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Easy access to diastereomerically pure platinacycles†

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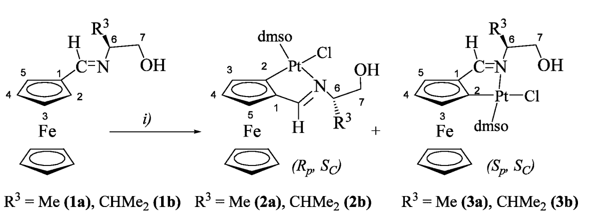
The synthesis of the first examples of diastereomerically pure platinacycles having simultaneously a chiral carbon and a σ[Pt–C(sp^2, ferrocene)] bond is described.

The synthesis and study of the potential applications of cycloplatinated compounds have attracted great interest in recent years.[1–4] Most of the articles published so far are focused on complexes having a σ(Pt–Csp^2, aryl), or to a lesser extent a σ(Pt–Csp^3) bond. Platinacycles with a σ(Pt–Csp^2, ferrocene) bond are not common.[5–9] Some authors have shown that chiral platinacycles can be potentially useful in asymmetric catalytic processes.[2] Although it is well known that cyclometallation of N-donor ferrocenyl ligands is expected to induce chirality, enantio- or diastereomerically pure platinacycles with a σ(Pt–Csp^2,ferrocene) bond are really scarce. Cycloplatination of [(η^5-C_5H_5)Fe{(η^5-C_5H_4)CH_2NMe_2}] **(I)** or [(η^5-C_5H_5)Fe{[(η^5-C_5H_4)C(R^1)=NR^2}] **(II)** (with R^1 = H, Me or Ph and R^2 = OH, $(CH_2)_3NMe_2$ or phenyl groups) lead to the enantiomers R_p and S_p.[5–7] Ryabov *et al.*[8] have reported that the reaction of equimolar amounts of **I** and the enantiopure platinum(II) sulfoxide: *cis*-[$PtCl_2${(S_S)–S(O)Me(C_6H_4-4-Me)}$_2$] produced the two diastereomers [(R_p,S_S) and (S_p,S_S)] of [Pt{[(η^5-C_5H_3)CH_2NMe_2]Fe(η^5-C_5H_5)}Cl(dmso)] [in a molar ratio (R_p,S_S)/(S_p,S_S) = 1.3].

In the view of these findings and due to our present interest in diastereomerically pure metallacycles derived from N-donor ferrocenyl ligands, we decided to use a different strategy to afford platinacycles with σ[Pt–Csp^2, ferrocene] bonds based on the use of ferrocene derivatives arising from **II** by incorporation of a stereogenic carbon atom in the vicinity of the imine nitrogen. With this aim we prepared the novel ferrocenyl Schiff bases (S_C)-[(η^5-C_5H_5)Fe{(η^5-C_5H_4)C(H)=NCH(R^3)CH_2OH}] {with R^3 = Me (**1a**) or $CHMe_2$ (**1b**)} (Scheme 1) and studied their reactivity with *cis*-[$PtCl_2$(dmso)$_2$][10] under different experimental conditions. Treatment of **1a** or **1b** with *cis*-[$PtCl_2$(dmso)$_2$] and NaOAc (in a **1**:Pt(II):OAc$^-$ molar ratio = 1:1:2) in a toluene/methanol mixture under reflux for 3 days, produced the two diastereomers of [Pt{[(η^5-C_5H_3)C(H)=N–CH(R^3)CH_2OH]Fe(η^5-C_5H_5)}Cl(dmso)] {with R^3= Me or $CHMe_2$ (**2,3a–b**) Scheme 1[11]} and small amounts of ferrocenecarboxaldehyde (FcCHO) as a by-product. In contrast with the results reported for the cycloplatination of **I**,[8] when the reactions were performed in the absence of NaOAc, [Pt{(η^5-C_5H_5)Fe{[(η^5-C_5H_4)C(H)=N–CH(R^3)CH_2OH]}-Cl_2(dmso)], (**4**) {R^3 = Me (**4a**) or $CHMe_2$ (**4b**)} were isolated.



Scheme 1 *cis*-[$PtCl_2$(dmso)$_2$] and NaAcO (in a ligand:Pt(II):OAc$^-$ molar ratio of 1:1:2) in a toluene/methanol mixture under reflux for 3 days (see text and reference 11).

Although **4** can be partially transformed in the corresponding platinacycles by treatment with the equimolar amount of NaOAc in methanol or toluene under reflux, longer reaction periods were required ($t \geq 6$ days), the yields were smaller and FcCHO and *cis*-[Pt{(η^5-C_5H_5)Fe[(η^5-C_5H_4)C(H)=NCH(R^3)CH_2O]Cl(dmso)], (**5**) {R^3 = Me (**5a**) or $CHMe_2$ (**5b**)} were also isolated. Besides that, when equimolar amounts of **1**, *cis*-[$PtCl_2$(dmso)$_2$] and NaOAc were refluxed in methanol, toluene (or mixtures of both) for different reaction periods (from 6 h to 10 days), FcCHO and **2–5**, were obtained. The molar ratios **4**:**5** and **4**:(**2** and **3**) decreased with time, thus suggesting that **4** may be an intermediate product in the formation of **2**, **3** and **5**.

Compound **3b** has been characterised by X-ray diffraction[12] (Fig. 1). In each molecule, the platinum atom is in a slightly distorted square-planar environment and bond lengths involving the platinum(II) are similar to those reported for related platinacycles.[16] The distances C(12)–H(12)···Cl and C(18)–H(18)···Cl suggest intramolecular C–H···Cl interactions. In the crystal the molecules are associated by hydrogen bonds involving the C(3)–H(3) bond and the O(2) atom of a proximal molecule thus leading to a chain which stacks along the *b*-axis.

Due to the increasing interest on the electrochemical properties of cycloplatinated complexes,[5,17] we have also undertaken an electrochemical study based on cyclic voltammetry for **1–3a,b**.[18] The formation of the σ[Pt–C(sp^2,ferrocene)] bond produces a shift of the ferrocene-centred transition to more cathodic potentials in good agreement with the results reported for [Pt{[(η^5-C_5H_3)C(Me)=NOH]Fe(η^5-C_5H_5)}Cl(dmso)].[5]

The work presented here has allowed us to establish the best experimental conditions required to prepare and isolate the diastereomers [(**2a,3a**) and (**2b,3b**)] of [Pt{[(η^5-C_5H_3)C(H)=N–CH(R^3)CH_2OH]Fe(η^5-C_5H_5)}Cl(dmso)] {R^3 = Me or $CHMe_2$}. Besides their potential interest in homogeneous catalysis,[2] they are also useful precursors for the synthesis of other platinacycles arising from **2–3a,b** by ligand exchange reactions. In addition, since it has been reported that [Pt{[(η^5-C_5H_3)–CH_2NMe_2]Fe(η^5-C_5H_5)}Cl(dmso)],[7] (in which the environment of the Pt(II) is very

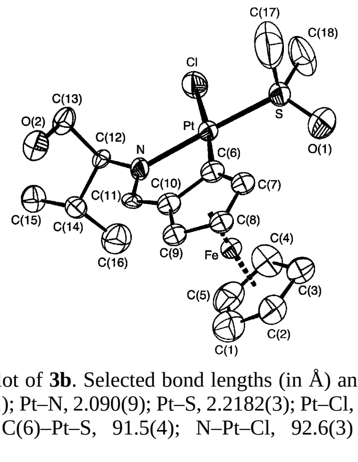


Fig. 1 ORTEP plot of **3b**. Selected bond lengths (in Å) and angles (deg.): Pt–C(6) 2.018(11); Pt–N, 2.090(9); Pt–S, 2.2182(3); Pt–Cl, 1.380(3); C(6)–Pt–N, 82.3(5); C(6)–Pt–S, 91.5(4); N–Pt–Cl, 92.6(3) and S–Pt–Cl, 93.57(11).

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b315157c/

similar to those of **2** and **3**) exhibits antitumour activity, the platinacycles presented here appear to be excellent candidates for future studies in this area.

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11 The diastereomers were separated by SiO_2 column chromatography using a CH_2Cl_2:MeOH (100:0.02) mixture as eluent. Yields: 30 (**2a**), 27 (**3a**), 16 (**2b**) and 27 (**3b**) %. *Characterisation data for* **2a**: ^{1}H-NMR data (500 MHz) δ = 8.20[s, 1H, –CH=N–, ^3J(Pt–H) = 110], 4.28[s, 5H, C_5H_5], 4.50[dd, 1H, J = 2.6 and J = 1.0, H^3], 4.58[t, 1H, J = 2.7, H^4], 5.22[dd, 1H, J = 2.5, J = 1.0 Hz, H^5], 4.73–4.82[br.m, 1H, H^6], 3.89–3.95 and 3.73–3.82 [br.m, 2H, H^7], 2.01[br.m, 1H, –OH], 1.29[d, 3H, J = 8.5, Me], 3.54 [s, 3H, ^3J(Pt–H) = 31, Me(dmso)] and 3.59[s, 3H, ^3J(Pt–H) = 28, Me(dmso)] ppm. ^{13}C{^{1}H}-NMR data (100.78 Hz): δ = 174.7[–CH=N–, J(Pt–C) = 60.2], 70.5[C_5H_5], 86.5[C^1], 86.1[C^2], 71.7[C^3], 68.1[C^4], 76.4[C^5], 59.7[C^6], 66.4[C^7], 16.6[Me], 47.0 and 47.1 [Me(dmso)] ppm. ^{195}Pt{^{1}H}NMR: δ = −3824 ppm. IR: ν(–CH=N–) = 1578 cm^{-1}. R_f [CH_2Cl_2:MeOH (100:0.1)] = 0.096. *For* **3a**: ^{1}H-NMR data (500 MHz) δ = 8.21[s, 1H, –CH=N–, ^3J(Pt–H) = 109], 4.25[s, 5H, C_5H_5], 4.55[dd, 1H, J = 2.5 and J = 1.0 Hz, H^3], 4.75[t, 1H, J = 2.5, H^4], 5.20[dd, 1H, J = 2.5, J = 1.0, H^5], 4.62–4.74[br.m, 1H, H^6], 3.70–3.82[br.m, 2H, H^7], 1.83[br.m, 1H, –OH], 1.44[d, 3H, J = 6.5, Me], 3.58 [s, 3H, ^3J(Pt–H) = 21, Me(dmso)] and 3.54[s, 3H, ^3J(Pt–H) = 23, Me(dmso)] ppm. ^{13}C{^{1}H}-NMR data (100.78 Hz): δ = 174.9[–CH=N–], 70.3 [C_5H_5], 86.3[C^1], 85.7[C^2], 68.2[C^3], 71.6[C^4], 76.4[C^5], 60.3[C^6], 65.3[C^7], 17.1[Me], 47.0[Me(dmso)] ppm. ^{195}Pt{^{1}H}-NMR: δ = −3814 ppm IR: ν(–CH=N–) = 1576 cm^{-1}. R_f [CH_2Cl_2:MeOH (100:0.1)] = 0.021. *For* **2b**: ^{1}H-NMR data (500 MHz) δ = 8.21[s, 1H, –CH=N–, ^3J(Pt–H) = 107], 4.37[s, 5H, C_5H_5], 4.60[s, H^3], 4.68[br, 2H, H^4 and H^6], 5.31[s, 1H, H^5], 3.84–3.90 and 3.95–4.01 [br.m, 2H, H^7], 2.20[br.m, 1H, –OH], 1.66 [br., 1H, H^8], 0.99[d, 3H, J = 6.5, Me], 0.95[d, 3H, J = 6.5, Me] and 3.54 [s, 6H, Me(dmso)] ppm. ^{13}C{^{1}H}-NMR data (100.78 Hz): δ = 176.4[–CH=N–], 70.0[C_5H_5], 86.3[C^1], 86.1[C^2], 67.8[C^3], 68.1[C^4], 71.2[C^5], 76.1[C^6], 75.3[C^7], 28.3[C^8], 19.5 and 19.9[Me] and 46.8[Me(dmso)] ppm.^{195}Pt{^{1}H}-NMR: δ = −3826 ppm. IR: ν(–CH=N–) = 1575 cm^{-1}. R_f [CH_2Cl_2:MeOH (100:0.2)] = 0.083. *For* **3b**: ^{1}H-NMR data (500 MHz) δ = 8.21[s, 1H, –CH=N–, ^3J(Pt–H) = 115], 4.29[s, 5H, C_5H_5], 4.51[s, 1H, H^3], 4.57[br., 2H, J = 2.5, H^4 and H^6], 5.22[s, 1H, H^5], 4.62–4.74[br.m, 1H, H^6], 3.70–3.82 and 3.90–4.10[br.m, 2H, H^7], 2.40[br.m, 1H, –OH], 1.08 [d, 6H, Me], 3.59 [s, 3H, ^3J(Pt–H) = 21, Me(dmso)] and 3.55[s, 3H, ^3J(Pt–H) = 23, Me(dmso)] ppm. ^{13}C{^{1}H}-NMR data (100.78 Hz): δ = 176.8[–CH=N–], 70.3[C_5H_5], 86.7[C^1], 85.8[C^2], 67.8[C^3], 71.2[C^4], 75.9[C^5], 75.3[C^6], 67.3[C^7], 28.2[C^8], 19.5 and 20.2[Me], 47.0[Me(dmso)] ppm. ^{195}Pt{^{1}H}NMR: δ = −3825 ppm. IR: ν(–CH=N–) = 1571 cm^{-1}. R_f [CH_2Cl_2:MeOH (100:0.2)] = 0.033.

12 Crystallographic data for **3b**: $C_{18}H_{25}ClFeNO_2PtS$, Mw = 605.855 Orthorhombic, $P2_12_12_1$, a = 7.1740(19), b = 9.6780(10), c = 28.8870(10) Å, $\alpha = \beta = \gamma = 90°$, V = 2005.6(4) $Å^3$ and Z = 4. For 6248 reflections the final R(on F) and wR(on F^2) factors were 0.0371 and 0.0876, respectively. The Flack coefficient[13] was 0.00(33). Data collected with a MAR345 diffractometer with a image plate detector. Intensities were collected with a graphite monochromatised Mo–K_α radiation. The structure was solved by Direct methods, using SHELXS computer program[14] and refined by full-matrix least-squares method using SHELX93 computer program.[15] CCDC 224295. See http://www.rsc.org/suppdata/cc/b3/b315157c/ for crystallographic data in .cif or other electronic format.

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18 Summary of electrochemical data: anodic (E^{ox}) and cathodic potentials (E^{red}), separation between peaks [$\Delta E = E^{ox} - E^{red}$] and intensity ratio I_{pa}/I_{pc} at 25 °C. (The potentials, in mV, are referred to the ferrocene/ferricinium couple): For **1a**: E^{ox} = 195, E^{red} = 58, ΔE = 135 and I_{pa}/I_{pc} = 1.62; for **1b**: E^{ox} = 105, E^{red} = 51, ΔE = 90, I_{pa}/I_{pc} = 1.49; for **2a**: E^{ox} = 100, E^{red} = 18, ΔE = 82, I_{pa}/I_{pc} = 1.41; for **3a**: E^{ox} = 118, E^{red} = 34, ΔE = 84, I_{pa}/I_{pc} = 1.43; For **2b**: E^{ox} = 97, E^{red} = 19, ΔE = 78, I_{pa}/I_{pc} = 1.26 and for **3b**: E^{ox} = 104, E^{red} = 31, ΔE = 73 and I_{pa}/I_{pc} = 1.40.