DOI: 10.1002/ejic.200901142

Synthesis and Characterisation of a Novel Chiral Bidentate Pyridine-N-Heterocyclic Carbene-Based Palladacycle

Minyi Chiang,[a] Yongxin Li,[a] Deepa Krishnan,[a] Pullarkat Sumod,[a] Kim Hong Ng,[a] and Pak-Hing Leung*[a]

Keywords: Carbene ligands / Nitrogen heterocycles / Palladium / Optical resolution

A novel chiral six-membered bidentate pyridine-N-heterocyclic carbene palladacycle was prepared via optical resolution of the racemic palladacycle. This is the first successful demonstration of the synthesis of a chiral carbene palladacycle via fractional crystallization of its chiral amino acid derivatives. Upon formation of (R_C,S_C) and (S_C,S_C)-phenylalanate derivatives, the (R_C,S_C)-phenylalanate diastereomer crystallized out spontaneously. Optically active (*R*)- and (*S*)-dichloropalladacycles can then be achieved by subsequent cleavage of the chiral amino acid auxiliary in the presence of aqueous HCl from their respective diastereomers. The absolute configurations of both the (*R*)- and (*S*)-palladacycles were determined by X-ray diffraction studies.

Introduction

Following the isolation of the stable carbene in crystalline form by Arduengo in 1991,[1] the chemistry of *N*-heterocyclic carbenes (NHC) has experienced unprecedented development. The popularity of NHC can be attributed to the fact that both their electronic and steric properties can be easily modified like phosphane ligands which have been the ligand of choice in the field of organometallic catalysis. Unlike phosphane ligands, NHCs are mainly σ donors and weak π accepting ligands.[2] Due to the strong metal–NHC bond, NHC-based catalytic systems exhibit a high degree of stability against heat, moisture and air during the course of their synthetic applications. Therefore NHC have emerged as a promising functional analogue to phosphanes for the design of organometallic catalysts.[3]

Recently, several groups have focused their efforts in the development of hemilabile chelating NHC metallacycles[4] like the S, N and O functionalized NHC bidentate ligands. This trend can be attributed to the fact that through introduction of the rigidity of a bidentate system and the options of chirality on the chelate backbone, a more promising catalyst can be developed.[5] One of the most common variant is the palladium system and these palladium complexes have shown average to excellent *ee* values in a variety of asymmetric reactions.[6] Pyridine-NHC chelating ligands are a popular class of hemilabile ligands. These ligands are usually coordinated to the palladium centre in a bidentate[7] or a tridentate fashion[8] and display excellent catalytic ability in C–C coupling reactions. However, to the best of our knowledge, none of the above-mentioned pyridine-NHC palladacycles exhibited any chirality in the carbon chelate backbone.

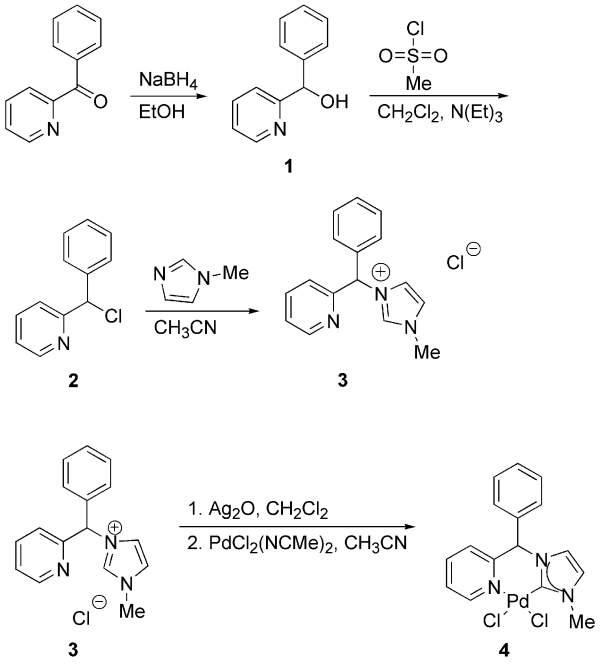
Realising that all the above-mentioned chiral palladium complexes were achieved via manipulation of chiral amines or other chiral starting materials and also due to the fact that a literature search yielded no results on any chiral bidentate pyridine-NHC palladacycle, we sought to achieve the synthesis of such a palladium system by the optical resolution of a racemic palladium complex via diastereomeric complex formation with chiral amino acids as the resolving agent, since this is a common method employed in the synthesis of palladacycles.[9] We envisaged that a more rigid chiral chelating system would be more effective in controlling the stereochemistry in an asymmetric reaction scenario. We hereby present the synthesis, resolution and characterisation of the first ever reported chiral NHC-pyridine palladium bidentate complex.

Results and Discussion

The synthesis of the new pyridine-functionalized imidazolium salt **3** was achieved by the initial reduction of the commercially available 2-benzoylpyridine followed by halogenation to give 2-[chloro(phenyl)methyl]pyridine. Subsequent reaction of 2-[chloro(phenyl)methyl]pyridine with 1-methylimidazole (Scheme 1) yielded the target imidazolium salt **3**. The imidazolium salt **3** was then subjected to the transmetalation method developed by Lin et al.[10] to give the racemic palladacycle complex (±)-**4**. The silver complex was generated in situ and its formation was confirmed by the absence of the characteristic imidazolium proton peak at δ = 10.15 in ^{1}H NMR spectroscopy. The crude silver

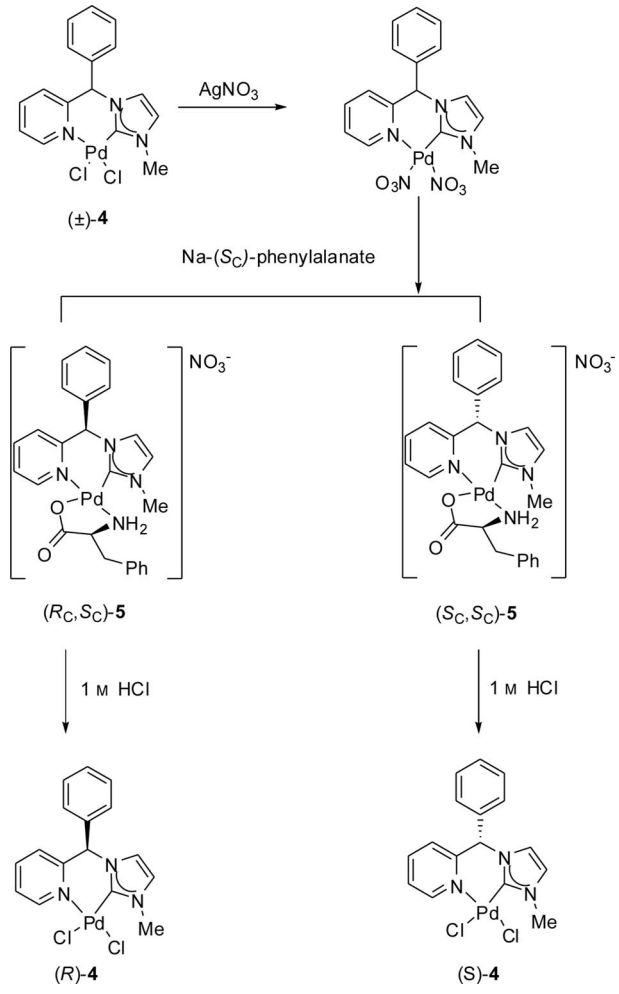
[a] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences,
Nanyang Technological University, 637371 Singapore
E-mail: pakhing@ntu.edu.sg

complex was filtered through a short plug of celite and was immediately subjected to the proceeding step to yield complex (±)-**4** as yellow solid (Scheme 1). X-ray crystallography grade single crystals of complex (±)-**4** can be obtained via slow diffusion of diethyl ether into a solution of complex (±)-**4** in methanol and dimethyl sulfoxide (DMSO). Racemic complex (±)-**4** can then be resolved via the formation of its diastereomeric derivatives with sodium-(S_C)-phenylalanate (Scheme 2). Complex (R_C,S_C)-**5** spontaneously crystallized out from the reaction mixture and was isolated as an off-white crystalline solid, leaving a (S_C,S_C)-**5**-enriched mother liquor. The diastereomeric derivatives were subsequently treated with aqueous 1 M HCl to give the optically active complexes (*R*)-**4** and (*S*)-**4** respectively.



Scheme 1.

The solubility of complex (±)-**4** posed as the main challenge in the course of the synthesis. Complex (±)-**4** was found to be insoluble in an array of organic solvents like CH_2Cl_2 and CH_3Cl; sparingly soluble in more polar solvents like tetrahydrofuran, acetonitrile and methanol; and was only completely soluble in DMSO. Due to the poor solubility of complex (±)-**4**, it is necessary to add a few drops of DMSO to the methanol solution to enable complex (±)-**4** to be completely soluble in the solvent. The X-ray diffraction study of complex (±)-**4** was performed (Figure 1) and the selected bond lengths and angles are provided in Table 1. The X-ray diffraction study of complex (±)-**4** showed that the six-membered ring is in the boat conformation, with the Ph ring in the axial position. The conformation of complex (±)-**4** in solution was determined by 2D ^{1}H-^{1}H ROESY NMR (Figure 2). The assignment of proton signals was made by a combination of COSY and HMQC. From the key correlations (A) and (B) observed in 2D ^{1}H-^{1}H ROESY NMR, namely between H5–H4 and H5–H13 (protons were numbered in accordance to the carbon numbers that they are directly attached to in Figure 1), it can be established that the six-membered ring remained locked in the boat conformation with no rotational conformers present in room temperature.



Scheme 2.

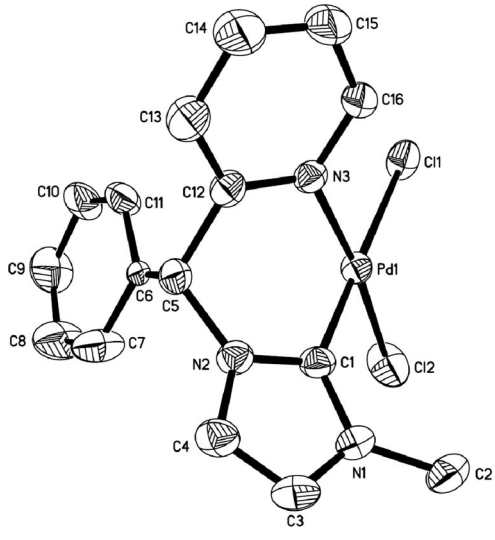


Figure 1. Molecular structure of complex (±)-**4**.

Table 1. Selected bond lengths selected bond lengths (Å) and angles (°) for racemic complex (±)-**4**.

Pd(1)–C(1)	1.951(3)	Pd(1)–N(3)	2.055(2)
Pd(1)–Cl(2)	2.310(7)	Pd(1)–Cl(1)	2.374(7)
C(1)–Pd(1)–N(3)	86.2(9)	C(1)–Pd(1)–Cl(2)	90.8(7)
N(3)–Pd(1)–Cl(2)	173.7(6)	C(1)–Pd(1)–Cl(1)	176.6(7)
N(3)–Pd(1)–Cl(1)	91.3(6)	Cl(2)–Pd(1)–Cl(1)	91.8(3)
N(1)–C(1)–Pd(1)	133.8(2)	N(2)–C(1)–Pd(1)	120.8(2)
C(16)–N(3)–Pd(1)	119.7(16)	C(12)–N(3)–Pd(1)	121.1(2)

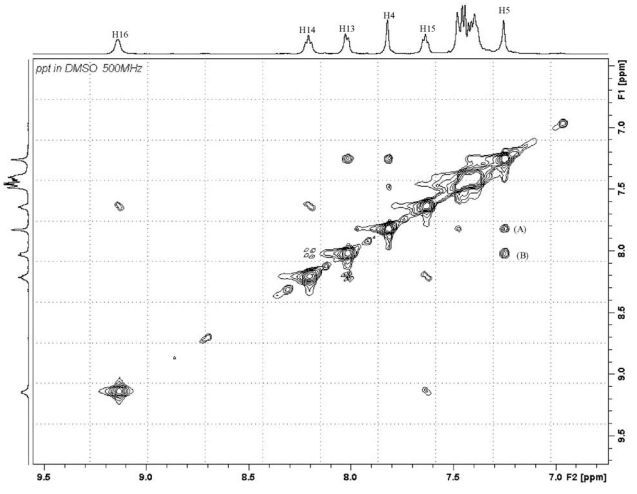


Figure 2. ROESY NMR of complex (±)-**4**.

After screening through a range of amino acid salts in different solvent systems, only sodium (S_C)-phenylalanate was found to be an effective resolving agent for the resolution of complex (±)-**4** in methanol. After the addition of 1 molar equivalent of sodium (S_C)-phenylalanate, the progress of the diastereomeric salt formation was monitored by ^{1}H NMR spectroscopy. The two resulting diastereomers could not be separated and kept crystallizing out together in several failed attempts at fractional crystallizations in different solvent system. The problem was circumnavigated by changing the counter anion present in the diastereomeric complexes. After switching the counter anion from chloride to nitrate, successful optical resolution of racemic complex (±)-**4** was achieved using sodium (S_C)-phenylalanate as the auxiliary ligand (Scheme 2). Sequential treatment of complex (±)-**4** with two molar equivalent of silver nitrate and one molar equivalent of sodium (S_C)-phenylalanate resulted in the formation of the expected 1:1 mixture of diastereomeric adducts (R_C,S_C)-**5** and (S_C,S_C)-**5** as evident from the presence of two distinct sets of proton resonances for each of the diastereomers. Fractional crystallization from methanol/diethyl ether afforded the less soluble diastereomer (R_C,S_C)-**5** in the form of off-white crystalline solid in 70% yield and > 99% *de* (according to the ^{1}H NMR spectrum) with $[a]_{436}$ = +83.3 (*c* = 0.5, DMSO). In [D_6]-DMSO, the 500-MHz ^{1}H NMR spectrum of complex (R_C,S_C)-**5** at room temperature presents itself as a sole geometric isomer in solution, which was indicated by the presence of a solitary set of resonance observed for each chemically nonequivalent proton.

Off white crystals of diastereomer (R_C,S_C)-**5** suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a methanol/DMSO solution of complex (R_C,S_C)-**5**. The molecular structure of diastereomer (R_C,S_C)-**5** is presented in Figure 3, selected bond lengths and bond angles are provided in Table 2. The X-ray crystallographic study revealed the *R* absolute configuration of the α-carbon stereocenter which was confirmed independently using (S_C)-phenylalanate as a reference point, as well as based on the anomalous X-ray scattering method with the Flack parameter of 0.003(18). The complex adopts a *trans*-(*N*,*N*) arrangement, with the α-phenyl group (C7–C12) occupying the axial position. The tetrahedral distortion of the palladium coordination environment is minimal, with an angle of 5.5° between the {Pd(1)–C(16)–N(1)} and {Pd(1)–N(4)–O(1)} planes.

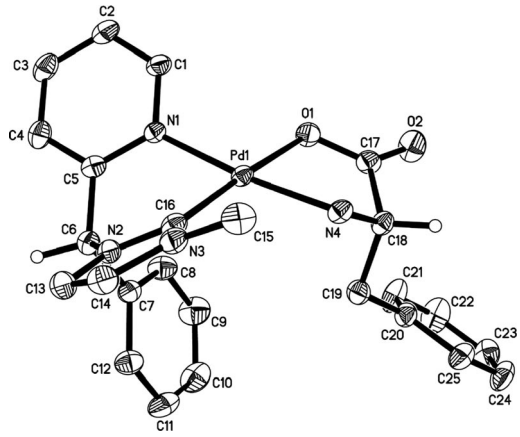


Figure 3. Molecular structure of complex (R_C,S_C)-**5**.

Table 2. Selected bond lengths (Å) and angles (°) for complex (R_C,S_C)-**5**.

Pd(1)–C(16)	1.960(4)	Pd(1)–N(1)	2.027(3)
Pd(1)–N(4)	2.028(3)	Pd(1)–O(1)	2.057(3)
C(16)–Pd(1)–N(1)	86.44(9)	C(16)–Pd(1)–N(4)	99.01(17)
N(1)–Pd(1)–N(4)	173.5(1)	C(16)–Pd(1)–O(1)	176.3(2)
N(1)–Pd(1)–O(1)	94.3(1)	N(4)–Pd(1)–O(1)	80.5(6)
N(2)–C(16)–Pd(1)	120.8(3)	N(3)–C(16)–Pd(1)	133.3(3)
C(1)–N(1)–Pd(1)	118.0(2)	C(5)–N(1)–Pd(1)	123.9(2)

Slow diffusion of diethyl ether into a methanol solution of the resulting diastereomer (S_C,S_C)-**5**-enriched mother liquid allowed all of the remaining diastereomer (R_C,S_C)-**5** to crystallize out. The resulting mother liquor comprised almost entirely of the other diastereomer (S_C,S_C)-**5** > 99% *de* (according to the ^{1}H NMR spectrum) with $[a]_{436}$ = +42.1 (*c* = 0.5, MeOH). Diastereomer (S_C,S_C)-**5** was subsequently isolated as a light yellow colored solid in 67% yield. Compared to (R_C,S_C)-**5**, (S_C,S_C)-**5** displayed far superior solubility in an array of solvents. Therefore, efforts to obtain X-ray grade crystals of (S_C,S_C)-**5** were unsuccessful. However, as demonstrated below, an optically pure complex can be obtained from the mother liquor (> 99% *de*) by the cleavage of the chiral auxiliary phenylalanate ligand thereby leading to the formation of the single crystals of the chiral complex (*S*)-**4**.

The optically active dichloro complex (*R*)-**4** was obtained by mixing a methanol solution of complex (R_C,S_C)-**5** with 1 M HCl and was isolated as a yellow powder in 51% yield with $[\alpha]_{436}$ = –12.5 (*c* = 0.5, DMSO) (Scheme 2). Yellow single crystals suitable for X-ray crystallography were obtained from a solution of (*R*)-**5** in methanol, DMSO and diethyl ether and its molecular structure is depicted in Figure 4. The selected bond lengths and angles are listed in Table 3. The X-ray crystallographic study confirmed the expected *R* absolute configuration of the α-phenyl stereocenter of the palladacycle. The coordination sphere of the palladium center is in a distorted square-planar geometry, with tetrahedral distortions of 1.5°.

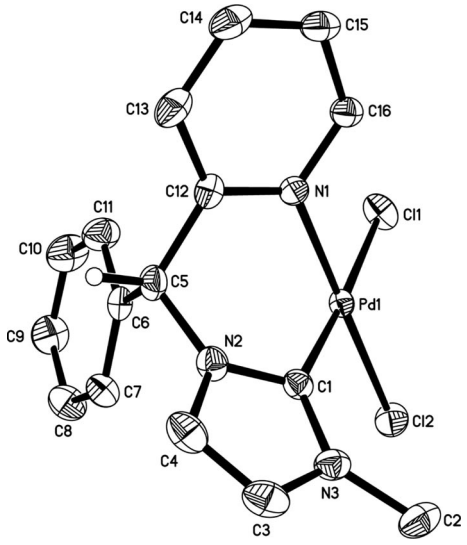


Figure 4. Molecular structure of complex (*R*)-**4**.

Table 3. Selected bond lengths (Å) and angles (°) for complex (R_C)-**4**.

Pd(1)–C(1)	1.980(2)	Pd(1)–N(1)	2.045(2)
Pd(1)–Cl(2)	2.292(5)	Pd(1)–Cl(1)	2.356(5)
C(1)–Pd(1)–N(1)	87.0(7)	C(1)–Pd(1)–Cl(2)	92.7(6)
N(1)–Pd(1)–Cl(2)	179.5(5)	C(1)–Pd(1)–Cl(1)	176.4(6)
N(1)–Pd(1)–Cl(1)	89.9(5)	Cl(2)–Pd(1)–Cl(1)	90.5(2)
N(3)–C(1)–Pd(1)	136.1(2)	N(2)–C(1)–Pd(1)	118.9(1)
C(16)–N(1)–Pd(1)	118.7(1)	C(12)–N(1)–Pd(1)	121.7(1)

The enantiomerically pure palladacycle (*S*)-**4** was prepared from complex (S_C,S_C)-**5** in a similar manner: $[\alpha]_{436}$ = +11.8 (*c* = 0.5, DMSO) (Scheme 2). Yellow colored single crystals were obtained from a methanol, DMSO and diethyl ether solution of complex (*S*)-**4**. The solid-state structure of the complex (*S*)-**4** was determined by X-ray crystallography (refer to Figure 5). Selected bond lengths and angles are listed in Table 4. The X-ray crystallographic study confirmed the *S* absolute configuration of the α-phenyl stereocenter of the palladacycle. The Pd center experienced a slight tetrahedral distortion and the dihedral angle between the {N(1)–Pd(1)–C(1)} and {Cl(1)–Pd(1)–Cl(2)} planes was 1.9°.

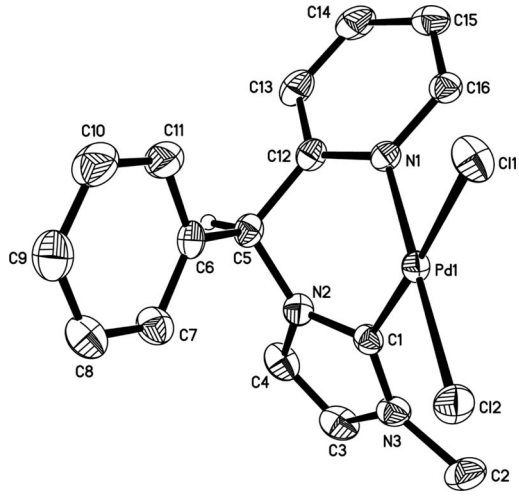


Figure 5. Molecular structure of complex (*S*)-**4**.

Table 4. Selected bond lengths (Å) and angles (°) for complex (S_C)-**4**.

Pd(1)–C(1)	1.984(2)	Pd(1)–N(1)	2.045(2)
Pd(1)–Cl(2)	2.292(5)	Pd(1)–Cl(1)	2.357(5)
C(1)–Pd(1)–N(1)	86.9(8)	C(1)–Pd(1)–Cl(2)	92.8(6)
N(1)–Pd(1)–Cl(2)	179.6(5)	C(1)–Pd(1)–Cl(1)	176.2(6)
N(1)–Pd(1)–Cl(1)	89.9(5)	Cl(2)–Pd(1)–Cl(1)	90.5(2)
N(3)–C(1)–Pd(1)	135.9(2)	N(2)–C(1)–Pd(1)	118.9(1)
C(12)–N(1)–Pd(1)	121.7(1)	C(16)–N(1)–Pd(1)	118.9(1)

Conclusions

In this paper, we have successfully demonstrated the viability of synthesizing novel chiral bidentate NHC-based palladacycles via efficient optical resolution of its diastereomeric salts. Resolution of other hemilabile palladacycles and catalytic applications of the synthesized chiral palladacycles are currently in progress.

Experimental Section

General: Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen using standard Schlenk techniques. All the commercially available chemicals and solvents were used without prior drying or purification. Phenyl(pyridin-2-yl)methanol[11] **1** and $PdCl_2(NCMe)_2$[12] were prepared according to literature methods. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on a Bruker Avance 300, 400 and 500 NMR spectrometers. Multiplicities were given as: s (singlet); b (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); m (multiplets) and etc. The number of protons (*n*) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Nuclear magnetic resonance spectra (^{1}H NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ = 0.0 ppm), relative to the signal of [D]chloroform (δ = 77.20, triplet) (^{13}C NMR). Phase-sensitive ROESY spectra were obtained with a Bruker AMX-500 spectrometer and were acquired into a 1024X512 matrix with a 250 ms spin lock time and a spin lock field strength such that $\gamma B1/2\pi$ = 5000 Hz and then transformed into 1024 × 1024 points by using a sine bell

weighting function in both dimensions. Mass spectra were recorded on a Thermo Finnigan MAT 95 XP Mass Spectrometer with EI mode and Waters Q-Tof Premimer Mass Spectrometer with ESI mode. Melting points were determined on SRS-Optimelt MPA-100 apparatus and were uncorrected. Optical rotations were measured on the specified solution in 0.1-dm cell at 25 °C with a Perkin–Elmer model 341 polarimeter. The Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at the Nanyang Technological University of Singapore performed elemental analyses.

2-[Chloro(phenyl)methyl]pyridine (2): Phenyl(pyridin-2-yl)methanol (**1**) (1.85 g, 10.5 mmol) and triethylamine (3.4 mL, 24.4 mmol) in 32 mL of dichloromethane was stirred in an ice bath. Methanesulfonyl chloride (1.2 mL, 15.8 mmol) was added dropwise to the stirring solution. The reaction mixture was allowed to warm up slowly to room temperature. The reaction mixture was left to stir overnight and was then poured into a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with chloroform. The combined organic layers were washed with H_2O, dried with anhydrous $MgSO_4$ and the solvents evaporated in vacuo to give a red liquid. The resultant red liquid was subjected to flash column chromatography (ethyl acetate/hexanes = 1:4, v/v) to give a yellow oil 1.7 g, 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.17 (s, 1 H, ClC*H*), 7.19–7.22 (m, 1 H, arom. H), 7.26–7.36 (m, 3 H, arom. H), 7.47–7.56 (m, 3 H, arom. H), 7.69–7.72 (m, 1 H, arom. H), 8.57–8.58 [d, *J*(H,H) = 4.0 Hz, 1 H, arom. H] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 64.58 (C-Cl), 122.11, 122.85, 127.81, 128.31, 128.67, 137.0, 139.96, 149.21, 159.71 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd. for $C_{12}H_{10}ClN$ 204.0580, found 204.0585.

1-Methyl-3-[phenyl(pyridin-2-yl)methyl]-1*H*-imidazolium Chloride (3): 1-Methylimidazole (1.8 mL, 22.6 mmol) was added to a stirring solution of compound **2** (4.35g, 21.3 mmol) in 50 mL of CH_3CN. The reaction mixture was heated at refluxing temperature for 48 h. The reaction mixture was reduced in vacuo and the resulting oil was stirred in diethyl ether. The diethyl ether layer was decanted to give a pink oil 4.3 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.01 (s, 3 H, CH_3), 7.25–7.34 (m, 4 H, arom. H), 7.41–7.43 (m, 2 H, arom. H), 7.52 (s, 1 H, arom. H), 7.61–7.64 (m, 2 H, arom. H), 7.68–7.72 (m, 2 H, arom. H), 8.57 (d, $J_{H,H}$ = 4.5 Hz, 1 H, arom. H), 10.15 (s, 1 H, carbenic proton) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.74 (N-CH_3), 66.06 (N-C-Ph), 121.90, 122.87, 123.95, 124.71, 129.07, 129.42, 129.56, 136.54, 137.82, 138.63, 149.60, 155.18 ppm. HRMS (ESI) *m*/*z*: $[M - Cl]^+$ calcd. for $C_{16}H_{16}N_3$ 250.1344, found 250.1345.

Racemic [Pd{1-methyl-3-{phenyl(pyridin-2-yl)methyl}-1*H*-imidazolin-2-ylideneCl$_2$}] (–)-4 and (+)-(4): To a solution of compound **3** (3.57g, 12.5 mmol) in 30 mL of dichloromethane, Ag_2O (1.59g, 6.9 mmol) was added in the dark. The reaction mixture was allowed to stir at room temperature for 12 hours and was filtered through celite. A $PdCl_2(NCMe)_2$ suspension (3.24g, 12.5 mmol in 100 mL of CH_3CN) was added to the filtrate in the dark. The reaction mixture was then allowed to stir overnight at room temperature and was filtered through a short plug of celite the next day. The filtrate was reduced in vacuo to approximately 50 mL and diethyl ether (200 mL) was added which resulted in the precipitation of an orange-yellow solid 3.3 g, 61%; m.p. 249.2–249.8 °C (dec.). ^{1}H NMR (400 MHz, DMSO): δ = 3.97 (s, 3 H, CH_3), 7.33–7.47 (m, 6 H, arom. H), 7.62 (t, 1 H, arom. H), 7.84 (s, 1 H, arom. H), 8.02 (d, $J_{H,H}$ = 7.6 Hz, 1 H, arom. H), 8.20 (t, 1 H, arom. H), 9.12 (d, $J_{H,H}$ = 5.6 Hz, 1 H, arom. H) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 37.86 (N-CH_3), 66.46 (N-C-Ph), 122.41, 124.11, 125.10, 126.34, 126.98, 128.29, 128.78, 138.19, 140.45, 150.37, 154.60, 155.10 ppm. $C_{16}H_{16}Cl_2N_3Pd{\cdot}C_4H_{10}O$ (501.77): calcd. C 47.87, H 5.22, N 8.37; found C 48.06, H 5.69, N 8.38.

Optical Resolution of the Racemic Complex 4: To a suspension of the racemic complex (2.45g, 5.7 mmol) in 20 mL of methanol, $AgNO_3$ (1.94 g, 11.4 mmol) was added. The reaction mixture was allowed to stir in the dark at room temperature for 3 h and was filtered through celite. The filtrate was treated with sodium (S_C)-phenylalanate (1.07 g, 5.7 mmol) in 100 mL of methanol. The reaction mixture was stirred for 2 h and was concentrated to approximately 50 mL and was left to stand overnight. Complex (R_C,S_C)-**5** which precipitated out as off-white crystals the next day was isolated and washed with methanol.

Diastereomer (R_C,S_C)-5: 1.2 g, 35%, $[\alpha]_{436}$ = +83.3 (*c* = 0.5, DMSO); m.p. 189.5–190.2 °C (dec.). ^{1}H NMR (500 MHz, DMSO): δ = 2.61–2.65 (m, 1 H), 3.16 (d, $J_{H,H}$ = 5.2 Hz, 1 H), 3.50–3.52 (m, 1 H), 3.82 (s, 3 H, CH_3), 5.00 (d, $J_{H,H}$ = 9.6 Hz, 1 H), 5.98–6.01 (m, 1 H), 6.94 (s, 1 H, arom. H), 6.96 (s, 1 H, arom. H), 7.15–7.23 (m, 5 H, arom. H), 7.35–7.38 (m, 2 H, arom. H), 7.47–7.50 (m, 2 H, arom. H), 7.59 (d, $J_{H,H}$ = 1.8 Hz, 1 H, arom. H), 7.76–7.79 (m, 1 H, arom. H), 7.90 (d, $J_{H,H}$ = 1.8 Hz, 1 H, arom. H), 8.16 (d, $J_{H,H}$ = 7.8 Hz, 1 H, arom. H), 8.33–8.36 (m, 1 H, arom. H), 8.71 (d, $J_{H,H}$ = 4.7 Hz, 1 H, arom. H) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 37.26, 49.06, 62.71, 66.34, 123.58, 124.62, 126.61, 126.79, 127.08, 127.65, 128.55, 128.91, 129.29, 129.57, 129.78, 137.35, 139.71, 142.10, 151.70, 153.07, 154.77, 179.24 ppm. $C_{25}H_{25}N_5O_5Pd$ (581.09): calcd. C 51.60, H 4.33, N 12.03; found C 50.44, H 4.33, N 12.05.

The mother liquor is enriched with the other diastereomer (S_C,S_C)-**5**.

Diastereomer (S_C,S_C)-5: 1.1 g, 34%. $[\alpha]_{436}$ = +42.1 (*c* = 0.5, MeOH); m.p. 189–190 °C (dec.). ^{1}H NMR (400 MHz, MeOD): δ = 2.56 (s, 2 H, CH_2), 2.80–2.86 (m, 1 H), 3.13–3.17 (m, 1 H), 3.27–3.29 (m, 1 H), 3.65 (s, 3 H, CH_3), 7.07 (s, 1 H, arom. H), 7.09–7.33 (m, 11 H, arom. H), 7.56–7.59 (m, 1 H, arom. H), 7.68 (d, $J_{H,H}$ = 7.7 Hz, 1 H, arom. H), 8.14–8.18 (m, 1 H, arom. H), 8.70 (d, $J_{H,H}$ = 5.5 Hz, 1 H, arom. H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 37.49, 40.62, 41.30, 63.24, 68.62, 124.35, 125.50, 127.27, 128.13, 128.21, 128.27, 130.03, 130.42, 130.67, 138.36, 140.43, 142.90, 154.12, 156.39, 181.86 ppm. HRMS (ESI) *m*/*z*: $[M–NO_3]^+$ calcd. for $C_{25}H_{25}N_4O_2{}^{106}Pd$ 519.1012, found 519.1013.

[Pd{1-methyl-3-{phenyl(pyridin-2-yl)methyl}-1*H*-(N-CH_3)imidazolin-2-ylideneCl$_2$}] {(*R*)-4}: To a suspension of complex (R_C,S_C)-**5** (0.50g, 0.86 mmol) in 50 mL of methanol, 1 M HCl (aq) (4.3 mL, 4.3 mmol) was added. The reaction mixture was stirred vigorously for approximately 1 hour and was concentrated down to give an orange yellow solid. The solid was washed three times with copious amount of methanol to give a pale yellow solid 0.2 g, 51%, $[\alpha]_{436}$ = –12.5 (*c* = 0.5, DMSO).

Similarly, complex (*S*)-**4** was achieved using the same method from complex (S_C, S_C)-**5** 0.2 g, 50%. $[\alpha]_{436}$ = +11.8 (*c* = 0.5, DMSO).

Crystal Structure Determinations of (±)-4, (R_C,S_C)-5, (*R*)-4, and (*S*)-4: Crystal data for all 4 complexes and a summary of the crystallographic analyses are given in Table 5. Diffraction data were collected on a Bruker X8 CCD diffractometer with Mo-K_α radiation (graphite monochromator). SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter.[13]

Table 5. Crystallographic data for complexes (±)-**4**, (R_C,S_C)-**5**, (*Rc*)-**4** and (*Sc*)-**4**.

	(±)-**4**	(R_C,S_C)-**5**	(*Rc*)-**4**	(*Sc*)-**4**
Formula	$C_{16}H_{15}Cl_2N_3Pd$	$C_{25}H_{25}N_5O_5Pd$	$C_{16}H_{15}Cl_2N_3Pd$	$C_{16}H_{15}Cl_2N_3Pd$
Formula weight	426.61	581.90	426.61	426.61
Space group	*Pbca*	*P*2(1)	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic
a /Å	12.1801(5)	9.3999(4)	9.7816(3)	9.7843(5)
b /Å	15.4613(7)	10.6789(4)	12.7776(3)	12.7883(6)
c /Å	17.8198(7)	11.9827(5)	13.0825(4)	13.0945(6)
V /Å^3	3355.8(2)	1182.87(8)	1635.12(8)	1638.44(14)
Z	8	2	4	4
T /K	223(2)	173(2)	173(2)	173(2)
$\rho_{calcd.}$ /g cm^{-3}	1.689	1.634	1.733	1.729
λ /Å	0.71073	0.71073	0.71073	0.71073
μ /mm^{-1}	1.423	0.832	1.460	1.457
Flack parameter		0.003(18)	–0.01(2)	–0.008(19)
R_1(obsd. data)[a]	0.0393	0.0265	0.0290	0.0234
wR_2(obsd. data)[b]	0.0821	0.0711	0.0741	0.0497

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F^2_o - F^2_c)^2]\}/\Sigma[w(F^2_o)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

CCDC-755570 (for (±)-**4**), -755571 (for (R_C,S_C)-**5**), -755572 (for (*R*)-**4**), -755573 (for (*S*)-**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[2] a) N. Fröhlich, U. Pidun, M. Stahl, G. Frenking, *Organometallics* **1997**, *16*, 442–448; b) H. Jacobsen, A. Correa, C. Costabile, L. Cavallo, *J. Organomet. Chem.* **2006**, *691*, 4350–4358; c) S. Díez-González, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874–883; d) S. Fantasia, J. L. Petersen, H. Jacobsen, L. Cavallo, S. P. Nolan, *Organometallics* **2007**, *26*, 5880–5889; e) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.

[3] V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619–636.

[4] a) W. A. Herrmann, L. J. Goossen, M. Spiegler, *Organometallics* **1998**, *17*, 2162–2168; b) J. J. V. Veldhuizen, S. B. Garber, J. S. Kingsbury, A. H. Hoveyda, *J. Am. Chem. Soc.* **2002**, *124*, 4954–4955; c) H. Seo, H. Park, B. Y. Kim, J. H. Lee, S. U. Son, Y. K. Chung, *Organometallics* **2003**, *22*, 618–620; d) K. Vladimir, D. Dioumaev, J. Szalda, J. Hanson, J. A. Franz, R. M. Bullock, *Chem. Commun.* **2003**, *14*, 1670–1671; e) S. Gischig, A. Togni, *Organometallics* **2004**, *23*, 2479–2487; f) L. G. Bonnet, R. Hodgson, J. Houghton, B. M. Kariuki, S. Simonovic, R. E. Douthwaite, *Dalton Trans.* **2004**, *21*, 3528–3535; g) M. Frøseth, K. A. Netland, K. W. Törnroos, A. Dhindsa, M. Tilset, *Dalton Trans.* **2005**, *9*, 1664–1674; h) E. Mas-Marzá, M. Sanaú, E. Peris, *Inorg. Chem.* **2005**, *44*, 9961–9967; i) C. H. Yeo, G. K. Tan, H. V. Huynh, *Chem. Commun.* **2006**, *36*, 3833–3835; j) C. Y. Liao, K. T. Chan, J. Y. Zeng, C. H. Hu, C. Y. Tu, H. M. Lee, *Organometallics* **2007**, *26*, 1692–1702; k) P. Y. Cheng, C. C. Lee, H. M. Lee, *Curr. Org. Chem.* **2007**, *11*, 1491–1524; l) O. Kaufhold, F. E. Hahn, T. Pape, A. Hepp, *J. Organomet. Chem.* **2008**, *693*, 3435–3440; m) D. Meyer, M. A. Taige, A. Zeller, K. Hohlfeld, S. Ahrens, T. Strassner, *Organometallics* **2009**, *28*, 2142–2149; n) C. Fliedel, G. Schnee, P. Braunstein, *Dalton Trans.* **2009**, *14*, 2474–2476; o) R. Corberán, E. Mas-Marzá, E. Peris, *Eur. J. Inorg. Chem.* **2009**, *13*, 1700–1716.

[5] O. Kühl, *Chem. Soc. Rev.* **2007**, *36*, 592–607.

[6] a) M. Jøgensen, S. Lee, X. Liu, J. P. Wolkowski, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 12557–12565; b) L. G. Bonnet, B. M. Kariuki, R. E. Douthwaite, *Organometallics* **2003**, *22*, 4187–4189; c) Y. Sato, T. Yoshino, M. Mori, *Org. Lett.* **2003**, *5*, 31–33; d) T. M. Seidal, Y. Jia, G. Bernardinelli, E. P. Kündig, *Angew. Chem. Int. Ed.* **2007**, *46*, 8484–8487; e) R. E. Douthwaite, *Coord. Chem. Rev.* **2007**, *251*, 702–717; f) A. Flahaut, P. Mangeney, S. Roland, *Tetrahedron: Asymmetry* **2007**, *18*, 229–236; g) Y. Jia, J. M. Hillgren, E. L. Watson, S. P. Marsden, E. P. Kündig, *Chem. Commun.* **2008**, *34*, 4040–4042; h) X. Liang, Y. Shi, *J. Org. Chem.* **2008**, *73*, 749–751; i) J. Dupont, M. Pfeffer, *Palladacycles: Synthesis characterization and applications*, Weinheim, Wiley-VCH, **2008**, p. 209; j) M. C. Jahnke, T. Pape, F. E. Hahn, *Eur. J. Inorg. Chem.* **2009**, *13*, 1960–1969.

[7] a) D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748; b) J. C. C. Chen, I. J. B. Lin, *Organometallics* **2000**, *19*, 5113–5121; c) A. A. D. Tolloch, A. A. Danopoulos, S. M. Cafferkey, S. Kleinhenz, M. B. Hursthouse, R. P. Tooze, *Chem. Commun.* **2000**, *14*, 1247–1248; d) A. A. D. Tulloch, S. Winston, A. A. Danopoulos, G. Eastham, M. B. Hursthouse, *Dalton Trans.* **2003**, *4*, 699–708; e) C. Y. Wang, Y. H. Liu, S. M. Peng, J. T. Chen, S. T. Liu, *J. Organomet. Chem.* **2007**, *692*, 3976–3983; f) A. A. Danopoulos, N. Tsoureas, S. A. Macgregor, C. Smith, *Organometallics* **2007**, *26*, 253–263; g) J. Jarusiewicz, K. S. Yoo, K. W. Jung, *Synlett* **2009**, *3*, 482–486.

[8] a) S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller, R. H. Crabtree, *Organometallics* **2001**, *20*, 5485–5488; b) J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 700–706; c) A. A. Danopoulos, A. A. Tulloch, A. D. Arran, S. Winston, G. Eastham, M. B. Hursthouse, *Dalton Trans.* **2003**, *5*, 1009–1015; d) F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, P. Morales-Morales, T. Pape, *Organometallics* **2005**, *24*, 6458–6463; e) D. J. Nielson, K. J. Cavell, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2006**, *359*, 1855–1869; f) D. Pugh, A. A. Danopoulos, *Coord. Chem. Rev.* **2007**, *251*, 610–641.

[9] a) V. V. Dunina, O. N. Gorunova, G. Kuz′mina, M. V. Livantsov, Y. K. Grishnin, *Tetrahedron: Asymmetry* **1999**, *10*, 3951–3961; b) J. K.-P. Ng, S. Chen, Y. Li, G.-K. Tan, L.-L. Koh, P.-H. Leung, *Inorg. Chem.* **2005**, *44*, 9874–9886.

[10] H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972–975.

[11] T. Kawano, M. Kurimoto, U. Hanatanaka, I. Ueda, *Chem. Pharm. Bull.* **1992**, *40*, 3067–3071.

[12] C. J. Mathews, P. J. Smith, T. Welton, *J. Mol. Catal. A* **2004**, *214*, 27–32.

[13] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881.

Received: November 25, 2009
Published Online: February 12, 2010

