Inorg. Chem. **1997,** *36,* 6094−6098

Chiral Cyclometalated Platinum(II) and Palladium(II) Complexes with Derivatives of Thienylpyridine as Ligands: Helical Distortion of the Square Planar (SP-4) Geometry

Michel Gianini,[1a] Alex von Zelewsky,*,[1a] and Helen Stoeckli-Evans[1b]

Institute of Inorganic Chemistry, University of Fribourg, Pérolles, CH-1700 Fribourg, Switzerland, and
Institute of Chemistry, University of Neuchâtel, Avenue de Bellevaux 51,
CH-2000 Neuchâtel, Switzerland

Received February 26, 1997[⊗]

Four *cis*-bis-cyclometalated complexes of platinum(II) and palladium(II) have been synthesized with chiral substituted thienylpyridine ligands. These ligands are (5a*R*,6a*S*)-5,5a,6a,7-tetrahydro-6,6-dimethyl-3-(2′-thienyl)-cyclopropa[*g*]isoquinoline (th4,5capy) (**1**), (6a*R*,7a*S*)-5,6,6a,7a-tetrahydro-7,7-dimethyl-2-(2′-thienyl)cyclopropa-[*h*]quinoline (th5,6capy) (**2**), (6*R*,8*R*)-5,6,7,8-tetrahydro-9,9-dimethyl-2-(2′-thienyl)-6,8-methanoquinoline (th5,6*β*ppy) (**3**), and (6*R*,8*R*)-5,6,7,8-tetrahydro-9,9-dimethyl-3-(2′-thienyl)-6,8-methanoisoquinoline (th4,5ppy) (**5**). Two complexes have a well-defined chirality at the metal center, due to the sterical interaction of the ligands. These complexes are Δ-Pt(th5,6capy)$_2$ (**8**) and Λ-Pt(th5,6*β*ppy)(thpy) (**9**). The crystal structure of **8** shows a strong distortion from the ideal square planar geometry. Crystals of Δ-Pt(th5,6capy)$_2$ (**8**) are tetragonal, space group $P4_32_12$, $a = 13.407(1)$ Å, $b = 13.407(1)$ Å, $c = 14.860(2)$ Å, $\alpha = \beta = \gamma = 90°$, and $Z = 4$. Final $R = 0.0237$ and $R_w = 0.0450$ for 2353 observed reflections. Compound **8** possesses a crystallographic C_2 symmetry.

Introduction

Interest in chiral inorganic compounds has recently increased, especially in enantiomeric catalysis,[2] bioinorganic chemistry,[3] and supramolecular chemistry.[4] However, it has been a long time since researchers have turned their attention to this class of compounds. Originally, the stereochemical concepts have been extensively developed in organic chemistry and applied, when it was possible, to metal compounds. Although specific terms have been defined to describe most of the chiral coordination compounds, there are still some possibilities to be explored. For instance, a few years ago, Deuschel demonstrated that it is possible to induce a chirality at the metal center of square planar (SP-4) *cis*-bis-cyclometalated platinum(II) complexes.[5] The bidentate ligand used in this case was 2,6-diphenylpyridine (dppy). After complexation, the two *cis* ligands strongly interact and create a sterical hindrance, mainly due to the two phenyl moieties in the six positions. The result is that the ideal square planar geometry is distorted in a helical way and a chirality is induced at the metal center (Figure 1). Other examples of such distortions are reported in the literature.[5,6] The problem is that the complex of Deuschel, Pt(dppy)$_2$, was obtained as a racemate, that is, a 1:1 mixture of Δ and Λ forms. Nothing in the chelating (dppy) ligands is likely to favor a unique form of chirality. A further step had to be carried out with stereocontrol, in other words, the predetermination of the chirality at the metal center.

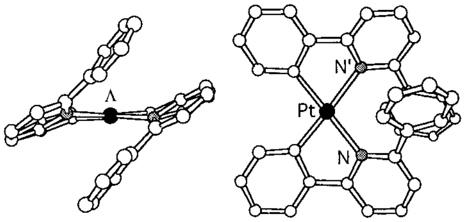


Figure 1. Crystal structure of Λ-*cis*-bis(2,6-diphenylpyridine)platinum(II).

In recent works, we proposed the synthesis of chiral "thienylpyridine" ligands substituted with bicyclic aliphatic groups (Figure 2).[7,8] Their ability to induce and predetermine a helical chirality was studied, and a first success was obtained with (5*R*,7*R*)-5,6,7,8-tetrahydro-9,9-dimethyl-2-(2′-thienyl)-5,7-methanoquinoline (th5,6ppy) (**6**). A *cis*-bis-cyclometalated platinum(II) complex was formed with this ligand, showing a Δ chirality as pointed out by X-ray analysis and circular dichroism.[7]

In this paper, we present the crystal structure of a very similar platinum(II) complex, Δ-Pt(th5,6capy)$_2$ (**8**). This compound, which was synthesized from (6a*R*,7a*S*)-5,6,6a,7a-tetrahydro-7,7-dimethyl-2-(2′-thienyl)cyclopropa[*h*]quinoline (th5,6capy) (**2**),[7] clearly shows a predetermined Δ chirality at the metal center. The synthesis of three other complexes is also presented: Pt(th4,5capy)$_2$ (**7**), Λ-Pt(th5,6*β*ppy)(thpy) (**9**), and Pd(th4,5ppy)$_2$ (**10**). Complex **9** is another example of a compound with a predetermined chirality at the metal center, whereas compounds **7** and **10** are not (Figure 3). In these latter cases, the sterical interaction between the two ligands is not strong enough to create a real distortion and the chirality of these compounds is only due to the presence of two asymmetric carbons on each ligand. The stereoselective synthesis of chiral inorganic compounds is a first step. A further study should follow, dealing with their application in chiral recognition.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) (a) University of Fribourg. (b) University of Neuchâtel.

(2) Brunner, A.; Zettlmeier, W. *Handbook of Enantioselective Catalysis with Transition Metal Complexes*; VCH Verlagsgesellschaft: Weinheim, 1993; Vols. I and II.

(3) (a) Frausto da Silva, J. J. R.; Williams, R. J. P. *The Biological Chemistry of the Elements. The Inorganic Chemistry of Life*; Clarendon Press, Oxford University Press: Oxford, 1993. (b) Kaim, W.; Schwederski, B. *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life. An Introduction and Guide*; John Wiley & Sons: Chichester, 1994.

(4) Balzani, V.; de Cola, L. *Supramolecular Chemistry*; NATO ASI Series; Kluwer Academic Publishers, Dordrecht, 1992.

(5) Deuschel-Cornioley, C.; Stoeckli-Evans, H.; von Zelewsky, A. *J. Chem. Soc., Chem. Commun.* **1990**, 121.

(6) Jolliet, P.; Gianini, M.; von Zelewsky, A.; Bernardinelli, G.; Stoeckli-Evans, H. *Inorg. Chem.* **1996**, *35*, 4883.

(7) Gianini, M.; Forster, A.; Haag, P.; von Zelewsky, A.; Stoeckli-Evans, H. *Inorg. Chem.* **1996**, *35*, 4889.

(8) Gianini, M.; von Zelwsky, A. *Synthesis* **1996**, 702.

S0020-1669(97)00228-0 CCC: $14.00

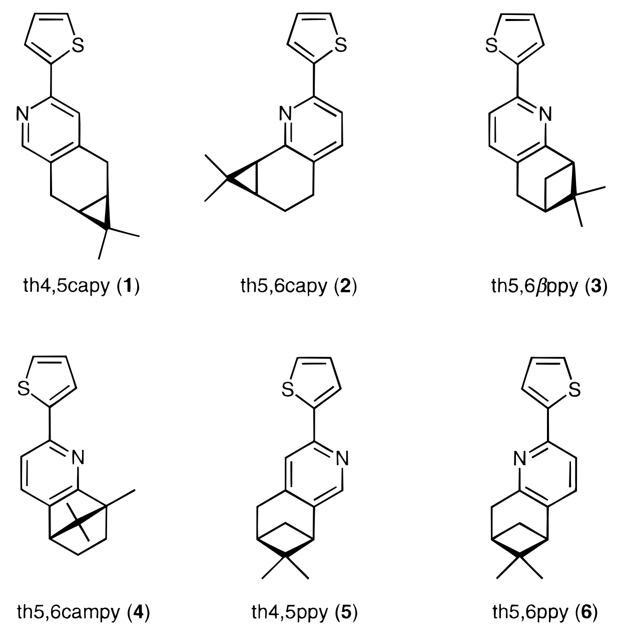


Figure 2. Chiral thienylpyridine ligands derived from natural monoterpenes.

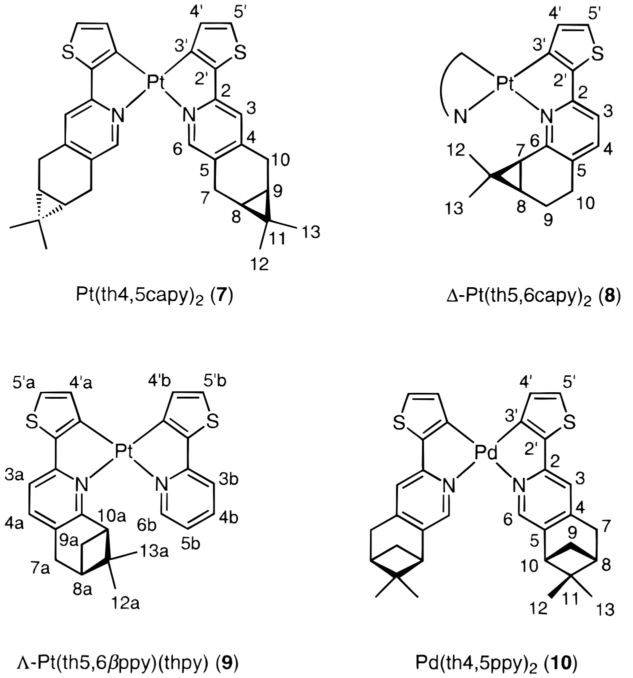


Figure 3. Synthesized complexes of platinum(II) and palladium(II).

Experimental Section

Products. The synthesis of the ligands th4,5capy (**1**), th5,6capy (**2**), th5,6βppy (**3**), th5,6campy (**4**), th4,5ppy (**5**), and th5,6ppy (**6**) is reported in two of our previous papers.[7,8] *tert*-Butyllithium 15% in pentane and *n*-butyllithium 1.6 M in hexane were bought from Merck and Fluka, respectively. The precursor platinum(II) and palladium(II) complexes, $M(Et_2S)_2Cl_2$, were prepared following procedures described by Livingstone[9] and Kauffman.[10] Chloro(diethyl sulfide)(thienylpyridine-$C^{3'}$,N)-platinum(II), Pt(thpy)(Et_2S)Cl, was synthesized according to a literature method.[11] Diethyl ether and THF were distilled from sodium.

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. Chemical shifts are reported in parts per million on the δ scale. Attribution 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 carried out by using DEPT (distortionless enhancement by polarization transfer) experiments. Infrared spectral data were collected using a Perking-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 photo-oxidation of complex **7** was performed in a quartz cell (1 cm section) placed at 5 cm of a 50 W halogen lamp. Dichloromethane was not degassed, and no interfering filter was placed between the cell and the lamp. The initial concentration of **7** was ~3 × 10^{-5} M, and the spectra were measured every 2 min. The CD spectra were measured on a Jobin Yvon autodichrograph Mark V spectrometer.

Table 1. Crystal Data and Structure Refinement for Δ-Pt(th5,6capy)$_2$ (**8**)

formula	$C_{32}H_{32}N_2PtS_2$	V (Å^3)	2671.1(5)
mol wt	703.82	Z	4
cryst size (mm)	0.38 × 0.34 × 0.27	ρ_{calcd} (g cm^{-3})	1.750
cryst syst	tetragonal	μ (cm^{-1})	54.35
space group	$P4_32_12$	λ(Mo Kα) (Å)	0.710 73
a (Å)	13.407(1)	no. of obsd reflns	2116
b (Å)	13.407(1)	final R value	0.0237
c (Å)	14.860(2)	weighted R value[a]	0.0450

[a] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$; $w = 1/[\sigma(F_o^2) + (0.016P)^2]$; $P = [\max(F_o^2,\phi) + 2F_c^2]/3$.

Suitable crystals for X-ray analysis were grown by diffusion (1−2 days) of hexane in dichloromethane at room temperature. Crystal data and details of the structure refinement of **8** are summarized in Table 1. 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 data using the program XABS2.[12] Transmission factors were 0.822 (min) and 1.246 (max). The structure was solved using the program SHELXS86[13] and refined by full-matrix least-squares on F^2 using SHELXL93.[14] The H atoms were included in calculated positions and treated as riding atoms.

Platinum(II) Homoleptic Cyclometalated Complexes: General Synthesis. 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 1/2 h. The reaction flask was protected from light, and $Pt(SEt_2)_2Cl_2$, dissolved in a minimum 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 10 mL of water, and after removal of the solvent, the resulting product was purified by flash chromatography on silica gel, 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.

Pt(th4,5capy)$_2$ (7). Th4,5capy (**1**) (726 mg, 2.84 mmol) was dissolved in dried ether (50 mL) and lithiated with 15% *tert*-butyllithium (2 mL, 2.94 mmol). $Pt(SEt_2)_2Cl_2$ (424 mg, 0.94 mmol) was added, and crystals were obtained by diffusion of hexane in dichloromethane. Yield: 11% (71 mg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.32 (s, 2H), 7.63 (d, 2H, ^3J = 4.8 Hz), 7.36 (d, 2H, ^3J = 4.8 Hz), 7.17 (s, 2H), 3.15−3.19 (m, 2H), 3.08−3.19 (m, 2H), 2.71 (s, 2H), 2.65 (s, 2H), 1.11 (s, 6H), 0.98−1.02 (m, 4H), 0.79 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.5 (qr), 149.1 (qr), 147.4 (te), 145.4 (qr), 142.4 (qr), 135.5 (te), 128.6 (qr), 126.3 (te), 117.0 (te), 28.5 (pr), 24.8 (se), 21.9 (se), 19.2 (se), 19.1 (te), 18.2 (qr), 14.6 (pr). MS (FAB) *m/z*: 704 (M^+), 448 (M^+ − th4,5capy), 256 (th4,5capy), 212 (th4,5capy − C_3H_7). IR (KBr), cm^{-1}: 3438w, 2992w, 2938m, 1614s, 1484s, 1436m, 1330w, 1252w, 1126w, 1012w, 990w, 876m 702m, 626w. UV−vis (CH_2Cl_2) [λ, nm (ϵ, M^{-1} cm^{-1})]: 305 (34 590), 320 (sh), 345 (sh), 410 (12 042),

---

(9) Livingstone, S. E. *Synth. Inorg. Met. Org. Chem.* **1971**, *1*, 1−7.
(10) Kauffman, G. B.; Cowan, D. O. *Inorg. Synth.* **1960**, *6*, 211.
(11) Deuschel-Cornioley, C. Thesis No. 938, University of Fribourg, 1988.
(12) Parkin, S.; Moezzi, B.; Hope, H. XABS2: an empirical absorption correction program. Department of Chemistry, University of California, Davis, California 95616.
(13) Sheldrick, G. M. *Acta. Crystallogr.* **1990**, A46, 467.
(14) Sheldrick, G. M. SHELXL93: Program for crystal structure refinement. University of Göttingen, Germany.

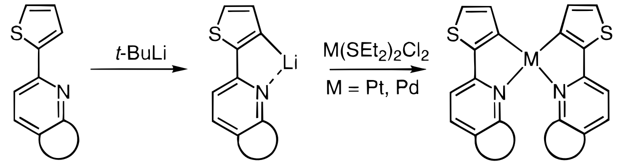
450 (sh). CD (CH_2Cl_2) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 297 (6.0), 361 (−0.2), 410 (−6.3), 450 (0.4).

Δ-Pt(th5,6capy)$_2$ (8). Th5,6capy (**2**) (726 mg, 2.84 mmol) was dissolved in dried ether (50 mL) and lithiated with 15% *tert*-butyllithium (2 mL, 2.94 mmol). Pt(SEt_2)$_2$$Cl_2$ (424 mg, 0.94 mmol) was added, and the final complex was precipitated from acetone. Crystals were obtained by slow diffusion of hexane in dichloromethane. Yield: 26% (171 mg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.66 (d, 2H, ^3J = 4.9 Hz), 7.33 (d, 2H, ^3J = 4.9 Hz), 7.27 (d, 2H, ^3J = 8.0 Hz), 7.08 (d, 2H, ^3J = 8.0 Hz), 2.71 (ddd, 2H, ^2J = 15.5 Hz, ^3J = 8.4 Hz, ^3J = 6.7 Hz), 2.44 (ddd, 2H, ^2J = 15.5 Hz, ^3J = 6.2 Hz, ^3J = 6.2 Hz), 2.29 (d, 2H, ^3J = 8.6 Hz), 1.96 (dddd, 2H, ^2J = 14.4 Hz, ^3J = 8.0 Hz, ^3J = 6.7 Hz, ^3J = 6.2 Hz), 1.69 (dddd, 2H, ^2J = 14.4 Hz, ^3J = 8.4 Hz, ^3J = 6.2 Hz, ^3J = 4.3 Hz), 1.15 (ddd, 2H, ^3J = 8.6 Hz, ^3J = 8.0 Hz, ^3J = 4.3 Hz), 0.75 (s, 6H), 0.70 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.6 (qr), 158.4 (qr), 146.0 (qr), 142.4 (qr), 137.7 (te), 135.1 (te), 128.5 (qr), 125.9 (te), 113.4 (te), 28.9 (se), 28.7 (te), 28.2 (pr), 26.8 (qr), 26.1 (te), 19.7 (se), 16.4 (pr). MS (FAB) *m/z*: 704 (M^+), 448 (M^+ − th5,6capy), 256 (th5,6capy), 212 (th5,6capy − C_3H_7). IR (KBr), cm^{-1}: 2920m, 2854w, 1584s, 1462s, 1256w, 1206w, 1162w, 1132w, 1064w, 906w, 874m, 822m, 794w, 772w, 712w, 692w, 644w. UV−vis (CH_2Cl_2) [λ, nm (ϵ, M^{-1} cm^{-1})]: 284 (sh), 313 (28 080), 332 (sh), 363 (14 630), 442 (7050). CD (CH_2Cl_2) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 279 (5.0), 312 (20.1), 329 (−2.3), 368 (13.5), 445 (−30.0).

Λ-Pt(thpy)(th5,6βppy) (9). This heteroleptic complex was formed similarly to the homoleptic complexes. Th5,6βppy (**3**) (128 mg, 0.5 mmol) was dissolved in dried ether (10 mL) and lithiated with 15% *tert*-butyllithium (0.4 mL, 0.6 mmol). Pt(thpy)(SEt_2)Cl (240 mg, 0.5 mmol) was added, and the final complex was precipitated by slow diffusion of hexane in dichloromethane. Yield: 10% (30 mg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.29 (dd, 1H, ^3J = 5.7 Hz, ^4J = 1.5 Hz), 7.68 (ddd, 1H, ^3J = 7.8 Hz, ^3J = 7.2 Hz, ^4J = 1.5 Hz), 7.68 (d, 1H, ^3J = 4.9 Hz), 7.60 (d, 1H, ^3J = 5.0 Hz), 7.46 (d, 1H, ^3J = 7.9 Hz), 7.46 (d, 1H, ^3J = 4.9 Hz), 7.41 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.4 Hz), 7.32 (d, 1H, ^3J = 5.0 Hz), 7.27 (d, 1H, ^3J = 7.9 Hz), 6.90 (ddd, 1H, ^3J = 7.2 Hz, ^3J = 5.7 Hz, ^4J = 1.4 Hz), 3.65 (dd, 1H, ^3J = 5.5 Hz, ^4J = 5.5 Hz), 2.96 (d, 2H, ^3J = 2.7 Hz), 2.67 (ddd, 1H, ^2J = 9.6 Hz, ^3J = 5.5 Hz, ^3J = 5.5 Hz), 2.29 (tdd, 1H, ^4J = 5.5 Hz, ^3J = 5.5 Hz, ^3J = 2.7 Hz), 1.50 (d, 1H, ^2J = 9.6 Hz), 1.27 (s, 3H), 0.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.4 (qr), 161.2 (qr), 157.9 (qr), 149.7 (te), 146.6 (qr), 145.3 (qr), 143.4 (qr), 141.9 (qr), 138.3 (te), 137.9 (te), 135.5 (te), 134.9 (te), 128.1 (te), 126.9 (qr), 126.0 (te), 119.2 (te), 117.5 (te), 114.9 (te), 50.2 (te), 39.9 (te), 39.1 (qr), 32.0 (se), 31.4 (se), 25.5 (pr), 21.4 (pr). MS (FAB) *m/z*: 609 (M^+), 448 (M^+ − thpy), 256 (th5,6βppy), 212 (th5,6βppy − C_3H_7). IR (KBr), cm^{-1}: 2922s, 2854m, 1650w, 1592s, 1468s, 1242m, 1148m, 908m, 876m, 820m, 768m, 714m, 626m, 528w. UV−vis (CH_2Cl_2) [λ, nm (ϵ, M^{-1} cm^{-1})]: 304 (17 890), 325 (sh), 350 (sh), 424 (5150), 461 (sh). CD (CH_2Cl_2) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 298 (−5.9), 319 (1.9), 343 (−1.3), 355 (−3.0), 369 (1.7), 423 (9.5).

Pd(th4,5ppy)$_2$ (10). Th4,5ppy (**5**) (383 mg, 1.5 mmol) was dissolved in dried ether (50 mL) in a "Schlenk" flask under argon. *n*-Butyllithium (1 mL, 1.6 mmol) was added at 0 °C, and the solution was stirred for 1/2 h. The reaction flask was protected from light, and Pd(SEt_2)$_2$$Cl_2$, dissolved in a minimum volume of ether, was added at −70 °C. The solution was stirred for 1 h at this temperature and the reaction quenched by the addition of water (10 mL). After removal of the solvent, the residue was dissolved in ether (100 mL) and dried over $MgSO_4$. The ether was removed, and the product was precipitated by diffusion of hexane in CH_2Cl_2 at −18 °C. Yield: 56% (208 mg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.03 (s, 2H), 7.62 (d, 2H, ^3J = 4.8 Hz), 7.36 (d, 2H, ^3J = 4.8 Hz), 7.29 (s, 2H), 3.01 (d, 4H, ^3J = 2.5 Hz), 2.83 (dd, 2H, ^4J = 5.5 Hz, ^3J = 5.5 Hz), 2.73 (ddd, 2H, ^2J = 9.6 Hz, ^3J = 5.5 Hz, ^3J = 5.5 Hz), 2.31 (tdd, 2H, ^4J = 5.5 Hz, ^3J = 5.5 Hz, ^3J = 2.5 Hz), 1.41 (s, 6H), 1.27 (d, 2H, ^2J = 9.6 Hz), 0.66 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.8 (qr), 156.6 (qr), 147.7 (qr), 143.7 (te), 141.7 (qr), 139.0 (qr), 135.8 (te), 124.9 (te), 117.6 (te), 44.7 (te), 39.9 (te), 39.6 (qr), 33.0 (se), 32.0 (se), 25.9 (pr), 21.4 (pr). MS (FAB) *m/z*: 614 (M^+), 360 (M^+ − th4,5ppy), 256 (th4,5ppy), 212 (th4,5ppy − C_3H_7). IR (KBr), cm^{-1}: 2922s, 1614s, 1490s, 1424m, 1366w, 1288w, 1260w, 1188w, 1128w, 1006w, 948w, 906w, 868m, 732w, 700m, 638w, 602w. UV−vis (CH_2Cl_2) [λ, nm (ϵ, M^{-1} cm^{-1})]: 292 (34 040), 314 (25 880), 382 (9390), 404 (sh). CD (CH_2Cl_2) [λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1})]: 290 (−11.3), 323 (5.7), 340 (0.9), 377 (9.2), 409 (−2.7).

Scheme 1



Results and Discussion

Synthesis. Scheme 1 features the pathway followed for the synthesis of complexes **7**, **8**, and **10**. Two steps can be distinguished: lithiation of the ligand on carbon C3′ of the thiophene ring[15] and metal exchange with M(SEt_2)$_2$$Cl_2$,[10] where M is either palladium or platinum. This method has already been applied in many cases reported in the literature.[5−7,16−18] In a recent work, Jolliet gives a probable mechanism for the formation of this type of compound.[6] Four consecutive substitutions occur according to an associative mechanism and are ruled by the *trans* effect. As a result, only *cis* compounds are formed, even if the complex is strongly crowded. The molecules presented in Figure 2 have all been tested as ligands to build *cis*-bis-cyclometalated palladium complexes. The problem is that these latter have a strong tendency to undergo reductive eliminations and palladium(0) is finally collected. As a matter of fact, it was impossible to build sterically hindered Pd^{II} complexes, and the only compound which was synthesized is Pd(th4,5ppy)$_2$ (**10**).

The bis-heteroleptic complex Λ-Pt(thpy)(th5,6βppy) (**9**) was synthesized in a traditional way from Pt(thpy)(SEt_2)Cl,[11] as depicted in Scheme 2. It is worth mentioning that the procedure proposed by Ryabov in a recent paper was tested in this case but gave no result.[19] The reason for this failure lies probably in the fact that compound **9** is strongly crowded.

^{1}H NMR. The bis-homoleptic complexes **7**, **8**, and **10** have C_2 symmetry in solution, giving rise to only one set of ^{1}H NMR signals for the two ligands. This is naturally not the case for the bis-heteroleptic complex **9**, where one can observe distinct signals for th5,6βppy (**3**) and for the thienylpyridine (thpy). In all cases, the disappearance of the H−C3′ signals on the thiophene rings shows that cyclometalations occurred. Otherwise, the spectra of these complexes are similar to parent compounds reported in the literature.[6,7]

UV−vis Spectroscopy. Table 2 gives a list of selected absorptions and molar extinction coefficients for complexes **7**−**10** and for the ligands they were synthesized from. The bands have been attributed by analogy with similar compounds described in the literature.[20] The ligands are colorless and do not absorb in the visible region. The platinum(II) complexes

---

(15) Kauffmann, T.; Mitschker, A.; Woltermann, A. *Chem. Ber.* **1983**, *116*, 992.

(16) Chassot, L; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 2814.

(17) Chassot, L.; Müller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249.

(18) Deuschel-Cornioley, C.; Ward, T.; von Zelewsky, A. *Helv. Chim. Acta* **1988**, *71*, 130.

(19) Ryabov, A. D.; van Eldik, R. *Angew. Chem.* **1994**, *106*, 798.

(20) (a) Gidney, M. P.; Gillard, R. D.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1973**, 132. (b) Chaudhurry, N.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *84*, 105. (c) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Am. Chem. Soc.* **1987**, *109*, 7720. (d) de Cola, L.; Credi, A.; Trovato, G.; Gianini, M.; von Zelewsky, A. Manuscript in preparation.

(21) Breu, J.; Range, K.-J.; von Zelewsky, A.; Yersin, H. *Acta Crystallogr.* **1997**, *C53*, 562.

Scheme 2

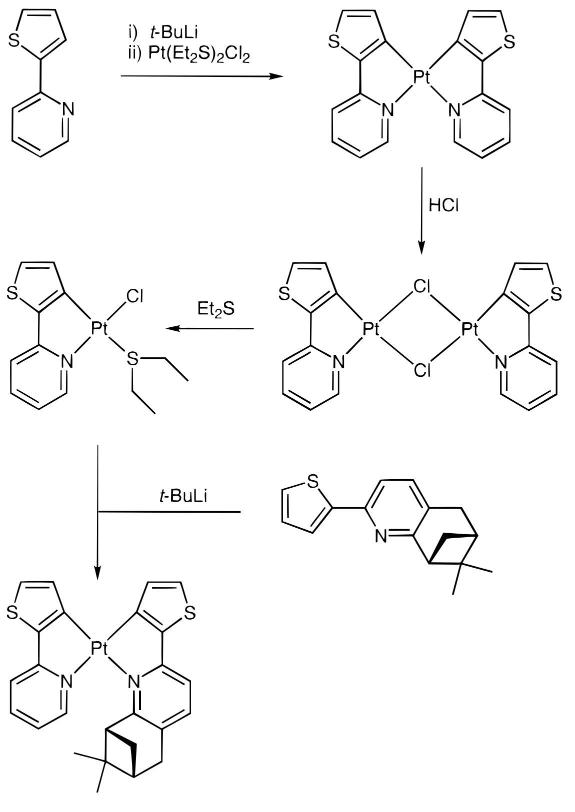


Table 2. Selected Absorptions (nm) and Molar Extinction Coefficients (l mol^{-1} cm^{-1}) of the Ligands and Complexes in CH_2Cl_2

	$\pi \to \pi^*$	$d \to \pi^*$
th4,5capy (**1**)	296 (12 500)	
th5,6capy (**2**)	314 (14 000)	
th5,6βppy (**3**)	312 (14 500)	
th4,5ppy (**5**)	308 (15 500)	
thpy	300 (17 700)	
Pt(th4,5capy)$_2$ (**7**)	305 (34 600)	410 (12 000), 450 (sh)
Δ-Pt(th5,6capy)$_2$ (**8**)	313 (28 100)	442 (7100)
Λ-Pt(th5,6βppy)(thpy) (**9**)	304 (17 900)	424 (5200), 461 (sh)
Pd(th4,5ppy)$_2$ (**10**)	292 (34 000)	382 (9400), 404 (sh)

have a strong reddish color due to absorptions between 410 and 461 nm. These low-energy absorptions were attributed to metal to ligand charge transfer transitions (MLCT, $d \to \pi^*$). The spectra of complexes **7**, **9**, and **10** present a shoulder due to the spin-forbidden transition $d_{z^2} \to \pi^*$. The $d \to \pi^*$ absorptions are weak, and the wavelengths at which they appear depend on the polarity of the solvent (solvatochromy).[6,20c] Other absorptions occur between 292 and 314 nm, due to internal ligand to ligand transitions ($\pi \to \pi^*$). As can be expected, the molar absorption coefficients of the bis-homoleptic complexes **7**, **8**, and **10** are twice as high as that of the free ligands in this region.

Figure 4 shows the photo-oxidation of Pt(th4,5capy)$_2$ (**7**) in CH_2Cl_2 followed by UV−vis spectroscopy. As the reaction progresses, the bands (410 and 305 nm) of the platinum(II) complex diminish, while two new maxima appear at 340 and 287 nm, corresponding to the formation of Pt(th4,5capy)$_2$(CH_2Cl)Cl. Three isosbestic points indicate that the reaction occurs in a clean way. The reaction was completed within 30 min, and there was no more trace of the starting complex **7**. More detailed photochemical investigations have been carried out with Δ-Pt(th5,6capy)$_2$ (**8**). These results will be reported elsewhere.[20d]

CD Spectroscopy. The absolute configuration of a compound can be determined by correlation with the CD spectrum of a known compound if they both have the same electronic configuration. For instance, the Δ chirality of Pt(th5,6capy)$_2$ (**8**) has been well established by X-ray analysis. The CD spectrum of this compound shows a strong negative Cotton effect ($\Delta\epsilon = -30.0$ l M^{-1}) at the MLCT transition wavelength (445 nm), whereas Pt(th5,6βppy)(thpy) (**9**) presents a positive Cotton effect ($\Delta\epsilon = 9.5$ l M^{-1}) at the MLCT transition wavelength (423 nm). Consequently, one can assign a Λ chirality for compound **9**. This correlation rule can only be applied in the case of crowded complexes, where a well-defined chirality is induced at the metal center in both solid and solution states. That is why no assignment of chirality was made for the less sterically hindered complexes **7** and **10**.

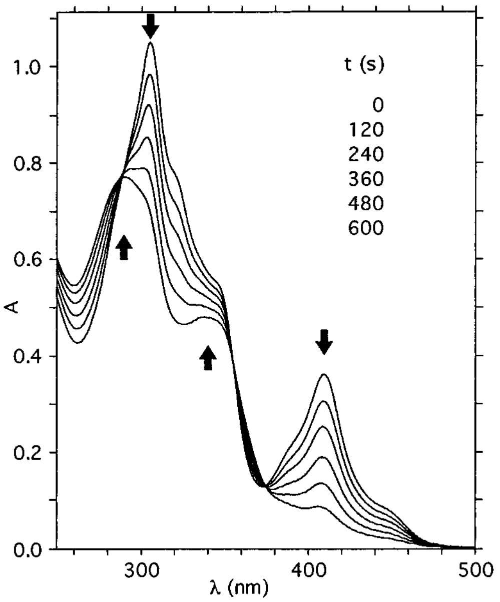


Figure 4. Photo-oxidation of Pt(th4,5capy)$_2$ (**7**) in CH_2Cl_2 followed by UV−vis spectroscopy.

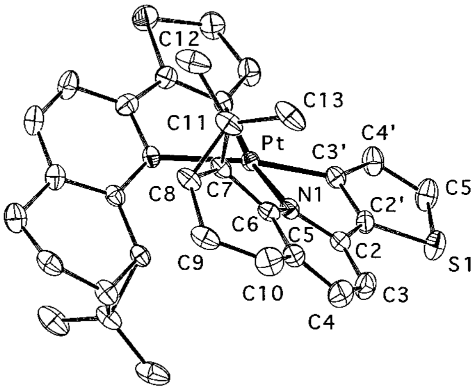


Figure 5. ORTEP plot and crystallographic numbering scheme of Δ-Pt(th5,6capy)$_2$ (**8**). The thermal ellipsoids are represented with a 50% probability level. Hydrogen atoms have been omitted for clarity.

Crystal and Molecular Structure. Figure 5 shows the numbering scheme for **8**, whereas Table 3 contains some selected distances and angles. Δ-Pt(th5,6capy)$_2$ (**8**) crystallized in the $P4_32_12$ space group with four molecules/unit cell. The shortest intermolecular Pt···Pt distance is 8.12 Å, which excludes any metal−metal interaction.

Compound **8** possesses a crystallographic C_2 axis. The interaction of the two chelating ligands causes the complex to distort in a helical way. This deformation is mainly due to the H−C7 and H−C8 protons which are pointing in the direction of their homologues on the second ligand. As a consequence of this distortion, a Δ chirality is induced at the metal center,

Table 3. Bond Lengths and Distortion Angles of Some Bis-Cyclometalated Platinum(II) Complexes

complex	Pt−N Pt−N′ (Å)	Pt−C Pt-C′ (Å)	$(C-Pt-C')_{yz}$ (deg)	$(N-Pt-N')_{yz}$ (deg)
$Pt(thpy)_2$[a]	2.160(4) 2.160(4)	1.989(5) 1.995(5)	1.8	1.4
$Pt(bhq)_2$[b]	2.149(9) 2.153(8)	1.975(9) 1.998(12)	7.2	5.9
$Pt(dppy)_2$[c]	2.153(8) 2.163(7)	2.008(10) 1.964(10)	9.4	7.9
$Pt(th4,5ppy)_2$[d]	2.147(7) 2.168(7)	1.984(10) 2.000(10)	13.3	11.4
Δ-$Pt(th5,6capy)_2$ (**8**)	2.185(3) 2.185(3)	1.986(4) 1.986(4)	18.7	16.2
Δ-$Pt(th5,6ppy)_2$[d]	2.166(13) 2.174(13)	1.975(14) 1.920(20)	22.5	18.3
$Pt(thq)_2$[b]	2.156(2) 2.156(2)	1.984(3) 1.984(3)	26.0	23.2

[a] Reference 21. [b] Reference 6. [c] Reference 5. [d] Reference 7.

and it is obvious that, for sterical reasons, the inverse Λ chirality cannot be formed.

The comparison with the crystal structures of similar compounds, synthesized from thienylpyridine or phenylpyridine ligands, is of great interest (Table 3). In a general way, the Pt−C bond lengths are shorter than the Pt−N distances. The Pt−C bond lengths vary from 1.920 to 2.008 Å (Δ = 0.088 Å), whereas the Pt−N distances lie between 2.147 and 2.185 Å (Δ = 0.038 Å). There is no relation between these bond lengths and the sterical hindrance in the complexes. However, the larger variation of the Pt−C distances indicates a stronger propensity for the Pt−C bonds to stretch themselves. The deformation of the square planar geometry can be determined by considering the Pt−C and Pt−N distances as vectors and projecting them onto the yz plane, which is defined by the Pt coordinates and the middle points of the C−C′ and N−N′ vectors. An angle is then calculated, which gives an idea of the distortion from the ideal square planar geometry. One can see that, for the same complex, the $(C-Pt-C')_{yz}$ angle is bigger than the $(N-Pt-N')_{yz}$ angle.

Conclusions. From (+)-2-carene, we synthesized (6a*R*,7a*S*)-th5,6capy (**2**), which, after complexation, generated a Δ-configured platinum(II) complex in a stereoselective way. To obtain the enantiomer of Δ-$Pt(th5,6capy)_2$ (**8**), that is a Λ-configured complex, one should use (−)-2-carene as a natural precursor to produce a ligand with inverse (6a*S*,7a*R*) chiral centers. The same is true for the heteroleptic complex Λ-Pt(thpy)(th5,6*β*ppy) (**9**), which was synthesized from (−)-*β*-pinene. The formation of the Δ complex implies the initial choice of (+)-*β*-pinene as starting material. To summarize, two conditions are required to predetermine the chirality in *cis*-bis-cyclometalated complexes: a strong sterical hindrance between the two ligands and the presence of chiral centers in the ligands to direct, in a unique way, the helical distortion. Complexes **8** and **9** fulfill these two conditions while compounds **7** and **10** are not crowded enough to present an intrinsically well defined chirality.

Acknowledgment. The authors thank the Swiss National Science Foundation for financial support.

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for Δ-$Pt(th5,6capy)_2$ (**8**) (6 pages). Ordering information is given on any current masthead page.

IC970228W