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2-Pyridylmetallocenes, part IV. Cycloplatination of 2-pyridyl-ferrocene, -ruthenocene and –cymantrene. Molecular structures of σ -Pt{CpM[C₅H₃(2-C₅H₄N)]}Cl (DMSO) (M = Fe, Ru) and σ -Pt{CpFe[C₅H₃ (2-C₅H₄N)]}(acac)

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ABSTRACT

The 2-pyridylmetallocenes $[C_5H_3R(2-C_5H_4N)]ML_n$ (**1a–e**, $ML_n = FeCp$, RuCp, $Mn(CO)_3$, R = H, CH_3) react with *cis*-[PtCl₂(DMSO)₂] to give the cycloplatinated complexes σ -Pt{ $L_nM[C_5H_2(2-C_5H_4N)(R)]$ }Cl (DMSO) ($ML_n = FeCp$ (R = H: **2a**; R = Me: **2b**), RuCp (R = H, **3a**; R = Me, **3b**), $Mn(CO)_3$ (R = H, **4**)). The reaction of **1a** with the chiral sulfoxide complexes *cis*-[PtCl₂{S(O)Me(*p*-C₆H₄Me)}₂] or K[PtCl₃S(O)Me(*p*-C₆H₄Me)] yields a mixture of σ -Pt{ $CpFe[C_5H_2(2-C_5H_4N)(R)]$ }Cl[S(O)Me(*p*-C₆H₄Me)] diastereomers (R_pR_S/S_pS_s)-and (R_pS_s/S_pR_s)-**5**. Treatment of **2a** with sodium pentane-2,4-dionate ("Na(acac)") gives the bischelate σ -Pt{ $CpFe[C_5H_3(2-C_5H_4N)]$ }(acac) (**6a**). Refluxing solutions of **2a** with glycine in the presence of sodium methoxide yields the amino acidato complex Pt{ $CpFe[C_5H_3(2-C_5H_4N)]$ }(gly) **6b**. The molecular structures of **2a**, **b**, **3a** and **6a** have been determined by X-ray diffraction. **2a**, **b** and **3a** show a *trans*-N, S configuration of the pyridine nitrogen and the DMSO sulfur atoms.

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1. Introduction

Cyclometalation reactions continue to receive considerable attention, as well from mechanistic and preparative aspects as from the numerous applications of the metallacycles that are produced by these reactions [1]. Known cyclometalated organometallic platinum complexes are mostly based on 2-arylpyridines, and have been tested mainly for their luminescence properties [2], but also for their antitumour activity [3], and very recently for interaction with amyloid-β-peptide in the context of Alzheimer's disease [4]. Usually it was found that the particular properties could be tuned by variations as well in the arvl part as in the pyridine part of the cyclometalating ligand. One possible modification of the aryl moiety would be the use of a substituted metallocene, e.g., ferrocene. There is a rather long tradition of cycloplatination of ferrocenylamines [5] and ferrocenylimines [6]. Cycloplatinated ferrocenylimines have been tested e.g., for their electrochemical properties [7], or their potential utility as molecular switches [8]. Several ferrocene derivatives have been shown to have antitumour activity [9], and among them a cycloplatinated ferrocenylamine [10]. However, there seem to be no reports on cycloplatinated

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metallocenylpyridines. With the rich chemistry of arylpyridines and their interesting physicochemical properties and their applications in mind, we decided it would be worthwhile to study the cycloplatination of some 2-pyridyl-metallocenes.

2. Experimental

All reactions were performed under argon, using standard Schlenk techniques. *cis*-[PtCl₂(DMSO)₂], *cis*-[PtCl₂{S(O)Me(p-C₆H₄Me)}₂] and K[PtCl₃S(O)Me(p-C₆H₄Me)] were prepared as described in the literature [11]. The 2-pyridylmetallocenes **1a**–**e** were prepared as recently described by us [12]. Solvents (analytical grade) were saturated with argon.

NMR: JEOL ECP-270 and ECX-400, all NMR spectra (except for **6b**) were recorded in CD₂Cl₂ and were referenced to the signal of residual CHDCl₂ δ (¹H) = 5.300 ppm, or CD₂Cl₂ δ (¹³C) = 53.8 ppm; DMSO-d⁶ was used for **6b**: reference was set to δ (¹H) = 2.49 ppm and δ (¹³C) = 39.5 ppm.

MS: Finnigan MAT 90 and JEOL Mstation 700.

UV/Vis: Ocean Optics USB 2000. Concentration: 1.0 mg in $10.0 \text{ mL CH}_2\text{Cl}_2$.

The elemental analyses were performed at the microanalytical laboratory at the chemistry department of Ludwig-Maximilians University, Munich.



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2.1. General procedure for the preparation of chlorido[2-(2-pyridinyl- κ N)metallocenyl- κ C]dimethylsulfoxide-platinum(II), σ -Pt{LM[C₅H₃(2-C₅H₄N)]}Cl(DMSO) **2-4**

The whole synthesis of **4** has to be performed in the dark. The 2pyridylmetallocene (0.25 mmol) and *cis*-[PtCl₂(DMSO)₂] (0.11 g, 0.25 mmol) were suspended in toluene (50 mL) and treated with a solution of NaOAc·3H₂O (0.068 g, 0.50 mmol) in methanol (1.0 mL). The mixture was refluxed (4 h for **2a,b** and **3b**, 6 h for **3a** and 5 h for **4**), and then the solvent completely removed in vacuo. The remaining solid was taken up in a small amount of CH₂Cl₂ and then chromatographed on silica gel. **2a** and **3a** were eluted with a CH₂Cl₂/EtOAc mixture (8:1 for **2a** and **3a**, 3:1 for **2b**, 5:1 for **3b**, 4:1 for **4**). After evaporation of the solvents the products were recrystallized from CH₂Cl₂/hexane. Yields: **2a**: 0.14 g (0.24 mmol, 98%); **2b**: 0.13 g (0.22 mmol, 93%); **3a**: 0.13 g (0.21 mmol, 82%); **3b**: 0.15 g (0.24 mmol, 95%), **4**: 0.15 g (0.23 mmol, 93%).

2a: Anal. Calc. for $C_{17}H_{18}$ CIFeNOPtS: C, 35.77; H, 3.18; N, 2.45; Fe, 9.78; S, 5.62. Found: C, 36.02; H, 3.28; N, 2.51; Fe, 9.39; S, 5.70%. MS (DEI⁺): m/z = 570.9 (M⁺), 537.1 (M⁺–Cl), 493.1 (M⁺–DMSO), 456.2 (M⁺–Cl–DMSO). ¹H NMR (270 MHz), $\delta = 9.30$ ("ddd", " J_{HH} " = 0.9, 1.5, 5.9 Hz; $J_{PtH} = 36$ Hz, H6), 7.74 ("dt", " J_{HH} " = 1.8, 8.0 Hz; H4), 7.32 ("ddd", " J_{HH} " = 0.9, 1.5, 8.0 Hz; $J_{PtH} = 9$ Hz, H3), 7.08 ("ddd", " J_{HH} " = 1.5, 5.9, 7.4 Hz; H5), 5.01 ("dd", " J_{HH} " = 1.2, 2.4 Hz; $J_{PtH} = 8$ Hz, H9), 4.66 ("dd", " J_{HH} " = 0.9, 2.7 Hz; H11), 4.50 ("t", " J_{HH} " = 2.4 Hz; $J_{PtH} = 13$ Hz, H10), 4.06 (s, Cp), 3.64/3.59 (2 s, $J_{PtH} = 25$ Hz/24 Hz, SCH₃). ¹³C NMR (100 MHz): $\delta = 167.8$ (C2), 150.0 ($J_{PtC} = 19$ Hz, C6), 139.8 (C4), 120.1 ($J_{PtC} = 30$ Hz, C5), 118.2 ($J_{PtC} = 31$ Hz, C3), 88.2 ($J_{PtC} = 62$ Hz, C7), 83.8 ($J_{PtC} = 1130$ Hz, C8), 74.2 ($J_{PtC} = 94$ Hz, C9), 70.4 (Cp), 70.0 ($J_{PtC} = 46$ Hz, C10), 65.0 ($J_{PtC} = 44$ Hz, C11), 47.7/47.3 ($J_{PtC} = 66$ Hz/71 Hz, SCH₃). ¹⁹⁵Pt NMR (CD₂Cl₂): $\delta = -3797$ ppm.

2b: MS (DEI⁺) m/z: 628.8 ($C_{20}H_{27}FeNO_2PtS_2^+$), 584.8 (M⁺, 75%), 506.8 (M⁺-DMSO, 100%), 468.9 ([M + H]⁺-Cl-DMSO, 42%). ¹H NMR (400 MHz): δ = 9.36 ("d", " J_{HH} " = 5.8 Hz; J_{PtH} = 36 Hz, H6), 7.73 ("dt", " J_{HH} " = 1.7, 7.7 Hz; H4), 7.53 ("d", " J_{HH} " = 7.4 Hz; H3), 7.09 ("dt", " J_{HH} " = 1.1, 6.7 HZ; H5), 4.89 ("d", " J_{HH} " = 2.5 Hz; H9), 4.42 ("d", " J_{HH} " = 2.2 Hz; H10), 3.99 (s, Cp), 3.59/3.54 (2 s, J_{PtH} = 24 - Hz/25 Hz, SCH₃), 2.32 (s, H_{Me}). ¹³C NMR (100 MHz): δ = 168.4 (J_{PtC} = 65 Hz, C2), 150.5 (J_{PtC} = 15 Hz, C6), 139.6 (C4), 120.0 (J_{PtC} = 30 Hz, C5), 118.7 (J_{PtC} = 33 Hz, C3), 86.3 (J_{PtC} = 70 Hz, C7), 84.3 (J_{PtC} = 1130 Hz, C8), 82.3 (J_{PtC} = 44 Hz, C11), 73.3 (J_{PtC} = 42 Hz, C10), 72.1 (J_{PtC} = 89 Hz, C9), 71.0 (Cp), 47.7/47.5 (J_{PtC} = 65 Hz/71 Hz, SCH₃), 15.4 (C_{Me}).

3a: Anal. Calc. for $C_{17}H_{18}$ CINOPtRuS: C, 33.15; H, 2.95; N, 2.27; S, 5.21. Found: C, 33.29; H, 3.10; N, 2.13; S, 5.39%. MS (DEI⁺): m/z = 616.2 (M⁺), 580.3 (M⁺-Cl), 537.2 (M⁺-DMSO), 502.3 (M⁺-Cl-DMSO). ¹H NMR (270 MHz), $\delta = 9.20$ ("ddd", " J_{HH} " = 0.9, 1.5, 5.9 Hz; $J_{PtH} = 36$ Hz, H6), 7.67 ("dt", " J_{HH} " = 1.5, 7.4 Hz; H4), 7.28 ("ddd", " J_{HH} " = 0.9, 1.2, 8.0 Hz; $J_{PtH} = 9$ Hz, H3), 7.05 ("dt", " J_{HH} " = 1.5, 5.9 Hz; H5), 5.21 ("dd", " J_{HH} " = 0.6, 2.4 Hz; $J_{PtH} = 8$ Hz, H9), 5.03 ("dd", " J_{HH} " = 0.9, 2.4 Hz; H11), 4.72 ("t", " J_{HH} " = 2.4 Hz; $J_{PtH} = 11$ Hz, H10), 4.45 (s, Cp), 3.54/3.49 (2 s, $J_{PtH} = 26$ Hz/25 Hz, SCH₃). ¹³C NMR (67.9 MHz): $\delta = 166.4$ ($J_{PtC} = 61$ Hz, C2), 149.8 ($J_{PtC} = 31$ Hz, C3), 93.5 ($J_{PtC} = 64$ Hz, C7), 83.2 ($J_{PtC} = 1130$ Hz, C8), 75.6 ($J_{PtC} = 98$ Hz, C9), 72.0 (Cp), 71.4 ($J_{PtC} = 44$ Hz, C10), 66.8 ($J_{PtC} = 44$ Hz, C11), 47.9/47.0 ($J_{PtC} = 72$ Hz/69 Hz, SCH₃). ¹⁹⁵Pt (CD₂-Cl₂): $\delta = -3755$ ppm.

3b: Anal. Calc. for $C_{18}H_{20}$ ClNOPtRuS: C, 34.31; H, 3.20; N, 2.22; S, 5.09%; found: C, 35.84; H, 3.55; N, 2.10; S, 4.68%. MS (DEI⁺): *m/z*: 645.0 ($C_{19}H_{22}$ ClNOPtRuS⁺), 630.4 (M⁺), 594.5 (M⁺–Cl), 553.3 (M^{+–}–DMSO), 530.0 (M⁺–Cl–Cp), 515.4 (M⁺–Cl–DMSO). ¹H NMR (400 MHz), δ = 9.30 ("ddd", "*J*_{HH}" = 0.6, 1.7, 6.0 Hz; *J*_{PtH} = 35 Hz, H6), 7.70 ("dt", "*J*_{HH}" = 1.7, 8.0 Hz; *J*_{PtH} = 26 Hz, H4), 7.49 ("td",

"J_{HH}" = 0.8, 8.0 Hz; J_{PtH} = 8 Hz, H3), 7.07 ("dt", "J_{HH}" = 1.4, 5.8 Hz; H5), 5.08 ("d", "J_{HH}" = 2.2 Hz; J_{PtH} \approx 8 Hz, H9), 4.73 ("d", "J_{HH}" = 2.2 Hz; J_{PtH} = 11 Hz, H10), 4.41 (s, Cp), 3.52/3.45 (2 s, J_{PtH} = 25 Hz/26 Hz, SCH₃), 2.32 (s, CH₃). ¹³C NMR (100 MHz): δ = 167.1 (C2), 150.3 (J_{PtC} \approx 14 Hz, C6), 139.8 (C4), 120.2 (J_{PtC} = 31 -Hz, C5), 118.6 (J_{PtC} = 33 Hz, C3), 92.3 (C7), 85.0 (J_{PtC} = 41 Hz, C11), 83.9 (C8), 75.4 (J_{PtC} = 70 Hz/66 Hz, SCH₃), 15.8 (CH₃).

4: Anal. Calc. for C₁₅H₁₃ClMnNO₄PtS: C, 30.60; H, 2.23; N, 2.38; S, 5.45. Found: C, 31.79; H, 2.43; N, 2.37; S, 5.37%. MS (DEI⁺): *m*/*z* = 589.1 (M⁺, 22%), 505.1 (M⁺-3CO, 100%), 427.1 (M⁺-3CO-DMSO, 23%). ¹H NMR (400 MHz), δ = 9.36 ("d", "*J*_{HH}" = 5.8 Hz; *J*_{PtH} = 34 Hz, H6), 7.87 ("t", "*J*_{HH}" = 6.9 Hz; H4), 7.37 ("d", "*J*_{HH}" = 7.7 Hz; H3), 7.25 ("t", "*J*_{HH}" = 6.0 Hz; H5), 5.20 (s, br, H9), 5.15 (s, br, H11), 4.99 ("t", "*J*_{HH}" = 2.8 Hz; H10), 3.59/3.56 (2 s, *J*_{PtH} = 24 Hz/24 Hz, SCH₃). ¹³C NMR (100 MHz): δ = 226.2 (CO), 161.2 (C2), 150.5 (*J*_{PtC} = 17 Hz, C6), 141.1 (C4), 122.4 (*J*_{PtC} = 28 Hz, C5), 118.8 (*J*_{PtC} = 29 Hz, C3), 105.2 (*J*_{PtC} = 57 Hz, C7), 99.1 (C8), 85.4 (*J*_{PtC} = 48 Hz, C10), 84.1 (*J*_{PtC} = 86 Hz, C9), 78.8 (*J*_{PtC} = 50 Hz, C11), 47.0/46.8 (*J*_{PtC} = 63 Hz/64 Hz, SCH₃). ¹⁹⁵Pt NMR (CD₂Cl₂): δ = -3673 ppm.

2.2. Chlorido[2-(2-pyridinyl- κ N)ferrocenyl- κ C]methyl-p-tolyl-sulfoxide-platinum(II), σ -Pt{CpFe[C₅H₃(2-C₅H₄N)]}Cl[S(O)Me(p-C₆H₄Me)], **5**

A solution of **1a** (0.066 g, 0.25 mmol) and (a) K[PtCl₃S(O)Me(p-C₆H₄Me)] (0.12 g, 0.25 mmol) or (b) *cis*-[PtCl₂{S(O)Me(p-C₆H₄Me)}₂] (0.14 g, 0.25 mmol) in toluene (50 mL) is treated with a solution of NaOAc·3H₂O (0.068 g, 0.50 mmol) in 1 mL MeOH. After refluxing for 24 h the solvent is evaporated in vacuo. The red residue is taken up in a minimum amount of CH₂Cl₂ and chromatographed on silicagel using a 4:1 mixture of CH₂Cl₂/EtOAc as eluent. **5** Elutes first and yields after evaporation a red solid (a: 0.080 g, 0.13 mmol, 50%; b: 0.11 g, 0.17 mmol, 68%).

MS (FAB⁺): m/z = 647.2 (M⁺), 611.2 (M⁺-Cl), 492.2 (M⁺⁻ -S(O)MeTol), 457.2 (M⁺-Cl-S(O)MeTol). ¹H NMR (400 MHz): δ = 9.41 (m, J_{PtH} = 36 Hz, H6, I + II), 8.14 ("d", " J_{HH} " = 8.5 Hz; C₆H₄, α -H, I), 8.01 ("d", " J_{HH} " = 8.3 Hz; C₆H₄, α -H, II), 7.70 (m, H4, I + II), 7.46 ("d", " J_{HH} " = 8.3 Hz; C₆H₄, β -H, I), 7.33 ("d", " J_{HH} " = 8.3 Hz; C_6H_4 , β -H, II) 7.30–7.26 m, H3, I + II***, 7.10 (m, H5, I + II), 4.83/ 4.63 (2× "dd", " I_{HH} " = 1.1, 2.2 Hz/0.8, 2.2 Hz; H9, I/II), 4.59/4.58 (m, H11, I + II), 4.40/4.38 (2× "t", " I_{HH} " = 2.5 Hz/2.5 Hz; H10, I/II), 4.10 (s, Cp, II), 3.67 (s, J_{PtH} = 20 Hz, SCH₃, I + II), 3.55 (s, Cp, I), 2.43/ 2.40 (2 s, Tol-CH₃, I/II). ¹³C NMR (67.9 MHz): δ = 168.0 (J_{PtC} = 65 Hz, C2, I + II), 149.9/149.8 (J_{PtC} = 20/20 Hz, C6, II/I), 143.6/143.5 (C_6H_4 -C_i, II/I), 142.7/142.4 (C₆H₄-C_γ, II/I), 139.8 (C4, I + II), 130.2/130.1 $(C_6H_4-C_\beta, I/II)$, 125.8/125.5 $(C_6H_4-C_\alpha, II/I)$, 120.0 $(J_{PtC} = 31 \text{ Hz}, C5, C_6H_4-C_\alpha, II/I)$ I + II), 118.1 (J_{PtC} = 32 Hz, C3, I + II), 88.1 (J_{PtC} = 57 Hz, C7, I + II), 84.7/84.0 (C8, I/II), 74.4/74.1 (J_{PtC} = 98/94 Hz, C9), 70.8/70.3 (Cp), 70.1/70.0 (J_{PtC} = 46/45 Hz, C10), 64.8/64.5 (J_{PtC} = 44/43 Hz, C11), 49.3/49.2 (J_{PtC} = 54/58 Hz, SCH₃, II/I), 21.5 (Tol-CH₃). Note: "I" corresponds to the slightly preferred $R_p S_s / S_p R_s$ diastereomer, while "II" represents the minor R_pR_s/S_pS_s diastereomer.

2.3. Acetylacetonato[2-(2-pyridinyl- κ N)ferrocenyl- κ C]-platinum(II), σ -Pt{CpFe[C₅H₃(2-C₅H₄N)]}(acac) **6a**

A solution of **2a** (0.23 g, 0.40 mmol) and Na(acac)·H₂O (0.056 g, 0.40 mmol) in acetone (40 mL) was refluxed 8 h. After addition of 50 mL water the precipitated red solid was isolated by filtration, washed with water and dried in vacuo. Recrystallization from CH_2Cl_2/n -hexane yielded **5** as dark red crystals (0.18 g, 0.33 mmol, 82%).

Anal. Calc. for C₂₀H₁₉FeNO₂Pt: C, 43.18; H, 3.44; N, 2.52; Fe, 10.04; Pt, 35.07. Found: C, 43.59; H, 3.66; N, 2.38; Fe, 10.47; Pt,

31.40%. MS (FAB⁺): m/z = 556.0 (M⁺), 457.1 (M⁺-acac). ¹H NMR (270 MHz), $\delta = 8.81$ ("d", " J_{HH} " = 5.9 Hz; $J_{PtH} = 44$ Hz, H6), 7.65 ("dt", " J_{HH} " = 1.2, 7.7 Hz; H4), 7.23 ("d" br, " J_{HH} " = 8.0 Hz; H3), 6.96 ("ddd", " J_{HH} " = 1.2, 5.9, 7.4 Hz; H5), 5.46 (s, H14), 4.67 ("d" br, " J_{HH} " = 2.4 Hz; H11), 4.49 ("d" br, " J_{HH} " = 2.1 Hz; H9), 4.45 ("t" br, " J_{HH} " = 2.2 Hz;H10), 4.01 (s, Cp), 1.95/1.92 (2s, H12 and H16). ¹³C NMR (67.9 MHz): $\delta = 185.0$ (C13), 184.2 ($J_{PtC} = 32$ Hz, C15), 170.2 (C2), 147.6 (C6), 137.8 (C4), 119.3 ($J_{PtC} = 36$ Hz, C5), 117.9 ($J_{PtC} = 39$ Hz, C3), 102.4 ($J_{PtC} = 61$ Hz, C14), 89.1 (C7), 75.7 (C8), 70.6 ($J_{PtC} = 96$ Hz, C9), 70.2 (C12), 68.8 ($J_{PtC} = 49$ Hz, C10), 64.1 ($J_{PtC} = 49$ Hz, C11), 28.4 (C12), 27.0 ($J_{PtC} = 49$ Hz, C16). ¹⁹⁵Pt NMR (CD₂Cl₂): $\delta = -4026$ ppm.

2.4. $(\eta^2-N,O-glycinato)$ [2-(2-pyridinyl- κ N)-ferrocenyl- κ C]platinum(II), σ -Pt{CpFe[C₅H₃(2-C₅H₄N)]}(gly) (**6b**)

A solution of **2a** (0.057 g, 0.10 mmol) in CH_2CI_2 (10 mL) was treated with a mixture of glycine (0.0080 g, 0.10 mmol) and NaOMe (0.010 g, 0.20 mmol) dissolved in MeOH (10 mL) and refluxed for 24 h. Thereafter dilute HCl (30 mL) was added and the aqueous phase extracted three times with CH_2CI_2 (20 mL each). The combined organic phases were vigorously stirred over MgSO₄, and, after filtering, evaporated to dryness in vacuo. The remaining red solid was taken up with Et_2O and chromatographed on silica gel. The eluted ethereal phase was discarded; the desired product was eluted with MeOH. After evaporation a red solid remained, which contained small amounts of an unidentified impurity (visible by additional ¹H NMR signals and peaks in the mass spectra) (0.032 g, <61%).

MS (FAB⁺): $m/z = 531.1 \text{ (M}^+\text{)}$, 457.0 (M⁺-glycine). ¹H NMR (in DMSO-d⁶, 270 MHz): $\delta = 8.54 \text{ ("d", "}J_{HH}" = 5.3 Hz; H6)$, 7.87 ("dt", " $J_{HH}" = 1.2$, 8.0 Hz; H4), 7.47 ("d", " $J_{HH}" = 8.0$ Hz; H3), 7.13 ("t", " $J_{HH}" = 7.6$ Hz; H5), 5.97 (s, br, NH₂), 4.76 ("d", " $J_{HH}" = 1.8$ Hz; H11), 4.37 ("t", " $J_{HH}" = 2.1$ Hz; H10), 4.29 ("d", " $J_{HH}" = 1.8$ Hz; H9), 3.99 (s, Cp). ¹³C NMR (in DMSO-d⁶, 67.9 MHz): $\delta = 180.8$

Table 1

Experimental parameters of the crystal structure determinations.

(COO), 167.3 (C2), 148.9 (C6), 138.4 (C4), 120.3 (C5), 118.0 (C3), 89.0 (C7), 73.3 (C8), 71.9 (C9), 69.5 (Cp), 68.7 (C10), 63.9 (C11), 47.7 (C_{α}).

2.5. X-ray structure determinations of 2a, b, 3a and 6a

Crystals of all compounds were grown from CH_2Cl_2/iso -hexane or $CHCl_3/hexane$ (**3a**). X-ray quality crystals were mounted on glass fibers and cooled to 173(3) K during measurement. The data were collected on an Oxford Xcalibur3 CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). A multi-scan absorption correction was applied using the ABSPACK program [13]. The structures were solved with the SIR-97 software as implemented in the WINGX software package [14]. Refinement (full matrix least square on F^2) was done with SHELXL 97 [15], also as implemented in WINGX. Further details can be seen in Table 1.

3. Results and discussion

3.1. Synthesis

For the preparation of mononuclear cycloplatinated complexes of the $[(C^N)Pt(L)(X)]$ type, the sulfoxide complex *cis*- $[PtCl_2$ (DMSO)₂] has been reported to be the reagent of choice [5,9c,17]. Thus, when the 2-pyridyl metallocenes **1a**–**e** were treated with this complex in the presence of two equivalents of sodium acetate as base, high yields of the cycloplatinated compounds **2**–**4** could be obtained [16]. We tested also the reaction of **1a** with K₂PtCl₄, which lead to an observable reaction followed by precipitation of a solid that was completely insoluble in all common solvents. The manganese compound **4** turned out to be light sensitive and also rather unstable in solution. All attempts of recrystallization, to obtain satisfactory combustion analysis data, lead to decomposition.

Compound	2a	2b	3a	6a
Empirical formula	C17H18ClFeNOPtS	C18H20ClFeNOPtS·CH2Cl2	C17H18CINOPtRuS·CHCl3	C20H19FeNO2Pt
Formula weight	570.77	669.73	735.36	1112.60
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	C2/c	$P2_1/a$	ΡĪ	C2/c
Unit cell dimensions				
a (Å)	9.6637(7)	9.3079(5)	9.8621(10)	16.2080(5)
b (Å)	27.927(2)	26.2435(11)	10.4803(8)	12.3572(4)
c (Å)	12.8174(5)	9.7687(5)	11.1942(11)	17.5616(5)
α (°)	90	90	100.706(7)	90
β (°)	96.645(7)	116.795(8)	96.331(8)	91.026(3)
γ (°)	90	90	97.819(7)	90
$V(Å^3)$	3476(2)	2130.00(18)	1115.33(18)	3516.8(2)
Ζ	8	4	2	8
D_{calc} (mg/m ³)	2.207	2.088	2.190	2.101
Absorption coefficient (mm ⁻¹)	9.257	7.726	7.523	8.785
F(000)	2176	1288	696	2128
Crystal size (mm)	$0.13 \times 0.08 \times 0.02$	$0.21 \times 0.18 \times 0.14$	$0.25\times0.18\times0.17$	$0.24 \times 0.22 \times 0.16$
θ range for data collection (°)	4.21 to 26.29	4.15 to 26.35	4.20 to 26.24	4.25 to 26.30°
Index ranges	$-8\leqslant h\leqslant 12$,	$-6 \leqslant h \leqslant 11$,	$-12 \leqslant h \leqslant 12$,	$-19\leqslant h\leqslant 20$,
	$-31 \leqslant k \leq 34$,	$-32\leqslant k\leqslant 28$,	$-11 \leqslant k \leqslant 13$,	$-15 \leqslant k \leqslant 11$,
	$-11 \leqslant l \leqslant 15$	$-12 \leqslant l \leqslant 8$	$-13 \leqslant l \leqslant 13$	$-21 \leqslant l \leqslant 21$
Reflections collected	6693	8652	8573	13359
Independent reflections (R_{int})	3476 (0.0512)	4322 (0.0424)	4462 (0.0356)	3564 (0.0378)
Completeness to θ_{max}	98.5%	99.2%	98.7%	99.4%
Maximum and minimum transmission	0.8310 and 0.5724	0.3390 and 0.2462	0.2783 and 0.1603	0.2452 and 0.1294
Data/parameters	3476/208	4322/249	4462/246	3564/229
Goodness-of-fit on F ²	0.759	0.947	0.943	0.813
$R_1/wR_2 \left[I > 2\sigma(I)\right]$	0.0335/0.0501	0.0375/0.0736	0.0339/0.0701	0.0222/0.0410
R_1/wR_2 (all data)	0.0668/0.0541	0.0540/0.0772	0.0473/0.0726	0.0347/0.0426
Largest difference peak and hole [e Å ⁻³]	1.160 and -0.922	2.065 and -1.703	2.327 and -1.220	0.823 and -0.615
CSD number	822045	886293	822046	822047



Scheme 1. Synthesis of 2–4.

The use of a chiral sulfoxide ligand should lead, in principle, to asymmetrically cycloplatinated ferrocenes [17]. The reaction of **1a** with either a diastereomeric mixture of (meso + RR/SS)-[PtCl₂(-S(O)Me(p-C₆H₄Me)]₂] or racemic K[PtCl₃{S(O)Me(p-C₆H₄Me)}] yielded a diastereomeric mixture of R_pR_s/S_pS_s - and R_pS_s/S_pR_s -**5** (Scheme 2) (for the assignment of diastereomers, vide infra).

The ferrocenyl compound **2a** gave after treatment with sodium pentanedionate (Na⁺acac⁻) the bis-chelate complex **6a**, while with glycine in the presence of NaOMe the bis-chelate complex **6b** could be obtained (Scheme 3). **6a** could be fully characterized, however, **6b** was always contaminated with an unknown impurity.

3.2. NMR spectra

The signal assignments (numbering scheme see Scheme 1) are based on HMQC measurements, a NOESY experiment on **3**, which showed the coupling of H3 and H11, and the ¹H and ¹³C NMR spectra of the mono-deuterated complex [D1]-**2a**, which contains deuterium at position 11.

The cyclopentadienyl protons H9–H11 form an AXY pattern, giving apparent "dd", "t" and "dd" patterns for **2a**, **3a** and **5** (two signal sets), which are partially unresolved in **4** and **6a,b**. In the methylated derivatives **2b** and **3b** the protons H9 and H10 appear as two doublets. In some cases ¹⁹⁵Pt satellites can be observed for protons H9 and H10, with coupling constants J_{PtH} of 8 Hz and 11–13 Hz, respectively, thus ${}^{3}J < {}^{4}J$. The protons of the unsubstituted cyclopentadienyl rings are observed (in CD₂Cl₂) as singlets at ca 4.05 ± 0.05 ppm in the ferrocenes and 4.43 ± 0.02 ppm in the ruthenocenes, except for one diastereomer of **5**, which shows a substantial high field shift two δ = 3.55 ppm. This was also observed for the R_pS_s diastereomer of the cycloplatinated dimethyl-aminomethylferrocene with the same sulfoxide ligand [17], and



Scheme 3. Synthesis of 6a and 6b.

was attributed to the ring current effect from the sulfoxide tolyl group. Since this signal integrates ca. 54:46 with respect to the "normal" Cp resonance at 4.10 ppm, and approximately the same integral ratio can be observed for several other resonances in the ¹H NMR spectrum of **5**, assignment of individual signals to both diastereomers is possible. In analogy to the literature assignment we assign the R_pS_S/S_PR_S configuration to the slightly preferred isomer.

The pyridine protons H3–H6 form an ABCX spin system, with the H6 proton next to the coordinated nitrogen showing a significant low field shift: $\delta(H6) \delta(H4) > \delta(H3) > \delta(H5)$. As was already observed earlier, $\delta(H6) > 9.30$ ppm, when a chloride ligand is in *cis*position at the coordinated Pt atom, while it is shifted to $\delta < 9.0$ ppm, when an oxygen atom is the *cis*-donor atom [18]. In all complexes with *cis* Pt-Cl groups this proton shows also coupling to platinum, with ${}^{3}J_{PtH} = 34-36$ Hz, while in the acetylacetonato complex **6a** a coupling constant of 44 Hz is observed. In the DMSO complexes, for the SCH₃ protons there are always two singlets with platinum satellites to be seen. The values for J_{PtH} of ca. 25 Hz indicate that the DMSO ligand is always S-bonded.

In the ¹³C NMR spectra the most prominent feature is the large low-field shift of the pyridine carbon C2, from $\delta \approx 160$ ppm in the free metallocene ligand to 166–170 ppm in the cycloplatinated complexes **2–6**, which was also observed in the cycloplatination of phenylpyridines [18a]. For compounds **2b**, **3a** and **5** platinum satellites could be observed for these resonances, with ²*J*_{PtC} = 61– 65 Hz. For the pyridine carbon C6 in all cycloplatinated complexes, except for **6a,b**, ²*J*_{PtC} = 14–20 Hz, while for the quaternary cyclopentadienyl carbon C7 the observed ²*J*_{PtC} amounted to 57–70 Hz and for C9 a ²*J*_{PtC} of 86–98 Hz was found. The ³*J*_{PtC} couplings within the pyridine ring were 31 ± 2 Hz for **2–5**, while within the cyclopentadienyl ring values of 47 ± 3 Hz were found. In the spectra of



Scheme 2. Synthesis of 5. It is only one enantiomer of both diastereomers ahown.

Table 2

Selected UV–Vis spectroscopic data: wavelengths (λ in nm) and molar extinction coefficients (ϵ in dm²/mol) (in parentheses).

Compound	λ_1	λ_2	λ_3	λ_4
2a 2b 3b 6a	282 (17300) 294 (14800)	343 (4280) 344 (2843) 344	415 (1580) 421 (990)	502 (2460) 519 (1770) 389 (1980) 505



Fig. 1. Molecular structure of 2b, 30% probability ellipsoids.



Fig. 2. Molecular structure of 6a, 30% probability ellipsoids.

2a,b and **3a** the ${}^{1}J_{PtC}$ could be observed, amounting to 1130 Hz in all three compounds. ${}^{1}J_{PtC}$ values of ca. 1100 Hz have been reported before [18b]. Thus, within the cyclopentadienyl ring a sequence of ${}^{1}J >> {}^{2}J > {}^{3}J$ is observed, while in the pyridine ring ${}^{2}J < {}^{3}J$ is found.

For compounds **2a**, **3a**, **4** and **6a** it was possible to obtain ¹⁹⁵Pt NMR spectra, with δ_{Pt} ranging from -3755 ppm (**3a**) to -4026 ppm (**6a**). ¹⁹⁵Pt NMR data have been reported for several cycloplatinated complexes, including ferrocene derivatives. High-field signals with $\delta - 3700$ to -4000 ppm (rel. H₂PtCl₆) have been regarded as typical for cycloplatinated complexes [18a,19].

Table 3

Important bond parameters of the Pt coordination sphere.

Compound	2a	2b	3a	6a
Pt–C [Å]	1.989(7)	1.981(7)	2.001(6)	1.967(4)
Pt–Cl [Å]	2.409(2)	2.4050(17)	2.417(2)	-
Pt–N [Å]	2.079(5)	2.095(5)	2.110(5)	2.018(3)
Pt–S [Å]	2.194(2)	2.2017(17)	2.205(2)	-
C–Pt–N [°]	80.3(2)	80.5(2)	81.3(2)	81.6(2)
C–Pt–Cl [°]	173.9(2)	172.7(2)	173.7(2)	-
<(cp),(py) [°]	3.1(4)	4.1(4)	6.7(3)	9.6(4)
C–Pt–S–O [°]	8.0(3)	-14.8(3)	6.1(3)	-
"H6"· · ·Cl [Å]	2.672(1)	2.615(1)	2.675(1)	-
"H _a "…O [Å]	2.421(1)	2.342(1)	2.435(1)	-
(Pt···Pt) _{min} [Å]	3.921	7.955	5.857	6.125



Fig. 3. View of the dimer in 3a.

3.3. UV-Vis spectra

The UV–Vis spectra of compounds **2a**, **2b**, **3b**, **6a** were measured in ca. 10^{-4} M CH₂Cl₂ solution. Up to 4 bands could be resolved (Table 2). The bands labeled as " λ_1 ", " λ_2 " and " λ_4 " are very similar to the bands observed in [Pt{[(C₅H₃)–CH = N–(CH₂–CH₂–OH)]Fe(C₅-H₅)]}Cl(dmso),[20] and can most likely be assigned the same way. It was also tried to obtain emission spectra of these 0.01% solutions in CH₂Cl₂, using excitation wavelengths of ca. 340 nm or 505 nm, at r.t., but no emissions could be observed.

3.4. Crystal structures

All complexes except for **4** have a high tendency to crystallize. The molecular structures of **2b** and **6a** are depicted in Figs. 1 and 2.

The geometry around the platinum atom is very similar in all complexes (see Table 3), and also similar to related platinacycles with ligands of the phenylpyridine type [2,21] or the ferrocenylimine type [7] As can be seen from the torsion angles C–Pt–S–O, the SO-bond of the sulfoxide ligand is coplanar with the cyclopentadienyl ring, the deviation increasing in the series **3a** < **2a** < **2b**. At the same time the distance H9…O decreases from **3a** to **2b**. This C–H…O hydrogen bond persists in solution as can be concluded from the substantial low-field shift of the CH proton in the ¹H NMR spectra.



Fig. 4. Top view of the head-to-tail dimer in the crystal of 2a.



Fig. 5. Side view of the dimer in 2a.

Another important structural feature for the usefulness of square-planar platinum (II) complexes as emitters in OLED applications is their "tendency ...to aggregate in higher concentration, resulting in quenching of emission in the solid state" and the observation "that inhibition of stacking... is beneficial to the emitting behavior" [22]. On the other hand, it has been claimed that "the photophysical properties associated with Pt…Pt and π - π interactions most often disappear in a diluted solution..." [23] Several cycloplatinated compounds with ligands of the phenylpyridine type have been shown to exhibit such π - π interactions with distances of ca. 3.4 Å [2a,21a,b,22-24]. The observed Pt...Pt distances varied at the same time between 2.91 and 5.99 Å. In some

instances, by deliberate choice of counterions or sterically hindered cyclometallating ligands the formation of π -stacks and Pt···Pt interactions could be avoided to enforce the monomer emissions [25]. Since the pi-coordinated (Cp-M)-fragment should make stacking of more than two platinacycles impossible we looked at the possibility of π -stacked dimers. The structures of **2b** and **6a** show no π - π interactions at all, and the Pt···Pt distances of more than 6 Å also exclude any metal-metal interactions. In the ruthenocene structure **3a** there are head-to-tail dimers with interplanar distances of 3.54 Å, but the Pt···Pt distance of nearly 6 Å still excludes any metal-metal interaction (Fig. 3). These parameters are very similar to the ones found in the crystal structure of [Pt(ppy)(DMSO)Cl] [21a].

In compound **2a** two molecules related by the symmetry operators (*x*,*y*,*z*) and (1-x, y, 3/2 - z) and having the same planar chirality approach each other to a Pt–Pt distance of 3.921 Å. Although there are also π – π interactions between these molecules, there is an interplanar angle of ca. 15° which reduces the overlap substantially (Figs. 4 and 5).

4. Conclusion

We could prepare cycloplatinated pyridylmetallocenes in good to excellent yields and characterize them by NMR and mass spectrometry. Crystal structure determinations prove the proposed structures and also show in some cases the formation of dimers with π - π interactions. All ferrocene compounds have dark red colors, while the ruthenocene derivative is yellow. Unfortunately none of the prepared compounds shows fluorescence neither in the solid state nor in solution, at least at room temperature. This might seem to be expected, since it is known that ferrocene itself is not luminescent and ruthenocene only at low temperatures [26], and also that ferrocene guenches triplet states of organic compounds [27]. On one hand, this property could be used for the construction of fluorescence switches [28], on the other hand it could be shown that with appropriately substituted ferrocene good fluorescent properties are obtainable [29]. This lends hope to further synthetic efforts, towards the preparation of luminescent pyridylmetallocenes by proper combination of metal and ring substituents. This effort seems particularly worthwhile in the light of recent research towards promising photoactive antitumoral platinum complexes [30].

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Appendix A. Supplementary material

The supplementary crystallographic data for this article can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.01.022.

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