Hydration of nitriles with Ghaffar-Parkins catalyst

Literature Seminar

2021/4/24

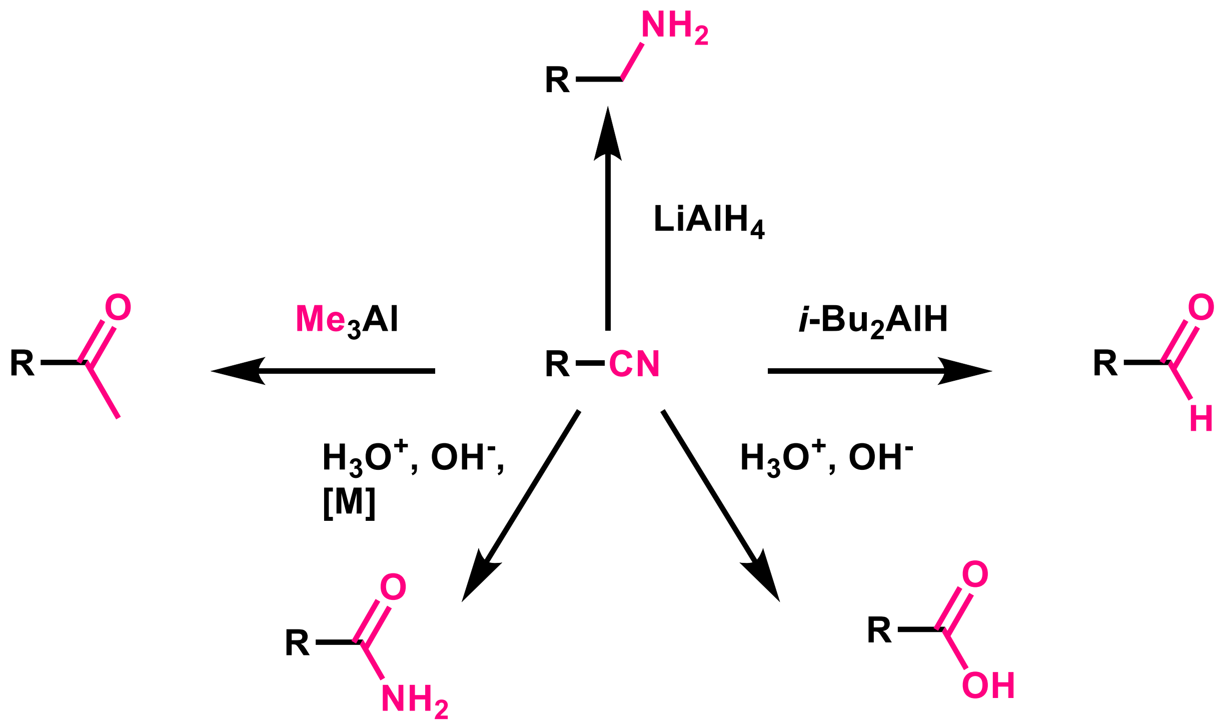
Takahiro Watanabe

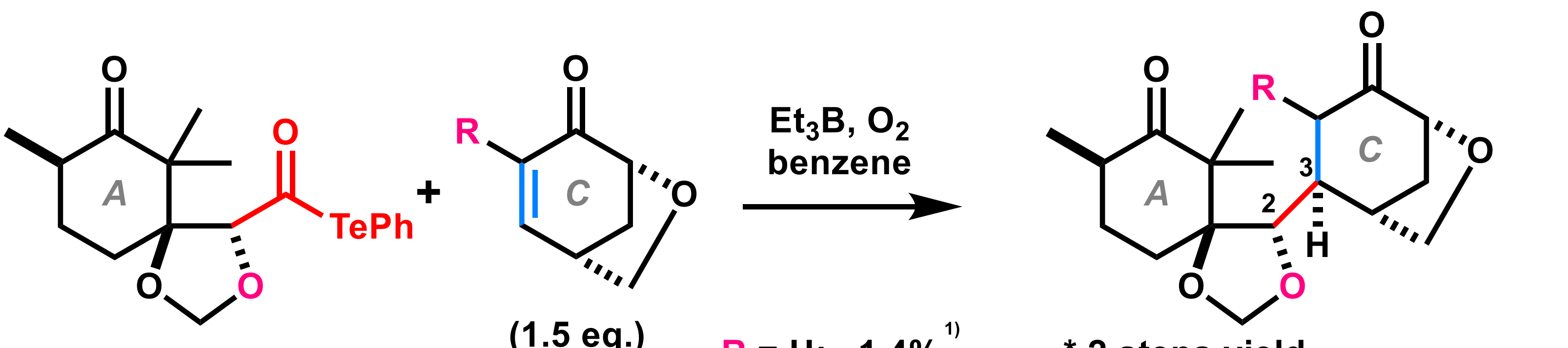
Contents

(Xing, X.; Xu, C; Chen, B.; Li, C.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2018**, *140*, 17782.)

Contents

Nitrile as a Versatile Fuctional Group





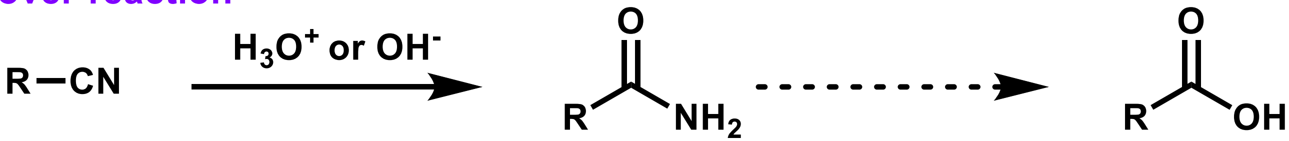
R = H: 1.4%[1)]
R = CN: 48%*

* 2 steps yield
after TBS enol ether formation

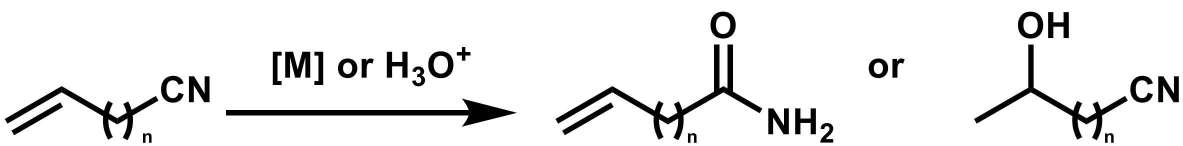
1) Matoba, H.; Watanabe, T.; Nagatomo, M.; Inoue, M. *Org. Lett.* **2018**, *20*, 7554.

Problems in Hydration of Nitriles

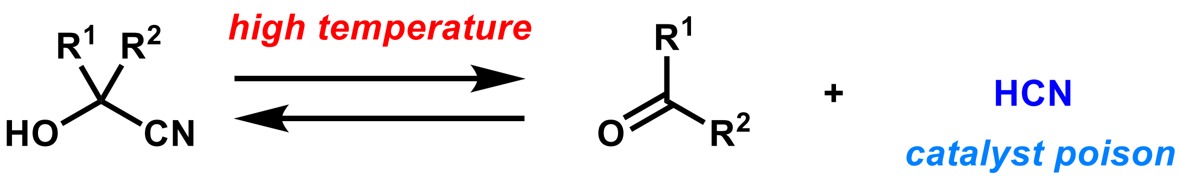
1. over-reaction

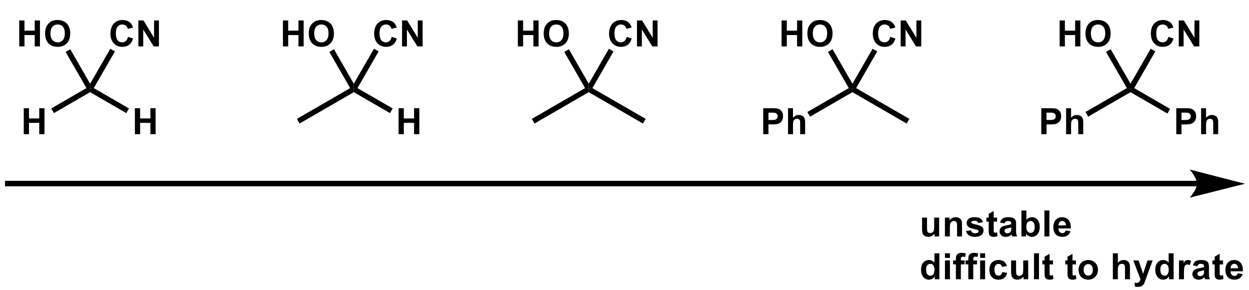


2. chemoselectivity



3. hydration of cyanohydrins

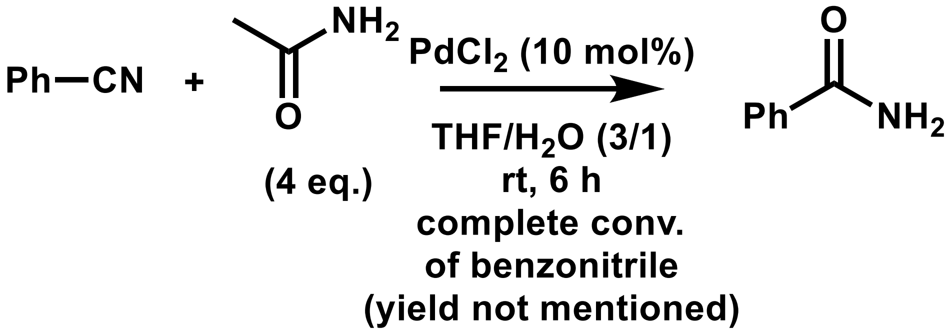


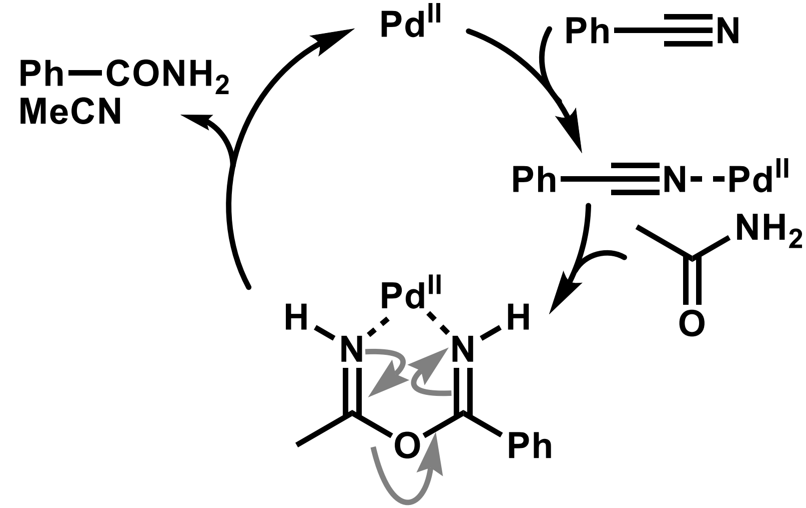


Though the reaction is fundamental, above problems remains (especially 3).
Mild and efficient conditions have been investigated.

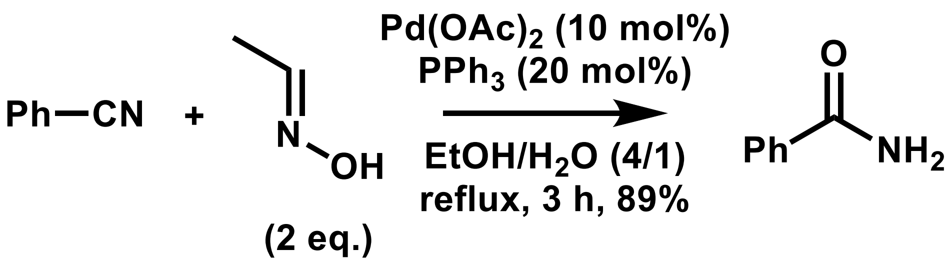
Conditions with Water Surrogates

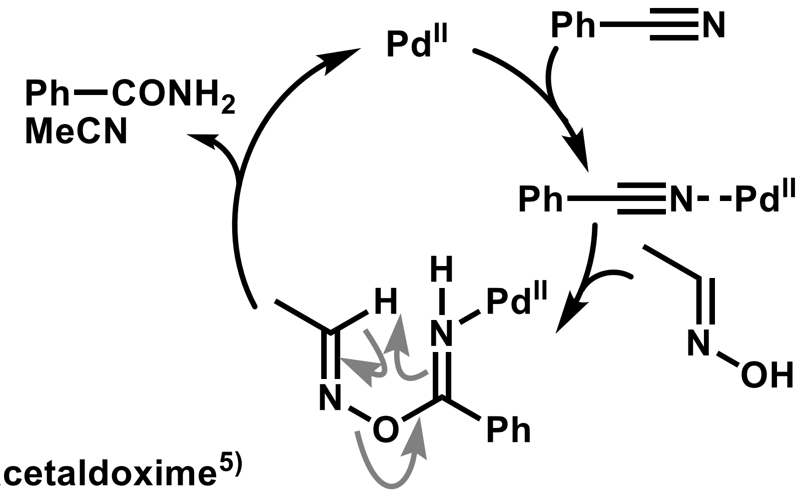
Drawbacks in hydration catalysts:
low nucleophilicity of water under neutral conditions
-Transfer hydration from amides
first example [1]:





-Transfer hydration from aldoximes
first example [2]:



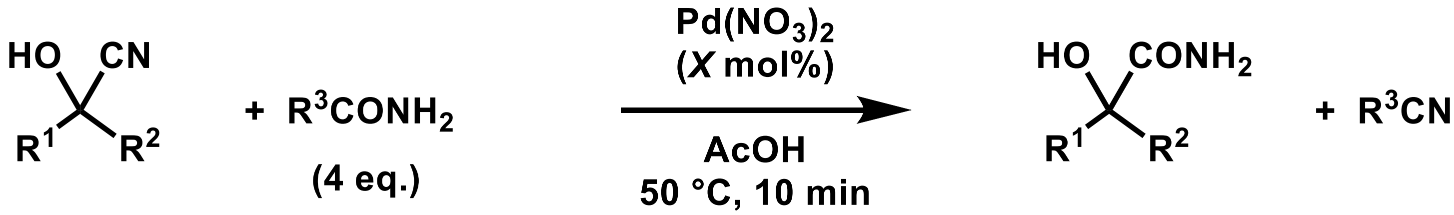


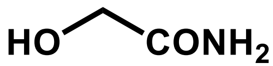
$RhCl(PPh_3)_3$/acetaldoxime[3], $InCl_3$/acetaldoxime[4], CuO/acetaldoxime[5] conditions were also reported.

*** The reaction also proceeded without PPh_3 (82% yield)**

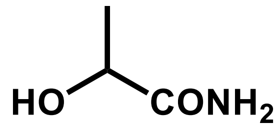
1) Maddioli, S. I.; Marzorati, E.; Marazzi, A. *Org. Lett.* **2005**, *7*, 5237. 2) Kim, E. S.; Kim, H. S.; Kim, J. N. *Tetrahedron Lett.* **2009**, *50*, 2973. 3) Lee, J.; Kim, M.; Chang, S.; Lee, H. Y. *Org. Lett.* **2009**, *11*, 5598. 4) Kim, E. S.; Lee, H. S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2010**, *51*, 1589. 5) Ma, X. Y.; He, Y.; Hu, Y. L.; Lu, M. *Tetrahedron Lett.* **2012**, *53*, 449.

Recent Progress in Cyanohydrin Hydration

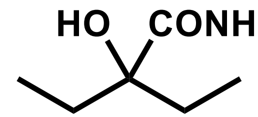




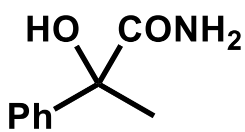
$R^3 = n\text{-}C_5H_{11}$
X = 2, 98%



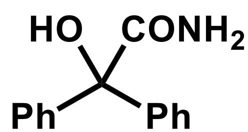
$R^3 = n\text{-}C_5H_{11}$
X = 2, 96%



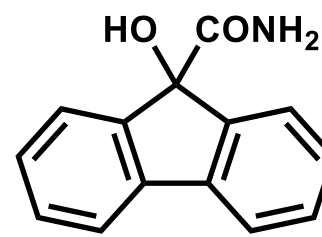
$R^3 = n\text{-}C_5H_{11}$
X = 3, 92%



$R^3 = n\text{-}C_5H_{11}$
X = 4, 98%



$R^3 = CH_3$
X = 5, 75%

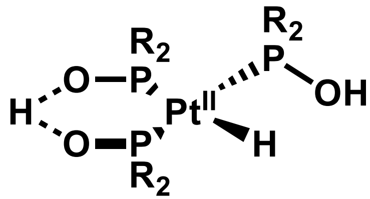


$R^3 = CH_3$
X = 10, 77%

Kanda, T.; Naraoka, A.; Naka, H. *J. Am. Chem. Soc*. **2019**, *141*, 825.

Contents

Ghaffar-Parkins Catalyst

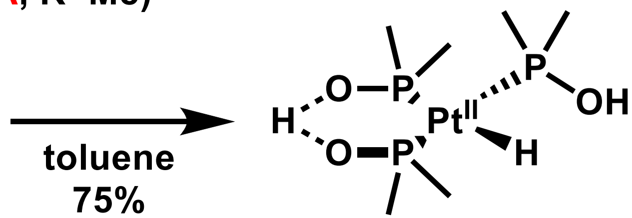


- air-stable
- three $Me_2P(O)H$ ligands, two of which are binded by hydrogen bonding
- described by Ghaffar and Parkins in 1995

Ghaffar-Parkins catalyst (A, R=Me)

Synthesis:

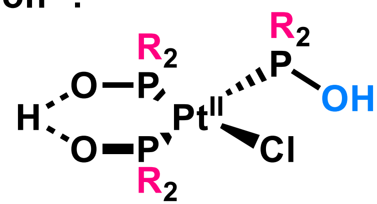
$Pt^0(PPh_3)_4$ + $Me_2P(O)H$ (5 eq.)



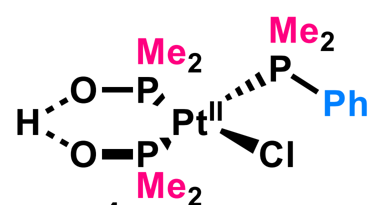
- Ph analogue (R=Ph) was known in 1975[1], and used in hydroformylation[2].

Comparison of TOF (mol of amides/(mol of cat h))

precursor	acetonitrile	acrylonitrile	benzonitrile
1b	20	68	35
2b	488	1800	610
3	90	670	140
4	186	310	230



R = Ph, 1b
R = Me, 2b (precursor of A)
R = $-(CH_2)_4-$, 3

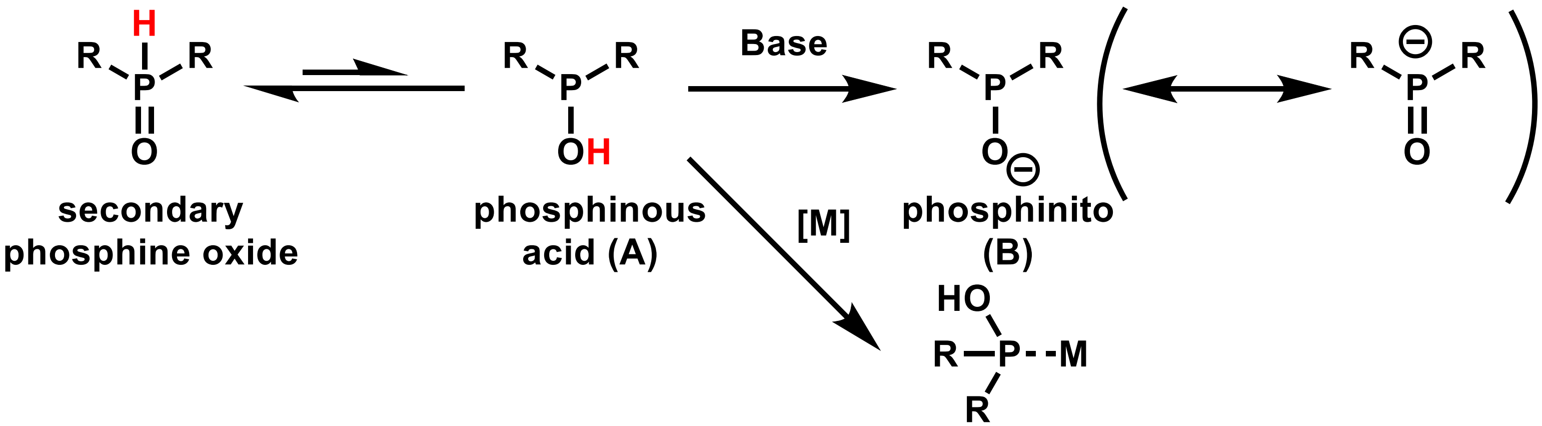


4

- Bulkiness of ligands affect the efficiency of the reaction.
- OH group plays important role in efficiency. (2b vs 4)

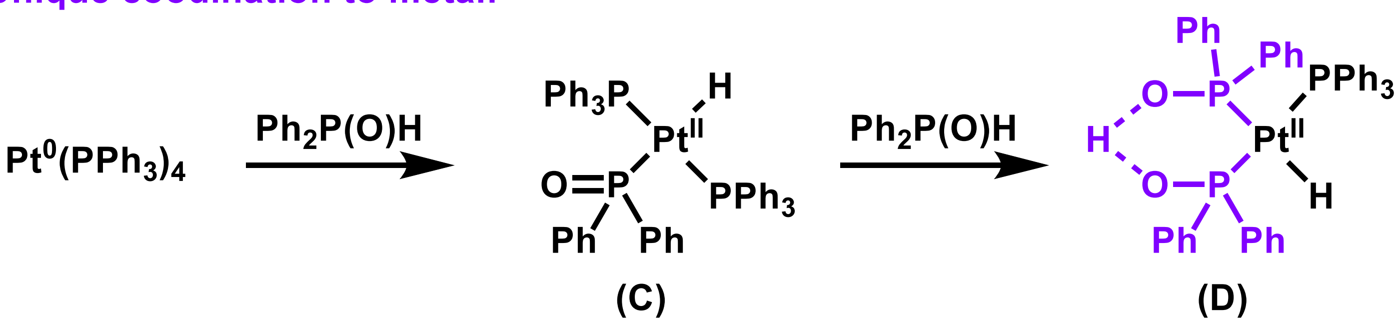
1) Beaulieu, W. B.; Rauchfuss, T. B.; Roundhill, T. B. *Inorg. Chem*. **1975**, *14*, 1732.
2) Van Leeuwen, P.W.N.M.; Roobeek, C.F. *Adv. Chem. Ser*. **1992**, *232*, 367.
Ghaffar, T.; Parkins, A. W. *J. Mol. Cat A* **2000**, *160*, 249.

Secondary Phosphine Oxide as a Ligand



Tri-coordinate form of (A) can coordinate to a metal ion like a tercially phosphine, and various metal complex with (A) or (B) have been synthesized.

Unique coodination to metal:

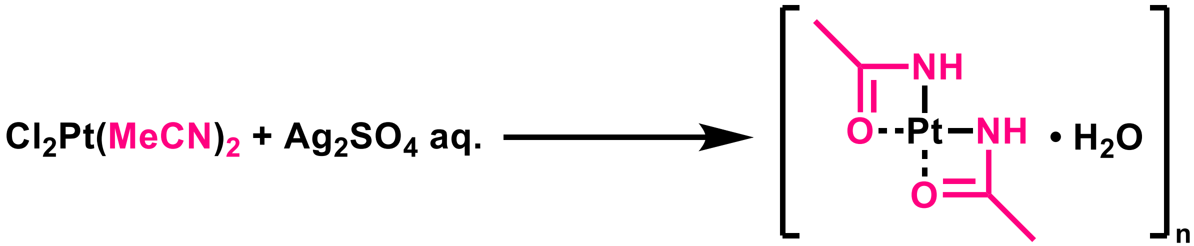


Commonly, protonation of compound Pt^0L_4 with HX leads to $[Pt^{II}HL_3]X$ or $Pt^{II}HXL_2$. However, in this case, (D) is obtained instead of (C).

Roundhill, D. M.; Sperline, R. P.; Beaulieu, W. B. *Coord. Chem. Rev.* **1978**, *26*, 263.

Early Work with Platinum Salts and Nitriles

- **First observation of acetamido formation [1]:**



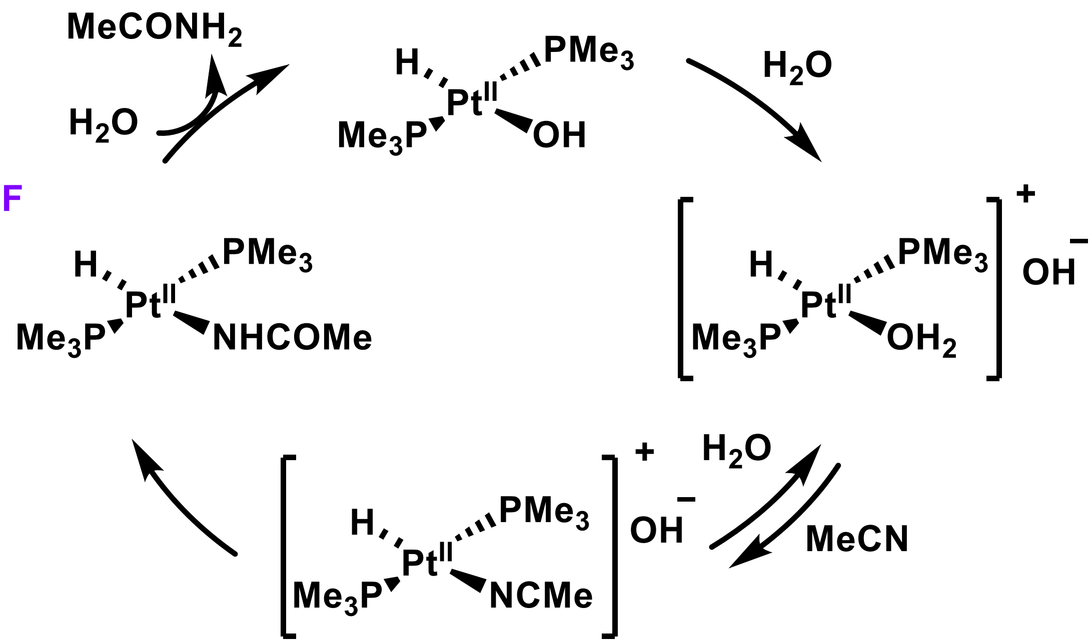
"platinblau"
(composition fomula)

The generated acetamido was not released from the coordination sphere.

- **The most efficient platinum catalyst for hydration of nitriles before Ghaffar-Parkins catalyst:** ***trans***-**[PtH(H_2O)(PMe_3)$_2$][OH] [2)]**

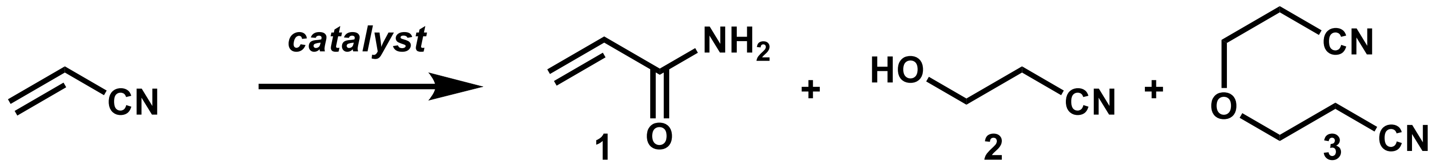
conditions:
PtHCl(PMe_3)$_2$, NaOH (1 eq.)
CH_3CN/H_2O (1/1), 78 °C

acetonitrile hydration at 78 °C: 178 TOF
(cf. NaOH cat. at 78 °C: 0.4 TOF)

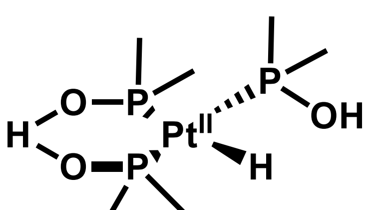


1) (a) Hofmann, K. A.; Bugge, G. *Chem. Ber.* **1907**, *40*, 1772. (b) Hofmann, K. A.; Bugge, G. *Chem. Ber.* **1908**, *41*, 312. 2) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723.

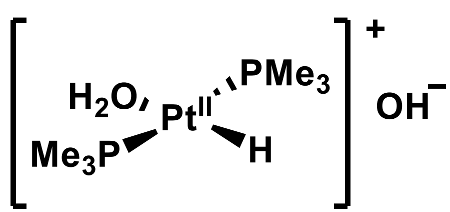
Comparison with Other Platinum Catlysts



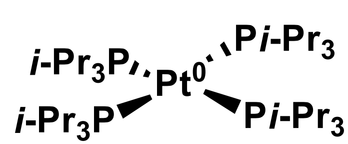
cat.	temp (°C)	TOF (mol. of product/mol. of cat h)			selectivity for nitrile
		1	2	3	
A	90	1485	-	-	>99
B	25	6.2	0.02	0.19	97
B	80	65.0	84.5	10.5	29
C	80	1.8	2.5	20.9	7.5
D	80	2.2	0.25	2.45	45



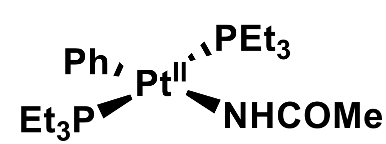
(Ghaffar-Parkins cat., A)



B



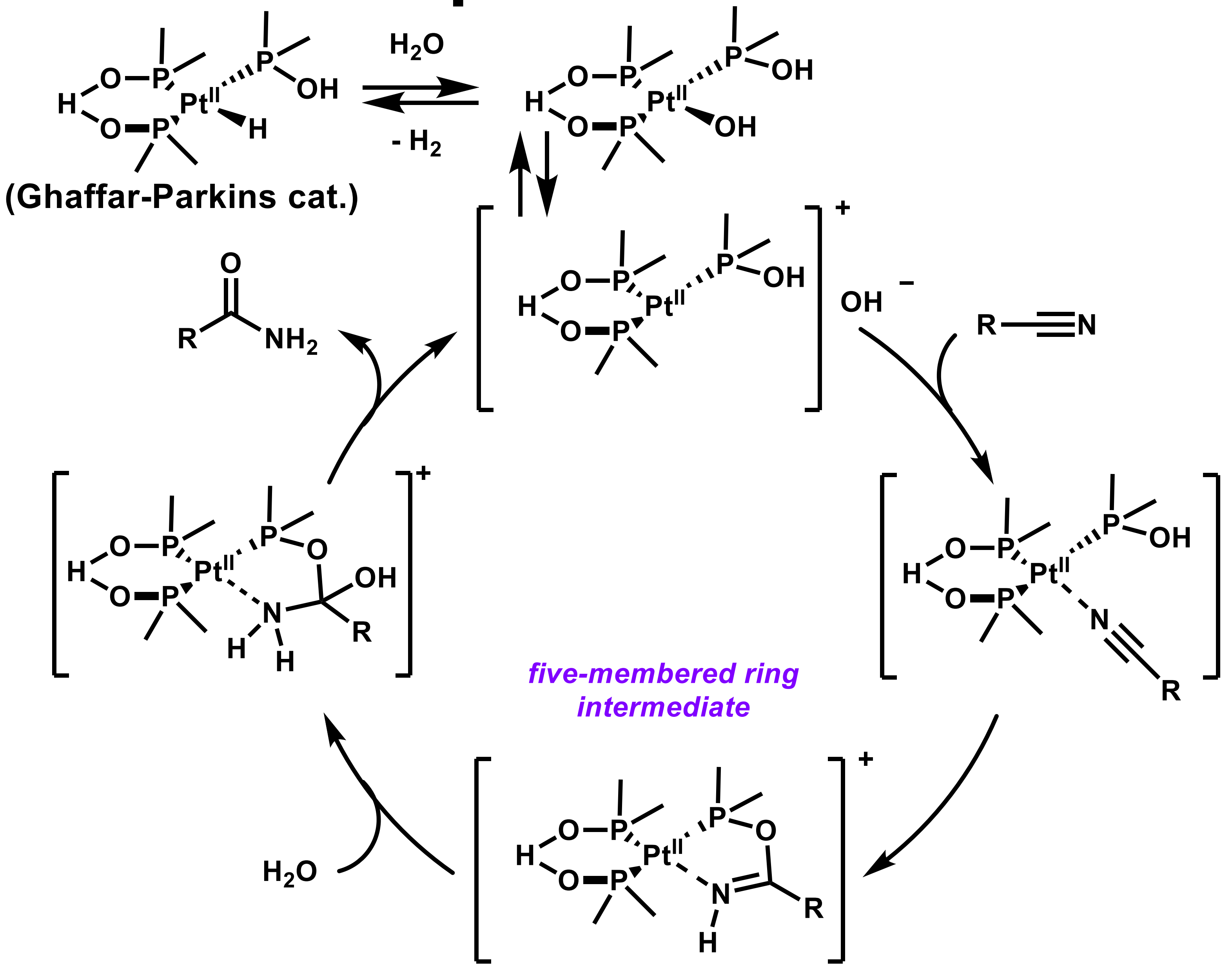
C



D

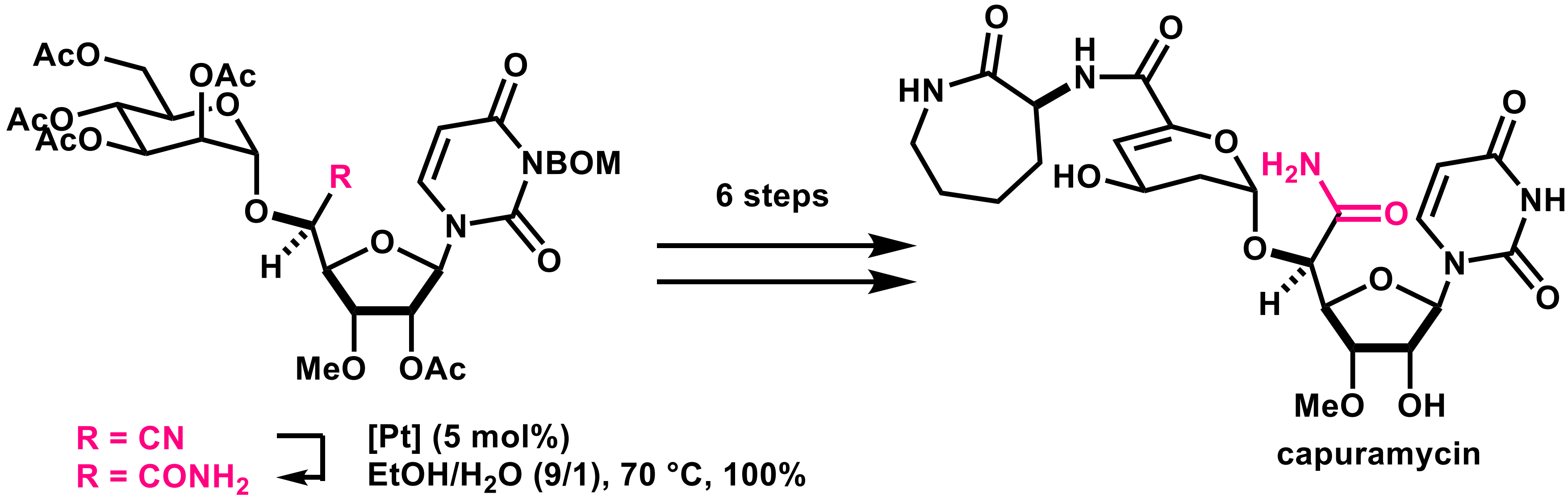
Ghaffar, T.; Parkins, A. W. *J. Mol. Cat A* **2000**, *160*, 249.

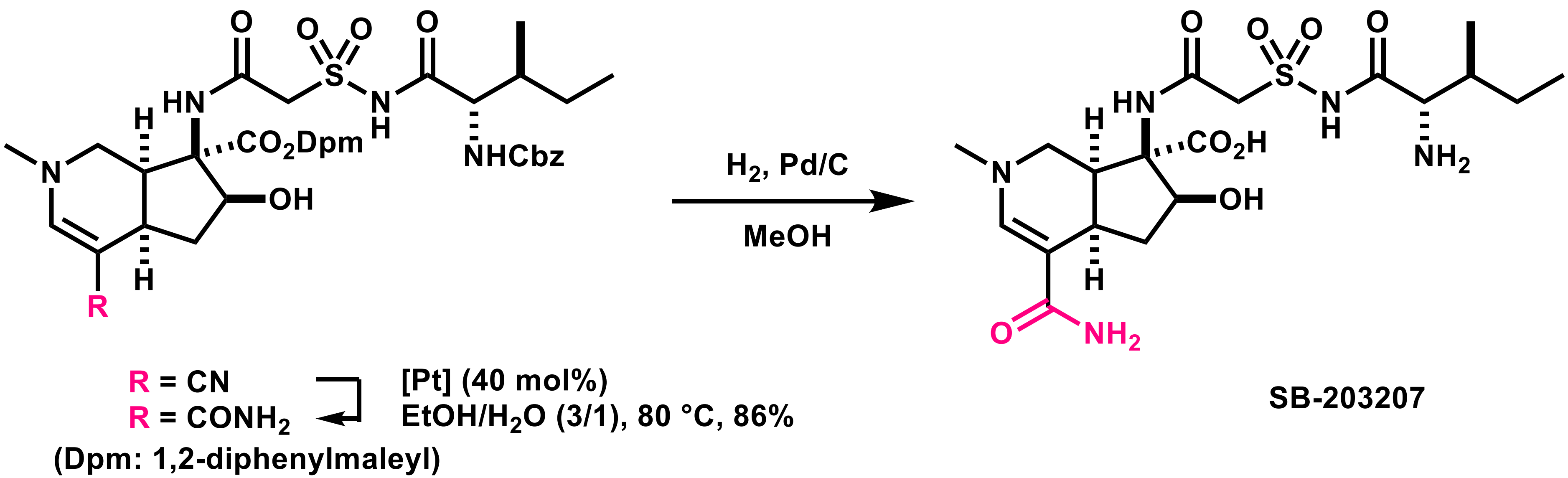
Proposed Mechanisms



Ghaffar, T.; Parkins, A. W. *J. Mol. Cat A* **2000**, *160*, 249.

Application in Total Syntheses

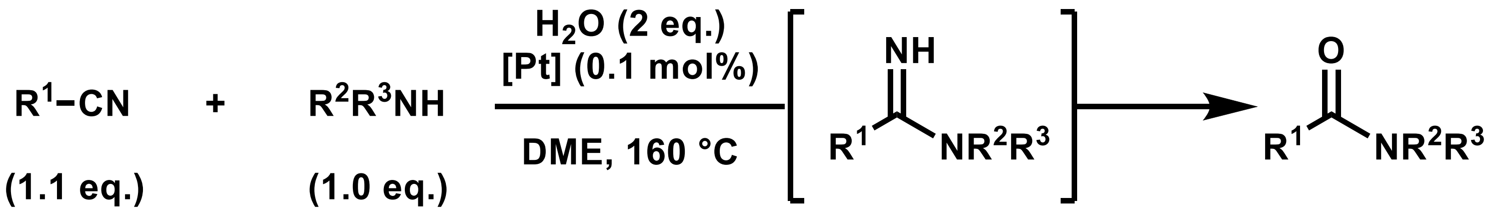




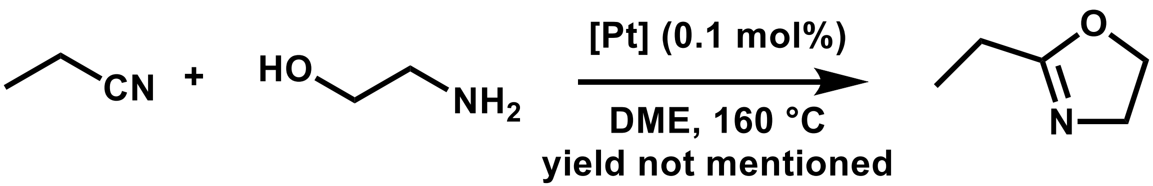
1) Kurosu, M.; Li, K.; Crick, D. C. *Org. Lett.* **2009**, *11*, 2393. 2) Kan, T.; Kawamoto, Y.; Asakawa, T.; Furuta, T; Fukuyama, T. *Org. Lett.* **2008**, *10*, 169.

Other Synthetic Applications

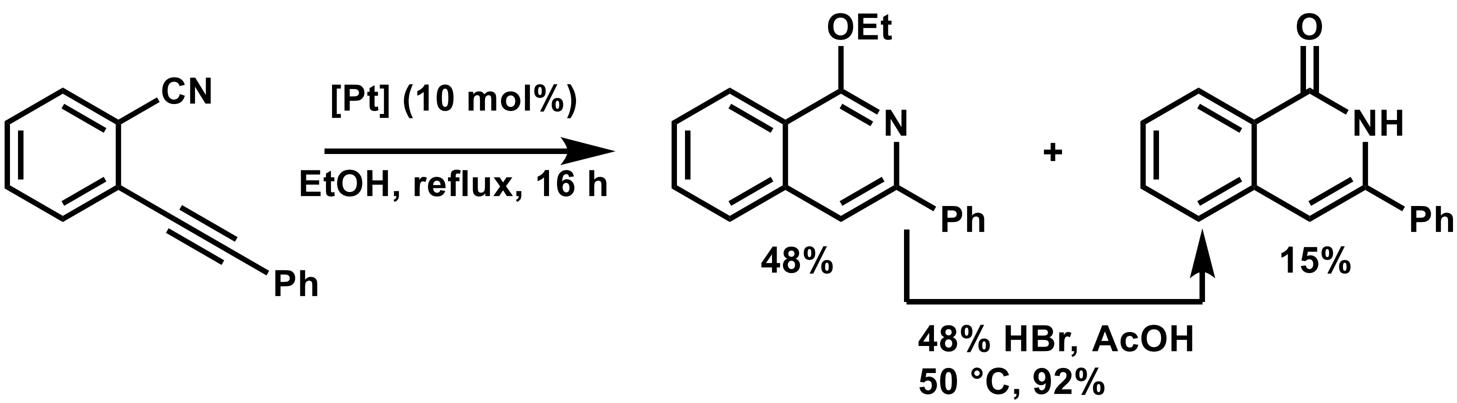
- Conversion of nitriles into *N*-substituted amides [1] ([Pt]=Ghaffar-Parkins cat.)



(R^1−CN = MeCN, PhCN, *n*-C_6H_{13}CN
R^2R^3NH = $PhNH_2$, *n*-$PrNH_2$, $BnNH_2$, pyrrolidine, piperidine, morpholine)



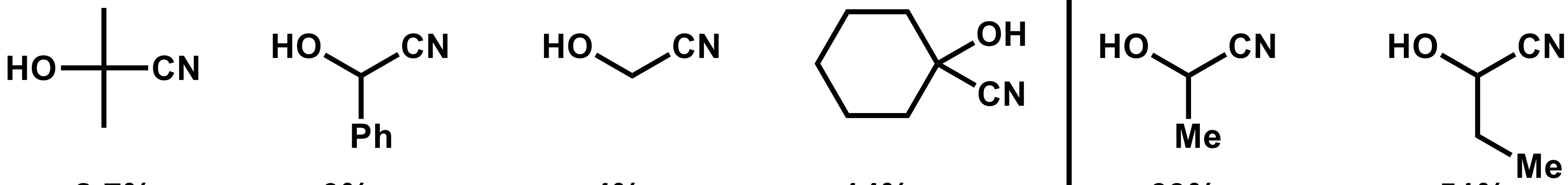
- Synthesis of isoquinolones by intramolecular cyclization [2]



1) Cobley, C. J.; van den Heuvel, M.; Abbadi, A.; de Vries, J. G. *Tetrahedron Lett.* **2000**, *41*, 2467. 2) Li, J.; Chen, L.; Chin, E.; Lui, A. S.; Zecic, H. *Tetrahedron Lett*. **2010**, *51*, 6422.

Limitations

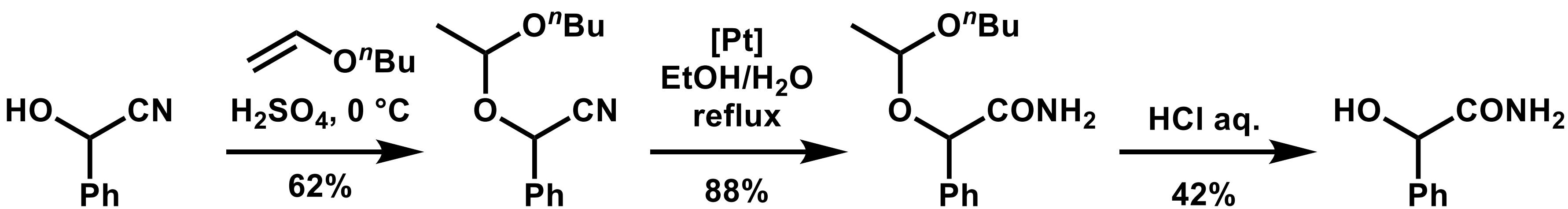
Hydration of cyanohydrins: limited scope[1)]



2.7%	0%	4%	14%	69%	51%
TON: 3	TON: 0	TON: 66	TON: 3	TON: 110	TON: 41

TON = mol. of amide/ mol. of cat.

Circumvention of above problems: protection of hydroxyl group [2)]



([Pt]: Ghaffar-Parkins cat.)

1) Ahmed, T.J.; Fox, B.R.; Knapp, S.M.M.; Yelle, R.B.; Juliette, J.J.; Tyler, D.R. *Inorg. Chem.* **2009**, *48*, 7828.
2) Papakyprianou, A.; Parkins, A.W.; Prince, P.D.; Steed, J.W. *Org. Prep. Proced. Int.* **2002**, *34*, 436.

Contents

1. Introduction

2. Ghaffar-Parkins catalyst

3. **Highly active platinum catalyst for nitrile and cyanohydrin hydration**

   (Xing, X.; Xu, C; Chen, B.; Li, C.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2018**, *140*, 17782.)

Robert H. Grubbs

- B.S. Chemistry, University of Florida, Gainesville, Florida (1963)
- M.S. Chemistry, with Prof. Merle Battiste, University of Florida, Gainesville, Florida (1965)
- Ph.D. Chemistry, with Prof. Ronald Breslow, Columbia University, New York, New York (1968)
- NIH Postdoctoral Fellow in Chemistry, with Prof. James P. Collman, Stanford University (1968-1969)
- Associate Professor, Michigan State University in East Lansing, Michigan (1969-1978)
- Professor, the California Institute of Technology in Pasadena, California

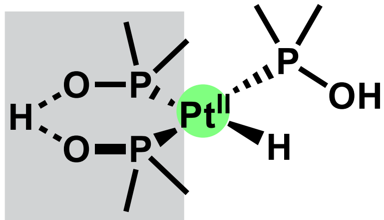
Research topics

1. Organometallic synthesis and mechanisms
- Catalysts for olefin metathesis

2. Organic synthesis
- Catalysts that provide high enantioselectivity in RCM and high stereoselectivity in cross metathesis
- Other metal-catalyzed reactions including oxidations and tandem metathesis/oxidation

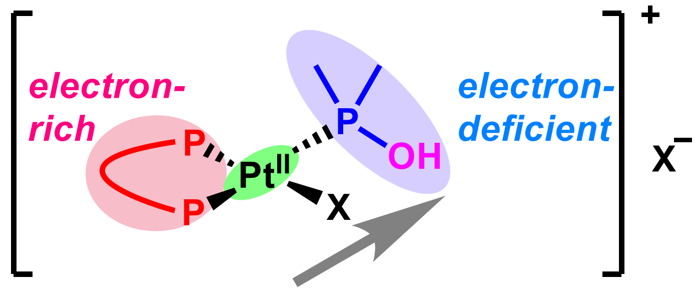
3. polymer synthesis

Concepts



Ghaffar-Parkins cat.

vs



"donor-acceptor"- type catalyst

Modification:

Introducing an electron-rich bidentate ligand instead of two bridging PMe_2OH ligands

Effect:

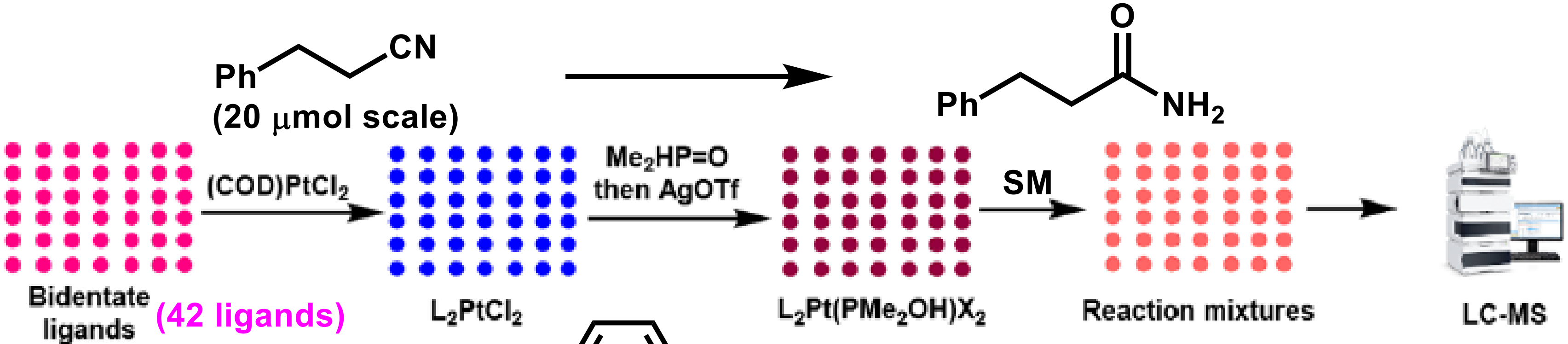
1. Enhancing nucleophilicity of OH group
2. more polarization→ softer cationic center→facilitation of CN activation

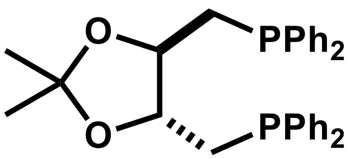
Expected advantages:

1. High TON and TOF
2. Reaction proceeds at ambient temperature
3. Cyanohydrin hydration

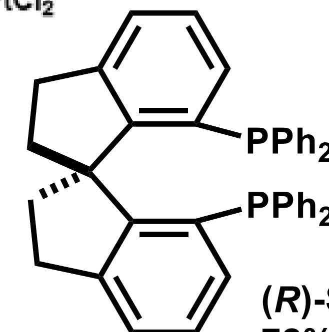
Xing, X.; Xu, C.; Chen, B.; Li, C.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2018**, *140*, 17782.

Screening of Bidentate Ligands

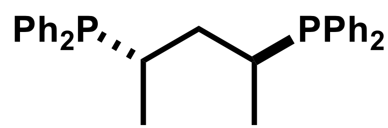




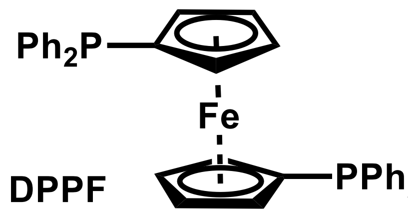
(*R*,*R*)-DIOP
66% conv.



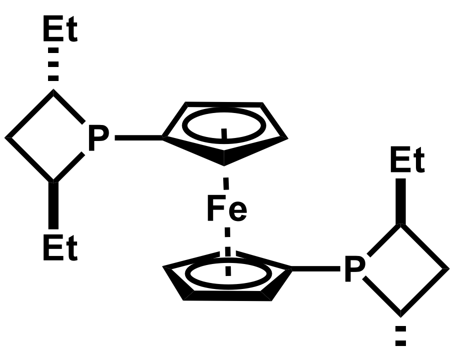
(*R*)-SDP
72% conv.



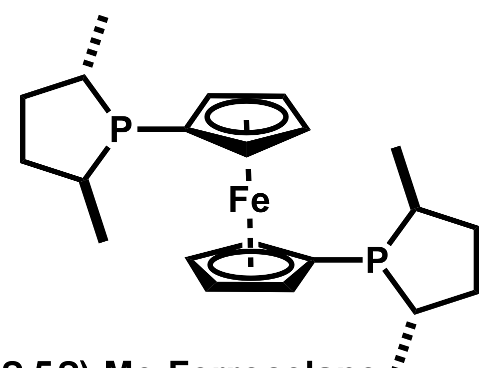
(*S*,*S*)-BDPP
66% conv.



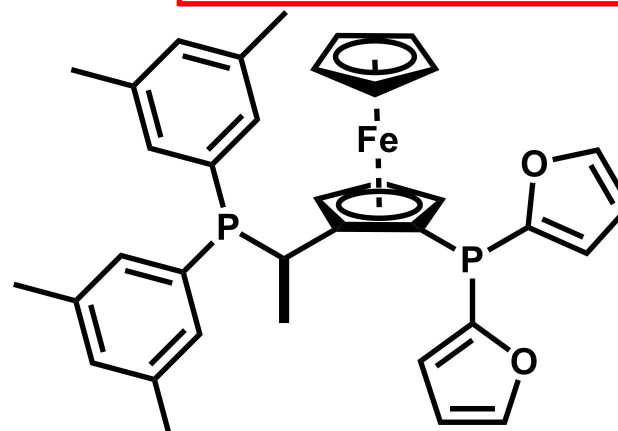
DPPF
69% conv.



(2*S*,4*S*)-Et-FerroTANE
64% conv.



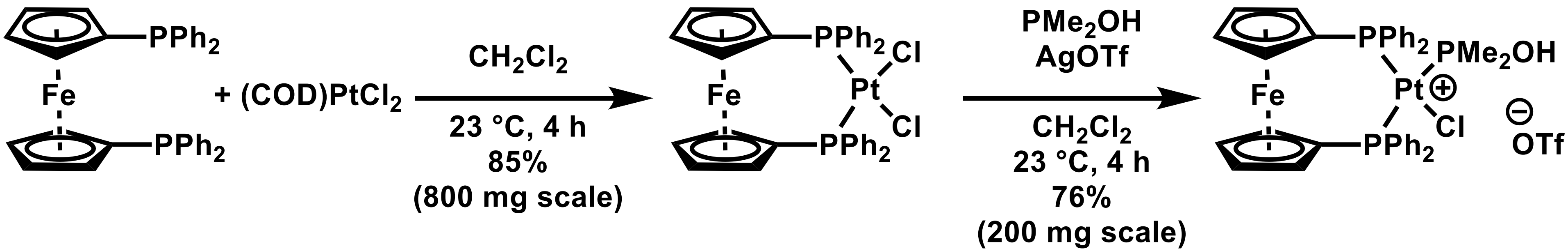
(2*S*,5*S*)-Me-Ferrocelane
64% conv.



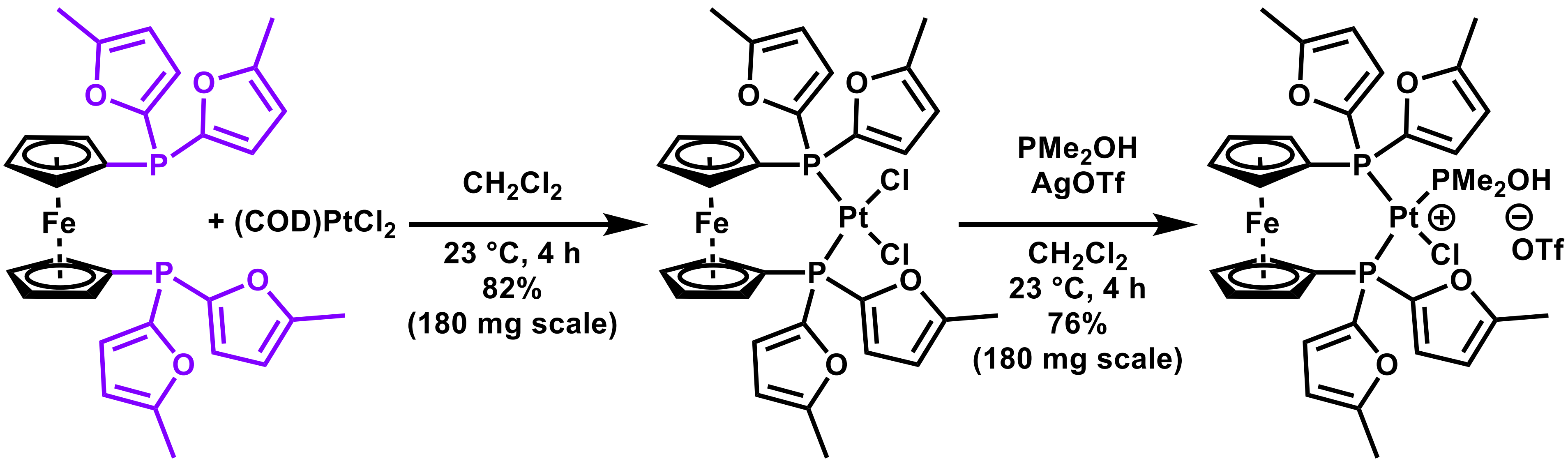
Josiphos SL-J015-1
65% conv.

Xing, X.; Xu, C.; Chen, B.; Li, C.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2018**, *140*, 17782.

Synthesis of Catalysts



- Synthesis of the catalyst with more electron-rich ligand



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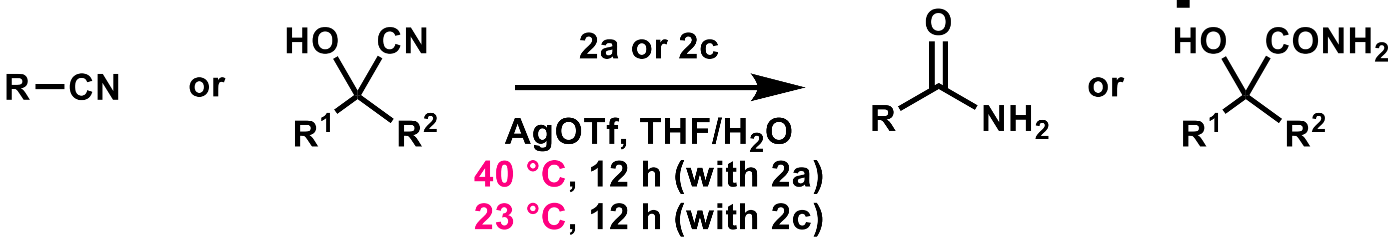
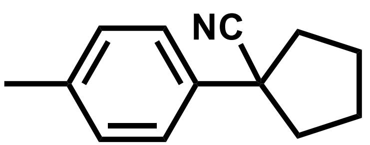
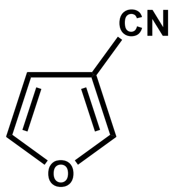
Substrate Scope

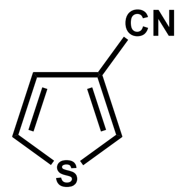




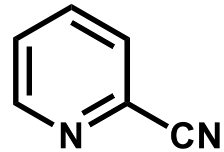
2a: 52%
TOF: 17
1a: 99%*, 97%**
TOF: 17*, 3.3**
***at 80 °C**
****at 45 °C**



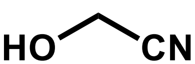
2a: 95%
TOF: 79
1a: 95%*, 96%**
TOF: 54*, 2.4**
***at 80 °C**
****at 25 °C**



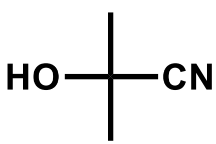
2a: 96%
TON: 960
2c: 95%
TON: 950



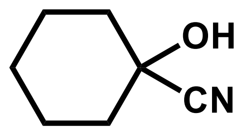
2a: 64%
TON: 254
2c: 45%
TON: 156



2a: 88%
TON: 880
2c: 98%
TON: 395
1a: 4%
TON: 66

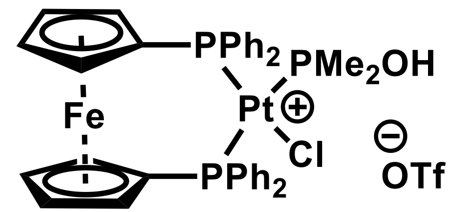


2a: 37%
TON: 112
2c: 54%
TON: 216
1a: 3%
TON: 3

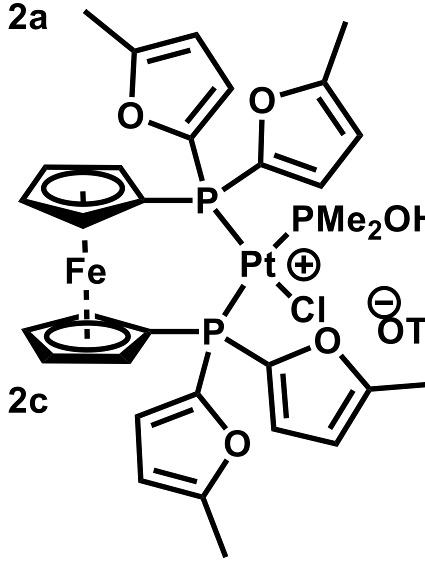


2a: 22%
TON: 43
2c: 37%
TON: 74
1a: 14%
TON: 3

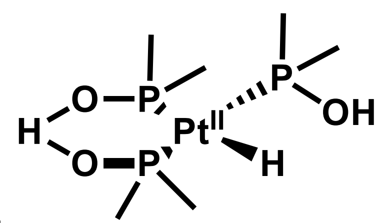
(TOF = TON/hour)



2a



2c



1a

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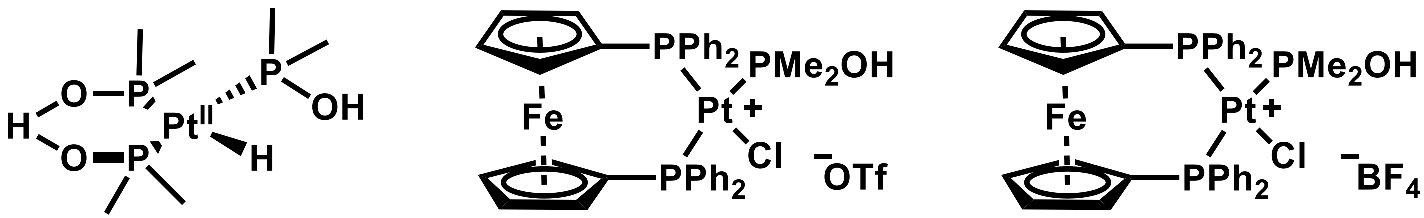
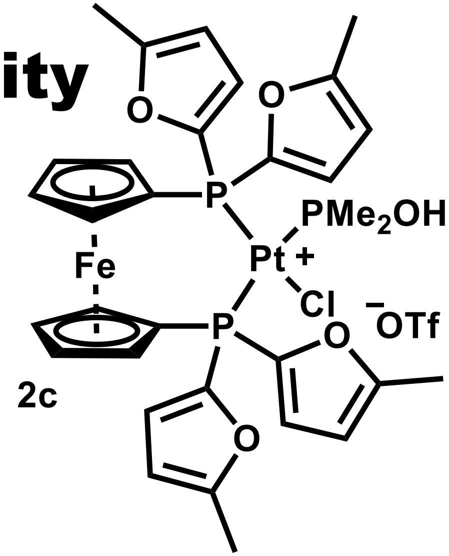
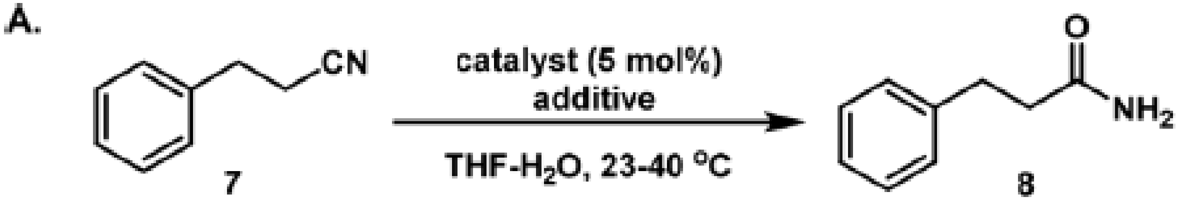
Jiang, X.-B.; Minnaard, A.J.; Feringa, B.L.; de Vries, J.G. *J. Org. Chem.* **2004**, *69*, 2327.

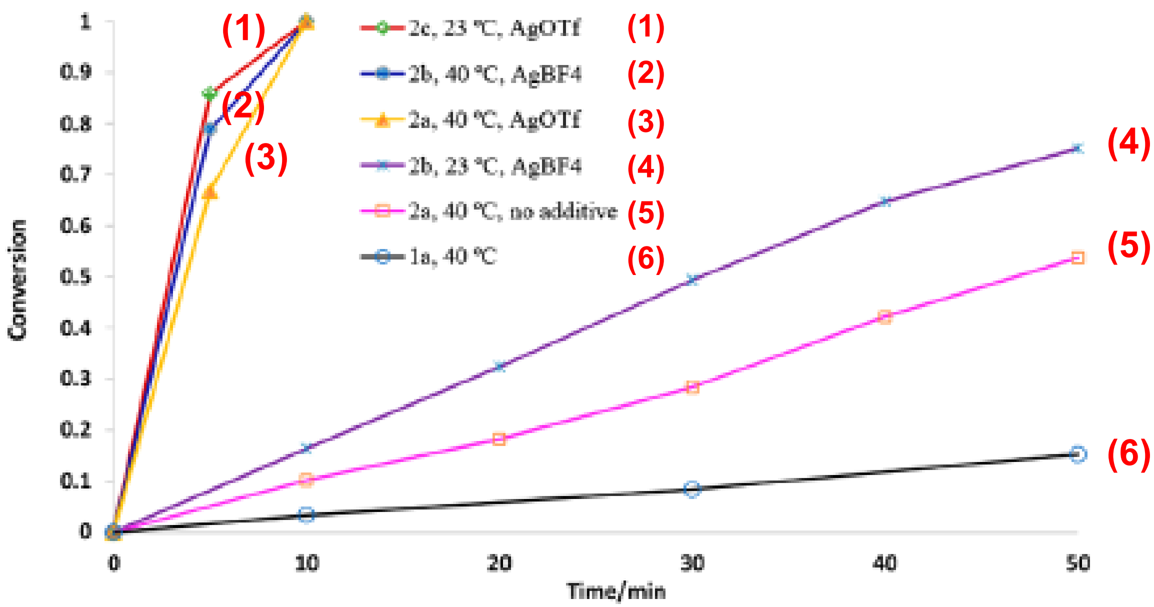
Comparison of Catalytic Activity





1a 2a 2b 2c





(1)~(5) vs (6):
TOF: 2a, 2b, 2c > 1a

(2) vs (4)
TOF: 40 °C > 23 °C

(1) vs (4)
TOF at 23 °C: 2c > 2b

(3) vs (5)
TOF: with AgOTf > no additive

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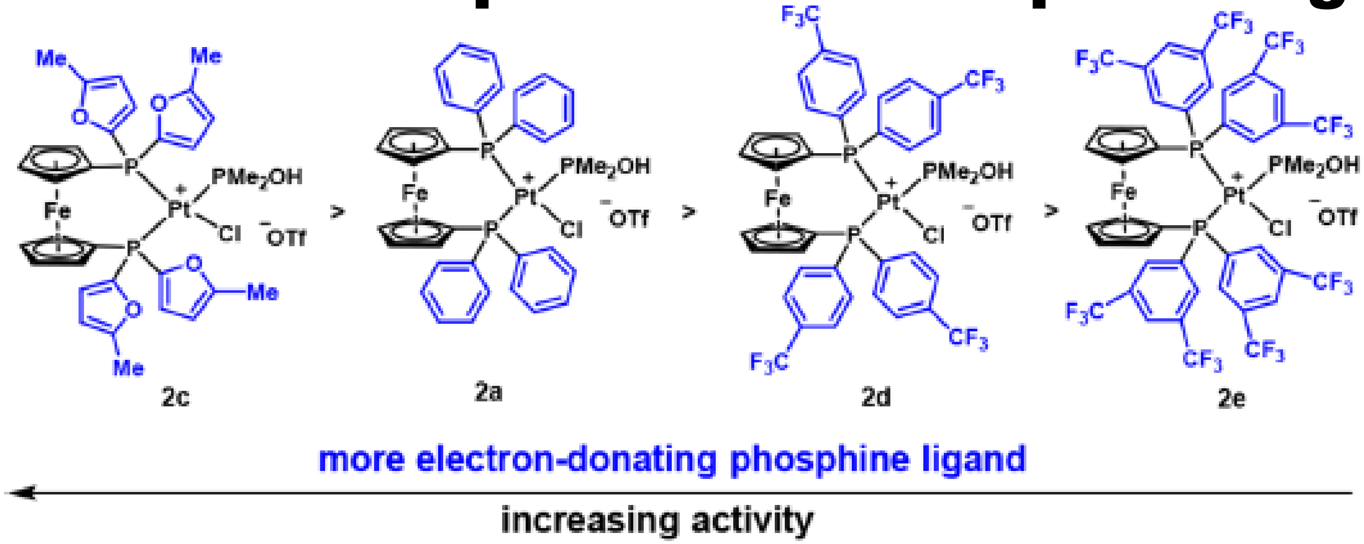
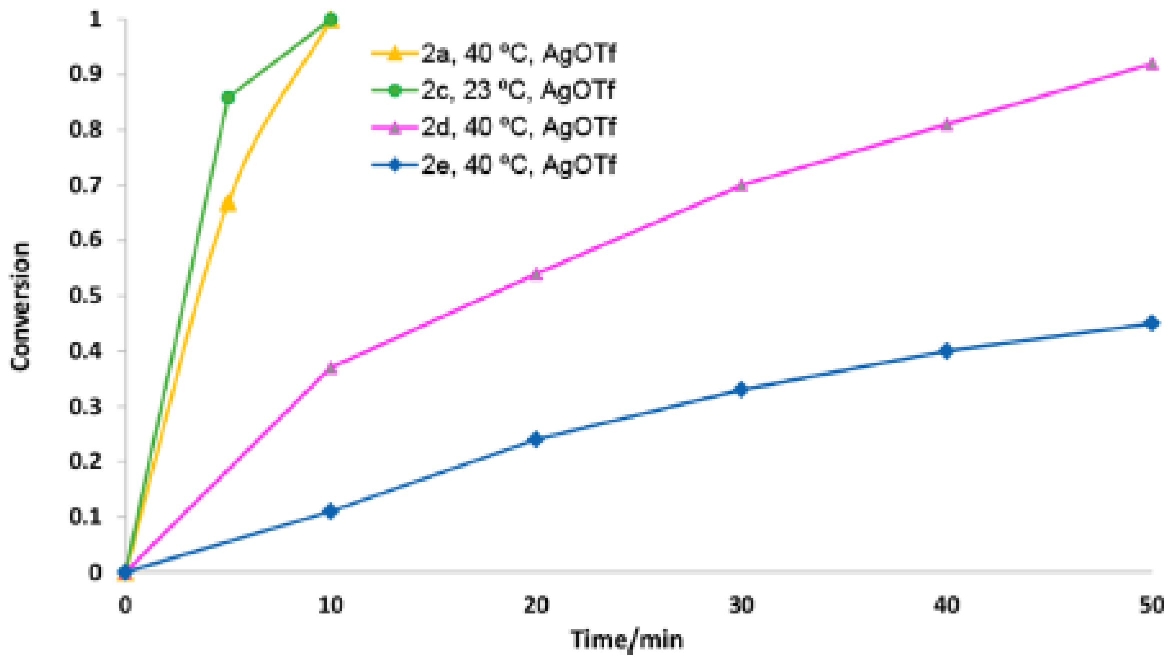
Relationship between Phosphine Ligands





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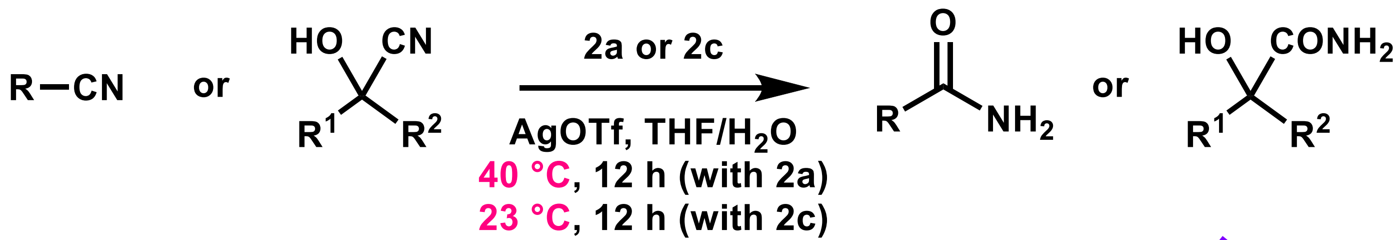
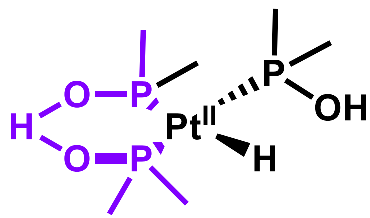
Summary

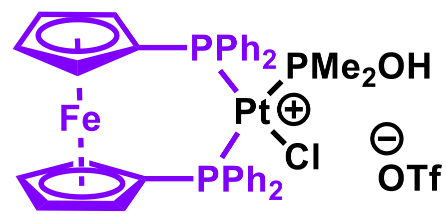


efficiency of the catalyst:



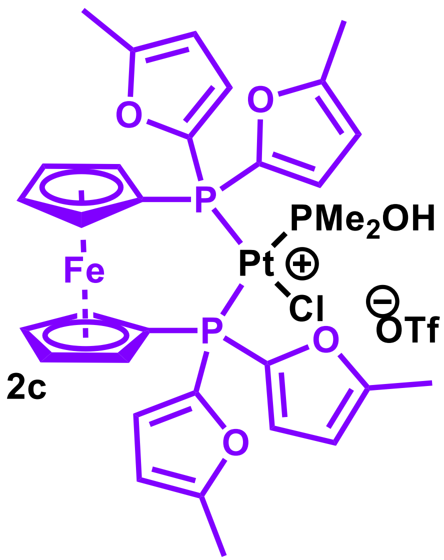
Ghaffar-Parkins cat.

<



2a

<



2c

more electron-rich ligand

- **Hydration of nitriles can proceed in lower temperature by changing ligands into more electron-rich bidentate ones.**

- **Substrate scope of cyanohydrins is expanded with 2c.**