*-PtCl$_2$(DMSO)[(η^5-C$_5$H$_4$CH$_2$NHPh)Fe(η^5-C$_5$H$_5$)], 4.** *cis*-$PtCl_2(DMSO)_2$ (21.1 mg; 0.05 mmol) was added to a solution of [(η^5-$C_5H_4CH_2NHPh$)Fe(η^5-C_5H_5)] (29.1 mg; 0.1 mmol) in dry, nitrogen flushed methanol (40 cm^3). The mixture was refluxed with stirring at 60–65 °C for 30 min, by which time tlc (solvent system: acetone/hexane, 1.5:3) indicated all of the *cis*-$PtCl_2(DMSO)_2$ had reacted. The product was cooled to room temperature, evaporated, and washed with hexane. The crude product was separated by preparative tlc (acetone/hexane, 2:3) to give pure yellow **4** (R_f = 0.42); yield 50%. Mp: 96–98 °C. Anal. Calcd for $C_{19}H_{23}NOSCl_2FePt$: C, 35.92; H, 3.65; N, 2.20; S, 5.05. Found: C, 35.92; H, 3.69; N, 2.16; S, 4.94. IR (KBr, cm^{-1}): 1145 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}): 333 ν_{Pt-Cl}, 374 ν_{Pt-S}. ^{1}H NMR ($CDCl_3$): δ 4.14–4.10 (2H, CH_2N), 3.33 (s, 6H, $^3J_{Pt-H}$ = 17 Hz, CH_3S), 4.21 (s, 5H, η^5-C_5H_5Fe), 4.32 (m, 2H, two of η^5-C_5H_4Fe), 4.19 (m, 2H, two of η^5-C_5H_4Fe), 5.90 (bs, 1H, N*H*), 7.26–7.39 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 44.42 and 44.51 (CH_3S), 53.74 (CH_2N), 68.82 (*C*H, η^5-C_5H_5Fe), 69.46 and 69.33 (*C*H, two of α-C of η^5-C_5H_4Fe), 68.93 (*C*H, two β-C of η^5-C_5H_4Fe), 80.91 (quaternary C), 143.98 (aromatic quaternary C). ^{195}Pt NMR ($CDCl_3$, 25 °C): δ −3102. UV–visible (CH_2Cl_2; λ_{max}, nm): 319 (ε = 608), 426 (ε = 150).

σ-Pt[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CH$_2$NMe$_2$)]Cl(DMSO), 5. *cis*-$Pt(DMSO)_2Cl_2$ (21.1 mg; 0.05 mmol) was added to a solution of [(η^5-$C_5H_4CH_2NMe_2$)Fe(η^5-C_5H_5)] (24.3 mg; 0.1 mmol) in dry methanol (40 cm^3). The mixture was refluxed at 70–80 °C for 30 min with stirring under N_2 in the absence of light and cooled to room temperature, and the solvent was evaporated *in vacuo*, until an orange solid formed. The orange solid was filtered out and washed with cold methanol. Recrystallization from CH_2Cl_2/methanol gave pure **5** as orange-yellow plates; yield 38%. Mp: 200 °C with dec. Anal. Calcd for $C_{15}H_{22}NOSClFePt$: C, 32.71; H, 4.03; N, 2.54; S, 5.82; Cl, 6.44. Found: C, 32.84; H, 4.30; N, 2.83; S, 6.00; Cl, 6.69. IR (KBr, cm^{-1}): 1126 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}): 293 ν_{Pt-Cl}, 358 ν_{Pt-S}. ^{1}H NMR (CD_2Cl_2): δ 2.88 (s, 3H, $^3J_{Pt-H}$ = 33 Hz, CH_3N), 3.19 (s, 3H, $^3J_{Pt-H}$ = 30 Hz, CH_3N), 3.49 (s, 3H, $^3J_{Pt-H}$ = 25 Hz, CH_3S), 3.55 (s, 3H, $^3J_{Pt-H}$ = 26 Hz, CH_3S), 3.57 (AB, 2H, J_{AB} = 14 Hz, Δν = 81.3 Hz, CH_2N), 4.13 (s, 5H, η^5-C_5H_5Fe), 4.11 (m, 2H, two of η^5-C_5H_3Fe), 4.50 (m, 1H, one of η^5-C_5H_3Fe). ^{13}C NMR (CD_2Cl_2): δ 47.45 (CH_3S, $^2J_{Pt-C}$ = 68 Hz), 47.83 (CH_3S, $^2J_{Pt-C}$ = 71 Hz), 53.84 (CH_3N), 69.49 (CH_2N), 62.55 (*C*H, $^3J_{Pt-C}$ = 43 Hz, one of η^5-C_5H_3Fe), 67.40 (*C*H, $^3J_{Pt-C}$ = 49 Hz, one of η^5-C_5H_3Fe), 69.83 (*C*H, five of η^5-C_5H_5Fe), 70.00 (*C*H, $^2J_{Pt-C}$ = 96 Hz, one of η^5-C_5H_3Fe), 82.16 (*C*—C—N, 95.69 (*C*—Pt). ^{195}Pt NMR ($CDCl_3$, 25 °C): δ −3763. UV–visible (CH_2Cl_2; λ_{max}, nm): 277 (ε = 8233), 449 (ε = 240).

The deuterated σ-platinum analogue of **5**, σ-Pt[(η^5-C_5H_5)Fe(η^5-$C_5H_3CH_2NMe_2$)]Cl(DMSO-d_6) was prepared from *cis*-$PtCl_2(DMSO\text{-}d_6)_2$ using the same procedure. IR (KBr, cm^{-1}): 1123 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}): 279 ν_{Pt-Cl}, 353 ν_{Pt-S}. ^{1}H NMR ($CDCl_3$): δ 2.88 (s, 3H, $^3J_{Pt-H}$ = 32 Hz, CH_3N), 3.18 (s, 3H, $^3J_{Pt-H}$ = 29 Hz, CH_3N), 3.59 (AB, 2H, J_{AB} = 14 Hz, Δν = 85.8 Hz, CH_2N), 4.14 (s, 5H, η^5-C_5H_5Fe), 4.12 (m, 2H, two of η^5-C_5H_3Fe), 4.51 (m, 1H, one of η^5-C_5H_3Fe). ^{13}C NMR ($CDCl_3$): δ 53.29 (CH_3N), 68.94 (CH_2N), 61.88 (*C*H, $^3J_{Pt-C}$ = 43 Hz, one of η^5-C_5H_3Fe), 66.87 (*C*H, $^3J_{Pt-C}$ = 49 Hz, one of η^5-C_5H_3Fe), 69.10 (*C*H, five of η^5-C_5H_5Fe), 69.34 (*C*H, $^2J_{Pt-C}$ = 92 Hz, one of η^5-C_5H_3Fe), 80.97 (one of quaternary C), 94.50 (one of quaternary C).

σ-Pt[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CH(Me)NMe$_2$)]Cl(DMSO), 6. [(η^5-$C_5H_4CH(Me)NMe_2$)Fe(η^5-C_5H_5)] (1.80 g; 7 mmol) in dry, nitrogen flushed methanol (320 cm^3) was added to *cis*-$Pt(DMSO)_2Cl_2$ (1.48 g; 3.5 mmol), and the mixture was heated at 50–55 °C until all *cis*-$Pt(DMSO)_2Cl_2$ dissolved. The mixture was cooled to room temperature in an ice bath and the solvent evaporated until an orange solid formed. The solid was collected and washed with cold methanol (5 cm^3 × 2) and dry ether (10 cm^3) and then dried *in vacuo*. Recrystallization was achieved by dissolving the solid in CH_2Cl_2, filtering through a Celite pad, and adding 20 cm^3 of methanol to the filtrate. Concentration of the mixture gave a yellow-orange solid; yield 33%. Mp: 195 °C with dec. Anal. Calcd for $C_{16}H_{24}NOSClFePt$: C, 34.02; H, 4.28; N, 2.48; S, 5.68. Found: C, 33.78; H, 4.29; N, 2.50; S, 5.93. IR (KBr, cm^{-1}): 1130 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}): 272 ν_{Pt-Cl}, 353 ν_{Pt-S}. ^{1}H NMR (CD_2Cl_2): δ 1.23 (d, 3H, *J* = 7 Hz, CH_3CH), 2.45 (s, 3H, $^3J_{Pt-H}$ = 36 Hz, CH_3N), 3.04 (s, 3H, $^3J_{Pt-H}$ = 32 Hz, CH_3N), 3.50 (s, 3H, $^3J_{Pt-H}$ = 25 Hz, CH_3S), 3.56 (s, 3H, $^3J_{Pt-H}$ = 26 Hz, CH_3S), 4.09 (s, 5H, η^5-C_5H_5Fe), 4.02 (m, 2H, two of η^5-C_5H_3Fe), 4.43 (m, 1H, one of η^5-C_5H_3Fe), 4.36 (q, 1H, *J* = 7 Hz, CH_3CH). ^{13}C NMR (CD_2Cl_2): δ 11.73 (CH_3CH), 47.55 (CH_3S), 47.85 (CH_3S), 44.23 (CH_3N), 50.18 (CH_3N), 71.80 (*C*H, one of η^5-C_5H_3Fe), 64.20 (*C*H, one of η^5-C_5H_3Fe), 66.31 (*C*H, one of η^5-C_5H_3Fe), 70.31 (*C*H, five of η^5-C_5H_5Fe), 70.40 ($CHCH_3$), 81.5 (one of quaternary C), 98.72 (one of quaternary C). ^{195}Pt NMR ($CDCl_3$, 25 °C): δ −3899. UV–visible (CH_2Cl_2; λ_{max}, nm): 278 (ε = 7353), 449 (ε = 470).

The deuterated analogue σ-Pt[(η^5-C_5H_5)Fe(η^5-$C_5H_3CH(Me)NMe_2$)]Cl(DMSO-d_6) was prepared by a similar method from *cis*-$PtCl_2(DMSO\text{-}d_6)_2$. IR (KBr, cm^{-1}): 1126 $\nu_{S=O}$, 2264 and 2252 ν_{CD_3}. Far IR (Nujol, cm^{-1}): 272 ν_{Pt-Cl}, 353 ν_{Pt-S}. ^{1}H NMR ($CDCl_3$): δ 1.25 (d, 3H, *J* = 6.9 Hz, CH_3CH), 2.48 (s, 3H, $^3J_{Pt-H}$ = 37 Hz, CH_3N), 3.08 (s, 3H, $^3J_{Pt-H}$ = 32 Hz, CH_3N), 4.10 (s, 5H, η^5-C_5H_5Fe), 4.07 (m, 2H, two of η^5-C_5H_3Fe), 4.50 (m, 1H, one of η^5-C_5H_3Fe), 4.41 (q, 1H, *J* = 7 Hz, CH_3CH). ^{13}C NMR ($CDCl_3$): δ 11.17 (CH_3CH), 43.63 (CH_3N), 49.60 (CH_3N), 63.38 (*C*H, one of η^5-C_5H_3Fe), 65.69 (*C*H, one of η^5-C_5H_3Fe), 71.10 (*C*H, one of η^5-C_5H_3Fe), 69.50 (*C*H, five of η^5-C_5H_5Fe), 69.70 ($CHCH_3$), 81.80 (one of quaternary C), 97.46 (one of quaternary C).

σ-Pt[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CH$_2$NMe$_2$)]Br(DMSO), 7. Lithium bromide (39.5 mg; 0.45 mmol) in acetone (20 cm^3) was added to a solution of **5** (50 mg; 9 × 10^{-2} mmol) in acetone (5 cm^3). The reaction mixture was stirred for 20 h at room temperature under nitrogen, after which time tlc (solvent system: acetone/hexane, 1:3) indicated that all of **1** had reacted. The solvent was removed *in vacuo*. Workup gave pure **7**; yield 73%. Mp: 198–200 °C. Anal. Calcd for $C_{15}H_{22}NOSFeBrPt$: C, 30.27; H, 3.73; N, 2.35. Found: C, 30.61; H, 3.83; N, 2.30. IR (KBr, cm^{-1}): 1126 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}): 198 ν_{Pt-Br}, 380 ν_{Pt-S}. ^{1}H NMR ($CDCl_3$): δ 2.93 (s, 3H, $^3J_{Pt-H}$ = 34 Hz, CH_3N), 3.29 (s, 3H, $^3J_{Pt-H}$ = 32 Hz, CH_3N), 3.64 (s, 3H, $^3J_{Pt-H}$ = 26 Hz, CH_3S), 3.68 (s, 3H, $^3J_{Pt-H}$ = 25 Hz, CH_3S), 3.60 (AB, 2H, J_{AB} = 14 Hz, Δν = 103.1 Hz, CH_2N), 4.42 (s, 5H, η^5-C_5H_5Fe), 4.11 (m, 2H, two of η^5-C_5H_3Fe), 4.64 (m, 1H, one of η^5-C_5H_3Fe). ^{13}C NMR ($CDCl_3$): δ 48.40 (CH_3S, $^2J_{Pt-C}$ = 70.9 Hz), 48.46 (CH_3S, $^2J_{Pt-C}$ = 73 Hz), 53.79 and 54.47 (CH_3N), 68.97 (CH_2N), 61.94 (*C*H, $^3J_{Pt-C}$ = 43 Hz, one of η^5-C_5H_3Fe), 66.63 (*C*H, $^3J_{Pt-C}$ = 49 Hz, one of η^5-C_5H_3Fe), 69.22 (*C*H, five of η^5-C_5H_5Fe), 69.42 (*C*H, $^2J_{Pt-C}$ = 96 Hz, one of η^5-C_5H_3Fe), 94.40 (one of quaternary C), 84.20 (one of quaternary C). ^{195}Pt NMR ($CDCl_3$, 25 °C): δ −3815. UV–visible (CH_2Cl_2; λ_{max}, nm): 281 (ε = 5566), 453 (ε = 223).

σ-Pt[(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CH$_2$NMe$_2$)]I(DMSO), 8. Lithium iodide (60.8 mg; 0.45 mmol) and **5** (50 mg; 9.1 × 10^{-2} mmol) in acetone (15 cm^3) were stirred for 20 h under nitrogen at room temperature in the dark. The reaction was followed using tlc (solvent system: acetone/hexane, 1:3). The solvent was evaporated and the solid was taken up in methanol and dried *in vacuo*. Yield: 68%. Mp: 198 °C with dec. Anal. Calcd for $C_{15}H_{22}NOSFeIPt$: C, 28.05; H, 3.45; N, 2.18. Found: C, 29.02; H, 3.63; N, 2.27. IR (KBr, cm^{-1}): 1126 $\nu_{S=O}$. Far IR (Nujol, cm^{-1}): 133.1 ν_{Pt-I}, 363 ν_{Pt-S}. ^{1}H NMR ($CDCl_3$): δ 2.95 (s, 3H, $^3J_{Pt-H}$ = 34.3 Hz, CH_3N), 3.42 (s, 3H, $^3J_{Pt-H}$ = 33 Hz, CH_3N), 3.82 (s, 3H, $^3J_{Pt-H}$ = 25 Hz, CH_3S), 3.83 (s, 3H, $^3J_{Pt-H}$ = 25.6 Hz, CH_3S), 4.15 (s, 5H, η^5-C_5H_5Fe), 4.14 (m, 2H, two of η^5-C_5H_3Fe), 4.67 (m, 1H, one of η^5-C_5H_3Fe). ^{13}C NMR ($CDCl_3$): δ 50.71 (CH_3S, $^2J_{Pt-C}$ = 75 Hz), 51.09 (CH_3S, $^2J_{Pt-C}$ = 77 Hz), 54.46 and 56.60 (CH_3N), 68.88 (CH_2N), 62.05 (*C*H, $^3J_{Pt-C}$ = 41 Hz, one of η^5-C_5H_3Fe), 66.15 (*C*H, $^3J_{Pt-C}$ = 48 Hz, one of η^5-C_5H_3Fe), 69.37 (*C*H, five of η^5-C_5H_5Fe), 69.59 (*C*H, one of η^5-C_5H_3Fe), 88.00 (one of quaternary C), 94.42 (one of quaternary C). ^{195}Pt NMR ($CDCl_3$, 25 °C): δ −3899. UV–visible (CH_2Cl_2; λ_{max}, nm): 281 (ε = 4513), 446 (ε = 391).

Conversion of Intermediate 1 to the Cyclometalated 5 in Different Solvents. 1 (0.020 g; 3.4×10^{-2} mmol) in *methanol* (10 cm^3) was left at room temperature for 20 h by which time orange-yellow crystals formed. Their ^1H NMR and IR data were identical to those the product **5**; yield 80%. A similar reaction at 20 °C using *ethanol, tert-butyl alcohol, or water* did not convert any of 1 but when the solution was heated to 60–70 °C for 30 min under nitrogen, the solvent evaporated and the residual oil (or, in the case of water, the precipitate) crystallized from CH_2Cl_2/methanol; a 65% yield of **5** was obtained. Incomplete conversion occurred in *DMSO* at 60 °C. The results are summarized in Table 6.

Reaction of 1 with Phosphines. Triphenylphosphine (2.55×10^{-3} mmol) was added to an equimolar solution of 1 in $CHCl_3$. The mixture was stirred for 15 min, the solvent was evaporated, and the white solid recrystallized from CH_2Cl_2/hexane. Yield: 93%. Mp: 260 °C with dec. Anal. Calcd for *trans*-$C_{36}H_{30}P_2Cl_2Pt$: C, 54.69; H, 3.82; P, 7.84; Cl, 8.97. Found: C, 54.41; H, 3.97; P, 6.63; Cl, 9.02. ^{31}P NMR ($CDCl_3$): δ 14.36 (J_{Pt-P} = 3658 Hz).[24] Other phosphines also gave *trans*-$PtCl_2L_2$ derivatives characterized from their known spectroscopic data.

σ-Pt[(η^5-C_5H_5)Fe(η^5-$C_5H_3CH_2NMe_2$)]Cl(PPh_3), 9. Triphenylphosphine (10.5 mg; 4×10^{-2} mmol) was added to a solution of **5** (20 mg; 3.6×10^{-2} mmol) in chloroform (1 cm^3). The mixture was stirred at room temperature under nitrogen for 30 min, and methanol (2 cm^3) was added. The volume of the solvent was then reduced by evaporation. The orange-yellow solid obtained was recrystallized from CH_2Cl_2/methanol to give pure **9**; yield 64%. Mp: 190 °C. Anal. Calcd for $C_{31}H_{31}NPClFePt$: C, 50.66; H, 4.25; N, 1.91; P, 4.21; Cl, 4.82. Found: C, 50.08; H, 4.62; N, 1.98; P, 4.03; Cl, 5.70. Far IR (Nujol, cm^{-1}): 285 ν_{Pt-Cl}, 260 ν_{Pt-P}. ^1H NMR ($CDCl_3$): δ 3.12 (d, 3H, $^3J_{P-H}$ = 3 Hz, CH_3N), 3.36 (d, 3H, $^4J_{P-H}$ = 3 Hz, CH_3N), 3.53 (AB, 2H, J_{AB} = 14 Hz, $\Delta\nu$ = 74.4 Hz, CH_2N), 3.74 (s, 5H, η^5-C_5H_5Fe), 3.65 (m, 1H, one of η^5-C_5H_3Fe), 3.81 (m, 1H, one of η^5-C_5H_3Fe), 4.02 (m, 1H, one of η^5-C_5H_3Fe), 7.39–7.77 (m, 15H, $P(C_6H_5)_3$). ^{31}P NMR ($CDCl_3$): δ 17.21 ($P(C_6H_5)_3$, $^1J_{Pt-P}$ = 4290 Hz). ^{195}Pt NMR ($CDCl_3$, 25 °C): δ −4173 ($^1J_{Pt-P}$ = 4297 Hz). UV–visible (CH_2Cl_2; λ_{max}, nm): 293 (ϵ = 8546), 465 (ϵ = 385).

σ-Pt[(η^5-C_5H_5)Fe(η^5-$C_5H_3CH_2NMe_2$)]Cl($P(OPh)_3$), 10. A solution of **5** (15 mg; 2.7×10^{-2} mmol) and triphenyl phosphite (8.1 mg; 2.6×10^{-2} mmol) in chloroform (1 cm^3) was stirred at room temperature for 15 min under nitrogen, after which time methanol (2 cm^3) was added. The solvent was evaporated *in vacuo* and dried. Recrystallization from CH_2Cl_2/methanol gave pure **10**; yield 68%. Mp: 175 °C with dec. Anal. Calcd for $C_{31}H_{31}NO_3PClFePt$: C, 47.56; H, 3.99; N, 1.79; Cl, 4.53. Found: C, 47.53; H, 4.05; N, 1.75; Cl, 5.02. Far IR (Nujol, cm^{-1}): 275 ν_{Pt-Cl}, 260 ν_{Pt-P}. ^1H NMR ($CDCl_3$): δ 2.67 (d, 3H, $^4J_{P-H}$ = 4.1 Hz, CH_3N), 3.10 (d, 3H, $^4J_{P-H}$ = 4.6 Hz, CH_3N), 3.51 (AB, 2H, J_{AB} = 14.0 Hz, $\Delta\nu$ = 68.8 Hz, $^4J_{P-H}$ = 4.2 Hz, CH_2N), 3.84 (s, 5H, η^5-C_5H_5Fe), 4.37 (m, 1H, one of η^5-C_5H_3Fe), 4.07 (m, 2H, two of η^5-C_5H_3Fe), 7.13–7.46 (m, 15H, $P(OC_6H_5)_3$). ^{13}C NMR ($CDCl_3$): δ 51.50 ($^3J_{P-C}$ = 4 Hz, CH_3N), 51.70 ($^3J_{P-C}$ = 4 Hz, CH_3N), 67.44 (CH_2N), 70.74 (*C*H, one of η^5-C_5H_3Fe), 67.28 (*C*H, one of η^5-C_5H_3Fe), 61.60 (*C*H, one of η^5-C_5H_3Fe), 69.13 (*C*H, five of η^5-C_5H_5Fe), 82.07 (one of quaternary C), 95.02 (one of quaternary C), 120.95–120.62 ($(C_6H_5O)_3P$). ^{31}P NMR ($CDCl_3$): 69.65 ($P(OC_6H_5)_3$, $^1J_{Pt-P}$ = 7155 Hz). ^{195}Pt NMR ($CDCl_3$, 25 °C): δ −4152 ($^1J_{Pt-P}$ = 7153 Hz). UV–visible (CH_2Cl_2; λ_{max}, nm): 281 (ϵ = 12537), 455 (ϵ = 261).

σ-Pt[(η^5-C_5H_5)Fe(η^5-$C_5H_3CH_2NMe_2$)]Cl(CO), 11. CO(g) was bubbled through a solution of **5** (70 mg) in CH_2Cl_2 (30 cm^3) over a period of 72 h. Evaporation of the solution to dryness gave an orange solid which was recrystallized from warm hexane to give red needles; yield 60%. Anal. Calcd for $C_{14}H_{16}NOClFePt$: C, 33.59; H, 3.22; N, 2.80. Found: C, 33.68; H, 3.15; N, 2.74. Mp: 96 °C. MS: *m/e* 500 (M^+). IR (cm^{-1}): 2095 $\nu_{C\equiv O}$. Far IR (Nujol mull): 484 ν_{Pt-CO}, 303 ν_{Pt-Cl}. ^1H NMR ($CDCl_3$): δ 2.80 (s, J_{Pt-H} = 14 Hz, CH_3N), 3.20 (s, J_{Pt-H} = 13 Hz), 3.60 (d, CH_2—N), 3.90 (d, CH_2—N), 4.06 (d, J_{H-H} = 16 Hz, *C*H), 4.17 (s, 5H, η^5-C_5H_5), 4.24 (s, 3H, CH_3—N). ^{13}C NMR ($CDCl_3$): δ 161.8 (C≡O). ^{195}Pt NMR ($CHCl_3$): δ −3929. UV (CH_2Cl_2; λ_{max}, nm): 303 (ϵ = 4016), 451 (ϵ = 327).

Table 1. Crystal Data, Data Collection, and Refinement of Compounds 1 and 5

	1	5
empirical formula	$C_{15}H_{25}ONSCl_2FePt$	$C_{15}H_{22}ONSClFePt$
M/g mol^{-1}	587.26	550.80
cryst syst	triclinic	monoclinic
space group[a]	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a/Å	10.385(2)	14.239(12)
b/Å	13.402(4)	10.990(17)
c/Å	14.482(5)	11.067(6)
α/deg	67.75(3)	90
β/deg	77.07(2)	105.33(6)
γ/deg	89.00(2)	90
V/Å^3	1814(1)	1670(3)
$D_c(D_m)$/g cm^{-3}	2.15	2.19
Z	4[b]	4
cryst size/mm	0.64 × 0.38 × 0.16	0.60 × 0.15 × 0.06
μ(Mo Kα) cm^{-1}	93.19	95.63
F(000)	1128	1056
diffractometer	Nicolet R3M	Nicolet R3M
temp/K	143 ± 5	173 ± 5
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
scan type	(ω–2θ)	Wycoff
scan speed/deg min^{-1}	5.86	7.32
data limits/deg	$4 < 2\theta < 50$	$4 < 2\theta < 50$
reflns measd	$h,\pm k,\pm l$	$h,k,\pm l$
cryst decay[c]/%	<7	<1
abs corr	empirical	empirical
transm	1.000 (max) 0.323 (min)	0.967 (max) 0.565 (min)
total no. of reflns[d]	6378	2941
no. of unique data ($I > 2\sigma I$)	4835	2439
method of solving	Patterson	Patterson
no. of variables	211	202
treatment of protons	calculated	calculated
R ($\Sigma\Delta F/\Sigma\|F_o\|$)	0.0446	0.0300
R_w [$\Sigma w^{1/2}(\Delta F)/\Sigma w^{1/2}F_o$]	0.0488	0.0408
weight (w)	[1.5103/(σ^2_F + 0.00087F^2)]	[0.9797/(σ^2_F + 0.001682F^2)]
residual dens/e Å^{-3}	+2.78, −1.77	+1.03, −1.01

[a] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1966; Vol. I. [b] Two unique molecules in the asymmetric unit. [c] Standard reflections: (216), (314), (−3,2,2) for **1**; (600), (080), (008) for **3**; (500), (060), (004) for **9** measured after every 100 reflections. [d] Lorentz and polarization corrections and empirical absorption corrections were applied using the SHELXTL system.

X-ray Structure Determinations of 1 and 5. Samples of **1** and **5** were prepared as detailed above. X-ray quality crystals were obtained for **1** from acetone layered with hexane at 273 K and for **5** from CH_2Cl_2/methanol. Both crystalline samples were in the form of thin, yellow plates. For **1** a triclinic unit cell was indicated and the structure was successfully solved in the centrosymmetric alternative $P\bar{1}$.[25] Precession photography (Cu Kα radiation) for **5** indicated a monoclinic unit cell and the systematic absences $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$, confirmed the space group $P2_1/c$.[25] Details of the crystals, data collections, and structure refinements are summarized in Table 1.

The structures were solved using the Patterson interpretation procedures of SHELXS-86[26] with the Pt and Fe atoms clearly located in the tangent expansion procedures. The remaining non-hydrogen atoms were found in a series of difference Fourier, least-squares refinement cycles. Refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$, was performed using SHELX-76.[27] In all cases hydrogen

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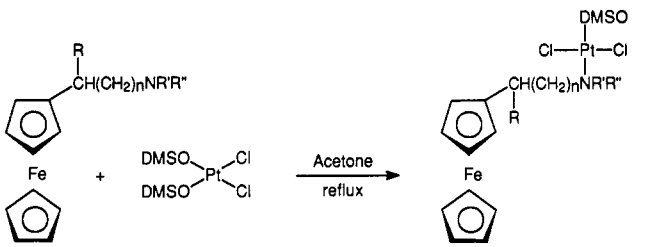
(25) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1966; Vol. 1.

(26) Sheldrick, G. M. SHELX-86, A program for the solution of crystal structures from diffraction data. University of Göttingen, 1986.

atoms were included in the refinements as fixed contributions to F_c, weighting schemes based on counting statistics were introduced, and the non-hydrogen atoms were refined anisotropically. For 1, the two unique molecules in the asymmetric unit were refined independently in alternating least-squares cycles. Final positional and equivalent thermal parameters for 1 and 5 are given in Tables 2 and 3.

Results and Discussion

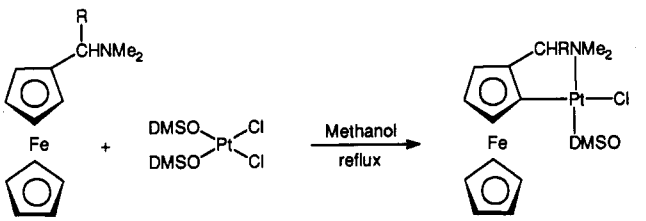
Reaction of *cis*-$Pt(DMSO)_2Cl_2$ with primary, secondary, and tertiary ferrocenylamines (η^5-$C_5H_4CHRNR'R''$)Fe(η^5-C_5H_5), in acetone or chloroform, produced *trans*-$PtCl_2(DMSO)$[(η^5-$C_5H_4CHRNR'R''$)Fe(η^5-C_5H_5)] in good yield (eq 1).



1 R = H; R' = R" = Me, n = 0
2 R = R' = R" = Me, n = 0
3 R = R' = R" = H, n = 1
4 R = R' = H; R" = Ph, n = 0

(1)

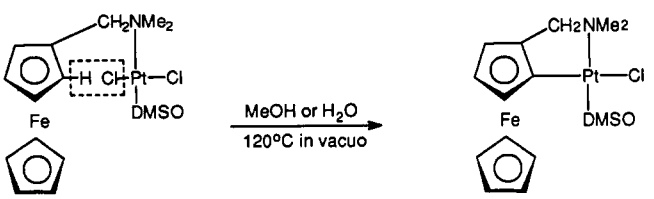
In basic solvents with heating, the reaction between *cis*-$PtCl_2(DMSO)_2$ and *tertiary* ferrocenylamines gave the novel platinocycles σ-Pt[(η^5-C_5H_5)Fe(η^5-$C_5H_3CHRNMe_2$)](DMSO)Cl (R = H, Me) (eq 2).



5 R = H
6 R = Me

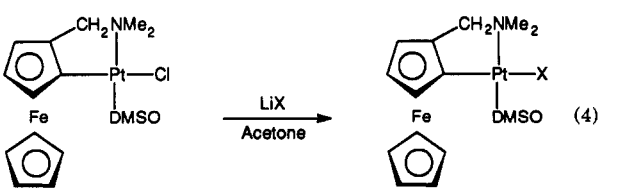
(2)

Yields are dependent on the solvent (*vide infra*) but were quantitative in methanol. The *trans* complexes 1 and 2 can be converted to their cycloplatinated analogues in the presence of water, methanol, or ethanol, or as a solid, by heating at 120 °C under reduced pressure (eq 3).



(3)

Despite the facility of these reaction with tertiary ferrocenylamines, no experimental procedure could be found for a cyclometalation transformation of the *trans* complexes of primary or secondary ferrocenylamines (3 and 4); a similar restriction is found in Pd(II) cyclometalation reactions.[3] Metathetical reactions of the chloro complex 5 and the appropriate lithium salt in acetone at room temperature gave the bromo and iodo derivatives in good yield (eq 4).



(4)

7 X = Br
8 X = I

All complexes 1–8 are yellow-orange, soluble in benzene, acetone, alcohols, and halogenated solvents, but insoluble in hexane. On standing in solution, they slowly oxidize denoted by the appearance of the characteristic green color of a ferrocenium species. Attempts to eliminate the remaining DMSO in the cyclometalated complexes by

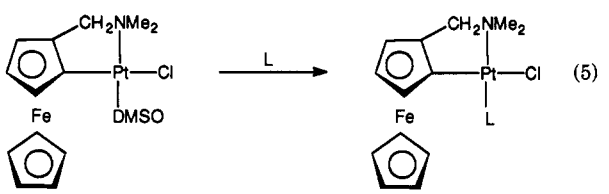
Table 2. Final Positional and Equivalent Thermal Parameters for 1

atom	*x/a*	*y/b*	*z/c*	$U_{eq}/U11$, Å^2
		Molecule 1		
Pt(1)	0.22232(4)	0.44137(3)	0.31722(3)	0.014
Cl(11)	0.1820(3)	0.3741(2)	0.2008(2)	0.024
Cl(12)	0.2742(2)	0.5000(2)	0.4365(2)	0.023
S(1)	0.1185(2)	0.2965(2)	0.4505(2)	0.018
O(1)	0.1985(7)	0.2292(6)	0.5185(6)	0.026
C(115)	0.024(1)	0.2114(9)	0.416(1)	0.026
C(116)	–0.012(1)	0.343(1)	0.522(1)	0.025
N(1)	0.3106(8)	0.5934(7)	0.1968(8)	0.020
C(113)	0.310(1)	0.603(1)	0.091(1)	0.027
C(114)	0.233(1)	0.6814(9)	0.217(1)	0.025
C(11)	0.4517(9)	0.6136(8)	0.1987(8)	0.015
C(12)	0.5402(9)	0.5242(9)	0.1912(9)	0.018
C(13)	0.573(1)	0.4398(9)	0.277(1)	0.025
C(14)	0.666(1)	0.378(1)	0.243(1)	0.034
C(15)	0.691(1)	0.423(1)	0.132(1)	0.029
C(16)	0.613(1)	0.513(1)	0.103(1)	0.028
Fe(1)	0.7381(1)	0.5368(1)	0.1831(1)	0.019
C(18)	0.789(1)	0.686(1)	0.178(1)	0.042
C(19)	0.816(1)	0.605(1)	0.264(1)	0.038
C(110)	0.906(1)	0.540(1)	0.232(1)	0.036
C(111)	0.935(1)	0.579(1)	0.122(1)	0.038
(C112)	0.862(1)	0.668(1)	0.090(1)	0.038
		Molecule 2		
Pt(2)	–0.40160(4)	0.05113(3)	0.69640(3)	0.014
Cl(21)	–0.2766(2)	–0.0146(2)	0.5809(2)	0.023
Cl(22)	–0.5169(3)	0.1250(2)	0.8072(2)	0.023
S(2)	–0.4172(2)	0.1956(2)	0.5586(2)	0.018
O(2)	–0.2946(7)	0.2602(6)	0.4954(7)	0.029
C(215)	–0.536(1)	0.2847(9)	0.586(1)	0.026
C(216)	–0.494(1)	0.153(1)	0.4802(9)	0.023
N(2)	–0.3855(8)	–0.0966(7)	0.8222(7)	0.021
C(213)	–0.448(1)	–0.1003(9)	0.9271(8)	0.021
C(214)	–0.452(1)	–0.1856(9)	0.807(1)	0.026
C(21)	–0.2399(9)	–0.1196(8)	0.8171(9)	0.017
C(22)	–0.1586(9)	–0.0323(8)	0.8219(8)	0.013
C(23)	–0.085(1)	0.0554(8)	0.7345(9)	0.020
C(24)	–0.014(1)	0.1179(9)	0.771(1)	0.025
C(25)	–0.046(1)	0.0712(9)	0.879(1)	0.024
C(26)	–0.135(1)	–0.0224(9)	0.9112(9)	0.019
Fe(2)	0.0376(1)	–0.0377(1)	0.8186(1)	0.017
C(28)	0.095(1)	–0.1820(9)	0.814(1)	0.027
C(29)	0.162(1)	–0.097(1)	0.723(1)	0.034
C(210)	0.234(1)	–0.029(1)	0.750(1)	0.035
C(211)	0.213(1)	–0.072(1)	0.859(1)	0.030
C(212)	0.1299(9)	–0.1659(9)	0.897(1)	0.026

Table 3. Final Positional and Equivalent Thermal Parameters for 5

atom	x/a	y/b	z/c	$U_{eq}/U11$, Å^2
Pt(1)	0.27757(2)	0.23815(2)	0.63696(2)	0.013
Cl(1)	0.3735(1)	0.0641(2)	0.6167(2)	0.023
S(1)	0.1388(1)	0.1510(2)	0.5425(2)	0.016
O(1)	0.0580(4)	0.1620(5)	0.6028(5)	0.022
C(15)	0.1488(6)	-0.0064(6)	0.5101(8)	0.023
C(16)	0.1007(7)	0.2099(7)	0.3887(7)	0.026
N(1)	0.4050(4)	0.3354(5)	0.7359(5)	0.016
C(13)	0.4582(7)	0.2657(7)	0.8483(8)	0.035
C(14)	0.4715(6)	0.3518(8)	0.6535(7)	0.027
C(1)	0.3807(6)	0.4580(7)	0.7779(7)	0.023
C(2)	0.2755(6)	0.4872(7)	0.7189(6)	0.020
C(3)	0.2107(5)	0.3935(7)	0.6544(6)	0.016
C(4)	0.1160(6)	0.4462(7)	0.6206(6)	0.021
C(5)	0.1227(6)	0.5680(6)	0.6645(7)	0.019
C(6)	0.2221(5)	0.5950(6)	0.7245(7)	0.019
Fe(1)	0.2061(1)	0.5484(1)	0.5435(1)	0.016
C(8)	0.3089(6)	0.5953(7)	0.4535(8)	0.029
C(9)	0.2453(7)	0.5057(7)	0.3823(7)	0.026
C(10)	0.1487(6)	0.5551(7)	0.3543(7)	0.025
C(11)	0.158(6)	0.6725(7)	0.4028(7)	0.026
C(12)	0.2496(6)	0.6982(7)	0.4662(7)	0.025

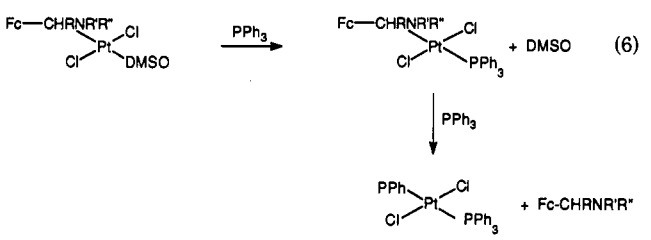
σ-donors, such as amines, were unsuccessful. That this is due to the intermediate *trans* effect and a relatively large *cis* effect of DMSO, compared to other ligands, was demonstrated by the facile substitution of DMSO by monodentate π-acceptor ligands to give σ-Pt[(η^5-C_5H_5)-Fe(η^5-$C_5H_3CH_2NMe_2$)]ClL′ (L′ = PPh_3, $P(OPh)_3$, CO) (eq 5). With chelate phosphines, coordination results in the displacement of both the DMSO and halide ion to give the salts [σ-Pt[(η^5-C_5H_5)Fe(η^5-$C_5H_3CH_2NMe_2$)]L-L]$^+X^-$.[28]



(5)

L = PPh_3, $P(OPh)_3$, CO
9 10 11

In contrast to the reactions with the cycloplatinated compounds, *trans*-$Pt(PPh_3)_2Cl_2$ is obtained from the reaction between PPh_3 and the *trans* derivatives 1–4. A possible route for this reaction is shown in eq 6; initial



(6)

substitution of the DMSO by the strongly *trans* directing π-acceptor leads to the elimination of the ferrocenylamine. Increased ligand lability in 1 compared to 5 is also shown by the rapid exchange reactions of 1 with other ferrocenylamines, but the extensive decomposition accompanying these reactions precludes their use in the synthesis of other *trans* derivatives.

(27) Sheldrick, G. M. SHELX-76, Program for crystal structure determination. University of Cambridge, 1976.
(28) Duffy, N. W.; McAdam, C. J.; Robinson, B. H.; Simpson, J. *Inorg. Chem.*, submitted for publication.

Table 4. Selected Bond Lengths and Angles for 3

Molecule 1			
Bond Lengths (Å)			
Pt(1)---Cl(11)	2.305(4)	N(1)---C(11)	1.50(1)
Pt(1)---Cl(12)	2.313(4)	N(1)---C(114)	1.50(2)
Pt(1)---S(1)	2.228(2)	N(1)---C(113)	1.49(2)
Pt(1)---N(1)	2.166(8)	S(1)---C(116)	1.77(1)
S(1)---O(1)	1.464(8)	S(1)---C(115)	1.79(2)
		C(11)---C(12)	1.51(2)
Bond Angles (deg)			
Cl(11)–Pt(1)–Cl(12)	175.9(1)	C(11)–C(12)–C(13)	124(1)
Cl(11)–Pt(1)–S(1)	92.4(1)	N(1)–C(11)–C(12)	114(1)
Cl(11)–Pt(1)–N(1)	92.3(3)	C(114)–N(1)–C(11)	108(1)
Cl(12)–Pt(1)–S(1)	86.5(1)	C(113)–N(1)–C(11)	107.6(8)
Cl(12)–Pt(1)–N(1)	89.2(3)	C(113)–N(1)–C(114)	107.5(9)
S(1)–Pt(1)–N(1)	173.3(3)	Pt(1)–N(1)–C(11)	111.3(6)
Pt(1)–S(1)–O(1)	117.0(3)	Pt(1)–N(1)–C(114)	107.4(6)
Pt(1)–S(1)–C(115)	113.6(4)	Pt(1)–N(1)–C(113)	114.9(8)
Pt(1)–S(1)–C(116)	107.0(4)	C(115)–S(1)–C(116)	99.3(6)
O(1)–S(1)–C(115)	108.9(5)	O(1)–S(1)–C(116)	109.5(6)
		C(11)–C(12)–C(16)	127.9(9)

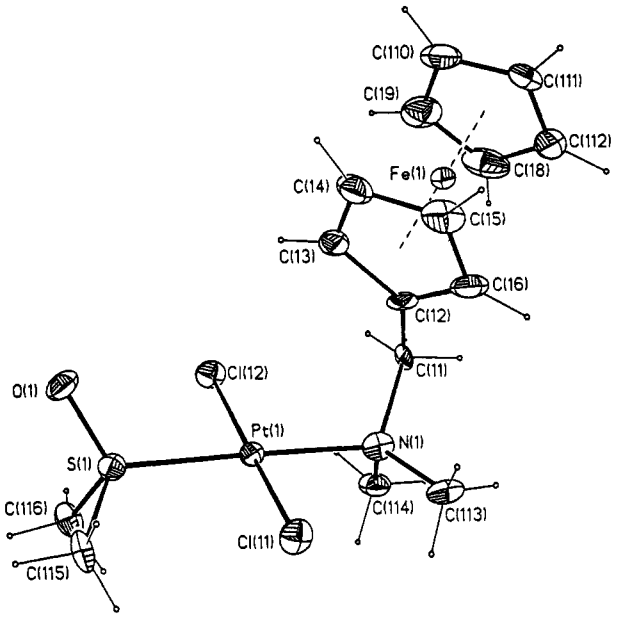
Characterization and Structure Determination. Characterization of these platinum complexes in solution has been achieved using ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR and IR but the solid state structures of 1 and 5 will be described first, as these give the fundamental stereochemistry of both the Pt(II) and ferrocenyl units and provide a basis for the interpretation of the spectroscopic data.

X-ray Crystal Structures of *trans*-$PtCl_2$(DMSO)[(η^5-$C_5H_4CH_2NMe_2$)Fe(η^5-C_5H_5)], 1, and σ-Pt[(η^5-C_5H_5)Fe(η^5-$C_5H_3CH_2NMe_2$)](DMSO)Cl, 5. Selected bond length and angle data for 1 are given in Table 4. Compound 1 crystallizes with two unique molecules in the asymmetric unit of the triclinic unit cell (Figure 1). Individual molecules in the unit cell are well separated with the closest contact, not involving hydrogen atoms, between C(116) and O(2) being 3.31(2) Å. Small differences in bond lengths and angles are likely to result from the effects of molecular packing. Molecular parameters for molecule 1 of 1 will be used in the subsequent discussion.

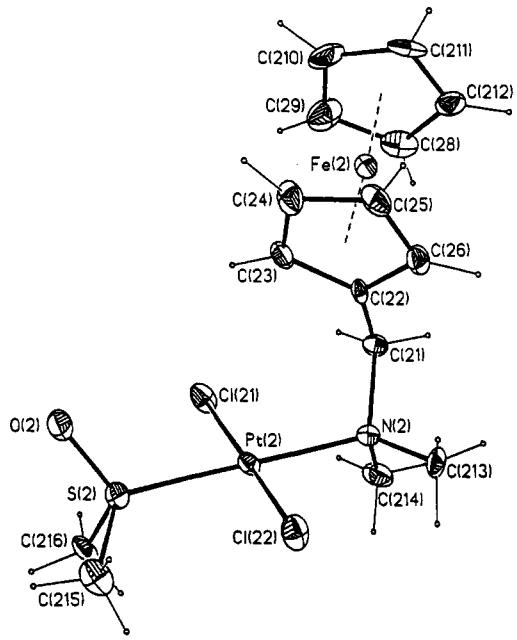
The platinum atom has the expected square-planar coordination with two mutually *trans* chloride ions, an S-bound DMSO, and the N-bound ferrocenylamine ligand completing the coordination sphere. Some deviation from idealized square-planar geometry is apparent with the angles Cl(11)–Pt(1)–Cl(12) 175.9(1)° and S(1)–Pt(1)–N(1) 173.3(3)° and deviations from the PtL_4 ring plane Pt(1) –0.0041(6), Cl(11) 0.076(3), Cl(12) 0.075(3), S(1) –0.0173(3), and N(1) –0.182(9). The Pt–Cl bonds are similar in length to those found in a variety of other *trans*-dichloroamino(sulfoxide)platinum(II) complexes[29-32] and, in contrast to the values observed for 5, the Pt(1)–S(1) bond (2.228(2) Å), lies in the normal range. Evidence for possible *trans* influence by the DMSO ligand in these systems is found in the long Pt–N bond, 2.166(8) Å, compared to values in the range 2.03–2.07 Å in similar compounds. Other features of the coordinated DMSO ligand are unremarkable.

Selected bond length and angle data for 5 are given in Table 5. Compound 5 consists of well separated monomeric molecules with no unusual intermolecular contacts. A perspective view of the molecule is shown in Figure 2

(29) Melanson, R.; Rochon, F. D. *Acta Crystallogr., Sect. C* **1984**, *C40*, 793.
(30) Lock, C. J. L.; Speranzini, R. A. *Can. J. Chem.* **1976**, *54*, 53.
(31) (a) Melanson, R.; Rochon, F. D. *Inorg. Chem.* **1978**, *17*, 679. (b) Melanson, R.; Rochon, F. D. *Acta Crystallogr.* **1978**, *B34*, 1125.
(32) Caruso, F.; Spagna, R.; Zambonelli, L. *Acta Crystallogr.* **1980**, *B36*, 713.



a



b

Figure 1. Perspective views of the two unique molecules of 1, showing the atom-numbering scheme: (a) molecule 1; (b) molecule 2.

which defines the atom numbering scheme. The Pt atom has a distorted square-planar environment; deviations of the donor atoms from the PtL_4 ring plane are Pt(1) 0.000(3), S(1) −0.005(2), N(1) −0.056(6), Cl(1) 0.005(2), and C(3) 0.090(7). In comparison to 1 one *trans* Cl^- ion is lost with the formation of a σ-Pt–C bond *ortho* to the amine functionality on the cyclopentadienyl ring. Thus, cycloplatination produces a five-membered $C_{Cp}CH_2N(Pt)C_{Cp}$ ring system and the coordination sphere of the Pt atom has a Cl^- ion *trans* to the metalated C atom with the N donor atom of the ferrocenylamine *trans* to the S atom of the coordinated DMSO. The metallocycle ring is non-

Table 5. Selected Bond Lengths and Angles for 5

Bond Lengths (Å)			
Pt(1)---Cl(1)	2.395(2)	C(1)---C(2)	1.50(1)
Pt(1)---S(1)	2.195(2)	C(2)---Fe(1)	2.046(7)
Pt(1)---N(1)	2.141(6)	C(3)---Fe(1)	2.091(7)
Pt(1)---C(3)	1.988(7)	C(4)---Fe(1)	2.052(7)
S(1)---O(1)	1.480(5)	C(5)---Fe(1)	2.022(7)
S(1)---C(15)	1.781(7)	C(6)---Fe(1)	2.022(7)
S(1)---C(16)	1.767(8)	Fe(1)---C(8)	2.043(7)
N(1)---C(13)	1.49(1)	Fe(1)---C(9)	2.060(7)
N(1)---C(14)	1.489(9)	Fe(1)---C(10)	2.038(7)
N(1)---C(1)	1.496(9)	Fe(1)---C(11)	2.060(7)
		Fe(1)---C(12)	2.026(7)
Bond Angles (deg)			
Cl(1)–Pt(1)–S(1)	94.1(1)	C(14)–N(1)–C(1)	108.5(6)
Cl(1)–Pt(1)–N(1)	91.1(2)	N(1)–C(1)–C(2)	110.1(6)
Cl(1)–Pt(1)–C(3)	173.8(2)	C(1)–C(2)–C(3)	119.8(6)
S(1)–Pt(1)–N(1)	174.6(2)	C(1)–C(2)–C(6)	130.1(7)
S(1)–Pt(1)–C(3)	91.6(2)	C(3)–C(2)–C(6)	109.8(7)
N(1)–Pt(1)–C(3)	83.4(3)	Pt(1)–C(3)–C(2)	113.7(5)
Pt(1)–S(1)–O(1)	117.3(2)	Pt(1)–C(3)–C(4)	140.2(6)
Pt(1)–S(1)–C(15)	114.2(3)	Pt(1)–C(3)–Fe(1)	125.7(3)
Pt(1)–S(1)–C(16)	107.9(3)	C(2)–C(3)–C(4)	106.1(6)
O(1)–S(1)–C(15)	106.4(3)	C(3)–C(4)–C(5)	108.7(7)
O(1)–S(1)–C(16)	109.1(4)	C(4)–C(5)–C(6)	108.9(7)
C(15)–S(1)–C(16)	100.5(4)	C(2)–C(6)–C(5)	106.4(6)
Pt(1)–N(1)–C(13)	110.3(5)	C(9)–C(8)–C(12)	107.0(7)
Pt(1)–N(1)–C(14)	109.7(4)	C(8)–C(9)–C(10)	106.9(7)
Pt(1)–N(1)–C(1)	112.0(4)	C(9)–C(10)–C(11)	109.6(7)
C(13)–N(1)–C(14)	108.1(7)	C(10)–C(11)–C(12)	107.7(7)
C(13)–N(1)–C(1)	108.2(6)	C(8)–C(12)–C(11)	108.7(7)

planar, with the methylene C atom displaced significantly from the PtL_4 plane. Formation of metallocyclic rings locks the conformation of both rings, such that the H atoms on the methylene group of the ferrocenylamine, the amine methyl groups, and the methyl groups of the DMSO ligands are no longer equivalent with respect to the PtL_4 ring plane; this is clearly evident in the NMR spectra (*vide infra*). Disubstitution of the cyclopentadienyl ring confers planar chirality on the molecule[33] and the structure shown in Figure 2 has an S configuration. However, both the *R* and *S* configurations occur in the centrosymmetric unit cell.

Bond lengths from Pt(II) to the ligated atoms can be compared with those for the closely related compound chloro(dimethyl sulfide)(2-picolinyl) (chloromethyl)-platinum(II),[34a] which has a donor set identical to that of **5**. There is excellent agreement between the Pt–C and Pt–Cl bond lengths in both compounds; Pt–C 1.988(7), Pt–Cl 2.395(2) Å for **5**, and Pt–C 1.987(10), Pt–Cl 2.397(3) Å for the dimethyl sulfide complex. The Pt–C bond distance in **5** is also similar to those found in a platinum–cyclooctadiene complex with two σ-bound 1,1′-dichloroferrocene ligands.[34b] Comparison of these relatively long Pt–Cl distances with the corresponding distances (Pt–Cl(1) 2.305(4), Pt–Cl(2) 2.313(4) Å) in **1**, where the two chloro ligands are mutually *trans*, attests to the significant *trans* influence of the σ-PtC functionality. While the DMSO ligand has a notable *trans* effect, its *trans* influence is generally small.[29] Surprisingly therefore, the Pt(1)–N(1) distance in **5** (2.141(6) Å) is long, in comparison to that observed in the dimethyl sulfide complex (Pt–N 2.044(7) Å). The corresponding Pt–S bond lengths, 2.195(2) Å for **5** and 2.266(3) Å for the dimethyl sulfide complex, show an inverse relationship. Whether these observations

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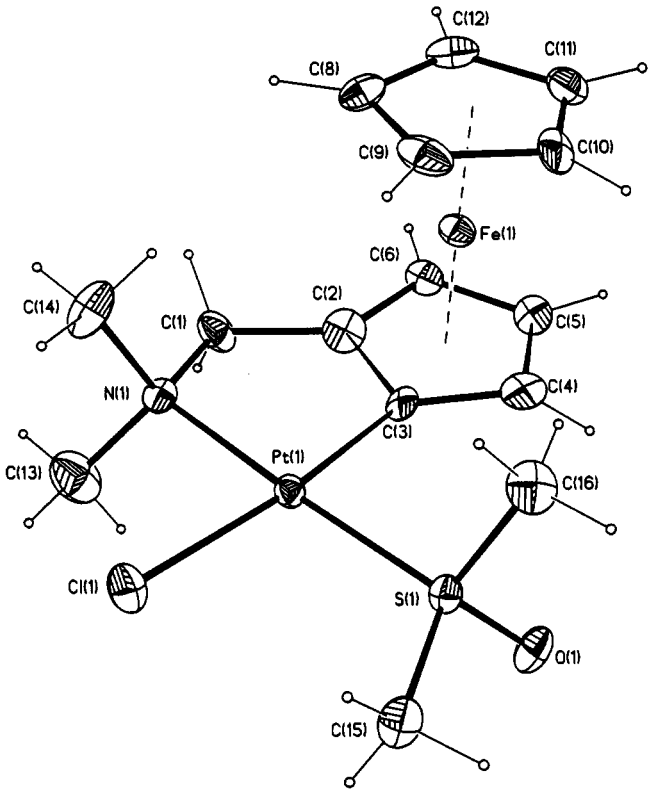

Figure 2. Perspective view of **5**, showing the atom-numbering scheme.

signal an unusual *trans* influence of the DMSO ligand in the cyclometalated ferrocene system or are a consequence of the steric strain imposed by the formation of the five-membered platinocyclic ring cannot be determined unambiguously. The S atom of the coordinated DMSO in **5** is in an approximately tetrahedral environment and the S–O and S–C distances are unremarkable and differ little from these found in the free ligand.[35]

The cyclopentadiene rings of the ferrocene moieties in both **1** and **5** are almost eclipsed. The rings are planar and the tilt angles between them are not exceptional; 1.9(5)° for **1** and 4.9(3)° for **5**. The Pt-bound cyclopentadiene ring in **5** is almost coplanar with the adjacent five-membered platinocyclic ring (interplanar angle 1.0(2)°). There are no systematic variations within the Fe–C and C–C bond distances with the exception of the Fe(1)–C(3) distance to the cyclometalated C atom which is significantly longer than the norm; Fe(1)–C(3) 2.101(7) Å. These observations are mirrored in two recently reported structures in which ferrocene moieties are involved in cyclometalated Pd complexes.[10,36]

Spectroscopy. IR. For complexes **1–4** the single ν_{Pt-X} band is consistent with a *trans*-dichloro configuration;[37] the ν_{Pt-Cl} modes of the platinocycles are of lower energy than those of *cis*-$Pt(DMSO)_2Cl_2$ and equivalent *trans* intermediates. For example, ν_{Pt-Cl} for *cis*-$Pt(DMSO)_2Cl_2$ are 320 and 333 cm^{-1}, and 339 cm^{-1} for **1**, whereas ν_{Pt-Cl} for the series of complexes σ-$PtCl[(\eta^5\text{-}C_5H_3CH_2NMe_2)Fe(\eta^5\text{-}C_5H_5)(L)]$ are in the range 272–303 cm^{-1}. The spectroscopic and structural data and unpublished electrochemical work[19] suggest that the σ-PtC_5H_3 interaction is particularly strong and this trend in ν_{Pt-Cl} may be attributed to the *trans* influence of the σ-C bond of the cycloplatinated complexes which causes the Pt—X bond to be weakened. The $\nu_{S=O}$ mode in DMSO complexes is generally obscured by overlap or mixing with other bands such as C—M rocking modes so the $\nu_{S=O}$ assignments were checked by comparison with the spectra of the corresponding DMSO-d_6 complexes. In metal–dialkyl sulfoxide complexes, the shift of the S=O stretching frequency of DMSO to lower values on binding to oxygen and to higher values on binding to sulfur is well established[38] and the $\nu_{S=O}$ values, which are all in the range 1122–1149 cm^{-1}, are consistent with a S-bonded DMSO configuration. Comparative spectra of the isotopically-substituted compounds also allowed an assignment of the ν_{Pt-S} mode between 353 and 380 cm^{-1}.

NMR. DEPT and HETCOR ^{13}C NMR data[1] and ^{31}P data confirmed the assignments and conclusions from the ^1H NMR and will not be discussed in detail; data are given for each complex in the Experimental Section. Methylene, NMe, and SMe resonances were differentiated using the DMSO-d_6 analogues, and the profile and chemical shifts of these resonances were diagnostic for the *trans* or cycloplatinated complexes.

^1H NMR. ^1H NMR spectra were well resolved and ^{195}Pt–^1H satellites were generally observed, making assignments straightforward. The appearance of satellites on the NMe resonances confirmed that coordination of the ferrocenylamine was via the nitrogen donor in all cases and the observation of SMe resonances at ~3.5 ppm is consistent with S-bound DMSO. The NMe and SMe groups in *trans* derivatives are stereochemically equivalent whereas in the cycloplatinated complexes they are inequivalent due to the planar chirality with respect to the coordination plane of the platinum atom. Hence the number of discrete resonances for a particular group readily distinguishes the two classes of compound, as does the chemical shift; for example, δ(NMe) for **1** is 2.66 ppm but 2.88 and 3.19 ppm for the NMe doublet of **5**. The latter resonance to lower field is assigned to the out-of-plane NMe group pointing toward the Pt(II) atom. Deshielding of the NMe resonance upon metalation and the fact that the coupling constants ($^3J_{Pt-H}$) are smaller are both indicative of a good donor group *trans* to the NMe and again reflect the strong σ-Pt–C interaction. For the series **5–7** the magnitude of the three-bond $^3J_{Pt-H}$ increases Cl < Br < I due to dependence of the coupling constants (J_{Pt-H}) on the mutual polarizability at the platinum, which in turn varies with the electronegativity of the *cis* halide.[39] The methylene protons of the amine moiety in the cycloplatinated complexes are similarly nonequivalent and give an AB system of doublets (J_{AB} = 14.2 Hz, $\Delta\nu_{AB}$ = 81.3 Hz). In general, the resonance of the unsubstituted Cp protons appear upfield of those for the Cp protons of the substituted ring for the trans intermediates **1–4** but an upfield shift of the latter set upon metalation makes an assignment for the ferrocenyl ring protons difficult. However, 2-D ^{13}C NMR readily distinguished the Cp ring carbon resonances (see Experimental Section).

^{195}Pt. ^{195}Pt NMR provided definitive data on the coordination sphere and structure. For the *trans* derivatives the ^{195}Pt chemical shift fell within the range −3040 to −3100 ppm, characteristic of a $PtNSX_2$ donor set[39] (an

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analogue is *trans*-$PtCl_2(NH_3)$(DMSO) for which ^{195}Pt is −3067 ppm; cf. −3075 ppm for **4**). A $PtNOX_2$ donor set is expected to give values in the range −1600 to −1800 ppm, confirming that the DMSO is S-bound in solution. Cycloplatination results in a large upfield shift to a range −3690 to −4580 ppm, making for easy identification of this type of product. There are no closely comparable data in the literature, but these chemical shifts are similar to those for compounds with a $PtCl_2R_2$ or PtR_2(COD) donor set.[39] A decrease in halide content normally causes a downfield ^{195}Pt shift, so the upfield shift upon cycloplatination is a direct consequence of σ-PtC bond formation. An upfield shift is typical of a strong donor interaction with Pt(II), and it substantiates the conclusion that fusion to the Cp ring polarizes the Pt(II) ion, producing a strong *trans* effect. Otherwise, empiricisms derived from earlier ^{195}Pt chemical shift data[40] hold for these ferrocenylamine complexes. Halogen dependence gives an upfield shift in the order I > Br > Cl, but the dependence is not so marked as in complexes where the halide is *cis* to the S-donor; for example, similar shifts in *trans*-[PtClX$(SMe)_2$] span 1700 ppm[24] compared with 100 ppm for the cycloplatinated derivatives **5**–**7**. Presumably, the mutual polarizability is dominated by the σ-PtC and Pt–S bonds counteracting any variation due to the halide. Substitution of DMSO by phosphine or CO causes the expected upfield shift to a range −3930 to −4173 ppm. Molecule **5** has planar and **6** both planar and central elements of chirality, and four configurations, *R,R*, *R,S*, *S,R*, *S,S*, could evolve in the formation of **6**. Nevertheless, for **5** and **6** only a single ^{195}Pt resonance is seen in the temperature range 100–320 K. This is not unexpected for **5** as the paramagnetic contribution to the ^{195}Pt chemical shift is unlikely to be significantly different for the two diastereoisomers. With **6** the C-methyl can have an "up" (*R*) or "down" (*S*) orientation with respect to the planar ring[41] and the individual ^{195}Pt chemical shifts should be resolvable. The observation of a single ^{195}Pt resonance implies that the cycloplatination reaction is stereoselective (*vide infra*).

Reaction Pathway of the Cycloplatination Reaction. Apart from their novelty for Pt(II) chemistry, these cycloplatination reactions involving ferrocenylamines provided a special opportunity to investigate the cyclometalation process, as the intermediate *trans* complexes have a finite lifetime. Questions raised by the cycloplatination reaction include the opportunistic role of the DMSO ligand, the role of the solvent and the stereochemical nuances. The reaction pathway was studied in detail by following the reaction between *cis*-Pt$(DMSO)_2Cl_2$ and (η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2NMe_2$) (≡FMA hereafter) by ^{195}Pt and ^1H NMR, as well as varying the synthetic parameters.

Pt(II) precursors other than Pt$(DMSO)_2Cl_2$ were tried without success. Nitrile complexes Pt$(RCN)_2X_2$ invariably underwent nucleophilic attack by the ferrocenylamine at the nitrile carbon to give imine complexes[19] while organoplatinum(II) complexes gave substitution products L_2PtX_2 in low yield or did not react. It seems that *cis*-Pt$(DMSO)_2X_2$ complexes provide the appropriate thermodynamic and kinetic environment to allow for the formation of the intermediates with a *cis* orientation of halide and Cp ring proton which then undergo intramolecular ring fusion. The halide leaving group has little influence in the reactions, as ^{195}Pt NMR studies show that similar *trans* complexes can be prepared from *cis*-Pt$(DMSO)_2X_2$, X = Br, I.

Table 6

Effect of Solvent on the Reaction between *cis*-Pt$(DMSO)_2Cl_2$ and FMA (1:2 Molar Ratio)

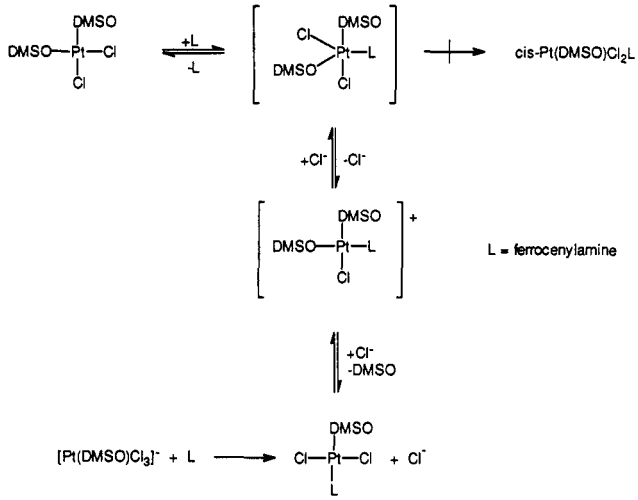
solvent	product	temp (°C)	time (min)	yield (%)
acetone	**1**	60–70	30	91
benzene	**1**	70	30	67
THF	**1**	60–70	30	60
chloroform	**1**	20	240	40
methanol	**5**	70–80	30	76
water	*a*	60–70	30	

Effect on Solvent for the Conversion of *trans*-Pt$(DMSO)Cl_2$[(η^5-$C_5H_4CH_2NMe_2$)Fe(η^5-C_5H_5)] to the Cycloplatinated Product σ-Pt[(η^5-C_5H_5)Fe(η^5-$C_5H_3CH_2NMe_2$)(DMSO)Cl]

solvent	product	temp (°C)	time (h)	yield (%)
methanol	**5**	20	16–20	80
water	**5**	60–70	0.5	60
water	*b*	20	27	
ethanol	*a*	20	27	
ethanol	**5**	60–70	0.5	65
tert-butyl alcohol	**5**	60–70	0.5	68
DMSO	*b*	45	1	

[a] Mixture of products (including **1** and **5**). [b] No reaction.

Scheme 1



Formation of Trans Intermediates. Table 6 shows how the product and yield obtained from the reaction between *cis*-Pt$(DMSO)_2Cl_2$ and FMA varies with the solvent. Nonpolar solvents offer the best medium for the isolation of the *trans* derivatives simply because cycloplatination does not occur in these solvents. Excess ligand has no effect on the rate of this step of the reaction, while, in water, protonation of the ligand effectively competed with complexation so that the salt $[FMAH]^+$ is preferentially formed.

Several studies of the reactions between *cis*-Pt$(DMSO)_2Cl_2$ and N-donors have shown[40,41] that the stereochemistry is determined by an interplay between *trans* effects, steric factors, and the involvement of cationic species. The reaction pathway proposed by Annibale et al.,[40] adapted for the reactions of ferrocenylamines, is given in Scheme 1. To test this scheme and to define the role of cationic species, NMR studies were carried out in different solvents. ^{195}Pt NMR spectra, recorded at 15-min intervals for reactions, in both $CDCl_3$ and acetone-d_6, show only one new ^{195}Pt resonance at −3044 ppm due to

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1, which grows smoothly at the expense of the resonance due to *cis*-$PtCl_2(DMSO)_2$ at −3466 ppm; after 4 h 1 is the sole product. The reactions were also followed by ^1H NMR at 1-min intervals in acetone and nitromethane at 20 °C using the NMe_2 and DMSO resonances as markers on the assumption that the chemical shifts for a *trans* FMA–Pt–Cl (σ-donor) linkage would be significantly different from a *trans* FMA–Pt–DMSO (π-acceptor) linkage; the SMe resonance should also show different J_{Pt-H} coupling depending on the coordination geometry. New resonances due to the *trans* product grew in concert with the disappearance of the SMe resonance of *cis*-$Pt(DMSO)_2Cl_2$. A good pseudo-first-order plot was obtained for the appearance of the *trans* product resonances with $k = (1.11 \pm 0.03) \times 10^4$ s^{-1} in acetone, which suggested that *cis*-$Pt(DMSO)Cl_2L$ is not an intermediate. These data do not preclude the intermediacy of the ionic species *cis*-$[Pt(DMSO)ClL]^+$, as the coordination of Cl^- to this species would be fast, but there is no evidence in the δ(SMe) resonance region for small concentrations of ionic products (cf. Figure 1 of ref 40). The reaction of FMA with $[Pt(DMSO)Cl_3]^-$, a counterion which is in equilibrium with *cis*-$[Pt(DMSO)_2Cl_2]$ once Cl^- ion abstraction begins, was also followed by ^{195}Pt and ^1H NMR. Again the only product resonances were those of 1 (eq 7) and in this respect the ferrocenylamine is behaving similarly to nucleoside ligands.[41]

$$[Pt(DMSO)Cl_3]^- + FMA \rightarrow \textit{trans}\text{-}[Pt(DMSO)(FMA)Cl_2] + Cl^- \quad (7)$$

The NMR data for the FMA reactions therefore show that there are no other observable products formed during the conversion of *cis*-$Pt(DMSO)_2Cl_2$ to the *trans* intermediate 1, and preliminary NMR data support this conclusion for primary and secondary ferrocenylamines as well. This is consistent with other work with N-donor ligands. Because basic and sterically nondemanding ligands react more rapidly with $[Pt(DMSO)_2Cl_2]$, kinetic control is determined by the greater *trans* effect of Cl^- than the N-donor, which assuming the intermediacy of the transient ionic species, leads to a *trans* configuration for the $[Pt(DMSO)Cl_2L]$ intermediates in the cycloplatination reaction. Since FMA is relatively congested around the N-donor site, this might influence the stability of the five-coordinate transition state[42] but the absence of an *ortho* substituent on the Cp ring would be necessary to drive the stereochemistry toward the *cis* isomer.

Cycloplatination. ^{195}Pt and ^1H NMR data confirm that 1 is converted directly to the cyclometalated product, 5, in a mixture of acetone-d_6/methanol-d_6. After $t = 2$ h, a new ^{195}Pt resonance begins to appear at −3763 ppm due to 5 and by $t = 6$ h the resonance due to the *trans* precursor had disappeared. Similarly, no resonances other than those of 1 or 5 were detected in the ^1H NMR spectra.

Table 6 shows that conversion to 5 is optimized in polar solvents and with excess ligand; the small yield in acetone is attributed to the presence of water in the solvent during the reaction. These results support an intramolecular mechanism whereby the HCl is removed under the influence of a base and the efficacy of the reaction does roughly follow the pK_a of the solvent. Nevertheless, this must be a simplification, as the presence of DMSO or PPh_3 in proportions >10% effectively blocks the cycloplatination reaction. Rather than a synchronous HCl removal, it is suggested that dissociation of Cl^- allows weak coordination of the solvent prior to ring fusion; presumably, coordination of the strongly bound, but weakly basic, DMSO or PPh_3 terminates this pathway. Base-assisted HCl removal is well-known in cyclopalladation reactions, and indirect support for this mechanism comes from recent work of Bednarski and co-workers[5a] who found that cycloplatination of a benzylamine ligand is driven by the hydrolysis of a Pt–Cl bond. A similar explanation can be given for the unusual cycloplatination of the primary amine, benzylamine, described by Avushu et al.,[5b] in which they utilized an iodide/$AgBF_4$ route to provide an aquo precursor. This synthetic methodology was tried using the *trans* primary ferrocenylamine complex 4 but with a Ba(II) salt as the halide precipitation agent as Ag(I) oxidizes the ferrocenyl unit. Unfortunately, the presumed iodo complex, prepared from 4 by a metathetical reaction with LiI, rapidly decomposed, even with free FMA present, with no evidence for cycloplatination. Several parameters distinguish the tertiary complexes from their primary or secondary analogues. First, intramolecular H-bonding can stabilize the *trans* precursor. Second, the ^{195}Pt NMR data indicate that the primary and secondary ferrocenylamines coordinate more strongly than tertiary ones. Third, the α-protons of the substituted ring for 1 are deshielded, that is more acidic, than those for 3 and 4 (4.52 (1), compared to 4.32 and 4.12 for 3 and 4, respectively). Fourth, in the case of 3, metalation would require the formation of a six-membered ring. Fifth, it is possible that the steric congestion around the Pt(II) plane in tertiary ferrocenylamine derivatives, clearly seen in computer models, would be relieved upon fusion to the Cp ring. From this viewpoint it is significant that cycloplatination reactions with a ferrocenylamine having a sterically-demanding $-CH(Me)NMe_2$ functionality are very rapid (the *trans* precursor has a half-life of ~1 min in boiling methanol) and it is not possible to isolate the *trans* precursor for the ferrocenylamine with a $-CH(Me)NMe_2$ functionality on both Cp rings.[18]

Metalation reactions of chiral ferrocenylamines are stereospecific, arising from a combination of the amine nitrogen directing electrophilic attack at the cyclopentadienyl ring and steric effects involving the movement of the *C*-methyl away from the interplane area.[21c,41] A similar proposal can be advanced to explain the stereospecificity for the cycloplatination of 6. Butler et al.[41] have shown that the *C*-methyl lies predominantly in the interplane region in solution and cycloplatination with this configuration would lead to the *R,S* or *S,S* diastereoisomers; the least favored conformation with the *C*-methyl outside the interplane region would give rise to the *R,R or S,R* diastereoisomers. This predisposition to orientate the *C*-methyl in the interplane area is also found in the bis(platinum) complexes.

Conclusion

Metallocene-based complexes are of particular interest[43] because they are likely to have a different cytotoxic

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mechanism and to show activity against cisplatin-resistant tumor systems.[44] The new ferrocenylamine complexes described herein offer a new versatile drug regime which may act on DNA either as a cisplatin type compound or as a metallocene. In particular, the addition of functionality on the Cp rings allows the synthesis of complexes with more than one Pt(II) center.[18] Preliminary cytotoxicity studies have demonstrated that complexes 1–8 are indeed less toxic, particularly toward kidney and liver damage, although their antiproliferative properties were disappointing.[15] In part, this is due to their poor solubility in water, necessitating delivery via a medium such as peanut oil. This has been overcome in a new sequence of complexes where the halide anion is replaced by carboxylate anions.[19] Oxidation of the ferrocenyl unit is also possible, giving added pharmacological value, and the ability to "tune" the redox potential from +0.8 to 0.0 V is potentially of great benefit. These aspects of cycloplatinated complexes will be delineated in future papers.

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Supplementary Material Available: Full tables of bond length and angle data, anisotropic thermal parameters, hydrogen positional and thermal parameters, and mean plane data (15 pages). Ordering information is given on any current masthead page.

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