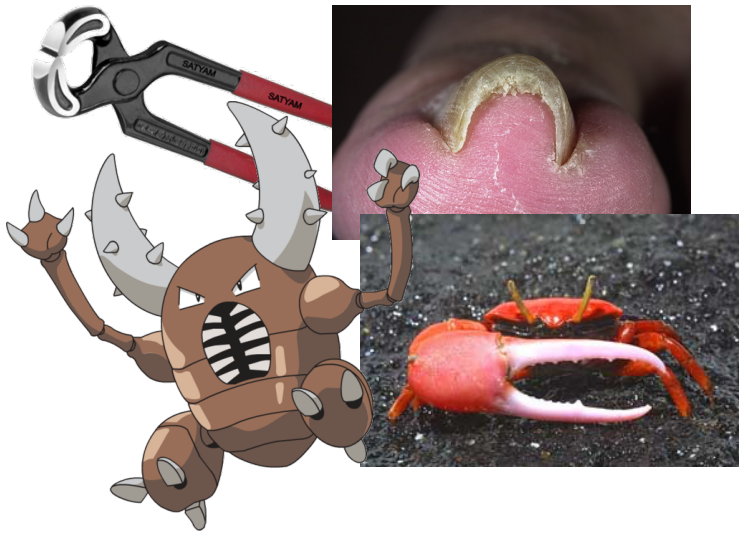
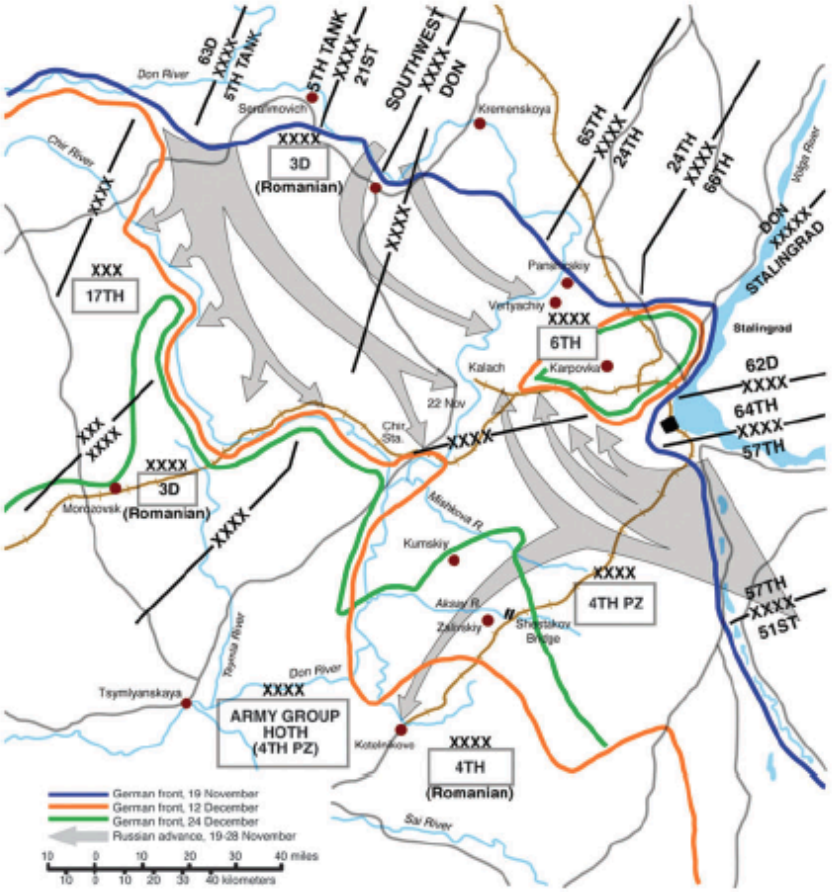
PINCER LIGANDS

John Gurak

4/21/16

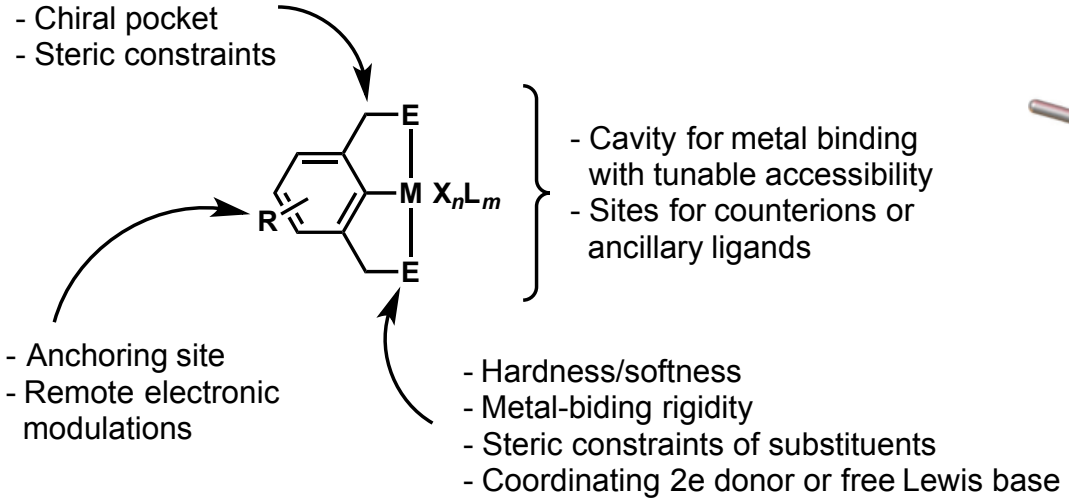
Origin of Pincer

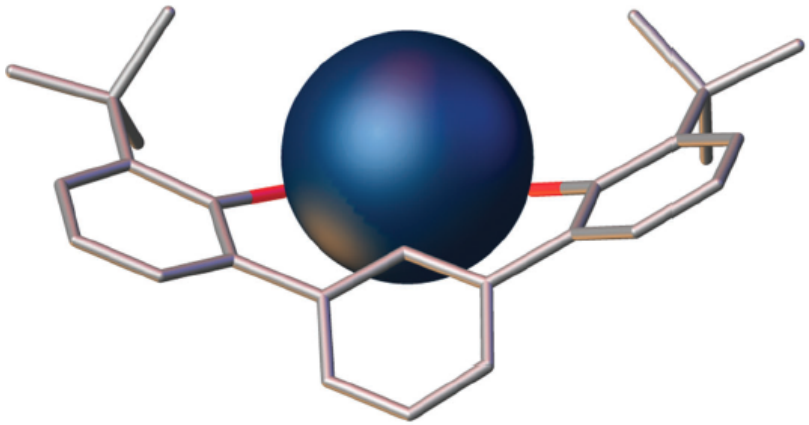




- Military tactic that involves the simultaneous attack of an advancing army by two flanking units at the sides in an effort to surround the enemy
- Hannibal's defeat of the Romans in 216 B.C. at the Battle of Cannae
- General Lee in the Battle of Chancellorsville
- The Soviet Army in the Battle of Stalingrad in WWII

General Structure





General Considerations:

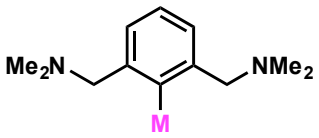
- Thermal stability
- High reactivity
- Hemilabile coordination
- Acid and base stable
- Air and moisture stable

Void Space Influences:

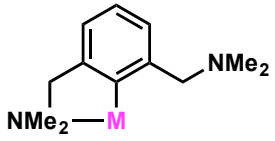
- Coordination mode
- Steric requirements
- Atomic radii of donor atoms
- Hybridization of donor atom
- E–M bond length
- Nature of E substituents

van Koten, G. *Top. Organomet. Chem.* **2013,** *40,* 1.
Albrecht, M.; van Koten, G. *Angew. Chem. Int. Ed.* **2001,** *40,* 3750.
O'Reilly, M. E.; Veige, A. S. *Chem. Soc. Rev.* **2014,** *43,* 6325.

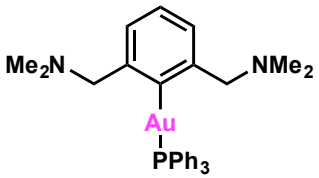
Coordination Modes

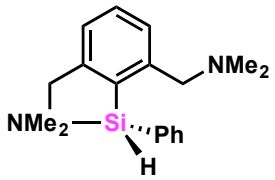


monodentate
M = Ni, Pt, Au



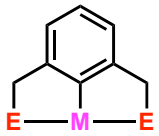
bidentate
M = Si, Ta, Co, Rh, Ir, Ru



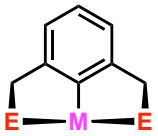


van Koten, G. *Top. Organomet. Chem.* **2013,** *40,* 1.

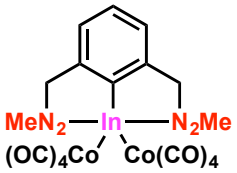
Coordination Modes - Terdentate

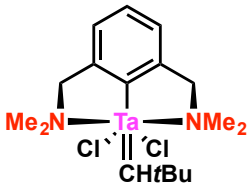


mer-terdentate
E = NR_2, PR_2, Sr, SeR
M = Ti, Ta, Fe, Co, Rh, Ir, Ru, Ni, Pd, Pt, Si, Sn, In



fac-terdentate
E = NR_2, PR_2
M = Ti, Ta, Lu, Ln, Re, Ru, Rh

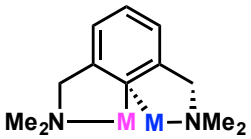




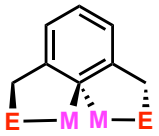
- *Fac*-terdentate binding mode not anticipated because of the presumed rigidity of the aryl ring
- Acute (between 110-120°) N–M–N bond angle and bending of the arene ring in some cases
- Binding can be imposed by selecting the right steric and/or electronic properties of the E donor group
- Similar structural features to corresponding Cp-metal complexes

van Koten, G. *Top. Organomet. Chem.* **2013,** *40,* 1.

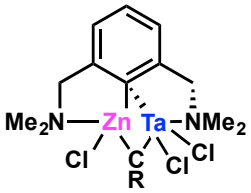
Coordination Modes - Bridging



bridging
M = Ta, M = Zn



bridging
E = NR_2, PR_2
M = Li, Cu



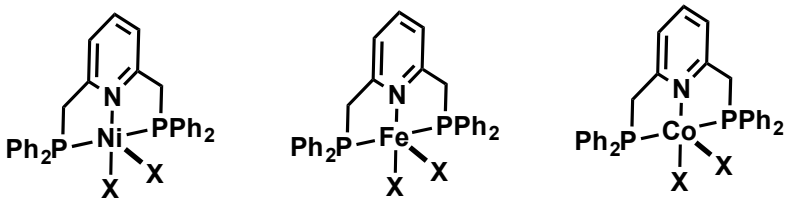
- Bridging systems are very sensitive to σ-donating character and steric size
- When same metals, 2 electrons are shared between 3 centers
- When different metals, C_{ipso} is σ-bonded to one metal and π-bonded to the other metal

van Koten, G. *Top. Organomet. Chem.* **2013,** *40,* 1.

Degrees of Anionic

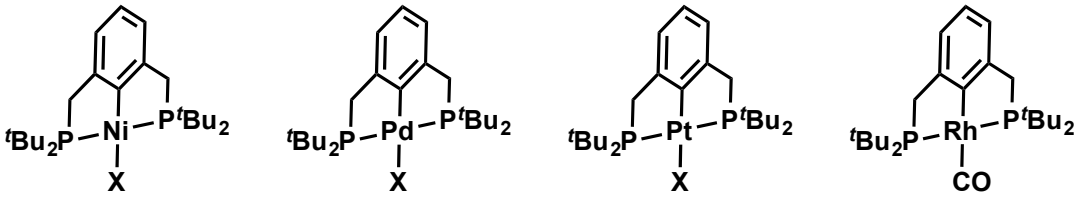
- Neutral
  - Include: SPS, NNN, PNP
- Monoanionic
  - Effective for metal ions in low oxidation states
  - Include: PCP^{-}, SCS^{-}, NCN^{-}, $SeCSe^{-}$, SPS^{-}
- Dianionic
  - Include: ONO^{2-}, NCN^{2-}, CNC^{2-}, NNN^{2-}, CCN^{2-}, SCS^{2-}
- Trianionic
  - Effective for metal ions in high oxidation states (M^{n+}; $n \geq 3$)
  - Include: NNN^{3-}, OCO^{3-}, NCN^{3-}, CCC^{3-}, ONO^{3-}, SNS^{3-}

First Pincer Complexes



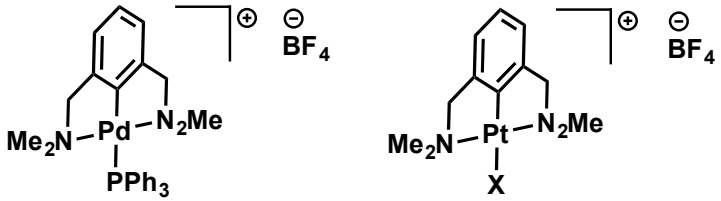
X = Cl, Br, I, NCS, ClO_4

Dahlhoff, W. V.; Nelson, S. M. *J. Chem. Soc.* **1971,** 2184.



X = Cl, Br, I, H, CN

Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976,** 1020.

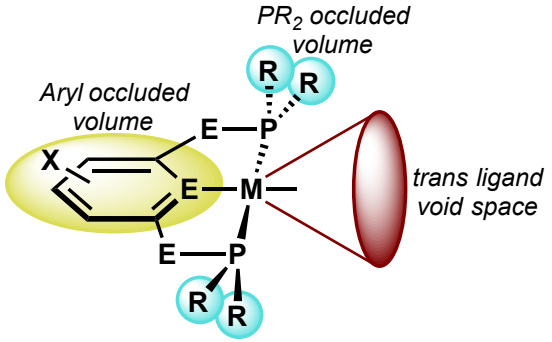


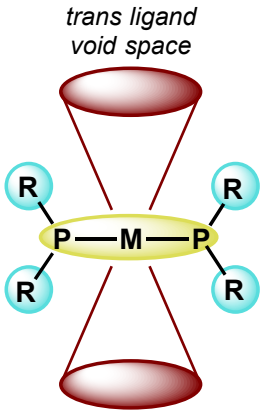
X = PPh_3, CO

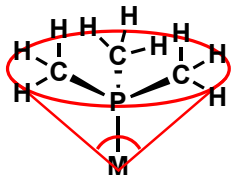
Timmer, K.; Spek, A. L.; van Koten, G.; Noltes, J. G. *J. Chem. Soc., Chem. Comm.* **1978,** 250.

Phosphine Pincer Ligands – A Case Study

- Percent Buried Volume ($\%V_{bur}$)
  - Measure of the 1st coordination sphere blocked by the ligand
  - Sensitive to nature of the metal and remaining coordination environment
  - Trends for $\%V_{bur}$:
    - Similar for different pincer frameworks with the same pendant phosphine groups
    - Generally follow expected steric influence and Tolman cone angle trends for pendant phosphine groups of 4-coordinate systems
    - 6-coordinate complexes are significantly smaller (2-10%) than comparable 4-coordinate systems



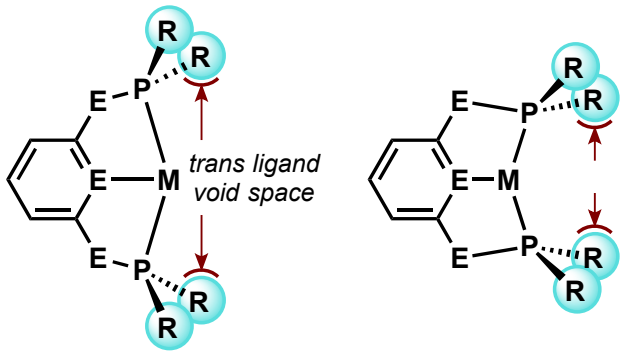




Roddick, D. M. *Top. Organomet. Chem.* **2013,** *40,* 49.

Phosphine Pincer Ligands – A Case Study

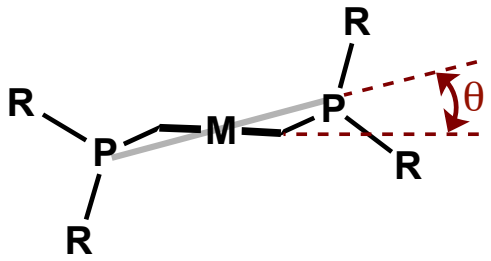
- Additional Void Space Influences
  - Degree of pincer “pull-back”
    - Controlled by metal bonding radii and subtending pincer arm metrics
  - For a given pincer ligand, smaller metals with shorter M–C(Ar) and M–P bond lengths are enfolded more
  - Smaller C(Ar)–O and O–P bond lengths result in pincer “pull-back” and afford greater steric access to the metal center



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

Phosphine Pincer Ligands – A Case Study

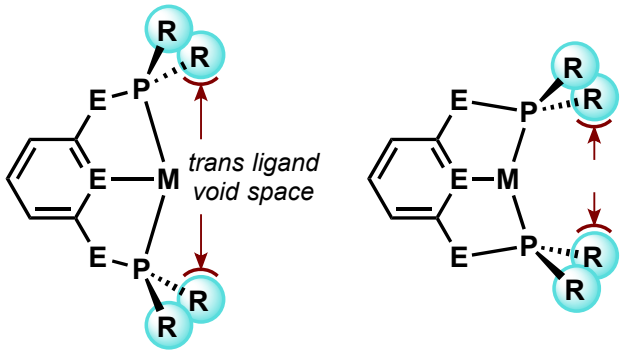
- Pincer C_2 Twists
  - For 4-coordinate systems, CH_2-bridged pincers (10.1° average) > NH-bridged pincers (4.2° average) > O-bridged pincers (2.4° average)
  - 6-Coordinate CH_2-bridged pincer complexes are significantly more twisted (19° average) than 4-coordinate counterparts



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

Phosphine Pincer Ligands – A Case Study

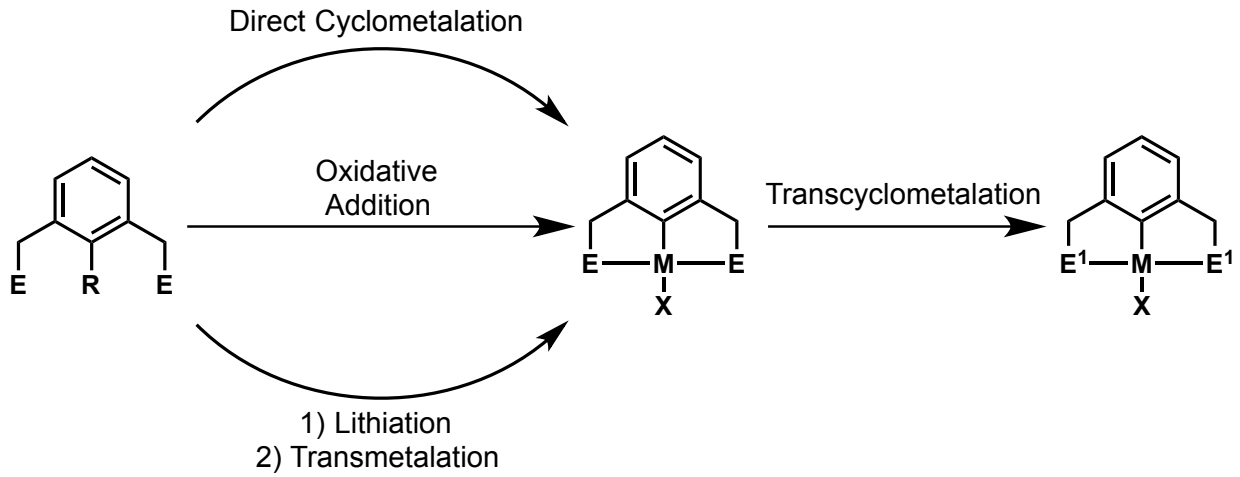
- P–M–P Angle Trends
  - Smallest P–M–P angles are associated with a bulky ligand (i.e. PPh_3)
  - In systems with undifferentiated steric demand above and below the plane decreases in P–M–P angles are due to bending toward the pincer aryl unit
    - In less symmetric complexes (5-coordinating), the P–M–P angle is usually a combination of bending both parallel and perpendicular to the C(Ar)–M bond axis
  - The largest P–M–P angles are associated with smaller transition metals
  - Rough inverse correlation between high C_2 twist and small P–M–P values
    - Higher distortions accompany a decrease in $\%V_{bur}$



"Pulled-back" Enfolding

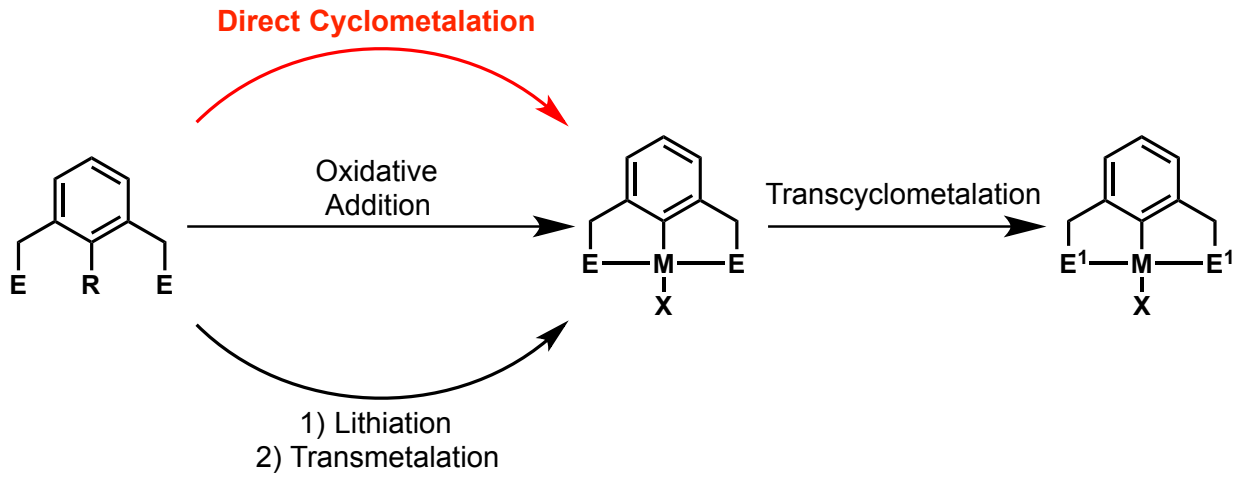
Roddick, D. M. *Top. Organomet. Chem.* **2013,** *40,* 49.

Pincer Complexes Syntheses



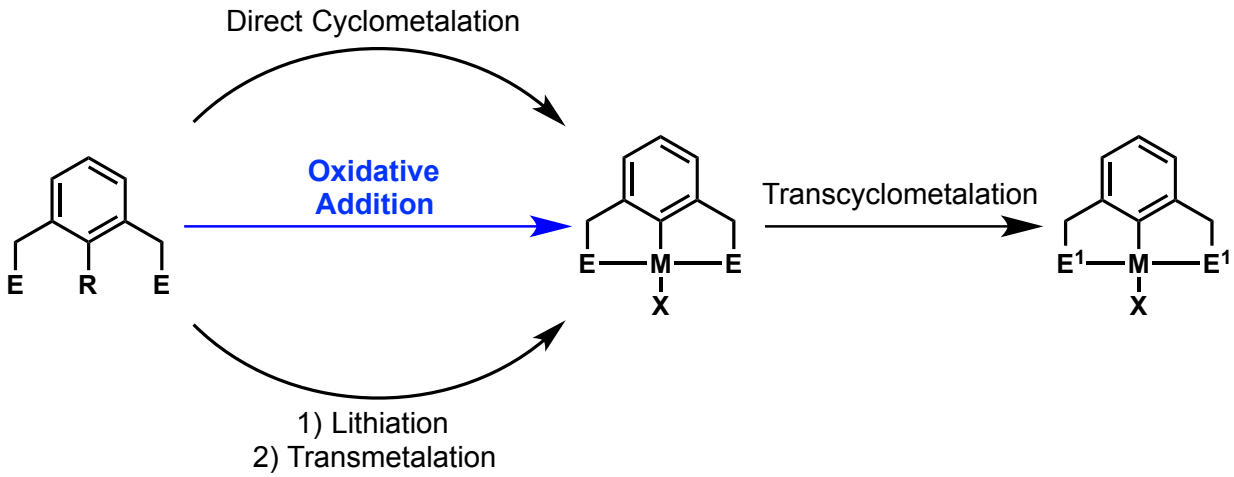
van Koten, G. *Top. Organomet. Chem.* **2013,** *40,* 1.
Albrecht, M.; van Koten, G. *Angew. Chem. Int. Ed.* **2001,** *40,* 3750.
Selander, N.; Szabó, K. J. *Chem. Rev.* **2011,** *111,* 2048.
Younus, H. A.; Su, W.; Ahmad, N.; Chen, S.; Verpoort, F. *Adv. Synth. Catal.* **2015,** *357,* 283.

Pincer Complexes Syntheses



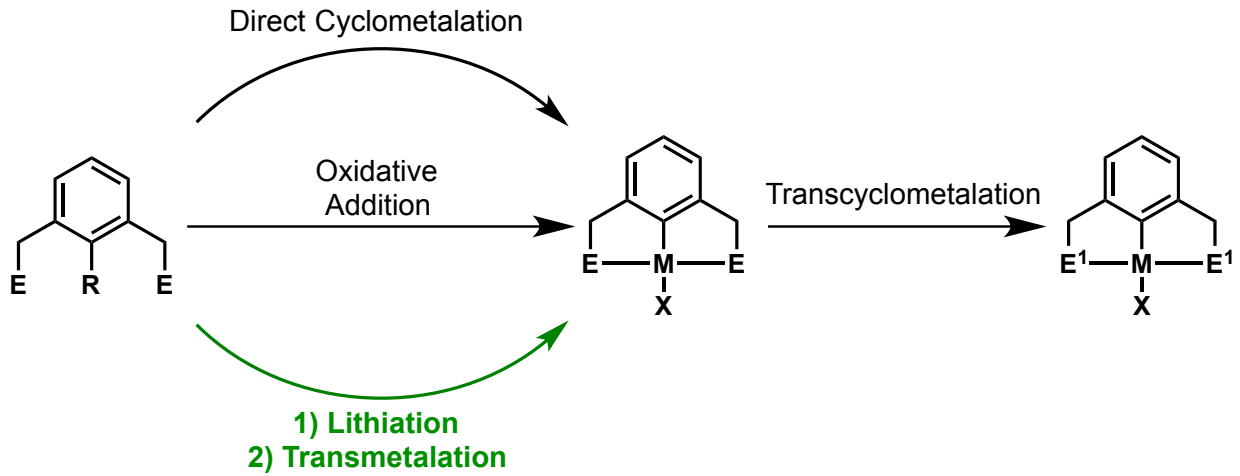
- Most effective with softer donor atoms
- Two potential mechanisms for C–R activation:
  - Oxidative addition
    - Typical of electron-rich, low-valent late transition metals
  - σ-Bond metathesis
    - Typical of electron-poor, high-valent early transition metals

Pincer Complexes Syntheses

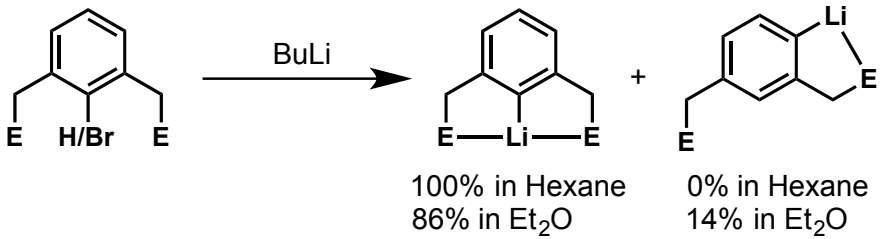


- Requires an electron-rich center
- Direct population of the anti-bonding σ* orbital of the C–H bond
- Useful for acid labile or thermally unstable substituents
- Utilized with NCN ligands

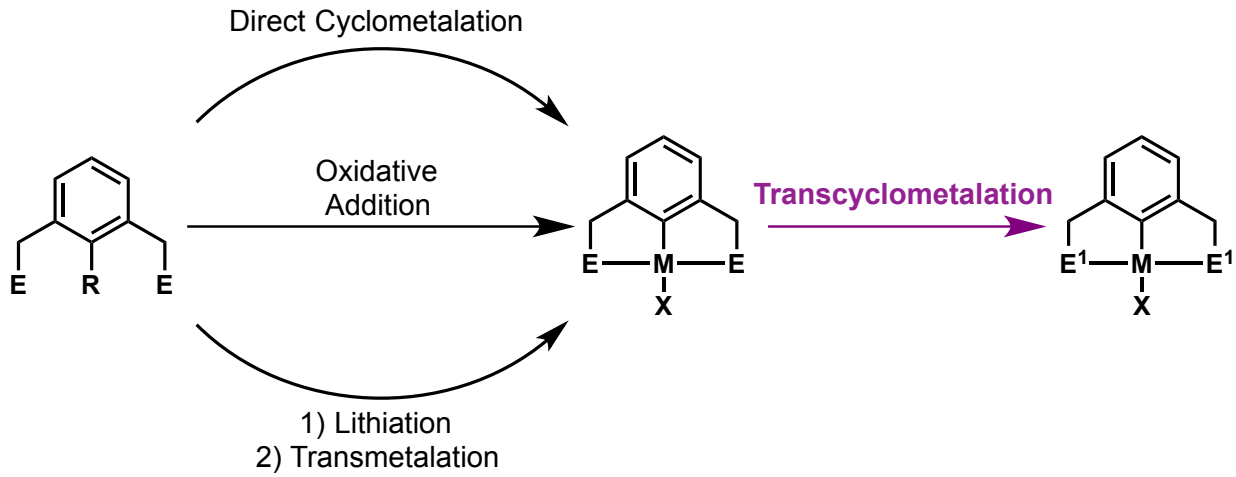
Pincer Complexes Syntheses



- Effective for NCN ligands
  - Lower M–N bond strength
- *Ortho-, para-* a competing pathway
  - Silyl substituents as directing group
  - Use apolar, non-coordinating solvents

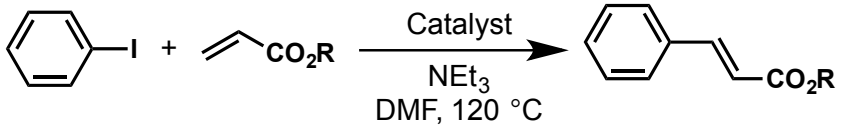


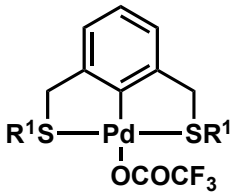
Pincer Complexes Syntheses

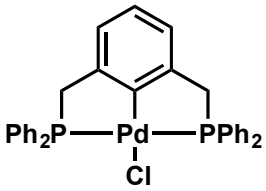


- A C–H activation mechanism with 2 possible precessions:
  - Inorganic intermediate (M–C cleavage before M–C' formation)
  - Diorgano metal complex (M–C' formation before M–C cleavage)
- NCN ligands are particularly good starting materials
  - Lower bond strength of M–N bond

Catalysis – Heck Reaction

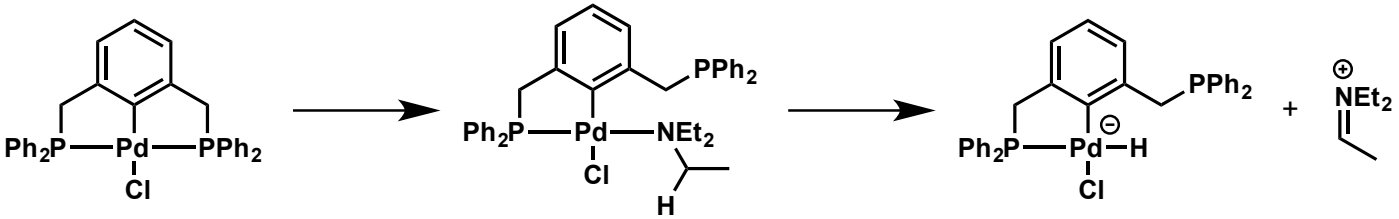






$R^1 = CH_2CH_2R_{f8}$

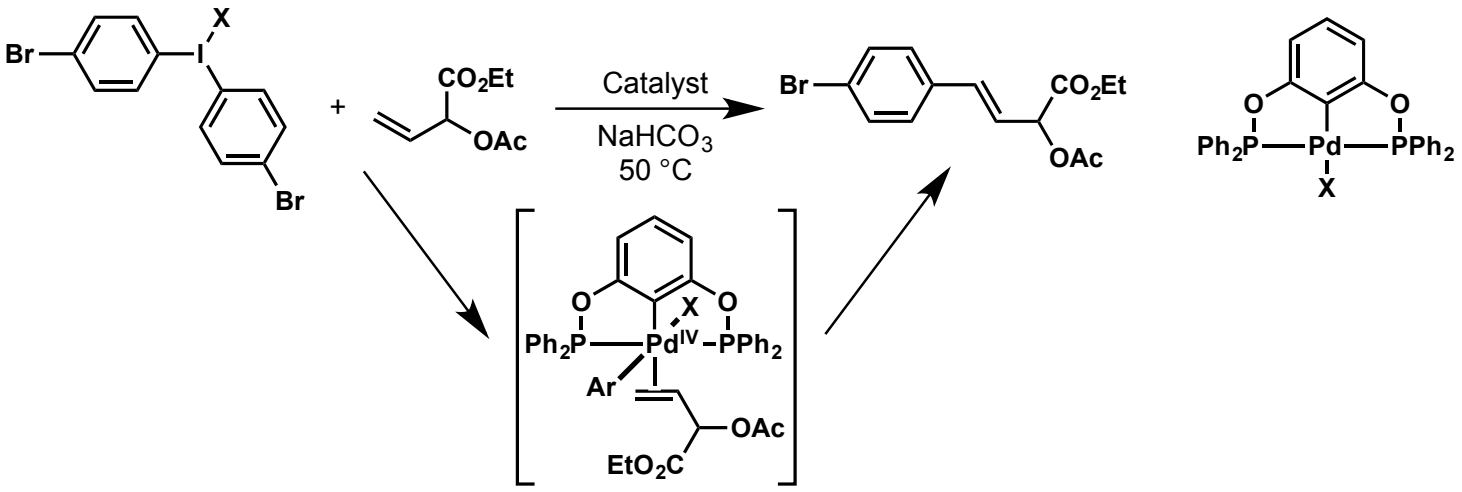
- Most likely the release of Pd(0) nanoparticles
- Pincer ligand controls the release of nanoparticles, and therefore, the rate of reaction



- Coordination of base by opening one of the side arm
- β-hydride elimination to produce the anionic complex
- Reductive deprotonation to yield Pd(0)

Sommer, W. J.; Yu, K.; Sears, J. S.; Ji, Y.; Zheng, X.; Davis, R. J.; Sherrill, C. D.; Jones, C.W.; Weck,M. *Organometallics* **2005,** *24,* 4351.
da Costa, R. C.; Jurisch, M.; Gladysz, J. A. *Inorg. Chim. Acta* **2008,** *361,* 3205.

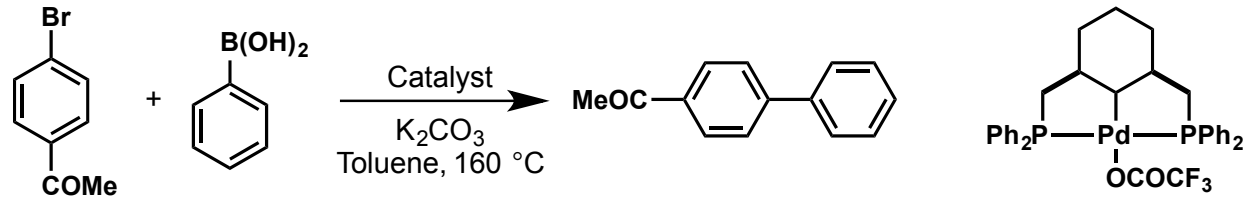
Catalysis – Heck Reaction



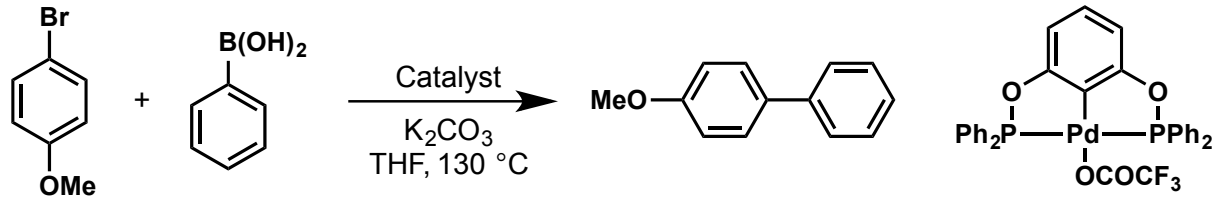
- Generally, oxidative potential of aryl halides is too low to efficiently oxidize Pd(II) to Pd(IV) without some unusual structural elements in the complex or some kind of additive
- No Pd(0) generated, therefore, no Pd(II) allyl palladium complex formed
- According to DFT calculations, the oxidation from Pd(II) to Pd(IV) for hypervalent iodides is exothermic, while the oxidation for aryl iodides is endothermic

Aydin, J.; Larsson, J. M.; Selander, N.; Szabo, K. J. *Org. Lett.* **2009,** *11,* 2852.

Catalysis – Suzuki-Miyaura Coupling



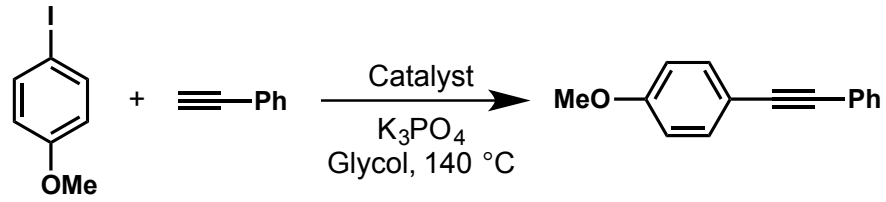
- Probably does not proceed via the usual Pd(0)/Pd(II) redox cycle, and instead is most likely a redox-free pathway
  - No irreversible dissociation of the pincer ligand
  - Substitution of the trifluoroacetate anion with a phenyl group results in a highly reactive palladium species that reacts directly with aryl bromides without a redox process

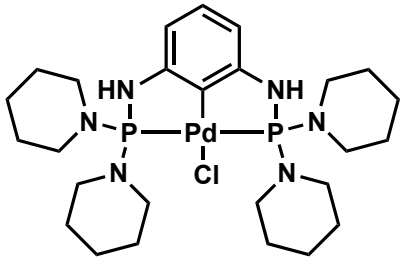


- Requires only 0.0001 mol% catalyst with TON of 190,000
- Oxidative addition not thought to be the rate-determining step
- Base-sensitive

Bedford, R. B.; Draper, S. M.; Scully, P. N.; Welch, S. L. *New J. Chem.* **2000,** *24,* 745.
Olsson, D.; Wendt, O. F. J. *Organomet. Chem.* **2009,** *694,* 3112.

Catalysis – Sonagashira Coupling

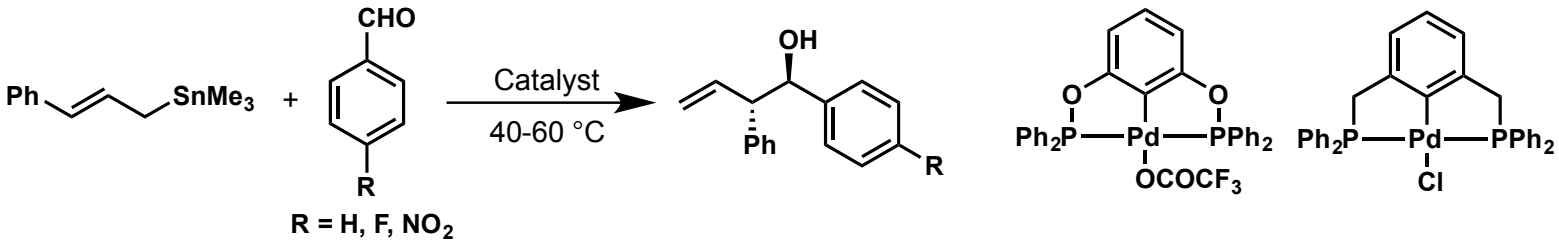




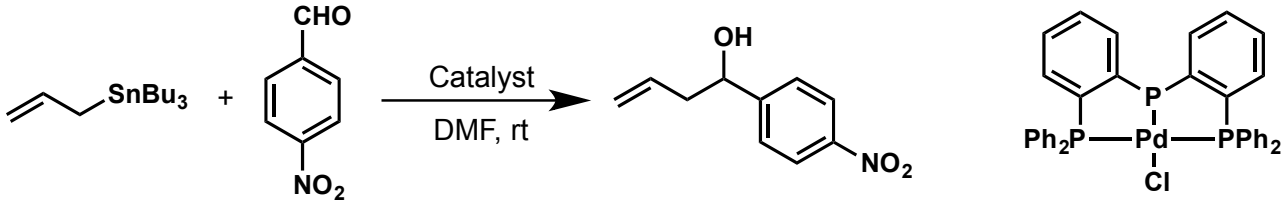
- No copper co-catalyst
- TON of 2 x 10^6
- Quantitative yield
- No Pd(0) formation
- Induction period
- Unclear if direct catalyst

Bolliger, J. L.; Frech, C. M. *Adv. Synth. Catal.* **2009,** *351,* 891.

Catalysis – Allylation of Aldehydes



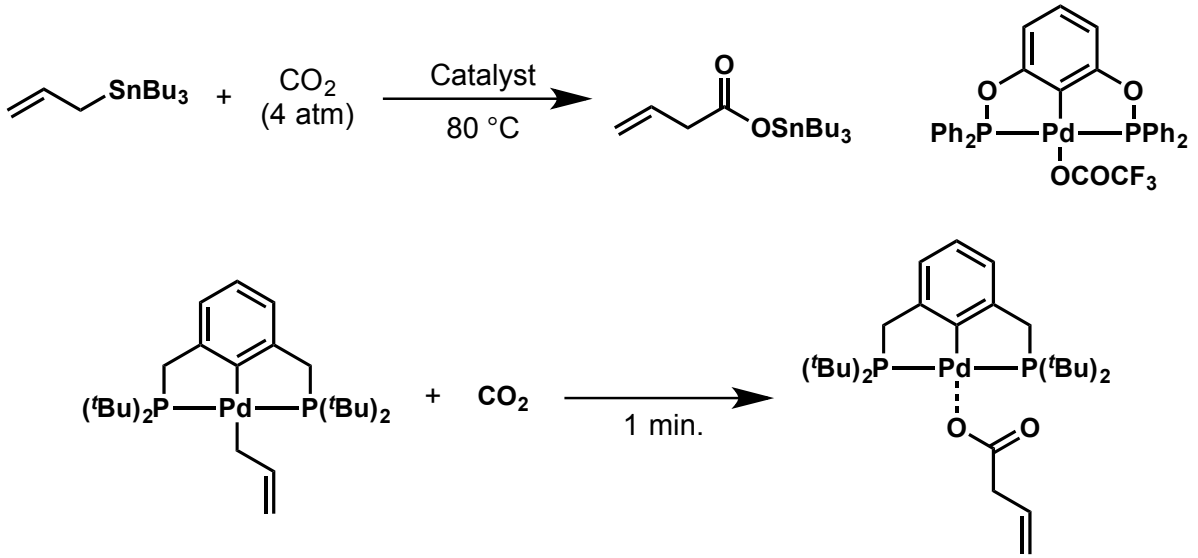
- Pincer complexes with a relatively electron-poor palladium atom performed well
- Higher catalytic activity for weaker coordinating counteranion



- Tridentate coordination of the pincer ligand forces the allyl fragment into an η^1-coordination mode
- Pincer ligand prevents reductive allyl-alyll reactions

Solin, N.; Kjellgren, J.; Szabo, K. J. *J. Am. Chem. Soc.* **2004,** *126,* 7026.
Mazzeo, M.; Lamberti, M.; Massa, A.; Scettri, A.; Pellechia, C.; Peters, J. C. *Organometallics* **2008,** *27,* 5741.

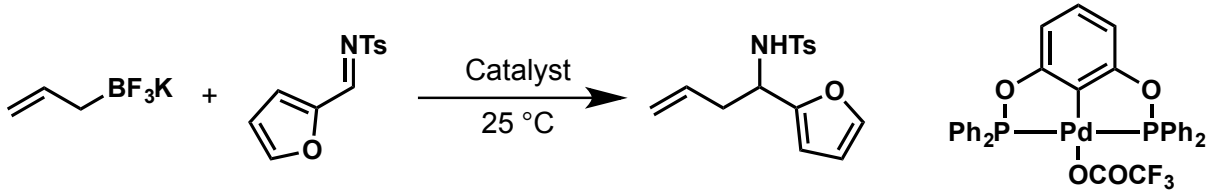
Catalysis – Allylation of CO_2



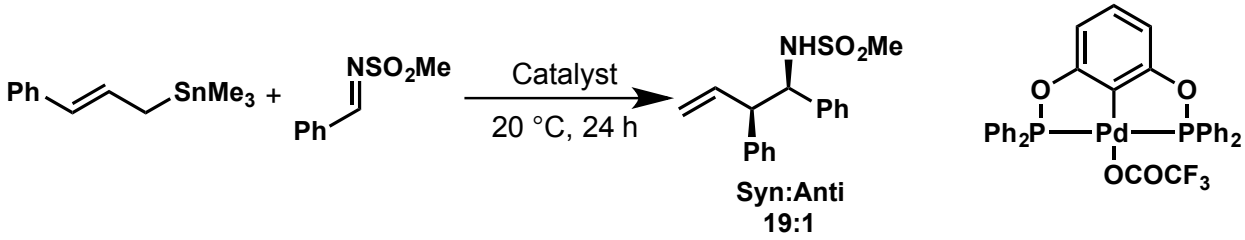
- No change in oxidation state
- A high electron density on palladium allows an efficient electron transfer to the double bond, which increases the nucleophilicity of the allyl moiety
- Usually a relatively electron-poor palladium atom is used because transmetalation is the rate-determining step
- If the electron density on palladium is too low, the electrophilic attack can become rate-determining or, in extreme cases, hinder the catalytic process

Johansson, R.; Wendt, O. F. *Dalton Trans.* **2007,** *488*.
Olsson, D.; Nilsson, P.; El Masnaouy, M.; Wendt, O. F. *Dalton Trans.* **2005,** *1924*.

Catalysis – Allylation of Imines



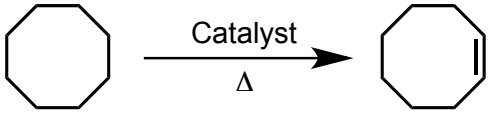
- Imines more reactive than aldehydes in palladium-catalyzed allyl reactions via bis-allyl palladium intermediates
- Can be carried out without the addition of water and base
- Form η^1-allyl palladium complexes

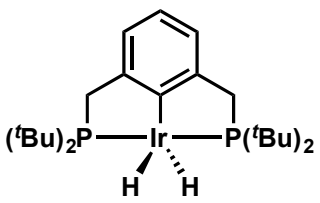


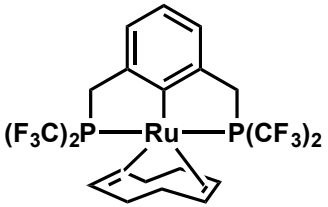
- Allylation of imines gives *syn* stereoselectivity, while the allylation of aldehydes gives *anti* stereoselectivity
- According to DFT modeling studies, the switch of the diastereoselectivity was attributed to the different transition state geometries for allylation of aldehydes and imines

Solin, N.; Wallner, O. A.; Szabo, K. J. *Org. Lett.* **2005,** *7,* 689
Wallner, O. A.; Szabo, K. J. *Chem.—Eur. J.* **2006,** *12,* 6976.

Catalysis – Alkane Dehydrogenation



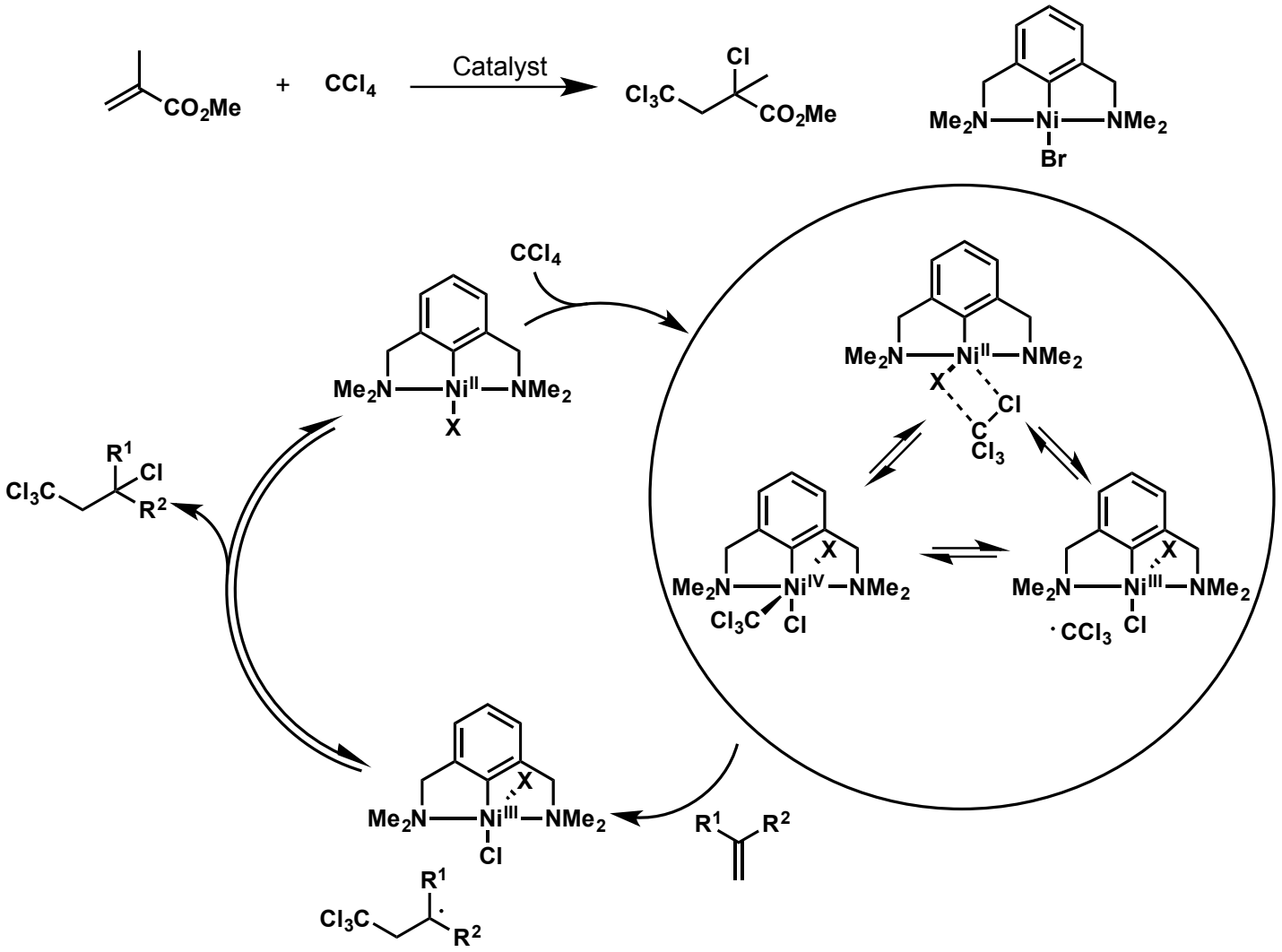




- With *tert*-butylethylene, rates of 180 (150 °C) and 1000 (200 °C) turnovers per hour
- Without *tert*-butylethylene, initial rate of 14 turnovers per hour
- Decrease in catalyst activity from thermal catalyst decomposition
- Iridium catalysts are generally more active because they more readily undergo C–H oxidative addition
- Nitrogen atmosphere kills the reaction via $[Ir(PCP)]_2(\mu\text{-}N_2)$, so reactions must be performed under argon

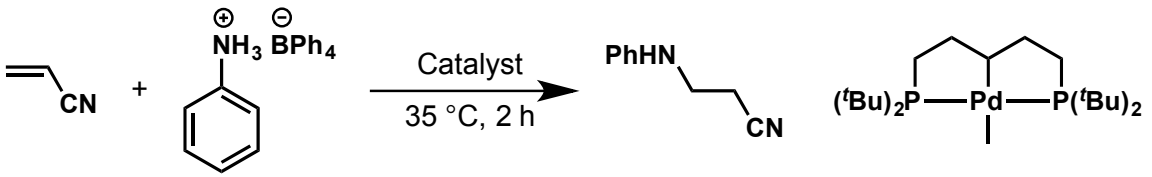
Gupta, M.; Hagen, C.; Kaska, W. C.; Crammer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997,** *119,* 840.
Gruver, B. C.; Adams, J. J.; Warner, S. J.; Arulsamy, N.; Roddick, D. M. *Organometallics* **2011,** *30,* 5133.

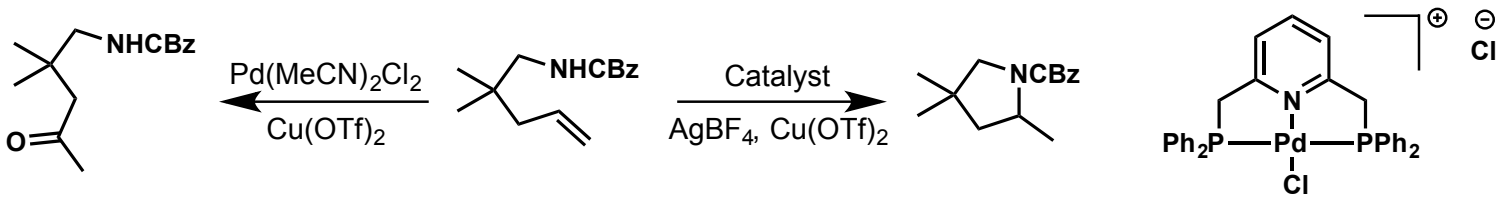
Catalysis – Kharasch Reaction

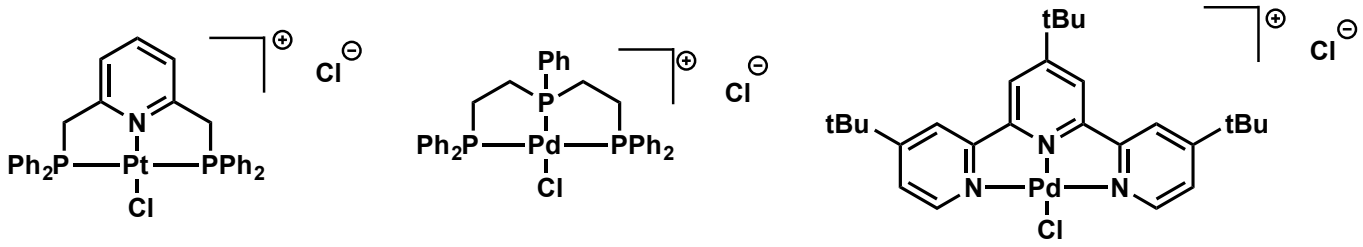


Van de Kuil, L. A.; Grove, D. M.; Gossage, R. A.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1997,** *16,* 4985

Catalysis – Hydroamination



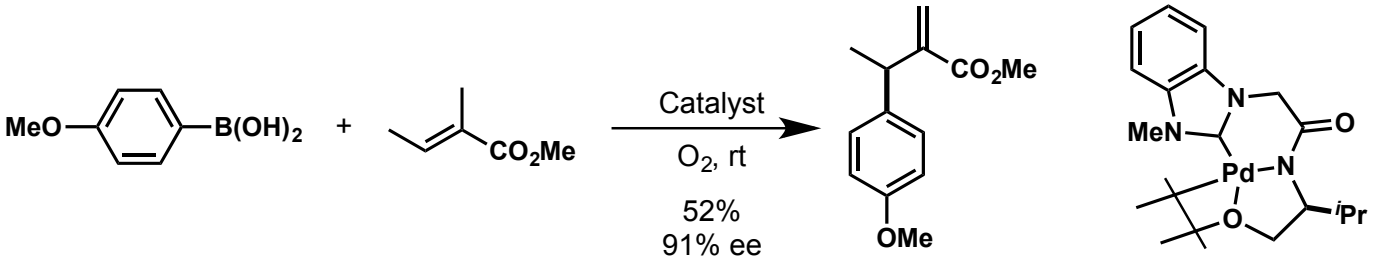




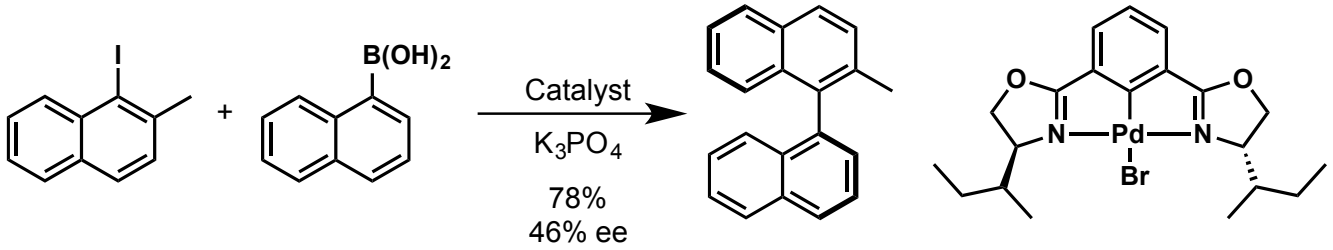
Seligson, A. L.; Trogler, W. C. *Organometallics* **1993,** *12,* 744.
Michael, F. E.; Cochran, B. M. *J. Am. Chem. Soc.* **2006,** *128,* 4246.

Asymmetric Couplings

- Heck

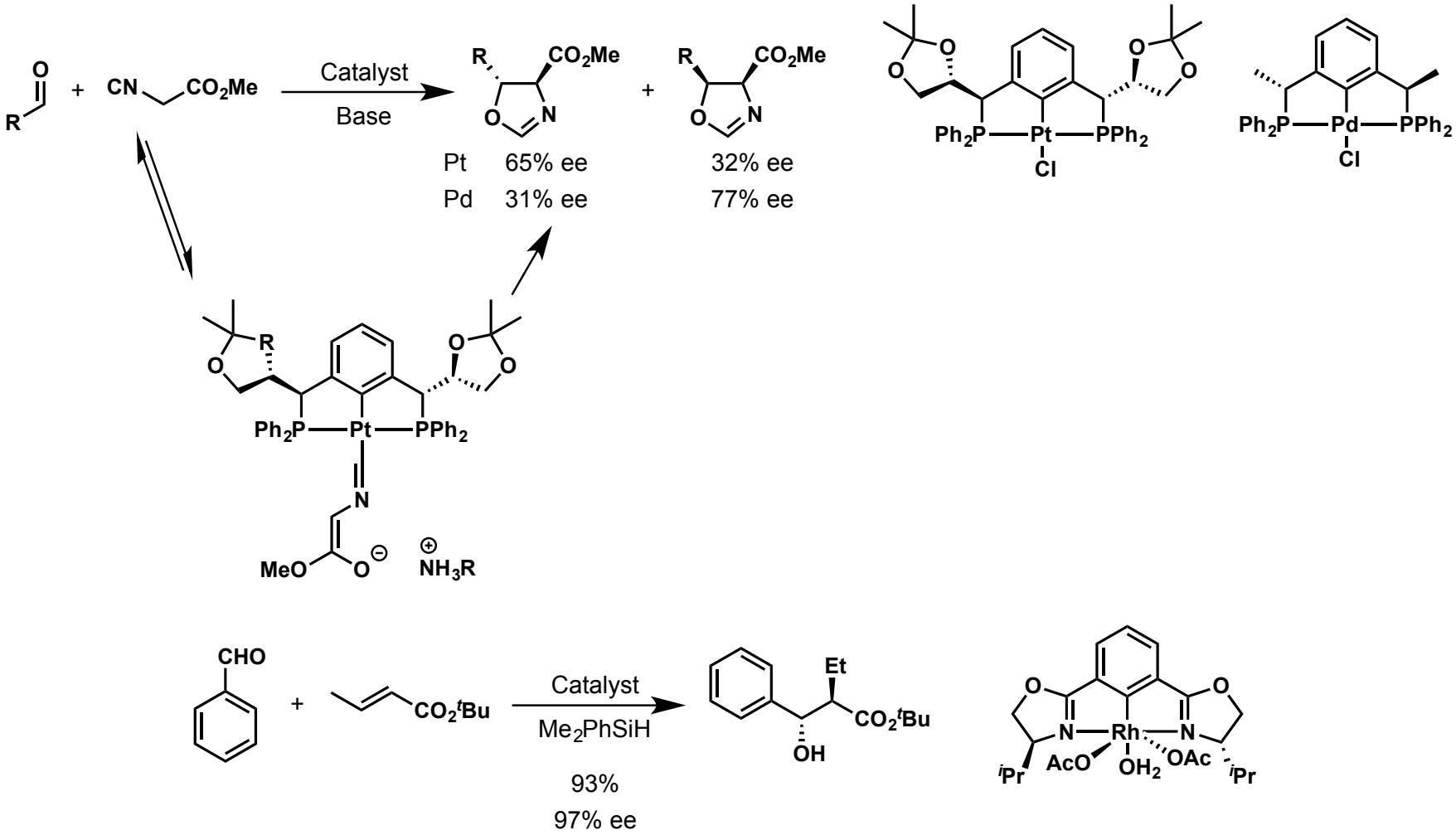


- Suzuki-Miyaura



Yoo, K. S.; O'Neill, J.; Sakaguchi, S.; Giles, R.; Lee, J. H.; Jung, K. W. *J. Org. Chem.* **2010,** *75,* 95.
Takemoto, T.; Iwasa, S.;Hamada, H.; Shibatomi, K.; Kameyama, M.; Motoyama, Y.; Nishiyama, H. *Tetrahedron Lett.* **2007,** *48,* 3397.

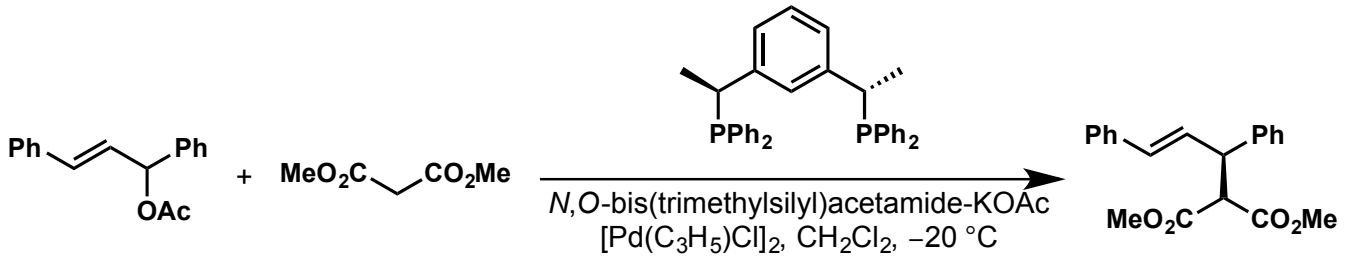
Asymmetric Aldol Reactions



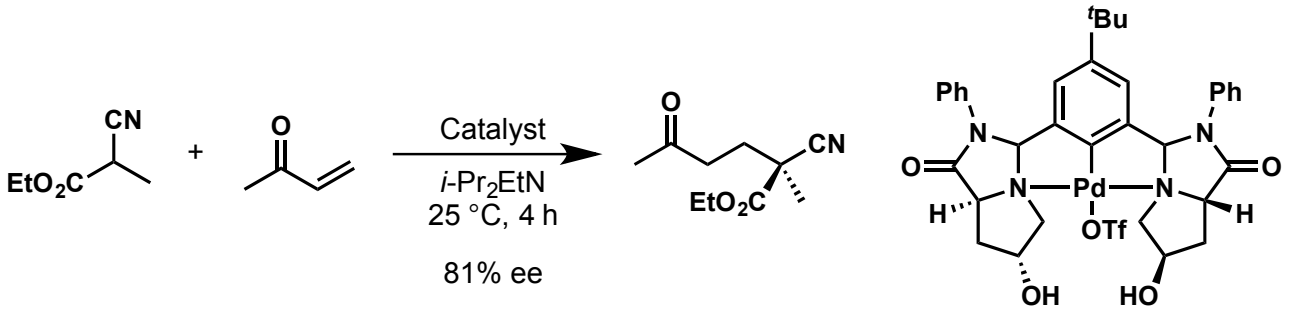
Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998,** *17,* 4374.
Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994,** *13,* 1607.
Nishiyama, H.; Shiomi, T.; Tsuchiya, Y.; Matsuda, I. *J. Am. Chem. Soc.* **2005,** *127,* 6972.

Asymmetric Additions

- Allylic Alkylation



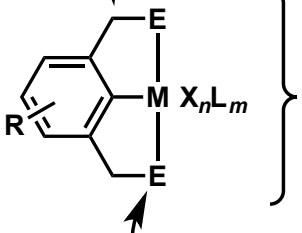
- Michael



Longmire, J. M.; Zhang, X. *Tetrahedron Lett.* **1997,** *38,* 1725.
Takenaka, K.; Minakawa, M.; Uozumi, Y. *J. Am. Chem. Soc.* **2005,** *127,* 12273.

Summary

- Chiral pocket
- Steric constraints



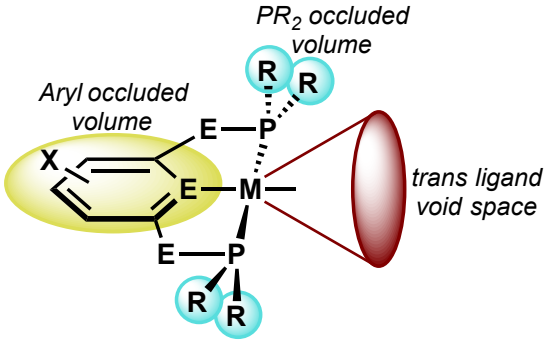
- Cavity for metal binding with tunable accessibility
- Sites for counterions or ancillary ligands

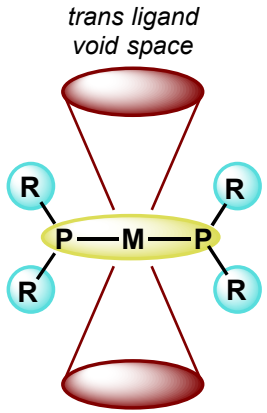
- Anchoring site
- Remote electronic modulations

- Hardness/softness
- Metal-biding rigidity
- Steric constraints of substituents
- Coordinating 2e donor or free Lewis base

Applications:

- Cross-couplings
- Additions
- Dehydrogenations
- Alkylations
- Hydroaminations





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