

Versatile syntheses of optically pure PCE pincer ligands : facile modifications of the pendant arms and ligand backbones

Pullarkat, Sumod Appukkuttan; Yang, Xiang-Yuan; Tay, Wee Shan; Li, Yongxin; Leung, Pak-Hing

2015

Yang, X.-Y., Tay, W. S., Li, Y., Pullarkat, S. A., & Leung, P.-H. (2015). Versatile syntheses of optically pure PCE pincer ligands : facile modifications of the pendant arms and ligand backbones. *Organometallics*, 34(8), 1582-1588.

<https://hdl.handle.net/10356/79347>

<https://doi.org/10.1021/acs.organomet.5b00132>

© 2015 American Chemical Society. This is the author created version of a work that has been peer reviewed and accepted for publication by *Organometallics*, American Chemical Society. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1021/acs.organomet.5b00132>].

Downloaded on 17 Jul 2024 18:31:47 SGT

Versatile Syntheses of the Optically Pure PCE Pincer Ligands: Facile Modifications of The Pendant Arms and Ligand Backbones

Xiang-Yuan Yang,^[a] Wee Shan Tay,^[a] Yongxin Li,^[a] Sumod A. Pullarkat*^[a] and Pak-Hing Leung*^[a]

Abstract

A series of chiral C-stereogenic PCP- and PCN-ligands were synthesized in good overall yields from inexpensive achiral starting materials *via* a simple catalytic asymmetric P-H addition reaction. This facile catalytic method of preparing the ligand backbones renders easy and economical modifications of the electronically crucial *para*-substituent, chiral functionalities, and donor atoms for different transition metal ions. A one-pot synthetic procedure was used efficiently to prepare the corresponding optically pure pincer complexes. All the new complexes were characterized by NMR and mass spectroscopy. The molecular structures of several selected complexes have also been elucidated by X-ray crystallography. Preliminary studies indicated that minor structural changes on these novel pincer complexes affect their chemical properties significantly when they were applied as catalysts for the reaction between diphenylphosphine and chalcone.

Introduction

In the 1970s, the pioneering work of Shaw,¹ van Koten and Noltes² on transition metal pincer complexes of the ECE' type, notably on PCP and NCN pincer complexes, generated interest in a new class of complexes that would later be regarded as a privileged ligand scaffold. Since then, a plethora of pincer complexes have been synthesized and studied in diversified catalytic applications,³ ranging from cross coupling reactions such as Heck reaction,⁴ to dehydrogenation,^{1,5} transfer hydrogenation,⁶ aldol⁷ and Michael^{7b, 8} reactions. Although pincer complexes have gone through an explosive period of development and exploitation, the future for its advancements remains optimistic due to their ability to generate an extremely broad, sterically, electronically and stereochemically diversified spectrum of ligands that is unmatched by most other systems. The existence of the M-C bond flanked by two neutral electron donors generally contributes to their higher stabilities towards air, heat and moisture,^{4a} which fulfils some of the most important criteria of an ideal catalyst. Furthermore, their reactivities and stereoselectivities may be tuned by a judicious choice of donor atoms (such as P, S and N), substituents on the donor atoms as well as chiral functionalities on the pendant arms.

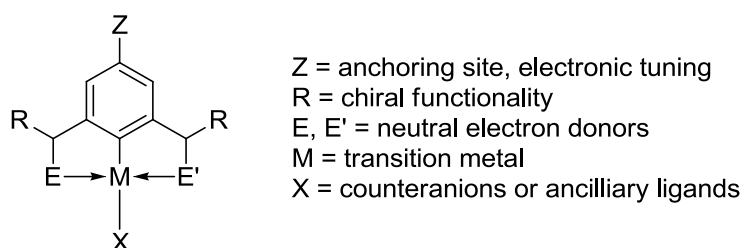


Figure 1. Schematic representation of pincer architecture.

A literature search reveals a record of about 370 examples for benzylic PCP-, 260 for benzylic NCN- and a mere 4 for benzylic PCN-pincers, amongst other types of tridentate ligands in existence.⁹ An investigation of literature^{3f, 10} for optically active PCP- and NCN-pincers turned up three broad categories of chiral moieties incorporated into these tridentate ligands: (1) oxazoline-(eg. *Phebox*, *Benbox*),^{7b, 8, 11} (2) BINOL-¹² and (3) TADDOL-derivatives.^{12a} It should be noted that these enantiopure ligands are often derived from optically pure amino acids,^{11c, 13} or through tedious synthetic protocols or resolution steps.¹⁴ The difficulties lies in the preparation of enantiomerically pure pincer ligands, and their corresponding metal complexes, which directly hampers progress in their application as catalysts in asymmetric transformations.

Over the last decade, tremendous progress has been achieved in the attempts to synthesize chiral *tertiary* phosphines catalytically.¹⁵ However, due to the profound affinity of phosphines towards most low valent late transition metal ions, they are often considered as *catalyst poisons*. Consequently, it is rare for the efficient generation of enantiopure tertiary phosphines *via* a metal catalyzed synthetic method, which is arguably the most economical and practical approach to generate these chiral molecules.¹⁶ It is noteworthy that reports on the synthesis of chiral PCN-complexes are limited and sporadic¹⁷ due to their relatively tedious synthesis. We have been involved in the development of an efficient protocol for the enantioselective generation of P-C bonds leading to the formation of new tertiary phosphine motifs. The idea of *direct* generation of tertiary phosphines circumventing the traditional borane, sulfide or oxide intermediates is attractive since it avoids the issues associated with the protection-deprotection steps which can adversely impact yield, optical purity and result in unwanted conversion of desired functional groups.¹⁸ In the current context of pincer complexes it allows the facile generation of a class of compounds with various transition metals.

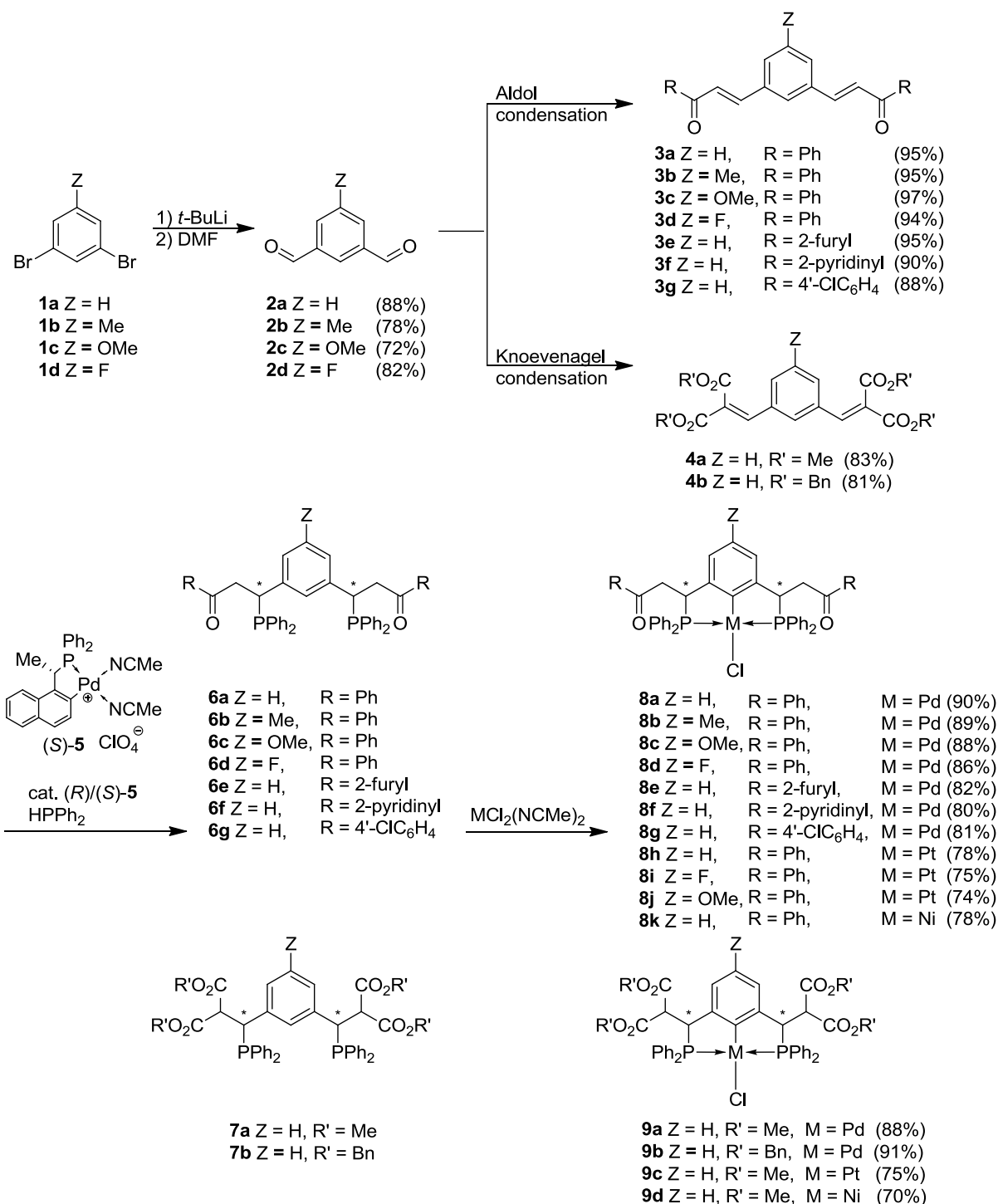
Herein, we report the synthesis of various optically pure PCP- and PCN-transition metal pincer complexes by utilizing a palladacycle catalyzed asymmetric hydrophosphination protocol.^{15d} Structural analysis of these complexes allow the systematic investigations of: (1) the electronic effects originated from the *para*-substituent *Z* (Figure 1), (2) the chiral functionalities *R*, (3) the steric effects of *R*, (4) the coordination chemistry of selected donor atoms and (5) the choices of suitable transition metal ions to form the pincer complexes. By developing a facile and direct synthesis based on a one-pot hydrophosphination/metalation reaction for the preparation of C-stereogenic PCP- and PCN-pincer complexes, a series of such complexes incorporating Pd, Pt and Ni metal ions with various functionalities have been prepared and examined.

Results and Discussion

Facile Syntheses of PCP-Transition Metal Pincer Complexes

The construction of benzylic PCP tridentate ligands started from commercially available dibromo derivatives **1** or substituted benzene-1,3-dicarboxaldehyde **2**. In a typical synthesis, the dibromo species **1** was subjected to dilithiation with *t*-BuLi at -78°C followed by

quenching with DMF to afford the corresponding dicarboxaldehyde **2** in high yields (72 - 88%). Treatment of aldehyde **2** with substituted methyl ketone *via* aldol condensation reaction gave the corresponding dienone **3**. The preparation of ester functionalized substrate **4** was done *via* Knoevenagel condensation of aldehyde **2** with dialkyl malonate in the presence of catalytic amounts of piperidine under Dean-Stark conditions. With the PCP ligand precursors in hand, the one-pot hydrophosphination/metalation reactions were attempted using catalyst (*S*)/(*R*)-**5** followed by the direct C-H activation/cyclometalation of the *air-sensitive* phosphine ligands **6** and **7** to palladium, platinum or nickel metals. We were pleased to realize the syntheses of all the corresponding pincer complexes *via* this protocol in excellent yields (70-91%) from substrates **3** and **4**. In contrast to their free ligands, all the isolated PCP pincer complexes **8** and **9** were stable in air and moisture, both in the solid state and in solution. They were fully characterized by elemental analysis, high resolution mass spectroscopy, ^1H , ^{13}C and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Single crystals of complexes **8b**, **d** and **9a-d** suitable for structural analyses were obtained from either DCM/diethyl-ether or DCM/n-hexanes. Selected bond lengths and angles are presented in Table 1. The chloro complex **8a** could not be induced to form single crystals directly. However, the analogous iodo complex (pincer **8a'**) can be characterized crystallographically. The X-ray structure of pincer **8d** is shown in Figure 2. The molecular structures of the iodo-derivative **8a'** and pincer **9a** have been previously reported by our group.¹⁹ The enantiomeric excess (*ee*) and diastereomeric excess (*de*) of the PCP ligands **3a-g** and **4a-b** were either determined earlier or ascertained using the same NMR and chromatography techniques described previously.^{15d}



Scheme 1. Syntheses of various PCP transition metal pincer complexes (Absolute configurations are not indicated due to the use of both enantiomers of the catalyst).

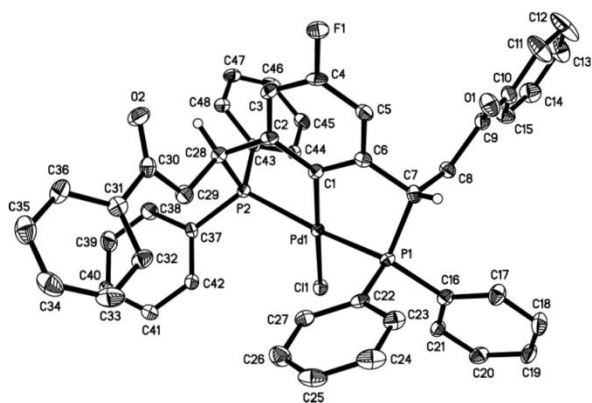
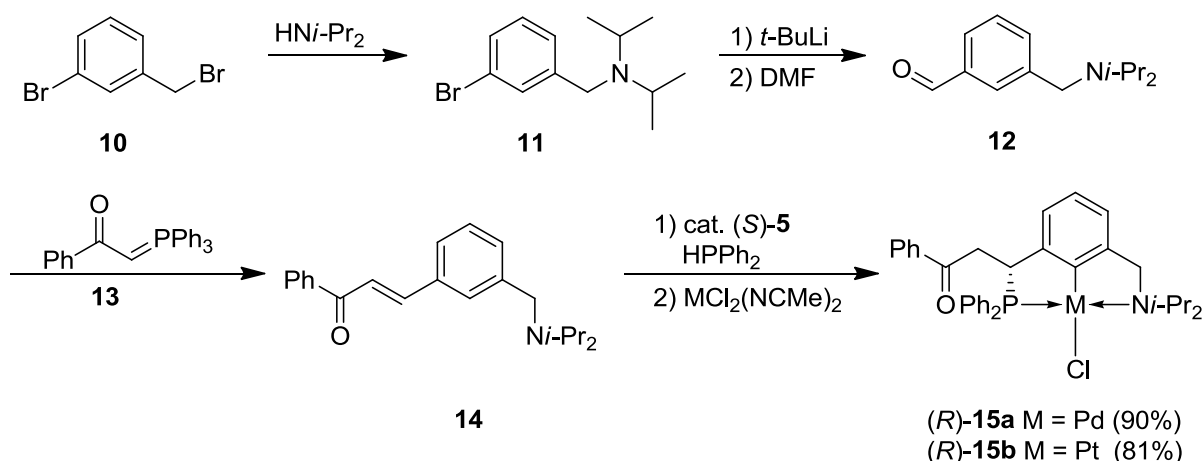


Figure 2. Molecular structure of (*S,S*)-**8d**. Hydrogen atoms except H(C7) and H(C28) were omitted for clarity.

It needs to be noted that there are multiple benefits of this synthetic approach. Firstly, any dibromo or dicarboxaldehyde derivative may be employed as building blocks (a screening of chemical catalogues turned up at least 200 suitable chemicals which are mostly inexpensive). Secondly, a variety of ligand precursors **3** and **4** may be conveniently obtained either *via* Aldol or Knoevenagel condensation with an appropriate choice of substituted methyl ketones or malonates respectively. Thirdly, the palladacycle (*S*)/(*R*)-**5** catalyzed hydrophosphination of the specially designed precursors afforded the optically active PCP diphosphine ligands **6** and **7** in quantitative yields with excellent *ee* and *de* of up to 99%, allowing an efficient one-pot hydrophosphination/metalation reaction to produce the enantiopure pincer complexes. From the viewpoint of catalyst design it should be noted that different transition metals such as Rh or Ru may also be selected for the metalation step. As a result of the aforementioned benefits, it allows multifarious configurations of the generic pincer architecture which facilitates the fine-tuning of the ligand scaffold especially for chemically and stereochemically demanding reactions. However, a limitation of this methodology is that the benzylic positions of the central aryl moiety must be sufficiently activated by electron-withdrawing groups for the catalytic P-H addition to ensue.

Facile Synthesis of PCN-Transition Metal Pincer Complexes

Motivated by our success in the syntheses of the symmetrical PCP ligands, we attempted the construction of a chiral, unsymmetrical PCN complex **15** using a similar methodology (Scheme 2). A mixture of 1-bromo-3-(bromomethyl)benzene **10** and diisopropylamine in toluene was refluxed to give quantitative yields of N-(3-bromobenzyl)-N-isopropylpropan-2-amine **11**. Subsequently, the lithiation of amine **11** with *t*-BuLi followed by addition of DMF gave aldehyde **12** in 90% isolated yield. The Wittig reagent **13** was prepared and refluxed with aldehyde **12** to produce the enone **14**. Interestingly, the catalyst (*S*)-**5** was tolerant of the amine functionality on the specially designed PCN ligand precursor **14**. Thus the catalytic addition of PPh₂H to **14** gave the optically pure PCN ligand (>99% *ee*) which was directly metalated to afford the PCN-pincer (*R*)-**15a-b** in high isolated yields. Single crystals of pincer **15a'** were obtained upon conversion of the chloride anion to a nitrate group. Selected bond lengths and angles are collated in Table 1. The X-ray structure of the PCN-pincer complex **15a'** is depicted in Figure 3.



Scheme 2. Preparation of PCN-transition metal pincer complexes.

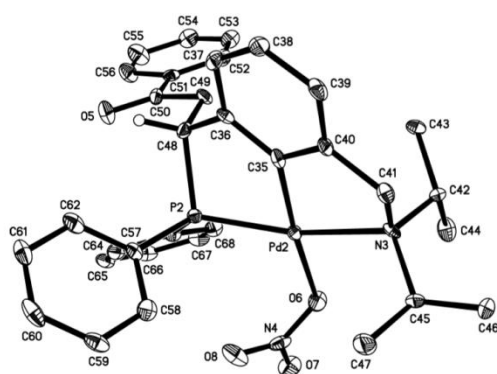


Figure 3. Molecular structure of PCN-Pd pincer complex **15a'**. Hydrogen atoms except H(C48) were omitted for clarity.

A literature review indicated that the scarcity of unsymmetrical PCN-pincer complexes may be due to the difficulties associated with the ligand synthesis.¹⁷ These hemilabile PCN-pincer complexes²⁰ are expected to be useful catalysts due to their unique reactivity.²¹ The efficient synthesis of the chiral PCN pincers (*R*)-**15a-b** therefore offered a simple approach to this class of important complexes. It should be noted that modification of the ligand scaffold could be easily achieved by an appropriate choice of reagents throughout the synthetic process thus affording significant flexibility in design. For example, the reaction between substrate **10** and diphenylamine would result in a less basic and sterically more demanding N-donor. With a wide variety of Wittig reagents available, it is clear that this approach provides a simple and versatile approach towards the preparation of PCN ligands.

Molecular Structures of PCP- and PCN-Transition Metal Pincer Complexes

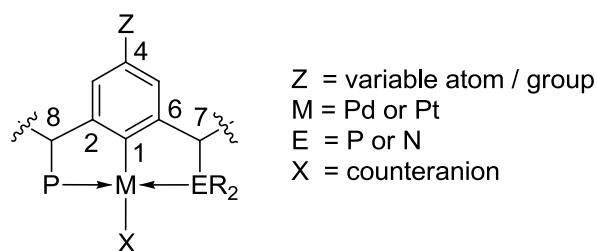


Figure 4. General numbering of pincer architecture.

For simplicity, a general atom numbering scheme is adopted for the comparison of the key structural features of complexes **8a'** (X = I), **b, d, 9a-d** and **15a'** (X = ONO₂). It should be noted that single crystals of the chloro complexes **8a** and **15a** could not be obtained despite multiple attempts. The two complexes were eventually crystallized as their iodo (**8a'**) and nitrato (**15a'**) derivatives, respectively. Selected bond lengths (Å), angles (°) and C₂ pincer twist parameters, θ (°) of the structures are presented below in Table 1.

Table 1. Selected bond lengths (Å), angles (°) and C₂ pincer twist parameters (°) of complexes **8a'**, **b, d, 9a-d** and **15a'**.^a

	8a'	8b	8d	9a	9b	9c	9d	15a'
M-X	2.671(1)	2.370(3)	2.382(1)	2.382(1)	2.368(1)	2.385(2)	2.208(1)	2.151(5)
M-C(1)	2.038(4)	2.040(10)	2.027(3)	2.017(2)	2.006(3)	2.007(6)	1.924(3)	1.954(6)
M-P	2.289(1)	2.273(3)	2.301(1)	2.287(1)	2.280(1)	2.272(2)	2.162(1)	2.236(2)
M-E	2.287(1)	2.310(3)	2.282(1)	2.302(1)	2.296(1)	2.282(2)	2.171(1)	2.198(5)
C(4)-Z	0.95	1.519(12)	1.365(3)	0.95	0.95	0.95	0.95	0.95
C(2)-C(8)	1.510(7)	1.521(16)	1.512(4)	1.517(3)	1.522(4)	1.534(9)	1.507(4)	1.511(8)
C(6)-C(7)	1.496(7)	1.510(16)	1.514(4)	1.511(2)	1.510(3)	1.525(9)	1.502(4)	1.498(9)
P-M-E	162.24(4)	161.30(11)	160.69(3)	161.05(2)	161.13(3)	162.03(6)	167.94(3)	161.82(14)
P-M-C(1)	81.05(17)	81.70(30)	80.44(9)	80.45(5)	80.55(8)	80.93(17)	83.90(9)	79.86(19)
P-M-X	98.86(3)	95.71(12)	102.44(3)	98.52(2)	99.13(3)	98.45(6)	84.04(9)	101.88(13)
E-M-C(1)	81.19(17)	79.80(30)	82.16(9)	80.69(5)	82.74(8)	81.16(17)	95.57(3)	82.20(20)
E-M-X	98.90(3)	102.88(12)	95.59(3)	100.43(2)	98.53(3)	99.52(6)	96.50(3)	96.26(18)
θ^b	19.64	20.51	19.62	19.64	17.43	18.85	11.68	-

^a For complexes **8a'**, M = Pd, X = I; **8b, d, 9a** and **b**, M = Pd and X = Cl; **9c**, M = Pt, X = Cl; **9d**, M = Ni, X = Cl and **15a'**, M = Pd, X = ONO₂. ^b The pincer twist parameters for the C₂ symmetrical P-C-P complexes were determined from the corresponding cif files using Mercury 3.1 software.

In general, all the complexes adopted distorted square-planar geometry around the transition metal centers. Due to restrictions by the metrics of the P-C(8)-C(2)-C(1)-C(6)-C(7)-E framework, all the P→M←E angles are smaller than 180°. A literature review of the bond parameters gave an average of 164° for 4-coordinated PCP pincers. The small P→M←E angles is a reflection of the steric strain imposed in pincers containing two-fused five-membered metallacycles.²² It was earlier deduced that in 4-coordinated pincer systems where

steric demand is similar both above and below the planes, changes in P→M←E angles are attributed to the inherent bending towards the aryl moiety of the ligand.²³ With the exception of pincer **9d** all the current complexes conform to this phenomenon with P-M-E angles of approximately 161°. The larger bond angle (168°) observed from complex **9d** may be attributed to the smaller covalent radii of nickel metal.

From the data obtained for complexes **8a'**, **b** and **d**, interestingly, the electronic properties originating from the *para*-substituent *Z* appears to affect the metal-carbon bond. When the strong electron-withdrawing fluorine atom is involved, the M-C(1) bond [2.027(3) Å] in complex **8d** is noticeably shorter than those in complexes **8a'** and **8b** [2.038(4) Å and [2.040(10) Å, respectively]. However, the effects of *Z* are not pronounced in other neighbouring bond lengths and angles.

A comparison of the structural features in Table 1 did not reveal any clear trends with regards to the effects of the chiral functionalities *R*. For example, the sterically bulkier malonate functionalities on pincers **9a** and **b** did not have significant influence on the architecture of the complexes when compared to the smaller ketone groups on compounds **8a'** and **b**. In contrast, the sizes of the central metal ions affect the structural features of the complexes significantly. For example, with the same pincer ligand, the nickel(II) complex **9d**, with the smallest metallic covalent radii of 1.24 Å, exhibited the shortest coordination bonds when compared with their palladium(II) (**9a**), and platinum(II) (**9c**) analogues. Interestingly, the Pt-C bond [2.007(6) Å] in **9c** is clearly shorter than the Pd-C bond [2.017(2) Å] in **9a**, despite the fact that carbon is located relatively further away from platinum in the periodic table and the two atoms have a larger difference in term of electron density. This observation in the solid state structures may be due to the respective covalent radii of platinum (1.36 Å) and palladium (1.39 Å), or a stronger electronic interaction within the Pt-C bond. Similarly, the Pt-P bonds in **9c** are also slightly shorter than the corresponding Pd-P bonds on complex **9a**.

Interestingly, the Pd←P bond [2.236(2) Å] in the unsymmetrical PCN pincer **15a'** is the shortest among all the Pd←P bonds [2.273(3) - 2.310(3) Å] listed in Table 1. This is probably due to the favourable electronic effect associated with the *trans* P→Pd←N arrangement in which the σ -donating N atom is coordinated *trans* to a π -accepting P donor. In all other palladium complexes, the competition between the two P atoms in the P→Pd←P moiety will somewhat weaken the Pd-P bonds due to competition for electrons from the same metal *d*-orbital.²⁴

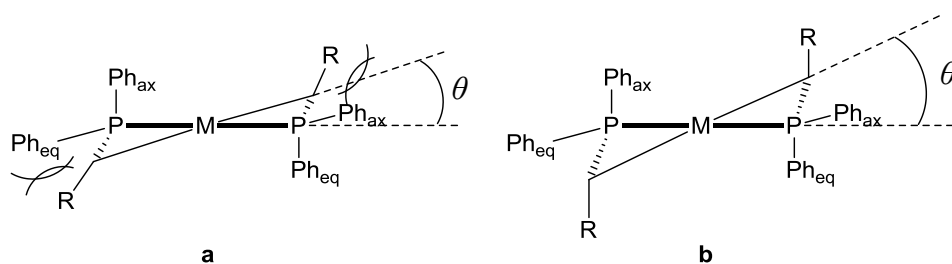


Figure 5. Diagrammatic representations of a) larger steric repulsion due to smaller θ , and b) lower repulsion due to a larger θ .

It is noted that steric properties of pincer complexes are also commonly measured by their characteristic twist angle θ ,²⁵ as illustrated in Figure 5. For a particular pincer system, a larger θ with a smaller P→M←P angle reflects a lower volume of coordination sphere blocked by the ligand (measured by percent buried volume, %V_{bur}). Therefore, this indicates a more compact conformation, which in turn restricts the access of a reagent to the metal center in the direction *trans* to the M-C(1) bond axis.²³ Consequently, these structural features influence the reactivity and stereoselectivity of the pincer complexes in their metal catalyzed asymmetric reactions.²⁶ By comparison, the C-C bonds that form the pincer arms [C(2)-C(8) and C(6)-C(7)] of all the pincer complexes listed in Table 1 are all in close agreement with the average value of 1.51 Å reported for analogous PCP systems.²³ However, their twist angles (11.7-20.5°) are all larger than the average θ of 10.1° for similar square-planar benzylic-CH₂-bridged pincers. The enlarged θ values may be attributed to steric repulsions between the P-phenyl rings and the substituents on the chiral carbon centers.

Preliminary Activity Test

We are interested to develop a series of chiral pincer complexes as catalysts for chemical transformation reactions. A possible approach is by the systematic modification of θ and %V_{bur} of the complexes. Prior to the dedicated structural fine tuning, the general chemical reactivity of the selected complexes **8a**, **h**, **9a**, **9d** and **15a** were examined. In this preliminary test, the complexes were used as catalysts in the reaction between diphenylphosphine and chalcone. Table 2 shows that the results of these tests were gratifying, with 4 out of 5 complexes exhibiting excellent reactivity to afford the product quantitatively without further optimization, albeit with low to moderate enantioselectivities.

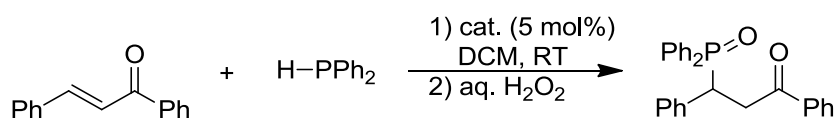


Table 2. Preliminary catalytic screening for pincer complexes.

Entry	Cat. ^a	t (h)	Conversion (%)	Yield ^b (%)	ee ^c (%)
1	8a	1	99	90	11
2	8h	4	99	95	3
3	9a	5	99	96	43
4	9d	48	99	76	0
5	15a	9	99	88	3

^a The catalysts were pre-treated with AgOAc in DCM for 1h. ^b Isolated yield. ^c ee was determined by chiral HPLC.

Interestingly, the palladium PCP-pincer **8a** is noticeably more reactive than its platinum analogous **8h** (Table 2, entries 1,2). Similarly, the heavily functionalized palladium complex **9a** is significantly more reactive than its nickel counterparts (**9d**) (entries 3,4). Clearly, the choice of the metal ion is a key factor that determines the chemical reactivity of a pincer complex, even though the same ligand is used. For the P-H addition reaction, palladium

appears to be a better choice than platinum and nickel. On the other hand, while palladium is used in both **8a** and **9a**, the sterically bulkier ester functional groups on the pendant arms also affects the reactivity and stereoselectivity of the complexes significantly (entries 1,3). Furthermore, the PCP pincers are clearly better ligands than the PCN system as complex **15a** is the least reactive palladium catalysts in Table 2. These preliminary tests revealed that the catalytic P-H addition reaction is indeed sensitive to the minor changes in the structure of the pincer catalysts.

Conclusion

The facile synthesis of the privileged PCP- and PCN-ligand scaffolds *via* the synthetic methodology presented (*vide supra*) serves as a functional and valuable synthetic tool to prepare a series of pincer ligands. This synthetic pathway allows straightforward modification of the *para*-substituent *Z* (Figure 1), functionalities *R*, bulkiness of *R*, donor atoms and the transition metal center, thereby allowing access to a broad spectrum of pincer analogues of varying electronic and chemical properties. Consequently, this enables the fine-tuning of both the stereochemical and electronic characteristics of the pincer ligands thus tailoring it to best suit a specific transformation scenario. By utilizing the highly efficient asymmetric double hydrophosphination, the one-pot synthesis procedure was realized, which resulted in the efficient synthesis of the functionalized C-stereogenic PCP- and PCN-pincer complexes in their enantiomerically pure form. In the current report, we have clearly illustrated the highly versatile synthesis of a variety of ligand scaffolds. In subsequent work, it will be shown that the information obtained in this preliminary study is crucial to the rational utilization of these readily modified PCP-complexes in some stereochemically highly demanding catalytic asymmetric transformations.

Acknowledgement

We wish to acknowledge the funding support for this project from Nanyang Technological University, W.-S. Tay thank the NTU Undergraduate Research Experience on CAmpus (URECA) programme for the support and X.-Y. Yang thank NTU for the award of a PhD scholarship.

References

- [1] Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.
- [2] van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc., Chem Commun.* **1978**, 250.
- [3] For selected reviews, see: a) Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New J. Chem.* **1997**, *21*, 751. b) Albrecht, M.; van Koten, G. *Angew. Chem. Int. Ed.* **2001**, *40*, 3750. c) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. d) Morales-Morales, D. *Mini-Rev. Org. Chem.* **2008**, *5*, 141. e) Selander, N.; Szabó, K. J. *Dalton Trans.* **2009**, 6267. f) Selander, N.; Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048.

[4] For selected examples, see: a) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. b) Beller, M.; Zapf, A. *Synlett* **1998**, 792. c) Morales-Morales, D.; Redón, R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1619. d) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379.

[5] For selected examples, see: a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083. b) Wang, K.; Goldman, M. E.; Emge, T. J.; Goldman, A. S. *J. Organomet. Chem.* **1996**, *518*, 55. c) Xu, W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273.

[6] Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem. Int. Ed.* **2000**, *39*, 743.

[7] For selected examples, see: a) Gorla, F.; Togni, A.; Venanzi, L. *Organometallics* **1994**, *13*, 1607. b) Stark, M. A.; Richards, C. J. *Tetrahedron Lett.* **1997**, *38*, 5881. c) Zhang, X.; Longmire, J. M.; Shang, M. *Organometallics* **1998**, *17*, 4374. d) Gimenez, R.; Swager, T. J. *Mol. Catal. A: Chem.* **2001**, *166*, 265.

[8] Stark, M. A.; Richards, C. J. *Organometallics* **2000**, *19*, 1282.

[9] Cambridge Crystallographic Data Base, www.ccdc.cam.ac.uk.

[10] For selected examples, see: a) Nishiyama, H. *Chem. Soc. Rev.* **2007**, *36*, 1133. b) *The Chemistry of Pincer Compounds*; Morales-Morales, D.; Jensen, C. M., Eds.; Elsevier: Amsterdam, 2007.

[11] For selected examples, see: a) Motoyama, Y.; Makihara, N.; Mikami, Y.; Aoki, K.; Nishiyama, H. *Chem. Lett.* **1997**, *26*, 951. b) Denmark, S. E.; Stavenger, R. A.; Faucher, A. - M, Edwards, J. P. *J. Org. Chem.* **1997**, *62*, 3375. c) Fossey, J. S.; Richards, C. J. *Organomet. Chem.* **2004**, *689*, 3056. d) Kanazawa, Y.; Tsuchiya, Y.; Kobayashi, K.; Shiomi, T.; Itoh, J.; Kikuchi, M.; Yamamoto, Y.; Nishiyama, H. *Chem. Eur. J.* **2006**, *12*, 63. e) Gerisch, M.; Krumper, J. R.; Bergman, R. G.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 5818.

[12] a) Wallner, O. A.; Olsson, V. J.; Eriksson, L.; Szabó, K. J. *Inorg. Chim. Acta* **2006**, *359*, 1767. b) Aydin, J.; Kumar, K. S.; Sayah, M. J.; Wallner, O. A.; Szabó, K. J. *J. Org. Chem.* **2007**, *72*, 4689. c) Aydin, J.; Conrad, C. S.; Szabó, K. J. *Org. Lett.* **2008**, *10*, 5175.

[13] Ito, J.; Shiomi, T.; Nishiyama, H. *Adv. Synth. Cat.* **2006**, *348*, 1235.

[14] Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43.

[15] For selected examples, see: a) Pullarkat, S. A.; Leung, P. -H. *Top. Organomet. Chem.* **2013**, *43*, 145. b) Huang, Y.; Pullarkat, S. A.; Li, Y.; Leung, P. H. *Chem. Commun.* **2010**, *46*, 6950. c) Koshti, V.; Gaikwad, S.; Chikkali, S. H. *Coord. Chem. Rev.* **2014**, *265*, 52. d) Huang, Y.; Chew, R. J.; Li, Y.; Pullarkat, S. A.; Leung, P. H. *Org. Lett.* **2011**, *13*, 5862. e) Rosenberg, L. *ACS Catal.* **2013**, *3*, 2845. f) Feng, J. -J.; Chen, X. -F.; Shi, M.; Duan, W. -L. *J. Am. Chem. Soc.* **2010**, *132*, 5562.

[16] For selected examples, see: a) Glueck, D. S. *Chem.-Eur. J.* **2008**, *14*, 7108. b) Scriban, C.; Kovacic, I.; Glueck, D. S. *Organometallics* **2005**, *24*, 4871. c) Wicht, D. K.; Kourkine, I. V.; Kovacic, I.; Nthenge, J. M.; Glueck, D. S. *Organometallics* **1999**, *18*, 5381. d) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607. e) Sadow, A. D.; Haller, I.; Fadini, L.; Togni, A. *J. Am. Chem. Soc.* **2004**, *126*, 14704. f) Sadow, A. D.; Togni, A. *J. Am. Chem. Soc.* **2005**, *127*, 17012.

[17] a) Motoyama, Y.; Shimozone, K.; Nishiyama, H. *Inorg. Chim. Acta* **2006**, *359*, 1725. b) Bonnet, S.; Li, J.; Siegler, M. A.; von Chrzanowski, L. S.; Spek, A. L.; van Koten, G.; Klein Gebbink, R. J. M. *Chem. Eur. J.* **2009**, *15*, 3340. c) Niu, J. -L.; Chen, Q. -T.; Hao, X. -Q.; Zhao, Q. -X.; Gong, J. -F.; Song, M. -P. *Organometallics* **2010**, *29*, 2148. d) Yang, M. -J.; Liu, Y. -J.; Gong, J. -F.; Song, M. -P. *Organometallics* **2011**, *30*, 3793.

[18] a) Busacca, C. A.; Raja, R.; Grinberg, N.; Haddad, N.; James-Jones, P.; Lee, H.; Lorenz, J. C.; Saha, A.; Sennanayake, C. H. *J. Org. Chem.* **2008**, *73*, 1524. b) Stankevič, M.; Pietrusiewicz, K. M. *Synthesis* **2005**, 1279. c) Busacca, C. A.; Farber, E.; DeYoung, J.; Campbell, S.; Gonnella, N. C.; Grinberg, N.; Haddad, N.; Lee, H.; Ma, S.; Reeves, D.; Shen, S.; Sennanayake, C. H. *J. Org. Chem.* **2009**, *74*, 5594. d) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 2368. e) Trepohl, V. T.; Mori, S.; Itami, K.; Oestreich, M. *Org. Lett.* **2009**, *11*, 1091.

[19] Yang, X. -Y.; Gan, J. H.; Li, Y.; Pullarkat, S. A.; Leung, P. -H. manuscript submitted.

[20] Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.

[21] a) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588. b) Poverenov, E.; Efremenko, I.; Frenkel, A. I.; Ben-David, Y.; Shimon, L. J. W.; Leitun, G.; Konstantinovski, L.; Martin, J. M. L.; Milstein, D. *Nature* **2008**, *455*, 1093. c) Poverenov, E.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Ben-David, Y.; Milstein, D. *Chem.-Eur. J.* **2004**, *10*, 4673.

[22] For examples, see: a) Inés, B.; SanMartin, R.; Churruca, F.; Dominguez, E.; Urtiaga, M. K.; Arriortua, M. I. *Organometallics* **2008**, *27*, 2833. b) Li, J.; Siegler, M.; Lutz, M.; Spek, A. L.; Klein Gebbink, R. J. M.; van Koten, G. *Adv. Synth. Catal.* **2010**, *352*, 2474. c) Zhang, B. S.; Wang, W.; Shao, D. -D.; Hao, X. -Q.; Gong, J. -F.; Song, M. -P. *Organometallics* **2010**, *29*, 2579.

[23] Roddick, D. M. *Top. Organomet. Chem.* **2013**, *40*, 49.

[24] Leung, P. H.; Martin, J. W. L.; Wild, S. B. *Inorg. Chem.* **1986**, *25*, 3396.

[25] a) Albert, P.; Biagio, C.; Andrea, C.; Simona, G.; Francesco, R.; Vittorio, S.; Luigi, C. *Eur. J. Inorg. Chem.* **2009**, 1759. b) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 841.

[26] For examples, see: a) Wallner, O. A.; Olsson, V. J.; Eriksson, L.; Szabó, K. J. *Inorg. Chim. Acta* **2006**, *359*, 1767. b) Li, J.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G.; Klein, G. R. J. M. *J. Organomet. Chem.* **2010**, *695*, 2618. c) Aydin, J.; Ryden, A. Szabó, K. J. *Tetrahedron: Asymmetry* **2008**, *19*, 1867. d) Baber, R. A.; Bedford, R. B.; Betham, M.; Blake, M. E.; Coles, S. J.; Haddow, M. F.; Hursthouse, M. B.; Orpen, A. G.; Pilarski, L. T.; Pringle, P. G.; Wingad, R. L. *Chem. Commun.* **2006**, 3880.