Journal of Organometallic Chemistry 862 (2018) 22–27

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Catalytic asymmetric synthesis of Pt- and Pd-PCP pincer complexes bearing a para-N pyridinyl backbone

Esther Hui Yen Wong, Yu-Xiang Jia, Yongxin Li, Sumod A. Pullarkat**, Pak-Hing Leung*

Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, 637371, Singapore

ARTICLE INFO

Article history:
Received 27 November 2017
Received in revised form
27 February 2018
Accepted 8 March 2018
Available online 10 March 2018

Keywords:
PCP pincer complexes
Para-N pyridinyl backbone
Catalytic synthesis
Asymmetric hydrophosphination
Metal-carbon bond

ABSTRACT

A diastereoselective catalytic asymmetric hydrophosphination reaction was performed using a palladacycle catalyst to produce chiral PCP phosphine ligand with high dr (95:5) and excellent enantioselectivity (>99% ee). Subsequent facile metalation of the chiral ligand with Pt and Pd metal salts yielded the desired pincer complexes. The protonated form of these pincer complexes was also synthesised, and their structures were confirmed through the use of X-ray crystal diffraction and NMR spectroscopy analyses.

1. Introduction

Ever since the synthesis of pincer complexes first appeared in the works of Moulton and Shaw in 1976 [1] and van Koten et al. in 1978 [2], many other research groups had begun working on the synthesis and application of chiral and non-chiral pincer complexes [3]. Today, pincer complexes are commonly used in catalysis, molecular recognition, material science and supramolecular chemistry [4]. One main factor for their extensive research and use till now is the ability to tune the electronic properties of the metal centre through modifications of the different sites of the ligand scaffold. For example, there were reports by van Koten and his co-workers that the reactivity of the metal centre was affected by *para* substituents on the backbone of NCN pincer complexes through their inductive and/or resonance effects [5]. Furthermore, such modifications do not affect the binding mode at the metal centre greatly.

In 1996, Milstein et al. had also suggested that the electron density and reactivity of the metal centre could be more effectively influenced *via* N-coordination of the free nitrogen atom in a palladium-PCP pincer complex of a 3,5-lutidine based phosphine ligand [6]. With such a convenient method to fine tune the reactivity of the metal centre, one would think that more research will be done in that direction. However, till date, only two other publications [7] were found to further investigate the effects of N-coordination on the metal centre. Moreover, the pincer complexes that were mentioned in these papers did not contain any chiral centres, which otherwise could potentially form a new class of easily tuneable pincer catalysts for the synthesis of chiral compounds.

Herein, we wish to report the synthesis and characterization of platinum(II) and palladium(II) chiral PCP pincer complexes incorporating a *para*-N-pyridinyl backbone. Even though there were concerns that the free nitrogen atom would affect the selectivity of the ligand as well as the coordination mode, results show that the heteroatom do not play a part in deciding the final configuration of the chiral ligand. The synthesis of these novel chiral pincer complexes would also serve as a stepping stone for future studies and modifications on the catalytic application for this class of chiral *para*-N-pyridinyl pincer complexes.

* Corresponding author. Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, 637371, Singapore.

** Corresponding author. Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, 637371, Singapore.

E-mail addresses: sumod@ntu.edu.sg (S.A. Pullarkat), pakhing@ntu.edu.sg (P.-H. Leung).

https://doi.org/10.1016/j.jorganchem.2018.03.010
0022-328X/

2. Experimental

2.1. General information

All reactions involving the use of air-sensitive compounds were conducted under a nitrogen atmosphere. All chemicals and solvents were used as received commercially without further purification. The solvents used for the reactions were degassed whenever necessary and dried according to literature procedures [8]. The Eyela Low Temp. Pairstirrer PSL-1800 was used for reactions conducted at −80 °C. Column chromatography was done on Silica Gel 60 (Merck). The determination of melting points was conducted on the SRS Optimelt Automated Melting Point System, SRS MPA100 with melting points of compounds determined in open capillary tubes and their values uncorrected. Optical rotation was performed on the Jasco P-1030 Polarimeter using cells of length 0.1 dm at 20 °C and a wavelength of 589 nm. The HRMS analysis was done on the Water Q-Tof Premier MS machine. The Bruker AV 300, 400 and 500 NMR machines were used to obtain the ^{1}H, ^{13}C and ^{31}P NMR spectra. All chemical shifts were reported in δ ppm, referencing chloroform-*d* ($\delta = 7.26$) for ^{1}H NMR, chloroform-*d* ($\delta = 77.2$) for ^{13}C NMR, and an external 85% H_3PO_4 standard ($\delta = 0.0$) for $^{31}P\{^{1}H\}$ NMR. Diamine **2** [9], catalyst **5** [10] and 1-phenyl-2-(triphenylphosphoranylidene)ethenone [11] were prepared according to literature methods.

2.2. Synthesis of pyridine-3,5-dicarbaldehyde 3

Diamide **2** (1.00 g, 3.95 mmol) was dissolved in dry THF (20 mL) and cooled to −78 °C under N_2 protection. A solution of diisobutylaluminium hydride (8.30 mL, 1 M in toluene) was added dropwise to the amide solution and the reaction was monitored by thin layer chromatography until no more starting material was observed. The reaction was carefully quenched using cold water (0.2 mL), 15% NaOH (0.2 mL) and then water (1.6 mL), and was left stirring for 15 min. The reaction was allowed to warm up to room temperature and magnesium sulfate was added with stirring for another 15 min. The mixture then passed through celite and washed with ethyl acetate (20 mL x 3). The filtrate was dried under vacuum and purified over silica gel (ethyl acetate: hexane = 1: 1), yielding a pale-yellow solid (0.29 g, 54%). M.p. 95–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.56 (t, 1H, $J = 2.1$ Hz, NCHCC*H*), 9.25 (d, 2H, $J = 2.0$ Hz, NC*H*CCH), 10.2 (s, 2H, NCHCC*H*O); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.4 (s, 2C, *C*CHO), 136.0 (s, 1C, *C*CHC), 155.5 (s, 2C, N*C*H), 189.5 (s, 2C, *C*HO); HRMS (ESI) calcd for $C_7H_6NO_2$ [$(M + H)^+$] 136.0399, found 136.0399.

2.3. Synthesis of (2E,2'E)-3,3'-(pyridine-3,5-diyl)bis(1-phenylprop-2-en-1-one) 4

Dialdehyde **3** (0.53 g, 3.93 mmol) and 1-phenyl-2-(triphenylphosphoranylidene)-ethanone (3.14 g, 8.25 mmol) were dissolved in CH_2Cl_2 (70 mL) and stirred for 20 h under reflux. Upon cooling, the reaction mixture was evaporated to dryness and methanol (50 mL) was added. The mixture was then filtered and the solid collected was washed with cold methanol (20 mL x 3) to afford the product as a pale yellow crystalline solid (1.21 g, 91%). M.p. 221–223 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.66 (m, 6H, Ar), 7.67 (d, 2H, $J = 15.9$ Hz, HCC*H*COPh), 7.84 (d, 2H, $J = 15.9$ Hz, *H*CCHCOPh), 8.08 (m, 4H, Ar), 8.16 (t, 1H, $J = 2.1$ Hz, NCHCC*H*), 8.88 (d, 2H, $J = 1.8$ Hz, NC*H*CCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.8 (s, 2C, CH*C*HCOPh), 128.6–137.6 (15C, Ar), 140.0 (s, 2C, *C*HCHCOPh), 150.8 (s, 2C, N*C*H), 189.6 (s, 2C, *C*OPh); HRMS (ESI) calcd for $C_{23}H_{18}NO_2$ [$(M + H)^+$] 340.1338, found 340.1337.

2.4. General procedure for the synthesis of free phosphine ligand 3,3'-(pyridine-3,5-diyl)bis(3-(diphenylphosphino)-1-phenylpropan-1-one) 1

Dienone **4** (33.9 mg, 0.1 mmol, 1.0 equiv.) in either toluene or CH_2Cl_2 (9.5 mL) was added into a toluene or CH_2Cl_2 (2 mL) solution of Ph_2PH (42.8 mg, 0.23 mmol, 2.3 equiv.) and chiral catalyst **5** (0.0063 g, 0.01 mmol, 10mol%). The reaction was stirred for 10 min at room temperature and then cooled to −80 °C. NEt_3 (27 μL, 0.2 mmol, 2.0 equiv.) in solvent (0.5 mL) was subsequently added in dropwise and the reaction continued to stir at −80 °C for 24 h. When the reaction had completed, the mixture was warmed to room temperature and was subsequently metallated to give the various pincer complexes.

2.5. General procedure for the synthesis of pincer complex 6a

To a toluene solution of the directly synthesised ligand **1** (0.1 mmol, 1.0 equiv.), $PtCl_2(NCCH_3)_2$ (0.1 mmol, 1.0 equiv.) was added into the reaction mixture. The reaction was heated to 90 °C and stirred for 4 h. The organic layer was washed with saturated $NaHCO_3$ (1 × 25 mL) and water (2 × 25 mL), dried over magnesium sulfate, filtered and evaporated to dryness. The crude product was purified via repeated precipitation using a mixture of CH_2Cl_2 and ethyl acetate to give the desired complex as a white solid.

(R,R)-6a 48%. $[\alpha]_D = -283°$ (*c* 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.06–3.30 (m, 4H, PCHCH_2), 5.08 (m, 2H, PC*H*), 7.19–8.18 (m, 32H, Ar); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 49.4 ($J_{Pt-P} = 2902$ Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 43.4 (s, 2C, CH_2), 44.1 (vt, 2C, P*C*H), 125.2–148.6 (40C, Ar), 162.3 (s, $J_{Pt-C} = 956$ Hz, 1C, C_{ipso}), 196.2 (s, 2C, *C*OPh); HRMS (ESI) calcd for $C_{47}H_{38}NO_2P_2Pt$ [$(M - Cl)^+$] 906.2026, found 906.2006.

2.6. General procedure for the synthesis of pincer complex 6b

To a CH_2Cl_2 solution of the directly synthesised ligand 1 (0.1 mmol, 1.0 equiv.), $PdCl_2(NCCH_3)_2$ (0.1 mmol, 1.0 equiv.) was added into the mixture and the reaction was stirred at room temperature for 20 hThe organic layer was washed with saturated $NaHCO_3$ (1 × 25 mL) and water (2 × 25 mL), dried over magnesium sulfate, filtered and evaporated to dryness. The crude product was purified over silica gel (CH_2Cl_2: ethyl acetate: hexane = 15: 6: 14) to give the desired product as a white solid.

(*R,R*)-6b 68%. $[\alpha]_D = -482°$ (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.18 (m, 4H, PCHCH_2), 5.01 (m, 2H, PC*H*), 7.18–8.24 (m, 32H, Ar); $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$): δ 47.7 (s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 44.4 (vt, 2C, $CH_2$45.4 (vt, 2C, P*C*H), 128.0–148.4 (40C, Ar), 170.0 (s, 1C, C_{ipso}), 196.7 (vt, 2C, *C*OPh); HRMS (ESI) calcd for $C_{47}H_{39}NO_2ClPdP_2$ [$(M + H)^+$] 852.1179, found 852.1204.

2.7. General procedure for the synthesis of pincer complexes 7

Complex **6** (0.1 mmol, 1.0 equiv.) was dissolved in a saturated solution of hydrochloride in chloroform (5 mL) and stirred for 30 min. Afterwards, the solution was evaporated to dryness to give the final product as a white solid.

(*R,R*)-7a >99%. $[\alpha]^{26}_D = -129°$ (*c* 0.62, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.11–13.35 (m, 4H, PCHCH_2), 5.15 (m, 2H, PC*H*), 7.23–8.29 (m, 32H, Ar). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 49.4 ($J_{Pt-P} = 2818$ Hz); ^{13}C NMR (121 MHz, $CDCl_3$): δ 42.8 (s, 2C, CH_2), 43.9 (vt, 2C, P*C*H), 124.8–151.1 (40C, Ar), 173.7 (s, $J_{Pt-C} = 999$ Hz, 1C, C_{ipso}), 194.8 (s, 2C, *C*OPh).

(*S,S*)-7b 98%. $[\alpha]^{26}_D = +302°$ (*c* 0.65, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (br, 4H, PCHCH_2), 5.11 (br, 2H, PC*H*), 7.30–38.41 (m, 32H, Ar); $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$): δ 47.7 (s); ^{13}C NMR

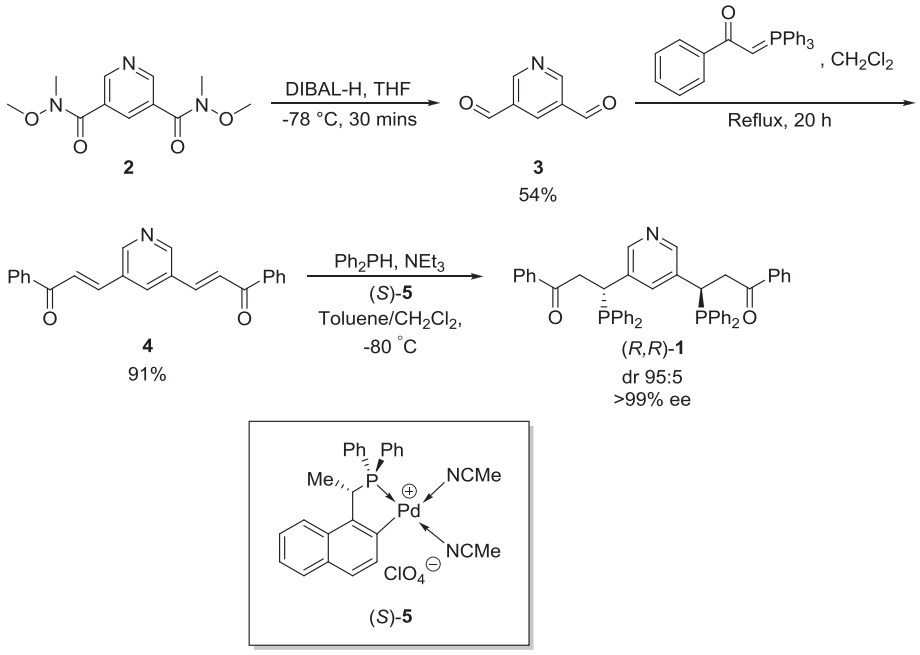
(100 MHz, $CDCl_3$): δ 43.7 (m, 2C, CH_2), 45.3 (vt, 2C, PCH), 126.3–151.4 (40C, Ar), 186.9 (s, 1C, C_{ipso}), 195.0 (m, 2C, COPh).

2.8. Crystallographic studies of (R,R)-7a and (S,S)-7b

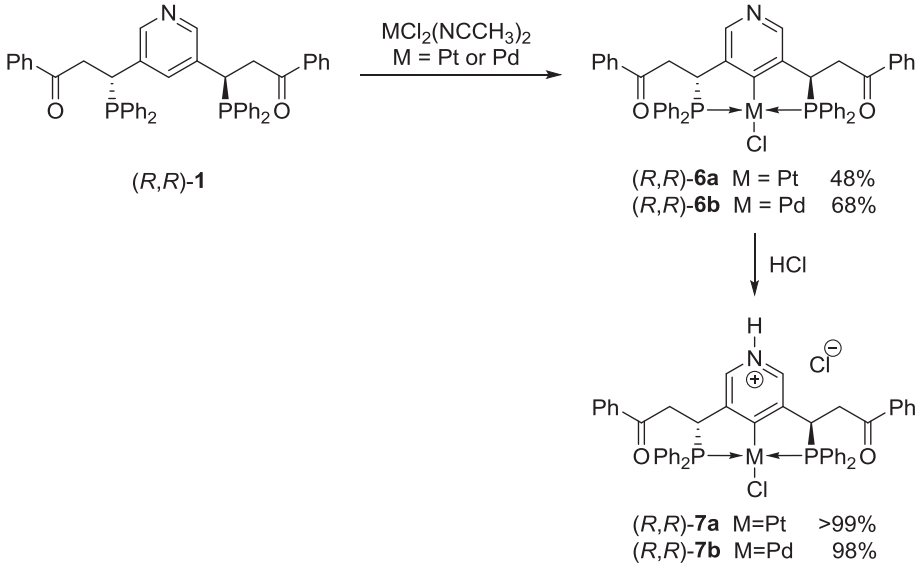
Crystal data for these 2 complexes and a summary of the crystallographic analyses are given in the electronic supporting information. Diffraction quality crystals were mounted onto quartz fibres for analysis. X-ray data were collected at 103 K on a Bruker X8 CCD diffractometer, using Mo-K_α radiation, with the Bruker SAINT software package using a narrow-frame algorithm. Data were processed and corrected for absorption effects with SADABS. Structural solution and refinement were carried out with the SHELXL-2014/6 refinement program. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined with a riding model. The absolute configuration of the chiral complexes was determined unambiguously by using the Flack parameter [12].

3. Results and discussion

Scheme 1 illustrates the pathway for the synthesis of the chiral PCP free phosphine ligand (*R*,*R*)-**1**. Diamide **2** was first reduced to dialdehyde **3**. The subsequent addition of the acetophenyl groups to **3** *via* the Wittig reaction gave a 91% yield of dienone **4**. (*R*,*R*)-**1** was



Scheme 1. Synthesis of the chiral PCP free phosphine ligand (*R*,*R*)-**1**.



Scheme 2. Synthesis of the chiral Pt- and Pd-PCP pincer complexes.

then synthesised from dienone **4** according to the methodology described previously [10].

To our delight, the synthesis of (*R*,*R*)-**1** gave us high dr (95:5) and >99% ee under the optimal condition that was established in the above-mentioned methodology. This result suggests that the presence of the free nitrogen on the pyridine backbone did not have much impact on the *dr* and *ee* of the synthesised ligand, since these values were similar to those reported for the normal aryl backbone containing ligands [10].

Next, we proceeded to synthesise two different types of chiral PCP pincer complex **6** using two different metal salts, namely $PtCl_2(NCCH_3)_2$ and $PdCl_2(NCCH_3)_2$ (Scheme 2). The metalation process took place with the use of the crude enantiomerically enriched ligand. The reaction mixture was purified *via* column chromatography and moderate yields of **6** were obtained (48% for **6a** and 68% for **6b**).

It should be noted that the enantiomeric forms of both complexes **6** and **7** can be equally prepared from their respective pincer ligands. For example, complex (*S*,*S*)-**6** and (*S*,*S*)-**7** were prepared from ligand (*S*,*S*)-**1**. Attempts to crystallise the neutral complexes **6** for X-ray crystal diffraction analysis were not successful. Interestingly, the cationic pincer complexes **7** could be easily crystallised when they were synthesised from the reaction with **6** and hydrochloric acid. Figs. 1 and 2 illustrate the molecular structures of (*R*,*R*)-**7a** and (*S*,*S*)-**7b**. Selected bond lengths and angles of these two complexes are also listed out in Table 1.

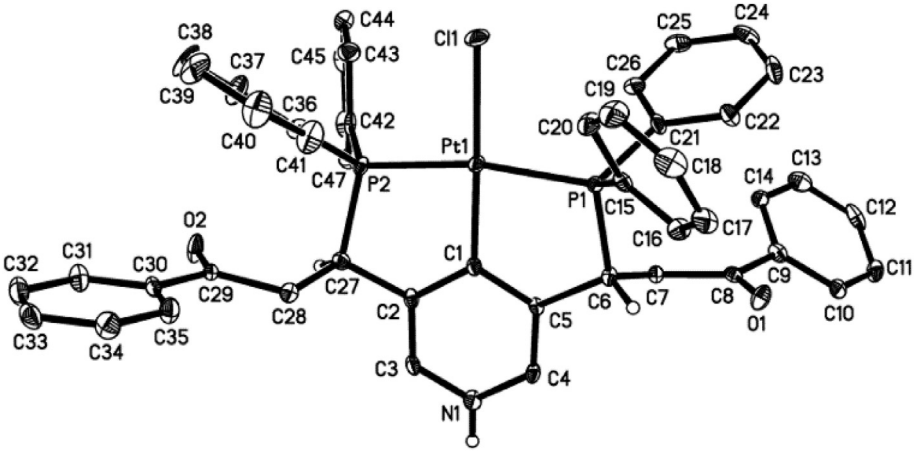


Fig. 1. X-ray crystal structure and the absolute stereochemistry of the protonated Pt-PCP pincer complex (*R*,*R*)-**7a**. The chloride counter anion and all other hydrogen atoms (except those on the chiral carbon centre) were omitted for clarity.

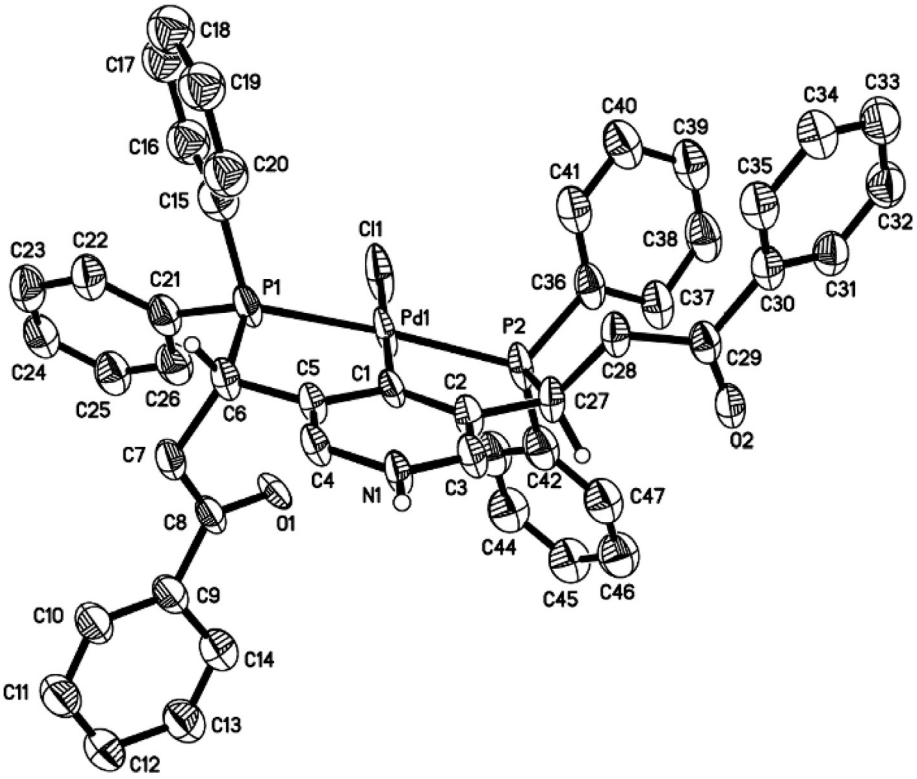
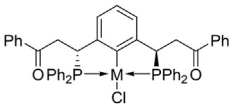
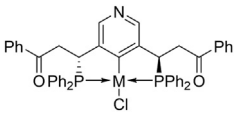
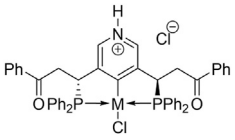


Fig. 2. X-ray crystal structure and the absolute stereochemistry of the protonated Pd-PCP pincer complex (*S*,*S*)-**7b**. The chloride counter anion and all other hydrogen atoms (except those on the chiral carbon centre) were omitted for clarity.

Table 1
Selected bond lengths [Å] and angles [°] of complexes (*R*,*R*)-**7a** and (*S*,*S*)-**7b**.

	(*R*,*R*)-7a (M = Pt)	(*S*,*S*)-7b (M = Pd)
M-C	1.995 (7)	2.033 (14)
M-Cl	2.377 (2)	2.363 (4)
M-P	2.281 (2)	2.310 (5)
M-P	2.276 (3)	2.285 (5)
C-M-Cl	178.2 (2)	179.1 (5)
P-M-P	169.1 (2)	166.7 (3)

Table 2
Selected chemical shifts[a] (δ_{Cipso}) and coupling constants ($^1J_{Pt\text{-}C}$) of the *ipso* carbon of (*R*,*R*)-benzylic-PCP pincer complexes, (*R*,*R*)-**6** and (*R*,*R*)-**7**.

		M = Pt	M = Pd
	δ_{Cipso} (ppm)	151.5[b]	158.3[c]
	$^1J_{Pt\text{-}C}$ (Hz)	936[d]	–
(*R*,*R*)-benzylic-PCP			
	δ_{Cipso} (ppm)	162.3	170.0
	$^1J_{Pt\text{-}C}$ (Hz)	956	–
(*R*,*R*)-**6**			
	δ_{Cipso} (ppm)	173.7	186.9
	$^1J_{Pt\text{-}C}$ (Hz)	999	–
(*R*,*R*)-**7**			

[a] All values were recorded in $CDCl_3$.
[b] Value as obtained from reference [10].
[c] Value as obtained from reference [13].
[d] Value as obtained from reference [14].

In both complexes, it is observed that the geometry around the metal centre is a distorted square planar, which is also supported by the bond angles C-M-Cl and P-M-P. Additionally, the phenyl rings on the phosphorus atoms in both complexes are noted to be puckered in opposite directions. Consequently, the rings on each P are positioned in a pseudo-axial-pseudo-equatorial manner.

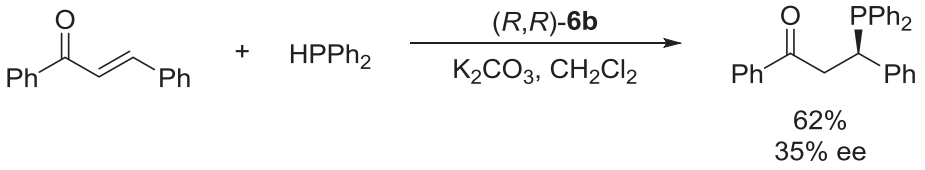
We also employed the ^{13}C NMR spectroscopy to help us better understand these complexes in the liquid state. Particular attention was paid to the chemical shifts and coupling constants (where applicable) of the *ipso* carbon, i.e. the carbon atom of the aryl backbone that is directly bonded to the metal centre, between the benzylic analogue, **6** and **7** (refer to Table 2). For both **6** and **7**, it was noted that the chemical shifts of the *ipso* carbon were significantly more downfield for the pyridinyl-backbone based complexes as compared to the benzylic-backbone based ones (151.5 ppm [10] vs. 162.3 and 173.7 ppm for the Pt complexes and 158.3 ppm [13] vs. 170.0 and 186.9 ppm for the Pd complexes). This suggests that the change of an atom at the *para* position of the aryl backbone from carbon to nitrogen could influence the electron density around the metal centre, which was similar to the observations made by Milstein et al. [6]. Additionally, as seen from the $^1J_{Pt\text{-}C}$ coupling constants in Table 2, a stronger coupling was observed when the nitrogen is at the *para* position instead.

Notably, the chemical shifts in the $^{31}P\{^1H\}$ NMR spectra of **6** and **7** were almost identical (49.4 ppm for **6a**/**7a** and 47.7 ppm for **6b**/**7b**). However, when the Pt-P coupling constants in the $^{31}P\{^1H\}$ NMR spectra of **6a** and **7a** were analysed, the difference became more apparent (2902 Hz vs 2818 Hz). The observed difference in the coupling constant values suggest that the additional presence of the proton could possibly affect the strength of the interaction between M and P.

The potential for the use of complex **6** as a chiral catalyst could be seen in the asymmetric hydrophosphination reaction of *trans*-chalcone. Preliminary result showed that the use of (*R*,*R*)-**6b** with K_2CO_3 as the base gave us 35% ee of the (R)-conformation of the tertiary phosphine with a yield of 62% without further optimization (Scheme 3).

4. Conclusion

The successful synthesis of chiral Pt- and Pd-PCP pincer complexes involved two main processes. Firstly, the synthesis of the chiral PCP free phosphine ligand, through a catalytic asymmetric hydrophosphination reaction, was performed. This process yielded free ligands that had high dr and ee. Secondly, the facile cyclometalation of the chiral ligand with Pt and Pd metal salts gave rise to our desired product. Furthermore, it was demonstrated that the pyridinyl nitrogen could be bonded to a proton to form variants of the chiral pincer complexes. Initial observations suggest that replacing the *para* atom of the aryl backbone with nitrogen could significantly decrease the electron density found in the metal centre and affect the coupling strength between the *ipso* carbon, M and P. As an extension to the current work, our group is now working to 1) further investigate the effects of the nitrogen atom on the electron density of the metal centre and 2) synthesise similar complexes with different functional groups attached to the nitrogen atom and to the ketone side arms. With the synthesis of these alternative complexes, we hope to further fine-tune the reactivity of and the stereoselectivity around the metal centre; and use these



Scheme 3. Synthesis of the (R)-conformation of the tertiary phosphine using (*R*,*R*)-**6b** as the catalyst.

complexes for different types of asymmetric reactions involving organic molecules.

Acknowledgement

We are grateful to Nanyang Technological University, MoE Tier I RG108/15 for supporting this research and the research scholarship to Y.-X. J.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2018.03.010.

SupportingReferences

[1] C.J. Moulton, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1976) 1020–1024.
[2] (a) G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, A.L. Spek, J.C. Schoone, J. Organomet. Chem. 148 (1978) 233–245;
(b) G. van Koten, K. Timmer, J.G. Noltes, A.L. Spek, J. Chem. Soc., Chem. Commun. (1978) 250–252.
[3] (a) H. Rimml, L.M. Venanzi, J. Organomet. Chem. 259 (1983) C6–C7;
(b) M. Gozin, M. Aizenberg, S.-Y. Liou, A. Weisman, Y. Ben-David, D. Milstein, Nature 370 (1994) 42–44;
(c) F. Gorla, A. Togni, L.M. Venanzi, A. Albinati, F. Lianza, Organometallics 13 (1994) 1607–1616;
(d) D. Morales-Morales, R.E. Cramer, C.M. Jensen, Organomet. Chem. 654 (2002) 44–50;
(e) Y. Motoyama, H. Kawakami, K. Shimozono, K. Aoki, H. Nishiyama, Organometallics 21 (2002) 3408–3416;
(f) S. Medici, M. Gagliardo, S.B. Williams, P.A. Chase, S. Gladiali, M. Lutz, A.L. Spek, G.P.M. van Klink, G. van Koten, Helv. Chim. Acta 88 (2005) 694–705;
(g) W. Baratta, M. Bosco, G. Chelucci, A. Del Zotto, K. Siega, M. Toniutti, E. Zangrando, P. Rigo, Organometallics 25 (2006) 4611–4620;
(h) V.A. Kozlov, D.V. Aleksanyan, Y.V. Nelyubina, K.A. Lyssenko, P.V. Petrovskii, A.A. Vasil'ev, I.L. Odinets, Organometallics 30 (2011) 2920–2932;
(i) R. Tian, Y. Ng, R. Ganguly, F. Mathey, Organometallics 31 (2012) 2486–2488;
(j) E. Kinoshita, K. Arashiba, S. Kuriyama, Y. Miyake, R. Shimazaki, H. Nakanishi, Y. Nishibayashi, Organometallics 31 (2012) 8437–8443;
(k) H. Valdés, L. González-Sebastián, D. Morales-Morales, J. Organomet. Chem. 845 (2017) 229–257.
[4] (a) D.E. Bergbreiter, P.L. Osburn, Y.-S. Liu, J. Am. Chem. Soc. 121 (1999) 9531–9538;
(b) D.E. Bergbreiter, P.L. Osburn, A. Wilson, E.M. Sink, J. Am. Chem. Soc. 122 (2000) 9058–9064;
(c) M. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750–3781;
(d) D. Morales-Morales, C.M. Jensen, The Chemistry of Pincer Compounds, Elsevier, Amsterdam, 2007;
(e) D. Benito-Garagorri, K. Kirchner, Acc. Chem. Res. 41 (2008) 201–213;
(f) D. Morales-Morales, Mini-Reviews Org. Chem. 5 (2008) 141–152;
(g) J.M. Serrano-Becerra, D. Morales-Morales, Curr. Org. Synth. (6) (2009) 169–192;
(h) K. Arashiba, Y. Miyake, Y. Nishibayashi, Nat. Chem. 3 (2011) 120–125;
(i) G. van Koten, D. Milstein, Organometallic Pincer Chemistry, vol. 40, Springer, Berlin, 2013;
(j) C. Gunanathan, D. Milstein, Chem. Rev. 114 (2014) 12024–12087;
(k) K.J. Szabo, O.F. Wendt, Pincer and Pincer-type Complexes: Applications in Organic Synthesis and Catalysis, WileyVCH, Germany, 2014;
(l) M. Assay, D. Morales-Morales, Dalton Trans. 44 (2015) 17432–17447;
(m) M.K. Salomon-Flores, I.J. Bazany-Rodriguez, D. Martinez-Otero, M.A. Garcia-Eleno, J.J. Guerra-Garcia, D. Morales-Morales, A. Dorazco-Gonzalez, Dalton Trans. 46 (2017) 4950–4959;
(n) L. Pocquet, N. Vologdin, G.F. Mangiatordi, I. Ciofini, O. Nicolotti, S. Thorimbert, M. Salmain, Eur. J. Inorg. Chem. 30 (2017) 3622–3634.
[5] L.A. van de Kuil, H. Luitjes, D.M. Grove, J.W. Zwikker, J.G.M. van der Linden, A.M. Roelofsen, L.W. Jenneskens, W. Drenth, G. van Koten, Organometallics 13 (1994) 468–477.
[6] A. Weisman, M. Gozin, H.-B. Kraatz, D. Milstein, Inorg. Chem. 35 (1996) 1792–1797.
[7] (a) H. Meguro, T.-a. Koizumi, T. Yamamoto, T. Kanbara, J. Organomet. Chem. 693 (2008) 1109–1116;
(b) K.T. Horak, D.G. VanderVelde, T. Agapie, Organometallics 34 (2015) 4753–4765.
[8] D.B.G. Williams, M. Lawton, J. Org. Chem. 75 (2010) 8351–8354.
[9] (a) T. Shibata, H. Morioka, S. Tanji, T. Hayase, Y. Kodaka, K. Soai, Tetrahedron Lett. 37 (1996) 8783–8786;
(b) J.P. Collman, R.A. Decréau, S. Costanzo, Org. Lett. 6 (2004) 1033–1036.
[10] Y. Huang, R.J. Chew, Y. Li, S.A. Pullarkat, P.-H. Leung, Org. Lett. 13 (2011) 5862–5865.
[11] D.-W. Wan, Y.-S. Gao, J.-F. Li, Q. Shen, X.-L. Sun, Y. Tang, Dalton Trans. 41 (2012) 4552–4557.
[12] H. Flack, Acta Crystallogr. 39 (1983) 876–881.
[13] J.-J. Feng, X.-F. Chen, M. Shi, W.-L. Duan, J. Am. Chem. Soc. 132 (2010) 5562–5563.
[14] Y.-X. Jia, X.-Y. Yang, W.S. Tay, Y. Li, S.A. Pullarkat, K. Xu, H. Hirao, P.-H. Leung, Dalton Trans. 45 (2016) 2095–2101.