Square Planar (*SP*-4) and Octahedral (*OC*-6) Complexes of Platinum(II) and -(IV) with Predetermined Chirality at the Metal Center

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cis-Bis-homoleptic platinum(II) complexes, with predetermined helical chirality at the metal center, can be obtained by using strongly sterically interacting ligands. With this aim, two new ligands, (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine, th4,5ppy (**2**), and (8*R*,10*R*)-2-(2′-thienyl)-5,6-pinenopyridine, th5,6ppy (**4**), were synthesized and coordinated to platinum. The structures of the resulting complexes, Pt(th4,5ppy)$_2$ (**5**) and Pt(th5,6ppy)$_2$ (**6**), were determined by X-ray diffraction, and it was found that they both crystallize with a Δ-*cis* configuration. Thermal oxidative additions (TOA) of alkyl halides were performed with both complexes leading, in the case of **5**, to a mixture of isomers and, in the case of **6**, to isomerically pure products. The predetermination of chirality at the metal center is therefore preserved in the octahedral (*OC*-6) platinum(IV) complexes. Crystals of Pt(th4,5ppy)$_2$ (**5**) are orthorhombic, of space group $P2_12_12_1$, with $a = 12.973(1)$ Å, $b = 13.619(2)$ Å, $c = 17.665(2)$ Å, $\alpha = \beta = \gamma = 90°$, and $Z = 4$. Final $R = 0.0268$ and $R_w = 0.0424$ for 3101 observed reflections. Crystals of Pt(th5,6ppy)$_2$ (**6**) are hexagonal, of space group $P6_1$, with $a = 11.5465(4)$ Å, $b = 11.5465(4)$ Å, $c = 35.356(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, and $Z = 6$. Final $R = 0.0424$ and $R_w = 0.0845$ for 2660 observed reflections. Neither molecule possesses a crystallographic C_2 symmetry.

Introduction

Square planar (*SP*-4) coordination geometry, very often exhibited by coordination species of metals with d^8 electronic configuration, constitutes basically an achiral structure. Nevertheless, under special circumstances, *SP*-4 complexes can become chiral. This is obviously the case if chiral ligands are involved. It occurs also in bis-heteroleptic complexes with bidentate ligands where symmetry elements, present in one of the chelates, are broken by the other non identical ligand. The well-known example is the complex [Pt(isobutylenediamine)(*meso*-stilbenediamine)]$^{2+}$.[2] A third possibility was observed with *cis*-bis-cyclometalated complexes if strong steric ligand interactions disturb the square planar geometry in such a way that it becomes a two-bladed helix.[3] In the cases described so far, these chiral helical *SP*-4 complexes were obtained as racemates. We therefore were interested to design ligands that predetermine the helical chirality at the metal center. Obviously, this can be achieved only by using ligands that have large steric interactions and are chiral themselves. The synthesis developed recently for chiral derivatives of bipyridine was easily transferable to ligands that can give cyclometalated complexes (Figure 1).[4,5] Two new ligands, (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine, th4,5ppy (**2**), and (8*R*,10*R*)-2-(2′-thienyl)-5,6-pinenopyridine, th5,6ppy (**4**), were coordinated to platinum. The resulting *cis*-bis-homoleptic complexes (Figure 2) were investigated in view of their predetermined helical chirality at the metal center.

SP-4 d^8 complexes often undergo oxidative addition reactions.[6] Thereby the formal oxidation number increases by 2, yielding a d^6-configured metal. Bis-homoleptic achiral complexes, with two cyclometalating ligands, yield in many cases

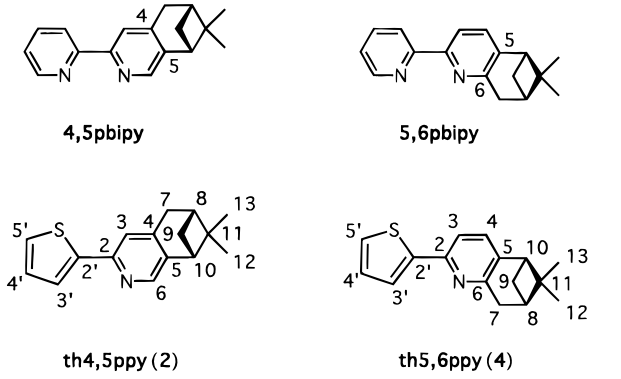

Figure 1. (8*R*,10*R*)-4,5-Pinenobipyridine, 4,5-pbipy, and (8*R*,10*R*)-5,6-pinenobipyridine, 5,6-pbipy, and the analogous thienylpyridine ligands **2** and **4**.

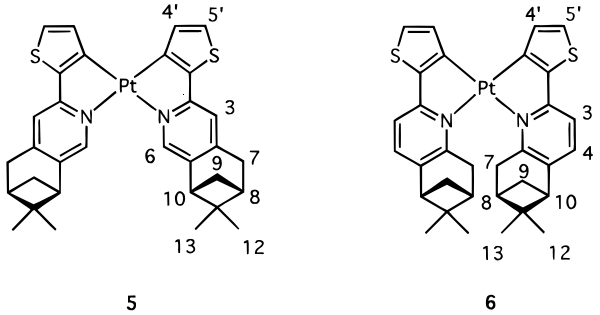

Figure 2. Number scheme of *cis*-bis[(8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine]platinum(II), Pt(th4,5ppy)$_2$ (**5**), and Δ-*cis*-bis[(8*R*,10*R*)-2-(2′-thienyl)-5,6-pinenopyridine]platinum(II), Pt(th5,6ppy)$_2$ (**6**).

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on addition three isomers.[6] If, instead of achiral bis-homoleptic complexes, the species with predetermined chiralities are used for oxidative addition reactions, only one of a pair of diastereomers is formed. Thus, the predetermination of the helical chirality in the *SP*-4 complexes is preserved upon changing the geometry from *SP*-4 to *OC*-6.

Experimental Section

Products. 2-Acetylthiophene, (−)-α-pinene, (−)-myrtenal, α-bromo-2,3,4,5,6-pentafluorotoluene, and iodomethane were purchased from Fluka and used without purification. *tert*-Butyllithium, 15% in pentane, was obtained from Merck. The precursor platinum complex $Pt(Et_2S)_2Cl_2$ was prepared by following procedures described by Kauffman[14] and Livingstone.[15] Diethyl ether and THF were distilled from sodium, while dichloromethane and tetrachloromethane were dried over a P_2O_5 dispersion.

Measurements. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with a Varian Gemini 300 instrument using solvent as the internal standard. The measurements at variable temperatures were made on an Avance DRX 500 Bruker spectrometer (500 MHz). Chemical shifts are reported in ppm on the δ scale. Assignment of the proton spectra was performed by COSY (COrrelation SpectroscopY) experiments, and the distinction between primary (pr), secondary (se), tertiary (te), and quaternary (qr) carbons was done using DEPT (Distortionless Enhancement by Polarization Transfer) experiments. Infrared spectral data were collected using a Perkin-Elmer 683 spectrometer with the samples (1%) in compressed KBr disks, and mass spectral data were obtained with a VG Instruments 7070E equipped with a FAB inlet system. UV−vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrometer. The CD spectra were measured on a Jobin Yvon autodichrograph Mark V spectrometer. Uncorrected melting point (mp) values were determined with a Buchi 520 apparatus. Microanalyses were obtained from Ciba-Geigy, Marly, Switzerland.

Suitable crystals for X-ray analysis were grown by diffusion (1−2 days) of hexane into dichloromethane at room temperature. Crystal data and details of the structure refinement of **5** and **6** are summarized in Table 4. The data were collected on a Stoe-Siemens AED2 four-circle diffractometer (graphite-monochromated Mo Kα radiation) at room temperature using the ω/θ scan mode. An empirical absorption correction was applied to the intensity data using the XABS2 and DIFABS subroutines in the respective cases of **5** and **6**. Both structures were solved with the SHELXS86 program.[18]

(2-Thienylacetyl)pyridinium Bromide (1). 2-Acetylthiophene (25.8 g, 204 mmol) in tetrachloromethane (200 mL) and a catalytic amount of iron filings were heated to 60 °C. Bromine (32.7 g, 204.4 mmol), diluted in tetrachloromethane (100 mL), was slowly added and the mixture stirred for 3 h at 60 °C with N_2 bubbling. The reddish solution was filtered through silica gel and the volume reduced to 100 mL. The resulting yellowish solution was cooled in an ice bath and pyridine (40 mL, 497 mmol) added. The solution was stirred overnight at room temperature and the pyridinium salt was filtered off, washed with ether, and dried at 80 °C under reduced pressure. Yield: 55% (31.9 g). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.02 (d×d, 2H, ^3J = 6.8 Hz, ^4J = 1.3 Hz), 8.72 (t×t, 1H, ^3J = 7.8 Hz, ^4J = 1.3 Hz), 8.27 (d×d, 2H, ^3J = 7.8 Hz, ^3J = 6.8 Hz), 8.23 (d×d, 1H, ^3J = 4.9 Hz, ^4J = 1.1 Hz), 8.21 (d×d, 1H, ^3J = 3.9 Hz, ^4J = 1.1 Hz), 7.41 (d×d, 1H, ^3J = 4.9 Hz, ^3J = 3.9 Hz), 6.40 (s, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 183.6 (qr), 146.5 (te), 146.2 (te, 2C), 139.2 (qr), 136.8 (te), 135.0 (te), 129.2 (te), 127.8 (te, 2C), 65.6 (se). Anal. Calcd for $C_{11}H_{10}BrNOS$: C, 46.49; H, 3.55; N, 4.93; Br, 28.12. Found: C, 46.30; H, 3.55; N, 4.87; Br, 28.08.

(+)-Pinocarvone (3). (+)-Pinocarvone was prepared from (−)-α-pinene, 97% (38.8 g, 285 mmol), by following a method of Mihelich,[9] and distilled under reduced pressure. Yield: 60% (25.5 g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.91 (d, 1H, ^2J = 1.7 Hz), 4.95 (d, 1H, ^2J = 1.7 Hz), 2.71 (d×d, 1H, ^3J = 6.0 Hz, ^4J = 6.0 Hz), 2.67−2.57 (m, 2H), 2.46 (d×d, 1H, ^2J = 19.2 Hz, ^3J = 3.1 Hz), 2.15 (t×d×d, 1H, ^3J = 6.3 Hz, ^3J = 6.0 Hz, ^3J = 3.1 Hz), 1.31 (s, 3H), 1.24 (d, 1H, ^2J = 10.3 Hz), 0.75 (s, 3H).

(8*R*,10*R*)-2-(2′-Thienyl)-4,5-pinenopyridine, th4,5ppy (2). A mixture of (2-thienylacetyl)pyridinium bromide (**1**) (7.10 g, 25 mmol) in formamide (40 mL), ammonium acetate (3.86 g, 50 mmol), and (−)-myrtenal (3.76 g, 25 mmol) was heated at 60 °C for 16 h. The reaction was quenched by addition of water (20 mL) and the brownish solution was extracted with hexane (8 × 100 mL). After the mixture was dried over $MgSO_4$, the solvent was removed and an orange oil that solidified at room temperature was isolated. Yield: 80% (5.05 g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.07 (s, 1H), 7.50 (d×d, 1H, ^3J = 3.7 Hz, ^4J = 1.2 Hz), 7.43 (s, 1H), 7.31 (d×d, 1H, ^3J = 5.0 Hz, ^4J = 1.2 Hz), 7.07 (d×d, 1H, ^3J = 5.0 Hz, ^3J = 3.7 Hz), 2.97 (d, 2H, ^3J = 2.7 Hz), 2.80 (d×d, 1H, ^4J = 5.6 Hz, ^3J = 5.6 Hz), 2.68 (d×d×d, 1H, ^2J = 9.6 Hz, ^3J = 5.6 Hz, ^3J = 5.6 Hz), 2.28 (t×d×d, 1H, ^3J = 5.6 Hz, ^4J = 5.6 Hz, ^3J = 2.7 Hz), 1.39 (s, 3H), 1.20 (d, 1H, ^2J = 9.6 Hz), 0.63 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.8 (qr), 145.7 (qr), 145.5 (qr), 145.2 (te), 141.2 (qr), 127.8 (te), 126.6 (te), 123.5 (te), 118.3 (te), 44.4 (te), 40.0 (te), 39.3 (qr), 32.8 (se), 31.9 (se), 26.0 (pr), 21.4 (pr). MS (EI), *m/z* (%): 255 (M^+, 14), 240 ($M^+ - CH_3$, 10), 212 ($M^+ - C_3H_7$, 100). IR (KBr), cm^{-1}: 2920s, 1596w, 1536w, 1474m, 1384m, 1262w, 1220w, 1128w, 1054w, 942w, 828w, 692s. UV−vis (CH_2Cl_2) [λ, nm (ϵ, M^{-1} cm^{-1})]: 229 (6281), 293 (sh), 308 (15 545). Mp: 118−119 °C. Anal. Calcd for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48. Found: C, 75.05; H, 6.75; N, 5.36.

(8*R*,10*R*)-2-(2′-Thienyl)-5,6-pinenopyridine, th5,6ppy (4). A mixture of (2-Thienylacetyl)pyridinium bromide (**1**) (6.93 g, 24.4 mmol), in acetic acid (25 mL), ammonium acetate (15.04 g, 195.1 mmol) and (+)-pinocarvone (**3**) (3.66 g, 24.4 mmol) was heated at 80 °C for 15 h. The reaction was quenched by addition of water (25 mL), and the brownish solution was extracted with hexane (8 × 100 mL). After the mixture was dried over $MgSO_4$, the solvent was removed and a brownish oil that solidified at room temperature was isolated. Yield: 71% (4.40 g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50 (d×d, 1H, ^3J = 3.7 Hz, ^4J = 1.1 Hz), 7.34 (d, 1H, ^3J = 7.7 Hz), 7.30 (d×d, 1H, ^3J = 5.1 Hz, ^4J = 1.1 Hz), 7.17 (d, 1H, ^3J = 7.7 Hz), 7.06 (d×d, 1H, ^3J = 5.1 Hz, ^3J = 3.7 Hz), 3.12 (d, 2H, ^3J = 2.7 Hz), 2.74 (d×d, 1H, ^4J = 5.7 Hz, ^3J = 5.7 Hz), 2.66 (d×d×d, 1H, ^2J = 9.4 Hz, ^3J = 5.7 Hz, ^3J = 5.7 Hz), 2.36 (t×d×d, 1H, ^4J = 5.7 Hz, ^3J = 5.7 Hz, ^3J = 2.7 Hz), 1.39 (s, 3H), 1.27 (d, 1H, ^2J = 9.4 Hz), 0.66 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.8 (qr), 149.9 (qr), 145.4 (qr), 140.4 (qr), 133.5 (te), 127.8 (te), 126.2 (te), 123.5 (te), 115.6 (te), 46.4 (te), 40.2 (te), 39.5 (qr), 36.6 (se), 32.0 (se), 26.0 (pr), 21.3 (pr). MS (EI), *m/z* (%): 255 (M^+, 43), 240 ($M^+ - CH_3$, 40), 226 ($M^+ - C_2H_5$, 19), 212 ($M^+ - C_3H_7$, 100). IR (KBr), cm^{-1}: 2962m, 2924m, 1570m, 1448m, 1420s, 1266w, 1218w, 1108m, 1050w, 1020w, 942w, 894w, 818m, 756w, 704s. UV−vis (CH_2Cl_2) [λ, nm (ϵ, M^{-1} cm^{-1})]: 228 (4139), 294 (sh), 311 (15 704). Mp: 70−2 °C. Anal. Calcd for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48. Found: C, 75.22; H, 6.70; N, 5.34.

Platinum(II) Bis-Homoleptic Cyclometalated Complexes. General Synthesis. The lithiation of the ligand at position 3′ on the thiophene ring was done following a procedure by Kauffmann.[12] The ligand was dissolved in dried ether in a "Schlenk" flask under argon. *tert*-Butyllithium was added at −70 °C and the solution was allowed to warm to room temperature for half an hour. The reaction flask was protected from the light and $Pt(SEt_2)_2Cl_2$, dissolved in a minimun volume of THF, was added at −70 °C. The solution was again allowed to warm to room temperature for 90 min. The reaction was quenched by addition of water (10 mL) and, after removal of the solvent, the resulting product was purified by flash chromatography on silicagel, using dichloromethane as eluent. The solvent was evaporated and the reddish complex was crystallized by either diffusion of hexane in dichloromethane or precipitation from acetone.

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Pt(th4,5ppy)$_2$ (5). Th4,5ppy (**2**) (726 mg, 2.84 mmol) dissolved in dried ether (50 mL) was lithiated with *tert*-butyllithium, 15% (2 mL, 2.94 mmol). Pt(SEt$_2$)$_2$Cl$_2$ (424 mg, 0.94 mmol) was added, and crystals were obtained by diffusion of hexane into dichloromethane. Yield: 26% (175 mg). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.16 (s, 2H), 7.65 (d, 2H, ^3J = 4.8 Hz), 7.38 (d, 2H, ^3J = 4.8 Hz), 7.29 (s, 2H), 3.02 (d, 4H, ^3J = 2.7 Hz), 2.82 (d×d, 2H, ^4J = 5.6 Hz, ^3J = 5.6 Hz), 2.75 (d×d×d, 2H, ^2J = 9.6 Hz, ^3J = 5.6 Hz, ^3J = 5.6 Hz), 2.31 (t×d×d, 2H, ^4J = 5.6 Hz, ^3J = 5.6 Hz, ^3J = 2.7 Hz), 1.41 (s, 6H), 1.30 (d, 2H, ^2J = 9.6 Hz), 0.65 (s, 6H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 160.1 (qr), 147.9 (qr), 145.7 (qr), 143.4 (te), 139.0 (qr), 135.6 (te), 126.4 (te), 118.0 (qr), 117.4 (te), 44.9 (te), 40.0 (te), 39.7 (qr), 33.1 (se), 32.1 (se), 26.0 (pr), 21,5 (pr). MS (FAB), *m/z*: 704 (M$^+$), 448 (M$^+$ − th4,5ppy), 256 (th4,5ppy), 212 (th4,5ppy − C$_3$H$_7$). IR (KBr), cm^{-1}: 2920s, 1616s, 1488s, 1434m, 1366w, 1330w, 1290w, 1260w, 1130w, 1008w, 906w, 874m, 730m, 706m, 640w, 618w. UV−vis (CH$_2$Cl$_2$) [λ, nm (ϵ, M^{-1} cm^{-1})]: 307 (36 762), 321 (sh), 346 (sh), 417 (11790), 458 (sh). CD (CH$_2$Cl$_2$) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 304 (−9.0), 320 (5.5), 356 (0.6), 415 (12.6), 462 (−1.4).

Δ-Pt(th5,6ppy)$_2$ (6). Th5,6ppy (**4**) (726 mg, 2.84 mmol) dissolved in dried ether (50 mL) was lithiated with *tert*-butyllithium, 15% (2 mL, 2.94 mmol). Pt(SEt$_2$)$_2$Cl$_2$ (424 mg, 0.94 mmol) was added, and the final complex was precipitated in acetone. Crystals were obtained by slow diffusion of hexane into dichloromethane. Yield: 42% (278 mg). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.64 (d, 2H, ^3J = 4.9 Hz), 7.34 (d, 2H, ^3J = 4.9 Hz), 7.21−7.13 (m, 4H, ^3J = 7.9 Hz), 3.36 (d×d, 2H, ^2J = 18.8 Hz, ^3J = 3.7 Hz), 2.96 (d, 2H, ^2J = 18.8 Hz), 2.71 (d×d, 2H, ^4J = 5.6 Hz, ^3J = 5.6 Hz), 2.63 (d×d×d, 2H, ^2J = 9.4 Hz, ^3J = 5.6 Hz, ^3J = 5.6 Hz), 2.18 (t×d×d, 2H, ^4J = 5.6 Hz, ^3J = 5.6 Hz, ^3J = 3.7 Hz), 1.29 (s, 6H), 1.16 (d, 2H, ^2J = 9.4 Hz), 0.50 (s, 6H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 159.6 (qr), 158.0 (qr), 145.5 (qr), 142.8 (qr), 138.8 (qr), 135.6 (te), 134.8 (te), 126.0 (te), 113.6 (te), 46.3 (te), 40.4 (qr), 40.0 (te), 36.0 (se), 30.5 (se), 25.8 (pr), 21.4 (pr). MS (FAB), *m/z*: 704 (M$^+$), 448 (M$^+$ − th5,6ppy), 256 (th5,6ppy), 212 (th5,6ppy − C$_3$H$_7$). IR (KBr), cm^{-1}: 2970w, 2918m, 1585s, 1452s, 1429m, 1224w, 1173w, 1115w, 1073m, 1050m, 876m, 814w, 705s, 632w. UV−vis (CH$_2$Cl$_2$) [λ, nm (ϵ, M^{-1} cm^{-1})]: 280 (sh), 312 (31859), 331 (sh), 356 (sh), 443 (7163). CD (CH$_2$Cl$_2$) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 280 (8.6), 310 (20.7), 325 (2.3), 333 (6.2), 355 (−3.3), 368 (9.0), 444 (−24.7).

Pt(th4,5ppy)$_2$F$_5$BzBr. α-Bromo-2,3,4,5,6-pentafluorotoluene (1.842 g, 7.06 mmol) in dichloromethane (100 mL) and Pt(th4,5ppy)$_2$ (**5**) (200 mg, 0.28 mmol) were stirred for 0.5 h at room temperature under argon in the dark. The solution was evaporated, and excess bromopentafluorotoluene was evacuated by heating to 80° C under reduced pressure. The resulting yellowish powder was composed of 25% of *trans*-Pt(th4,5ppy)$_2$F$_5$BzBr (**7**), 25% of Δ-*cis*-*fac*-Pt(th4,5ppy)$_2$F$_5$BzBr (**8**), and 50% of Λ-*cis*-*fac*-Pt(th4,5ppy)$_2$F$_5$BzBr (**9**). Complex **7** went through a *trans* → *cis* isomerization within a few days and was not isolated. The separation of **8** and **9** was done by either crystallization (CH$_2$Cl$_2$/hexane) or precipitation at room temperature.

***trans*-Pt(th4,5ppy)$_2$F$_5$BzBr (7) (Not Isolated).** ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.35 (s, 1H), 8.33 (s, 1H), 7.77 (d, 1H, ^3J = 5.1 Hz), 7.75 (d, 1H, ^3J = 5.1 Hz), 7.49 (d, 1H, ^3J = 5.1 Hz), 7.47 (d, 1H, ^3J = 5.1 Hz), 7.40 (s, 1H), 7.34 (s, 1H), 3.11 (d, 4H, ^3J = 2.8 Hz), 2.91 (d×d, 2H, ^4J = 5.5 Hz, ^3J = 5.5 Hz), 2.85 (m, 2H), 2.78 (d×d×d, 2H, ^2J = 10.0 Hz, ^3J = 5.5 Hz, ^3J = 5.5 Hz), 2.35 (t×d×d, 2H, ^4J = 5.5 Hz, ^3J = 5.5 Hz, ^3J = 2.8 Hz), 1.49 (s, 3H), 1.46 (s, 3H), 1.32 (d, 2H, ^2J = 10.0 Hz), 0.74 (s, 3H), 0.70 (s, 3H).

Δ-*cis*-*fac*-Pt(th4,5ppy)$_2$F$_5$BzBr (8). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.19 (s, 1H), 7.53−7.60 (m, 2H, ^3J = 4.9 Hz), 7.28 (s, 1H), 7.13 (s, 1H), 6.98 (d, 1H, ^3J = 4.9 Hz), 6.81 (s, 1H), 6.11 (d, 1H, ^3J = 4.9 Hz), 4.15 (d, 1H, ^2J = 10.0 Hz), 3.61 (d, 1H, ^2J = 10.0 Hz), 3.10 (d, 2H, ^3J = 2.8 Hz), 3.03 (d×d, 1H, ^4J = 5.5 Hz, ^3J = 5.5 Hz), 2.94 (d, 2H, ^3J = 2.8 Hz), 2.83 (d×d×d, 1H, ^2J = 10.1 Hz, ^3J = 5.5 Hz, ^3J = 5.5 Hz), 2.48 (d×d×d, 1H, ^2J = 9.8 Hz, ^3J = 5.5 Hz, ^3J = 5.5 Hz), 2.37 (t×d×d, 1H, ^4J = 5.5 Hz, ^3J = 5.5 Hz, ^3J = 2.8 Hz), 2.20 (d×d, 1H, ^4J = 5.5 Hz, ^3J = 5.5 Hz), 2.17 (t×d×d, 1H, ^4J = 5.5 Hz, ^3J = 5.5 Hz, ^3J = 2.8 Hz), 1.47 (s, 3H), 1.32 (d, 1H, ^2J = 10.1 Hz), 1.26 (s, 3H), 0.99 (d, 1H, ^2J = 9.8 Hz), 0.72 (s, 3H), 0.59 (s, 3H). MS (FAB), *m/z*: 884 (M$^+$ − Br), 783 (M$^+$ − F$_5$Bz), 702 (Pt(th4,5ppy)$_2$), 448 (Pt(th4,5ppy)), 256 (th4,5ppy). IR (KBr), cm^{-1}: 3446w, 2928s, 2362w, 1618s, 1496s, 1428m, 1380w, 1294w, 1246w, 1122m, 1034w, 968s, 878m, 712w. UV−vis (CH$_2$Cl$_2$) [λ, nm (ϵ, M^{-1} cm^{-1})]: 285 (27 906), 307 (sh), 350 (15 993), 358 (sh). CD (CH$_2$Cl$_2$) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 308 (−1.24), 331 (−5.30), 336 (−4.99), 364 (−18.1), 400 (1.73).

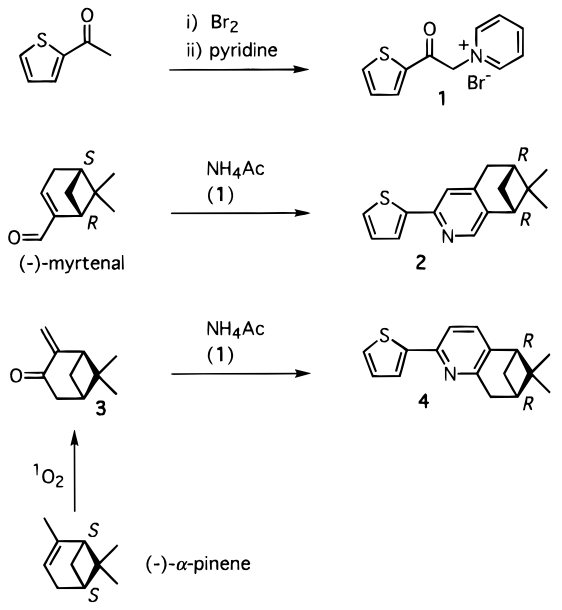
Λ-*cis*-*fac*-Pt(th4,5ppy)$_2$F$_5$BzBr (9). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.22 (s, 1H), 7.65−7.58 (m, 2H, ^3J = 5.0 Hz), 7.29 (s, 1H), 7.20 (s, 1H), 6.92 (d, 1H, ^3J = 5.0 Hz), 6.83 (s, 1H), 6.11 (d, 1H, ^3J = 5.0 Hz), 4.05 (d, 1H, ^2J = 10.3 Hz), 3.66 (d, 1H, ^2J = 10.3 Hz), 3.16 (d, 2H, ^3J = 2.8 Hz), 3.05 (d×d, 1H, ^4J = 5.5 Hz, ^3J = 5.5 Hz), 2.94 (d, 2H, ^3J = 2.8 Hz), 2.79 (d×d×d, 1H, ^2J = 10.3 Hz, ^3J = 5.5 Hz, ^3J = 5.5 Hz), 2.55 (d×d×d, 1H, ^2J = 10.3 Hz, ^3J = 5.5 Hz, ^3J = 5.5 Hz), 2.39−2.34 (m, 2H), 2.17 (t×d×d, 1H, ^4J = 5.5 Hz, ^3J = 5.5 Hz, ^3J = 2.8 Hz), 1.46 (s, 3H), 1.25 (s, 3H), 1.24 (d, 1H, ^2J = 10.3 Hz), 1.12 (d, 1H, ^2J = 10.3 Hz), 0.80 (s, 3H), 0.40 (s, 3H). MS (FAB), *m/z*: 884 (M$^+$ − Br), 783 (M$^+$ − F$_5$Bz), 702 (Pt(th4,5ppy)$_2$), 448 (Pt(th4,5ppy)), 256 (th4,5ppy). IR (KBr), cm^{-1}: 3446w, 2928s, 2362w, 1618s, 1496s, 1428m, 1380w, 1294w, 1246w, 1122m, 1034w, 968s, 878m, 712w. UV−vis (CH$_2$Cl$_2$) [λ, nm (ϵ, M^{-1} cm^{-1})]: 285 (27 906), 307 (sh), 350 (15 993), 358 (sh). CD (CH$_2$Cl$_2$) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 308 (5.16), 316 (4.54), 327 (5.47), 340 (4.07), 364 (17.3), 396 (−1.24).

Δ-*cis*-*fac*-Pt(th5,6ppy)$_2$F$_5$BzBr (10). α-Bromo-2,3,4,5,6-pentafluorotoluene (400 mg, 1.53 mmol) in dichloromethane (50 mL) and Δ-Pt(th5,6ppy)$_2$ (**6**) (50 mg, 0.07 mmol) were stirred for 3 h at room temperature under argon in the dark. The orange solution was evaporated, and excess bromopentafluorotoluene was evacuated by heating to 80 °C under reduced pressure. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.63 (d, 1H, ^3J = 5.3 Hz), 7.53 (d, 1H, ^3J = 5.3 Hz), 7.39 (d, 1H, ^3J = 7.8 Hz), 7.29 (d, 1H, ^3J = 7.8 Hz), 7.07−7.13 (m, 2H, ^3J = 7.9 Hz), 6.78 (d, 1H, ^3J = 5.0 Hz), 5.91 (d, 1H, ^3J = 5.0 Hz), 4.70 (d×d, 1H, ^2J = 19.6 Hz, ^3J = 3.2 Hz), 4.27 (d, 1H, ^2J = 10.5 Hz), 4.07 (d, 1H, ^2J = 10.5 Hz), 3.88 (d, 1H, ^2J = 19.6 Hz), 2.82−2.88 (m, 2H), 2.71 (d×d×d, 1H, ^2J = 9.6 Hz, ^3J = 5.4 Hz, ^3J = 5.4 Hz), 2.53−2.65 (m, 2H), 2.45 (d×d×d, 1H, ^2J = 9.6 Hz, ^3J = 5.4 Hz, ^3J = 5.4 Hz), 1.78 (t×d×d, 1H, ^4J = 5.4 Hz, ^3J = 5.4 Hz, ^3J = 2.4 Hz), 1.72 (d×d, 1H, ^2J = 17.6 Hz, ^3J = 2.4 Hz), 1.43 (s, 3H), 1.17 (s, 3H), 1.16 (d, 1H, ^2J = 9.6 Hz), 0.99 (d, 1H, ^2J = 9.6 Hz), 0.92 (s, 3H), 0.05 (s, 3H). MS (FAB), *m/z*: 884 (M$^+$ − Br), 783 (M$^+$ − F$_5$Bz), 702 (Pt(th5,6ppy)$_2$), 448 (Pt(th5,6ppy)), 256 (th5,6ppy). IR (KBr), cm^{-1}: 3440w, 2924s, 1592s, 1516s, 1496s, 1450s, 1298w, 1226m, 1120m, 1026w, 966s, 878m, 820w, 758w, 710w, 644w, 622w. UV−vis (CH$_2$Cl$_2$) [λ, nm (ϵ, M^{-1} cm^{-1})]: 230 (23683), 283 (11 846), 356 (11 473). CD (CH$_2$Cl$_2$) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 272 (−1.9), 324 (−7.3), 373 (−18.2).

Δ-*cis*-*fac*-Pt(th5,6ppy)$_2$Br$_2$ (11). The same reaction as above was done by directly dissolving Δ-Pt(th5,6ppy)$_2$ (**6**) in α-bromo-2,3,4,5,6-pentafluorotoluene (400 mg, 1.53 mmol). After 1 h of stirring and elimination of excess pentafluorotoluene, two products were isolated in the same proportions. An unexpected complex, Δ-*cis*-*fac*-Pt(th5,6ppy)$_2$Br$_2$ (**11**), was precipitated by diffusion of hexane into dichloromethane, whereas Δ-*cis*-*fac*-Pt(th5,6ppy)$_2$BrF$_5$Bz (**10**) remained in solution. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.85 (d, 1H, ^3J = 5.1 Hz), 7.50 (d, 1H, ^3J = 5.1 Hz), 7.29−7.39 (m, 2H, ^3J = 7.8 Hz), 7.16−7.24 (m, 2H), 7.02 (d, 1H, ^3J = 5.0 Hz), 5.74 (d, 1H, ^3J = 5.0 Hz); 4.52 (d×d, 1H, ^2J = 19.8 Hz, ^3J = 3.0 Hz), 4.08 (d, 1H, ^2J = 19.8 Hz), 3.20 (d×d, 1H, ^2J = 17.8 Hz, ^3J = 3.2 Hz), 2.82 (d×d, 1H, ^4J = 5.7 Hz, ^3J = 5.7 Hz), 2.73 (d×d×d, 1H, ^2J = 9.6 Hz, ^3J = 5.7 Hz, ^3J = 5.7 Hz), 2.65 (d×d, 1H, ^4J = 5.7 Hz, ^3J = 5.7 Hz), 2.46−2.56 (m, 2H), 2.16 (d×d, 1H, ^2J = 17.8 Hz, ^3J = 2.3 Hz), 1.90 (t×d×d, 1H, ^4J = 5.7 Hz, ^3J = 5.7 Hz, ^3J = 2.3 Hz), 1.40 (s, 3H), 1.23 (s, 3H), 1.20 (d, 1H, ^2J = 9.9 Hz), 1.15 (d, 1H, ^2J = 9.6 Hz), 0.73 (s, 3H), 0.22 (s, 3H). MS (FAB), *m/z*: 864 (M$^+$), 783 (M$^+$ − Br), 703 (Pt(th5,6ppy)$_2$), 448 (Pt(th5,6ppy)), 256 (th5,6ppy). IR (KBr), cm^{-1}: 2926s, 2362m, 2336m, 1594s, 1496m, 1450s, 1418w, 1226m, 1120w, 1076w, 1028w, 878m, 820w, 712w. UV−vis (CH$_2$Cl$_2$) [λ, nm (ϵ, M^{-1} cm^{-1})]: 229 (32 516), 279 (sh), 284 (21 008), 302 (sh), 350 (12 162). CD (CH$_2$Cl$_2$) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 262 (1.7), 281 (9.6), 309 (−3.5), 325 (0.6), 360 (−13.9).

Δ-*cis*-*fac*-Pt(5′-Brth5,6ppy)$_2$Br$_2$ (12). Bromine (122 mg, 0.76 mmol) in tetrachloromethane (50 mL) and Δ-Pt(th5,6ppy)$_2$ (**6**) (25 mg, 0.04 mmol) were stirred for 90 min at room temperature under argon in the dark. The reddish solution was evaporated, and excess bromine was removed under reduced pressure. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.80 (s, 1H), 7.37 (d, 1H, ^3J = 7.8 Hz), 7.23 (d, 1H, ^3J = 7.8 Hz), 7.17 (d, 1H, ^3J = 7.8 Hz), 7.12 (d, 1H, ^3J = 7.8 Hz), 5.83 (s, 1H), 4.47 (d×d, 1H, ^2J = 19.6 Hz, ^3J = 3.2 Hz), 4.02 (d×d, 1H, ^2J = 19.6 Hz,

Scheme 1



^3J = 3.2 Hz), 3.15 (d×d, 1H, ^2J = 17.9 Hz, ^3J = 3.0 Hz), 2.82 (d×d, 1H, ^4J = 5.7 Hz, ^3J = 5.7 Hz), 2.66−2.77 (m, 2H), 2.48−2.55 (m, 2H), 2.09 (d×d, 1H, ^2J = 17.9 Hz, ^3J = 3.0 Hz), 1.87−1.92 (m, 1H), 1.40 (s, 3H), 1.24 (s, 3H), 1.11−1.21 (m, 2H), 0.71 (s, 3H), 0.27 (s, 3H). MS (FAB), *m/z*: 941 (M^+ − Br), 861 (M^+ − 2Br), 529 (M^+ − 2Br − (5′-Brth5,6ppy)). IR (KBr), cm^{-1}: 3412w, 2966m, 2926s, 1592s, 1498w, 1448s, 1416s, 1260w, 1224s, 1184w, 1098m, 1074m, 1028m, 974w, 948w, 820m. UV−vis (CH_2Cl_2) [λ, nm (ϵ, M^{-1} cm^{-1})]: 228 (31 652), 295 (22 651), 362 (22 811). CD (CH_2Cl_2) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 238 (15.3), 288 (11.9), 327 (3.2), 367 (−20.1).

Δ-*cis*-*fac*-Pt(th5,6ppy)$_2$CH$_3$I (13). Iodomethane (40 mg, 0.28 mmol) in dichloromethane (50 mL) and Δ-Pt(th5,6ppy)$_2$ (**6**) (40 mg, 0.06 mmol) were stirred for 2 h at room temperature under argon in the dark. The solvent and the iodomethane were then evaporated. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48 (d, 1H, ^3J = 5.0 Hz); 7.36 (d, 1H, ^3J = 7.8 Hz), 7.28 (d, 1H, ^3J = 7.8 Hz), 7.25 (d, 1H, ^3J = 5.0 Hz), 7.22 (d, 1H, ^3J = 7.8 Hz), 7.09 (d, 1H, ^3J = 7.8 Hz), 6.93 (d, 1H, ^3J = 5.0 Hz), 5.66 (d, 1H, ^3J = 5.0 Hz), 4.65 (d×d, 1H, ^2J = 19.4 Hz, ^3J = 2.9 Hz), 3.80 (d, 1H, ^2J = 19.4 Hz), 3.02 (d×d, 1H, ^2J = 17.6 Hz, ^3J = 2.7 Hz), 2.80 (d×d, 1H, ^4J = 5.7 Hz, ^3J = 5.7 Hz), 2.70 (d×d×d, 1H, ^2J = 9.6 Hz, ^3J = 5.7 Hz, ^3J = 5.7 Hz), 2.62 (d×d, 1H, ^4J = 5.7 Hz, ^3J = 5.7 Hz), 2.45−2.55 (m, 2H), 1.96 (d×d, 1H, ^2J = 17.6 Hz, ^3J = 2.7 Hz), 1.86 (s, 3H), 1.84−1.89 (m, 1H), 1.40 (s, 3H), 1.21 (s, 3H), 1.12−1.22 (m, 2H), 0.69 (s, 3H), 0.20 (s, 3H). MS (FAB), *m/z*: 846 (M^+), 831 (M^+ − CH_3), 719 (M^+ − I), 703 (Pt(th5,6ppy)$_2$), 463 (Pt(th5,6ppy)(CH_3)), 449 (Pt(th5,6ppy)), 256 (th5,6ppy). IR (KBr), cm^{-1}: 2966m, 2928s, 2870w, 2362m, 2338w, 1592s, 1490m, 1450s, 1418w, 1226m, 1118w, 880m, 836w, 820w, 728m, 712m, 644w. UV−vis (CH_2Cl_2) [λ, nm (ϵ, M^{-1} cm^{-1})]: 295 (20 692), 355 (14 426). CD (CH_2Cl_2) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 262 (2.2), 289 (15), 367 (−30.8).

Results and Discussion

Synthesis. Two new thienylpyridine ligands were synthesized according to Scheme 1. These ligands have a common precursor, (2-thienylacetyl)pyridinium bromide (**1**), prepared by bromination of acetylthiophene,[7] followed by addition of pyridine. It is well-known that such salts can easily undergo condensation with α,*β*-ene aldehydes or α,*β*-methylene ketones.[8] Consequently, (8*R*,10*R*)-2-(2′-thienyl)-4,5-pinenopyridine, th4,5ppy (**2**), was obtained from (−)-myrtenal and (8*R*,10*R*)-2-(2′-thienyl)-5,6-pinenopyridine, th5,6ppy (**4**), from (+)-pinocarvone (**3**), which was prepared by oxidation of (−)-α-pinene.[9] As they are derived from natural products, taken from the "chiral pool", ligands **2** and **4** have a known absolute configuration. In both cases, the C8 and C10 chiral carbons present an *R* configuration, while carbons C7, C9, and C11 are prochiral.

Table 1. Alkyl Halides, R−X, Used for the Thermal Oxidation of Pt(th4,5ppy)$_2$ (**5**) and Pt(th5,6ppy)$_2$ (**6**)[a]

Pt(II) complex	R−X	Pt(IV) complexes
5	F_5Bz−Br	*trans*-Pt(th4,5ppy)$_2F_5$BzBr (**7**) + Δ-*cis*-*fac*-Pt(th4,5ppy)$_2F_5$BzBr (**8**) + Λ-*cis*-*fac*-Pt(th4,5ppy)$_2F_5$BzBr (**9**)
6	F_5Bz−Br	Δ-*cis*-*fac*-Pt(th5,6ppy)$_2F_5$BzBr (**10**)
	F_5Bz−Br[b]	**10** + Δ-*cis*-*fac*-Pt(th5,6ppy)$_2Br_2$ (**11**)
	Br_2	Δ-*cis*-*fac*-Pt(5′-Brth5,6ppy)$_2Br_2$ (**12**)
	CH_3I	Δ-*cis*-*fac*-Pt(th5,6ppy)$_2CH_3I$ (**13**)

[a] *cis* or *trans* is used to determine the position of R and X in the Pt(IV) complexes; *fac* or *mer* indicates the CCR arrangement. [a] Reactioneaction done without any solvent; **6** is dissolved in F_5Bz−Br.

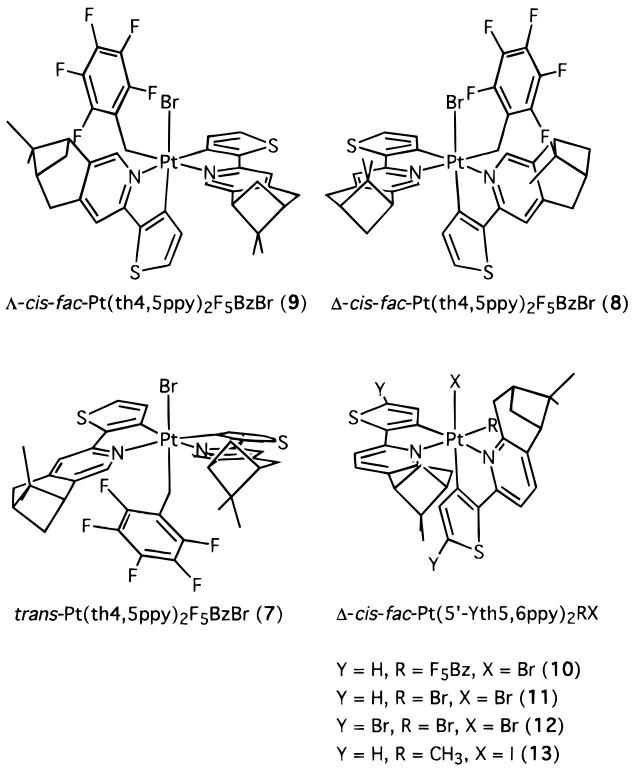


Figure 3. Platinum(IV) complexes synthesized by thermal oxidative addition (TOA) reactions from Pt(th4,5ppy)$_2$ (**5**) and Pt(th5,6ppy)$_2$ (**6**).

A systematic study by Kauffmann showed that, in the case of thienylpyridine, it is possible to make a selective lithiation on the thiophene ring at position 3′, being the correct position for a cyclometalation to occur.[10] This reaction was successfully performed with ligands **2** and **4**. According to a previously used method,[11−13] the *cis*-bis-homoleptic platinum(II) complexes Pt(th4,5ppy)$_2$ (**5**) and Pt(th5,6ppy)$_2$ (**6**) (Figure 2) were formed by metal exchange with bis(diethyl sulfide)dichloroplatinum-(II).[14,15]

Oxidative additions with *cis*-bis[2-(2′-thienyl)pyridine]platinum(II) have already been studied, using alkyl halides as reagents.[6] The result was that, among the eleven possible combinations, only three isomers were typically formed. The thermal oxidative addition (TOA) of α-bromo-2,3,4,5,6-pentafluorotoluene with **5** similarly led to the formation of three isomers, consistent with previous results. These isomers were identified as the *trans*-, Δ-*cis*-*fac*-, and Λ-*cis*-*fac*-bromo-2,3,4,5,6-pentafluorobenzyl−bis(th4,5ppy)platinum(IV) complexes (**7**−**9**). ^{1}H NMR showed that complexes **7**−**9** are present in solution in the ratio 1:1:2, respectively. The *trans* product **7** was not isolated because it went through a *trans* → *cis* isomerization within 1 week at room temperature. The Δ-*cis*-*fac* **8** and Λ-*cis*-*fac* **9** diastereomers were separated by either precipitation or crystallization. The same TOA was performed with **6**, and this time, only one isomer was observed, Δ-*cis*-

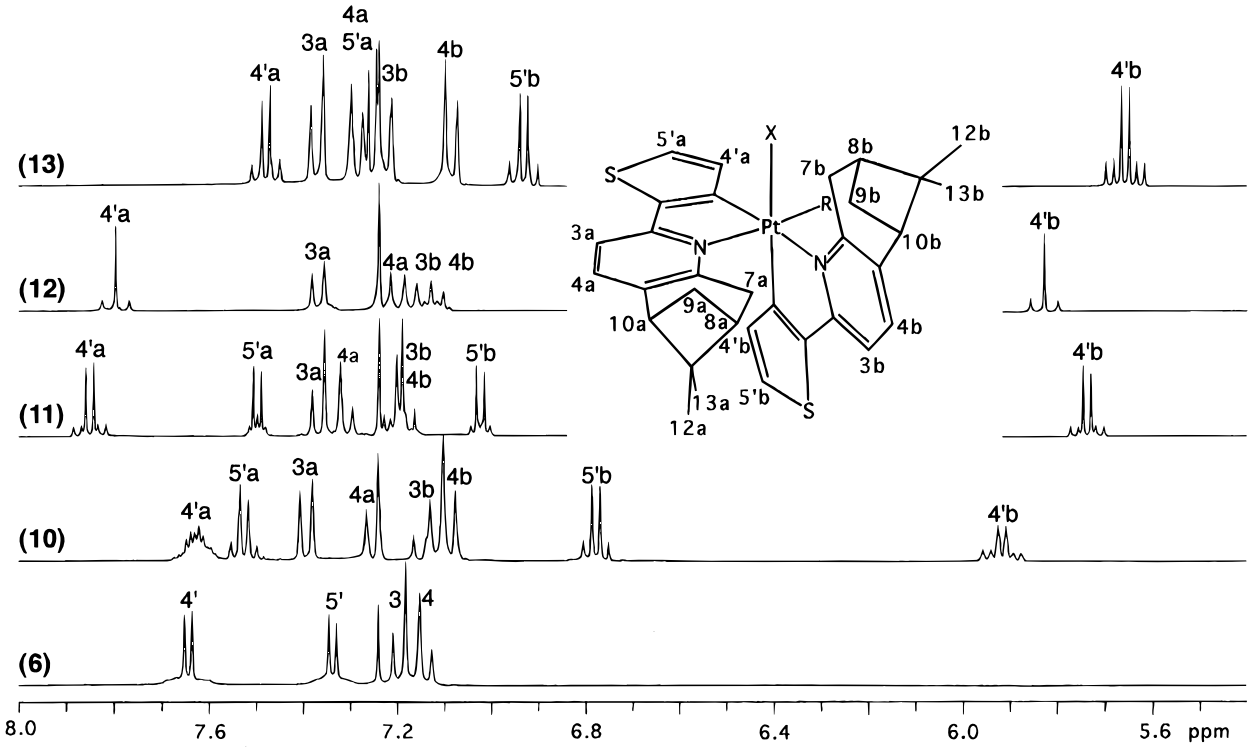


Figure 4. ^{1}H NMR spectra in the aromatic region of Pt(th5,6ppy)$_2$ (**6**), Δ-*cis*-*fac*-Pt(th5,6ppy)$_2$F$_5$BzBr (**10**), Δ-*cis*-*fac*-Pt(th5,6ppy)$_2$Br$_2$ (**11**), Δ-*cis*-*fac*-Pt(5′-Brth5,6ppy)$_2$Br$_2$ (**12**), and Δ-*cis*-*fac*-Pt(th5,6ppy)$_2$ (**13**).

Table 2. ^{1}H NMR Chemical Shifts (δ, ppm) in the Aromatic Region of Ligands **2** and **4** and of Complexes **5**−**13**

	H−C										
	6b	6a	3′	4′a	4′b	5′a	5′b	3a	3b	4a	4b
2	8.07		7.50	7.07		7.31		7.43			
4			7.50	7.06		7.30		7.70		7.17	
5	8.16			7.65		7.38		7.29			
6				7.64		7.34		*a*		*a*	
7	8.35	8.33		7.77	7.75	7.49	7.47	7.40	7.34		
8	9.19	6.82		*b*	6.11	*b*	6.98	7.29	7.13		
9	9.22	6.83		*a*	6.11	*b*	6.92	7.29	7.20		
10				7.63	5.91	7.53	6.78	7.39	*c*	7.29	*c*
11				7.85	5.74	7.50	7.02	*d*	*c*	*d*	*e*
12				7.80	5.83			7.37	7.17	7.23	7.12
13				7.48	5.66	7.25	6.93	7.36	7.22	7.28	7.09

[a] 7.21−7.13. [b] 7.65−7.58. [c] 7.13−7.07. [d] 7.39−7.29. [e] 7.24−7.16.

fac-bromo-2,3,4,5,6-pentafluorobenzyl−bis(th5,6ppy)platinum-(IV) (**10**). To confirm this result, other oxidative addition reactions were carried out with **6**, and the formation of only the Δ-*cis*-*fac* isomers was always observed. Table 1 and Figure 3 present the reactions performed with both **5** and **6** and the resulting products. The yields for the formation of the platinum-(IV) complexes are quantitative.

^{1}H NMR. Figure 4 shows the aromatic region of complexes **6** and **10**−**13**, while Table 2 lists the chemical shift values (δ, ppm) of the aromatic protons of ligands **2** and **4** and those of complexes **5**−**13**. The disappearance of the H−C3′ signal, on the thiophene, confirmed that cyclometalation occurred. Complex **12** is brominated at the C5′ carbon, explaining the differences in the spectrum. As compounds **5** and **6** have a C_2 symmetry in solution, the two ligands cannot be differentiated. However, there is no element of symmetry in the *trans* Pt(IV) complex **7**, leading to a small inequivalence of the signals for the two ligands. The same occurs with the **8**−**13** Δ or Λ Pt-(IV) complexes, but with a larger enhancement of the splitting effect.

In the platinum(II) complexes, the metal center exerts a deshielding effect, which explains the downfield position of the

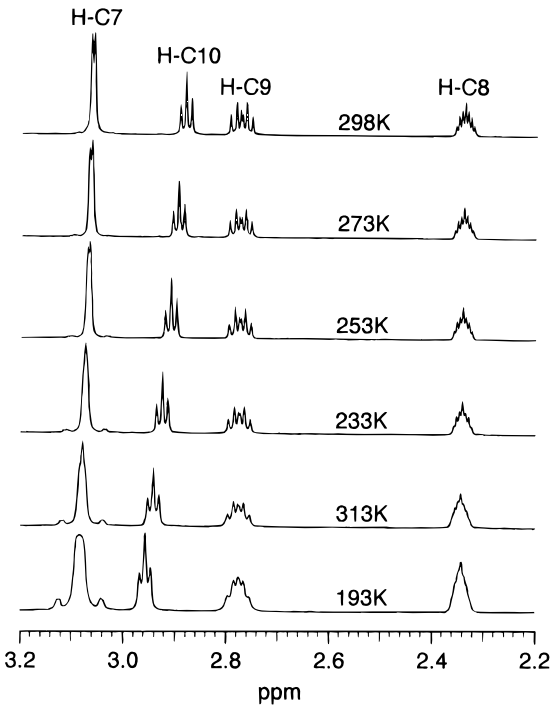


Figure 5. ^{1}H NMR temperature dependence of Pt(th4,5ppy)$_2$ (**5**).

H−C4′, H−C5′, or H−C6 proton signals in comparison with those of the free ligands. This is not the case for the H−C3 and H−C4 protons, whose signals appear upfield. It seems that complexation of ligands **2** and **4** causes the thiophene and the pyridine rings to be coplanar, which implies a greater interaction, and so, a larger shielding effect is experienced. The same observations were made with the related complex *cis*-bis[2-(2′-thienyl)pyridine]platinum(II).[16] The spectrum of complex **7** is very similar to that of complex **5**, except that all aromatic signals are duplicated and shifted downfield. These effects were attributed to the loss of symmetry and to the higher charge of the platinum(IV) center, respectively. Compounds **8**−**13** H−C4′b

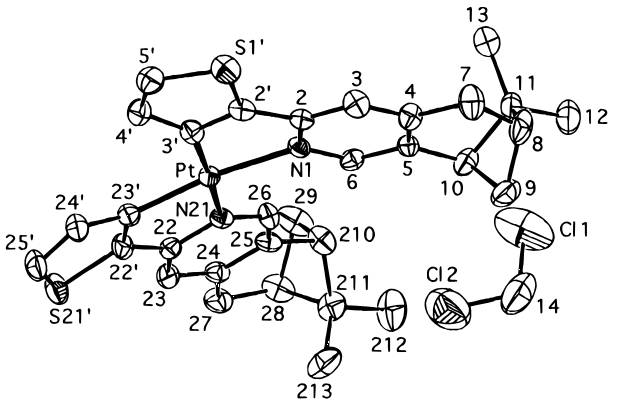


Figure 6. Number scheme and ORTEP plot of Pt(th4,5ppy)$_2$ (**5**). The thermal ellipsoids are represented with a 50% probability. Hydrogen atoms have been omitted for clarity.

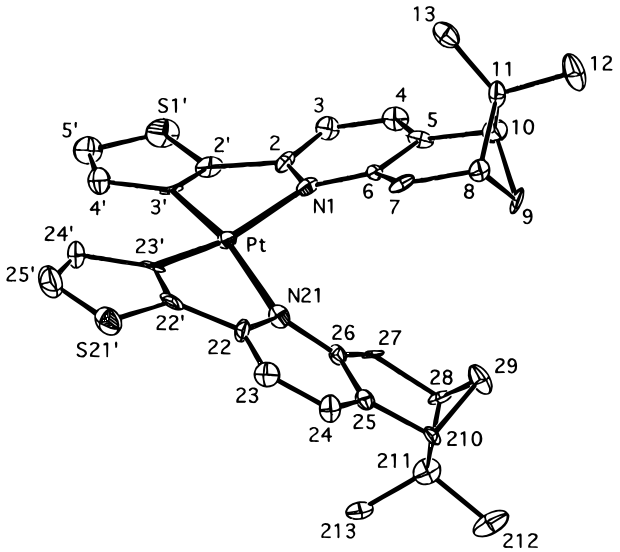


Figure 7. Number scheme and ORTEP plot of Pt(th5,6ppy)$_2$ (**6**). The thermal ellipsoids are represented with a 50% probability. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Pt(th4,5ppy)$_2$ (**5**) and Pt(th5,6ppy)$_2$ (**6**)

	5	**6**
Pt−N1	2.168(7)	2.166(13)
Pt−N21	2.147(7)	2.174(13)
Pt−N^a	2.157(7)	2.170(13)
Pt−C3′	1.984(10)	1.975(14)
Pt−C23′	2.000(10)	1.92(2)
Pt−C^a	1.992(10)	1.947(17)
C2−C2′	1.409(15)	1.48(2)
C22−C22′	1.450(14)	1.46(2)
N1−Pt−C3′	80.2(4)	79.0(6)
N21−Pt−C23′	80.0(3)	78.9(6)
Pt−Pt	8.643^b	6.323
(N1−Pt−N21)$_{yz}$	11.4	18.3
(C3′−Pt−C23′)$_{yz}$	13.3	22.5

^{a} Mean values. ^{b} Shortest distance.

and H−C5′b signals appear upfield of the H−C4′a and H−C5′a signals, since they are pointing to the inside of the thiophene ring of the other ligand. In complexes **8** and **9**, the same effect is observed with the H−C6a proton, which is pointing to the inside of the pyridine ring of the other ligand. All these observations confirmed the expected configurations for complexes **5**−**13**.

Figure 5 presents an interesting region of complex **5**, recorded over a range of temperatures from 298 to 193 K. At 298 K, both H−C7 protons are accidentally equivalent and their signal

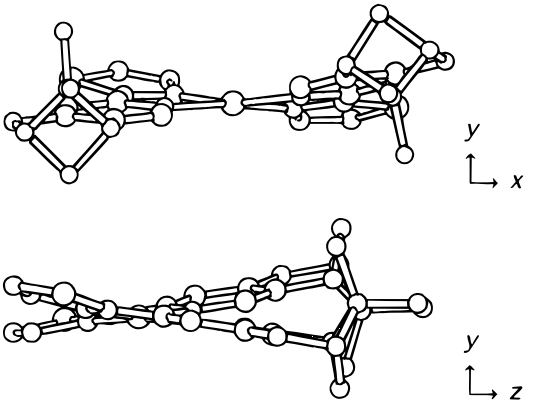


Figure 8. Front and side views of Pt(th4,5ppy)$_2$ (**5**).

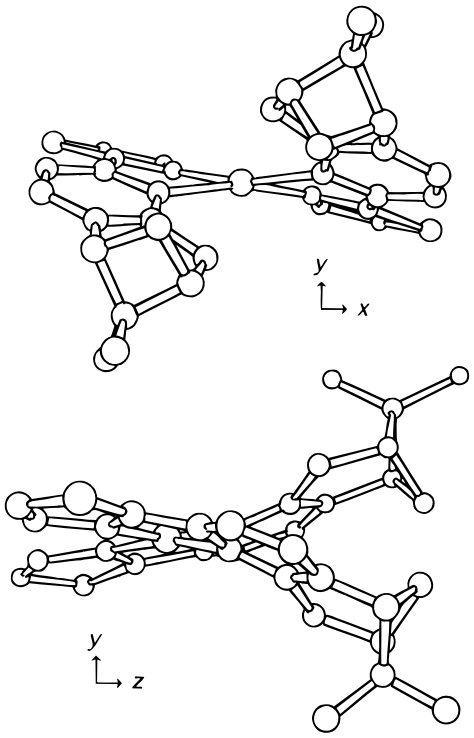


Figure 9. Front and side views of Pt(th5,6ppy)$_2$ (**6**).

Table 4. Crystallographic Data for Pt(th4,5ppy)$_2$·CH_2Cl_2 (**5**) and Pt(th5,6ppy)$_2$ (**6**)

	5	**6**
empirical formula	$C_{33}H_{34}Cl_2N_2PtS_2$	$C_{32}H_{32}N_2PtS_2$
mol wt	788.75	703.82
crystal size, mm	0.38 × 0.27 × 0.25	0.72 × 0.49 × 0.30
crystal system	orthorhombic	hexagonal
space group	$P2_12_12_1$	$P6_1$
a, Å	12.973(1)	11.5465(4)
b, Å	13.619(2)	11.5465(4)
c, Å	17.665(2)	35.356(3)
V, Å^3	3121.0(6)	4082.2(4)
Z	4	6
ρ_{calcd}, g·cm^{-3}	1.679	1.718
μ, cm^{-1}	46.63	51.47
λ(Mo Kα), Å	0.710 73	0.710 73
no. of obsd reflcns	3101	2660
final R value	0.0268	0.0424
weighted final R value^a	0.0584	0.0845

^{a} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{0.5}$; $w = 1/[\sigma(F)]^2$.

appears as a doublet at 3.08 ppm with a coupling constant $J_{7,8}$ = 2.7 Hz. At 253 K, the double signal of H−C7 becomes a singlet while, as temperature decreases, a doublet forms on either side of the broadening central peak. From 253 to 193 K, the two H−C7 protons become inequivalent and their signals appear

Table 5. Absorption Wavelengths (nm) and Molar Extinction Coefficients (L cm^{-1} mol^{-1}) for Compounds **2**, **4**, and **5**−**13**

th4,5ppy (**2**)	229 (6281)	293 (sh)	308 (15 545)
th5,6ppy (**4**)	228 (4139)	294 (sh)	311 (15 704)
$Pt(th4,5ppy)_2$ (**5**)	307 (36 762)	321 (sh)	346 (sh)
	417 (11 790)	458 (sh)	
$Pt(th5,6ppy)_2$ (**6**)	280 (sh)	312 (31 859)	331 (sh)
	356 (sh)	443 (7163)	
cis-fac-$Pt(th4,5ppy)_2F_5BzBr$ (**8**, **9**)	285 (27 906)	307 (sh)	350 (15 993)
	358 (sh)		
Δ-*cis-fac*-$Pt(th5,6ppy)_2F_5BzBr$ (**10**)	230 (23 683)	283 (18 146)	356 (11 473)
Δ-*cis-fac*-$Pt(th5,6ppy)_2Br_2$ (**11**)	229 (32 516)	279 (sh)	284 (21 008)
	302 (sh)	350 (12 162)	
Δ-*cis-fac*-$Pt(5'-Brth5,6ppy)_2Br_2$ (**12**)	228 (31 652)	295 (22 811)	362 (22 811)
Δ-*cis-fac*-$Pt(th5,6ppy)_2CH_3I$ (**13**)	295 (20 692)	355 (14 426)	

at 3.06 and 3.10 ppm. As a consequence of this inequivalence, a mean geminal coupling constant of 20.0 Hz is observed and both signals have the form of a doublet of doublets. The same accidental equivalence of the H−C7 protons was observed in the case of ligands **2** and **4**.

X-ray Analysis. Figures 6 and 7 show the numbering schemes and molecular structures of **5** and **6**, whereas Table 3 contains some selected bond lengths and bond angles. Both complexes do not have identical Pt−N and Pt−C bond lengths, and there is no C_2 crystallographic symmetry in the solid state, as would be expected. The mean Pt−N and Pt−C bond lengths of **5** are very similar to those observed in related complexes. For instance, the same bond lengths are 2.151 and 1.984 Å in *cis*-bis[2-(2′-thienyl)quinoline]platinum(II), $Pt(thq)_2$, and 2.156 and 1.987 Å in *cis*-bis[benzo[*h*]quinoline]platinum(II), $Pt(bhq)_2$.[13] However, complex **6** has longer Pt−N distances and shorter Pt−C distances. All of these complexes present a deformation of the square planar (*SP*-4) geometry, as can be seen in Figures 8 and 9. In the case of **5**, this distortion is mainly due to the steric interaction of the two 4′-protons on the thiophene rings (H−C4′···H−C24′ = 2.17 Å) and the two 6-protons on the pyridine rings (H−C6···H−C26 = 1.99 Å). Complex **6** has a more distorted structure caused by a stronger steric interaction of the pinene fragments. It is possible to quantify this distortion by considering the Pt−N and Pt−C distances as vectors and projecting them onto the *yz* plane. It was found that, in the case of **5**, the $(C3'-Pt-C23')_{yz}$ and $(N1-Pt-N21)_{yz}$ angles are 13.3 and 11.4°, respectively, whereas the same angles for **6** are 22.5 and 18.3°. A direct consequence of this distortion is that a helix is generated and the metal center becomes chiral. The structures of **5** and **6** clearly show, in both cases, a Δ-*cis* configuration which is predetermined by the precursors of the ligands. If (+)-α-pinene instead of (−)-α-pinene had been chosen, complex **6** should have the opposite Λ chirality. The angles mentioned above imply that distortions in the ligands themselves are occurring. Deformations were observed at the thienyl−pyridine bond (C2′−C2) and at the junction of the pyridine with the pinene fragment.

Complex **5** was found to crystallize in the $P2_12_12_1$ space group with four molecules per unit cell. Each of these molecules is accompanied by a dichloromethane molecule. The shortest intermolecular Pt···Pt distance is 8.64 Å, which excludes any metal−metal interaction. Complex **6** crystallized in the hexagonal space group $P6_1$. Pt···Pt distances were found to be 6.32 Å, which, again excludes any overlapping of the platinum orbitals. Additional data and results for **5** and **6** are given in Table 4.

Absorption Spectroscopy. Table 5 lists the absorption wavelengths and molar extinction coefficients of ligands **2** and **4** and those of complexes **5**−**13**. The spectra of the platinum(II) compounds **5** and **6** are similar to the spectrum of *cis*-bis[2-(2′-thienyl)pyridine]platinum(II),[17] $Pt(thpy)_2$. In these three cases, absorptions which are not present in the free ligands occur in the visible region between 420 and 442 nm. These bands were attributed to the metal to ligand charge transfer (MLCT), d → π*, and are at the origin of a deep reddish color. In the cases of $Pt(thpy)_2$ and $Pt(th4,5ppy)_2$ (**5**), a shoulder appears around 460 nm and was attributed to the spin-forbidden, $d_{z^2} \rightarrow \pi^*$ transition. Other absorptions occur at wavelengths smaller than 340 nm. They are present in both ligands and complexes of platinum(II) and were assigned as ligand-centered π → π* transitions. The values of the molar extinction coefficients for these bands are twice as large in the complexes than in the free ligands, which was to be expected since there are two ligands coordinated to the platinum.

The thermal oxidative addition of α-bromo-2,3,4,5,6-pentafluorotoluene with **6** was followed by UV−vis spectroscopy. The MLCT band of **6** was seen to disappear as the reaction progressed, while a new maximum appeared at 356 nm. This band of complex **10** was attributed to a ligand to metal, π* → d, charge transfer (LMCT). It was found that, in the case of the $Pt(thpy)_2RX$ complexes, the LMCT bands are virtually independent of the RX alkyl halide attached to the platinum(IV) metal center.[6] It is almost the case of complexes **10**, **11**, and **13**, where the LMCT bands vary from 350 to 356 nm.

CD Spectra. It was found that ligands **2** and **4** are not circular dichroic in the wavelength range from 250 to 800 nm. However, complex **5** presents a positive Cotton effect, $\Delta\epsilon$ = 12.6 (412 nm), while complex **6** has a strong negative effect, $\Delta\epsilon = -24.7$ (444 nm), at the MLCT wavelength. As seen with X-ray analysis, both complexes crystallize with Δ configurations. Therefore, they should have similar CD spectra with the same positive or negative Cotton effects. So, it appears that one of these complexes behaves differently in solution. For steric reasons, complex **6** cannot undergo a Δ/Λ inversion in solution, but this process can be considered for the less sterically hindered complex **5**. The Δ configuration of **5**, observed in the solid state, is therefore probably a consequence of packing effects. In **6**, it is a molecular property, leading to an intrinsically well-defined configuration.

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **5** and **6** (15 pages). Ordering information is given on any current masthead page.

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