Electrophilic Reactions with Dicationic Platinum

D. Luke Nelsen

A dissertation submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry.

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Approved by

Advisor: Professor Michel R. Gagné

Reader: Professor Maurice Brookhart

Reader: Professor Jeffrey S. Johnson

Professor Joseph L. Templeton

Professor Cynthia K. Schauer

Abstract

D. Luke Nelsen: Electrophilic Reactions with Dicationic Platinum (Under the Direction of Michel R. Gagné)

In situ generated $[(PPP)Pt][BF_4]_2$ (PPP = triphos) catalyzes the cycloisomerization of 1,6-enyne-ols by initiative π-activation of the alkyne. This generates an isolable cationic Pt-alkenyl species which subsequently participates in turnover limiting protonolysis with in situ generated acid. This latter reactivity contrasts cationic Pt-alkyls which are more difficult to protonolyze. Mechanistic studies on isolated Pt-alkenyls, and deuterium labeling helped to elucidate the mechanistic details.

A new class of *tropos* 3,3'-bis(diphenylphosphino)-2,2'-bipyridine ligated Pt(II) complexes was developed. Their ability to coordinate to chiral H-donor auxiliaries through the bipyridine moiety was examined. While d.r. was low for weak H-donors like BINOL and TADDOL, more acidic H-donors (L-DBT) afforded a 1.0:5.5 d.r. for bulkier bipyridine moieties. A single diastereomer of this complex crystallized from solution. These ligands could also be resolved across the metal by forming the (*S*)-BINOLate complex. However, upon cleavage of the chiral auxiliary, racemization was too rapid for the complex to be used for catalysis.

Acknowledgements

First I would like to thank Mike Gagné for giving me an opportunity to work in his lab. I would also like to thank Mike for his constant support. For five and a half years he helped me develop as a chemist. His insights helped me see the forest is spite of the trees, a lesson that not all advisors are capable of teaching, but relevancy can be appreciated in all aspects of life, including chemistry. I thank the Gangé group members, past and present, for providing an environment in which good chemistry is appreciated and the motivation to work long hours, because you know you won't be working alone. I would also like to thank the chemistry faculty and staff at UNC, especially my committee members Professors Brookhart, Johnson, Schauer, and Templeton.

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sacrificing time and help I would have gladly given if not for my studies and distance. Last but certainly not least, to my “darling” Alison, who not only made this worthwhile, but also possible.

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List of Abbreviations

18-C-6	1,4,7,10,13,16-hexaoxacyclooctadecane
2D	two dimensional
3°	tertiary
Å	angstrom
atm	atmospheres
benzo-18-C-6	2,3,5,6,8,9,11,12,14,15-decahydrobenzo-[b][1,4,7,10,13,16]hexaoxacyclooctadecine
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINOL	1,1’-binapthyl-2,2’-diol
BINAM	1,1'-binaphthyl-2,2'-diamine
BIPHEP	2,2'-bis(diphenylphosphino)biphenyl
bpyPHOS	3,3'-bis(diphenylphosphino)-2,2'-bipyridine
bpyPHOS-^{i}Bu	3,3'-bis(diphenylphosphino)-6,6'-diisobutyl-2,2'-bipyridine
bpyPHOS-Et	3,3'-bis(diphenylphosphino)-6,6'-diethyl-2,2'-bipyridine
bpyPHOS-Me	3,3'-bis(diphenylphosphino)-6,6'-dimethyl-2,2'-bipyridine
bpyPHOS-OMe	3,3'-bis(diphenylphosphino)-6,6'-dimethoxy-2,2'-bipyridine
Bz	benzoyl
COD	1,5-cyclooctadiene
d	doublet
dd	doublet of doublets
δ	chemical shift
$\Delta G^{\ddagger}$	transition state free energy

DABCO	1,4-diazabicyclo[2.2.2]octane
deg	degrees
DBT	dibenzoyl tartaric acid
DFT	density functional therory
DMAP	N,N-dimethyl-4-aminopyridine
DM-BINAM	3,3'-dimethyl-1,1'-binaphthyl-2,2'-diamine
DMF	N,N-dimethylformamide
DPEN	1,2-diphenylethane-1,2-diamine
dppe	1,2-bis-(diphenylphosphino)ethane
dppf	1,1’-bis-(diphenylphosphino)ferrocene
d.r.	diastereomer ratio
e.e.	enantiomer excess
e.g.	exempli gratia
EI	electron impact
endo	endocyclic
eq	equation
equiv	equivalent
ESI	electrospray ionization
Et	ethyl
EtOAc	ethylacetate
exo	exocyclic
g	gram
GC	gas chromatography
h	hour
$HNTf_2$	bis-trifluoromethansulfonamide

HOTf	trifluoromethanesulfonic acid
HR	high resolution
Hz	hertz
^{i}Bu	isobutyl
IPA	isopropyl alcohol
(II)	divalent
J	three-bond H-H coupling constant
$J_{H\text{-}Pt}$	three-bond H-Pt coupling
$J_{P\text{-}Pt}$	one-bond P-Pt coupling
k	rate constant
kcal	kilocalorie
μL	microliter
m	multiplet
m	meta
M	molarity
M^{+}	molecular ion
Me	methyl
MeO-BIPHEP	(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)
Me-SoniPHOS	6,6'-bis(diphenylphosphino)biphenyl-2,2'-diyldiacetate
mg	milligram
MHz	megahertz
min	minutes
mL	milliliter
mmHg	millimeters of mercury

mmol	millimole
mol	mole
mol%	molar percentage
MS	mass spectrometry
m/z	mass-to-charge ratio
N	normality
NEt_3	triethylamine
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect
NOESY	nuclear Overhauser and exchange spectroscopy
o	ortho
OAc	acetate
OMe	methoxy
ORTEP	anisotropic displacement ellipsoid plot
p	para
Ph	phenyl
Ph_2NMe	N,N-diphenylmethylamine
ppm	parts per million
P-Phos	2,2′,6,6′-Tetramethoxy-4,4′-bis(diphenylphosphino)-3,3′-bipyridine
PPP	bis-(2-diphenylphosphinoethyl) phenylphosphine
PTFE	polytetrafluoroethylene
py	pyridine
q	quartet
rac	racemic

RT	room temperature
s	singlet
SEGPHOS	5,5′-Bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole[4(*R*)-(4,4′-bi-1,3-benzodioxole)-5,5′-diyl]bis[diphenylphosphine]
t	triplet
TADDOL	2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol)
^{t}Bu	tertbutyl
td	triplet of doublets
THF	tetrahydrofuran
TLC	thin layer chromatography
Ts	(4-methylphenyl)sulfonamide
tt	triplet of triplets
μmol	micromole
VAPOL	2,2’-diphenyl-[3,3’-biphenanthrene]-4,4’-diol

Chapter 1

Stereo-controlled Systems: Taking Inspiration from Enzymes

In terms of pure synthetic efficiency, enzymes are the pinnacle of reactivity and selectivity. They are capable of distinguishing the appropriate substrate from a complex reaction mixture. Through a multitude of interactions (acid, base, hydrophobic and hydrophilic, H-donors or H-acceptors, metal coordination, etc.) enzymes orient the desired substrate to lower its transition state energy and produce a single, stereodefined product. The rate and control with which enzymes convert a plethora of relatively simple substrates into complex products has led to many fields of research aimed at mimicking such impressive transformations.

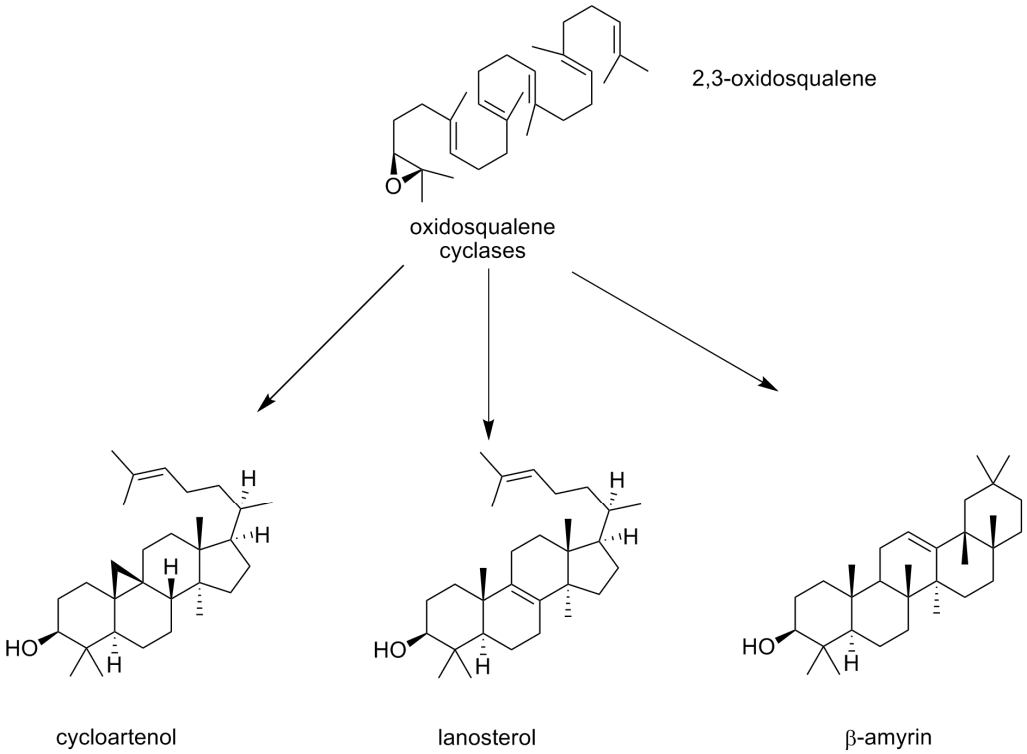
1.1. Cation-Olefin Cyclization Reactions

A. Enzymatic cyclization of triterpenes. An impressive example of enzyme efficiency is the cyclization of triterpenes or triterpene oxides.[1] In particular, the class of enzymes which convert squalene (and squalene derivatives) to hopene (and many other polycyclic products) has been especially well studied.[1b] In bacteria, squalene is directly cyclized into the steroid hopene, a process that is initiated by proton transfer to the terminal alkene. In plants, animals and fungi, squalene is first enantioselectively oxidized into 2,3-

1. (a) Abe, I.; Rhomer, M.; Prestwhich, G. D. *Chem. Rev.* **1993**, *93*, 2189-2206. (b) Wendt, K. U.; Schulz, G. E.; Corey, E. J.; Liu, D. R. *Angew. Chem. Int. Ed.* **2000**, *39*, 2812-2833. (c) Yoder, R. A.; Johnston, J. N. *Chem. Rev.* **2005**, *105*, 4730-4756.

oxidosqualene. There are numerous oxidosqualene cyclases, each capable of producing a unique natural product (Scheme 1.1).

Scheme 1.1

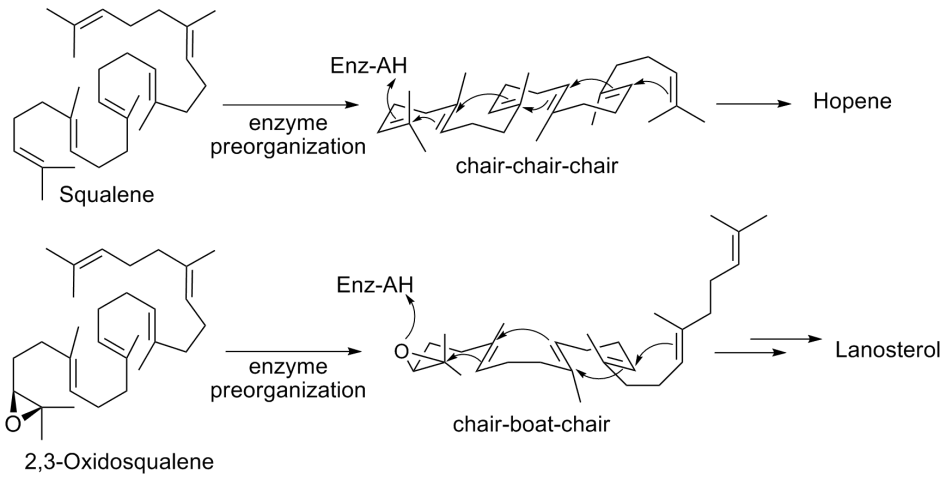


Because the formation of a 6-membered ring from an olefin is exothermic (ca. -20 kcal/mol) and has a low barrier to activation (ca. 1 kcal/mol), a number of cyclic products derived from the enzyme catalyzed cyclization for 2,3-oxidosqualene can be envisioned to be energetically competitive.[2] However, each enzyme is capable of forming a single product with very high selectivity. In the examples shown in Scheme 1.1, up to 5 new rings and 8 new stereocenters are generated with compete selectivity. This reflects the tight enzymatic control of the substrate. As exemplified in Scheme 1.2, a chair-chair-chair conformation is

2. Jensen, C.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 10846-10854.

enforced by squalene-hopene cyclase and a chair-boat-chair conformation is imposed by lanosterol synthase; each unique conformation leads to the observed stereochemical outcome.

Scheme 1.2



B. Biomimetic Cation-Olefin Reactions. Chemists strive to develop biomimetic polyolefin cascade reactions analogous to those seen in nature due to the impressive increases in molecular complexity that can be achieved. The efficiency, selectivity, and specificity with which these transformations occur are the envy of the most skilled scientists. Utilizing olefin cascade initiators such as Brønsted acids (eq 1.1),[3] Lewis acids (eq 1.2),[4] and Hg^{2+} salts (eq 1.3)[5] biomimetic cyclizations occur with good yields and good control of stereochemistry. However, there are fewer examples of polyolefin asymmetric catalysis.[6]

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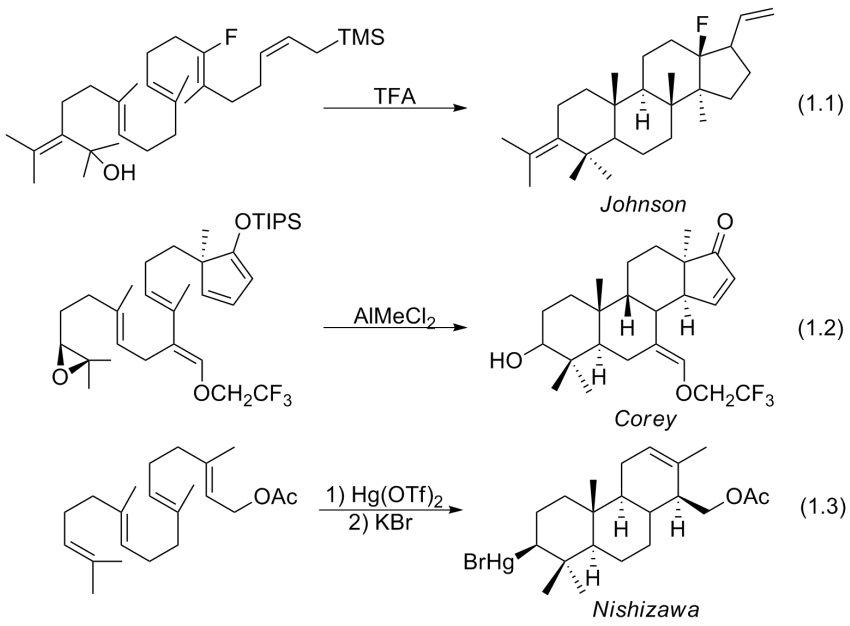
3. (a) Corey, E. J.; Lee, J. *J. Am. Chem. Soc.* **1993**, *115*, 8873-8874. (b) Corey, E. J.; Lin, S. *J. Am. Chem. Soc.* **1996**, *118*, 8765-8766. (c) Corey, E. J.; Wood, H. B. *J. Am. Chem. Soc.* **1996**, *118*, 11982-11983. (d) Johnson, W. S. *Acc. Chem. Res.* **1968**, *1*, 1-8. (e) Johnson, W. S. *Angew. Chem., Int. Ed.* **1976**, *15*, 9-17. (f) Johnson, W. S.; Bartlett, W. R.; Czeskis, B. A.; Gautier, A.; Lee, C. H.; Lemoine, R.; Leopold, E. J.; Luedtke, G. R.; Bancroft, K. J. *J. Org. Chem.* **1999**, *64*, 9587-9595. (g) Mi, Y.; Schreiber, J. V.; Corey, E. J. *J. Am. Chem. Soc.* **2002**, *124*, 11290-11291.

4. (a) Ishihara, K.; Ishibashi, H.; Yamamoto, H. *J. Am. Chem. Soc.* **2002**, *124*, 3647-3655. (b) Nakamura, S.; Ishihara, K.; Yamamoto, H. **2000**, *122*, 8131-8140.

5. (a) Hoye, T. R.; Kurth, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 5065-5067. (b) Nishizawa, M.; Takenaka, H.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 806-813.

6. (a) Grütter, C.; Alonso, E.; Chougnet, A.; Woggon, W.-D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1126-1130. (b) Ishibashi, H.; Ishihara, K.; Yamamoto, H. *J. Am. Chem. Soc.* **2004**, *126*, 11122-11123. (c) Kumazawa, K.; Ishihara,



Without an enzyme pocket to stabilize intermediate carbocations formed from polyolefin cyclizations, the Stork-Eschenmoser postulate predicts the stereochemistry of the cyclized product.[7] If an E-olefin is cyclized, then a trans ring juncture should be formed; a cis ring juncture results from the cyclization of a Z-olefin (Figure 1.1). This effect is due to the favorable anti addition of the nucleophile and electrophile across the double bond. However, it is important to have good neighboring group participation as this lowers the energy of the transition state (and intermediates)and avoids the formation of a full carbocation which can erode stereochemical information. Additionally, highly reactive initiators can also negate the effect of neighboring group participation by lowering the activation energy of the cyclization and producing a stereomixture of products.

K.; Yamamoto, H. *Org. Lett.* **2004**, *6*, 2551-2554. (d) Sakakura, A.; Ishihara, K. *Chim. Oggi* **2007**, *25*, 9-12. (e) Sakakura, A.; Ukai, A.; Ishihara, K. *Nature* **2007**, *445*, 900-903. (f) Uyanik, M.; Ishihara, K.; Yamamoto, H. *Org. Lett.* **2006**, *8*, 5649-5652. (g) Zhao, Y.-J.; Loh, T.-P. *J. Am. Chem. Soc.* **2008**, *130*, 10024-10029.

7. (a) Eschenmoser, A.; Ruzika, L.; Jeger, O.; Arigoni, D. *Helv. Chim. Acta* **1955**, *38*, 1890-1904. (b) Stork, G.; Burgstahler, A. W. *J. Am. Chem. Soc.* **1955**, *77*, 5068-5077.

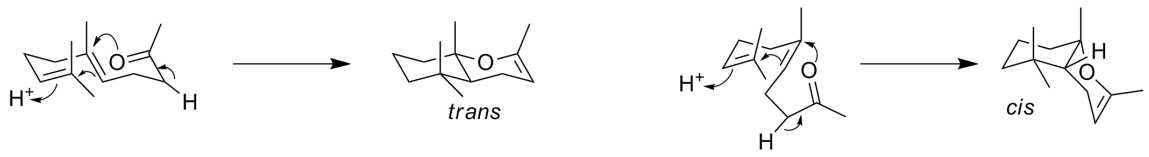


Figure 1.1. Stork-Eschenmoser postulate.

C. Pt(II) and Pd(II) cycloisomerization reactions. Another means of initiating polyolefin cascade cyclizations is the use of transition metals. Pt(II) and Pd(II), unlike Lewis and Brønsted acids and Hg^{2+} salts, have been shown to preferentially activate the least substituted olefin [8] for nucleophilic attack (eq 1.4). [9, 10] Their ability to selectively electrophilically activate one olefin over another can be used as a means to direct activation to a specific olefin in a substrate. For example, in substrates such as the dienyl phenol shown in eq 1.4, activation selectively occurs at the terminus. [11] This electrophilic activation initiates a cascade cyclization wherein the tertiary carbocation is ultimately trapped by the pendant phenol, generating a Pt-alkyl, **1**, and an equivalent of ammonium acid. **1** is stable to β-H elimination even at elevated temperatures because both of the *cis* coordination sites are

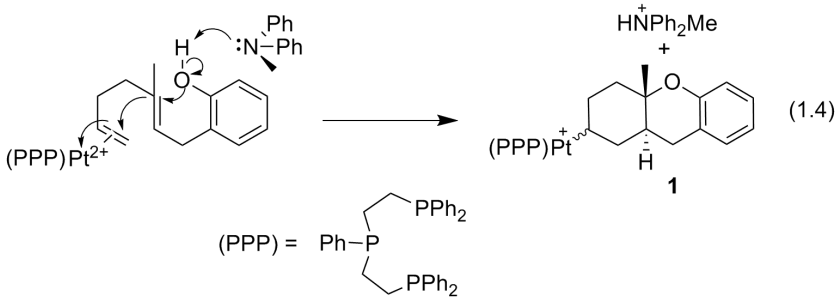
8. (a) Chianese, A. R.; Lee, S. J.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 4042-4059. (b) Cucciolito, M. E.; D'Amora, A.; Vitagliano, A. *Organometallics* **2005**, *24*, 3359-3361. (c) Liu, C.; Han, X.; Wang, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 3700-3701. (d) Overman, L. E.; Knoll, F. M. *J. Am. Chem. Soc.* **1980**, *102*, 865-867.

9. (a) Hegedus, L. S. *Comprehensive Organic Synthesis*. Trost, B. M.; Fleming, I., Eds. Pergamon Press: Oxford, 1990; Vol. 4, pp 571-583. (b) Hegedus, L. S. In *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; p 199-236.

[10] For examples of Pd(II) and Pt(II) activation of alkenes for nucleophilic attack, see: (a) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009-3066. (b) Brunet, J.-J.; Chu, N. C.; Diallo, O. *Organometallics* **2005**, *24*, 3104-3110. (c) Hahn, C. *Chem. Eur. J.* **2004**, *10*, 5888-5899. (d) Hahn, C.; Cucciolito, M. E.; Vitagliano, A. *J. Am. Chem. Soc.* **2002**, *124*, 9038-9039. (e) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 12640-12646. (f) Liu, C.; Bender, C. F.; Han, X.; Widenhoefer, R. A. *Chem. Commun.* **2007**, 3607-3618. (g) McKeown, B. A.; Foley, N. A.; Lee, J. P. *Organometallics* **2008**, *27*, 4031-4033. (h) Michael, F. E.; Cochran, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 4246-4247. (i) Michael, F. E.; Cochran, B. M. *J. Am. Chem. Soc.* **2008**, *130*, 2786-2792. (j) Minatti, A.; Mũniz, K. *Chem. Soc. Rev.* **2007**, *36*, 1142-1152. (k) Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285-2309.

11. Koh, J. H.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 3459-3461.

occupied thus blocking the low energy pathway for hydride migration.[12] The ammonium acid is not sufficiently acidic to protonolyze the cationic Pt-alkyl and the organic product must be recovered by stoichiometric reductive cleavage.



1.2 Research Objective 1

We have demonstrated that dicationic (PPP)Pt can cyclize polyolefins to form a transient Pt-alkyl carbocation which is intramolecularly trapped by a nucleophilic pendant phenol. The (PPP)Pt-alkyl is stable to protonolysis with the in situ generated acid. A model system has shown that protonolysis from a cationic (PPP)Pt-alkyl (e.g., **1**) is not feasible even with a very electron rich PPP derivative.[13] Increasing the acid strength promotes a Brønsted acid catalyzed cyclization of the substrate and is therefore ineffectual.

It was later found that a similar oxidative cyclization could be performed with a dicationic (P_2)Pt catalyst.[14] This cyclization involved a β-hydride elimination from an

12. For other examples of triphosphine ligands inhibiting β-H elimination, see: (a) Arai, I.; Daves, G. D. J., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 7683. (b) Arnek, R.; Zetterberg, K. *Organometallics* **1987**, *6*, 1230-1235. (c) Cucciolito, M. E.; D'Amora, A.; Vitagliano, A. *Organometallics* **2005**, *24*, 3359-3361. (d) Hahn, C.; Morvillo, P.; Herdtweck, E.; Vitagliano, A. *Organometallics* **2002**, *21*, 1807-1818. (e) Oestreich, M.; Dennison, P. R.; Kodanko, J. J.; Overman, L. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 1439-1442. (f) Zhang, L.; Zetterberg, K. *Organometallics* **1991**, *10*. (g) Feducia, J. A.; Campbell, A. N.; Doherty, M. Q.; Gagné, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 13290-13297.

13. Feducia, J. A.; Campbell, A. N.; Anthis, J. W.; Gagné, M. R. *Organometallics* **2006**, *25*, 3114-3117.

14. Mullen, C. A.; Gagné, M. R. *J. Am. Chem. Soc.* **2007**, *129*, 11880-11881.

intermediate (P_2)Pt-alkyl cation to generate a putative $(P_2)PtH^+$. The hydride was abstracted using a stoichiometric amount of Ph_3CBF_4 to regenerate the catalyst. The use of Ph_3CBF_4 produced an effective catalytic cycle, but requiring a molecule as heavy as Ph_3CBF_4 to abstract a hydride detracts from the atom efficiency normal associated with cyclizations. Although numerous other oxidants were screened, only Ph_3CBF_4 was capable of turning over the catalytic cycle.

This work was initiated to develop an alternative approach for protonolyzing a cationic (PPP)Pt-C bond. Utilizing a cationic (PPP)Pt-alkenyl generated from the cyclization of an enyne-ol seemed to provide an alternative means of protonolysis. The resting state and mechanism of the catalytic cycle that resulted from this area of study are herein examined and will be elucidated in chapter 2.

1.3 Tropos Ligands

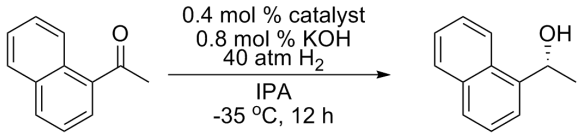
Another research goal was to use outersphere techniques to modify the chiral pocket around a catalytic metal allowing for asymmetric induction via chiral auxiliaries. To best achive this goal we wished to utilize *tropos* ligands. *Tropos* is the Greek word for 'turn;' *a* is Greek for 'not.' These words have included themselves into the chemical lexicon to describe molecules containing an axis. If there is free rotation about the axis at RT, the molecule is considered to be *tropos*; when rotation is hindered, the molecule is considered *atropos*.[15] This terminology is often utilized to describe ligands bound to metals that are used for catalysis. Chiral ligands (e.g. BINAP, P-Phos, MeO-BIPHEP) are referred to as atropisomeric and can be used as the sole source of chirality in an asymmetric reaction.

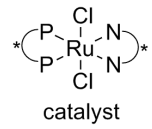
15. Rotation energy barrier of greater than 22.3 kcal/mol at 300K is considered *atropos*: See Oki, M.; Yamamoto, G. *Bull. Chem. Soc. Jpn.* **1971,** *44*, 266-270**.**

Tropos ligands may remain *tropos* when attached to a metal ((dppf)$PtCl_2$) or become atropisomeric upon coordination to a metal ((BIPHEP)$PtCl_2$).

Many ligands contain an axis with a rotational barrier too low to be useful in asymmetric catalysis.[16] However, these *tropos* ligands can be used in conjunction with chiral auxiliaries to generate greater enantioselectivity. The first report of BIPHEP being used as a chiral ligand was for the hydrogenation of methyl naphthyl ketone (Table 1.1).[17] The enantiomeric increase is 4%; however BIPHEP did not require a resolution step like BINAP.

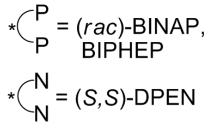
Table 1.1. A comparison of Ru hydrogenation catalysts containing a *tropos* or *atropos* ligand.[a]





catalyst

catalyst	% yield	% *e.e*
(BIPHEP)$RuCl_2$((*S,S*)-DPEN)	99	92
((*rac*)-BINAP)$RuCl_2$((*S,S*)-DPEN)	99	89



[a]Catalyst was allowed to stir in IPA for 3 h, in order to reach thermodynamic equilibrium.

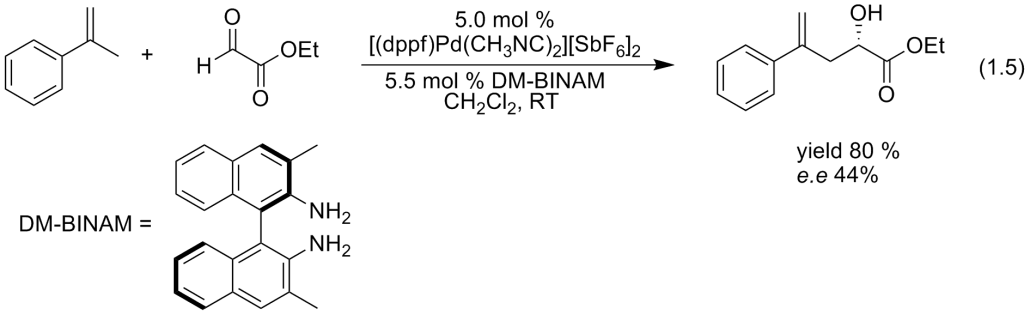
Another important example of using a chiral auxiliary to generate an enantioselective reaction with a *tropos* ligand is the glyoxylated-ene reaction catalyzed by (dppf)Pd^{2+} (eq 1.5).[18] It is believed that during the course of the catalytic cycle DM-BINAM reversibly coordinates to (dppf)Pd^{2+} and sets the stereo-axis of dppf. The DM-BINAM is then dissociated with the association of the ethyl glyoxylate. The set stereo-axis of dppf offers an

16 . For review see: (a)Walsh, P. J.; Lurain, A. E.; Balsells, J. *Chem. Rev.* **2003,** *103*, 3297-3344. (b) Mikami, K.; Yamanaka, M. *Chem. Rev.* **2003,** *103*, 3369-3400 and references therein.

17. Mikami, K.; Korenaga, T.; Terada, M.; Ohkuma, T.; Pham, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1999,** *38*, 495-497

18. Mikami, K.; Aikawa, K. *Org. Lett.* **2002,** *4*, 99-101.

enantioenriched catalyst, and its chirality is subsequently transferred to the product. (dppf)Pd^{2+} has a fast rotation around the C_2 axis that can be resolved by other chiral nitrogen donors (e.g., DPEN, BINAM). The resolution induced by DPEN is slower for this complex and the enantioenrichment also suffers 27% compared to 44% with DM-BINAM demonstrating the need for fast resolution in this system.



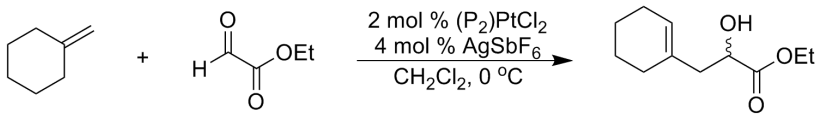
(1.5)

We have formed enantioresolved ((*R* and *S*)-BIPHEP)$PtCl_2$ catalysts by performing a ligand exchange on (COD)$PtCl_2$ followed by forming diastereomers upon reaction of ((*rac*)-BIPHEP)$PtCl_2$ with Na_2(*S*)-BINOLate. The 1:1 mixture of diastereomers was separated through crystallization and treated with HCl releasing the (*S*)-BINOL and generating the precatalyst with the stereodefined axis set.[19] The atropisomeric complexes were used as catalysts for the Diels-Alder and glyoxylate-ene reaction (Table 1.2).[20] Both catalyst generated the desired product with good *e.e.* and moderate to good yields.

19. Tudor, M. D.; Becker, J. J.; White, P. S.; Gagné, M. R. *Organometallics* **2000,** *19*, 4376-4384.

20. Becker, J. J.; White, P. S.; Gagné, M. R. *J. Am. Chem. Soc.* **2001,** *123*, 9478-9479.

Table 1.2. The use of resolved (BIPHEP)$PtCl_2$ as a chiral catalyst[a]



$(P_2)PtCl_2$	% conversion	% *e.e.*[b]	stereochemistry
(*S*)-(BIPHEP)$PtCl_2$	90	70	*S*
(*R*)-(BIPHEP)$PtCl_2$	62	70	*R*

[a]Reactions were run with 3:1 equiv of methylene cyclohexane to ethyl glyoxylate for 4 h. [b]Determined by chiral GC.

1.4 Research Objective 2

We and others have demonstrated the *tropos* nature of BIPHEP can be attenuated through coordination to a substitutionally inert metal such as Pt to form an atropisomeric complex. Once resolved, enantiopure (BIPHEP)Pt^{2+} performs as a chiral Lewis acid catalyst, capable of catalyzing Diels-Alder or glyoxylate-ene reactions with moderate to good yields and moderate e.e.

This work describes the synthesis of a new tropos ligand analogous to BIPHEP but with nitrogen atoms in the 2,2' position allowing for free rotation on the metal or off. The nitrogen atoms, in addition to allowing free rotation, afford the opportunity to control the stereochemistry of the biaryl axis though H-bond interactions. The screening of H-donors to create a stereopreference and the use of this system as a catalyst in the glyoxylate-ene reaction are examined. The results are presented in chapter 3.

Chapter 2

Probing the Mechanism of Platinum(II) Enyne Cycloisomerization

2.1 Introduction

In nature enzymes can convert polyolefins into a wide array of cyclic products.[1] For example, squalene-hopene cyclase catalyzes the cycloisomerization of the polyolefin squalene to the plant steroid hopene.[1a] Secondary effects in the enzyme pocket allow for pre-organization of the substrate prior to the cascade cyclization, resulting in the generation of five rings and nine new stereocenters with perfect stereocontrol (Scheme 2.1). Similarly, triterpene cyclization is an important biological process for the formation of compounds such as *cis*-thujane (eq 2.1), (-)-3-isothujone (eq 2.2), *cis*-sabinene hydrate, (+)-sabinol, and (+)-sabinene.[2] These cyclopropane derivatives are synthetically relevant in perfume and food chemistry as well as agricultural industry.[3]

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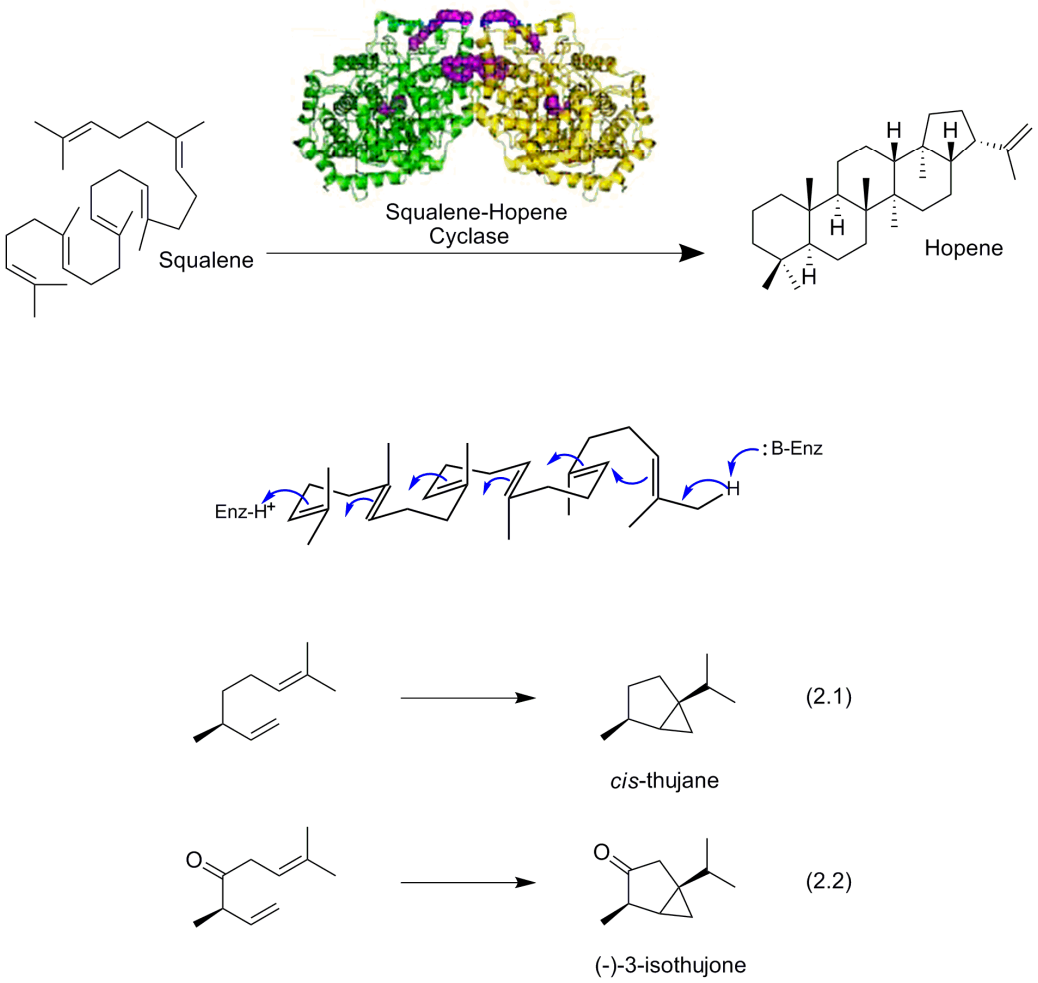
1. (a) Abe, I.; Rhomer, M.; Prestwhich, G. D. *Chem. Rev.* **1993**, *93*, 2189-2206. (b) Wendt, K. U.; Schulz, G. E.; Corey, E. J.; Liu, D. R. *Angew. Chem. Int. Ed.* **2000**, *39*, 2812-2833. (c) Yoder, R. A.; Johnston, J. N. *Chem. Rev.* **2005**, *105*, 4730-4756.

2. Crouteau, R. *Chem. Rev.* **1987**, *87*, 929-954.

3. Crouteau, R. *Recent Developments in Flavor and Fragrance Chemistry: Proceedings of the 3rd International Harmann & Reimer Symposium*; VCH: Weinheim, 1993; p 263-273.

Scheme 2.1



The incorporation of oxygen as a nucleophilic trap allows for the synthesis of other classes of biologically relevant molecules.[4] These types of compounds offer an alternative means of terminating the cascade cyclization. The cyclized variants of these compounds are

4. (a) Alvarez-Manzaneda, E. J.; Chahboun, R.; Cabrera, E.; Alvarez, E.; Haidour, A.; Ramos, J. M.; Alvarez-Manzaneda, R.; Hmamouchi, M.; Bouanou, H. *J. Org. Chem.* **2007**, *72*, 3332-3339. (b) Laird, D. W.; Poole, R.; Wikstrom, M.; van Altena, I. A. *J. Nat. Prod.* **2007**, *70*, 671-674. (c) Mente, N. R.; Neighbors, J. D.; Wiemer, D. F. *J. Org. Chem.* **2008**, *73*, 7963-7970. (d) Pecchio, M.; Solis, P. N.; Lopez-Perez, J. L.; Vasquez, Y.; Rodriguez, N.; Olmedo, D.; Correa, M.; San Feliciano, A.; Gupta, M. P. *J. Nat. Prod.* **2006**, *69*, 410-413. (e) Yamamoto, H.; Inoue, K.; Li, S.-M.; Heide, L. *Planta* **2000**, *210*, 312-317.

naturally occurring biomolecules that have shown properties as antimicrobials,[4d] anticancer agents (Schweinfurthins),[4a,4c] as well as antioxidants (Flavonoids) (Figure 2.1).[5]

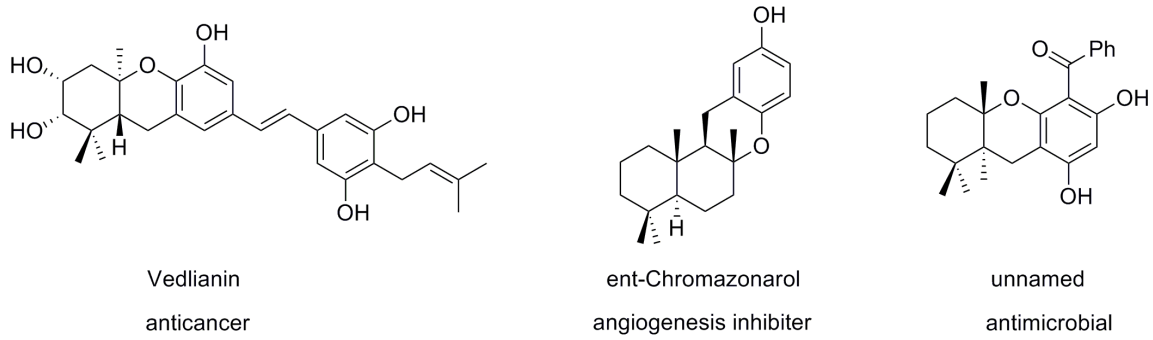


Figure 2.1 Examples of medicinally important natural products that contain cyclic ethers.

Biomimetic cycloisomerization reactions are of great synthetic interest due to their ability to convert simple unsaturated starting materials into useful complex polycyclic products.[1c] These reactions have gained attention due to their atom efficiency. Attempts at achieving enzyme-like selectivity have focused on protonation with Brønsted acids (eq 2.3),[6] ionization with Lewis acids (eq 2.4)[7] and even addition of Hg^{+2} (eq 2.5).[8] In all of these

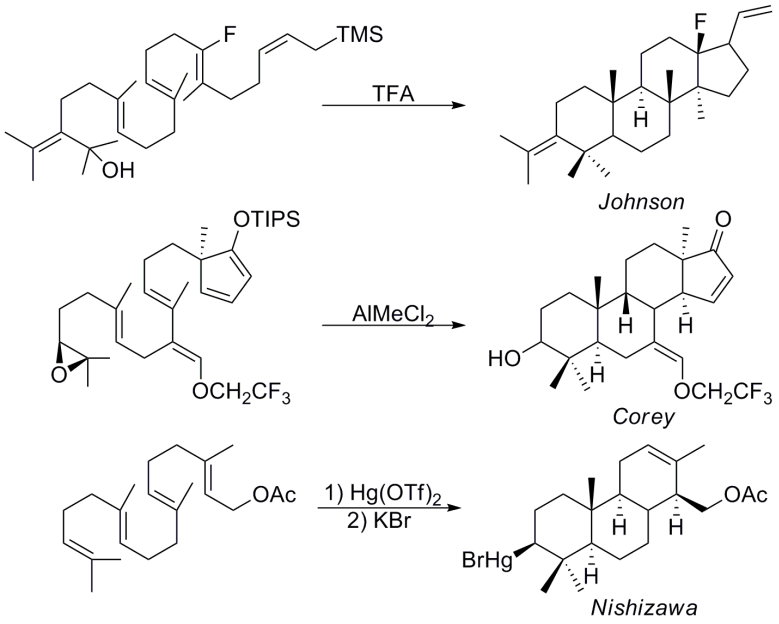
5. (a) Corbett, J. R. *The Biochemical Mode of Action of Pesticides*; Academic Press: New York, 1974. (b) Matsumura, F. *Toxicity of Insecticides*; Plenum Press: New York, 1985. (c) O'Brien, R. D. *Insecticides, Action and Metabolism*; Academic Press: New York, 1967.

6. (a) Corey, E. J.; Lee, J. *J. Am. Chem. Soc.* **1993**, *115*, 8873-8874. (b) Corey, E. J.; Lin, S. *J. Am. Chem. Soc.* **1996**, *118*, 8765-8766. (c) Corey, E. J.; Wood, H. B. *J. Am. Chem. Soc.* **1996**, *118*, 11982-11983. (d) Johnson, W. S. *Acc. Chem. Res.* **1968**, *1*, 1-8. (e) Johnson, W. S. *Angew. Chem., Int. Ed.* **1976**, *15*, 9-17. (f) Mi, Y.; Schreiber, J. V.; Corey, E. J. *J. Am. Chem. Soc.* **2002**, *124*, 11290-11291. (g) Johnson, W. S.; Bartlett, W. R.; Czeskis, B. A.; Gautier, A.; Lee, C. H.; Lemoine, R.; Leopold, E. J.; Luedtke, G. R.; Bancroft, K. J. *J. Org. Chem.* **1999**, *64*, 9587-9595.

7. (a) Ishihara, K.; Ishibashi, H.; Yamamoto, H. *J. Am. Chem. Soc.* **2002**, *124*, 3647-3655. (b) Nakamura, S.; Ishihara, K.; Yamamoto, H. **2000**, *122*, 8131-8140.

8. (a) Hoye, T. R.; Kurth, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 5065-5067. (b) Nishizawa, M.; Takenaka, H.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 806-813.

examples, the cyclization cascade is initiated at the most substituted olefin. Asymmetric examples are more limited but offer a greater degree of stereocontrol.[9]



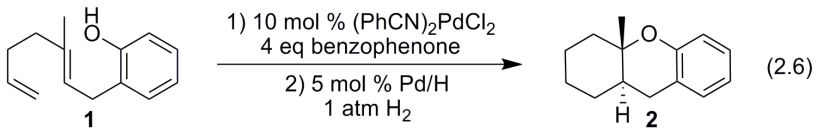
With traditional Lewis acids the cyclization is initiated at the most substituted olefin. Transition metal catalysts offer access to a wide variety of polycyclization mechanisms. Group 10 metal catalysts (e.g., Pd(II), Pt(II)) are unique in their ability to activate the least substituted olefin.[10,11,12] As shown in eq 2.6, the oxidative cyclization of **1** is initiated by

9. (a) Grütter, C.; Alonso, E.; Chougnet, A.; Woggon, W.-D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1126-1130. (b) Ishibashi, H.; Ishihara, K.; Yamamoto, H. *J. Am. Chem. Soc.* **2004**, *126*, 11122-11123. (c) Kumazawa, K.; Ishihara, K.; Yamamoto, H. *Org. Lett.* **2004**, *6*, 2551-2554. (d) Sakakura, A.; Ishihara, K. *Chim. Oggi* **2007**, *25*, 9-12. (e) Sakakura, A.; Ukai, A.; Ishihara, K. *Nature* **2007**, *445*, 900-903. (f) Uyanik, M.; Ishihara, K.; Yamamoto, H. *Org. Lett.* **2006**, *8*, 5649-5652. (g) Zhao, Y.-J.; Loh, T.-P. *J. Am. Chem. Soc.* **2008**, *130*, 10024-10029.

10. (a) Hegedus, L. S. In *Comprehensive Organic Synthesis*. Trost, B. M.; Fleming, I., Eds. Pergamon Press: Oxford, 1990; Vol. 4, pp 571-583. (b) Hegedus, L. S. In *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; p 199-236.

11. For examples of Pd(II) activation of alkenes, see: (a) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009-3066. (b) Hahn, C. *Chem. Eur. J.* **2004**, *10*, 5888-5899. (c) Michael, F. E.; Cochran, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 4246-4247. (d) Michael, F. E.; Cochran, B. M. *J. Am. Chem. Soc.* **2008**, *130*, 2786-2792. (e) Minatti, A.; Mũniz, K. *Chem. Soc. Rev.* **2007**, *36*, 1142-1152. (f) Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285-2309.

Pd(II) which selectively activates the terminal olefin for nucleophilic attack.[13] This results in a cascade cyclization reaction in which the 3° carbocation is intramolecularly trapped by the pendant phenol. The mixture of olefin isomers were hydrogenated to yield **2**, which is the core fragment of many natural products (Figure 2.1).



(2.6)

We have previously shown that (PPP)Pt(II) Lewis acids are similarly capable of cyclizing diene-ols to generate poly-heterocyclic (PPP)Pt-alkyls (eq 2.7).[14] The resulting (PPP)Pt-alkyls are stable to β-hydride elimination due to the coordinatively saturated Pt.[15] Furthermore, the in situ generated acid is not sufficiently acidic to protonate the Pt-C bond to release the product and regenerate the catalyst.[16] Although the organic product can be cleaved with $NaBH_4$, the net process is stoichiometric in Pt.

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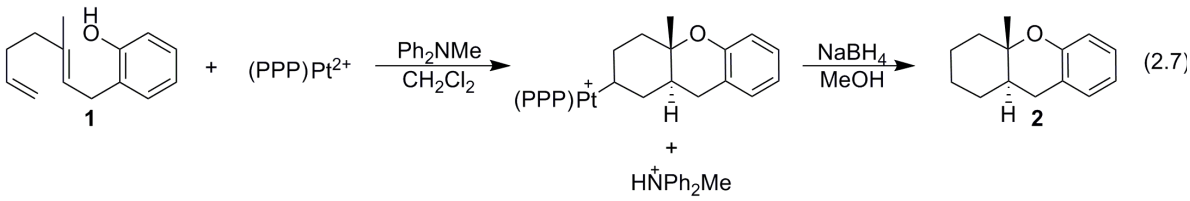
12. For examples of Pt(II) activation of alkenes, see: (a) Brunet, J.-J.; Chu, N. C.; Diallo, O. *Organometallics* **2005**, *24*, 3104-3110. (b) Hahn, C.; Cucciolito, M. E.; Vitagliano, A. *J. Am. Chem. Soc.* **2002**, *124*, 9038-9039 and references therein. (c) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 12640-12646. (d) Liu, C.; Bender, C. F.; Han, X.; Widenhoefer, R. A. *Chem. Commun.* **2007**, 3607-3618. (e) McKeown, B. A.; Foley, N. A.; Lee, J. P. *Organometallics* **2008**, *27*, 4031-4033.

13. (a) Koh, J. H.; Mascarenhas, C.; Gagné, M. R. *Tetrahedron* **2004**, *60*, 7405-7410. (b) Korotchenko, V. N.; Gagné, M. R. **2007,** *72*, 4877-4881.

14. Koh, J. H.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 3459-3461.

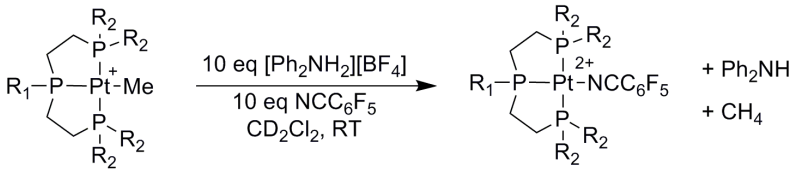
15. For other examples of triphosphine ligands inhibiting β-H elimination, see: (a) Arai, I.; Daves, G. D. J., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 7683. (b) Arnek, R.; Zetterberg, K. *Organometallics* **1987**, *6*, 1230-1235. (c) Cucciolito, M. E.; D'Amora, A.; Vitagliano, A. *Organometallics* **2005**, *24*, 3359-3361. (d) Hahn, C.; Morvillo, P.; Herdtweck, E.; Vitagliano, A. *Organometallics* **2002**, *21*, 1807-1818. (e) Oestereich, M.; Dennison, P. R.; Kodanko, J. J.; Overman, L. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 1439-1442. (f) Zhang, L.; Zetterberg, K. *Organometallics* **1991**, *10*. (g) Feducia, J. A.; Campbell, A. N.; Doherty, M. Q.; Gagné, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 13290-13297.

16. Cationic Pt-alkyls are notoriously difficult to protonolyze: (a) Annibale, G.; Bergamini, P.; Cattabriga, M. *Inorg. Chim. Acta.* **2001**, *316*, 25-32. (b) Butikofer, J. L.; Hoerter, J. M.; Peters, R. G.; Roddick, D. M. *Organometallics* **2004**, *23*, 400-408. (c) Heyduk, A. F.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**,



Efforts to alter the substituents on the phosphines of the PPP ligand yielded a series of electron rich (PPP)Pt(II) species which did significantly accelerate the protonolysis of a model (PPP)Pt-Me with an ammonium acid (Scheme 2.2).[17,18] However, this methodology was not amenable to more complex Pt-alkyls, and protonolysis was still not a viable option for catalyst turnover of more catalytically relevant polyenes. To induce protonolysis of a Pt-C bond it appeared that ligand modification would prove insufficient; therefore, an alternative substrate would be needed.

Scheme 2.2



R_1	R_2	half-life (min)
Et	Et	<5
Ph	Et	10
Et	Ph	195
Ph	Ph	445

125, 6366-6367. (d) Peters, R. G.; White, S.; Roddick, D. M. *Organometallics* **1998**, *17*, 4493-4499. (e) Thom, D. L. *Organometallics* **1998**, *17*, 348-352.

17. Feducia, J. A.; Campbell, A. N.; Anthis, J. W.; Gagné, M. R. *Organometallics* **2006**, *25*, 3114-3117.

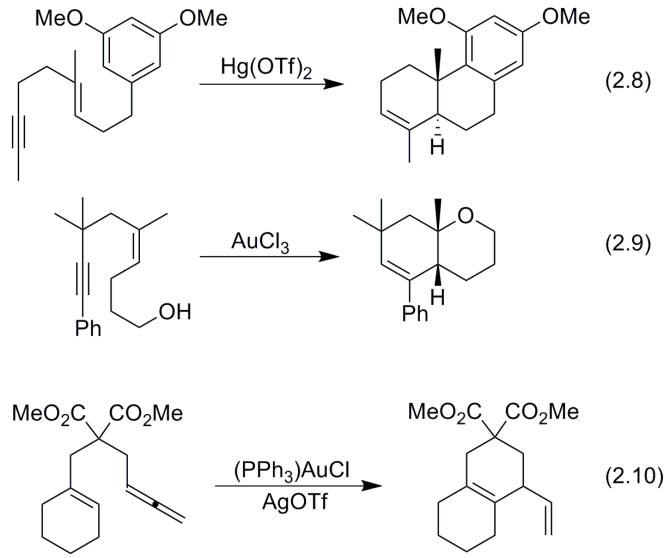
18. $[Ph_2NH_2][BF_4]$, pKa = 0.8; see: Stewart, R.; Dolman, D. *Can. J. Chem.* **1967**, *45*, 925-928.

The cycloisomerizations of enynes by transition metals often produce metal vinyl intermediates.[19] These metal-alkenyl species have been shown to undergo protonolysis[20] while their metal-alkyl analogs are acid stable. For example, eq 2.5 shows a cyclization that uses stoichiometric $Hg(OTf)_2$ to promote a cascade cyclization of a diene yielding a Hg-alkyl complex stable to protonolysis. As exemplified by eq 2.8, the Hg-alkenyl created though the cyclization of an enyne has increased reactivity toward acid, and the Hg-C bond is efficiently cleaved with the in situ generated triflic acid.[20a] This reactivity is not unique to Hg-alkenyl bonds. Many other metal-vinyl intermediates generated by enyne cycloisomerization can undergo protonolysis as a turnover mechanism, including Pt,[20b,20g] Pd,[20c] and Au (eq 2.9).[20b, 20d-g] Au catalyzed allenene cycloisomerizations also form transient Au-alkenyl intermediates that readily undergo protonolysis of the Au-C bond (eq 2.10).[21]

19. For review on transition metal catalyzed enyne cycloisomerizations, see: (a) Fürstner, A.; Davies, P. W. *Angew. Chem. Int. Ed.* **2007**, *46*, 3410-3449. (b) Michelet, V.; Toullec, P. Y.; Genêt, J.-P. *Angew. Chem. Int. Ed.* **2008**, *47* 4268-4315. (c) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1-16. (d) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271-2296 and references therein.

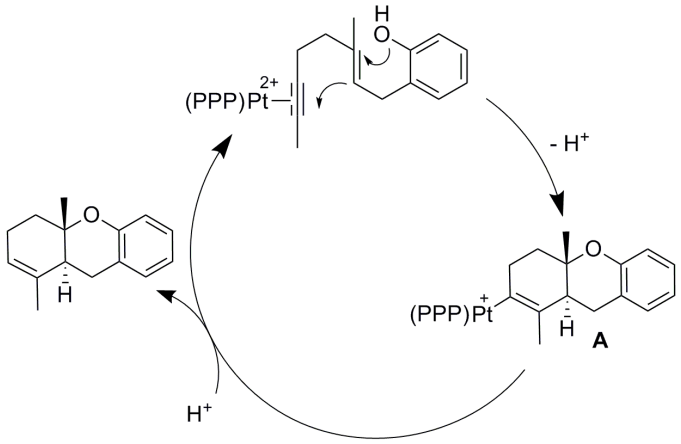
20. (a) Imagawa, H.; Iyenaga, T.; Nishizawa, M. *Org. Lett.* **2005**, *7*, 451-453. (b) Nevado, C.; Cárdena, D. J.; Echavarren, A. M. *Chem. Eur. J.* **2003**, *9*, 2627-2635. (c) Nevado, C.; Charruault, L.; Michelet, V.; Nieto-Oberhuber, C.; Muñoz, M. P.; Méndez, M.; Mager, M.-N.; Genêt, J.-P.; Echavarren, A. M. *Eur. J. Org. Chem.* **2003**, 706-713. (d) Toullec, P. Y.; Genin, E.; Leseurre, L.; Genêt, J.-P.; Michelet, V. *Angew. Chem. Int. Ed.* **2006**, *45*, 7427-7430. (e) Yao, T.; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 11164-11165. (f) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 11806-11807. (g) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2006**, *128*, 9705-9710.

21. (a) Tarselli, M. A.; Chianese, A. R.; Lee, S. J.; Gagné, M. R. *Angew. Chem. Int. Ed.* **2007**, *46*, 6670-6673. (b) Tarselli, M. A.; Gagné, M. R. *J. Org. Chem.* **2008**, *73*, 2439-2441.



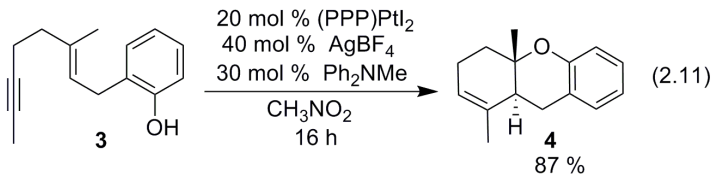
By using an enyne for cycloisomerization, we believed that the $(PPP)Pt^{2+}$ would initiate a Pt(II) mediated cyclization analogous to eq 2.7. First, coordination of the Pt-catalyst to the electron rich alkyne would electrophilically activate the alkyne for nucleophilic attack by the alkene. The 3^{o} cation would be trapped by the alcohol generating a Pt-alkenyl and releasing a proton. The resulting Pt-alkenyl (**A**, Scheme 2.3) is expected to be protonated by the in situ generated acid resulting in the release of product and regeneration of the active catalyst (Scheme 2.3).

Scheme 2.3



2.2 Results and Discussion

To test the hypothesis that a Pt-alkenyl would be more susceptible to protonolysis (as compared to analogous Pt-alkyls which are inert to protonolysis), an enyne-ol substrate analogous to **1** was prepared (**3**). The active Pt catalyst was generated by iodide abstraction from (PPP)PtI_2 with 2.0 equiv $AgBF_4$ in nitromethane to form a (PPP)Pt^{2+}-nitromethane adduct in situ (δ = 77 ppm, $J_{Pt\text{-}P}$ = 3500 Hz).[22] 5.0 equiv of **3** and 1.5 equiv Ph_2NMe (to mediate proton transfer)[23] were added to the activated catalyst (eq 2.11). Monitoring by in situ ^{31}P NMR revealed two distinct Pt-complexes present in a 1:1 ratio. The observed Pt-P coupling constants and ^{31}P NMR chemical shifts (δ = 91 and 86 ppm, $J_{Pt\text{-}P}$ = 1400 Hz) were consistent with the expected coupling constants for a (PPP)Pt-alkenyl cation.[24] These (PPP)Pt-alkenyl resonances remained in a 1:1 ratio until substrate consumption was complete (^1H and ^{31}P NMR) and yielded the (PPP)Pt^{2+}-nitromethane adduct. A single product (**4**) was isolated from the reaction mixture which was consistent with a 6-endo cyclization followed by protonolysis.



(2.11)

Because two seemingly distinct Pt-alkenyls yielded a single organic product, the identity of these two species was investigated. The Pt-alkenyls could be isolated from the

22. $J_{Pt\text{-}P}$ coupling constants are reported for the central P of the triphos ligand that is *trans* to the reactive site.

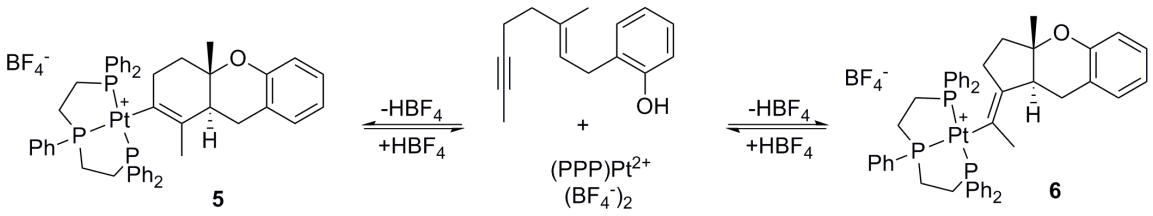
23. In the absence of Ph_2NMe, the acid byproduct of cyclization can cause Brønsted cyclization processes to initiate.

24. (PPP)Pt-alkyl cations typically have coupling constants for the *trans* P between 1300 and 1500 Hz, see footnotes 14 and 17.

catalytic cycle through precipitation upon addition of Et_2O. While this afforded the desired intermediates, trace amounts of Ag byproducts contaminated the Pt-complexes. The Pt complexes could be made independently by reacting $[(PPP)Pt(NCC_6F_5)][BF_4]_2$ with 1.5 equiv of piperidinomethyl polystyrene resin and 1.5 equiv of **3**. Filtering off the base followed by precipitation of the Pt-alkenyls with Et_2O and recrystallization by slow evaporation of a mixture of CH_2Cl_2 and Et_2O produced fine white needles. The crystals were taken up in CD_2Cl_2 at -78 ^oC, and ^{31}P and ^1H NMR spectra indicated that a single Pt-species had crystallized and persisted up to -18 ^oC, where upon the other platinum complex began to grow in until the 1:1 ratio was reestablished.

At first we postulated that the two Pt-alkenyls arose from a 6-endo (**5**) and a 5-exo (**6**) cyclization of the substrate which were in equilibrium through proton coupled retrocyclization (Scheme 2.4).[25] If retrocyclization of **6** and protonolysis of **5** were faster than protonolysis of **6**, then the catalytic results could be rationalized. However, this seemed less likely as the low temperature NMR studies revealed that the two Pt species could interconvert in the absence of acid.

Scheme 2.4



To further probe the nature of the two Pt species, the organic fragment was cleaved. Protonolysis with 2.0 equiv of HCl was carried out at low temperature (-78 ^oC) to avoid

25. (a) Feducia, J. A.; Gagné, M. R. *J. Am. Chem. Soc.* **2008**, *130*, 592-599. (b) Mullen, C. A.; Campbell, A. N.; Gagné, M. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 6011-6014.

isomerization. This yielded (PPP)$PtCl_2$ and **4**. Because proton coupled isomerization might still be an active pathway, an acid free method of cleaving the organic product was necessary. Reductive cleavage with 2.0 equiv $LiHBEt_3$ yielded the organic fragment cleanly as a single product (**4**). This experiment indicated that both Pt-alkenyls contain the 6-endo organic fragment.

An X-ray quality crystal of **5** was produced by layering pentane over a saturated solution of Pt-alkenyls in CH_2Cl_2 (Figure 2.2). The X-ray structure of **5** provided a possible explanation for the two Pt-alkenyl isomers. The C1/C14/C16 alkenyl plane is orientated orthogonal to the square plane of the Pt center. The alkenyl methyl (C16) can orientate *syn* to the central P-Ph (shown) or *anti*. If Pt-C bond rotation were slow on the NMR time scale, this would lead to two rotational isomers. Protonolysis or reductive cleavage of either rotamer would thus produce the same product, **4**. Hindered rotation around the Pt-C bond has not been seen in similar Pt-alkyls. For (PPP)Pt^{2+} catalyzed oxidative cyclizations of substrates which possess a substituent on the C14 position other than hydrogen, olefin coordination is the rate determining step, and therefore the Pt-alkyls have not been observed by spectroscopic techniques and could not be made independently. To determine if the hindered rotation around the Pt-C bond was the source of the two Pt complexes observed by ^{31}P and ^{1}H NMR, a new substrate with a terminal alkyne **7** was synthesized.

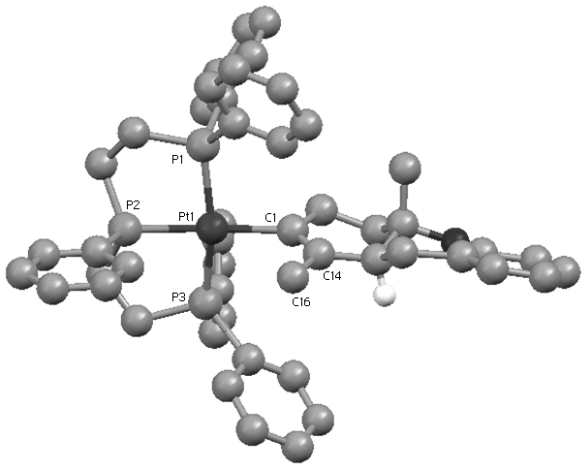
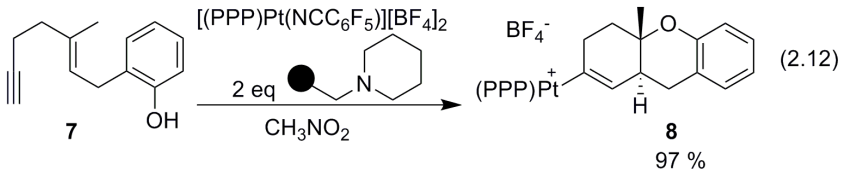


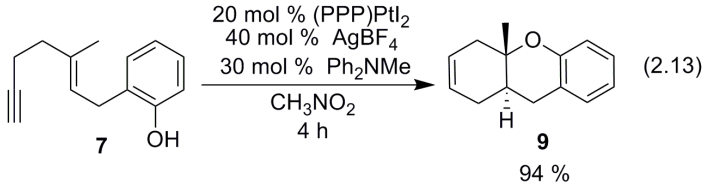
Figure 2.2 Chem3D representation of **5**. BF_4^- anion removed for clarity. Selected bond lengths (Å): Pt-P_1 = 2.283(6), Pt-P_2 = 2.275(6), Pt-P_3 = 2.284(6), Pt-C_1 = 2.10(2), C_1-C_{14} = 1.33(3). Selected bond angles (deg): C_1-Pt-P_1 = 97.6(5), C_1-Pt-P_3 = 93.0(5), P_1-Pt-P_2 = 84.4(2), P_2-Pt-P_3 = 85.4(2).

Reacting $[(PPP)Pt(NCC_6F_5)][BF_4]_2$ with 2.0 equiv of **7** and 2.0 equiv of piperidinomethyl polystyrene resin in CH_3NO_2 yielded a single Pt-alkenyl by ^{31}P and ^1H NMR (eq 2.12). This provided further evidence that the two Pt-alkenyls produced from substrate **3** were rotational isomers and that the methyl on C14 caused the rotational hindrance.



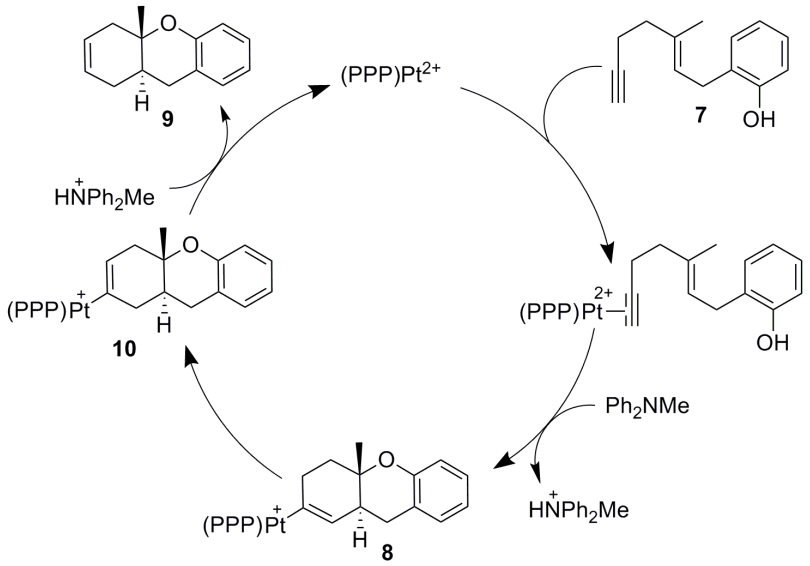
The terminal alkyne, **7**, was subjected to catalytic conditions (eq 2.13). The reaction time for this substrate was substantially faster as compared to **3** with complete consumption of **7** in 4 h. However, the expected cycloisomerization product was not observed. During the course of the reaction an olefin isomerization occurred producing only the

thermodynamically favored alkene **9**.[26] When the reaction was monitored by ^{31}P NMR, the resting state was found to be a single Pt-alkenyl. There were two likely possibilities for the resting state of the catalyst. The first was the unisomerized Pt-alkenyl **8** resulting from a slow isomerization and a fast protonolysis (Scheme 2.4). The second possibility was the isomerized Pt-alkenyl **10** which would result from a fast isomerization and a slow protonolysis.



(2.13)

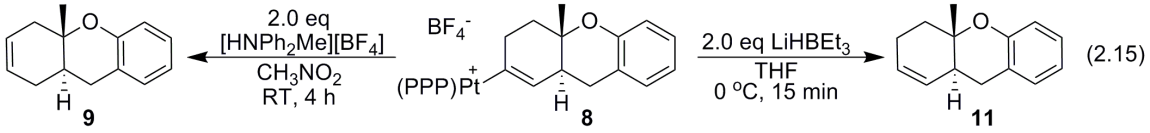
Scheme 2.5



The mechanism of this transformation was probed using stoichiometric reactions. Treatment of the isolated Pt-alkenyl with $LiHBEt_3$ in THF yielded the unisomerized product

26. DFT calculations on the products (B3LYP/6-31G*) indicated that **9** was more stable than **11** by 1.0 kcal/mol (MacSpartan 06).

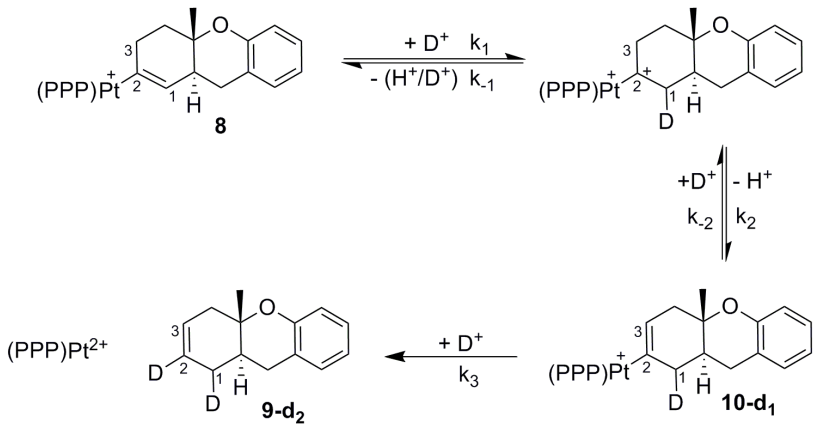
11 (eq 2.15). This indicated that the resting state was **8** and that olefin isomerization was the rate determining step. To ensure that the Pt-alkenyl isolated was the resting state along the catalytic cycle, it was treated with 2 equiv of $[HNPh_2Me][BF_4]$ in CD_3NO_2 to initiate turnover (eq 2.15). The reaction showed conversion of the Pt complex to the (PPP)Pt-nitromethane adduct and product **9**, further confirming that the catalyst rests as **8**.



(2.15)

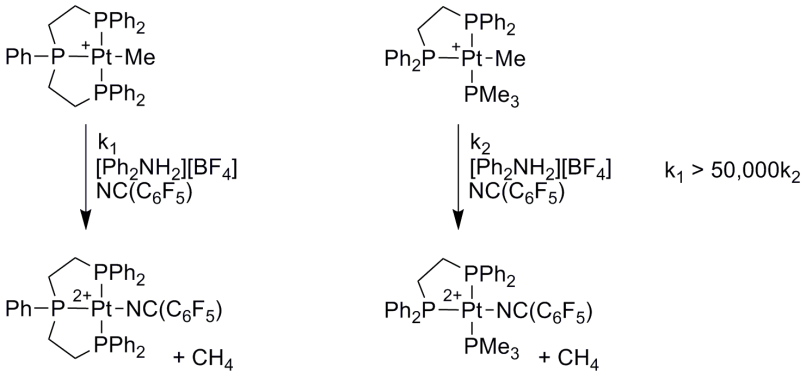
With the resting state elucidated, the mechanism of olefin migration and protonolysis was investigated. To determine the details regarding the reversibility of this process deuterium labeling experiments were performed by reacting **8** with DBF_4 in a mixture of CD_2Cl_2/CD_3OD. This reaction yielded a dideuterated product. The result is consistent with an irreversible deuteration of the olefin yielding an α-cation followed by irreversible ejection of a proton at the C3 position yielding the 2,3 alkene (Scheme 2.6). The reaction proceeds forward with the deuterolysis of the isomerized Pt-alkenyl bond to generate the dideuterated product. The fact that there is a 1:1 d.r. for deuterium incorporation at C1 (from ^2H NMR spectroscopy) indicates that the deuteration at either diastereotopic position is equally feasible and argues that k_{-1} is not competitive with k_2. Furthermore, the little to no deuterium incorporation at C3 was interpreted to mean that k_3 is faster than k_{-2}. This reaction process is also proposed to be active in the catalytic cycle.

Scheme 2.6



By deconstructing the triphos ligand into the combination of a diphosphine and a monophosphine (P_2P), it was possible to generate a modular system amenable to rapid screening of chiral diphosphine derivatives while maintaining three phosphines coordinated to Pt. Earlier work had shown that $(P_2P)Pt\text{-}Me^+$ undergoes protonolysis 50,000 times slower than the $(PPP)Pt\text{-}Me^+$ analog (Scheme 2.7).[17] However, (PPP)Pt-alkenyls cations have shown increased reactivity towards protonolysis.

Scheme 2.7



A series of chiral $(P_2P)Pt$-dications were tested for their ability to render the cycloisomerization reaction asymmetric. Catalysis with $(P_2)(PMe_3)Pt^{2+}$ (P_2 = dppe, (*S*)-

BINAP, (*S*)-MeO-BIPHEP, (*S*)-Me-SoniPHOS), 5.0 equiv of **7** and 1.5 equiv Ph_2NMe in CD_3NO_2 led to reactions that were complete within 4 h and yielded **9**. Unfortunately, the product was racemic. Consistent with a markedly different protonolysis mechanism, catalytic reactions with the P_2P family of catalysts were equally efficient and yielded **9** with similar reaction times to $(PPP)Pt^{2+}$.

In the course of catalyst screening it was found that in some reactions where $[(P_2)(PMe_3)PtCl][Cl]$ was the pre-catalyst, 6 to 12 % of the olefin produced was the nonisomerized product **11**. It was believed that a small portion of the precatalyst was converted to a $(P_2)PtCl^+$ species. This catalyst would form a neutral Pt-alkenyl after enyne cyclization, in contrast to the cationic Pt-alkenyl complexes initiating with a $(P_2P)Pt^{2+}$ catalyst (Figure 2.3). It is known the neutral Pt-alkyls protonate more rapidly than their cationic analogs. To test this hypothesis a $(P_2)PtCl^+$ was generated and used for the cycloisomerization of **7**. $[(dppe)PtCl][NTf_2]$ cleanly catalyzed the cycloisomerization of **7** to a 1:1 ratio of the olefin isomers **9** and **11**. This result indicates that the more electron rich catalyst had a rate of protonolysis which is competitive with the rate of olefin isomerization.

Figure 2.3 Proposed intermediates comparing the cationic (P_2P)Pt-alkenyl to the neutral (P_2Cl)Pt-alkenyl.

2.3 Conclusion

We have developed a catalyst for the cycloisomerization of 1,6-enyne-ols wherein the turnover limiting step is protonolysis of the Pt-alkenyl bond that results from an electrophilic cascade cyclization. Mechanistic studies revealed that, for a terminal alkyne, a slow,

irreversible, olefin isomerization preceded a fast protonolysis. When the alkyne was internal, protonolysis was turnover limiting and no olefin migration was detected. These results stand in stark contrast to the protonolysis of Pt-alkyls, which do not proceed under similar conditions.

2.4 Experimental

General Procedures

Synthetic procedures were carried out under nitrogen using standard Schlenk techniques or in a nitrogen filled glove box. CD_2Cl_2 and CD_3NO_2 were distilled from CaH_2 and feeze-pump-thaw degassed before use. $MeNO_2$ was purified as previously described[27] and distilled from CaH_2. TriPHOS, dppe, and BINAP were purchased from Aldrich and used as received. (*S*)-Me-SoniPHOS and (*S*)-MeOBIPHEP were purchased from Strem and used as received. The piperidinomethyl polystyrene resin was purchased from NovaBiochem. $(COD)PtI_2$,[28] $(P_2)(PMe_3)PtI_2$,[15g] $(PPP)PtI_2$, and $[(PPP)Pt(NCC_6F_5)][BF_4]_2$[17] were prepared according to literature procedures. NMR spectra were recorded on a Bruker 400 MHz Avance or Bruker 500 MHz Avance spectrometer; chemical shifts are reported in ppm and referenced to residual solvent peaks (^1H, ^{13}C) or to an external standard (85% H_3PO_4 for ^{31}P NMR). GC was performed on an HP-6890. Elemental microanalyses were performed by Robertson-Microlit Laboratories, Madison, NJ. High-resolution mass spectrometry was performed by the mass spectrometry service laboratory at the University of Illinois.

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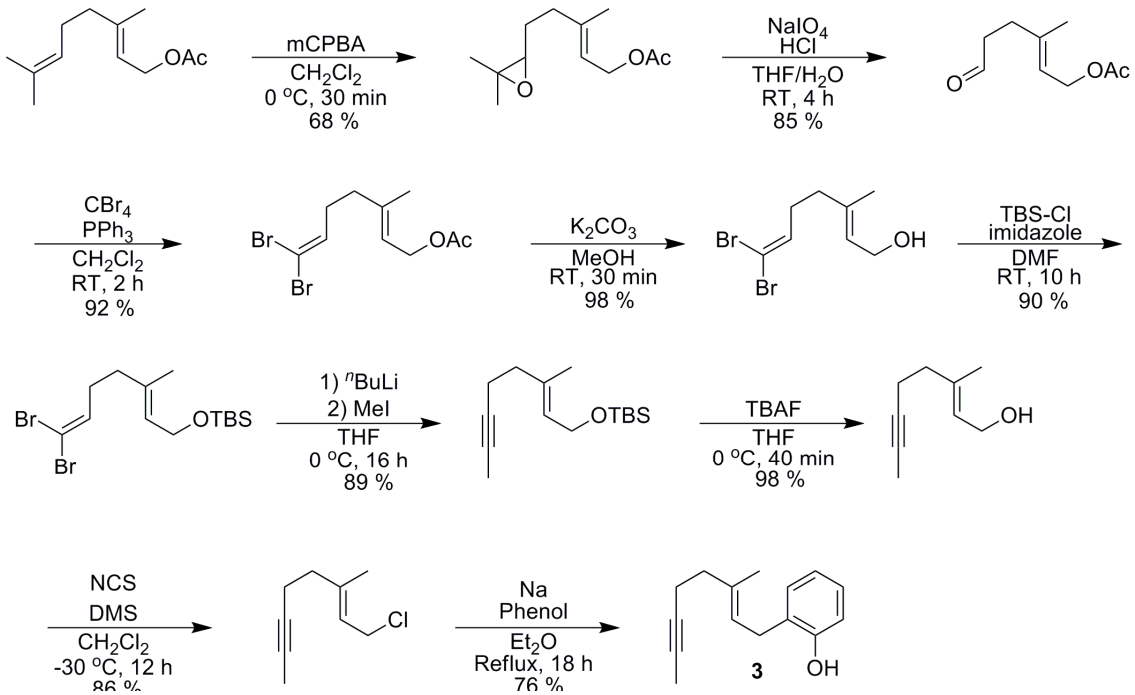
27. Commercial nitromethane contains traces of propionitrile which poison the catalyst. For purification, see: Parrett, F. W.; Sun, M. S. *J. Chem. Educ.* **1977**, *54*, 448-449.

28. Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411-428.

Scheme 2.8



Synthesis of 3: The (2E)-7,7-dibromo-3-methylhepta-2,6-dien-1-ol was obtained following a modified procedure established by Malacria (Scheme 2.8).[29] The substrate was protected with a TBS group, followed by a Corey-Fuchs to the methyl alkyne. Cleavage of the TBS group with TBAF generated the free alcohol, which was converted to the allyl chloride with treatment of NCS/DMS. Nucleophilic displacement of the chloride with sodium phenoxide yielded the desired product (**1**) (E)-2-(3-methyloct-2-en-6-ynyl)phenol.

(E)-2-(3-methyloct-2-en-6-ynyl)phenol (3) was isolated as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.6 Hz, 2H), 6.84 (t, *J* = 7.6Hz, 1 H), 6.79 (d, *J* = 7.6Hz, 1H), 5.37 (t, *J* = 6.8 Hz, 1H), 5.04 (s, 1H), 3.36 (d, 7.2 *J* = Hz, 2H), 2.27-2.18 (m, 4H), 1.75 (s, 6H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 154.2, 136.3, 129.7, 127.2, 127.0, 122.8, 120.5, 115.6,

29. Elliot, M. R.; Dhimane, A.-L.; Hamon, L.; Malacria, M. *Eur. J. Org. Chem.* **2000**, 155-163.

78.5, 76.3, 38.7, 29.2, 17.5, 15.6, 3.3. HRMS (ESI+) *m/z* $[M+H]^+$: observed 215.1234, calculated. 215.1436 for $C_{15}H_{19}O$.

(E)-2-(3-methylhept-2-en-6-ynyl)phenol (7) was prepared analogously to **3** and isolated as a colorless oil. ^1H NMR: (400 MHz, $CDCl_3$) δ 7.01 (t, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.42 (td, *J* = 8.0 and 1.0 Hz, 1H), 5.04 (s, 1H), 3.40 (d, *J* = 7.1 Hz, 2H), 2.37-2.27 (m, 4H), 1.98 (t, *J* = 2.5 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 154.1, 136.1, 129.9, 127.4, 126.8, 123.1, 120.7, 115.7, 83.8, 68.9, 38.2, 29.4, 17.3, 15.8. HRMS (EI+) *m/z* $[M]^+$: observed 200.1199, calcd. 200.1201 for $C_{14}H_{17}O$.

General Procedure for Isolation of Pt-alkenyls.

To a solution of $[(PPP)Pt(NCC_6F_5)][BF_4]_2$ (0.60 mmol) and piperidinomethyl polystyrene resin (1.20 mmol) in CH_2Cl_2 was added enyne (**3** or **7**) (0.70 mmol). The solution was allowed to stir for 15 min in air then the basic resin was filtered off and the Pt-alkenyl precipitated with Et_2O.

(PPP)Pt-alkenyl (5). After following the procedure described above, the resulting white solid was washed with Et_2O, dissolved in CH_2Cl_2 and diluted with Et_2O. The solvent was allowed to evaporate, yielding colorless needles (95 %). The NMRs for this complex were taken at -68 °C. $^1H\{^{31}P\}$ NMR: (400 MHz, CD_2Cl_2,) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.51-7.45 (m, 8H), 7.32-7.19 (m, 13H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 8.0 Hz, 1H), 6. 60 (t, *J* = 8.0 Hz, 1H), 3.45 (b, 2H), 2.87 (b, 2H), 2.55 (b, 4H), 2.11 (b, 2H), 2.08 (m, 2H), 1.80, (s, 2H), 1.52 (m, 1), 0.77 (s, 3H), -0.33(s, 3H).

$^{31}P\{^{1}H\}$ NMR: (162 MHz, $CDCl_3$). δ 88.09 (s, $J_{Pt\text{-}P}$ = 1398 Hz, 1P), 39.79 (s, $J_{Pt\text{-}P}$ = 2775 Hz, 2P).

(PPP)Pt-alkenyl (8). After following the procedure described above, the resulting solid was washed with Et_2O and dried in vacuo yielding desired product in 97 %. $^{1}H\{^{31}P\}$ NMR: (400 MHz, $CDCl_3$,) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.50-7.42 (m, 21H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 8.0 Hz, 1H), 6. 66 (t, *J* = 8.0 Hz, 1H), 4.59 (d, *J* = 12 Hz, $J_{Pt\text{-}H}$ = 44.0 Hz, 1H) 3.24 (b, 2H), 2.93 (m, 2H), 2.53 (m, 4H), 2.11 (m, 2H), 2.08 (m, 2H), 2.01 (m, 1H), 1.41 (m, 1H), 1.33(m, 1H), 0.55 (s, 3H). $^{31}P\{^{1}H\}$ NMR: (162 MHz, $CDCl_3$). δ 89.82 (s, $J_{Pt\text{-}P}$ = 1438 Hz, 1P), 38.52 (s, $J_{Pt\text{-}P}$ = 2812 Hz, 2P).

General Procedure for Catalysis.

To a solution of $(PPP)PtI_2$ (0.30 mmol) in CD_3NO_2 was added $AgBF_4$ (0.60 mmol). The reaction was stirred for 1 h, then the catalyst was filtered away from the silver salts via a PTFE syringe filter into a solution of **3** or **7** (1.5 mmol) and Ph_2NMe (0.45 mmol) in CD_3NO_2. The reaction was monitored by ^{31}P and ^{1}H NMR. Once the substrate was consumed the product was extracted with 1 mL pentane (2x). The pentane was removed via rotary evaporation to yield the isolated product.

1,4a-dimethyl-4,4a,9,9a-tetrahydro-3H-xanthene (4) was prepared as described above and isolated as a colorless oil in 87 % yield. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.12-7.07 (m, 2H), 6.82 (td, *J* = 8.4 and 2.8 Hz, 2H), 5.38 (s, 1H), 2.86 (m, 1H), 2.52 (m, 2H), 2.17 (m, 2H), 1.96-1.82 (m, 2H), 1.52 (s, 3H), 1.10 (s, 3H). δ ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.7, 133.6, 129.8, 127.4, 122.5, 121.5, 119.7, 117.4, 76.0, 42.0, 35.5, 25.9, 24.1, 19.8, 16.6. HRMS (ESI+) *m*/*z* $[M+H]^+$: observed 215.1234, calcd. 215.1436 for $C_{15}H_{19}O$.

4a-methyl-4,4a,9,9a-tetrahydro-1H-xanthene (9) was prepared as described above and isolated as a colorless oil in 96 % yield. ^{1}H and ^{13}C NMR matched previously reported data.[30]

General Procedure for Protonolysis/Deuterolysis of Pt-alkenyl

To a solution of **3** or **6** in CH_2Cl_2/CD_2Cl_2 was added HBF_4 as a solution in Et_2O and CH_3OH/CD_3OD. The reaction stirred for 10 min. Solution was then washed with H_2O/D_2O, extracted with pentane, dried over $MgSO_4$, and filtered. The solvent was removed via rotary evaporation yielding the desired product.

1,4a-dimethyl-4,4a,9,9a-tetrahydro-3H-xanthene (4) was isolated as a colorless oil in 96 % yield; ^{1}H and ^{13}C NMR matched above spectra.

4a-methyl-4,4a,9,9a-tetrahydro-1H-xanthene (9) was isolated as a colorless oil in 95 % yield; ^{1}H and ^{13}C NMR matched previously reported data.[30]

4-d$_1$: was isolated as a colorless oil in 96 % yield. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.07 (m, 2H), 6.81 (m, 2H), 2.86 (m, 1H), 2.50 (m, 2H), 2.19 (m, 2H), 1.92 (m, 2H), 1.71 (s, 3H), 1.10 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.6, 133.5, 129.9, 127.5, 122.5, 121.5 (C-D), 119.7, 117.4, 76.1, 41.9, 35.5, 25.9, 24.0, 19.8, 16.6. ^{2}H NMR: (500 MHz, $CHCl_3$) δ 5.42 (s, 1D). HRMS (EI+) *m*/*z* $[M]^+$: observed 215.1423, calcd. 215.1420 for $C_{14}H_{17}DO$.

9-d$_2$: was isolated as a colorless oil in 94 % yield. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.07 (t, J = 8.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.82 (m, 2H), 5.49 (s, 1H), 2.71 (d, J = 4.0 Hz, 1H), 2.48 (m, 3.5H), 2.13 (m, 1H), 1.78 (m, 0.5H), 1.10 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$)

δ 153.9, 129.7, 127.2, 125.5 (C-D), 125.3, 125.1, 120.0, 117.0, 76.0, 39.9, 34.2, 31.8 (C-D), 31.1, 16.1. ^{2}H NMR: (500 MHz, $CHCl_3$) δ 5.49 (s, 1D), 2.36 (s, 0.5D), 1.77 (s, 0.5D). HRMS (EI+) *m*/*z* $[M]^+$: observed 202.1325, calcd. 202.1327 for $C_{14}H_{14}D_2O$.

General Procedure for Reductive Cleavage of Organic Fragment.

To a solution of **5** or **8** in THF at 0 ^{o}C was added $LiHBEt_3$ in THF. The reaction was stirred for 30 min. Solvent was removed via rotary evaporation and the product was extracted with pentane and filtered through celite. The solvent was then removed via rotary evaporation to yield the desired product.

4a-methyl-4,4a,9,9a-tetrahydro-3H-xanthene (11) was isolated as a colorless oil in 89 % yield. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.07 (m, 2H), 6.82 (t, *J* = 9.6 Hz, 2H), 5.65 (d, *J* = 12.8 Hz, 1H), 5.47 (d, *J* = 12.8 Hz, 1H), 2.69 (d, *J* = 14.0 Hz, 1H), 2.52 (m, 2H), 2.22 (m, 3H), 1.91 (m, 2H), 1.14 (s, 3H). δ ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.2, 132.9, 130.1, 127.7, 122.7, 122.0, 119.3, 118.4, 75.2, 42.7, 35.5, 24.5, 19.6, 15.6. HRMS (EI+) *m*/*z* $[M]^+$: observed 200.1204, calcd. 200.1201 for $C_{14}H_{16}O$.

4a-methyl-4,4a,9,9a-tetrahydro-1H-xanthene (9) was isolated as a colorless oil in 87 % yield. ^{1}H and ^{13}C NMR matched previously reported data.[30]

30. Mullen, C. A.; Gagné, M. R. *J. Am. Chem. Soc.* **2007**, *129*, 11880-11881.

Chapter 3

A New Set of Tropos Ligands

3.1 Introduction

Classically, transition metal Lewis acid promoted asymmetric catalysis requires chiral catalysts derived from enantio-resolved ligands on the transition metal. It is possible, however, to achieve asymmetric reactions with achiral ligands through the addition of chiral auxiliaries.[1] The benefits to this approach are numerous. Preparation of asymmetric ligands generally requires resolution of a racemic mixture along the ligand synthetic route. This separation is performed by generating diastereomers and using their differing chemical properties as a means of resolution as shown in eqs 3.1 and 3.2 for the preparation of chiral BINAP[2] and P-Phos,[3] respectively. These steps add to the cost and efficiency of the preparation of enantiopure ligands. Often, diphosphine ligands must be altered with different substituents for optimal reactivity and selectivity. These optimizations require the independent synthesis of a multitude of ligands. Developing a catalytic system where nonchiral ligands can be used in conjunction with chiral inexpensive, readily available

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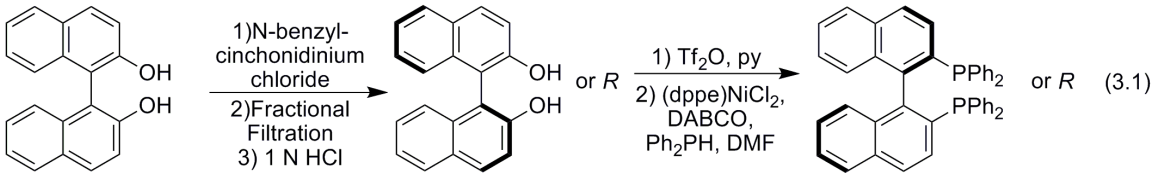
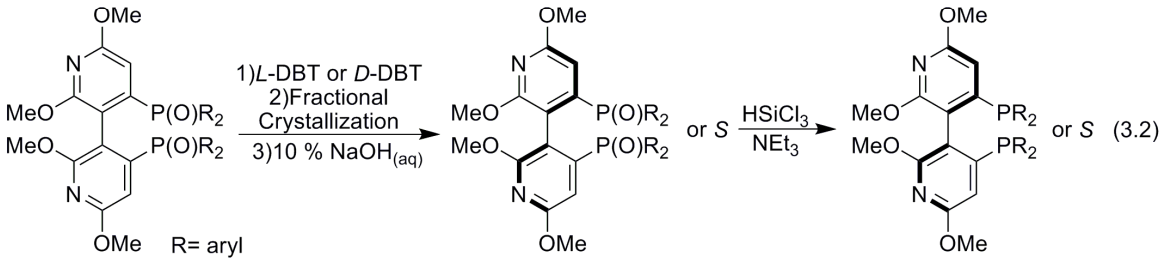
1. (a) Mikami, K.; Aikawa, K. *Org. Lett.* **2002,** *4*, 99-101. (b) Pasquini, C.; Desvergnes-Breuil, V.; Jodry, J. J.; Dalla, C. A.; Lacour, J. *Tet. Lett.* **2002,** *43*, 423-426. (c) Roelfes, G.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2005,** *44*, 3230-3232.

2. (a) Vondenhof, M.; Mattay, J. *Tet. Lett.* **1990,** *31*, 985. (b) Cai, D.; Payack, J. F.; Bender, D. R.; L. Hughes, D.; Verhoeven, T. R.; Reider, P. J. *J. Org. Chem.* **1994,** *59*, 7180.

3. Wu, J.; Chan, A. S. C. *Acc. Chem. Res.* **2006,** *39*, 711-720.

auxiliaries would afford the opportunity to perform rapid screening of the naturally abundant chiral molecules.





Asymmetric ligands that contain axial chirality (e.g., BINAP, MeO-BIPHEP, SEGPHOS, P-Phos, Me-SoniPHOS) are atropisomeric,[4] meaning the barrier to rotation around the axis is sufficiently high to prevent racemization.[5] Conversly, *tropos* ligands (e.g., BIPHEP, dppf) have a lower rotational barrier, and therefore readily undergo racemization at RT. *Tropos* ligands can be separated as diastereomers through coordination of a chiral auxiliary; however, once they are cleaved into the free ligand, racemization occurs rapidly.[6]

Mikami has shown that (BIPHEP)$RuCl_2$((*S,S*)-DPEN) complexes are capable of increasing the enatioselectivity of ketone hydrogenations as compared to the ((*rac*)-

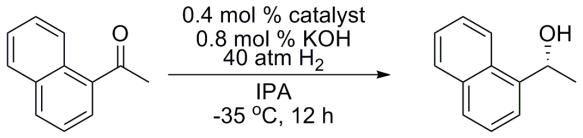
4. Derived from the Greek words *tropos* meaning "turn" and *a* meaning "not"

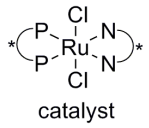
5. 22.3 kcal/mol at 300 K:see Oki, M.; Yamamoto, G. *Bull. Chem. Soc. Jpn.* **1971,** *44*, 266-270.

6. For review see: (a) Walsh, P. J.; Lurain, A. E.; Balsells, J. *Chem. Rev.* **2003,** *103*, 3297-3344. (b) Mikami, K.; Yamanaka, M. *Chem. Rev.* **2003,** *103*, 3369-3400 and references therein.

BINAP)$RuCl_2$((*S,S*)-DPEN) analog (Table 3.1).[7] The practicality of this reaction is that the *tropos* nature of BIPHEP allows for the formation of a favorable thermodynamic mixture (3:1 d.r.) while the analogous (*rac*)-BINAP complex can form only a 1:1 mixture of diastereomers and requires isolation and purification to generate greater selectivity.

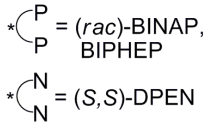
Table 3.1. A comparison of Ru hydrogenation catalysts containing a *tropos* or *atropos* ligand.[a]





catalyst

catalyst	% yield	% *e.e*
(BIPHEP)$RuCl_2$((*S,S*)-DPEN)	99	92
((*rac*)-BINAP)$RuCl_2$((*S,S*)-DPEN)	99	89



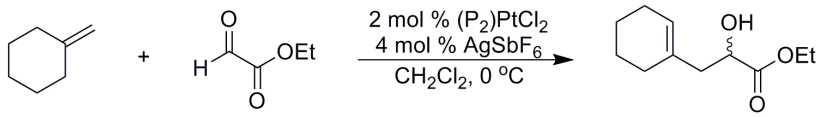
[a]Catalyst was allowed to stir in IPA for 3 h, in order to reach thermodynamic equilibrium.

In the aforementioned example by Mikami, the BIPHEP ligand remains *tropos* even after coordination to the metal. By using a more substitutionally inert metal such as Pt it was hypothesized that BIPHEP would become an atropisotopic ligand and could be used as the sole source of chirality for asymmetric catalysis. Reacting ((*rac*)-BIPHEP)$PtCl_2$ with (*S*)-BINOLate led to the formation of a 1:1 mixture of diastereomers which could be separated by crystallization.[8] After separation, protonolysis of the BINOLate with HCl generated the enantiomerically resolved ((*S*)-BIPHEP)$PtCl_2$ and ((*R*)-BIPHEP)$PtCl_2$ and (*S*)-BINOL. These resolved (BIPHEP)$PtCl_2$ species were used as asymmetric catalyst for Lewis acid

7. Mikami, K.; Korenaga, T.; Terada, M.; Ohkuma, T.; Pham, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1999,** *38*, 495-497.
8. Tudor, M. D.; Becker, J. J.; White, P. S.; Gagné, M. R. *Organometallics* **2000,** *19*, 4376-4384.

catalyzed Diels-Alder and glyoxylate-ene reactions (Table 3.2).[9] This was the first report of the use of a *tropos* ligand as the sole source of chirality for asymmetric catalysis.

Table 3.2. The use of resolved (BIPHEP)$PtCl_2$ as a chiral catalyst[a]



$(P_2)PtCl_2$	% conversion	% *e.e.*[b]	stereochemistry
(*S*)-(BIPHEP)$PtCl_2$	90	70	*S*
(*R*)-(BIPHEP)$PtCl_2$	62	70	*R*

[a]Reactions were run with 3:1 equiv of methylene cyclohexane to ethyl glyoxylate for 4 h. [b]Determined by chiral GC.

Having shown that the BIPHEP ligand was *atropos* once bound to Pt, we sought to prepare a ligand that would be capable of remaining *tropos* once coordinated to Pt (Figure 3.1). We envisioned a ligand similar to BIPHEP but with a 2,2'-bipyridine backbone instead of a biphenyl backbone. With nitrogen atoms in the 2,2'-positions, a low barrier to rotation around the bipyridyl axis was expected, even upon coordination to Pt. The nitrogen atoms would serve a dual purpose. Not only should the lack of H's in the 2,2' position help the ligand remain *tropos* on the metal, but the N's could also act as hydrogen bond acceptors. This motif would afford the opportunity to control the orientation of the stereo axis through added chiral H-donors.

9. Becker, J. J.; White, P. S.; Gagné, M. R. *J. Am. Chem. Soc.* **2001,** *123*, 9478-9479.

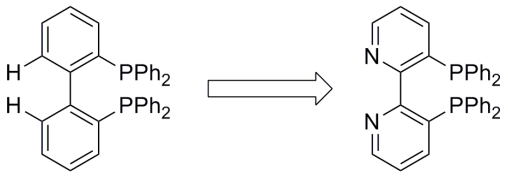
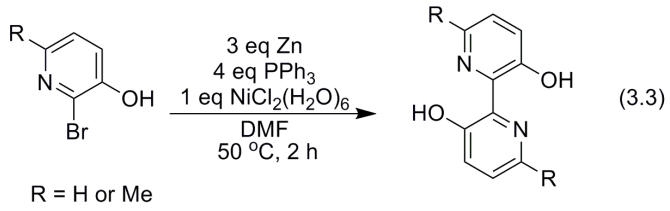


Figure 3.1 Design of a *tropos* ligand based on BIPHEP

Results and Discussion

The first step in the ligand synthesis began with the preparation of 2,2'-bis(3-pyridinols). These compounds have been extensively studied for their fluorescent properties and a stoichiometric nickel promoted diaryl coupling was used to synthesize the bipyridinols from the corresponding 2-bromo-3-pyridin-ols (eq 3.3).[10]

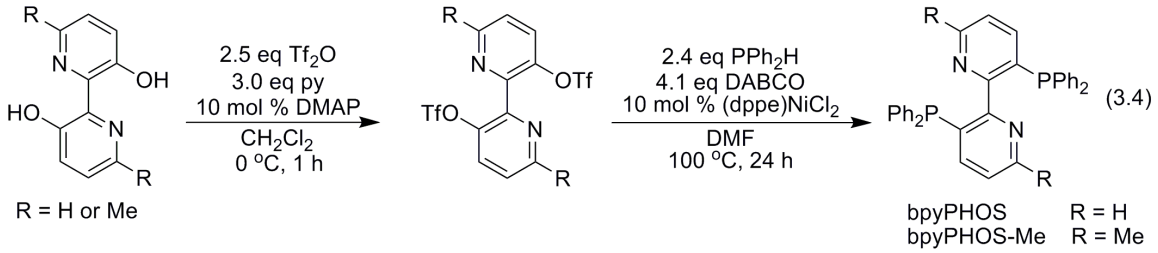


(3.3)

Using methods developed by Mattay,[2a] the bipyridinol was converted to the ditriflate by treatment with 2.5 eq of Tf_2O, 3.0 eq py and 10 mol % DMAP. Synthesis of the desired ligand was completed using Cai's Ni coupling conditions to generate the diphosphine (eq 3.4).[2b] This diphosphine ligand (3,3'-bis(diphenylphosphino)-2,2'-bipyridine) will be henceforth referred to as bpyPHOS for the bipyridine back bone. Ligands with substituents

10. (a) Naumann, C.; Langhals, H. *Synthesis* **1990**, 279-281. (b) Mongin, F.; Trécourt, F.; Mongin, O.; Quéguiner, G. *Tetrahedron* **2002,** *58*, 309-314. (c) Langhals, H. U.S. Patent 5,266,700, **1993**.

at the 6,6' positions will be labeled as bpyPHOS-R, where R is the substituent at the 6,6' position (3,3'-bis(diphenylphosphino)-6,6'-dimethyl-2,2'-bipyridine is abbreviated as bpyPHOS-Me).



(3.4)

Reacting bpyPHOS with 1.0 eq of $(COD)PtI_2$ in CH_2Cl_2 yielded $(bpyPHOS)PtI_2$. The downfield shift of the ^{31}P NMR resonance together with the splitting of the resonance by the 33 % spin active ^{195}Pt nuclei yielded a pseudotriplet (δ = 5.32 ppm $J_{Pt\text{-}P}$ = 3300 Hz) characteristic of a diphosphine coordinated to Pt. The new metal complex was crystallized by slow evaporation of CH_2Cl_2. X-ray structural analysis showed coordination of the Pt through the phosphines rather than the nitrogens, further confirming the desired mode of coordination (Figure 3.2). Adventitious water was found to bridge two different $(bpyPHOS)PtI_2$ molecules, through hydrogen bonding to the pyridine fragments with a H-N bond distance of 2.01 Å.[11]

11. Emsley, J. *Chem. Soc. Rev.* **1980,** *9*, 91-124 and references therein.

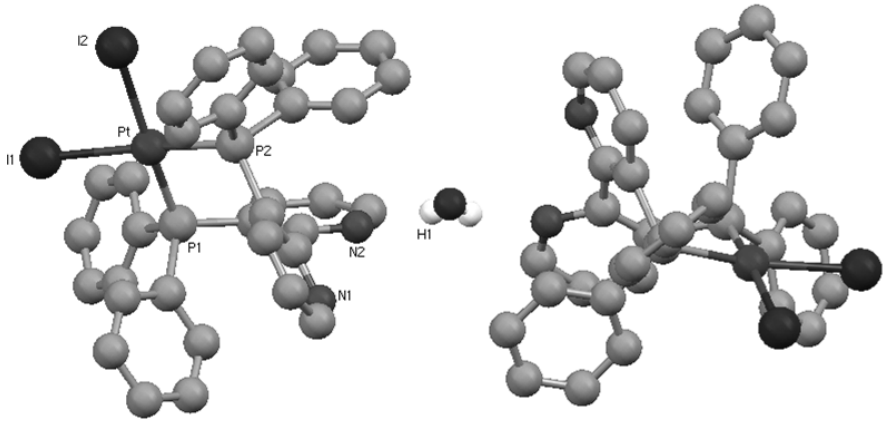
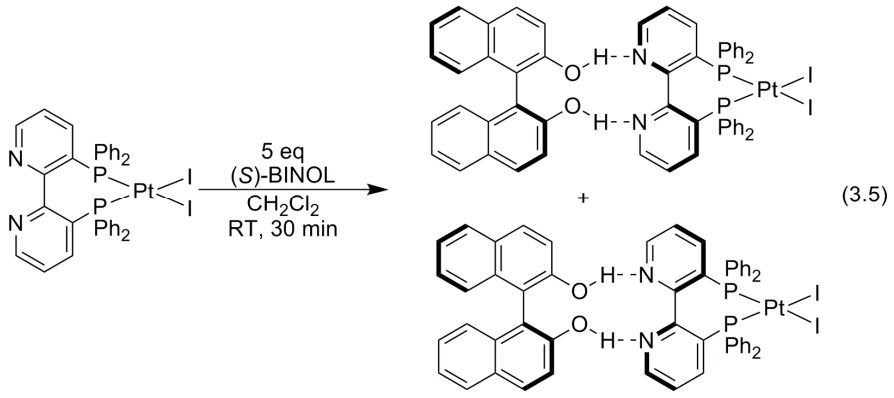


Figure 3.2 Chem3D representation of (bpyPHOS)PtI_2. Selected bond lengths (Å); Pt1-P1 = 2.2634, Pt1-P2 = 2.2669, Pt1-I1 = 2.6572, Pt1-I2 = 2.6709, Selected angles (deg); P1-Pt1-P2 = 92.54, P1-Pt1-I2 = 90.62, P2-Pt1-I1 =91.13, I1-Pt1-I2 =87.195.

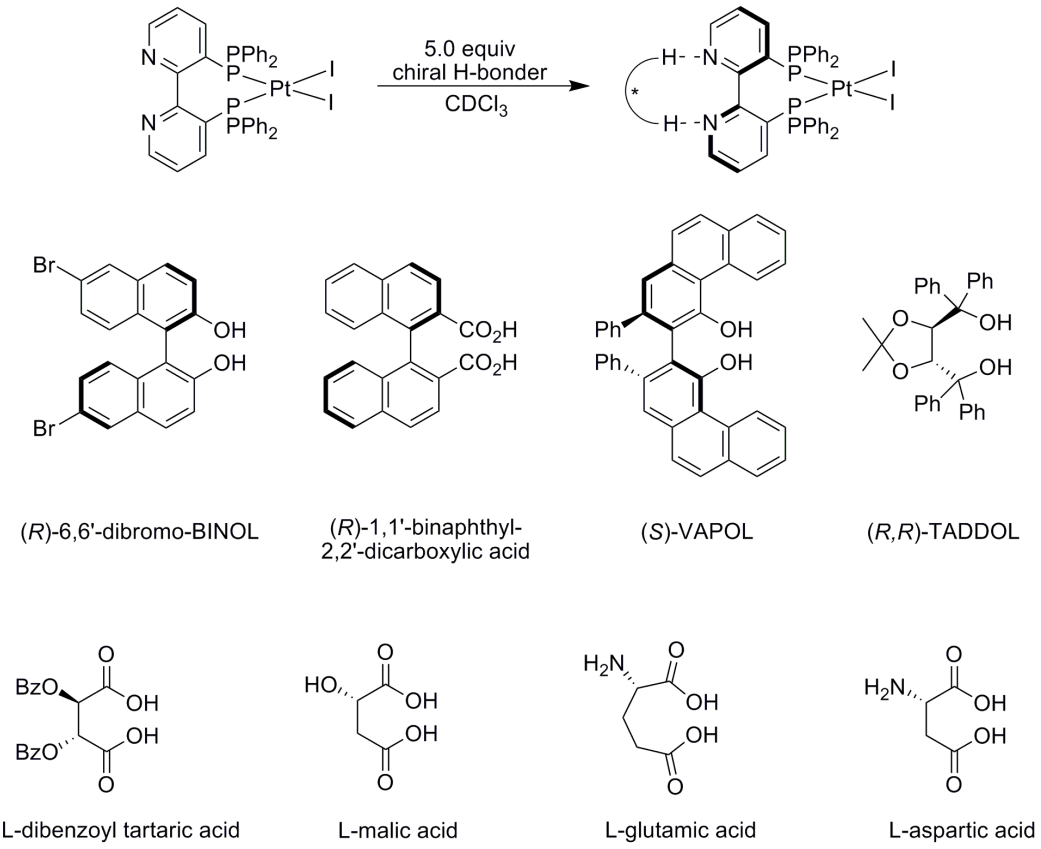
The X-ray structure proved that the bipyridyl moiety was capable of hydrogen bonding to hydrogen donors, at least in the solid state. Solution experiments were preformed with the chiral hydrogen donor (*S*)-BINOL to determine if the biaryl axis of bypPHOS could be resolved while complexed to Pt(eq 3.5). ^{31}P NMR spectra showed no coordination at RT when only 1.0 eq (*S*)-BINOL was added. When the mixture was cooled to -78 ^{o}C, the ^{31}P resonance split into two peaks in a 1:1 ratio suggesting the formation of 2 diastereomers (derived from the diastereomeric combination of (*S*)- and (*R*)-bpyPHOS together with the (*S*)-BINOL). The same effect could be achieved by adding 5.0 eq of (*S*)-BINOL at RT. The 1:1 d.r. was stable at elevated temperatures, upon addition of more (*S*)-BINOL (10.0 eq), and after extended times (1 month).



While coordination of the BINOL to the bipyridine moiety of the ligand was confirmed by the generation of two diastereomers in the ^{31}P NMR, no thermodynamic preference was observed and therefore no resolution was achieved. This could be attributed to two scenarios and each was examined in turn (Scheme 3.1). First, to increase the interaction between the chiral H-donor and the H-acceptor ligand, the acidity of the donor was increased. Using either 5.0 eq of (*R*)-dibromo-BINOL or (*R*)-1,1'-binaphthyl-2,2'-dicarboxylic acid as an H-donor yielded a 1:1 mixture of diastereomers. Alkyl dicarboxylic acids were screened next as they are more acidic than the previously tested aryl H-donors and contain a more flexible backbone which may allow for better chelation. Malic, glutamic, and aspartic acids did not interact with (bpyPHOS)PtI_2. However, L-DBT generated a 1:1 d.r. even at low concentrations of H-donor (1.0 eq)[12] but still gave no resolution. Next, hoping to create a greater steric preference upon binding and thereby increase the d.r., (*R,R*)-TADDOL and (*S*)-VAPOL (5.0 eq) were used as the H-donors. While both donors bound to the bipyridine moiety as evidenced by ^{31}P NMR, no diastereomer preference was observed.

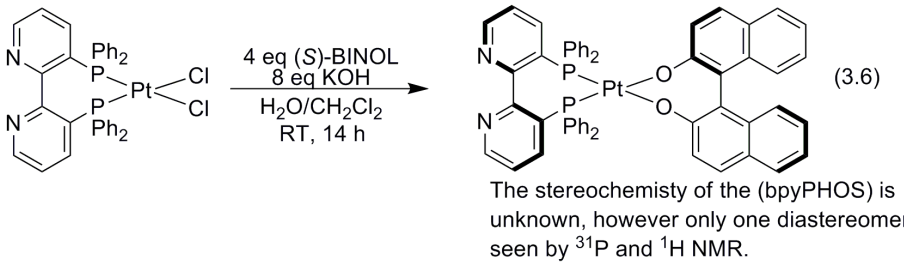
12. Only 1.0 equiv of L-DBT was required for a baseline separation in ^{31}P NMR. For less acid H-Donors, 5.0 equiv or greater is necessary for this degree of separation.

Scheme 3.1



Because, even after an extensive screen of H-donors, (bpyPHOS)PtI_2 had yet to show any resolution in the presence of these chiral auxiliaries, we began to suspect that restricted rotation of the biaryl axis upon coordination to the Pt prevented resolution. To test this hypothesis a (bpyPHOS)Pt((*S*)-(BINOLate) was synthesized (eq 3.6). At short times (4 h) the reaction mixture existed as three complexes by ^{31}P NMR: starting material ((bpyPHOS)$PtCl_2$) and the two different diastereomers of the (bpyPHOS)Pt((*S*)-(BINOLate). However, once the reaction was complete, only one diastereomer remained. The formation of a single diastereomer over time stood in stark contrast to the reaction of (BIPHEP)$PtCl_2$ with (*S*)-(BINOLate) which produced two diastereomers that did not interconvert at RT due

to the *atropos* behavior of the ligand on the metal. BpyPHOS, on the other hand, remained *tropos* while coordinated to Pt and could be converted to a single diastereomer upon formation of the BINOLate.



The conformational stability of the biaryl axis in (bpyPHOS)Pt in the absence of the chiral auxiliary was probed by BINOLate cleavage. The removal of the BINOLate with HOTf, HCl, and $AgSbF_6$ all yielded a racemic mixture of (bpyPHOS)PtX_2 (X =OTf, Cl, or SbF_6). Even at low temperatures (-78 ^oC) racemization was complete within 10 min.[13] These experiments further confirmed that the bipyridyl axis remains *tropos* on the metal and in fact has a barrier to rotation that is too low to easily work with.

With the tropos nature of (bpyPHOS) confirmed, the lack of diastereomeric preference was hypothesized to be the result of insignificant thermodynamic energy differences between the diastereomers formed, regardless of the bulk placed on the H-donor. To create a greater thermodynamic preference for one diastereomer over the other, the more sterically demanding (bpyPHOS-Me)PtI_2 was synthesized. Reacting (bpyPHOS-Me)PtI_2 with 5.0 eq of (*S*)-BINOL yielded a 1:1 ratio of products by ^{31}P NMR. However upon the addition of 1.0 eq of L-DBT a d.r. of 1.0:5.5 was observed. A single diastereomer was crystallized by slow evaporation of $CDCl_3$ (Figure 3.3). Diffraction data showed that the

13. This was observed by ^{31}P NMR through the 1:1 d.r. produced upon the complexation of *S,S*-DPEN.

complex crystallized in the chiral space group $P2_1$. A H-N distance of 1.97 Å indicated a H-bond between the DBT and (bpyPHOS-Me)$PtCl_2$ bipyridine backbone (Figure 3.3). Unfortunately, the L-DBT H-donor did not behave as a chelate; instead, the second carboxylic acid functional group formed an H-bond to an adjacent molecule of (bpyPHOS-Me)$PtCl_2$ resulting in extended H-bonding arrays (Figure 3.4).

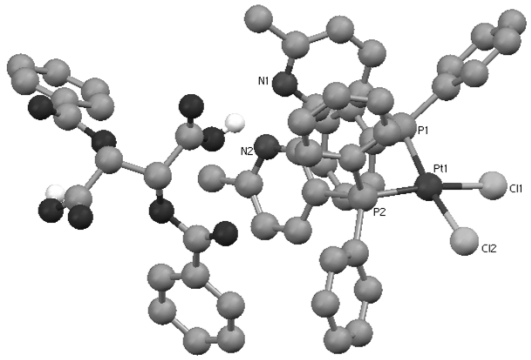


Figure 3.3 Chem3D representation of (bpyPHOS)$PtCl_2$ and L-DBT. Selected bond lengths (Å); Pt1-P1 = 2.2424, Pt1-P2 = 2.2533, Pt1-Cl1 = 2.3506, Pt1-Cl2 = 2.3651, Selected angles (deg); P1-Pt1-P2 = 92.07, P1-Pt1-Cl2 = 92.53, P2-Pt1-Cl1 =88.94, Cl1-Pt1-Cl2 =87.82.

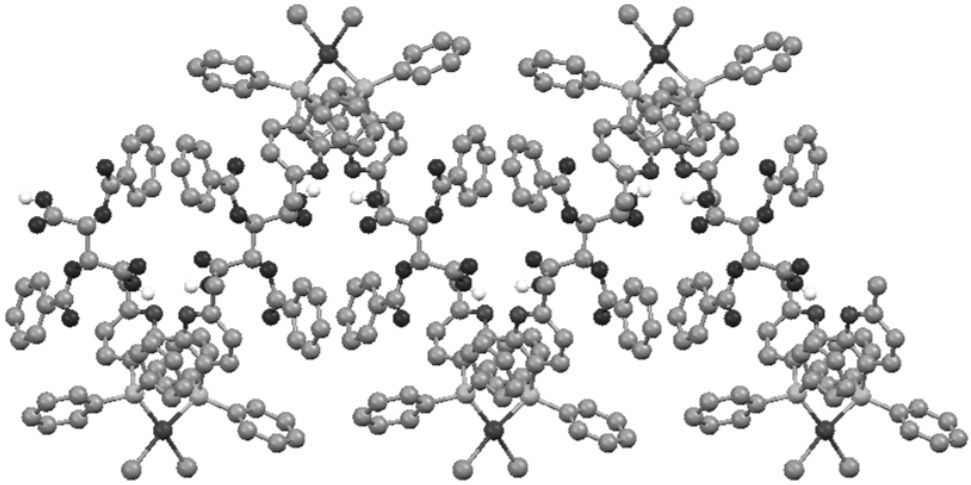
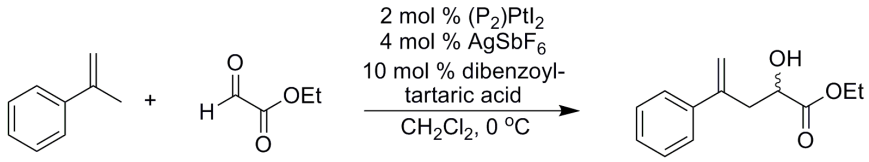


Figure 3.4 Extended H-Bonding array of (bpyPHOS)$PtCl_2$ and L-DBT.

Nevertheless, the L-DBT was capable of resolving the bpyPHOS-Me and to determine if this resolved system was amenable to asymmetric catalysis, a glyoxylate-ene reaction was carried out. The $(P_2)PtI_2$ (P_2 = BIPHEP, bpyPHOS, and bpyPHOS-Me) was stirred with $AgSbF_6$ for 1 h. The resulting active catalyst was filtered into a solution of L-DBT in CH_2Cl_2 and stirred for 15 min. The reaction was then cooled to 0 ^oC, ethyl glyoxylate added, and the reaction stirred for 15 min, followed by addition of α-methyl styrene. The reactions were monitored by chiral GC (Table 3.3). The highest e.e. was seen with the control catalyst $(BIPHEP)PtI_2$, which should have had no interaction with L-DBT. It was assumed that the 4 % *e.e.* was due to background Brønsted acid catalysis by the L-DBT. The bpyPHOS catalysts that gave essentially no e.e.

Table 3.3. Asymmetric glyoxylate-ene reaction with P_2PtI_2 and L-DTB[a]

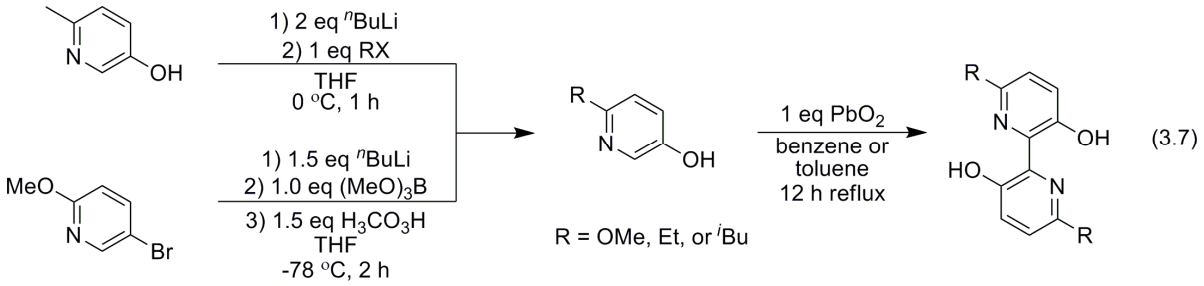


$(P_2)PtCl_2$	% conversion	% *e.e.*[b]
$(bpyPHOS)PtI_2$	90	2
$(bpyPHOS\text{-}Me)PtI_2$	91	2
$(BIPHEP)PtI_2$	92	4

[a]Reactions were run with 3:1 equiv of methylene cyclohexane to ethyl glyoxylate for 4 h. [b]Determined by chiral GC.

In an effort to avoid undesirable Brønsted acid catalysis a weaker acid was needed; however, none of the weaker acids tested were able to resolve the (bpyPHOS)Pt complexes. A new synthetic route for the preparation of more sterically bulky or more basic bipyridinols was required. A PbO_2 radical biaryl coupling afforded the opportunity to substitute the 6 and 6' positions starting from easily modified commercially available starting materials (eq

3.7).[14] The bipyridinols could be readily converted into their corresponding diphosphines using the previously described procedures (eq 3.4).



All the new (bpyPHOS-R)PtI_2 complexes were synthesized and their diastereoselectivity was tested by the addition of either (*S*)-BINOL or (*R,R*)-TADDOL. Like the previous derivatives both (bpyPHOS-^{i}Bu) and (bpyPHOS-Et)PtI_2 showed a 1:1 d.r. upon addition of the H-donors. (bpyPHOS-OMe)PtI_2 showed no interaction between the H-donor and the bipyridine moiety. This is most likely due to an unfavorable interaction between the H-donor and the OMe functional group. Even with the additional steric bulk next to the H-acceptor, these new ligands could not be resolved with weakly acidic H-donors.

Conclusions

A new set of tropos ligands was synthesized. It was demonstrated that these ligands remained tropos while coordinated to Pt and formed a single diastereomer upon complexation of (*S*)-BINOLate. However, cleaving the BINOLate led to immediate racemization of the (bpyPHOS)Pt complex, even at low temperatures, indicating a low barrier of rotation. When alkyl substituents were incorporated into the 6,6' position of the bipyridine backbone, the (bpyPHOS-alkyl)Pt complex exhibited a diastereomeric preference

14. Wirth, J. G. U.S. Patent 3,676,448, **1970.**

with sufficiently acidic H-donors. These Lewis acid complexes were used as glyoxylate-ene catalysts, but unfortunately this led to a racemic mixture of products. Addition of larger substituents (Et, ^{i}Bu) to the 6,6' position did not lead to catalysts which could be resolved with relatively weak H-donors (e.g., BINOL, TADDOL).

3.3 Experimental

General Procedures. Synthetic procedures were carried out under nitrogen using standard Schlenk techniques or in a nitrogen filled glove box. CD_2Cl_2 was distilled from CaH_2 and freeze-pump-thaw degassed before use. CH_2Cl_2 and toluene were dried by passage through a column of alumina. THF was dried over sodium/benzophenone and distilled prior to use. DMF was freeze-pump-thaw degassed before use. DABCO was freshly sublimed. 2,2'-bis(3-pyridinols)[9, 13] and (COD)PtI_2[15] were prepared according to literature procedures. (*S*)-VAPOL was generously donated by Professor William Wulff. All of the other chiral H-bond donors were commercially available and used as received. The ethyl glyoxylate was freshly distilled. NMR spectra were recorded on a Bruker 400 MHz Avance or Bruker 500 MHz Avance spectrometer; chemical shifts are reported in ppm and referenced to residual solvent peaks (^{1}H, ^{13}C) or to an external standard (85% H_3PO_4 for ^{31}P NMR, flourobenzene for ^{19}F). GC was performed on an HP-6890.

2,2'-bipyridine-3,3'-diyl bis(trifluoromethanesulfonate): To a solution of 2,2'-bipyridine-3,3'-diol (1.36 g, 7.23 mmol) in 20 ml CH_2Cl_2 was added 1.8 ml pyridine (22.3 mmol) and 10 mol% DMAP (0.723 mmol). Solution was cooled to 0 °C and 3.0 ml triflic anhydride (6.34 mmol) was added via cannula. Solution stirred for 2 hr at 0 °C and was then allowed to warm to room temperature. The reaction mixture was stirred for an additional 1 h

15. Clark, H. C.; Manzer, L. *E. J. Organomet. Chem*. **1973**, *59*, 411-428.

^{1}H NMR: ($CDCl_3$, 400 MHz) δ and then the solvent was removed *in vacuo*. The solid was taken up in 20 ml EtOAc and washed once with 50 ml of 5% HCl. The organic layer was dried with $MgSO_4$, filtered, and the solvent was removed via vacuum. The solid was dissolved in CH_2Cl_2 and purified via flash chromatography, eluted with 10% EtOAc in hexanes to yield 2.86 g (6.32 mmol, 87%) of the ditriflate.

6,6'-dimethyl-2,2'-bipyridine-3,3'-diyl bis(trifluoromethanesulfonate): Prepared as described above to yield a white powder in 90%. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.67 (d, 2H, J = 8.0 Hz), 7.39 (d, 2H, J = 8.0 Hz), 2.62 (s, 6H). ^{13}C{^{1}H} NMR: ($CDCl_3$, 100 MHz) δ 158.6, 156.0, 143.3, 130.5, 125.3, 118.4 (q, 2C, $J_{C\text{-}F}$ = 319 Hz), 23.3. ^{19}F NMR: ($CDCl_3$, 471 MHz) δ -74.3.

6,6'-dimethoxy-2,2'-bipyridine-3,3'-diyl bis(trifluoromethanesulfonate): Prepared as described above to yield a white powder in 92%. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.62 (d, 2H, J = 8.0 Hz), 6.88 (d, 2H, J = 8.0 Hz), 4.00 (s, 6H). ^{13}C {^{1}H} NMR: ($CDCl_3$, 100 MHz) δ 162.1, 143.9, 139.6, 133.2, 118.4 (q, 2C, $J_{C\text{-}F}$ = 320 Hz), 113.5, 54.3. ^{19}F NMR: ($CDCl_3$, 471 MHz) δ -75.0 (s, 6F).

6,6'-diethyl-2,2'-bipyridine-3,3'-diyl bis(trifluoromethanesulfonate): Prepared as described above to yield a white powder in 88%. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.65 (d, 2H, J = 8.0 Hz), 7.35 (d, 2H, J = 8.0 Hz), 2.93 (q, 4H, J = 8.0 Hz), 1.32 (t, 6H, J = 8.0 Hz). ^{13}C {^{1}H} NMR: ($CDCl_3$, 100 MHz) δ 163.4, 146.2, 143.3, 130.5, 123.9, 118.3 (q, 2C, $J_{C\text{-}F}$ = 318 Hz), 30.5, 13.2. ^{19}F NMR: ($CDCl_3$, 471 MHz) δ -74.8 (s, 6F).

6,6'-diisobutyl-2,2'-bipyridine-3,3'-diyl bis(trifluoromethanesulfonate): Prepared as described above to yield a white powder in 80%. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.66 (d, 2H, J = 8.0 Hz), 7.31 (d, 2H, J = 8.0 Hz), 2.78 (d, 4H, J = 4.0 Hz), 2.17 (m, 2H), 0.95 (d, 12

H, J = 8.0 Hz). ^{13}C {^{1}H} NMR: ($CDCl_3$, 100 MHz) δ 161.7, 146.4, 143.3, 130.1, 125.2, 123.1, 118.3, (q, 2C, J_{C-F} = 319 Hz), 46.6, 28.8, 22.2. ^{19}F NMR: ($CDCl_3$, 471 MHz) δ -74.5 (s, 6F).

3,3'-bis(diphenylphosphino)-2,2'-bipyridine (bpyPHOS) : To a solution of the ditriflate (50 mg, 0.11 mmol), (dppe)$NiCl_2$ (5.8 mg, 0.01mmol), and DABCO (50.9 mg, 0.45 mmol) in 0.75 ml DMF in a J-young tube was added 46 μL (0.26 mmol) diphenylphosphine. Reaction was heated to 100 °C and was monitored by ^{31}P NMR. Once reaction was complete the solution was taken up into 2 mL degassed CH_2Cl_2 and washed with twice with 1 mL degassed H_2O. The organic layer was dried with MgSO4, filtered, and solvent was removed by rotatory evaporation. The yellow oil was purified via flash chromatography with an eluent of 10% EtOAc in hexanes yielding the desired product in 87% yield. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 8.38 (d, 2H, J = 4.0 Hz), 7.38 (d, 2H, J = 8.0 Hz), 7.31 (s, 20 Hz), 7.10 (dd, 2H, J = 4.0, 8.0 Hz). ^{13}C {^{1}H} NMR: ($CDCl_3$, 100 MHz) δ 160.3, 146.9, 142.4, 138.2, 133.7, 128.3, 122.6. ^{31}P{^{1}H} NMR: ($CDCl_3$, 162 MHz) δ -12.1.

3,3'-bis(diphenylphosphino)-6,6'-dimethyl-2,2'-bipyridine (bpyPHOS-Me): Prepared as described above to yield a yellow solid in 85%. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.34 (s, 20H), 7.24 (d, 2H, J = 8.0 Hz), 6.92 (d, 2H, J = 8.0 Hz), 2.17 (s, 6H).). ^{13}C {^{1}H} NMR: ($CDCl_3$, 100 MHz) δ 159.6, 156.2, 143.2, 139.3, 133.7, 129.5, 128.1, 122.2, 22.6. ^{31}P{^{1}H} NMR: ($CDCl_3$, 162 MHz) δ -12.1.

3,3'-bis(diphenylphosphino)-6,6'-dimethoxy-2,2'-bipyridine (bpyPHOS-OMe): Prepared as described above to yield a yellow solid in 89%. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.44 (m, 20H), 6.77 (d, 4H, J = 8.0 Hz) 3.44 (s, 6H). ^{13}C {^{1}H} NMR: ($CDCl_3$, 100 MHz) δ

162.9, 161.5, 161.1, 145.2, 138.2, 133.3, 133.1, 128.1, 123.0, 122.8, 111.0, 53.0. $^{31}P\{^{1}H\}$ NMR: ($CDCl_3$, 162 MHz) δ -17.5.

3,3'-bis(diphenylphosphino)-6,6'-diethyl-2,2'-bipyridine (bpyPHOS-Et): Prepared as described above to yield a yellow solid in 85%. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.36 (s, 20H), 7.25 (d, 2H, *J* = 8.0 Hz), 6.94 (d, 2H, *J* = 8.0 Hz), 2.22 (q, 4H, J= 8.0) 1.10 (t, 6H, J= 8.0). $^{31}P\{^{1}H\}$ NMR: ($CDCl_3$, 162 MHz) δ -9.04

3,3'-bis(diphenylphosphino)-6,6'-diisobutyl-2,2'-bipyridine (bpyPHOS-^{i}Bu): Prepared as described above to yield a yellow solid in 82%. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.38 (s, 20H), 7.26 (d, 2H, *J* = 8.0 Hz), 6.95 (d, 2H, *J* = 8.0 Hz), 2.19 (d, 2H, *J* = 8 Hz) 1.16 (t, 12H, *J* = Hz). $^{31}P\{^{1}H\}$ NMR: ($CDCl_3$, 162 MHz) δ -10.2.

(bpyPHOS)PtI_2: To a solution of (COD)PtI_2 (500 mg, 897 mmol) in CH_2Cl_2 was added mg bpyPHOS (470 mg, 897 mmol) in CH_2Cl_2. The reaction was stirred for 15 min, and then a yellow-green solid was precipitated from the CH_2Cl_2 with pentane. After copious repeated washing with pentane, the solid was dried under vacuum to yield (bpyPHOS)PtI_2 in 95% yield (830 mg). X-Ray quality crystals were grown by slow evaporation of CH_2Cl_2. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.87 (m, 2H), 7.42 (d, 4H, *J* = 7.2 Hz), 7.40 (m, 4H), 7.27 (m, 14H), 6.89 (d, 2H, *J* = 8.0 Hz). $^{13}C\ \{^{1}H\}$ NMR: ($CDCl_3$, 100 MHz) δ 162.3, 141.6, 137.0, 135.2, 132.1, 131.4, 129.4, 127.6, 127.2, 126.9, 126.8, 126.5, 122.7. $^{31}P\ \{^{1}H\}$ NMR: ($CDCl_3$, 162 MHz) δ 5.2 (s, 2P, $J_{Pt\text{-}P}$ = 3350 Hz).

(bpyPHOS-Me)PtI_2: Prepared as above to produce the complex in 92% yield. ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 7.87 (m, 3H), 7.59 (d, 4H, *J* = 8.0 Hz), 7.40 (m, 8H), 7.28 (m, 4H), 7.10 (d, 2H, *J* = 12.0 Hz), 6.69 (d, 2H, *J* = 8.0 Hz), 2.34 (s, 6H). $^{13}C\ \{^{1}H\}$ NMR:

($CDCl_3$, 100 MHz) δ 162.2, 140.8, 136.1, 134.8, 131.7, 131.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 122.7, 24.2. ^{31}P {^1H} NMR: ($CDCl_3$, 162 MHz) δ 5.2 (s, 2P, J_{Pt-P} = 3300 Hz).

(bpyPHOS-OMe)PtI$_2$: Prepared as above to produce the complex in 94% yield. ^1H NMR: ($CDCl_3$, 400 MHz) δ 7.92 (d,4H, *J* = 8.0 Hz), 7.67 (d, 4H, *J* = 8.0 Hz), 7.43 (m, 8H), 7.33 (t, 4H, *J* = 8.0 Hz), 7.04 (d, 2H, *J* = 4.0 Hz), 6.30 (d, 2H, *J* = 8.0 Hz), 3.76 (s, 6H). ^{31}P {^1H} NMR: ($CDCl_3$, 162 MHz) δ 4.30 (J_{Pt-P} = 3480 Hz).

(bpyPHOS-Et)PtI$_2$: Prepared as above to produce the complex in 90% yield. ^1H NMR: ($CDCl_3$, 400 MHz) δ 7.87 (s 4H,), 7.45 (m, 18H), 6.76 (d, 2H, *J* = 8.0 Hz), 1.90 (t, 4H, *J* = 8.0 Hz), 1.19 (t, 6H, *J* = 6 Hz). ^{31}P {^1H} NMR: ($CDCl_3$, 162 MHz) δ 5.04 (J_{Pt-P} = 3453 Hz).

(bpyPHOS-^{i}Bu)PtI$_2$: Prepared as above to produce the complex in 94% yield. ^1H NMR: ($CDCl_3$, 400 MHz) δ 7.89 (s 4H,), 7.42 (m, 18H), 6.77 (d, 2H, *J* = 8.0 Hz), 1.95 (d, 2H, *J* = 8.0 Hz), 1.14 (t, 6H, *J* = 12 Hz). ^{31}P {^1H} NMR: ($CDCl_3$, 162 MHz) δ 5.18 (J_{Pt-P} = 3432 Hz).

General procedure for addition of chiral H-bonders to (bpyPHOS-R)PtI$_2$. To a solution of (bpyPHOS-R)PtI_2 in $CDCl_3$ (0.6 mL) was added 5.0 equiv chiral H-bonder. The reaction was monitored by ^{31}P NMR.

(bpyPHOS-Me)PtI$_2$ + L-DBT: To a solution of (bpyPHOS-Me)PtI_2 in $CDCl_3$ (0.6mL) was added 1.0 equiv L-DBT. After 3 h at RT a 5.5:1 ratio of diastereomers was observed by by ^{31}P NMR. An X-ray quality crystal of a single diastereomer of the adduct was form by slow evaporation of $CDCl_3$. ^{31}P{^1H} NMR: ($CDCl_3$, 162 MHz) δ 9.28 (J_{Pt-P} 3650 Hz 1P), 9.21 (J_{Pt-P} 3650 Hz 5P).

(bypPHOS)Pt(BINOLate): To a suspension of (bypPHOS)PtI_2 (197 mg, 0.25 mmol) in 15 mL of CH_2Cl_2 in air was added 5 mL of a red water solution containing (*S*)-BINOL (143 mg, 0.50 mmol) and KOH (56 mg, 1.00 mmol). The reaction was complete after stirring in air for 12 h (^{31}P NMR). After addition of 10 mL of CH_2Cl_2, the deep red organic layer was separated. The aqueous layer was twice extracted with 5 mL portions of CH_2Cl_2. The combined organic fractions were back extracted with 5 mL of H_2O, dried over $MgSO_4$, filtered and the solvent then removed to a calculated volume of 15 mL, whereupon 7 mL of MeOH was added. The solvent was then removed *in vacuo* and the solid was dried for 12 h under vacuum (< 10 mmHg) to afford **8** (147 mg, 84% yield) as a red crystalline solid.

BINOLate Cleavage: To a solution of (bypPHOS)Pt((*S*)-BINOLate) (30 mg, .030 mmol) in CH_2Cl_2 at -78 ^oC was added HCl (1 M in ether) (60 μL, .060 mmol) followed by the addition of (*S,S*)-DPEN (25.5 mg, 0.12 mmol). ^{31}P NMR showed a 1:1 d.r.

General Catalytic Procedures. To a solution of (P_2)PtI_2 (P_2 = BIPHEP, bpyPHOS, bpyPHOS-Me) (2 mol%) in CH_2Cl_2 was added $AgSbF_6$ (4 mol%). The resulting active catalyst was filtered into a solution of L-DBT (10 mol% equiv) in CH_2Cl_2 and stirred for 15 min. The reaction mixture was then cooled to 0 °C and ethyl glyoxylate (3.0 equiv) was added and then stirred for 15 min. α-methyl styrene (1.0 equiv) was added and the reaction was monitored by chiral GC (Agilent, β-cyclosil, 140 ^oC for 1 min, 20 ^oC/min, 200 ^oC for 10 min): t_R: 19.8 min, t_R: 20.4 min.

Appendix A

Synthesis and Characterization of Bifunctional Compounds: Templates for Metal Crown Ether Assemblies

A.1. Introduction

Enzymes are capable of distinguishing the appropriate substrate from a complex mixture, orienting it in such a manner as to lower its transition state energy, and then initiate a chemical reaction. Once complete, the product is released and the process is repeated. The functionality and selectivity of enzymes are due to the multiple functional sites (acids, bases, H-bond donors, acceptors, metals, etc.) which act upon the substrate. In an effort to mimic the multiple interactions of an enzyme, our lab has focused work on molecular imprinted polymers (MIPs).[1,2] This method utilizes a host-guest duet where the host contains polymerizable functional groups and a cleavable guest. The host-guest molecule is copolymerized to form rigid porous polymers wherein the guest can be cleaved leaving a template of similar shape in the MIP.[3] Like the active site of an enzyme a MIP has increased recognition of its templated guest.[4]

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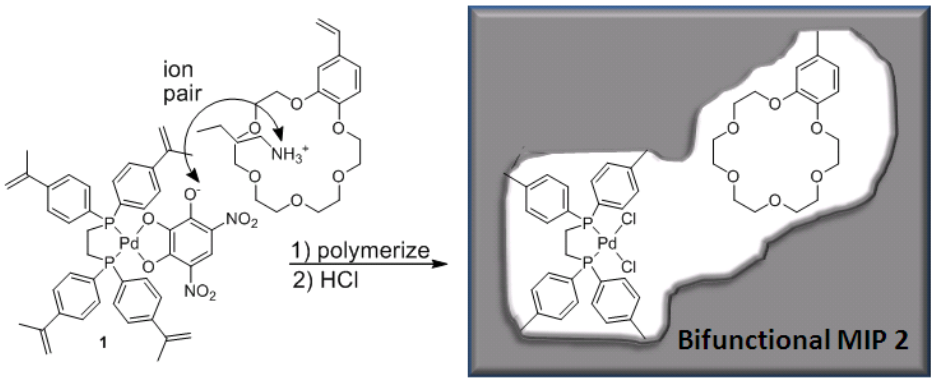
1. (a) Koh, J. H.; Larsen, A. O.; White, P. S.; Gagné, M. R. *Organometallics* **2002**, *21*, 7-9. (b) Viton, F.; Gagné, M. R. *Chem. Commun.* **2003**, 3040-3041. (c) Becker, J. J.; Gagné, M. R. *Acc. Chem. Res.* **2004**, *37*, 798-804. (d) Polborn, K.; Severin, K. *Chem. Commun.* **1999**, 2481-2482. (e) Polborn, K.; Severin, K. *Eur. J. Inorg. Chem.* **2000**, 1687-1692. (f)Polborn, K.; Severin, K. *Chem. Eur. J.* **2000**, *6*, 4604-4611. (g) Santora, B. P.; Gagné, M. R.; Moloy, K. G.; Radu, N. S. *Macromolecules* **2001**, *34*, 658-661. (h) Sherrington, D. C. *Chem. Commun.* **1998**, 2275-2286.

2. The broader field of catalysis in imprinted polymers has been reviewed: (a) Alexander, C.; Davidson, L.; Hayes, W. *Tetrahedron* **2003**, *59*, 2025-2057. (b) Davis, M. E.; Katz, A.; Ahmad, W. R. *Chem. Mater.* **1996**, *8*, 1820-1839. (c) Tada, M.; Iwasawa, Y. *J. Mol. Cat. A: Chem.* **2003**, *3953*, 1-23. (d) Wulff, G. *Chem. Rev.* **2002**, *102*, 1-27.

3. (a) Molecularly Imprinted Polymers: Manmade mimics of antibodies and their applications in analytical chemistry; Sellergren, B., Ed. Elsevier: Amsterdam, 2001. (b) Molecularly Imprinted Materials-Sensors and

To obtain greater selectivity/reactivity, a new generation of MIPs were produced with a Pd center and a crown ether in the outer coordination sphere (Scheme A.1); these bifunctional MIPs showed greater reactivity.[5,6] This is similar to the homogeneous catalyst that Hayashi and Ito have developed.[7] Their multifunctional Pd catalyst contains chiral ferrocenyl diphosphine ligands with pendent polyols or crown ethers that exhibit increased reactivity in conjunction with increased enantioselectivity. This suggests that these systems have an optimal arrangement of both metal and receptor that stabilizes the transition state.[8]

Scheme A.1



Other Devices; Shea, K. J.; Yan, M.; Roberts, M. J., Eds. Materials Research Society: Warrendale, PA, 2002; Vol. 723. (c) Wulff, G. *Angew. Chem. Int. Ed.* **1995**, *34*, 1812-1832.

4. Santora, B. P.; Gagné, M. R. *Chem. Innov.* **2000**, 23-29.

5. Viton, F.; White, P. S.; Gagné, M. R. *Chem. Commun.* **2003**, 3040-3041.

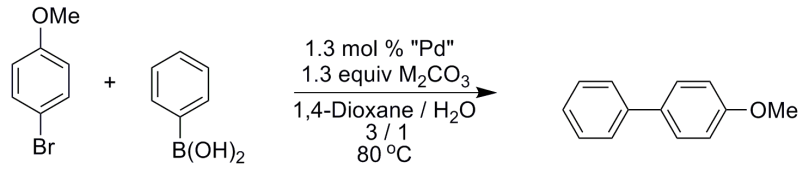
6. Metal ammine and aquo complexes are known to bind crown ethers. See, for example: (a) Colquhoun, H. M.; Lewis, D. F.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc. Dalton Trans.* **1983**, 607-613. (b) Vance Jr., T. B.; Holt, E. M.; Varie, D. L.; Holt, S. L. *Acta Crst.* **1980**, *B36*, 153-155.

7. Hayashi, T.; Kanehira, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1988**, *53*, 113-120. (b) Sawamura, M.; Nagata, H.; Sakamoto, H.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2586-2592. (c) Sawamura, M.; Nakayama, Y.; Tang, W.-M.; Ito, Y. *J. Org. Chem.* **1996**, *61*, 9090-9096.

8. Many conceptually similar approaches have been reviewed: (a) Ma, J.-A.; Cahard, D. *Angew. Chem. Int. Ed.* **2004**, *43*, 4566-4583. (b) Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857-871. (c) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem. Int. Ed.* **1997**, *36*, 1236-1256.

The bifunctional MIP (CE-MIP-Pd) was tested against an MIP that only contained the Pd-pyrogallate (MIP-Pd) template for comparative rates of the Suzuki coupling reaction (Table A.1). The rate enhancements seen for the bifunctional MIP corresponded to the 18-c-6 binding affinity for the alkali metal carbonate bases (K>Rb>Cs>Na> Li). Presuming that a more well-defined template would lead to even better imprinting results, we designed several third-generation templates that physically attached the ammonium linker to the ligand with the goal of generating a more spatially precise assembly of catalyst and crown ether. This report focuses on the synthesis and structural characterization of compounds that lend themselves to future molecular imprinting experiments while also providing a molecular visualization of the crown/catalyst assembly that may be relevant to the Hayashi/Ito allylation reactions.

Table A.1. Comparative rates of reaction between functionalized and unfuctionalized MIPs



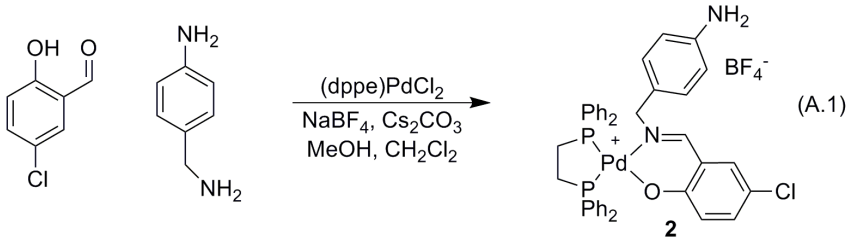
M_2CO_3	MIP-Pd (% converion)	CE-MIP-Pd (% conversion)	Comparitive rates
K_2CO_3	26	66	2.5
Rb_2CO_3	48	77	1.6
Cs_2CO_3	49	70	1.4
Na_2CO_3	57	71	1.2
Li_2CO_3	42	44	1.1

A.2. Results and Discussion

At the onset we desired a ligand framework that would be modular and amenable to a variety of derivatization techniques. A salicylimine seemed to provide both the scaffold for attaching multiple donor acceptor-type functionalities and the means for a convergent

synthesis. Concurrent work in our laboratory had demonstrated that salicylimines were stable on $P_2Pt(II)$ and $P_2Pd(II)$-fragments,[9] and so we were confident that this ligand set would be amenable to functionalization and derivatization.[10]

Salicylimine/Crown Ether Complexes. Following a procedure developed for unfunctionalized derivatives, a combination of 4-amino-benzylamine, 5-Cl-salicylaldehyde, Cs_2CO_3, $NaBF_4$ and $(dppe)PdCl_2$ in a 1:1 mixture of CH_2Cl_2:MeOH for 2 h cleanly provided a new product, **2**, in good yield (84%) after aqueous workup (eq A.1). The pair of doublets in the ^{31}P NMR ($J_{P\text{-}P}$ = 28 Hz) were consistent with the formulation of the product as a salicylimine. Of course, two isomers were possible: an *N*-benzyl-imine and an *N*-aryl-imine. Based on the key C*H*$_2$N resonance in the ^1H NMR, and model compounds (*N*-phenyl and *N*-benzyl), the *N*-benzyl-imine isomer was obtained, consistent with previous experiments showing a strong preference for an electron donating imine-substituent.[9] Compound **2** was air and moisture stable.



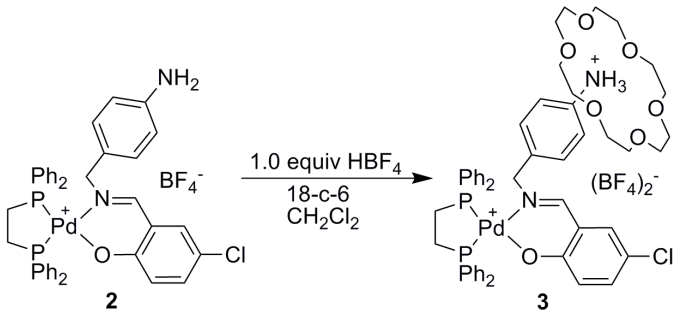
(A.1)

Attempts to protonate **2** with ethereal HBF_4 led to extensive decomposition, however, in the presence of 18-c-6, a relatively stable monoprotonated adduct, **3**, was obtained (eq A.2). Repeated washings with ether and/or crystallizations from MeOH/^{t}BuOMe did not dislodge the single equivalent of the crown from **3**. Most diagnostic in the ^1H NMR was the

9. Kerber, W. D.; Nelsen, D. L.; White, P. S.; Gagné, M. R. *J. Chem. Soc. Dalton Trans.* **2005**, 1948-1951.

10. Electron withdrawing groups on the salicylaldehyde were found to provide enhanced stabilization to the complexes in their protonated state so the 5-Cl derivative was utilized throughout (see footnote 5).

broadened resonance at 9.0 ppm (3H), characteristic of a $PhNH_3^+$•18-c-6 host-guest complex.[11] In contrast, the N*H* of $PhCH_2NH_3^+$•18-c-6 resonates at ~7.4 ppm, suggesting that **3** resulted from aniline protonation and subsequent trapping with the crown ether. ^{1}H NMR analysis of **3** indicates that even to –56 °C, the crown ether decomplexes and recomplexes faster than the NMR time scale as only a single resonance is observed for the two faces of the crown. Standing CD_2Cl_2 or $CDCl_3$ solutions of **3** begin to decompose at extended times (>12 h), though X-ray quality crystals could be obtained by the overnight vapor diffusion of ^{t}BuOMe into a saturated MeOH solution (Figure A.1).



(A.2)

11. Gokel, G. W.; Abel, E. In *Comprehensive Supramolecular Chemistry*; Gokel, G. W., Ed.; Elsevier: New York, NY, 1996; Vol. 1, p 511-535.

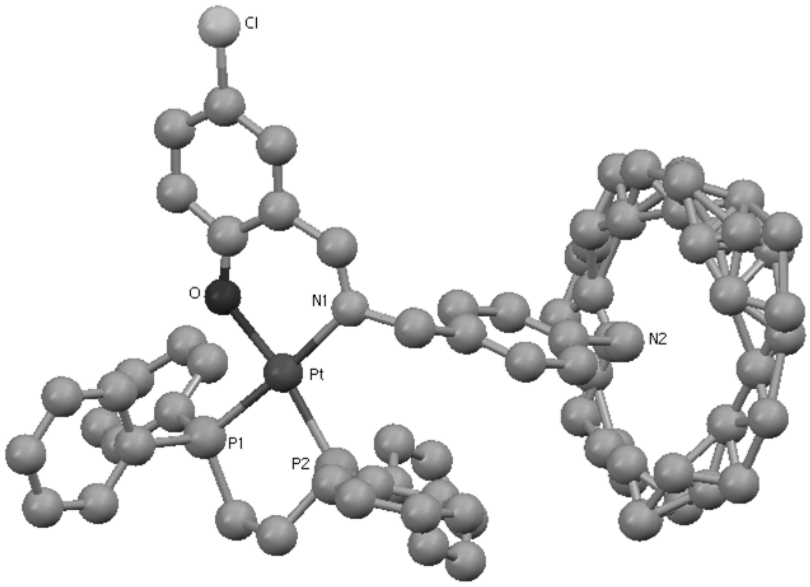
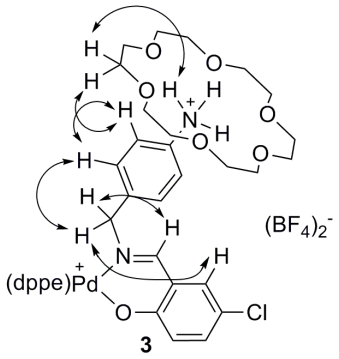


Figure A.1. Plot of **3** showing the atom connectivity of the organometallic complex; however, extensive disorder is seen in the crown ether.

As with many crown ether structures, disorder in the crown was extensive and a structural refinement leading to reliable metrical parameters was not possible despite significant effort. Nevertheless, the structure was sufficient to unambiguously establish the atom connectivity shown in Figure A.1.

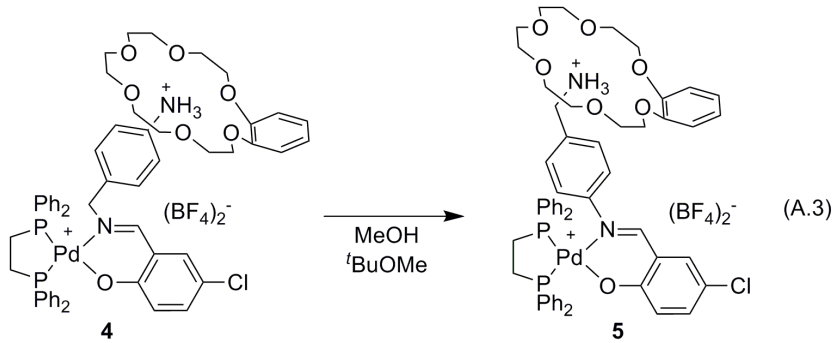
The gross features of the solid-state structure's connectivity are maintained in the solution state as judged by the NOESY spectrum. As shown in Scheme A.2, the key cross peaks are indicative of crown ether coordination to the anilinium ion at the terminus of the ligand. Cross peaks between the P-Ph and NCH_2 and the P-Ph and OCH_2 (weak) resonances were also observed. The solution and solid state structures of **3** are adequately represented by the 2-dimensional picture in eq A.2.

Scheme A.2 nOe cross peaks in NOSEY spectrum of **3** ($CDCl_3$, -56 °C)



3

Protonation of **2** with HBF_4 in the presence of benzo-18-c-6 led to an analogous product, **4**, which also contained the distinctive resonance at 9.0 ppm for the ArNH_3^+•crown. Adduct **4** was considerably more sensitive than **3** to polar solvents (e.g. MeOH), and attempts to crystallize the product invariably led to decomposition. Most of the decomposition products were unidentified, but one crown ether-containing compound proved to be exceptionally crystalline and was subjected to X-ray analysis. Unfortunately, like compound **3**, **5** was disordered and only atom connectivity information was obtained at a confidence level sufficient for publication (Figure A.2). Surprisingly, this compound proved to be an isomer of **4** wherein the two nitrogen positions were exchanged, i.e. *N*-arylimine/$ArCH_2NH_3^+$•crown complex **5** (eq A.3).



4 **5**

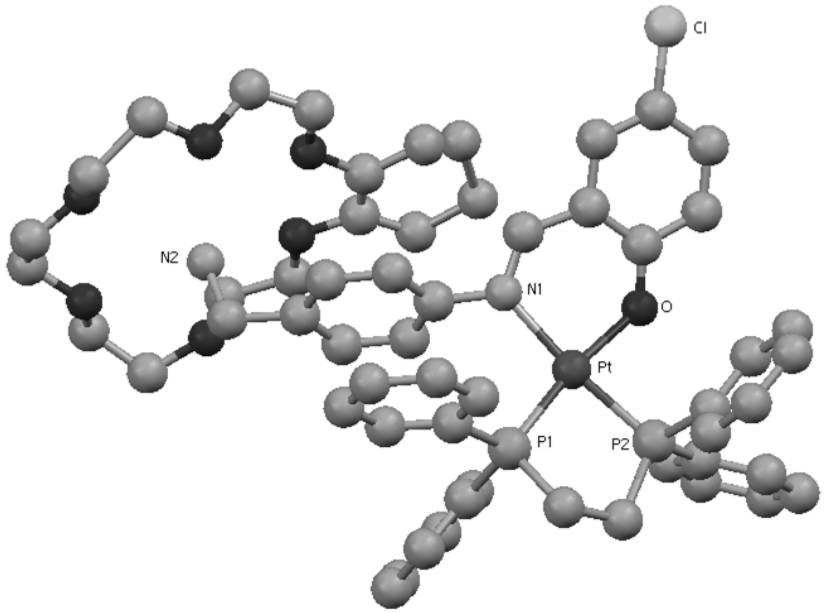


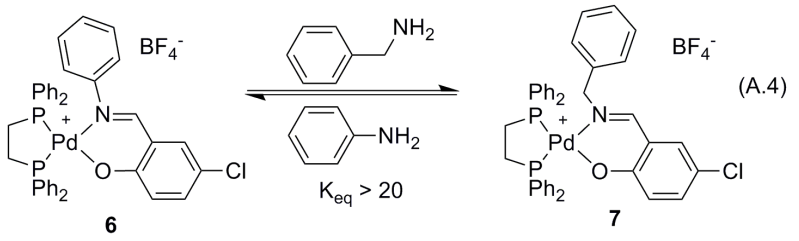
Figure A.2. While the crown ether is disordered, the connectivity of **5** clearly show an isomerization of 4-amino-benzylamine

An assessment of their comparative thermodynamic stability was not obvious since two key factors, $ArNH_3^+$•crown vs. $ArCH_2NH_3^+$•crown and Pd-N-CH_2Ar vs. Pd-N-Ar, ran counter to one another, i.e. Pd prefers the more basic *N*-alkyl substituent[12] while the crown prefers to bind $ArCH_2NH_3^+$.[13] For arguments that are primarily steric in nature, 18-c-6 binds to a primary alkyl ammonium ion slightly better (log K_A = 3.99; MeOH) than the more acidic anilinium ion (log K_A = 3.80; MeOH).[13] To determine the magnitude of the bias for *N*-benzyl over *N*-phenyl imine, 1 equivalent of benzyl amine was added to **6**, and the solution heated to promote imine interchange (CH_3NO_2, eq A.4). As expected, the *N*-benzylsalicylate complex **7** was favored by >20:1 at 60°C, suggesting that **5** likely results from a

12. No trace of the alternative form of **3** was observed in the crude reaction mixture during its synthesis (eq A.2).

13. Izatt, R. M.; Lamb, J. D.; Izatt, N. E.; Rossiter Jr., B. E.; Christensen, J. J.; Haymore, B. L. *J. Am. Chem. Soc.* **1979**, *101*, 6273-6276.

crystallization induced process and not by being significantly favored on thermodynamic grounds.



(A.4)

The lack of stability of protonated complexes in the absence of crown ether, the enhanced stability of the 18-c-6 complex (**3**) over the benzo-18-c-6 (**4**), the stability of the adducts in non-polar solvents (e.g. *o*-$Cl_2C_6H_4$) coupled with their instability in polar solvents is consistent with a scenario wherein the crown ether attenuates the effective acidity of the ammonium ions towards an otherwise acid sensitive metal fragment. In the case of the two crown ether types, 18-c-6 is known to bind ammonium ions ~60-times more strongly than benzo-18-c-6 (log K_A = 5.9 versus 4.1 (MeOH)).[14,15] Similarly, strong solvent effects are known to be operative in ammonium-crown binding, with polar protic solvents being significantly less stabilizing than non-protic and non-polar solvents (acetone > CH_3CN > MeOH > H_2O).[11,16] Thus, factors tending to increase the strength of the ammonium-crown interaction (and concomitantly decreasing the concentration of the uncomplexed anilinium ion) serve to increase the stability of the metal-crown aggregate towards decomposition. For

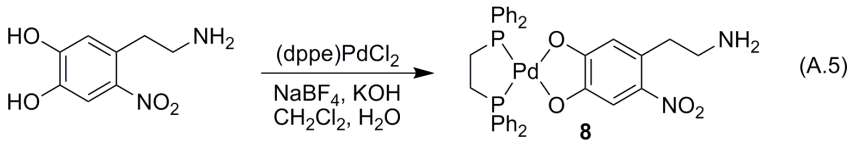
14. Timko, J. M.; Moore, S. S.; Walba, D. M.; Hiberty, P. C.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 4207-4219.

15. This proved to also be the case with the metal complexes as the addition of 1 equivalent of 18-c-6 to **4** led to quantitative displacement of benzo-18-c-6 as judged by the collapse of the pair of multiplets in the aromatic portion of the benzo-18-c-6; the free crown exhibits a broad singlet in the aromatic region.

16. de Boer, J. A. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1985**, *107*, 5347-5351.

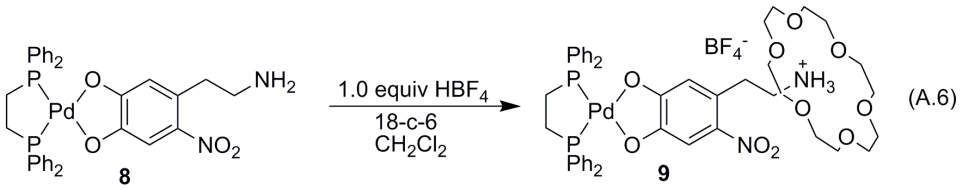
example, even the relatively sensitive complex **4** is stable to 60°C overnight in a non-polar solvent like *o*-$Cl_2C_6H_4$ (c.f. MeOH).

Nitro-Dopamine/Crown-Ether Complexes. Another ligand class that was examined for attaching functional groups was the catechols. In particular, 5-nitro-dopamine proved to be particularly well behaved, both towards formation of the free base metal complex (**8**, eq A.5) and to the protonated 18-c-6 adduct (**9**, eq A.6). Perhaps reflecting the poor nucleophilicity of the nitrocatecholate, reaction of (dppe)$PdCl_2$ with one equivalent of the anion in a biphasic mixture of CH_2Cl_2 and H_2O was sluggish, but proceeded quicker and cleaner with 2 equivalents of the ligand to generate blood red solutions of the Pd-catecholate (eq A.5). The excess ligand and salts were conveniently removed in the aqueous workup.



(A.5)

As before, protonation with ethereal HBF_4 in the presence of 1.1 equivalents of 18-c-6 provided the ammonium ion-crown ether host-guest complex **9**, which persisted even after several washings with ether and recrystallization. Based on the spectroscopic data (broad ammonium signal at 7.3 ppm), we suggest the solution structure shown in eq A.6.



(A.6)

The stability of **9** was initially surprising since previous experiments[17] had shown that the protonated parent dopamine complex was prone to decomposition (data not shown). As before,[10] an electron withdrawing group (NO_2) appeared to resolve this sensitivity and the resulting complexes were stable and well-behaved. In fact, **9** was indefinitely stable even in the presence of protic solvents like methanol (c.f. **3-5**), suggesting that for stability reasons, it may be the best candidate for imprinting experiments.

In summary, we report a series of complexes wherein dangling primary amine groups can be protonated to non-covalently bind crown ethers. In general, the salicylimines and the catecholates are moderately acid sensitive; however, binding of the crown ether to the primary ammonium ion serves to make the desired supramolecular aggregate and attenuate the ion's acidity, which stabilizes the metal-ligand complex.

A.3 Experimental

General Methods. All reactions were performed under nitrogen using standard Schlenk techniques unless otherwise mentioned. Dichloromethane and ether were passed through a column of activated alumina before use. Methanol was distilled from sodium methoxide prior to use. (dppe)$PdCl_2$, [18] 5-nitrodopamine, [19] and (dppe)Pd(2-(*N*-phenyliminomethyl)phenolate)(BF_4)[9] were prepared according to the literature procedures. All other materials were purchased from Aldrich. NMR solvents ($CDCl_3$ and CD_3NO_2,) were purchased from Cambridge Isotope labs. All ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on

17. Kerber, W. D.; Viton, F., unpublished results.

18. Gugger, P.; Limmer, S. O.; Watson, A. A.; Willis A. C.; Wild S. B. *Inorg. Chem*., **1993**, *32*, 5692-5696.

19. Napolitano, A.; d'Ischia, M.' Costantini, C.; Prota, G. *Tetrahedron*, **1992**, *48*, 8515-8522.

a Bruker AMX 400 or AMX 300 spectrometer, and chemical shifts were referenced to the residual solvent peaks (^{1}H, ^{13}C) or 85% H_3PO_4 external standard (^{31}P). Some complexes were unstable in solution at times long enough to acquire carbon NMR. Elemental analysis was performed by Complete Analysis Laboratories, Inc., Parsippany, NJ

(dppe)Pd(chlorosalicylimine) 2. To a suspension of $NaBF_4$ (225 mg, 2.05 mmol), (dppe)$PdCl_2$ (492 mg, 0.854 mmol), 4-aminobenzylamine (80 mg, 0.854 mmol), and 5-chloro-2-hydroxybenzaldehyde (134 mg, 0.854 mmol) in a mixture of 48 mL 1:1 CH_2Cl_2/MeOH was added Cs_2CO_3 (306 mg, 0.940 mmol). The reaction was stirred at room temperature and monitored periodically by ^{31}P NMR until complete (4 h). To the solution was added 25 mL H_2O, the layers were separated and the aqueous phase was back extracted three times with 5 mL CH_2Cl_2. The organics were combined and dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo* yielding a solid which was dissolved in hot MeOH and cooled to afford orange crystals in 84% yield. $^{1}H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.6 Hz, 4H), 7.91 (d, J = 8.0 Hz, 4H), 7.76 (m, 12H), 7.12 (dd, J = 10.8, 2 Hz, 1H), 7.16 (d, J = 2.8, 1H), 6.65 (d, J = 8.0 Hz, 2H), 6.57 (d, J = 8.8 Hz, 3H), 4.42 (s, 2H), 3.92 (s, 2H), 3.02 (br, 2H), 2.77 (br, 2H); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 63.5 (d, $J_{p\text{-}p}$ = 27.8 Hz), 59.2 (d, $J_{p\text{-}p}$ = 27.8 Hz); $^{13}C\ \{^{1}H\}\{^{31}P\}$ NMR (75 MHz, $CDCl_3$): δ 164.5, 162.6, 146.9, 135.6, 133.4, 133.2, 132.8, 130.1, 129.5, 129.2, 126.1, 125.2, 124.5, 122.7, 120.7, 120.0, 115.2, 67.3, 32.0, 24.6. Anal. Calcd. for $C_{40}H_{36}BClF_4N_2OP_2Pd$: C, 56.43; H, 4.26; N, 3.29. Found: C, 56.29; H, 4.12; N, 3.35.

2·HBF_4·18-c-6, 3. To a solution of **2** (90 mg, 0.106 mmol) and 18-C-6 (31 mg, 0.117 mmol) in 5 mL of CH_2Cl_2 was added 54 % HBF_4 in diethyl ether (14.6 μL, 0.106 mmol). The solution was stirred for 5 min, and then 10 mL of diethyl ether was added to precipitate a

yellow solid. The solid was filtered and washed three times with 5 mL portions of diethyl ether, and then dried under vacuum (< 10 mmHg) for 12 h. The solid was crystallized from MeOH/^{t}BuOMe to afford yellow crystals in 92% yield. $^{1}H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): □ 8.96 (br, 3H), 8.05 (s, 2H), 7.78 (m, 4H), 7.57 (m, 16H), 7.28, (s, 1H), 7.13 (d, J = 9.2 Hz, 2H), 6.96 (m, 2H), 6.38 (d, J = 9.2 Hz, 2H), 4.72 (s, 2H), 3.67 (s, 24H), 2.76 (br, 2H), 2.58 (br, 2H); $^{13}C\ \{^{1}H,^{31}P\}$ NMR (75 MHz, -40°C, $CDCl_3$): δ 167.9, 167.8, 162.5, 138.3, 135.9, 134.0, 132.9, 129.9, 129.5, 129.3, 127.8, 125.3, 124.4, 122.9, 122.3, 120.7, 120.1, 69.8, 66.4, 30.9, 24.5; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 66.6 (d, $J_{p\text{-}p}$ = 29.9 Hz), 60.1 (d, $J_{p\text{-}p}$ = 29.8 Hz). Anal. Calcd. for $C_{52}H_{61}B_2ClF_8N_2O_7P_2Pd$: C, 51.90; H, 5.11; N, 2.33. Found: C, 51.63; H, 5.04; N, 2.34.

2·HBF$_4$·Benzo-18-c-6, 4. To a solution of **2** (90 mg, 0.106 mmol) and benzo-18-c-6 (36 mg, 0.117 mmol) in 5 mL of CH_2Cl_2 was added 54 % HBF_4 in diethyl ether (14.6 mg, 0.106 mmol). The solution was stirred for 5 min and the solvent was removed *in vacuo*. The yellow solid was washed three times with 5 mL portions of diethyl ether and dried under vacuum (< 10 mmHg) for 12 h. The solid was obtained in quantitative yield. $^{1}H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 9.31 (br, 3H), 7.97 (br, 1H), 7.75 (m, 4H), 7.62 (m, 12H), 7.39 (br, 6H), 7.15, (m, 2H), 6.93 (br, 4H), 6.78 (m, 2H), 6.36 (m, 1H), 4.64, (br, 2H), 4.23 (br, 4H), 3.92 (br, 4H), 3.74 (m, 12H), 2.69 (br, 2H), 2.53 (br, 2H); $^{13}C\ \{^{1}H,^{31}P\}$ NMR (75 MHz, -40°C, $CDCl_3$): δ 167.7, 167.6, 162.5, 147.8, 145.7, 135.9, 133.9, 133.3, 133.0, 132.8, 129.8, 129.5, 128.9, 127.7, 125.2, 124.2, 122.5, 122.0, 120.5, 120.0, 111.4, 70.2, 70.0, 69.6, 68.7, 67.0, 66.6, 66.4, 53.6, 30.8, 24.4; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 64.8 (d, $J_{p\text{-}p}$ = 27.9 Hz), 58.1 (d, $J_{p\text{-}p}$ = 27.6 Hz). Anal. Calcd. for $C_{52}H_{61}B_2ClF_8N_2O_7P_2Pd$: C, 53.74; H, 4.91; N, 2.24. Found: C, 53.52; H, 4.82; N, 1.99.

2·HBF$_4$·Benzo-18-c-6 (isomer), 5. To a solution of (dppe)Pd(chlorosalicylimine) (90 mg, 0.106 mmol) and 18-c-6 (36 mg, 0.117 mmol) in 5 mL of CH_2Cl_2 was added 54 % HBF_4 in diethyl ether (14.6 μL, 0.106 mmol). The solution was stirred for 5 min, and then precipitated by addition of 10 mL of diethyl ether. The solid was filtered and washed three times with 5 mL portions of diethyl ether. The solid was dissolved in MeOH and crystallized by slow diffusion of ^{t}BuOMe to afford yellow crystals in low yield. $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 7.93 (br, 1H), 7.75 (m, 3H), 7.62 (m, 12H), 7.51 (m, 8H), 7.40, (s, 1H), 7.21 (s, 1H), 7.10 (m, 2H), 6.73 (s, 4H), 6.40 (br, 1H), 6.34, (m, 2H), 4.59 (s, 2H), 4.32 (br, 4H), 3.95 (br, 4H), 3.81 (m, 12H), 2.76 (br, 2H), 2.58 (br, 2H); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 66.4 (d, $J_{p\text{-}p}$ = 28.9 Hz), 60.0 (d, $J_{p\text{-}p}$ = 28.7 Hz).

Compound 7. To a suspension of $NaBF_4$ (37 mg, 0.38 mmol), (dppe)$PdCl_2$ (81 mg, 0.141 mmol), benzylamine (16 μL, 0.141 mmol), and 2-hydroxybenzaldehyde (12 μL, 0.141 mmol) in 12 mL of a 1:1 mixture of CH_2Cl_2/MeOH was added Cs_2CO_3 (46 mg, 0.141 mmol). The reaction was stirred at room temperature and was monitored by ^{31}P NMR until complete (4 h). The solution was added to 6 mL water and separated. The aqueous layer was extracted three times with 5 mL portions of CH_2Cl_2. The organics were combined and dried over $MgSO_4$. The solvent was removed *in vacuo* and the solid was crystallized by vapor diffusion of ^{t}BuOMe into CH_2Cl_2 to afford yellow crystals in 96% yield (97 mg). $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 7.85 (m, 5H), 7.55 (m 16H), 7.16 (m, 5H), 6.66 (d, J = 7.2 Hz, 2H), 6.60 (t, J = 7.2 Hz, 1H), 6.46 (d, J = 8.4, 1H), 4.48 (s, 2H), 2.80 (br, 2H), 2.58 (br, 2H); $^{31}P\{^1H\}$ (162 MHz, $CDCl_3$): δ 63.03 (d, $J_{p\text{-}p}$ = 28.5 Hz), 58.29 (d, $J_{p\text{-}p}$ = 28.6); $^{13}C\{^{31}P\}\{^1H\}$ (75 MHz, $CDCl_3$): δ 167.1, 167.0, 164.2, 136.6, 136.2, 135.5, 133.2, 132.7, 130.0, 129.5, 128.7, 127.8, 126.8, 126.7, 125.2, 125.0, 121.2, 119.9, 116.2, 67.4, 31.7, 24.5.

(dppe)Pd(5-nitrodopamine) 8. To a suspension of (dppe)$PdCl_2$ (144 mg, 0.25 mmol) and $NaBF_4$ (65 mg, 0.60 mmol) in 15 mL of CH_2Cl_2 in air was added 5 mL of a red water solution containing 5-nitrodopamine (99mg, 0.50 mmol) and KOH (56 mg, 1.00 mmol). The reaction was complete after stirring in air for 1 h (^{31}P NMR). After addition of 10 mL of CH_2Cl_2, the deep red organic layer was separated. The aqueous layer was twice extracted with 5 mL portions of CH_2Cl_2. The combined organic fractions were back extracted with 5 mL of H_2O, dried over $MgSO_4$, filtered and the solvent then removed to a calculated volume of 15 mL, whereupon 7 mL of MeOH was added. The solvent was then removed *in vacuo* and the solid was dried for 12 h under vacuum (< 10 mmHg) to afford **8** (147 mg, 84% yield) as a red crystalline solid. $^{1}H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 8.00-7.95 (m ,8H), 7.56 (m, 12H), 7.38 (s, 1H), 6.40 (s, 1H), 2.9 (m, 4H), 2.59 (s, 4H), 1.51 (br, 2H); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 55.0 (q_{AB}, $\Delta\nu_{AB}$, 66.6 Hz, J_{AB} 32.4 Hz); $^{13}C\{^{1}H\}\{^{31}P\}$ NMR (75 MHz, $CDCl_3$): δ 171.8, 161.9, 136.7, 132.9, 132.2, 129.4, 128.2, 127.2, 117.9, 111.9, 43.2, 39.2, 25.9. Calcd. for $C_{34}H_{32}N_2O_4P_2Pd$: C, 58.25; H, 4.60; N, 4.00; Found: C, 58.05; H, 4.36; N, 4.39.

8·HBF_4·18-c-6, 9. To a solution of **7** (39mg, 0 .055 mmol) and 18-c-6 (16 mg, 0.060 mmol) in 5 mL of CH_2Cl_2 was added 54% HBF_4 in diethyl ether (7.6 μL, 0.055 mmol). The solution was stirred for 5 min and a light orange solid was precipitated by the addition of 20 mL of diethyl ether. The solid was filtered and washed twice with 5 mL portions of diethyl ether yielding compound **9** (56 mg, 93% yield). 1H$\{^{31}P\}$ NMR (400 MHz, $CDCl_3$): δ 7.95 (br, 8H), 7.58 (s, 1H), 7.41 (br, 12H), 7.22 (br, 3H), 6.42 (s, 1H), 3.62 (br, 24H), 3.03 (br, 4H), 2.67 (br, 4H); $^{31}P\{^{1}H\}$ (162 MHz, $CDCl_3$) δ 56.0 (q_{AB}, $\Delta\nu_{AB}$, 44.7 Hz, J_{AB} 23.6 Hz);

$^{13}C\{^{1}H\}\{^{31}P\}$ (75 MHz, $CDCl_3$): δ 172.8, 163.1, 136.0, 133.0, 132.1, 129.4, 128.3, 128.2, 123.2, 117.8, 112.0, 70.1, 40.3, 34.0, 26.0, 25.9. Anal. Calcd. for $C_{46}H_{57}BF_4N_2O_{10}P_2Pd$: C, 52.46; H, 5.46; N, 2.66. Found: C, 52.53; H, 5.58; N, 2.81.

Equilibrium measurements (typical procedure)

To a solution of **7** (17.9 mg, 0.025 mmol) in 1.0 mL of in $CDCl_3$ was added 2.3 μL aniline (0.025 mmol). The solution was placed and sealed in a J-Young NMR tube and heated at 60 °C. The reaction was monitored by ^{31}P NMR. Equilibrium concentrations were calculated from the molar ratio of the two $P_2Pd(N,O)$ complexes.

Appendix B

Crystal Structure of 5 (Chapter 2)

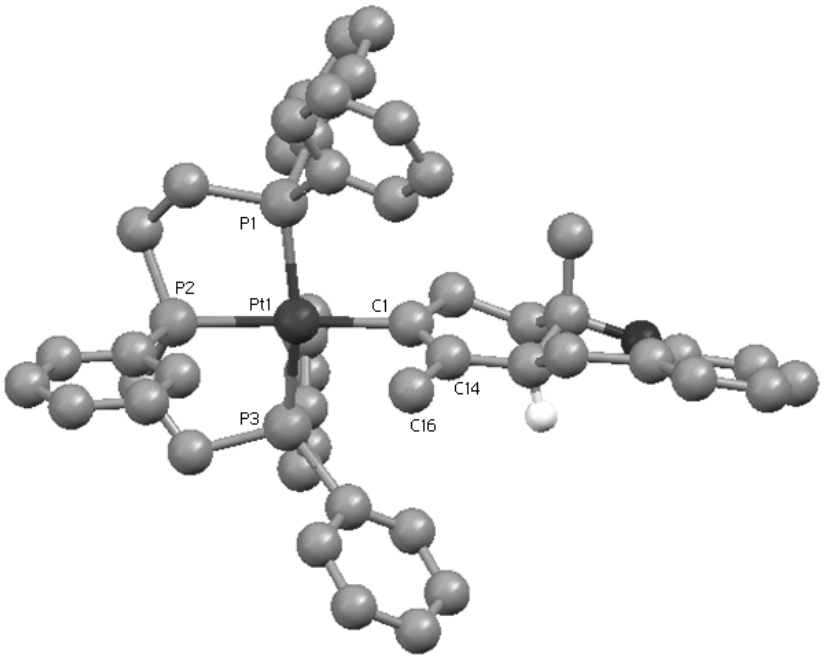


Figure B.1. Chem3D representation of **5**. Counterion is not shown.

Table B.1. Bond distances (Å) for **5**.

Bond	Length (Å)	Bond	Length (Å)
Pt(1)-C(1)	2.10(2)	C(19)-C(20)	1.39
Pt(1)-P(2)	2.275(6)	C(20)-C(21)	1.39
Pt(1)-P(1)	2.283(6)	C(21)-C(22)	1.39
Pt(1)-P(3)	2.284(6)	C(23)-C(24)	1.4109
P(1)-C(23)	1.835(11)	C(23)-C(28)	1.4206
P(1)-C(29)	1.84(2)	C(24)-C(25)	1.395
P(1)-C(17)	1.846(11)	C(25)-C(26)	1.4479
P(2)-C(31)	1.777(14)	C(26)-C(27)	1.4215
P(2)-C(30)	1.81(3)	C(27)-C(28)	1.3596
P(2)-C(37)	1.82(2)	C(29)-C(30)	1.53(3)
P(3)-C(38)	1.85(2)	C(31)-C(32)	1.39
P(3)-C(39)	1.889(16)	C(31)-C(36)	1.39
P(3)-C(45)	1.913(15)	C(32)-C(33)	1.39
C(1)-C(14)	1.33(3)	C(33)-C(34)	1.39
C(1)-C(2)	1.53(3)	C(34)-C(35)	1.39
C(2)-C(3)	1.54(3)	C(35)-C(36)	1.39
C(3)-C(4)	1.48(3)	C(37)-C(38)	1.51(4)
C(4)-O(5)	1.45(2)	C(39)-C(40)	1.39
C(4)-C(13)	1.51(3)	C(39)-C(44)	1.39
C(4)-C(15)	1.52(3)	C(40)-C(41)	1.39
O(5)-C(6)	1.37(3)	C(41)-C(42)	1.39
C(6)-C(11)	1.33(3)	C(42)-C(43)	1.39
C(6)-C(7)	1.43(3)	C(43)-C(44)	1.39
C(7)-C(8)	1.37(3)	C(45)-C(50)	1.3648
C(8)-C(9)	1.29(3)	C(45)-C(46)	1.5091
C(9)-C(10)	1.39(3)	C(46)-C(47)	1.3913
C(10)-C(11)	1.39(3)	C(47)-C(48)	1.4115
C(11)-C(12)	1.59(3)	C(48)-C(49)	1.3956
C(12)-C(13)	1.55(3)	C(49)-C(50)	1.4141
C(13)-C(14)	1.52(3)	B(1)-F(4)	1.348(10)
C(14)-C(16)	1.52(3)	B(1)-F(2)	1.351(10)
C(17)-C(18)	1.39	B(1)-F(1)	1.354(10)
C(17)-C(22)	1.39	B(1)-F(3)	1.355(10)
C(18)-C(19)	1.39		

Table B.2. Bond angles (°) for **5**.

Bonds	Angle (°)	Bonds	Angle (°)
C(1)-Pt(1)-P(2)	177.6(5)	C(13)-C(14)-C(16)	114(2)
C(1)-Pt(1)-P(1)	97.6(5)	C(18)-C(17)-C(22)	120
P(2)-Pt(1)-P(1)	84.4(2)	C(18)-C(17)-P(1)	119.7(5)
C(1)-Pt(1)-P(3)	93.0(5)	C(22)-C(17)-P(1)	120.3(5)
P(2)-Pt(1)-P(3)	85.4(2)	C(19)-C(18)-C(17)	120
P(1)-Pt(1)-P(3)	162.9(3)	C(18)-C(19)-C(20)	120
C(23)-P(1)-C(29)	103.1(9)	C(21)-C(20)-C(19)	120
C(23)-P(1)-C(17)	106.0(4)	C(20)-C(21)-C(22)	120
C(29)-P(1)-C(17)	106.5(9)	C(21)-C(22)-C(17)	120
C(23)-P(1)-Pt(1)	111.8(4)	C(24)-C(23)-C(28)	123.3
C(29)-P(1)-Pt(1)	107.7(7)	C(24)-C(23)-P(1)	118.8(3)
C(17)-P(1)-Pt(1)	120.4(4)	C(28)-C(23)-P(1)	117.8(3)
C(31)-P(2)-C(30)	102.8(11)	C(25)-C(24)-C(23)	116.4
C(31)-P(2)-C(37)	104.9(10)	C(24)-C(25)-C(26)	123.2
C(30)-P(2)-C(37)	116.6(12)	C(27)-C(26)-C(25)	115.4
C(31)-P(2)-Pt(1)	115.0(7)	C(28)-C(27)-C(26)	124.2
C(30)-P(2)-Pt(1)	109.1(9)	C(27)-C(28)-C(23)	117.5
C(37)-P(2)-Pt(1)	108.6(8)	C(30)-C(29)-P(1)	112.1(17)
C(38)-P(3)-C(39)	112.1(11)	C(29)-C(30)-P(2)	105.9(17)
C(38)-P(3)-C(45)	102.4(10)	C(32)-C(31)-C(36)	120
C(39)-P(3)-C(45)	103.3(7)	C(32)-C(31)-P(2)	119.4(11)
C(38)-P(3)-Pt(1)	106.6(9)	C(36)-C(31)-P(2)	120.6(11)
C(39)-P(3)-Pt(1)	121.0(4)	C(31)-C(32)-C(33)	120
C(45)-P(3)-Pt(1)	109.8(4)	C(34)-C(33)-C(32)	120
C(14)-C(1)-C(2)	119.1(19)	C(33)-C(34)-C(35)	120
C(14)-C(1)-Pt(1)	121.5(17)	C(34)-C(35)-C(36)	120
C(2)-C(1)-Pt(1)	119.0(14)	C(35)-C(36)-C(31)	120
C(1)-C(2)-C(3)	113.6(17)	C(38)-C(37)-P(2)	107.1(16)
C(4)-C(3)-C(2)	108.3(19)	C(37)-C(38)-P(3)	111.8(16)
O(5)-C(4)-C(3)	107(2)	C(40)-C(39)-C(44)	120
O(5)-C(4)-C(13)	107.8(18)	C(40)-C(39)-P(3)	108.3(5)
C(3)-C(4)-C(13)	108.8(17)	C(44)-C(39)-P(3)	131.7(5)
O(5)-C(4)-C(15)	106.7(16)	C(41)-C(40)-C(39)	120
C(3)-C(4)-C(15)	111(2)	C(40)-C(41)-C(42)	120
C(13)-C(4)-C(15)	115(2)	C(43)-C(42)-C(41)	120
C(6)-O(5)-C(4)	117.1(19)	C(42)-C(43)-C(44)	120
C(11)-C(6)-O(5)	125(2)	C(43)-C(44)-C(39)	120
C(11)-C(6)-C(7)	120(2)	C(50)-C(45)-C(46)	122.1
O(5)-C(6)-C(7)	115(2)	C(50)-C(45)-P(3)	115.2(5)
C(8)-C(7)-C(6)	117(2)	C(46)-C(45)-P(3)	121.0(5)

C(9)-C(8)-C(7)	124(3)	C(47)-C(46)-C(45)	115.6
C(8)-C(9)-C(10)	121(2)	C(46)-C(47)-C(48)	119.4
C(9)-C(10)-C(11)	118(3)	C(49)-C(48)-C(47)	124
C(6)-C(11)-C(10)	121(3)	C(48)-C(49)-C(50)	117.7
C(6)-C(11)-C(12)	120(2)	C(45)-C(50)-C(49)	120.2
C(10)-C(11)-C(12)	118(3)	F(4)-B(1)-F(2)	108(2)
C(13)-C(12)-C(11)	107(2)	F(4)-B(1)-F(1)	106(3)
C(4)-C(13)-C(14)	112.8(19)	F(2)-B(1)-F(1)	101(3)
C(4)-C(13)-C(12)	110.2(18)	F(4)-B(1)-F(3)	109(2)
C(14)-C(13)-C(12)	114(2)	F(2)-B(1)-F(3)	109(3)
C(1)-C(14)-C(13)	123(2)	F(1)-B(1)-F(3)	123(3)
C(1)-C(14)-C(16)	123(2)		

Table B.3. Torsion angles (°) for **5**.

Bonds	Angle (°)	Bonds	Angle (°)
C(1)-Pt(1)-P(1)-C(23)	70.9(7)	C(22)-C(17)-C(18)-C(19)	0
P(2)-Pt(1)-P(1)-C(23)	-110.5(4)	P(1)-C(17)-C(18)-C(19)	178.9(4)
P(3)-Pt(1)-P(1)-C(23)	-56.9(9)	C(17)-C(18)-C(19)-C(20)	0
C(1)-Pt(1)-P(1)-C(29)	-176.6(11)	C(18)-C(19)-C(20)-C(21)	0
P(2)-Pt(1)-P(1)-C(29)	2.0(10)	C(19)-C(20)-C(21)-C(22)	0
P(3)-Pt(1)-P(1)-C(29)	55.7(13)	C(20)-C(21)-C(22)-C(17)	0
C(1)-Pt(1)-P(1)-C(17)	-54.5(7)	C(18)-C(17)-C(22)-C(21)	0
P(2)-Pt(1)-P(1)-C(17)	124.1(5)	P(1)-C(17)-C(22)-C(21)	-178.9(4)
P(3)-Pt(1)-P(1)-C(17)	177.8(7)	C(29)-P(1)-C(23)-C(24)	107.8(9)
C(1)-Pt(1)-P(2)-C(31)	53(14)	C(17)-P(1)-C(23)-C(24)	-3.9(9)
P(1)-Pt(1)-P(2)-C(31)	-92.9(6)	Pt(1)-P(1)-C(23)-C(24)	-136.8(5)
P(3)-Pt(1)-P(2)-C(31)	100.8(6)	C(29)-P(1)-C(23)-C(28)	-72.7(8)
C(1)-Pt(1)-P(2)-C(30)	167(14)	C(17)-P(1)-C(23)-C(28)	175.6(4)
P(1)-Pt(1)-P(2)-C(30)	21.8(10)	Pt(1)-P(1)-C(23)-C(28)	42.6(4)
P(3)-Pt(1)-P(2)-C(30)	-144.4(10)	C(28)-C(23)-C(24)-C(25)	1.1
C(1)-Pt(1)-P(2)-C(37)	-65(14)	P(1)-C(23)-C(24)-C(25)	-179.5(5)
P(1)-Pt(1)-P(2)-C(37)	149.9(10)	C(23)-C(24)-C(25)-C(26)	1.1
P(3)-Pt(1)-P(2)-C(37)	-16.4(10)	C(24)-C(25)-C(26)-C(27)	-2.1
C(1)-Pt(1)-P(3)-C(38)	171.1(12)	C(25)-C(26)-C(27)-C(28)	1
P(2)-Pt(1)-P(3)-C(38)	-7.1(11)	C(26)-C(27)-C(28)-C(23)	0.9
P(1)-Pt(1)-P(3)-C(38)	-60.6(14)	C(24)-C(23)-C(28)-C(27)	-2.1
C(1)-Pt(1)-P(3)-C(39)	41.5(9)	P(1)-C(23)-C(28)-C(27)	178.5(5)
P(2)-Pt(1)-P(3)-C(39)	-136.7(7)	C(23)-P(1)-C(29)-C(30)	87.4(19)
P(1)-Pt(1)-P(3)-C(39)	169.8(8)	C(17)-P(1)-C(29)-C(30)	-161.3(18)
C(1)-Pt(1)-P(3)-C(45)	-78.6(7)	Pt(1)-P(1)-C(29)-C(30)	-31(2)
P(2)-Pt(1)-P(3)-C(45)	103.2(5)	P(1)-C(29)-C(30)-P(2)	48(2)

P(1)-Pt(1)-P(3)-C(45)	49.7(10)	C(31)-P(2)-C(30)-C(29)	77.3(19)
P(2)-Pt(1)-C(1)-C(14)	-41(15)	C(37)-P(2)-C(30)-C(29)	-168.7(16)
P(1)-Pt(1)-C(1)-C(14)	103.9(16)	Pt(1)-P(2)-C(30)-C(29)	-45(2)
P(3)-Pt(1)-C(1)-C(14)	-89.5(16)	C(30)-P(2)-C(31)-C(32)	63.1(12)
P(2)-Pt(1)-C(1)-C(2)	131(14)	C(37)-P(2)-C(31)-C(32)	-59.2(13)
P(1)-Pt(1)-C(1)-C(2)	-83.5(14)	Pt(1)-P(2)-C(31)-C(32)	-178.5(7)
P(3)-Pt(1)-C(1)-C(2)	83.0(14)	C(30)-P(2)-C(31)-C(36)	-118.4(12)
C(14)-C(1)-C(2)-C(3)	14(3)	C(37)-P(2)-C(31)-C(36)	119.2(12)
Pt(1)-C(1)-C(2)-C(3)	-158.8(14)	Pt(1)-P(2)-C(31)-C(36)	-0.1(10)
C(1)-C(2)-C(3)-C(4)	-49(2)	C(36)-C(31)-C(32)-C(33)	0
C(2)-C(3)-C(4)-O(5)	-177.1(17)	P(2)-C(31)-C(32)-C(33)	178.4(11)
C(2)-C(3)-C(4)-C(13)	67(2)	C(31)-C(32)-C(33)-C(34)	0
C(2)-C(3)-C(4)-C(15)	-61(2)	C(32)-C(33)-C(34)-C(35)	0
C(3)-C(4)-O(5)-C(6)	-162.3(18)	C(33)-C(34)-C(35)-C(36)	0
C(13)-C(4)-O(5)-C(6)	-45(2)	C(34)-C(35)-C(36)-C(31)	0
C(15)-C(4)-O(5)-C(6)	78(2)	C(32)-C(31)-C(36)-C(35)	0
C(4)-O(5)-C(6)-C(11)	10(3)	P(2)-C(31)-C(36)-C(35)	-178.4(11)
C(4)-O(5)-C(6)-C(7)	-168.5(18)	C(31)-P(2)-C(37)-C(38)	-81.8(19)
C(11)-C(6)-C(7)-C(8)	2(3)	C(30)-P(2)-C(37)-C(38)	165.3(19)
O(5)-C(6)-C(7)-C(8)	-180(2)	Pt(1)-P(2)-C(37)-C(38)	42(2)
C(6)-C(7)-C(8)-C(9)	0(4)	P(2)-C(37)-C(38)-P(3)	-49(2)
C(7)-C(8)-C(9)-C(10)	-1(4)	C(39)-P(3)-C(38)-C(37)	170.2(17)
C(8)-C(9)-C(10)-C(11)	0(4)	C(45)-P(3)-C(38)-C(37)	-80(2)
O(5)-C(6)-C(11)-C(10)	179(2)	Pt(1)-P(3)-C(38)-C(37)	36(2)
C(7)-C(6)-C(11)-C(10)	-3(3)	C(38)-P(3)-C(39)-C(40)	-45.0(11)
O(5)-C(6)-C(11)-C(12)	7(3)	C(45)-P(3)-C(39)-C(40)	-154.5(5)
C(7)-C(6)-C(11)-C(12)	-175(2)	Pt(1)-P(3)-C(39)-C(40)	82.2(5)
C(9)-C(10)-C(11)-C(6)	2(3)	C(38)-P(3)-C(39)-C(44)	135.1(13)
C(9)-C(10)-C(11)-C(12)	174(2)	C(45)-P(3)-C(39)-C(44)	25.6(11)
C(6)-C(11)-C(12)-C(13)	14(3)	Pt(1)-P(3)-C(39)-C(44)	-97.7(9)
C(10)-C(11)-C(12)-C(13)	-159(2)	C(44)-C(39)-C(40)-C(41)	0
O(5)-C(4)-C(13)-C(14)	-165.0(18)	P(3)-C(39)-C(40)-C(41)	-179.9(5)
C(3)-C(4)-C(13)-C(14)	-49(3)	C(39)-C(40)-C(41)-C(42)	0
C(15)-C(4)-C(13)-C(14)	76(2)	C(40)-C(41)-C(42)-C(43)	0
O(5)-C(4)-C(13)-C(12)	66(2)	C(41)-C(42)-C(43)-C(44)	0
C(3)-C(4)-C(13)-C(12)	-178(2)	C(42)-C(43)-C(44)-C(39)	0
C(15)-C(4)-C(13)-C(12)	-53(3)	C(40)-C(39)-C(44)-C(43)	0
C(11)-C(12)-C(13)-C(4)	-49(2)	P(3)-C(39)-C(44)-C(43)	179.9(7)
C(11)-C(12)-C(13)-C(14)	-177.4(19)	C(38)-P(3)-C(45)-C(50)	99.9(10)
C(2)-C(1)-C(14)-C(13)	4(3)	C(39)-P(3)-C(45)-C(50)	-143.5(5)
Pt(1)-C(1)-C(14)-C(13)	176.6(15)	Pt(1)-P(3)-C(45)-C(50)	-13.1(5)
C(2)-C(1)-C(14)-C(16)	-178.0(19)	C(38)-P(3)-C(45)-C(46)	-65.6(12)
Pt(1)-C(1)-C(14)-C(16)	-5(3)	C(39)-P(3)-C(45)-C(46)	51.0(9)

C(4)-C(13)-C(14)-C(1)	14(3)	Pt(1)-P(3)-C(45)-C(46)	-178.6(6)
C(12)-C(13)-C(14)-C(1)	140(2)	C(50)-C(45)-C(46)-C(47)	10.3
C(4)-C(13)-C(14)-C(16)	-164.5(19)	P(3)-C(45)-C(46)-C(47)	174.8(6)
C(12)-C(13)-C(14)-C(16)	-38(3)	C(45)-C(46)-C(47)-C(48)	-11.1
C(23)-P(1)-C(17)-C(18)	-92.3(6)	C(46)-C(47)-C(48)-C(49)	9.7
C(29)-P(1)-C(17)-C(18)	158.5(8)	C(47)-C(48)-C(49)-C(50)	-5.8
Pt(1)-P(1)-C(17)-C(18)	35.8(5)	C(46)-C(45)-C(50)-C(49)	-7
C(23)-P(1)-C(17)-C(22)	86.7(7)	P(3)-C(45)-C(50)-C(49)	-172.3(6)
C(29)-P(1)-C(17)-C(22)	-22.6(9)	C(48)-C(49)-C(50)-C(45)	4.5
Pt(1)-P(1)-C(17)-C(22)	-145.3(4)		

Appendix C

Crystal Structure of (bpyPHOS)PtI_2

(Chapter 3)

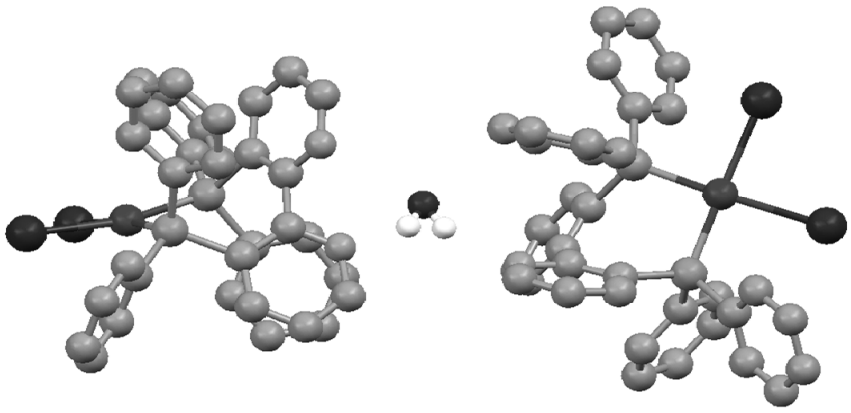


Figure C.1. Chem3D representation of (bpyPHOS)PtI_2.

Table C.1. Bond distances (Å) for (bpyPHOS)PtI_2.

Bond	Length (Å)	Bond	Length (Å)
Pt(1)-P(1)	2.2634(11)	N(17)-C(18)	1.349(6)
Pt(1)-P(2)	2.2669(10)	C(18)-C(19)	1.499(6)
Pt(1)-I(1)	2.6572(3)	C(19)-N(19)	1.349(6)
Pt(1)-I(2)	2.6709(3)	C(19)-C(24)	1.407(6)
P(1)-C(7)	1.819(4)	N(19)-C(21)	1.342(7)
P(1)-C(1)	1.831(4)	C(21)-C(22)	1.388(8)
P(1)-C(13)	1.849(4)	C(22)-C(23)	1.387(7)
P(2)-C(25)	1.818(4)	C(23)-C(24)	1.406(6)
P(2)-C(31)	1.827(4)	C(25)-C(26)	1.403(6)
P(2)-C(24)	1.843(4)	C(25)-C(30)	1.408(6)
C(1)-C(6)	1.399(6)	C(26)-C(27)	1.395(7)
C(1)-C(2)	1.403(6)	C(27)-C(28)	1.390(8)
C(2)-C(3)	1.394(6)	C(28)-C(29)	1.402(8)
C(3)-C(4)	1.395(7)	C(29)-C(30)	1.393(7)
C(4)-C(5)	1.385(8)	C(31)-C(32)	1.401(6)
C(5)-C(6)	1.408(7)	C(31)-C(36)	1.408(6)
C(7)-C(12)	1.396(6)	C(32)-C(33)	1.400(7)
C(7)-C(8)	1.404(6)	C(33)-C(34)	1.399(8)
C(8)-C(9)	1.396(6)	C(34)-C(35)	1.396(8)
C(9)-C(10)	1.392(7)	C(35)-C(36)	1.396(7)
C(10)-C(11)	1.389(8)	C(41)-Cl(42)	1.769(6)
C(11)-C(12)	1.401(7)	C(41)-Cl(43)	1.769(7)
C(13)-C(14)	1.410(6)	C(44)-Cl(46)	1.702(10)
C(13)-C(18)	1.411(6)	C(44)-Cl(45)	1.718(12)
C(14)-C(15)	1.396(7)	Cl(49)-C(48)	1.682(5)
C(15)-C(16)	1.391(8)	C(48)-Cl(49)#1	1.682(5)
C(16)-N(17)	1.337(7)		

Table C.2. Bond angles (°) for (bpyPHOS)PtI_2.

Bonds	Angle (°)	Bonds	Angle (°)
P(1)-Pt(1)-P(2)	92.54(4)	C(15)-C(14)-C(13)	119.9(4)
P(1)-Pt(1)-I(1)	169.50(3)	C(16)-C(15)-C(14)	118.4(4)
P(2)-Pt(1)-I(1)	91.13(3)	N(17)-C(16)-C(15)	123.3(4)
P(1)-Pt(1)-I(2)	90.62(3)	C(16)-N(17)-C(18)	118.2(4)
P(2)-Pt(1)-I(2)	171.22(3)	N(17)-C(18)-C(13)	123.5(4)
I(1)-Pt(1)-I(2)	87.195(11)	N(17)-C(18)-C(19)	113.2(4)
C(7)-P(1)-C(1)	108.3(2)	C(13)-C(18)-C(19)	123.2(4)
C(7)-P(1)-C(13)	105.23(19)	N(19)-C(19)-C(24)	122.8(4)
C(1)-P(1)-C(13)	101.74(19)	N(19)-C(19)-C(18)	112.9(4)
C(7)-P(1)-Pt(1)	113.95(14)	C(24)-C(19)-C(18)	124.3(4)
C(1)-P(1)-Pt(1)	112.27(14)	C(21)-N(19)-C(19)	118.6(5)
C(13)-P(1)-Pt(1)	114.43(13)	N(19)-C(21)-C(22)	122.9(5)
C(25)-P(2)-C(31)	105.64(19)	C(23)-C(22)-C(21)	118.4(5)
C(25)-P(2)-C(24)	106.71(19)	C(22)-C(23)-C(24)	120.2(4)
C(31)-P(2)-C(24)	101.94(19)	C(23)-C(24)-C(19)	117.0(4)
C(25)-P(2)-Pt(1)	113.60(14)	C(23)-C(24)-P(2)	119.9(3)
C(31)-P(2)-Pt(1)	113.81(14)	C(19)-C(24)-P(2)	123.0(3)
C(24)-P(2)-Pt(1)	114.10(14)	C(26)-C(25)-C(30)	119.6(4)
C(6)-C(1)-C(2)	119.6(4)	C(26)-C(25)-P(2)	117.6(3)
C(6)-C(1)-P(1)	122.9(3)	C(30)-C(25)-P(2)	122.7(3)
C(2)-C(1)-P(1)	117.5(3)	C(27)-C(26)-C(25)	119.7(4)
C(3)-C(2)-C(1)	120.4(4)	C(28)-C(27)-C(26)	120.8(5)
C(2)-C(3)-C(4)	119.6(4)	C(27)-C(28)-C(29)	119.6(4)
C(5)-C(4)-C(3)	120.7(4)	C(30)-C(29)-C(28)	120.2(4)
C(4)-C(5)-C(6)	119.9(4)	C(29)-C(30)-C(25)	120.0(4)
C(1)-C(6)-C(5)	119.8(4)	C(32)-C(31)-C(36)	119.7(4)
C(12)-C(7)-C(8)	119.5(4)	C(32)-C(31)-P(2)	121.6(3)
C(12)-C(7)-P(1)	121.5(3)	C(36)-C(31)-P(2)	118.7(3)
C(8)-C(7)-P(1)	119.0(3)	C(33)-C(32)-C(31)	120.0(4)
C(9)-C(8)-C(7)	120.1(4)	C(34)-C(33)-C(32)	120.2(5)
C(10)-C(9)-C(8)	119.6(4)	C(35)-C(34)-C(33)	119.8(4)
C(11)-C(10)-C(9)	120.9(4)	C(36)-C(35)-C(34)	120.4(5)
C(10)-C(11)-C(12)	119.4(5)	C(35)-C(36)-C(31)	119.9(4)
C(7)-C(12)-C(11)	120.4(5)	Cl(42)-C(41)-Cl(43)	111.2(3)
C(14)-C(13)-C(18)	116.6(4)	Cl(46)-C(44)-Cl(45)	116.6(6)
C(14)-C(13)-P(1)	121.1(3)	Cl(49)#1-C(48)-Cl(49)	122.6(7)
C(18)-C(13)-P(1)	122.2(3)		

Table C.3. Torsion angles (°) for (bpyPHOS)PtI_2.

Bonds	Angle (°)	Bonds	Angle (°)
P(2)-Pt(1)-P(1)-C(7)	82.86(16)	C(15)-C(16)-N(17)-C(18)	-0.5(8)
I(1)-Pt(1)-P(1)-C(7)	-166.82(18)	C(16)-N(17)-C(18)-C(13)	1.3(7)
I(2)-Pt(1)-P(1)-C(7)	-88.95(16)	C(16)-N(17)-C(18)-C(19)	178.7(4)
P(2)-Pt(1)-P(1)-C(1)	-153.61(15)	C(14)-C(13)-C(18)-N(17)	-0.9(7)
I(1)-Pt(1)-P(1)-C(1)	-43.3(2)	P(1)-C(13)-C(18)-N(17)	177.4(4)
I(2)-Pt(1)-P(1)-C(1)	34.58(15)	C(14)-C(13)-C(18)-C(19)	-178.0(4)
P(2)-Pt(1)-P(1)-C(13)	-38.30(15)	P(1)-C(13)-C(18)-C(19)	0.2(6)
I(1)-Pt(1)-P(1)-C(13)	72.0(2)	N(17)-C(18)-C(19)-N(19)	-58.6(6)
I(2)-Pt(1)-P(1)-C(13)	149.89(15)	C(13)-C(18)-C(19)-N(19)	118.8(5)
P(1)-Pt(1)-P(2)-C(25)	84.10(15)	N(17)-C(18)-C(19)-C(24)	120.1(5)
I(1)-Pt(1)-P(2)-C(25)	-86.06(15)	C(13)-C(18)-C(19)-C(24)	-62.5(6)
I(2)-Pt(1)-P(2)-C(25)	-164.9(2)	C(24)-C(19)-N(19)-C(21)	-0.2(8)
P(1)-Pt(1)-P(2)-C(31)	-154.96(15)	C(18)-C(19)-N(19)-C(21)	178.6(5)
I(1)-Pt(1)-P(2)-C(31)	34.89(15)	C(19)-N(19)-C(21)-C(22)	-0.3(9)
I(2)-Pt(1)-P(2)-C(31)	-44.0(3)	N(19)-C(21)-C(22)-C(23)	0.5(9)
P(1)-Pt(1)-P(2)-C(24)	-38.53(15)	C(21)-C(22)-C(23)-C(24)	-0.2(8)
I(1)-Pt(1)-P(2)-C(24)	151.32(15)	C(22)-C(23)-C(24)-C(19)	-0.2(7)
I(2)-Pt(1)-P(2)-C(24)	72.5(2)	C(22)-C(23)-C(24)-P(2)	177.3(4)
C(7)-P(1)-C(1)-C(6)	-5.4(4)	N(19)-C(19)-C(24)-C(23)	0.4(7)
C(13)-P(1)-C(1)-C(6)	105.1(4)	C(18)-C(19)-C(24)-C(23)	-178.2(4)
Pt(1)-P(1)-C(1)-C(6)	-132.1(3)	N(19)-C(19)-C(24)-P(2)	-177.1(4)
C(7)-P(1)-C(1)-C(2)	172.9(3)	C(18)-C(19)-C(24)-P(2)	4.3(6)
C(13)-P(1)-C(1)-C(2)	-76.5(4)	C(25)-P(2)-C(24)-C(23)	130.2(4)
Pt(1)-P(1)-C(1)-C(2)	46.3(4)	C(31)-P(2)-C(24)-C(23)	19.6(4)
C(6)-C(1)-C(2)-C(3)	-1.0(7)	Pt(1)-P(2)-C(24)-C(23)	-103.5(3)
P(1)-C(1)-C(2)-C(3)	-179.4(3)	C(25)-P(2)-C(24)-C(19)	-52.4(4)
C(1)-C(2)-C(3)-C(4)	1.8(7)	C(31)-P(2)-C(24)-C(19)	-163.0(4)
C(2)-C(3)-C(4)-C(5)	-1.4(7)	Pt(1)-P(2)-C(24)-C(19)	73.9(4)
C(3)-C(4)-C(5)-C(6)	0.3(7)	C(31)-P(2)-C(25)-C(26)	-96.4(4)
C(2)-C(1)-C(6)-C(5)	-0.2(7)	C(24)-P(2)-C(25)-C(26)	155.6(3)
P(1)-C(1)-C(6)-C(5)	178.2(4)	Pt(1)-P(2)-C(25)-C(26)	29.0(4)
C(4)-C(5)-C(6)-C(1)	0.5(7)	C(31)-P(2)-C(25)-C(30)	81.6(4)
C(1)-P(1)-C(7)-C(12)	63.7(4)	C(24)-P(2)-C(25)-C(30)	-26.3(4)
C(13)-P(1)-C(7)-C(12)	-44.4(4)	Pt(1)-P(2)-C(25)-C(30)	-152.9(3)
Pt(1)-P(1)-C(7)-C(12)	-170.6(4)	C(30)-C(25)-C(26)-C(27)	-2.0(7)
C(1)-P(1)-C(7)-C(8)	-119.3(4)	P(2)-C(25)-C(26)-C(27)	176.2(4)
C(13)-P(1)-C(7)-C(8)	132.6(4)	C(25)-C(26)-C(27)-C(28)	1.7(8)
Pt(1)-P(1)-C(7)-C(8)	6.4(4)	C(26)-C(27)-C(28)-C(29)	0.0(9)
C(12)-C(7)-C(8)-C(9)	-0.8(7)	C(27)-C(28)-C(29)-C(30)	-1.4(9)
P(1)-C(7)-C(8)-C(9)	-177.9(4)	C(28)-C(29)-C(30)-C(25)	1.1(8)

C(7)-C(8)-C(9)-C(10)	0.0(7)	C(26)-C(25)-C(30)-C(29)	0.5(7)
C(8)-C(9)-C(10)-C(11)	0.1(8)	P(2)-C(25)-C(30)-C(29)	-177.5(4)
C(9)-C(10)-C(11)-C(12)	0.6(9)	C(25)-P(2)-C(31)-C(32)	-11.6(4)
C(8)-C(7)-C(12)-C(11)	1.6(8)	C(24)-P(2)-C(31)-C(32)	99.8(4)
P(1)-C(7)-C(12)-C(11)	178.5(4)	Pt(1)-P(2)-C(31)-C(32)	-136.9(3)
C(10)-C(11)-C(12)-C(7)	-1.5(9)	C(25)-P(2)-C(31)-C(36)	168.7(3)
C(7)-P(1)-C(13)-C(14)	128.7(4)	C(24)-P(2)-C(31)-C(36)	-79.9(4)
C(1)-P(1)-C(13)-C(14)	15.9(4)	Pt(1)-P(2)-C(31)-C(36)	43.4(4)
Pt(1)-P(1)-C(13)-C(14)	-105.4(3)	C(36)-C(31)-C(32)-C(33)	0.1(7)
C(7)-P(1)-C(13)-C(18)	-49.5(4)	P(2)-C(31)-C(32)-C(33)	-179.6(4)
C(1)-P(1)-C(13)-C(18)	-162.3(3)	C(31)-C(32)-C(33)-C(34)	-0.2(7)
Pt(1)-P(1)-C(13)-C(18)	76.3(4)	C(32)-C(33)-C(34)-C(35)	0.5(8)
C(18)-C(13)-C(14)-C(15)	-0.3(7)	C(33)-C(34)-C(35)-C(36)	-0.7(8)
P(1)-C(13)-C(14)-C(15)	-178.6(4)	C(34)-C(35)-C(36)-C(31)	0.6(7)
C(13)-C(14)-C(15)-C(16)	1.0(8)	C(32)-C(31)-C(36)-C(35)	-0.3(7)
C(14)-C(15)-C(16)-N(17)	-0.6(8)	P(2)-C(31)-C(36)-C(35)	179.4(4)

Appendix D

Crystal Structure of (bpyPHOS-Me)$PtCl_2$ + L-DBT

(Chapter 3)

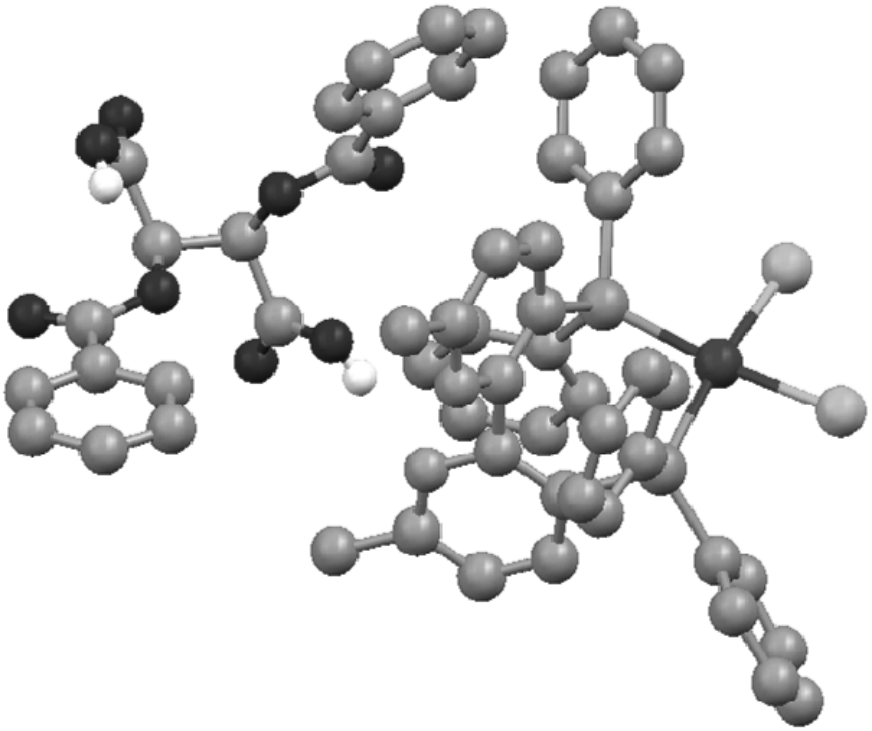


Figure D.1. Chem3D representation of (bpyPHOS-Me)Cl_2 + L-DBT.

Table D.1. Bond distances (Å) for (bpyPHOS-Me)Cl_2 + L-DBT.

Bond	Length (Å)	Bond	Length (Å)
Pt(1)-P(1)	2.2424(11)	C(34)-C(39)	1.397(7)
Pt(1)-P(2)	2.2533(11)	C(34)-C(35)	1.410(7)
Pt(1)-Cl(1)	2.3506(11)	C(35)-C(36)	1.390(7)
Pt(1)-Cl(2)	2.3651(11)	C(36)-C(37)	1.384(7)
P(1)-C(1)	1.827(4)	C(37)-C(38)	1.374(8)
P(1)-C(7)	1.830(5)	C(38)-C(39)	1.411(6)
P(1)-C(13)	1.854(5)	C(40)-C(45)	1.386(8)
P(2)-C(28)	1.809(5)	C(40)-C(41)	1.388(11)
P(2)-C(34)	1.836(4)	C(41)-C(42)	1.371(14)
P(2)-C(20)	1.841(4)	C(42)-C(43)	1.364(15)
C(1)-C(6)	1.404(6)	C(43)-C(44)	1.419(10)
C(1)-C(2)	1.410(7)	C(44)-C(45)	1.387(9)
C(2)-C(3)	1.403(7)	C(45)-C(46)	1.488(8)
C(3)-C(4)	1.373(8)	C(46)-O(58)	1.212(7)
C(4)-C(5)	1.400(7)	C(46)-O(47)	1.351(6)
C(5)-C(6)	1.399(6)	O(47)-C(48)	1.430(6)
C(7)-C(12)	1.379(6)	C(48)-C(59)	1.522(6)
C(7)-C(8)	1.411(6)	C(48)-C(49)	1.531(7)
C(8)-C(9)	1.397(7)	C(49)-O(50)	1.444(6)
C(9)-C(10)	1.377(7)	C(49)-C(62)	1.541(7)
C(10)-C(11)	1.395(8)	O(50)-C(51)	1.363(6)
C(11)-C(12)	1.401(7)	C(51)-O(65)	1.200(6)
C(13)-C(18)	1.394(6)	C(51)-C(52)	1.505(7)
C(13)-C(14)	1.401(6)	C(52)-C(53)	1.370(8)
C(14)-C(15)	1.377(7)	C(52)-C(57)	1.392(7)
C(15)-C(16)	1.403(6)	C(53)-C(54)	1.387(8)
C(16)-N(17)	1.349(6)	C(54)-C(55)	1.383(9)
C(16)-C(19)	1.496(7)	C(55)-C(56)	1.392(9)
N(17)-C(18)	1.363(6)	C(56)-C(57)	1.402(9)
C(18)-C(25)	1.489(6)	C(59)-O(61)	1.217(6)
C(20)-C(21)	1.400(6)	C(59)-O(60)	1.323(6)
C(20)-C(25)	1.400(6)	C(62)-O(63)	1.199(6)
C(21)-C(22)	1.383(6)	C(62)-O(64)	1.315(6)
C(22)-C(23)	1.409(6)	C(71)-Cl(73)	1.758(6)
C(23)-N(27)	1.341(6)	C(71)-Cl(74)	1.759(7)
C(23)-C(26)	1.507(7)	C(71)-Cl(72)	1.791(7)
C(25)-N(27)	1.340(6)	C(75)-Cl(78)	1.749(6)
C(28)-C(33)	1.394(7)	C(75)-Cl(76)	1.761(7)
C(28)-C(29)	1.397(7)	C(75)-Cl(77)	1.765(7)
C(29)-C(30)	1.384(7)	C(79)-Cl(81)	1.743(6)

C(30)-C(31)	1.402(9)	C(79)-Cl(82)	1.761(7)
C(31)-C(32)	1.352(9)	C(79)-Cl(80)	1.772(7)
C(32)-C(33)	1.408(7)		

Table D.2. Bond angles (°) for (bpyPHOS-Me)Cl_2 + L-DBT.

Bonds	Angle (°)	Bonds	Angle (°)
P(1)-Pt(1)-P(2)	92.07(4)	C(29)-C(28)-P(2)	119.3(4)
P(1)-Pt(1)-Cl(1)	92.53(4)	C(30)-C(29)-C(28)	120.5(5)
P(2)-Pt(1)-Cl(1)	171.29(4)	C(29)-C(30)-C(31)	119.4(5)
P(1)-Pt(1)-Cl(2)	169.91(4)	C(32)-C(31)-C(30)	120.5(5)
P(2)-Pt(1)-Cl(2)	88.94(4)	C(31)-C(32)-C(33)	120.9(6)
Cl(1)-Pt(1)-Cl(2)	87.82(4)	C(28)-C(33)-C(32)	119.2(5)
C(1)-P(1)-C(7)	106.7(2)	C(39)-C(34)-C(35)	120.8(4)
C(1)-P(1)-C(13)	102.2(2)	C(39)-C(34)-P(2)	121.2(4)
C(7)-P(1)-C(13)	107.7(2)	C(35)-C(34)-P(2)	118.0(3)
C(1)-P(1)-Pt(1)	114.58(15)	C(36)-C(35)-C(34)	119.0(5)
C(7)-P(1)-Pt(1)	114.85(15)	C(37)-C(36)-C(35)	120.7(5)
C(13)-P(1)-Pt(1)	109.92(15)	C(38)-C(37)-C(36)	120.3(4)
C(28)-P(2)-C(34)	108.2(2)	C(37)-C(38)-C(39)	121.0(5)
C(28)-P(2)-C(20)	103.8(2)	C(34)-C(39)-C(38)	118.2(5)
C(34)-P(2)-C(20)	102.6(2)	C(45)-C(40)-C(41)	120.6(8)
C(28)-P(2)-Pt(1)	114.90(15)	C(42)-C(41)-C(40)	119.5(8)
C(34)-P(2)-Pt(1)	111.92(15)	C(43)-C(42)-C(41)	120.9(7)
C(20)-P(2)-Pt(1)	114.45(14)	C(42)-C(43)-C(44)	120.7(9)
C(6)-C(1)-C(2)	119.8(4)	C(45)-C(44)-C(43)	118.1(7)
C(6)-C(1)-P(1)	121.8(3)	C(40)-C(45)-C(44)	120.2(6)
C(2)-C(1)-P(1)	118.3(3)	C(40)-C(45)-C(46)	118.8(6)
C(3)-C(2)-C(1)	119.1(5)	C(44)-C(45)-C(46)	121.0(5)
C(4)-C(3)-C(2)	121.0(5)	O(58)-C(46)-O(47)	123.3(5)
C(3)-C(4)-C(5)	120.3(4)	O(58)-C(46)-C(45)	124.7(5)
C(6)-C(5)-C(4)	119.9(5)	O(47)-C(46)-C(45)	112.0(5)
C(5)-C(6)-C(1)	119.9(4)	C(46)-O(47)-C(48)	116.5(4)
C(12)-C(7)-C(8)	120.6(4)	O(47)-C(48)-C(59)	114.2(4)
C(12)-C(7)-P(1)	118.5(3)	O(47)-C(48)-C(49)	106.0(4)
C(8)-C(7)-P(1)	120.8(4)	C(59)-C(48)-C(49)	108.7(4)
C(9)-C(8)-C(7)	118.3(4)	O(50)-C(49)-C(48)	105.0(4)
C(10)-C(9)-C(8)	121.0(5)	O(50)-C(49)-C(62)	113.4(4)
C(9)-C(10)-C(11)	120.6(5)	C(48)-C(49)-C(62)	109.4(4)
C(10)-C(11)-C(12)	119.0(5)	C(51)-O(50)-C(49)	116.6(4)
C(7)-C(12)-C(11)	120.4(4)	O(65)-C(51)-O(50)	122.3(5)
C(18)-C(13)-C(14)	117.2(4)	O(65)-C(51)-C(52)	126.9(5)

C(18)-C(13)-P(1)	122.4(3)	O(50)-C(51)-C(52)	110.8(4)
C(14)-C(13)-P(1)	120.3(3)	C(53)-C(52)-C(57)	121.6(5)
C(15)-C(14)-C(13)	119.7(4)	C(53)-C(52)-C(51)	121.9(5)
C(14)-C(15)-C(16)	120.6(4)	C(57)-C(52)-C(51)	116.5(5)
N(17)-C(16)-C(15)	120.1(4)	C(52)-C(53)-C(54)	119.6(6)
N(17)-C(16)-C(19)	118.0(4)	C(55)-C(54)-C(53)	120.5(6)
C(15)-C(16)-C(19)	121.9(4)	C(54)-C(55)-C(56)	119.5(5)
C(16)-N(17)-C(18)	119.3(4)	C(55)-C(56)-C(57)	120.5(5)
N(17)-C(18)-C(13)	123.2(4)	C(52)-C(57)-C(56)	118.1(6)
N(17)-C(18)-C(25)	113.6(3)	O(61)-C(59)-O(60)	125.3(4)
C(13)-C(18)-C(25)	123.2(4)	O(61)-C(59)-C(48)	120.1(5)
C(21)-C(20)-C(25)	116.2(4)	O(60)-C(59)-C(48)	114.6(4)
C(21)-C(20)-P(2)	122.5(3)	O(63)-C(62)-O(64)	126.3(5)
C(25)-C(20)-P(2)	121.3(3)	O(63)-C(62)-C(49)	119.6(5)
C(22)-C(21)-C(20)	120.7(4)	O(64)-C(62)-C(49)	114.1(4)
C(21)-C(22)-C(23)	119.1(4)	Cl(73)-C(71)-Cl(74)	110.1(4)
N(27)-C(23)-C(22)	120.5(4)	Cl(73)-C(71)-Cl(72)	109.6(4)
N(27)-C(23)-C(26)	117.4(4)	Cl(74)-C(71)-Cl(72)	109.8(3)
C(22)-C(23)-C(26)	122.1(4)	Cl(78)-C(75)-Cl(76)	110.7(3)
N(27)-C(25)-C(20)	123.6(4)	Cl(78)-C(75)-Cl(77)	110.8(3)
N(27)-C(25)-C(18)	113.9(4)	Cl(76)-C(75)-Cl(77)	106.8(4)
C(20)-C(25)-C(18)	122.4(4)	Cl(81)-C(79)-Cl(82)	111.5(4)
C(25)-N(27)-C(23)	119.9(4)	Cl(81)-C(79)-Cl(80)	109.7(3)
C(33)-C(28)-C(29)	119.5(4)	Cl(82)-C(79)-Cl(80)	109.0(4)
C(33)-C(28)-P(2)	121.0(4)		

Table D.3. Torsion angles (°) for (bpyPHOS-Me)Cl_2 + L-DBT.

Bonds	Angle (°)	Bonds	Angle (°)
P(2)-Pt(1)-P(1)-C(1)	159.18(17)	N(17)-C(18)-C(25)-N(27)	62.3(5)
Cl(1)-Pt(1)-P(1)-C(1)	-28.22(17)	C(13)-C(18)-C(25)-N(27)	-116.2(5)
Cl(2)-Pt(1)-P(1)-C(1)	63.6(3)	N(17)-C(18)-C(25)-C(20)	-119.4(4)
P(2)-Pt(1)-P(1)-C(7)	-76.80(16)	C(13)-C(18)-C(25)-C(20)	62.0(6)
Cl(1)-Pt(1)-P(1)-C(7)	95.80(16)	C(20)-C(25)-N(27)-C(23)	-1.1(7)
Cl(2)-Pt(1)-P(1)-C(7)	-172.4(3)	C(18)-C(25)-N(27)-C(23)	177.2(4)
P(2)-Pt(1)-P(1)-C(13)	44.80(15)	C(22)-C(23)-N(27)-C(25)	-2.3(7)
Cl(1)-Pt(1)-P(1)-C(13)	-142.59(15)	C(26)-C(23)-N(27)-C(25)	177.4(5)
Cl(2)-Pt(1)-P(1)-C(13)	-50.8(3)	C(34)-P(2)-C(28)-C(33)	-61.3(4)
P(1)-Pt(1)-P(2)-C(28)	-86.47(16)	C(20)-P(2)-C(28)-C(33)	47.2(4)
Cl(1)-Pt(1)-P(2)-C(28)	151.7(3)	Pt(1)-P(2)-C(28)-C(33)	172.9(3)
Cl(2)-Pt(1)-P(2)-C(28)	83.48(16)	C(34)-P(2)-C(28)-C(29)	123.4(4)
P(1)-Pt(1)-P(2)-C(34)	149.61(16)	C(20)-P(2)-C(28)-C(29)	-128.2(4)

Cl(1)-Pt(1)-P(2)-C(34)	27.8(3)	Pt(1)-P(2)-C(28)-C(29)	-2.5(4)
Cl(2)-Pt(1)-P(2)-C(34)	-40.43(16)	C(33)-C(28)-C(29)-C(30)	-1.2(7)
P(1)-Pt(1)-P(2)-C(20)	33.47(17)	P(2)-C(28)-C(29)-C(30)	174.2(4)
Cl(1)-Pt(1)-P(2)-C(20)	-88.4(3)	C(28)-C(29)-C(30)-C(31)	0.8(7)
Cl(2)-Pt(1)-P(2)-C(20)	-156.58(17)	C(29)-C(30)-C(31)-C(32)	0.8(8)
C(7)-P(1)-C(1)-C(6)	13.6(4)	C(30)-C(31)-C(32)-C(33)	-2.0(8)
C(13)-P(1)-C(1)-C(6)	-99.3(4)	C(29)-C(28)-C(33)-C(32)	0.0(7)
Pt(1)-P(1)-C(1)-C(6)	141.8(3)	P(2)-C(28)-C(33)-C(32)	-175.3(4)
C(7)-P(1)-C(1)-C(2)	-169.6(4)	C(31)-C(32)-C(33)-C(28)	1.6(8)
C(13)-P(1)-C(1)-C(2)	77.5(4)	C(28)-P(2)-C(34)-C(39)	5.0(4)
Pt(1)-P(1)-C(1)-C(2)	-41.3(4)	C(20)-P(2)-C(34)-C(39)	-104.3(4)
C(6)-C(1)-C(2)-C(3)	2.4(7)	Pt(1)-P(2)-C(34)-C(39)	132.6(3)
P(1)-C(1)-C(2)-C(3)	-174.5(4)	C(28)-P(2)-C(34)-C(35)	-176.2(4)
C(1)-C(2)-C(3)-C(4)	-2.2(8)	C(20)-P(2)-C(34)-C(35)	74.6(4)
C(2)-C(3)-C(4)-C(5)	0.3(8)	Pt(1)-P(2)-C(34)-C(35)	-48.6(4)
C(3)-C(4)-C(5)-C(6)	1.4(8)	C(39)-C(34)-C(35)-C(36)	1.8(7)
C(4)-C(5)-C(6)-C(1)	-1.2(7)	P(2)-C(34)-C(35)-C(36)	-177.1(4)
C(2)-C(1)-C(6)-C(5)	-0.7(7)	C(34)-C(35)-C(36)-C(37)	-2.1(8)
P(1)-C(1)-C(6)-C(5)	176.1(4)	C(35)-C(36)-C(37)-C(38)	1.0(8)
C(1)-P(1)-C(7)-C(12)	114.2(4)	C(36)-C(37)-C(38)-C(39)	0.5(8)
C(13)-P(1)-C(7)-C(12)	-136.7(4)	C(35)-C(34)-C(39)-C(38)	-0.3(7)
Pt(1)-P(1)-C(7)-C(12)	-13.9(4)	P(2)-C(34)-C(39)-C(38)	178.5(4)
C(1)-P(1)-C(7)-C(8)	-67.7(4)	C(37)-C(38)-C(39)-C(34)	-0.8(8)
C(13)-P(1)-C(7)-C(8)	41.3(4)	C(45)-C(40)-C(41)-C(42)	-2.2(9)
Pt(1)-P(1)-C(7)-C(8)	164.1(3)	C(40)-C(41)-C(42)-C(43)	1.3(10)
C(12)-C(7)-C(8)-C(9)	-0.6(7)	C(41)-C(42)-C(43)-C(44)	-0.2(11)
P(1)-C(7)-C(8)-C(9)	-178.6(4)	C(42)-C(43)-C(44)-C(45)	0.0(10)
C(7)-C(8)-C(9)-C(10)	1.9(7)	C(41)-C(40)-C(45)-C(44)	2.0(8)
C(8)-C(9)-C(10)-C(11)	-2.8(8)	C(41)-C(40)-C(45)-C(46)	-178.5(5)
C(9)-C(10)-C(11)-C(12)	2.4(7)	C(43)-C(44)-C(45)-C(40)	-0.8(8)
C(8)-C(7)-C(12)-C(11)	0.2(7)	C(43)-C(44)-C(45)-C(46)	179.7(5)
P(1)-C(7)-C(12)-C(11)	178.3(3)	C(40)-C(45)-C(46)-O(58)	-10.6(7)
C(10)-C(11)-C(12)-C(7)	-1.1(7)	C(44)-C(45)-C(46)-O(58)	168.9(5)
C(1)-P(1)-C(13)-C(18)	158.6(4)	C(40)-C(45)-C(46)-O(47)	168.3(4)
C(7)-P(1)-C(13)-C(18)	46.4(4)	C(44)-C(45)-C(46)-O(47)	-12.2(7)
Pt(1)-P(1)-C(13)-C(18)	-79.3(4)	O(58)-C(46)-O(47)-C(48)	0.5(7)
C(1)-P(1)-C(13)-C(14)	-26.1(4)	C(45)-C(46)-O(47)-C(48)	-178.3(4)
C(7)-P(1)-C(13)-C(14)	-138.3(4)	C(46)-O(47)-C(48)-C(59)	76.6(5)
Pt(1)-P(1)-C(13)-C(14)	95.9(4)	C(46)-O(47)-C(48)-C(49)	-163.7(4)
C(18)-C(13)-C(14)-C(15)	-0.6(6)	O(47)-C(48)-C(49)-O(50)	-62.6(4)
P(1)-C(13)-C(14)-C(15)	-176.1(4)	C(59)-C(48)-C(49)-O(50)	60.6(5)
C(13)-C(14)-C(15)-C(16)	-1.3(7)	O(47)-C(48)-C(49)-C(62)	59.5(5)
C(14)-C(15)-C(16)-N(17)	2.3(7)	C(59)-C(48)-C(49)-C(62)	-177.3(4)

C(14)-C(15)-C(16)-C(19)	-177.7(5)	C(48)-C(49)-O(50)-C(51)	-162.4(4)
C(15)-C(16)-N(17)-C(18)	-1.3(7)	C(62)-C(49)-O(50)-C(51)	78.1(5)
C(19)-C(16)-N(17)-C(18)	178.7(4)	C(49)-O(50)-C(51)-O(65)	-4.1(7)
C(16)-N(17)-C(18)-C(13)	-0.7(6)	C(49)-O(50)-C(51)-C(52)	177.0(4)
C(16)-N(17)-C(18)-C(25)	-179.3(4)	O(65)-C(51)-C(52)-C(53)	-178.9(5)
C(14)-C(13)-C(18)-N(17)	1.7(6)	O(50)-C(51)-C(52)-C(53)	-0.1(7)
P(1)-C(13)-C(18)-N(17)	177.1(3)	O(65)-C(51)-C(52)-C(57)	0.0(8)
C(14)-C(13)-C(18)-C(25)	-179.9(4)	O(50)-C(51)-C(52)-C(57)	178.9(4)
P(1)-C(13)-C(18)-C(25)	-4.5(6)	C(57)-C(52)-C(53)-C(54)	-0.7(8)
C(28)-P(2)-C(20)-C(21)	-133.1(4)	C(51)-C(52)-C(53)-C(54)	178.2(5)
C(34)-P(2)-C(20)-C(21)	-20.5(4)	C(52)-C(53)-C(54)-C(55)	-0.6(9)
Pt(1)-P(2)-C(20)-C(21)	101.0(4)	C(53)-C(54)-C(55)-C(56)	1.8(9)
C(28)-P(2)-C(20)-C(25)	48.1(4)	C(54)-C(55)-C(56)-C(57)	-1.8(8)
C(34)-P(2)-C(20)-C(25)	160.7(4)	C(53)-C(52)-C(57)-C(56)	0.7(8)
Pt(1)-P(2)-C(20)-C(25)	-77.8(4)	C(51)-C(52)-C(57)-C(56)	-178.3(4)
C(25)-C(20)-C(21)-C(22)	-0.5(6)	C(55)-C(56)-C(57)-C(52)	0.6(7)
P(2)-C(20)-C(21)-C(22)	-179.3(4)	O(47)-C(48)-C(59)-O(61)	178.2(4)
C(20)-C(21)-C(22)-C(23)	-2.7(7)	C(49)-C(48)-C(59)-O(61)	60.1(6)
C(21)-C(22)-C(23)-N(27)	4.2(7)	O(47)-C(48)-C(59)-O(60)	-0.6(6)
C(21)-C(22)-C(23)-C(26)	-175.5(5)	C(49)-C(48)-C(59)-O(60)	-118.7(5)
C(21)-C(20)-C(25)-N(27)	2.5(6)	O(50)-C(49)-C(62)-O(63)	-175.2(5)
P(2)-C(20)-C(25)-N(27)	-178.7(3)	C(48)-C(49)-C(62)-O(63)	67.9(7)
C(21)-C(20)-C(25)-C(18)	-175.6(4)	O(50)-C(49)-C(62)-O(64)	5.2(6)
P(2)-C(20)-C(25)-C(18)	3.2(6)	C(48)-C(49)-C(62)-O(64)	-111.8(5)

Appendix E

Crystal Structure of **5**

(Appendix A)

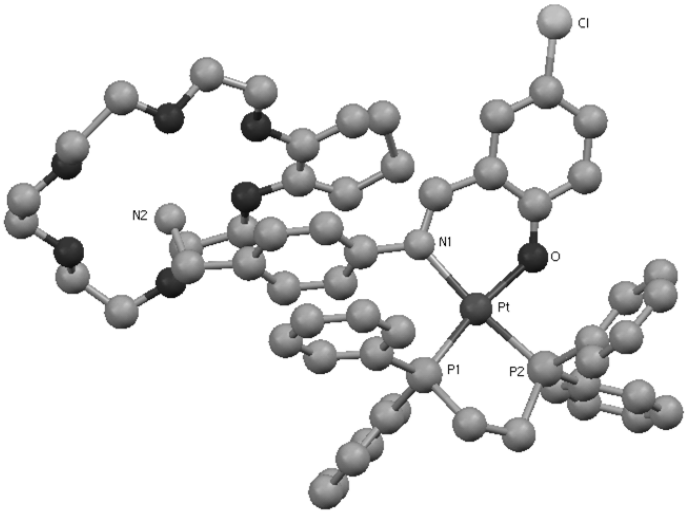


Figure E.1. ORTEP representation of **5**.

Table E.1. Bond distances (Å) for **5**.

Bond	Length (Å)	Bond	Length (Å)
Pd(1) - P(1)	2.2482(9)	C(35) - C(36)	1.400(6)
Pd(1) - P(2)	2.2518(10)	C(35) - C(40)	1.377(6)
Pd(1) - N(1)	2.099(3)	C(36) - C(37)	1.369(8)
Pd(1) - O(9)	2.040(2)	C(36) - H(361)	0.97
P(1) - C(21)	1.836(4)	C(37) - C(38)	1.362(9)
P(1) - C(23)	1.812(4)	C(37) - H(371)	1.00
P(1) - C(29)	1.810(4)	C(38) - C(39)	1.396(8)
P(2) - C(22)	1.841(4)	C(38) - H(381)	0.98
P(2) - C(35)	1.818(4)	C(39) - C(40)	1.400(6)
P(2) - C(41)	1.813(4)	C(39) - H(391)	0.97
Cl(1) - C(5)	1.747(4)	C(40) - H(401)	0.99
N(1) - C(2)	1.301(5)	C(41) - C(42)	1.390(7)
N(1) - C(10)	1.438(5)	C(41) - C(46)	1.395(8)
C(2) - C(3)	1.446(5)	C(42) - C(43)	1.389(7)
C(2) - H(21)	0.99	C(42) - H(421)	0.97
C(3) - C(4)	1.415(5)	C(43) - C(44)	1.379(11)
C(3) - C(8)	1.416(5)	C(43) - H(431)	1.00
C(4) - C(5)	1.368(6)	C(44) - C(45)	1.380(12)
C(4) - H(41)	0.97	C(44) - H(441)	1.04
C(5) - C(6)	1.391(6)	C(45) - C(46)	1.395(9)
C(6) - C(7)	1.375(6)	C(45) - H(451)	0.93
C(6) - H(61)	0.99	C(46) - H(461)	0.98
C(7) - C(8)	1.420(5)	C(51) - C(52)	1.417(11)
C(7) - H(71)	1.01	C(51) - C(56)	1.262(10)
C(8) - O(9)	1.316(4)	C(51) - O(72)	1.411(8)
C(10) - C(11)	1.391(5)	C(52) - C(53)	0.75(3)
C(10) - C(15)	1.391(5)	C(52) - H(521)	0.99
C(11) - C(12)	1.380(6)	C(53) - C(54)	1.71(4)
C(11) - H(111)	0.98	C(53) - H(531)	0.93
C(12) - C(13)	1.385(6)	C(54) - C(55)	1.540(17)
C(12) - H(121)	0.99	C(54) - H(541)	0.91
C(13) - C(14)	1.387(6)	C(55) - C(56)	1.326(10)
C(13) - C(16)	1.511(6)	C(55) - H(551)	0.89
C(14) - C(15)	1.387(5)	C(56) - O(57)	1.378(7)
C(14) - H(141)	1.00	O(57) - C(58)	1.396(7)
C(15) - H(151)	0.98	C(58) - C(59)	1.484(8)
C(16) - N(17)	1.506(6)	C(58) - H(581)	1.06
C(16) - H(161)	0.98	C(58) - H(582)	0.98
C(16) - H(162)	1.02	C(59) - O(60)	1.417(6)
N(17) - H(171)	1.01	C(59) - H(591)	1.04

N(17) - H(172)	0.97	C(59) - H(592)	0.99
N(17) - H(173)	0.98	O(60) - C(61)	1.428(7)
C(21) - C(22)	1.516(6)	C(61) - C(62)	1.474(10)
C(21) - H(211)	0.98	C(61) - H(611)	1.00
C(21) - H(212)	1.01	C(61) - H(612)	0.97
C(22) - H(221)	0.99	C(62) - O(63)	1.447(10)
C(22) - H(222)	1.01	C(62) - H(621)	0.98
C(23) - C(24)	1.397(6)	C(62) - H(622)	1.04
C(23) - C(28)	1.390(6)	O(63) - C(64)	1.406(10)
C(24) - C(25)	1.381(6)	C(64) - C(65)	1.545(16)
C(24) - H(241)	1.00	C(64) - H(641)	1.01
C(25) - C(26)	1.393(7)	C(64) - H(642)	0.89
C(25) - H(251)	0.99	C(65) - O(66)	1.379(11)
C(26) - C(27)	1.370(7)	C(65) - H(651)	0.99
C(26) - H(261)	0.97	C(65) - H(652)	1.00
C(27) - C(28)	1.395(7)	O(66) - C(67)	1.420(12)
C(27) - H(271)	0.97	C(67) - C(68)	1.702(17)
C(28) - H(281)	0.99	C(67) - H(671)	0.96
C(29) - C(30)	1.383(6)	C(67) - H(672)	1.07
C(29) - C(34)	1.390(6)	C(68) - O(69)	1.322(12)
C(30) - C(31)	1.404(7)	C(68) - H(681)	0.99
C(30) - H(301)	1.00	C(68) - H(682)	0.92
C(31) - C(32)	1.365(9)	O(69) - C(70)	1.462(8)
C(31) - H(311)	0.97	C(70) - C(71)	1.428(10)
C(32) - C(33)	1.373(8)	C(70) - H(701)	1.05
C(32) - H(321)	1.01	C(70) - H(702)	1.01
C(33) - C(34)	1.392(7)	C(71) - O(72)	1.393(8)
C(33) - H(331)	0.98	C(71) - H(711)	0.90
C(34) - H(341)	1.00	C(71) - H(712)	1.00

Figure E.2. Bond angles (°) for **5**.

Bonds	Angle (°)	Bonds	Angle (°)
P(1) - Pd(1) - P(2)	84.91(4)	C(62) - C(61) - H(612)	119.4(3)
C(62) - C(61) - H(612)	170.50(9)	C(62) - C(61) - H(612)	120.4(3)
C(62) - C(61) - H(612)	99.25(8)	C(62) - C(61) - H(612)	120.1(4)
C(62) - C(61) - H(612)	86.20(7)	C(62) - C(61) - H(612)	119.6(5)
C(62) - C(61) - H(612)	171.10(7)	C(62) - C(61) - H(612)	120.7
C(62) - C(61) - H(612)	89.58(10)	C(62) - C(61) - H(612)	119.7
C(62) - C(61) - H(612)	110.15(14)	C(62) - C(61) - H(612)	120.7(5)
C(62) - C(61) - H(612)	108.26(12)	C(62) - C(61) - H(612)	125.7
C(62) - C(61) - H(612)	108.19(18)	C(62) - C(61) - H(612)	113.4
C(62) - C(61) - H(612)	115.97(13)	C(62) - C(61) - H(612)	120.9(5)
C(62) - C(61) - H(612)	106.67(18)	C(62) - C(61) - H(612)	119.9
C(62) - C(61) - H(612)	107.34(18)	C(62) - C(61) - H(612)	119.2
C(62) - C(61) - H(612)	108.16(14)	C(62) - C(61) - H(612)	118.6(5)
C(62) - C(61) - H(612)	115.41(13)	C(62) - C(61) - H(612)	119.5
C(62) - C(61) - H(612)	103.12(18)	C(62) - C(61) - H(612)	121.8
C(62) - C(61) - H(612)	116.55(15)	C(62) - C(61) - H(612)	120.0(4)
C(62) - C(61) - H(612)	104.6(2)	C(62) - C(61) - H(612)	119.6
C(62) - C(61) - H(612)	107.6(2)	C(62) - C(61) - H(612)	120.4
C(62) - C(61) - H(612)	120.2(2)	C(62) - C(61) - H(612)	122.8(4)
C(62) - C(61) - H(612)	124.5(2)	C(62) - C(61) - H(612)	117.7(4)
C(62) - C(61) - H(612)	115.2(3)	C(62) - C(61) - H(612)	119.4(5)
C(62) - C(61) - H(612)	128.0(3)	C(62) - C(61) - H(612)	120.5(6)
C(62) - C(61) - H(612)	115.7	C(62) - C(61) - H(612)	119.2
C(62) - C(61) - H(612)	116.3	C(62) - C(61) - H(612)	120.3
C(62) - C(61) - H(612)	115.8(3)	C(62) - C(61) - H(612)	119.8(7)
C(62) - C(61) - H(612)	123.7(3)	C(62) - C(61) - H(612)	118.4
C(62) - C(61) - H(612)	120.0(3)	C(62) - C(61) - H(612)	121.8
C(62) - C(61) - H(612)	120.0(4)	C(62) - C(61) - H(612)	120.2(6)
C(62) - C(61) - H(612)	121.3	C(62) - C(61) - H(612)	121.5
C(62) - C(61) - H(612)	118.7	C(62) - C(61) - H(612)	118.2
C(62) - C(61) - H(612)	120.0(3)	C(62) - C(61) - H(612)	120.5(7)
C(62) - C(61) - H(612)	118.6(3)	C(62) - C(61) - H(612)	114.2
C(62) - C(61) - H(612)	121.3(4)	C(62) - C(61) - H(612)	125.2
C(62) - C(61) - H(612)	119.4(4)	C(62) - C(61) - H(612)	119.4(7)
C(62) - C(61) - H(612)	118.4	C(62) - C(61) - H(612)	122
C(62) - C(61) - H(612)	122.2	C(62) - C(61) - H(612)	118.6
C(62) - C(61) - H(612)	121.9(4)	C(62) - C(61) - H(612)	122.7(11)
C(62) - C(61) - H(612)	118.8	C(62) - C(61) - H(612)	116.1(11)
C(62) - C(61) - H(612)	119.3	C(62) - C(61) - H(612)	121.2(7)
C(62) - C(61) - H(612)	117.4(3)	C(62) - C(61) - H(612)	147(4)

C(62) - C(61) - H(612)	124.9(3)	C(62) - C(61) - H(612)	107.5
C(62) - C(61) - H(612)	117.6(3)	C(62) - C(61) - H(612)	105.4
C(62) - C(61) - H(612)	123.3(2)	C(62) - C(61) - H(612)	106(3)
C(62) - C(61) - H(612)	122.0(3)	C(62) - C(61) - H(612)	141.4
C(62) - C(61) - H(612)	117.3(3)	C(62) - C(61) - H(612)	112.6
C(62) - C(61) - H(612)	120.7(3)	C(62) - C(61) - H(612)	111.9(9)
C(62) - C(61) - H(612)	118.8(4)	C(62) - C(61) - H(612)	118.3
C(62) - C(61) - H(612)	119.7	C(62) - C(61) - H(612)	129.7
C(62) - C(61) - H(612)	121.5	C(62) - C(61) - H(612)	116.8(11)
C(62) - C(61) - H(612)	121.5(4)	C(62) - C(61) - H(612)	130
C(62) - C(61) - H(612)	118.8	C(62) - C(61) - H(612)	113.2
C(62) - C(61) - H(612)	119.7	C(62) - C(61) - H(612)	115.2(7)
C(62) - C(61) - H(612)	119.0(4)	C(62) - C(61) - H(612)	114.0(6)
C(62) - C(61) - H(612)	121.5(4)	C(62) - C(61) - H(612)	130.8(7)
C(62) - C(61) - H(612)	119.4(4)	C(62) - C(61) - H(612)	111.6(5)
C(62) - C(61) - H(612)	120.7(4)	C(62) - C(61) - H(612)	108.8(4)
C(62) - C(61) - H(612)	117.7	C(62) - C(61) - H(612)	110.6
C(62) - C(61) - H(612)	121.5	C(62) - C(61) - H(612)	107.7
C(62) - C(61) - H(612)	119.3(3)	C(62) - C(61) - H(612)	112.6
C(62) - C(61) - H(612)	120	C(62) - C(61) - H(612)	111.1
C(62) - C(61) - H(612)	120.8	C(62) - C(61) - H(612)	105.9
C(62) - C(61) - H(612)	109.5(4)	C(62) - C(61) - H(612)	107.4(4)
C(62) - C(61) - H(612)	111.4	C(62) - C(61) - H(612)	112.4
C(62) - C(61) - H(612)	108.6	C(62) - C(61) - H(612)	108.1
C(62) - C(61) - H(612)	110	C(62) - C(61) - H(612)	111.3
C(62) - C(61) - H(612)	108.1	C(62) - C(61) - H(612)	110.4
C(62) - C(61) - H(612)		C(62) - C(61) - H(612)	107.1
C(62) - C(61) - H(612)	107.9	C(62) - C(61) - H(612)	113.7(4)
C(62) - C(61) - H(612)	107.3	C(62) - C(61) - H(612)	113.1(5)
C(62) - C(61) - H(612)		C(62) - C(61) - H(612)	105.2
C(62) - C(61) - H(612)	107.3	C(62) - C(61) - H(612)	107.7
C(62) - C(61) - H(612)		C(62) - C(61) - H(612)	108.9
C(62) - C(61) - H(612)		C(62) - C(61) - H(612)	110.1
C(62) - C(61) - H(612)	109.3(3)	H(611) - C(61) - H(612)	111.7
C(62) - C(61) - H(612)	108.7	C(61) - C(62) - O(63)	109.9(5)
C(62) - C(61) - H(612)	111.2	C(61) - C(62) - H(621)	111.9
C(62) - C(61) - H(612)	108.2	O(63) - C(62) - H(621)	112.5
C(62) - C(61) - H(612)	109.4	C(61) - C(62) - H(622)	107.5
C(62) - C(61) - H(612)		O(63) - C(62) - H(622)	106.7
C(62) - C(61) - H(612)	108.8(3)	H(621) - C(62) - H(622)	108.1
C(62) - C(61) - H(612)	108.1	C(62) - O(63) - C(64)	116.3(7)
C(62) - C(61) - H(612)	112.8	O(63) - C(64) - C(65)	108.8(8)
C(62) - C(61) - H(612)	106.6	O(63) - C(64) - H(641)	107.3

C(62) - C(61) - H(612)	111.2	C(65) - C(64) - H(641)	105
C(62) - C(61) - H(612)		O(63) - C(64) - H(642)	109.1
C(62) - C(61) - H(612)	118.9(3)	C(65) - C(64) - H(642)	107.3
C(62) - C(61) - H(612)	121.0(3)	H(641) - C(64) - H(642)	118.8
C(62) - C(61) - H(612)	119.9(3)	C(64) - C(65) - O(66)	108.8(7)
C(62) - C(61) - H(612)	120.1(4)	C(64) - C(65) - H(651)	112.5
C(62) - C(61) - H(612)	120.7	O(66) - C(65) - H(651)	110.8
C(62) - C(61) - H(612)	119.1	C(64) - C(65) - H(652)	104.6
C(62) - C(61) - H(612)	119.6(4)	O(66) - C(65) - H(652)	110.3
C(62) - C(61) - H(612)	118.4	H(651) - C(65) - H(652)	109.8
C(62) - C(61) - H(612)	122	C(65) - O(66) - C(67)	109.5(9)
C(62) - C(61) - H(612)	120.6(4)	O(66) - C(67) - C(68)	105.0(6)
C(62) - C(61) - H(612)	119.5	O(66) - C(67) - H(671)	109.7
C(62) - C(61) - H(612)	119.9	C(68) - C(67) - H(671)	115
C(62) - C(61) - H(612)	120.3(4)	O(66) - C(67) - H(672)	103.1
C(62) - C(61) - H(612)	118.1	C(68) - C(67) - H(672)	115.9
C(62) - C(61) - H(612)	121.4	H(671) - C(67) - H(672)	107.3
C(62) - C(61) - H(612)	119.5(4)	C(67) - C(68) - O(69)	110.9(7)
C(62) - C(61) - H(612)	120.1	C(67) - C(68) - H(681)	101.6
C(62) - C(61) - H(612)	120.4	O(69) - C(68) - H(681)	101
C(62) - C(61) - H(612)	121.1(3)	C(67) - C(68) - H(682)	113
C(62) - C(61) - H(612)	118.2(3)	O(69) - C(68) - H(682)	111.8
C(62) - C(61) - H(612)	120.5(4)	H(681) - C(68) - H(682)	117.6
C(62) - C(61) - H(612)	119.0(5)	C(68) - O(69) - C(70)	110.6(8)
C(62) - C(61) - H(612)	120.7	O(69) - C(70) - C(71)	115.4(5)
C(62) - C(61) - H(612)	120.3	O(69) - C(70) - H(701)	108
C(62) - C(61) - H(612)	120.2(5)	C(71) - C(70) - H(701)	105.4
C(62) - C(61) - H(612)	123.8	O(69) - C(70) - H(702)	109.9
C(62) - C(61) - H(612)	116	C(71) - C(70) - H(702)	112.7
C(62) - C(61) - H(612)	120.8(5)	H(701) - C(70) - H(702)	104.6
C(62) - C(61) - H(612)	118.2	C(70) - C(71) - O(72)	108.5(6)
C(62) - C(61) - H(612)	120.9	C(70) - C(71) - H(711)	110.6
C(62) - C(61) - H(612)	120.1(5)	O(72) - C(71) - H(711)	110.6
C(62) - C(61) - H(612)	118	C(70) - C(71) - H(712)	103
C(62) - C(61) - H(612)	121.9	O(72) - C(71) - H(712)	105.1
C(62) - C(61) - H(612)	119.3(4)	H(711) - C(71) - H(712)	118.4
C(62) - C(61) - H(612)	118	C(51) - O(72) - C(71)	121.5(7)
C(62) - C(61) - H(612)	122.6		

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