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Chiral Pt(II)/Pd(II) pincer complexes that show C–H···Cl hydrogen bonding: Synthesis and applications to catalytic asymmetric aldol and silylcyanation reactions

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Abstract

A chiral C_2-symmetric NCN ligand, (5*R*,7*R*)-1,3-bis(6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)benzene has been synthesized. A direct cyclometalation of this ligand with K_2MCl_4 (M = Pt, Pd) in dry acetic acid offered the corresponding pincer complexes, [(5*R*,7*R*)-1,3-bis(6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)phenyl]platinum(II) chloride **5a** and its palladium(II) analogue **5b**. The Pt(II) and Pd(II) complexes **5** were characterized by NMR spectroscopy, and X-ray crystal structure analysis was done for the Pt(II) complex. The NMR data for both the complexes and X-ray crystal structural data for the chloro-Pt(II) complex indicate the existence of intramolecular C–H···Cl hydrogen bonding both in solution and in solid states. Chloride abstraction from **5a** by treatment with silver triflate resulted in the corresponding triflate complex **6a**, which generates the corresponding cationic aqua complex **7a** in the presence of water molecules. The Pt(II) complex **6a**/**7a** was used as asymmetric catalyst in the aldol reaction between methyl isocyanoacetate and aldehydes and also in the silylcyanation of aldehydes.

Keywords: Chiral NCN pincer ligand; Pt(II)/Pd(II) complexes; C–H···Cl hydrogen bonding; Crystal structure; Catalytic asymmetric reactions

1. Introduction

There has been an increasing interest in metal pincer complexes containing terdentate ligands which include one metal–carbon bond [1]. Particularly, platinum group metal based pincer complexes of general structure **1** are currently the subject of much attention due to their application as catalyst, novel organometallic materials and biomarkers [2]. A major subcategory of **1** is terdentate NCN complexes of Pd or Pt where N ligands are amino (**2**), oxazolinyl (**3**) and pyridinyl (**4**) *trans*–chelating functionalities [3–5]. In the synthesis of these pincer complexes, the metals are introduced by either (i) *trans*-metalation of M(II) (M = Ni, Pd or Pt) [6]; (ii) oxidative addition of M(0) (M = Ni, Pd or Pt) [7] or (iii) directing group mediated cyclometalation of M(II) (M = Pd) [8]. Though various methods have been developed for the metalation of pincer ligands, direct cyclometalation is a particularly attractive method for the formation of a new metal–carbon bond, since it does not require prefunctionalization of the pincer ligand in order to achieve regioselective metalation [9].

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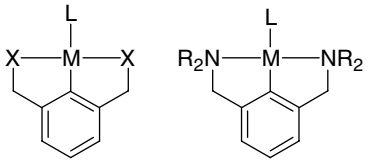
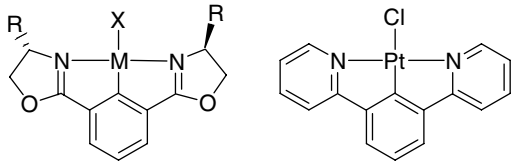


1 2
(M = Ni, Pt, Pd)



3 4
(M = Pd, Pt; X = Cl, Br)

Direct cyclometalation of NCN pincer ligands is less common in the literature. The reduced tendency for cyclometalation with these ligands may be explained by the relatively low bond strength of the M–N bond [10]. Moreover, this situation results in kinetically rather than thermodynamically controlled reaction pathways, and consequently, (ortho,para)-doubly metalated products rather than (ortho,ortho)-biscyclometallated species result [11]. Accordingly, we studied on the possibility of performing direct cyclometalation of NCN pincer ligands by screening appropriate metal sources and recently communicated our successful result in the synthesis of metal pincer complexes of achiral NCN ligands [12]. We also realized that chiral metal pincer complexes based on pyridine-based NCN ligands are rare, and thus initiated the synthesis of such metal pincer complexes for their potential applications to catalytic asymmetric reactions.

Various homogeneous catalytic processes with pincer complexes have been reported, including Kharasch addition [13], Heck olefin arylation [14], Suzuki biaryl coupling [15], dehydrogenation of alkanes [16] and transfer hydrogenation [17]. Despite considerable progress, very little attention has been focused on chiral version of NCN pincer ligands for asymmetric catalytic reactions. van Koten and co-workers reported the synthesis of enantiomeric (oxo-functionalized) C_2-symmetric NCN pincer ligands containing chiral information on the benzylic carbons and their Pt(II) and Pd(II) complexes via lithiation [18]. Further, direct cycloplatination of chiral C_2-symmetyric bis(imidazoline) NCN pincer ligand has been reported by Song [19].

As a part of our continuing efforts on the synthesis, structural study and catalytic activity of pincer complexes [12], we report here the Pt(II)/Pd(II) complexes derived from the chiral pyridine based NCN pincer ligand. After completion of this work, we have found that the same but enantiomeric chloro-Pt(II)/Pd(II) complexes have been coincidentally pursued by other research group and their X-ray single crystal structures have been reported very recently [20]. In addition to the important finding that there exist C–H···Cl hydrogen bonding in the pincer complexes, we have evaluated the new triflate analogue of platinum(II) NCN pincer complex as catalyst for the asymmetric aldol reaction and silylcyanation of aldehydes.

2. Experimental

2.1. 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 purified and distilled prior to use according to standard methods. The pincer ligand, (5*R*,7*R*)-1,3-Bis(6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)benzene, was synthesized starting from commercially available (*S*)-(−)-β-pinene, following the literature procedures used for the synthesis of a chiral terpyridine system [21]. HRMS (FAB) was performed by Daegu Branch of Korea Basic Science Institute. K_2PtCl_4 and K_2PdCl_4 were purchased from Aldrich and used without further purifications.

2.2. X-ray crystallography

All measurements were made with a Siemens CCD area detector using graphite monochromatized Mo Kα ($\lambda = 0.71073$Å) radiation. Intensities were corrected for Lorentz and polarization effects and for absorption. The structure was solved by direct methods 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.

2.3. Synthesis of the NCN ligand **9** and its Pt(II) and Pd(II) pincer complexes **5** and **6**

1,3-Bis(pyridinioacetyl)benzene diiodide (8). A solution of 1,3-diacetylbenzene (1.56 g, 9.62 mmol) and iodine (5.0 g, 19.7 mmol) in pyridine was refluxed for 7 h under argon. After being cooled, the precipitate was filtered off, and washed with methanol and diethyl ether. The solid was dried under vacuo to give pure **8** as a white solid. Yield: 5.13 g (93%). MP: 246–247 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.60 (s, 4H, ArCH_2), 7.99 (t, $J = 7.8$ Hz,1H, Ar–H), 8.32 (t, $J = 7.0$ Hz, 4H, Py–H), 8.47 (d, $J = 7.9$ Hz, 2H, Ar–H), 8.56 (s, 1H, Ar–H), 8.78 (t, $J = 7.8$ Hz, 2H, Py–H), 9.04 (d, $J = 5.9$ Hz, 4H, Py–H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 190.3, 146.6, 146.3, 134.3, 133.9, 130.2, 127.9, 127.1, 66.4.

(5*R*,7*R*)-1,3-Bis(6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)benzene (9). A solution of the pyridinium iodide **8** (0.49 g, 0.86 mmol), (+)-pinocarvone (0.26 g, 1.71 mmol) synthesized from commercially available (*S*)-(−)-β-pinene, and ammonium acetate (1.72 g, 22.3 mmol)

in glacial acetic acid (1.7 mL) was heated at 120–125 °C for 8 h under argon. Then, most of the acetic acid was removed under reduced pressure, and the residue was taken up with water (40 mL) and extracted with ethyl acetate (2 × 40 mL). The organic phase was washed with a 5% NaOH solution and then with H_2O. After being dried over anhydrous Na_2SO_4, the solvent was evaporated and the residue was purified by chromatography on silica gel (ethyl acetate/*n*-hexane = 1/9) to give pure **9** as a white solid. Yield: 0.15 g (42%). MP: 145–146 °C. $[\alpha]_D^{25}$ −115.8 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.70 (s, 6H,CH_3), 1.33 (d, $J = 9.5$ Hz, 2H, CHH_{endo}), 1.43 (s, 6H, CH_3), 2.41 (m, 2H, CH), 2.71 (m, 2H, CHH_{exo}), 2.80 (t, $J = 5.5$ Hz, 2H, CH), 3.21 (d, $J = 2.7$ Hz, 4H, CH_2), 7.28 (d, $J = 7.8$ Hz, 2H, Py–H), 7.51 (m, 3H, Py–H), 7.98 (d, $J = 7.8$ Hz, Py–H), 8.51 (s, 1H, Ar–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.3, 154.4, 140.0, 139.9, 133.1, 128.6, 126.3, 124.8, 117.0, 45.8, 39.8, 39.1, 36.3, 31.6, 25.6, 20.9. HRMS (FAB) Calcd. for $C_{30}H_{33}N_2$ $(M + H)^+$: 421.2644, found 421.2639.

[(5*R*,7*R*)-1,3-Bis(6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)phenyl]platinum chloride (5a) and its triflate analogue 6a. A solution of the NCN ligand **9** (0.37 g, 0.87 mmol) and K_2PtCl_4 (0.36 g, 0.87 mmol) in acetic acid (12 ml) was refluxed for 3 days. The progress of the reaction was monitored by thin layer chromatography after taking small aliquots and treating them with water. The mixture was allowed to cool to room temperature (The appearance of a red color indicated the presence of unreacted K_2PtCl_4). The bright yellow solid was filtered and washed sequentially with water, MeOH, and Et_2O to give pure **5a**. Yield: 0.47 g (83%). MP > 328 °C (dec.). $[\alpha]_D^{25}$ −260.8 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.72 (s, 6H,CH_3), 1.29 (d, $J = 9.6$ Hz, 2H, CHH_{endo}), 1.38 (s, 6H, CH_3), 2.44 (m, 2H, CH), 2.63 (m, 2H, CHH_{exo}), 2.78 (t, $J = 5.8$ Hz, 2H, CH), 4.30 and 4.12 (ABX, $J_{AB} = 19.3$ Hz, $\Delta v = 0.18$ Hz, 4H, CH_2), 7.14 (m, 1H, Ar–H), 7.25 (d, 2H, Ar–H), 7.37 (s, 4H, Py–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.9, 163.6, 154.5, 143.4, 142.1, 135.8, 123.4, 122.6, 115.7, 47.4, 40.3, 38.9, 38.8, 30.9, 25.8, 21.7. HRMS (FAB) calcd. for $C_{30}H_{31}N_2Pt$ $(M - Cl)^+$: 614.2135, found 614.2139.

A solution of the chloroplatinum pincer complex **5a** (0.44 g, 0.67 mmol) and silver triflate (0.17 g, 0.67 mmol) in dichloromethane (20 mL) was stirred at 25 °C for 2 h, by which time all the starting complex was consumed. The mixture was filtered through Celite to remove silver chloride and washed with dichloromethane. The solvent was evaporated to give air-stable **6a** as a pale yellow crystalline solid. Yield: 0.52 g (98%). MP: 192–193 °C. $[\alpha]_D^{25}$ −244.2 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.73 (s, 6H, CH_3), 1.30 (d, $J = 9.8$ Hz, 2H, CHH_{endo}), 1.40 (s, 6H, CH_3), 1.69 (bs, 2H, H_2O), 2.44 (m, 2H, CH), 2.67 (m, 2H, CHH_{exo}), 2.81 (t, $J = 5.6$ Hz, 2H, CH), 3.72 and 3.57 (ABX, $J_{AB} = 18.9$ Hz, $\Delta v = 0.16$ Hz, 4H, CH_2), 7.17 (m, 3H, Ar–H), 7.39 (m, 4H, Py–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.5, 162.8, 144.0, 142.0, 136.5, 124.7, 122.7, 118.0, 116.2, 47.3, 40.1, 39.0, 36.5, 30.9, 25.7, 21.6. HRMS (FAB) calcd. for $C_{30}H_{31}N_2Pt$ $(M - OTf)^+$: 614.2135, found 614.2139.

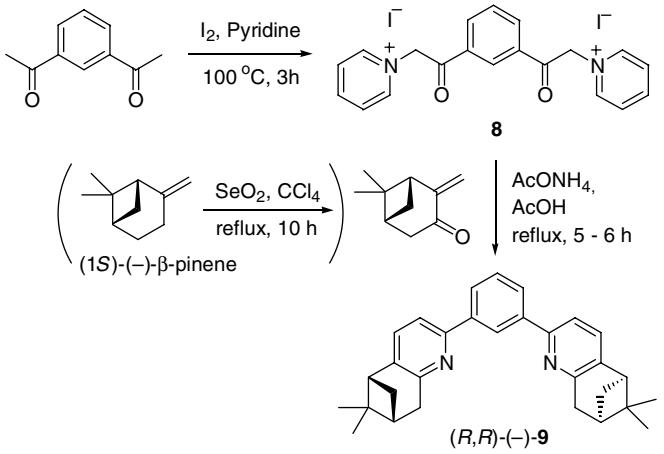
[(5R,7R)-1,3-Bis(6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)phenyl]palladium chloride (5b). A mixture of the NCN ligand **9** (0.10 g, 0.24 mmol), K_2PdCl_4 (0.08 g, 0.24 mmol), and glacial acetic acid (5 mL) was refluxed for 3 days. The mixture was allowed to cool to room temperature. The bright grey solid was filtered off and washed sequentially with H_2O, MeOH, and Et_2O to give the pure **5b** as a bright yellow solid in 57% yield (0.075 g). MP 312–313 °C. $[\alpha]_D^{25}$ −197.0 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.72 (s, 6H,CH_3), 1.29 (d, $J = 9.6$ Hz, 2H, CHH_{endo}), 1.39 (s, 6H, CH_3), 2.43 (m, 2H, CH), 2.62 (m, 2H, CHH_{exo}), 2.77 (t, $J = 5.7$ Hz, 2H, CH), 4.11 and 3.99 (ABX, $J_{AB} = 19.2$ Hz, $\Delta v = 0.12$ Hz, 4H, CH_2), 7.10 (m, 1H, Ar–H), 7.22 (d, 2H, Ar–H), 7.34 (s, 4H, Py–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.1, 162.5, 161.9, 144.2, 143.3, 135.6, 124.8, 122.5, 115.5, 47.3, 40.2, 39.0, 38.8, 31.2, 25.8, 21.7. HRMS (FAB) calcd. for $C_{30}H_{31}N_2Pd$ $(M - Cl)^+$ 525.1522, found 525.1534.

3. Results and discussion

3.1. Synthesis and structure analysis

The enantiomerically pure ligand was prepared according to Scheme 1. 1,3-Bis(pyridinoacetyl)benzene diiodide was obtained in 93% yield from 1,3-diacetylbenzene by reacting with iodine in pyridine [22]. (1*R*)-(+)-β-pinocarvone was prepared in 70–80% yield from commercially available (1*S*)-(−)-β-pinene (97% ee) following the literature procedure [23]. The promising NCN pincer ligand was readily accessible in 42% yield by reaction of 1,3-bis(pyridinoacetyl)benzene diiodide (**8**) with (1*R*)-(+)-pinocarvone following the Kröhnke condensation [24]. The ligand was purified by chromatography on silica gel (ethyl acetate/*n*-hexane=1/9) as a white solid ($[\alpha]_D^{25}$ − 115.8 (*c* 1.0, $CHCl_3$)).

With the chiral bis(pyridine) based NCN pincer ligand **9** in hand, we decided to synthesize the cyclometallated

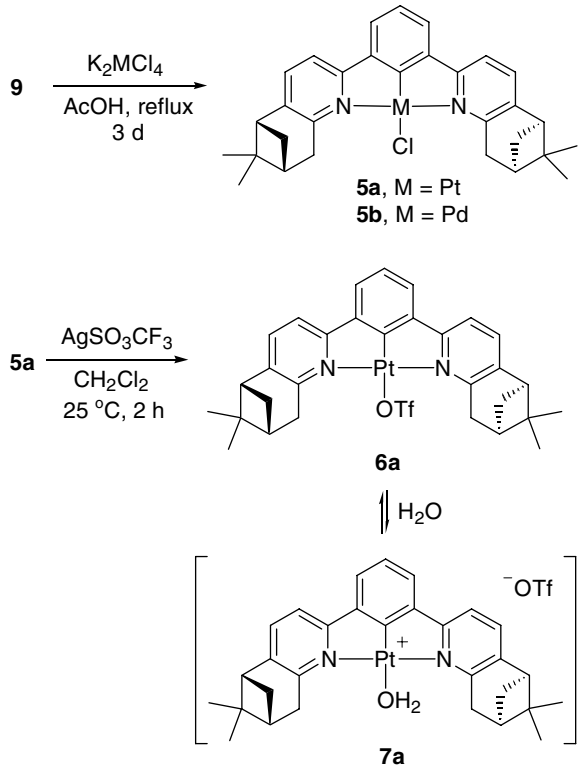


Scheme 1. Synthesis of the chiral NCN pincer ligand (*R*,*R*)-(−)-**9**.

Pt(II)/Pd(II) complexes considering that tridentate cyclometallated Pt(II)/Pd(II) complexes have promising performance as catalysts. The direct cycloplatination reaction was carried out with the chiral ligand **9** in the presence of an equimolar amount of K_2PtCl_4 in acetic acid under reflux for 3 days. After removal of solvents, the Pt(II) pincer complex **5a** was successfully obtained in 83% as bright yellow solid by column chromatography. Similarly, the Pd(II) pincer complex **5b** was prepared by using $KPdCl_4$ in 57% yield as bright grey solid. Attempted cyclopalladation of the NCN ligand **9** with other palladium sources such as $PdCl_2(CH_3CN)_2$, $PdCl_2(PPh_3)_2$, and $Pd(OAc)_2$/LiCl were not successful.

Further, chloride abstraction from complex **5a** by addition of silver trifluoromethanesulfonate (AgOTf) followed by removal of silver chloride by filtration afforded the triflate analogue **6a** in 98% isolated yield as white-yellow, air stable crystalline solid (Scheme 2). An aqueous work-up seems to generate the corresponding ionic aqua complex **7a**.

The formation of platinum pincer complexes **5** and **6a/7a** from the ligand **9** was clearly indicated by their NMR spectral changes (see Fig. 1.). Thus, the formation of pincer complex **5a** from the NCN ligand **9** is indicated by two distinct changes: (1) the benzene singlet proton in the ligand **9** (δ 8.5 ppm) disappeared in the chloroplatinum complex **5a**; (2) the α-pyridyl methylene protons showed significant downfield shift and split into a ABX pattern (**9**: δ 3.21 ppm, doublet, $J = 2.7$ Hz; **5a**: δ 4.30 and 4.12 ppm, AB system only, $J_{AB} = 19.3$ Hz, $\Delta\nu = 0.18$ Hz). These two changes clearly show the formation of a metal pincer complex. The formation of triflate analogue **6a/7a** from the chloro complex **5a** was also indicated by an upfield chemical shift of the α-pyridyl methylene protons: (**6a/7a**: δ 3.72 and 3.57 ppm, AB system only, $J_{AB} = 18.9$ Hz, $\Delta\nu = 0.16$ Hz), owing to a change in the chemical environment near the methylene protons [25]. Also, the ^{1}H NMR spectrum of the triflate analogue showed a water peak at 1.84 ppm, which is not observed in the case of the chloro complex **5a**, indicating that the aqua complex **7a** forms in this case. The corresponding palladium complex **5b** also showed a similar spectral change compared to that of the ligand **9**, indicating the formation of metal pincer complex.



Scheme 2. Synthesis of metal pincer complexes **5** and **6a/7a**.

Of particular note is that the unusual down field shifts ($\Delta\delta = 0.9$–1.0 ppm) of the α-pyridyl methylene protons in **5a** (H17a, H17b; H25a, H25b in the crystal structure) compared to those in the ligand **9**. Such a large downfield shift is not likely due to an inductive effect from the metal which is four-bond away from the hydrogens. The unusual downfield shift of the CH_2 protons can only be explained by evoking the presence of C–H···Cl hydrogen bonding between the chloride and the methylene protons in solution.

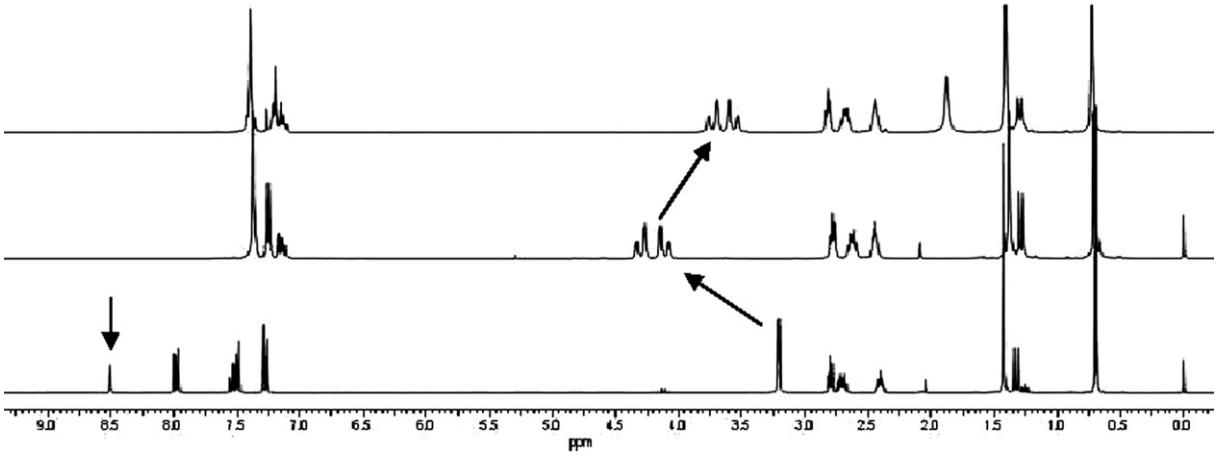


Fig. 1. ^{1}H NMR spectra of the ligand **9** and Pt(II) pincer complexes **5a** and **6a/7a** (from the bottom).

The existence of C–H···Cl hydrogen bonding has been supported by a number of crystal structures. Attractive hydrogen bonding interactions, particularly C–H···Cl^- and C–H···Cl–M (M: metal), have been identified by crystal structures of salt-like and covalently bound complexes [26–29]. Most of these examples are, however, based on solid structures, and to date only two examples including our recent report are known in which the hydrogen bonding has been identified both in the solid and solution states [30,31]. The magnitude of the chemical shift (0.9–1.0 ppm) due to the C–H···Cl hydrogen bonding in the present system is the largest value so far observed, compared to that of our recent report (0.7 ppm) and that of literature (0.11 ppm). The existence of C–H···Cl hydrogen bonding in the pincer complexes was further supported by an X-ray structure analysis for the chloroplatinum complex **5a**, as described below.

X-Crystallography. The structure of the chloroplatinum(II) complex **5a** was further confirmed by a single-crystal X-ray analysis, and the refinement data are given in Table 1. The selected bond angles, bond lengths, and data of hydrogen bonding interactions are given in Table 2. Single crystals suitable for diffraction were obtained by slow evaporation of the solvents, dichloromethane and hexane.

Table 1
Crystal data and structure refinement of the chloroplatinum(II) complex **5a**

Empirical formula	$C_{30}H_{31}ClN_2Pt$
Formula weight	650.11
Temperature (K)	243(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*P*2(1)2(1)2(1)
Unit cell dimensions	
a(Å)	10.2028(6)
b(Å)	14.1841(9)
c(Å)	17.5880(11)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	2545.3(3)
Z	4
Density (calculated) (Mg/m^3)	1.697
Absorption coefficient (mm^{-1})	5.639
F (000)	1280
Crystal size (mm^3)	$0.56 \times 0.32 \times 0.26$
θ Range for data collection (°)	1.84–23.25
Index ranges	$-11 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 15$, $-19 \leqslant l \leqslant 19$
Reflections collected	11 488
Independent reflections	3656 [$R_{int} = 0.0238$]
Completeness to theta = 23.25°	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3656/0/311
Goodness-of-fit on F^2	1.036
Final *R* indices [$I > 2$sigma(I)]	$R1 = 0.0252$, $wR_2 = 0.0647$
R indices (all data)	$R1 = 0.0255$, $wR_2 = 0.0648$
Absolute structure parameter	0.00
Largest difference in peak and hole ($e\,Å^{-3}$)	0.570 and −0.343

Table 2
Selected bond angles, bond lengths and structure data of hydrogen bonding interactions in the chloroplatinum(II) complex **5a**

Bond lengths (Å)		Bond angles (°)	
Pt–C(6)	1.921(7)	C(6)–Pt–N(1)	80.0(3)
Pt–N(1)	2.102(6)	C(6)–Pt–N(2)	80.1(3)
Pt–N(2)	2.095(5)	N(1)–Pt–N(2)	159.0(2)
Pt–Cl(1)	2.427(17)	C(6)–Pt–Cl(1)	160.5(2)
N(1)–C(1)	1.347(9)	N(1)–Pt–Cl(1)	100.25(17)
N(1)–C(5)	1.375(9)	N(2)–Pt–Cl(1)	100.77(15)
N(2)–C(12)	1.398(9)		
N(2)–C(16)	1.356(9)		
C(6)–C(7)	1.388(11)		
C(6)–C(11)	1.384(10)		
C–H···Cl	C–H	H···Cl	Cl···C
C(17)–H(17B)···Cl	0.98	2.56	3.1711
C(25)–H(25A)···Cl	0.98	2.37	3.1529

An ORTEP view of complex **5a** shows clearly that the chiral NCN pincer ligand is coordinated to the Pt(II) center via two pyridyl nitrogens and one aryl carbon in a tridentate fashion (Fig. 2). The Pt(II) center adopts a distorted square-planar configuration with bond angles and distances for the metal coordination sphere similar to those reported in the literature [19,20]. A further structural analysis for the bond distances between Cl(1) and methylene protons (H17, H25) shows that the hydrogen bonding is apparent between Cl(1) and two $H17_{endo}$ and $H25_{exo}$ hydrogens. In the case of other hydrogens, $H17_{exd}$ and $H25_{endo}$, rather longer distances from the Cl(1) are observed. Initially, we were curious about the tilted chloride ligand, which is 10.9° out of the metal coordination plane. It is clear that the distinct hydrogen bond in the solid state cause the chloride out of the metal coordination plane. In other words, C–H···Cl hydrogen bonding can cause the distortion of normal coordination bonds in the solid state. In the solution, however, the conformational change involving the hydrogen bond interactions should be faster than the NMR time scale, and thus no discrimination between the methylene protons is observed.

3.2. Asymmetric catalysis

As mentioned above, Pt(II)/Pd(II) pincer complexes are interesting due to their potential catalytic activity in organic reactions. We have used Pt(II) triflate complex **6a/7a** as asymmetric catalyst for the aldol reaction and silylcyanation of aldehydes. It has been observed that the complex shows higher reactivity in the catalytic reactions compared to that of chloride complex of **5a** and Pd(II) species. The aldol reaction was performed with a variety of aldehydes under various conditions. Optimization of the reaction conditions were carried out using benzaldehyde as the substrate and DIPEA or DBU as base (Table 3). The active catalystic species seems to be the corresponding aqua complex **7a**, which would readily form a vacant site for the binding of methyl isocyanoacetate. The *trans* isomers were major

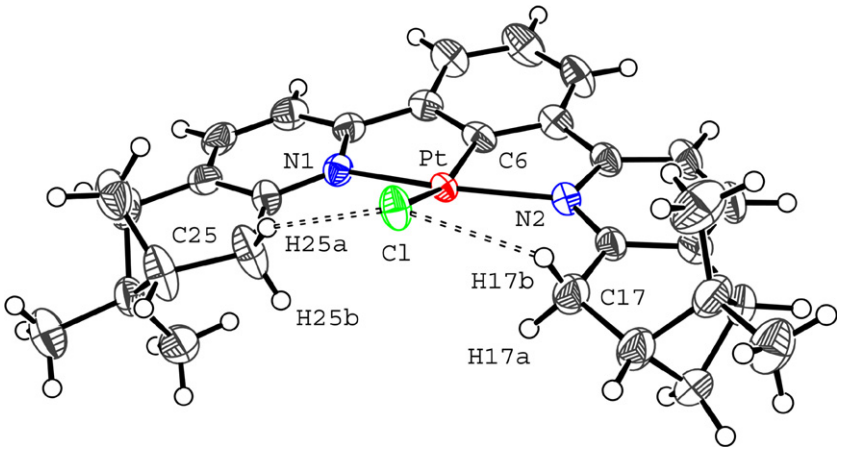
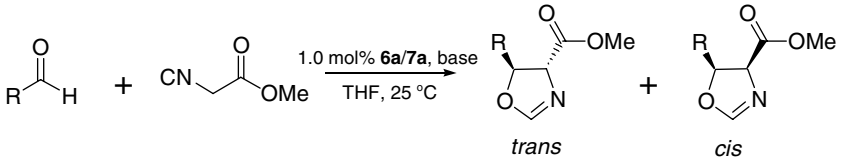


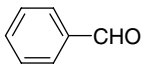
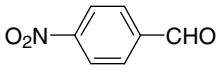
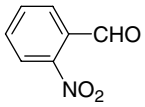
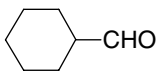
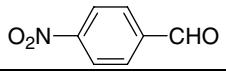
Fig. 2. An Ortep view of crystal structure of **5a**.

products for the aldehydes examined. The chiral Pt(II) pincer complex showed good conversions but with a low level of enantioselectivity for certain substrates. An explanation for the low enantioselectivity is not clear at the moment, but a possible reason may be found from the fact that the enolate derived from isocyanoacetate that is coordinated to the Pt center through isocyano carbon [32] is relatively away from the chiral pocket formed by the fused pyridines during the enantio-discriminating carbon–carbon bond formation stage.

Further, the catalytic efficiency of the Pt(II) pincer complex **6a**/**7a** in the silylcyanation of several aldehydes in presence of trimethylsilyl cyanide (TMSCN) has been evaluated [33]. There was no detectable cyanohydrin obtained in the presence of aldehyde with 1.2 equivalents of TMSCN only. However, under the same conditions in dichloromethane, addition of 1.0 mol% of complex **6a**/**7a** resulted in the clean formation of cyanohydrin after hydrolyzing the initially formed trimethylsilyl ether. It is notable that the reaction in dichloromethane gives better conversions than in toluene. Again, a low level of enantioselectivity was observed for some substrates (Table 4). Such types of pincer complexes seem to give low enantioselectivity in the examined reactions in general, compared to non-pincer type metal complexes known for the reactions. A further study to screen suitable reactions for such pincer metal complexes is necessary to fully address their catalytic efficiency.

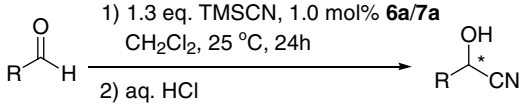
Table 3
Aldol reaction of methyl isocyanoacetate and aldehydes

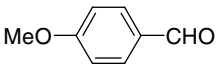
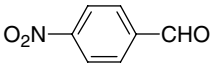
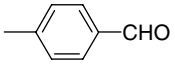
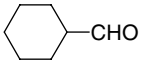
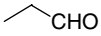


Entry	Aldehyde	Base	Reaction Time	Yield (%)	Er[a]	*Trans*/*Cis*
1		DBU	1 h	70	56:44	90/10
2		DIPEA	6 h	90	50:50	70/30
3		DIPEA	10 h	90	50:50	95/5
4		DBU	2 d	40	50:50	95/5
5		DBU	2 d	40	55:45	95/5

[a] Enantiomeric ratio determined by ^{1}H NMR integration of the methyl ester peak.

Table 4
Catalytic silylcyanation of aldehydes



Entry	Aldehyde	Conversion yield (%)[a]	Er[b]
1		64	52:48
2		9	50:50
3		57	57:43
4		62	50:50
5		98	58:42

[a] Determined by ^{1}H NMR analysis for the crude product using Eu(hfc)$_3$ as chiral shift agent.
[b] Conversion was determined by ^{1}H NMR analysis.

4. Conclusion

New Pt(II)/Pd(II) pincer complexes **5** and **6a/7a** have been synthesized from the chiral pincer ligand (5*R*,7*R*)-1,3-bis(6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)benzene **9** by direct cyclometalation using K_2PtCl_4/K_2PdCl_4 as the metal sources. Both the Pt(II) and Pd(II) complexes **5** show C–H···Cl hydrogen bonding in solution, being judged from ^{1}H NMR analysis. An X-ray crystal structure of the chloroplatinum(II) complex **5a** was resolved, which indicates the presence of a distorted square-planar geometry due to the C–H···Cl hydrogen bonding. The catalytic efficiency of the pincer complexes was evaluated by using **6a/7a** as catalysts in the asymmetric aldol and silylcyanation reactions, which shows reasonable conversions but with low to poor enantioselectivity. A further investigation on design and synthesis of new pincer ligands to improve the enantioselectivity is undergoing.

Acknowledgements

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Appendix A. Supplementary material

CCDC 615495 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] (a) M.C. Langunas, R.A. Gossage, W.J.J. Smeets, A.L. Speck, G. van Koten, Eur. J. Inorg. Chem. (1998) 163;
(b) M. Gerisch, J.R. Krumper, R.G. Bergmann, T.D. Tilley, J. Am. Chem. Soc. 123 (2001) 5818;
(c) J.S. Fossey, C.J. Richards, Organometallics 23 (2004) 367.
[2] (a) P. Steenwinkel, R.A. Gossage, G. van Koten, Chem. Eur. J. 4 (1998) 759;
(b) M. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750;
(c) G. Guillena, C.A. Kruithof, M.A. Casado, M.R. Egmond, G. van Koten, J. Organomet. Chem. 668 (2003) 3.
[3] (a) G. van Koten, K. Timmer, J.G. Noltes, A.L. Spek, J. Chem. Soc., Chem. Commun. (1978) 250;
(b) G. Guillena, G. Rodriguez, G. van Koten, Tetrahedron. Lett. 43 (2002) 3895.
[4] M.A. Stark, G. Jones, C.J. Richards, Organometallics 19 (2000) 1282.
[5] A.J. Canty, J. Patel, B.W. Skelton, A.H. White, J. Organomet. Chem. 607 (2000) 194.
[6] Y. Motoyama, Y. Mikami, H. Kawakami, K. Aoki, H. Nishiyama, Organometallics 18 (1999) 3584.
[7] T. Tsubomura, T. Tanihata, T. Yamakawa, R. Ohmi, T. Tamane, A. Higuchi, A. Kotoh, K. Sakai, Organomettalics 20 (2001) 3833.
[8] P. Steenwinkel, R.A. Gossage, T. Maunula, D.M. Grove, G. van Koten, Chem. Eur. J. 4 (1998) 763.
[9] A.D. Ryabov, Chem. Rev. 90 (1990) 403.
[10] G. van Koten, M. Albrecht, Angew. Chem., Int. Ed. 40 (2001) 3750.
[11] P. Steenwinkel, R.A. Gossage, G. van Koten, Chem. Eur. J. 4 (1998) 759.
[12] M.S. Yoon, D. Ryu, J. Kim, K.H. Ahn, Organometallics 25 (2006) 2409.
[13] G. van Koten, J.T.B.H. Jastrzebski, J. Mol. Catal. A. Chem. 146 (1999) 317.
[14] M. Ohff, A. Ohff, M.E. van der Boom, D. Milstein, J. Am. Chem. Soc. 119 (1997) 11687.
[15] R.B. Bedford, S.M. Draper, S.P. Noelle, S.L. Welch, New. J. Chem. 24 (2000) 745.
[16] M. Gupta, C. Hagen, R.J. Flesher, W.C. Kaska, C.M. Jensen, Chem. Commun. (1996) 2083.
[17] P. Dani, T. Karlen, R.A. Gossage, S. Gladiali, G. van Koten, Angew. Chem., Int. Ed. 39 (2000) 743.
[18] M. Albrecht, B.M. Kocks, A.L. Spek, G. van Koten, J. Organomet. Chem. 624 (2001) 271.
[19] X.-Q. Hao, J.-F. Gong, C.-X. Du, L.-Y. Wu, Y.-J. Wu, M-P. Song, Tetrahedron. Lett. 47 (2006) 5033.
[20] B. Soro, S. Stoccoro, G. Minghelti, A. Zucca, M.A. Cinellu, M. Manassero, S. Gladiali, Inorg. Chim. Acta 359 (2006) 1879, The enantiomeric complexes were synthesized starting from (*R*)-(+)-β-pinene, which is much more expensive than its enantiomer. Unfortunately, no optical rotation and ^{13}C NMR data for the enantiomeric metal complexes are given in the report.
[21] M. Ziegler, V. Monney, H. Stoekli-Evans, A. Von Zelewsky, I. Sasaki, G. Dupic, J.C. Daran, G.G.A. Galavoine, J. Chem. Soc. Dalton Trans. (1999) 667.
[22] G. Chelucci, A. Saba, D. Vignola, C. Solinas, Tetrahedron 51 (2001) 1099.
[23] E.D. Mihelich, D.J. Eickhoft, J. Org. Chem 48 (1983) 4135, Under this oxidation conditions, a side product of enal, instead of the enone, was formed as minor component, plausibly through the migration of double bond in the pinene, which gave the corresponding pincer

ligand along with the desired one. The minor side product could be removed by column chromatography.
[24] F. Kröhnke, Synthesis (1976) 1.
[25] Only the geminal couplings (J^2) are described. The vicinal couplings were relatively small ($J^3 \sim 3$ Hz) because the dihedral angles are in the range of $55 \sim 64°$.
[26] C.B. Aakeroy, T.A. Evans, K.R. Seddon, I. Palinko, New. J. Chem. (1999) 145.
[27] P.K. Thallapally, A. Nangia, Cryst. Eng. Commun. 27 (2001) 1.
[28] R. Taylor, O. Kennard, J. Am. Chem. Soc. 104 (1982) 5063.
[29] T. Spaniel, H. Görls, J. Scholz, Angew. Chem., Int. Ed. 37 (1998) 1862.
[30] J.C.M. Rivas, R.T. de Roseles, S. Parsons. Dalton Trans. (2003) 2156.
[31] Y.S. Kang, J.-H. Son, I.-C. Hwang, K.H. Ahn, Polyhedron 25 (2006) 3025.
[32] Y. Ito, M. Sawamura, T. Hayashi, J. Am. Chem. Soc. 108 (1986) 6405.
[33] For a recent review on asymmetric cyanohydrin formations, see M. North, Tetrahedron: Asymmetry. 14 (2003) 147.