Cyclometalated Platinum(II) Complexes Derived from a Chiral Pyridine Ligand: Synthesis, Structure, and Catalytic Activity†

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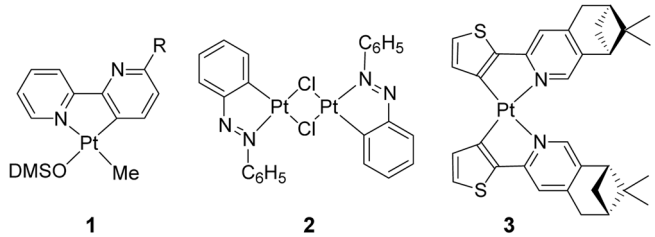
A direct cyclometalation of a chiral pyridine derivative, (5*R*,7*R*)-5,6,7,8-tetrahydro-6,6-dimethyl-2-phenyl-5,7-methanoquinoline (**L**), with K_2PtCl_4 in acetic acid is described. A chiral mononuclear cyclometalated platinum(II) complex (**6**) was obtained, in which second **L** was simply coordinated by nitrogen. This new platinum(II) complex was characterized by ^1H and ^{13}C NMR spectroscopy, and further by X-ray crystallography. Both the solution and solid structures show C-H···Cl hydrogen bonding, which explains a distorted square-planar geometry in the solid state. A reactive cationic platinum(II) species (**8**) was generated from the chloro complex by treatment with silver triflate, whose catalytic efficiency was evaluated in asymmetric aldol and silylcyanation reactions of aldehydes.

Key Words : Chiral ligand, Cycloplatination, X-ray structure, C-H···Cl hydrogen bonding, Asymmetric reactions

Introduction

Intramolecular activation of C-H bonds through the action of transition metal ions was first described by Kleiman and Dubeck.[1] The intramolecular C-H activation or cyclometalation/orthometalation reaction, which is a major achievement of organometallic chemistry, provides access to metallacyclic derivatives of the transition metals.[2-5] Conventionally, this reaction has involved one ligating group holding a metal center close to C-H bond and subsequent closure of the ring *via* the formation of carbon to metal bond.[6-8] Cyclometalated compounds have been used as effective catalysts for the Heck[9] and Suzuki coupling reactions.[10] In addition, cyclometalated compounds show important applications as new mesogenic[11] and biologically active compounds.[12] The most widely studied examples are platinum and palladium compounds with nitrogen donors in which C-H activation takes place at phenyl ortho position to produce five-membered metallacycles.[13-16] A number of reports are available on mononuclear platinum(II) cyclometalated compounds such as **1**, and very few are focused on dimeric compounds such as **2** or bis-cycloplatinated complexes such as **3** in the literature.[17,18]



1 **2** **3**

Particularly, square-planar cyclometalated platinum(II) complexes are of interest for several reasons such as their interesting photochemical and photophysical properties, their potential use as molecular devices, and more generally as products or intermediates in catalytic reactions.[19,20] The square-planar geometry, very often exhibited by coordination species of metals with d^8 electronic configuration, constitutes basically an achiral structure. Nevertheless, under special circumstances, square-planar complexes can become chiral. This is obviously the case if chiral ligands are involved. We therefore interested in the synthesis of chiral cyclometalated platinum(II) complexes from a suitable chiral ligand.

Chiral derivatives of bipyridines and their metal complexes were reported by Hayoz and co-workers where α-pinene was used as a source of chirality.[21,22] Alex von Zelewsky reported platinum(II) cyclometalated compounds obtained from the reaction of a chiral thienylpyridine and a platinum(II) precursor *via* lithiation.[18] Recently, the synthesis of chiral cyclometalated platinum(II) complexes with thienylimines and the oxidative addition of alkyl halides to this complex were reported by Margarita Crespo.[23]

As a part of our continuing efforts on the study of cyclometalated complexes,[24] we describe here the synthesis of chiral mononuclear cyclometalated platinum(II) complexes containing a chiral pyridine ligand derived from β-pinene. Further, the catalytic efficiency of one of the complexes was evaluated in asymmetric aldol reaction between methyl isocyanoacetate and aldehydes and in silylcyanation of aldehydes.

Results and Discussion

Continuing our interest in the synthesis and application of cyclometalated complexes, attempts were first made to synthesize bis-cyclometalated platinum(II) complexes of

† This paper is dedicated to Professor Sang Chul Shim at Kyungpook National University on the occasion of his honorable retirement.

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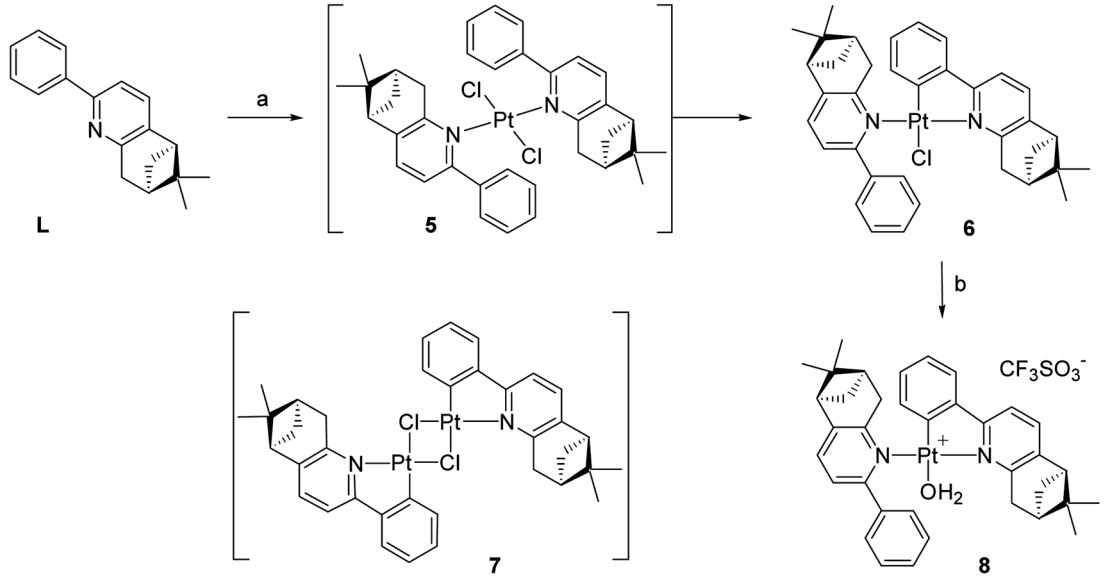


Scheme 1. Synthesis of Pt(II) cyclometalated complexes. Reagents and conditions: a) K_2PtCl_4, AcOH, reflux, 3 d; b) $AgOSO_2CF_3$, CH_2Cl_2, 25 °C, 4 h.

such a type as complex **3** *via* direct metallation by taking the chiral ligand and K_2PtCl_4 in a molar ratio of 2:1 in acetic acid under reflux (Scheme 1). But the present ligand system underwent only mono metallation, leading to the formation of chiral mononuclear cyclometalated platinum(II) complex **6**, in which an additional chiral ligand was coordinated to the platinum by nitrogen. Interestingly, complex **6** was formed through an intermediate of *trans* dichloro(dipyridyl)-platinum(II) complex **5**, which was identified by NMR spectroscopy for the isolated product after 2 days' reflux. When the reaction mixture was further refluxed, however, the mono-cyclometalated complex **6** was formed as the sole product after 3 days. We could not observe the chloro bridged dimeric complex **7** under the reaction conditions. When we carried out the same reaction for a 1:1 mixture of the ligand (**L**) and K_2PtCl_4, again we could not observe the chloro bridged dimer **7** during the reaction period, and again obtained complex **6** as the only product eventually. The formation of mononuclear cyclometalated platinum(II) instead of the dimmer or bis-cyclo metallated compound is probably due to the steric hindrance of β-pinene moiety, which interferes the platinum insertion to the second aromatic ring.

The formation of metallacyle **6** could be followed by ^1H NMR analysis for the reaction products. When a mixture of K_2PtCl_4 and pyridine ligand (**L**) in acetic acid was heated to reflux for 2 days, a solid began to precipitate, which was found to be *trans*-dichloro(dipyridyl)platinum(II) complex **5** by ^1H and ^{13}C NMR analyses after filtration and washing with solvents. No cyclometalated compounds were observed

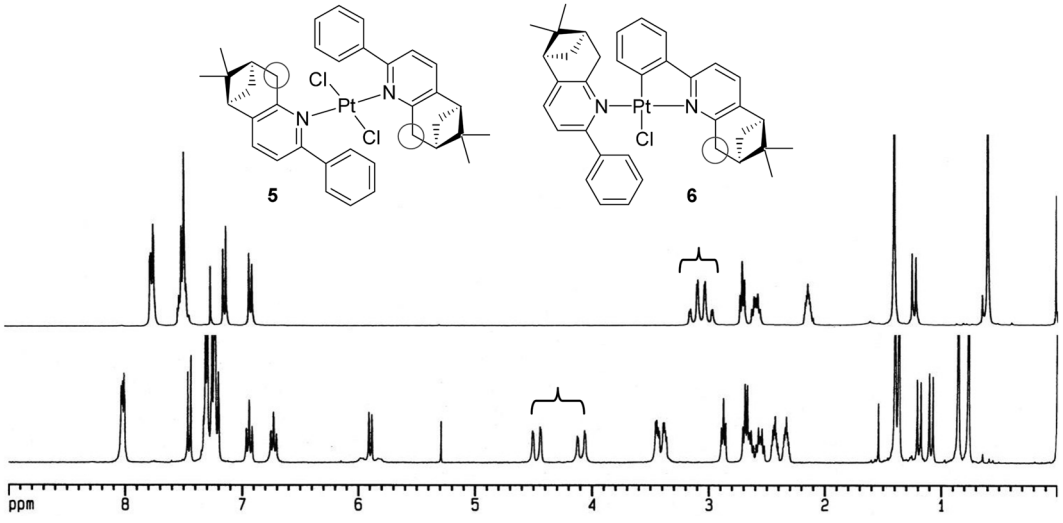


Figure 1. ^1H NMR spectra of complexes **5** (upper) and **6** (lower), obtained in $CDCl_3$. The methylene protons in the circle show a dramatic shift to the downfield in the case of **6** due to the C-H···Cl hydrogen bonding.

in the solid. The complex **5** showed two sets of benzene ring peaks (as multiplets, at δ 7.7 and 7.5 ppm) in a ratio of 2:3 and two doublets for the pyridine ring peaks (δ 7.1 and 6.9 ppm), from which the formation of metallacylic bonds could be excluded (Figure 1). Other peaks conformed to the C_2 symmetric structure of **5**. When the same reaction was carried out for longer time such as 3 days, the product obtained was found to be monocylometallated complex **6**. Complex **6** was obtained by washing the filtered solid sequentially with water, methanol, and diethyl ether, and then re-dissolving it in dichloromethane and purification by column chromatography. The ^{1}H and ^{13}C NMR spectra of **6** showed no C_2 symmetry but more split pattern, which clearly indicated that an unsymmetrical dipyridylplatinum complex was formed. Of particular note is that the α-pyridyl methylene protons of one pyridine ligand (the methylene protons adjacent to the pyridine ring) appear at much downfield (two doublets at 4.5 and 4.1 ppm; J = 19.5 Hz) compared to other α-methylene protons (two sets of multiplets at 3.3-3.5 ppm) (Figure 1).

The α-methylene protons in non-cyclometalated platinum complex **5** appeared as AB-type peaks around 3.0 ppm. The unusual downfield shifts of the CH_2 protons can be explained by the existence of C-H···Cl hydrogen bonding in solution. Attractive hydrogen bonding interactions, particularly C-H···Cl$^-$ and C-H···Cl-M (M: metal) types, have been identified in a number of crystal structures of salt-like and covalently bound complexes.[26,27] However, only two examples including our recent report are known in which the hydrogen bonding has been identified both in solid and in solution states.[28,29] Recently, we have also found another example of such a hydrogen bond in pincer complexes derived from chiral bis(pyridine) ligands, both in solid and solution states.[30] A molecular model and an X-ray crystal structure of **6** (in the following section) indicate that the α-pyridyl methylene protons of the cyclometalated ligand are involved in the C-H···Cl hydrogen bonding. The downfield shift due to the hydrogen bonding (0.8-1.0 ppm) is larger than known values (0.11 ppm)[28] and similar to our recent observations (0.7-1.0 ppm).[29,30]

Interestingly, similar downfield shifts were observed in the case of aqua complex **8**, although the shifts were smaller than that of the chloroplatinum complex (doublets at 4.14 and 3.60 ppm). In this case, we may also expect C-H···O hydrogen bonding in which O is provided by an aqua ligand coordinated to the platinum. The aqua complex showed two sets of NMR peaks for most of the protons, indicating an equilibrium mixture of conformational isomers. Two extreme conformers are possible for both complexes **6** and **8**, if we take into account the hindered rotation of non-chelating pyridine ligand around the metal. In the solid structure of chloride complex **6** in the following shows a conformational isomer in which both the gem-dimethyl substituents in the two pyridine ligands are in the same side. The other conformer is found to have almost the same stability by molecular mechanics calculations. Therefore, the conformational isomerism is expected to be fast compared to NMR time scale in the case of the chloroplatinum complex, while it is rather slow in the case of the aqua complex at room temperature.

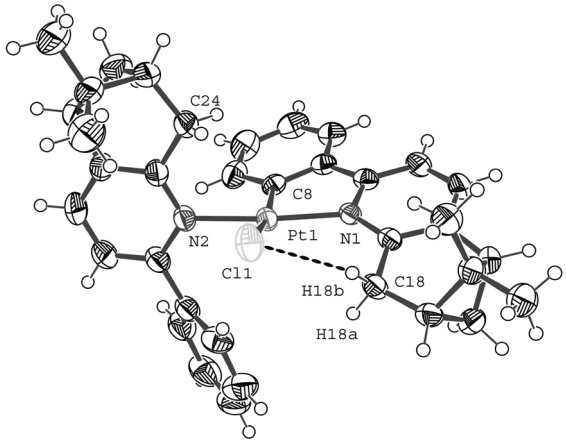


Figure 2. Molecular structure of complex **6**. The C-H···Cl hydrogen bond between C11 and H18b is indicated by a dashed line.

X-ray crystal structure. To find out the coordination mode of the chiral ligand in these complexes as well as the absolute stereochemistry of the complexes, the structure of one of the complexes, compound **6**, has been determined by X-ray crystallography and an ORTEP view of this complex is shown in Figure 2. The summary of single crystal X-ray structure refinement (Table 1) and selected bond angles and bond lengths are given (Table 2). It is clear that the present ligand system coordinates to platinum through bidentate as well as monodentate fashions in the cyclometalation reaction. The chiral ligand acts as bidentate, binding the metal centre at N(1) and C(8) forming one five membered chelate ring with bite angle of 81.23(10) (N(1)–Pt(1)–C(8)). The other unit of the chiral ligand acts as monodentate and binds to the metal through pyridine nitrogen N(2). The bond distances of Pt(1)-N(2) and Pt(1)-Cl(1) are 2.028(2) Å and 2.437(8) Å respectively. The overall N(1), C(8), N(2) and Cl(1) coordination sphere around the central platinum is a distorted square-planar, which is reflected in all the bond parameters around platinum. Of notable feature is the C-H···Cl hydrogen bonding between the chloride Cl(1) and one of the methylene hydrogen H(18b), as indicated with a dotted line. The distance between H(18b) and Cl(1) is 2.495 Å based on a calculated hydrogen position (confer H(18a)-Cl(1) = 3.242 Å), and the bond angle of Cl(1)-H(18b)-C(18) is 132.3 Å, conforming to the previously reported values observed for related C-H···Cl hydrogen bonds.[26,27] This solid structure also supports the unusual downfield shifts observed for the protons H(18a) and H(18b) in the ^{1}H NMR spectrum of complex **6**. A small distortion from the square-planar geometry around the metal centre seems to be due to the preferred hydrogen bonding involving one methylene hydrogen atom (H18b) in the solid state.

The crystal structure shows that the second pyridyl ligand coordinates to the metal plane formed by the cyclometalating ligand with dihedral angle of 83°. Because the

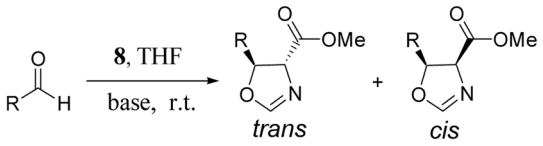
Table 1. Crystal data and structure refinement for **6**

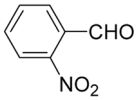
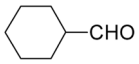
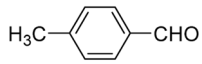
Empirical formula	$C_{36}H_{37}ClN_2Pt$
Formula weight	728.22
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.4163(10) Å α = 90°
	b = 11.1156(12) Å β = 90°
	c = 28.847(3) Å γ = 90°
Volume	3019.3(6) Å^3
Z	4
Density (calculated)	1.602 Mg/m^3
Absorption coefficient	4.763 mm^{-1}
F(000) 1448	
Crystal size	0.56 × 0.32 × 0.26 mm^3
Theta range for data collection	1.96 to 28.28°
Index ranges	−12 ≤ h ≤ 12, −14 ≤ k ≤ 14,
	−38 ≤ l ≤ 38
Reflections collected	31007
Independent reflections	7493 [R(int) = 0.0253]
Completeness to theta = 28.28°	99.9%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7493 / 0 / 365
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0183, wR2 = 0.0417
R indices (all data)	R1 = 0.0202, wR2 = 0.0421
Absolute structure parameter	0.004(5)
Largest diff. peak and hole	0.659 and 0.584 e.Å^{-3}

Table 2. Selected bond lengths (Å) and bond angles (°) of complex **6**

Bond lengths (Å)		Bond angles (°)	
Pt(1)-Cl(1)	2.437(8)	N(1)-Pt(1)-N(2)	171.91(9)
Pt(1)-N(1)	2.051(19)	N(1)-Pt(1)-C(8)	81.23(10)
Pt(1)-N(2)	2.028(2)	N(1)-Pt(1)-Cl(1)	102.56(7)
Pt(1)-C(8)	1.982(2)	N(2)-Pt(1)-C(8)	90.72(10)
N(1)-C(13)	1.375(3)	N(2)-Pt(1)-Cl(1)	85.11(7)
N(1)-C(17)	1.355(3)	C(8)-Pt(1)-Cl(1)	166.37(8)
N(2)-C(6)	1.343(4)		
N(2)-C(2)	1.374(4)		
C(2)-C(32)	1.494(4)		
C(8)-C(9)	1.403(4)		
C(8)-C(7)	1.415(4)		
C(9)-C(13)	1.461(4)		

Table 3. Aldol Reaction of Methylisocyanoacetate and Aldehydes



Entry	Aldehyde	Base	Reaction Time	Yield (%)	Er[a]	*Trans*/*Cis*[b]
1		DIPEA	1 d	68	50:50	93/7
2		DBU	4 d	11	50:50	96/4
3		DBU	1 d	87	53:47	98/2

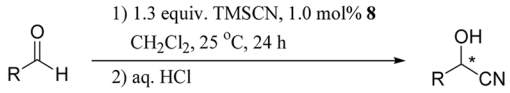
[a]Enantiomer ratio, determined by ^{1}H NMR spectroscopy using Eu(hfc)$_3$ as a chiral shift reagent. [b]Determined by integrating the methyl ester peak of each isomer on ^{1}H NMR spectrum.

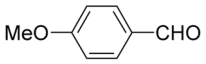
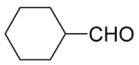
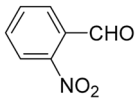
monodentate pyridyl ligand can rotate around the metal coordination bond, two typical conformers are possible depending on the relative position of the second pyridyl ligand with respect to the cyclometalated pyridyl moiety. In the case of chloroplatinum complex **6**, two conformers were not differentiated at room temperature, judging from the fact that its NMR spectrum showed single set of peaks. We did not carry out VT-NMR experiments to observe two conformers; however, we were able to observe that two conformers exist in the case of the corresponding aqua complex **8** as described above, even at room temperature. It is likely that the aqua complex undergoes a slow conformational change on the NMR time scale.

Catalytic activity. To evaluate the catalytic efficiency of the new complexes, we briefly studied the asymmetric aldol reaction and the silylcyanation reaction of aldehydes. In the case of the aldol reaction, optimizations of the reaction conditions were performed using benzaldehyde as the substrate and DIPEA (diisopropylethylamine) or DBU (1,8-diazobicyclo[5.4.0]undec-7-ene) as a base. The active catalytic species was formed in the reaction by abstracting the chloride with silver triflate, generating a vacant site for binding of methyl isocyanoacetate. The effects of solvents on the reaction were also investigated. It was found that the reaction in THF gave higher enantioselectivity than in CH_2Cl_2 or in toluene. A variety of organic bases were investigated (*i.e.*, DMAP, pyridine, ethanolamine, morpholine), and it was found that they affected very little on the enantioselectivity. Other factors such as concentration, amount of base used, addition rate, and order of substrate addition had no significant effect on the enantioselectivity. Under optimized conditions (1.0 mol % complex **8**, 100 mol % methylisoyanoacetate, 110 mol % aldehyde, and 10 mol % diisopropylethylamine in THF), the asymmetric aldol reaction was performed with a variety of aldehydes (Table 3).

In seeking further applications of this complex **8**, we chose to investigate its potential as catalyst for the silylcyanation of aldehydes. The reaction was carried out using **8** as the asymmetric catalyst. Optimizations of the reaction conditions were performed using benzaldehyde as the substrate and TMSCN. In the absence of a catalyst, combining benzaldehyde with 1.3 equivalents of TMSCN did not result in the formation of cyanohydrin. Under the same conditions in CH_2Cl_2, addition of 1.0 mol% of **8** resulted in the clean formation of cyanohydrin after the addition of 3 N HCl to

Table 4. Catalytic silylcyanation of aldehydes



Entry	Aldehyde	Conversion Yield (%)[a]	Er[b]
1		81	54:46
2		83	50:50
3		4	50:50

[a]Determined by ^{1}H NMR analysis. [b]Enantiomer ratio, determined by ^{1}H NMR spectroscopy using Eu(hfc)$_3$ as a chiral shift reagent.

hydrolyze the TMS ether initially formed in the reaction. The effects of solvents on the reaction were investigated and found that the reaction in CH_2Cl_2 gave higher conversion than in toluene. Under optimized conditions (1 mol % complex **8** 1.3 equiv. TMSCN in CH_2Cl_2), the asymmetric silylcyanation was performed with a series of aldehydes. The *trans* isomers were major products for the aldehydes examined in aldol reaction and in silylcyanation (Table 4).

The present results of asymmetric reactions show reasonable conversions by the Pt(II) cyclometalated complex but disappointingly low enantioselectivity in both the reactions. At this stage, we tentatively conclude that the chiral pyridine ligand of the cyclometalated complexes may not provide a distinctive chiral environment in the above reactions. A structural variation of the chiral pyridine ligand is necessary for a further study of the cyclometalated complex as an asymmetric catalyst.

Conclusion

In conclusion, mononuclear cyclometalated Pt(II) complexes are generated from a cyclometalation reaction between a chiral pyridine ligand and a platinum source, K_2PtCl_4. A chloroplatinum(II) complex (**6**) was structurally characterized by X-ray crystallography, which indicated the presence of a distorted square-planar geometry due to the C-H···Cl-Pt hydrogen bond. The unusual hydrogen bonding was also identified in solution by ^{1}H NMR analysis. The catalytic efficiency of its aqua complex (**8**) was evaluated in the aldol and silylcyanation reactions.

Experimental

Materials and physical measurements. All air sensitive experiments were performed under a positive pressure of argon atmosphere. Solvents such as dichloromethane, THF or DMF were distilled and purified prior to use according to standard methods. The chiral ligand, (5*R*,7*R*)-5,6,7,8-tetrahydro-6,6-dimethyl-2-phenyl-5,7-methanoquinoline, was prepared based on the literature procedures.[25] HRMS (FAB) was performed by Daegu Branch of Korea Basic Science Institute. K_2PtCl_4 was purchased from Aldrich and was used without further purifications.

X-ray crystallography. All measurements were made with a Siemens CCD area detector using graphite monochromatized Mo-Kα (λ = 0.71073 Å) radiation. Intensities were corrected for Lorentz and polarization effects and for absorption. The structure was solved by direct methods using SHELXS, and refined on F^2 using all data by full matrix least-squares procedures with SHELXS-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. CCDC 620197 contains the supplementary crystallographic data for the structure reported in this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of cyclometalated platinum(II) complexes 6 and 8 from (5*R*,7*R*)-5,6,7,8-tetrahydro-6,6-dimethyl-2-phenyl-5,7-methanoquinoline (L). A mixture of (5*R*,7*R*)-5,6,7,8-tetrahydro-6,6-dimethyl-2-phenyl-5,7-methanoquinoline (0.54 g, 2.17 mmol), K_2PtCl_4 (0.43 g, 1.03 mmol), and acetic acid (10 mL) was refluxed for 3 days. The mixture was allowed to cool to room temperature. The bright yellow solid was filtered off and washed sequentially with H_2O, MeOH, and Et_2O to give pure compound **6**. Yield: 0.72 g (96%). Mp: 282-284 °C. $[\alpha]_D^{25}$ −57.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.77 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 1.09 (d, *J* = 9.4 Hz, 1H, CHH_{endo}), 1.19 (d, *J* = 9.6 Hz, 1H, CHH_{endo}), 1.36 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 2.31-2.39 (m, 1H, CH), 2.39-2.47 (m, 1H, CH), 2.51-2.59 (m, 1H, CHH_{ex}), 2.60-2.73 (m, 1H, CHH_{ex}), 2.69 (t, *J* = 5.9 Hz, 1H, CH), 2.88 (t, *J* = 5.9 Hz, 2H, CH), 3.34-3.55 (m, 2H, CH_2), 4.09 (d, *J* = 19 Hz, 1H, CH_2), 4.48 (d, *J* = 19 Hz, 1H, CH_2), 5.81-6.09 (m, 1H, Ar-H), 6.86 (dd, *J* = 1.2, 7.4 Hz, 1H, Ar-H), 6.95 (dd, *J* = 1.0, 8.5 Hz, 1H, Ar-H), 7.20-7.38 (m, 7H, Ar-H, Py-H), 7.45 (d, *J* = 7.7 Hz, 1H, Py-H), 8.01-8.10 (m, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.7, 163.3, 160.4, 160.3, 146.3, 144.6, 141.9, 141.8, 138.8, 135.7, 135.1, 131.1, 130.9, 128.8, 128.7, 127.9, 124.1, 123.5, 122.9, 115.1, 47.8, 47.6, 40.9 (two peaks overlapped), 40.8, 40.4, 39.8, 39.1, 32.7, 31.7, 26.4, 26.3, 22.8, 22.4. MS (FAB) calcd for $C_{36}H_{37}N_2Pt$ (M-Cl)$^+$ 692.26, found 692.43.

A mixture of chloroplatinum complex **6** (0.71 g, 0.97 mmol) and silver triflate (0.25 g, 0.97 mmol) in dichloromethane (20 mL) was stirred for 7 h, by which time all the starting complexes had been consumed. The mixture was filtered through Celite to remove silver chloride and washed with dichloromethane. The solvent was evaporated to give the corresponding cationic complex **8** as a pale yellow solid. This cationic complex seems to be the corresponding aqua complex rather than the triflate (see the text). Complex **8** shows two sets of ^{1}H NMR peaks, consisting of a slow equilibrium mixture of two isomers that are different in the relative orientation of the second ligand with respect to the

metalacylic moiety. Yield: 0.71 g (85%). Mp: 152-154 °C. $[\alpha]_D^{25}$ −8.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) for the major component: δ 0.51 (s, 3H, CH_3), 0.74 (s, 3H, CH_3), 1.27 (d, J = 9.6 Hz, 1H, CHH_{endo}), 1.36 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.74 (d, J = 9.8 Hz, 1H, CHH_{endo}), 2.21-2.39 (m, 2H, CH), 2.50-2.80 (m, 4H), 2.90 (t, J = 5.6 Hz, 1H, CH), 3.17 (d, J = 18.5 Hz, 1H, CH_2), 3.60 (d, J = 19.3 Hz, 1H, CH_2), 4.15 (d, J = 19.3 Hz, 1H, CH_2), 6.04-6.32 (m, 1H, Ar-H), 6.79 (t, J = 7.6 Hz, 1H, Ar-H), 7.00 (t, J = 7.4, Hz, 1H, Ar-H), 7.21-7.40 (m, 7H, Ar-H, Py-H), 7.48-7.59 (m, 1H, Py-H), 7.70-7.91 (m, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz) for the major component: δ 165.7, 163.3, 160.4, 160.3, 146.3, 144.6, 141.9, 141.8, 138.8, 135.7, 135.1, 131.1, 130.9, 128.8, 128.7, 127.9, 124.1, 123.5, 122.9, 115.1, 47.8, 47.6, 40.9 (two peaks overlapped), 40.8, 40.4, 39.8, 39.1, 32.7, 31.7, 26.4, 26.3, 22.8, 22.4. HRMS (FAB) calcd for $C_{36}H_{37}N_2$ Pt (M H_2O OTf)$^+$ 692.2604, found 692.2604.

A representative procedure for the Pt(II)-catalyzed aldol reaction. A stirred solution of **8** (12.6 mg, 0.015 mmol, 1.5 mol %) in THF (5 mL) was treated sequentially with methyl α-isocyanoacetate (0.09 mL, 1.0 mmol), an aldehyde (1.0 mmol), and diisopropylethylamine (22 μL, 13 mol %). The colorless reaction mixture was stirred at room temperature for 1-4 d (monitored by TLC with a stain solution of $KMnO_4$/0.1 M NaOH). The solvent was evaporated *in vacuo*, and the remaining residue was purified by column chromatography on silica gel (EtOAc/hexane = 1/3) to give a pure *cis*/*trans*-mixture of the corresponding 4,5-oxazoline. The *cis*/*trans* ratio was determined by integrating the methyl ester peak of each isomer on the ^{1}H NMR spectrum. The enantiomeric excess was determined by ^{1}H NMR spectroscopy using Eu(hfc)$_3$ as a chiral shift reagent.

A representative procedure for the Pt(II)-catalyzed silylcyanation of aldehyde. To a solution of **8** (0.031 g, 0.036 mmol, 1.0 mol %) and an aldehyde (3.6 mmol) in CH_2Cl_2 (10 mL) was added TMSCN (0.6 mL, 4.5 mmol), and the resulting solution was stirred at room temperature for 24 h. A trap containing sodium hypochlorite was equipped with the reaction flask, and the reaction mixture was treated cautiously with 3*N* hydrochloric acid (10 mL), and the resulting solution was vigorously stirred for 12 h. The organic phase was separated, dried ($MgSO_4$) and evaporated *in vacuo*. Purification by column chromatography (gradient elution, 10% EtOAc/petroleum ether → 100% EtOAc) gave a pure cyanohydrin and unreacted aldehyde. The conversion percentage was determined by comparing the integrated ratio of the methine proton of the cyanohydrin with respect to the aryl protons of the cyanohydrin and the unreacted benzaldehyde on the ^{1}H NMR spectrum. The enantiomeric ratio were determined by ^{1}H NMR spectroscopy using Eu(hfc)$_3$ as a chiral shift reagent.

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