Literature Report

Reporter: Zhen Wang

Supervisor: Prof. Yong Huang

2016/04/13

ACS Catalysis
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Cobalt-Catalyzed C–H Activation

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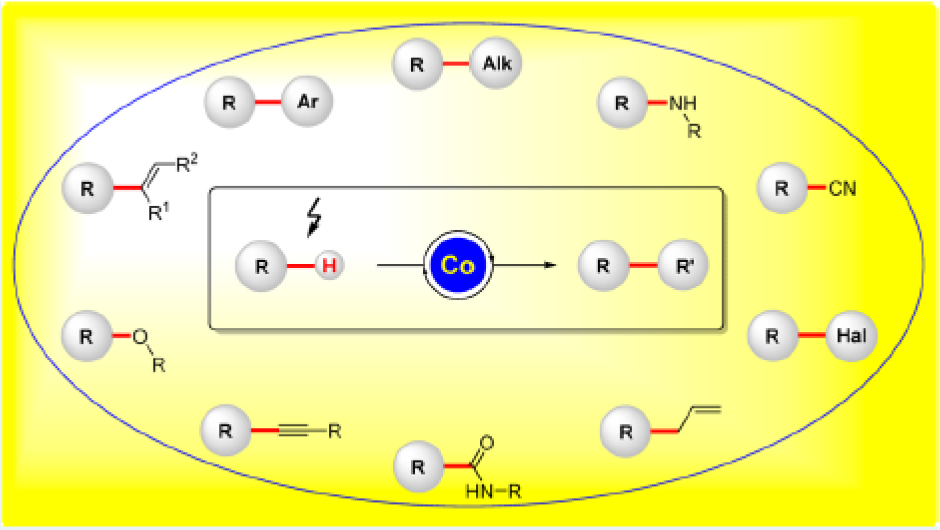


DOI: 10.1021/acscatal.5b02344
ACS Catal. 2016, 6, 498−525

Introduction

Lutz.Ackermann

Motomu Kanai

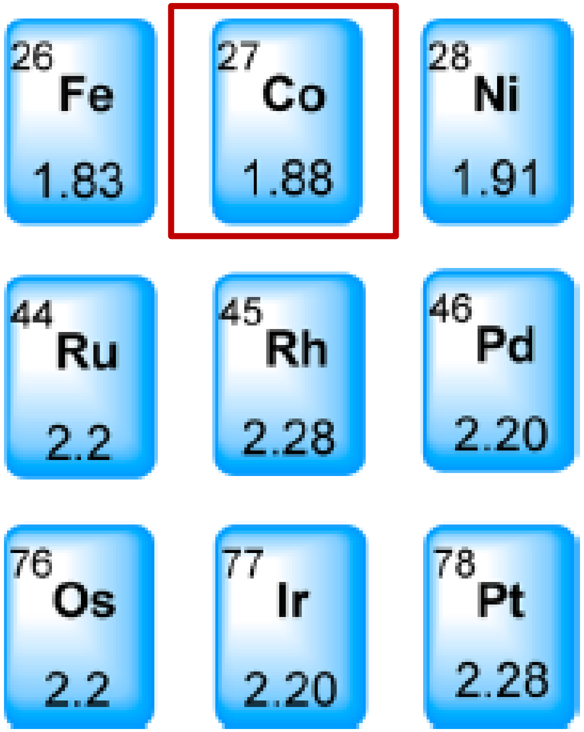


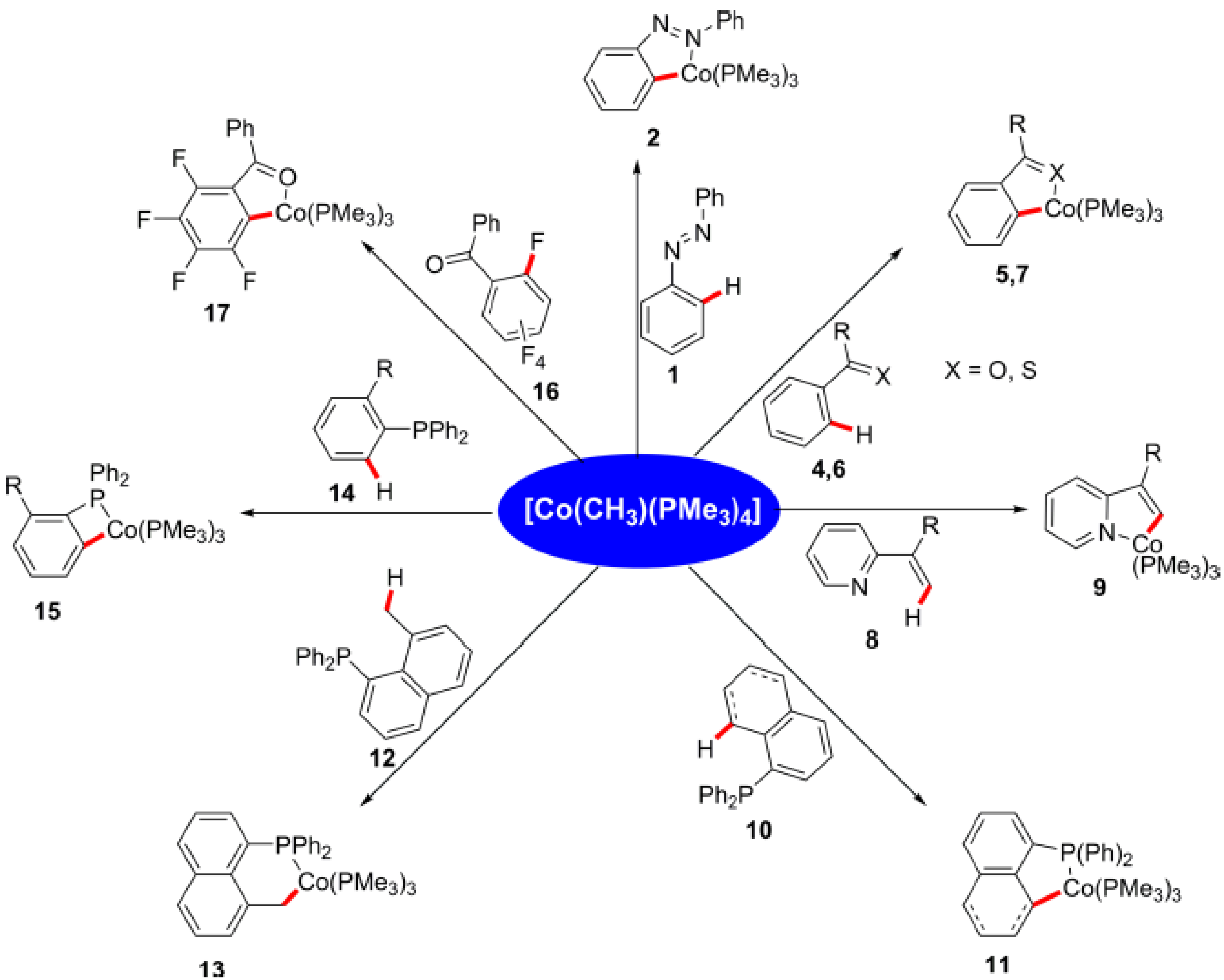
Figure 1. Electronegativities of Group 8, 9, and 10 elements according to the Pauling scale.

Naohiko Yoshikai

Frank Glorius

Stoichiometric C-H Activation

Scheme 1. Cyclocobaltated Compounds by Stochiometric C−H or C−F Cleavage Using $[Co(CH_3)(PMe_3)_4]$ (3)



Klein, H. F.; Helwig, M.; Koch, U.; Florke, U.; Haupt, H. J. Z.Naturforsch., *B: J. Chem. Sci*. **1993**, *48*, 778−784.

Catalytic C-H Activation

I: Catalysis with Low-Valent Cobalt Complexes

Addition Reactions
C-H Arylations
C-H Alkenylations
C-H Alkylations

II: Catalysis with Cp*Co(III) Complexes

Hydroarylations
C-H Amidations
C-H Cyanations
C-H Allylations

III: Oxidative C-H Functionalizations and Annulations

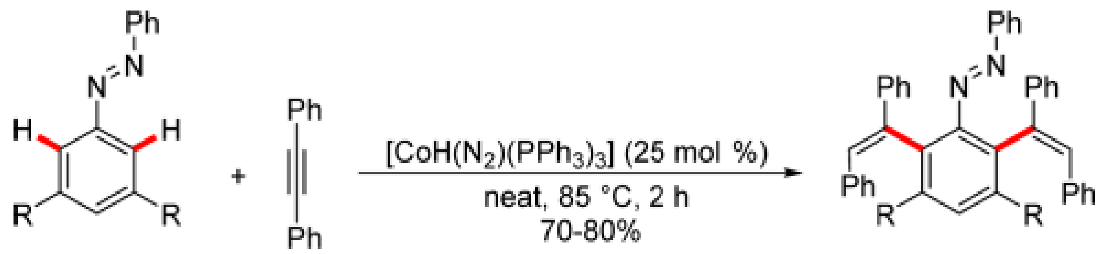
IV: Organometallic C-H Activation by Cobalt Carbenoids

Catalysis with Low-Valent Cobalt Complexes

Addition Reactions: *Hydroarylation Reactions*

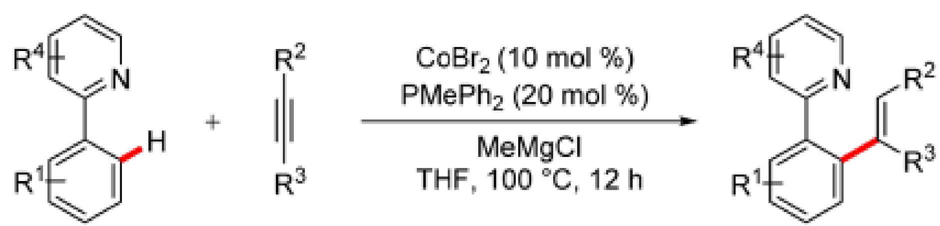
Co I

Co II
Phosphine ligand
Stoichiometric reductant
(RMgCl)



1 20a 21

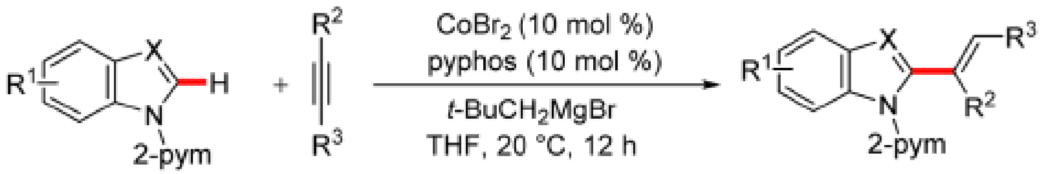
Halbritter, G.; Knoch, F.; Wolski, A.; Kisch, H. *Angew. Chem., Int. Ed. Engl*. **1994,** *33*, 1603−1605.



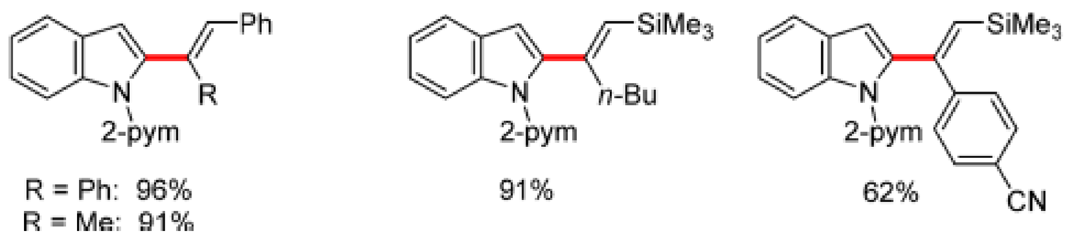
22 20 23

Gao, K.; Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc*. **2010**, *132*, 12249−12251.

Catalysis with Low-Valent Cobalt Complexes



24, 25 **20** **26, 27**

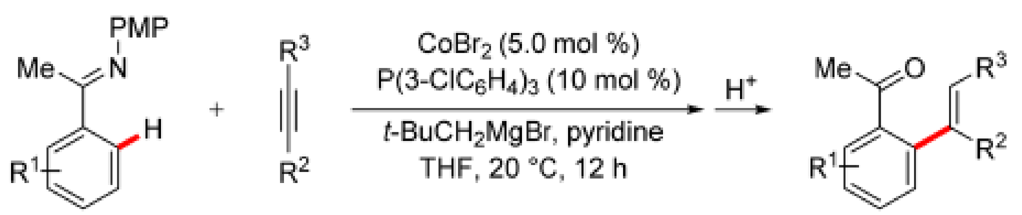


R = Ph: 96%
R = Me: 91%

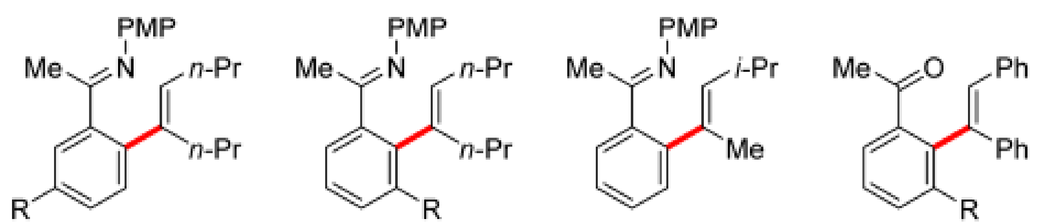
91%

62%

Ding, Z.; Yoshikai, N. *Angew. Chem., Int. Ed*. **2012**, *51*, 4698−4701.



28 **20** **30**



R = Me: 94%
R = CF_3: 85%

R = OMe: 87%
R = F: 92%

without hydroylsis

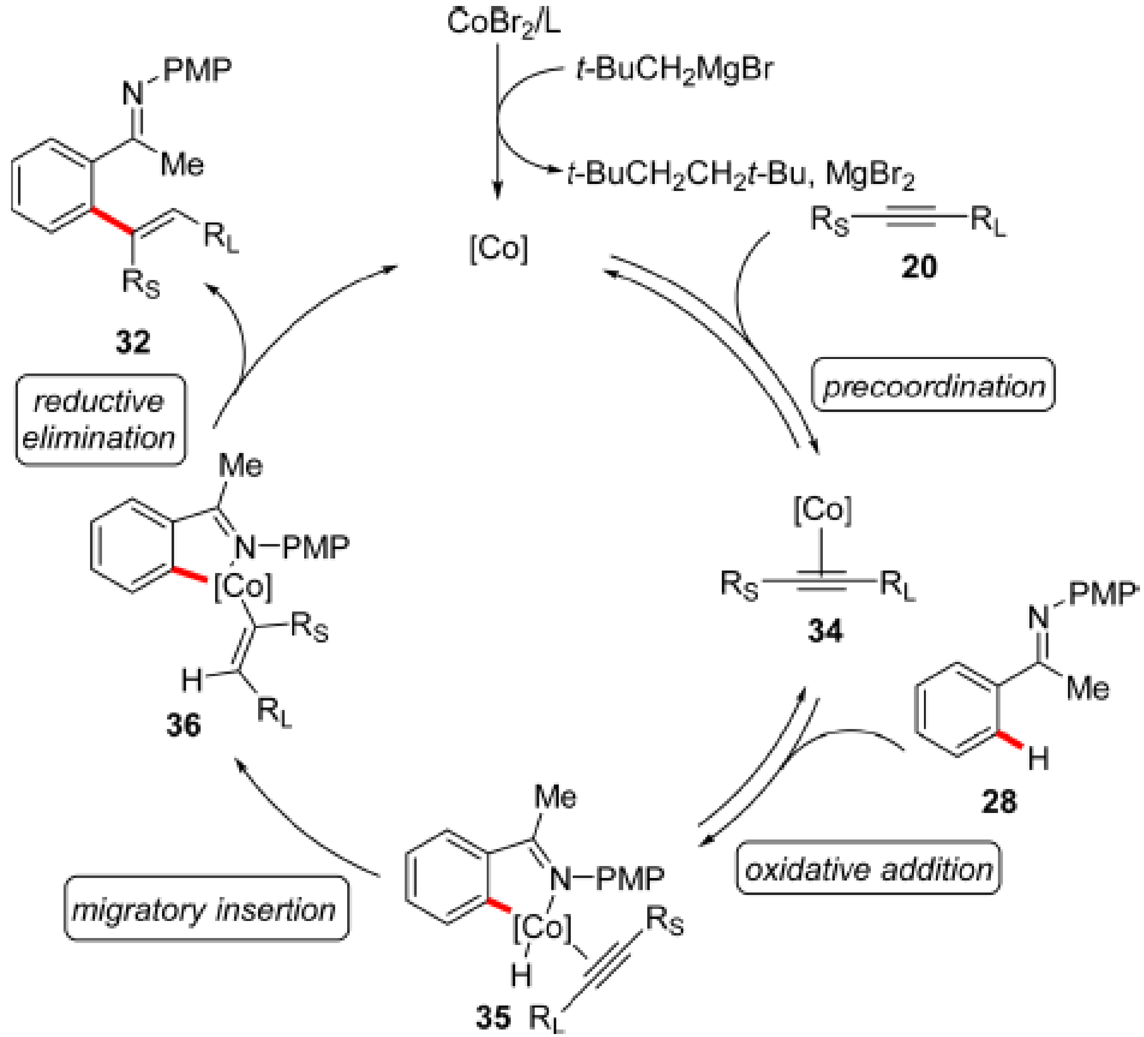
82%

R = F (**30aa**): 64%
R = Cl (**30ba**): 70%
R = Br (**30ca**): 20%
R = CN (**30da**): 76%

Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc*. **2011**, *133*, 17283−17295.

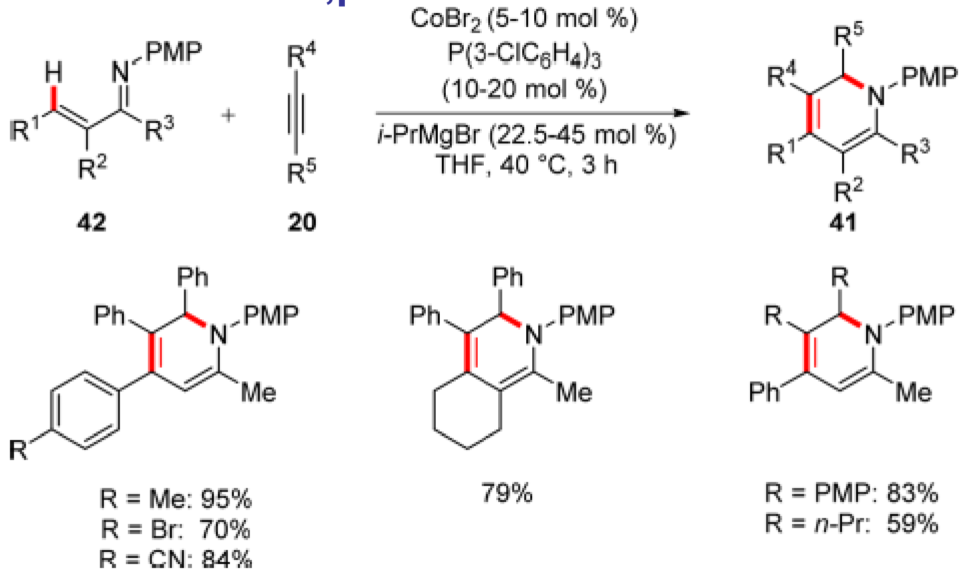
Catalysis with Low-Valent Cobalt Complexes

Scheme 7. Plausible Catalytic Cycle for the Cobalt-Catalyzed Hydroarylation of Internal Alkynes 20



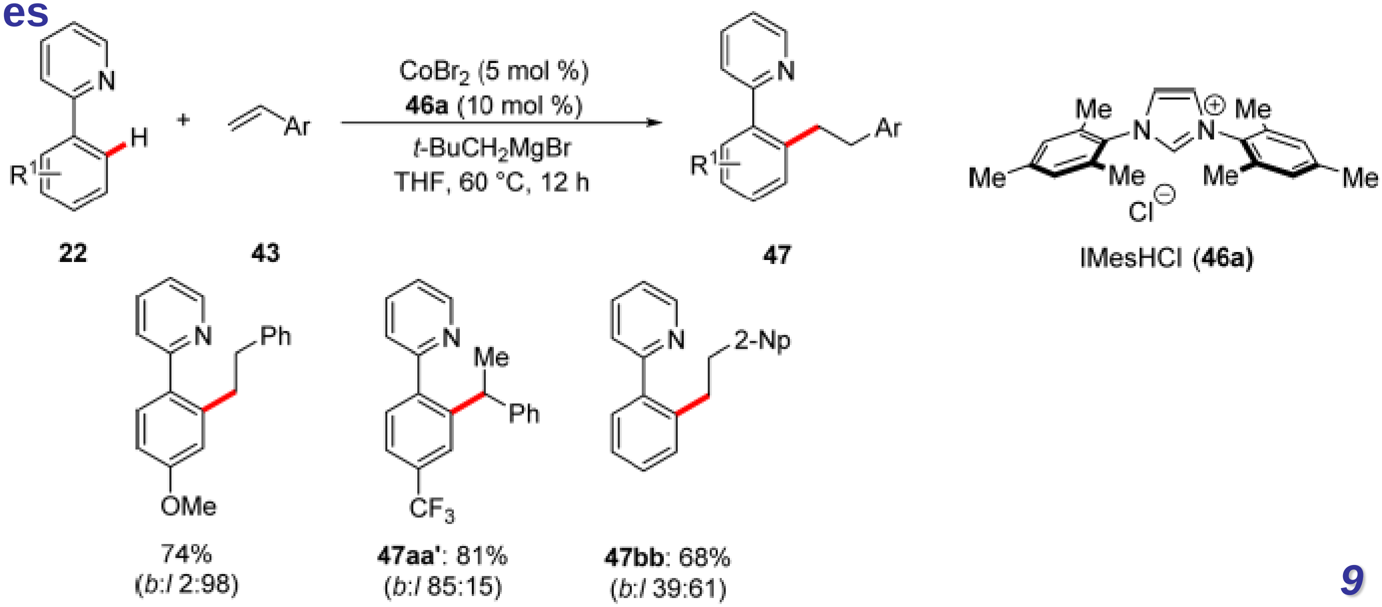
Catalysis with Low-Valent Cobalt Complexes

Cobalt-Catalyzed Annulations with α,β-Unsaturated Imines 42



Yamakawa, T.; Yoshikai, N. *Org. Lett*. **2013**, *15*, 196−199.

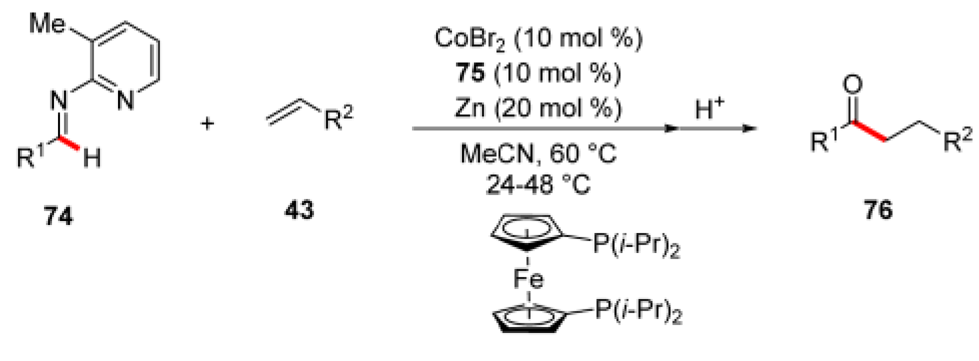
Hydroarylation of Alkenes

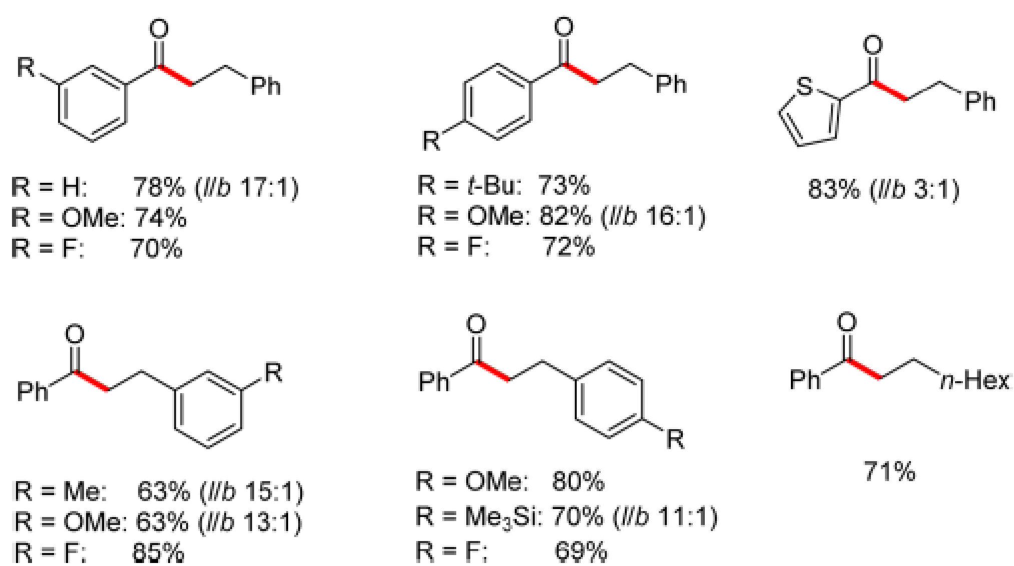


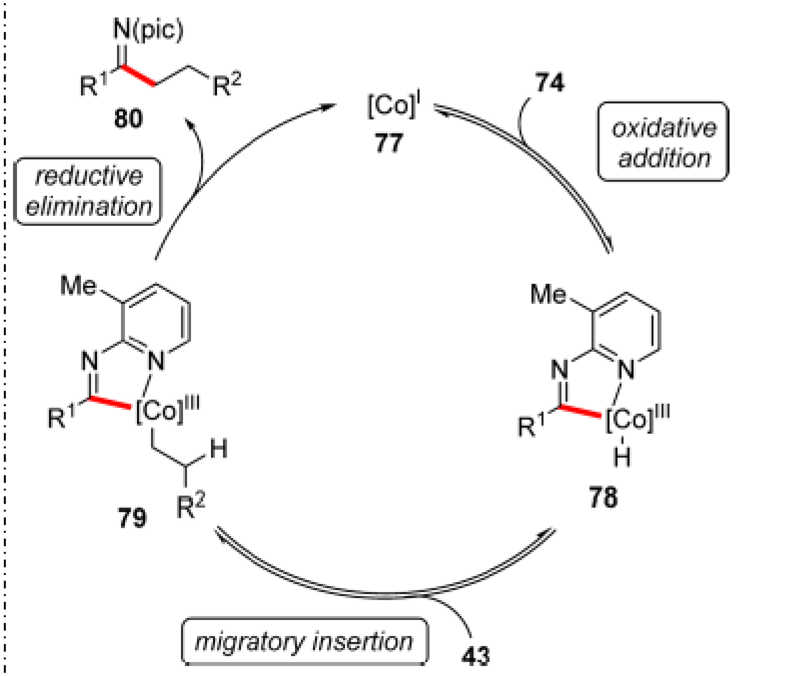
Gao, K.; Yoshikai, N. *J. Am. Chem. Soc*. **2011**, *133*, 400−402.

Catalysis with Low-Valent Cobalt Complexes

Addition Reactions: *Hydroacylation Reactions*





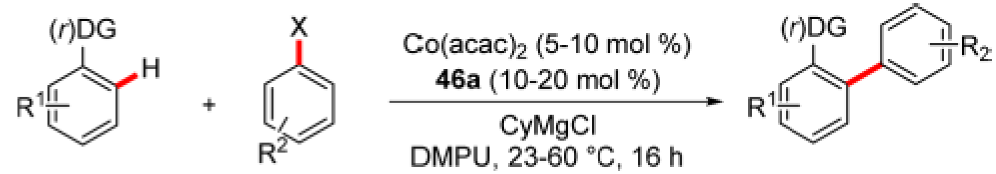


Yang, J.; Seto, Y. W.; Yoshikai, N. *ACS Catal*. **2015** , *5*, 3054−3057.

Catalysis with Low-Valent Cobalt Complexes

C-H Arylations:

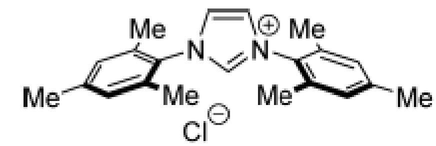
C−H Arylation with Aryl Carbamates 85, Sulfamates 86, and Chlorides 87



22 or **24**

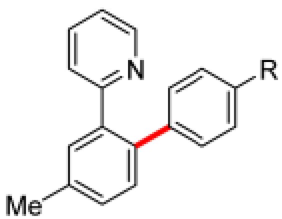
X = OC(O)NMe$_2$ **85**
X = OSO_2NMe_2 **86**
X = Cl **87**

88 or **89**

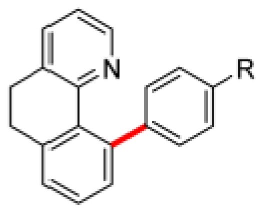


IMesHCl (**46a**)

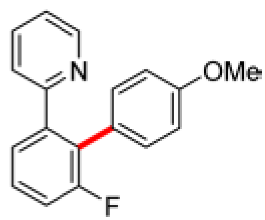
(a) aryl carbamates



R = H (**88da**): 71%
R = OMe (**88db**): 90%
R = Me (**88dc**): 81%

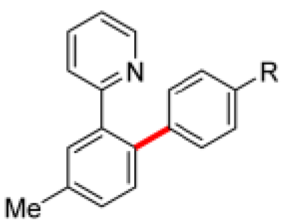


R = OMe: 96%
R = Me: 86%
R = F: 82%

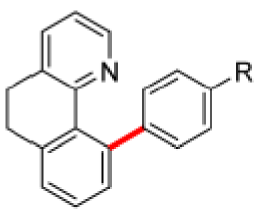


88eb: 90%

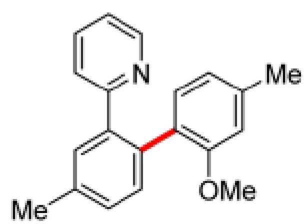
(b) aryl sulfamates



R = H (**88da**): 70%
R = Me (**88dc**): 80%

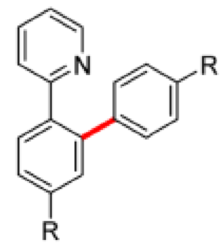


R = OMe: 95%
R = Me: 88%
R = F: 84%

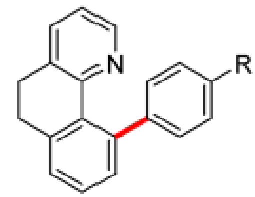


88dd: 83%

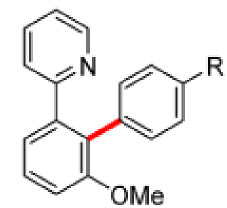
(c) aryl chlorides



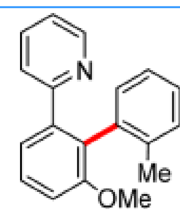
R = CF_3: 73%
R = OMe: 66%



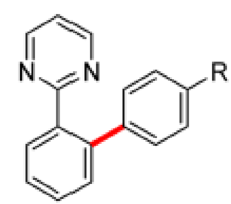
R = OMe: 94%
R = Me: 95%
R = F: 88%



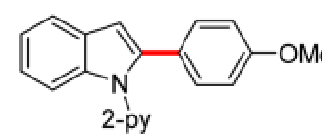
R = H (**88fa**): 79%
R = Me (**88fc**): 88%
R = F (**88fe**): 77%



88ff: 76%



R = OMe: 85%
R = Me: 76%
R = F: 66%

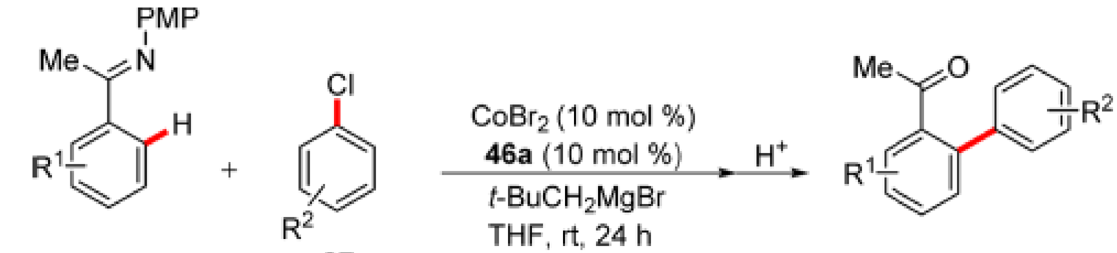


75%

Song, W.; Ackermann, L. *Angew. Chem., Int. Ed*. **2012**, *51*, 8251−8254.

Catalysis with Low-Valent Cobalt Complexes

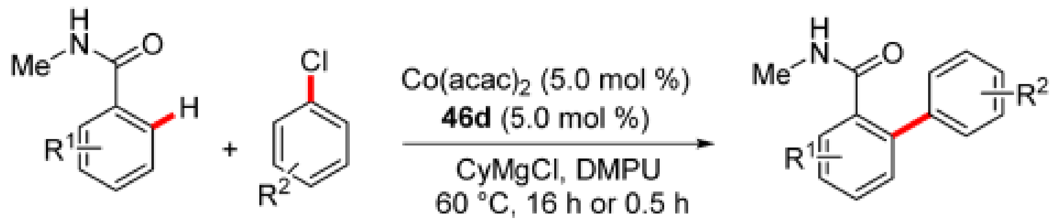
ketimines



28 87 90

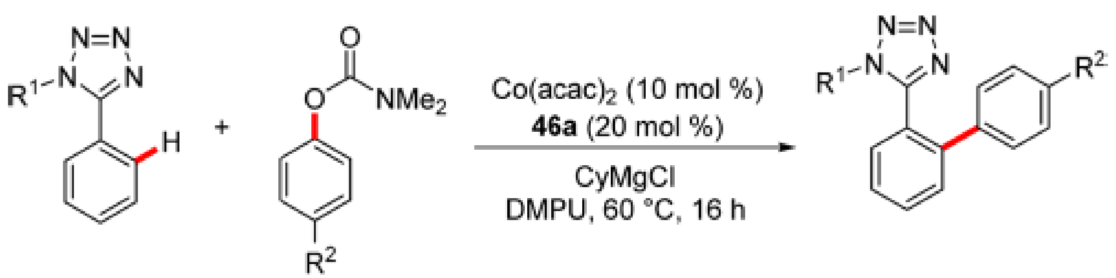
Gao, K.; Lee, P.-S.; Long, C.; Yoshikai, N. *Org. Lett*. **2012**, *14*, 4234−4237.

amides



44 87 92

tetrazoles

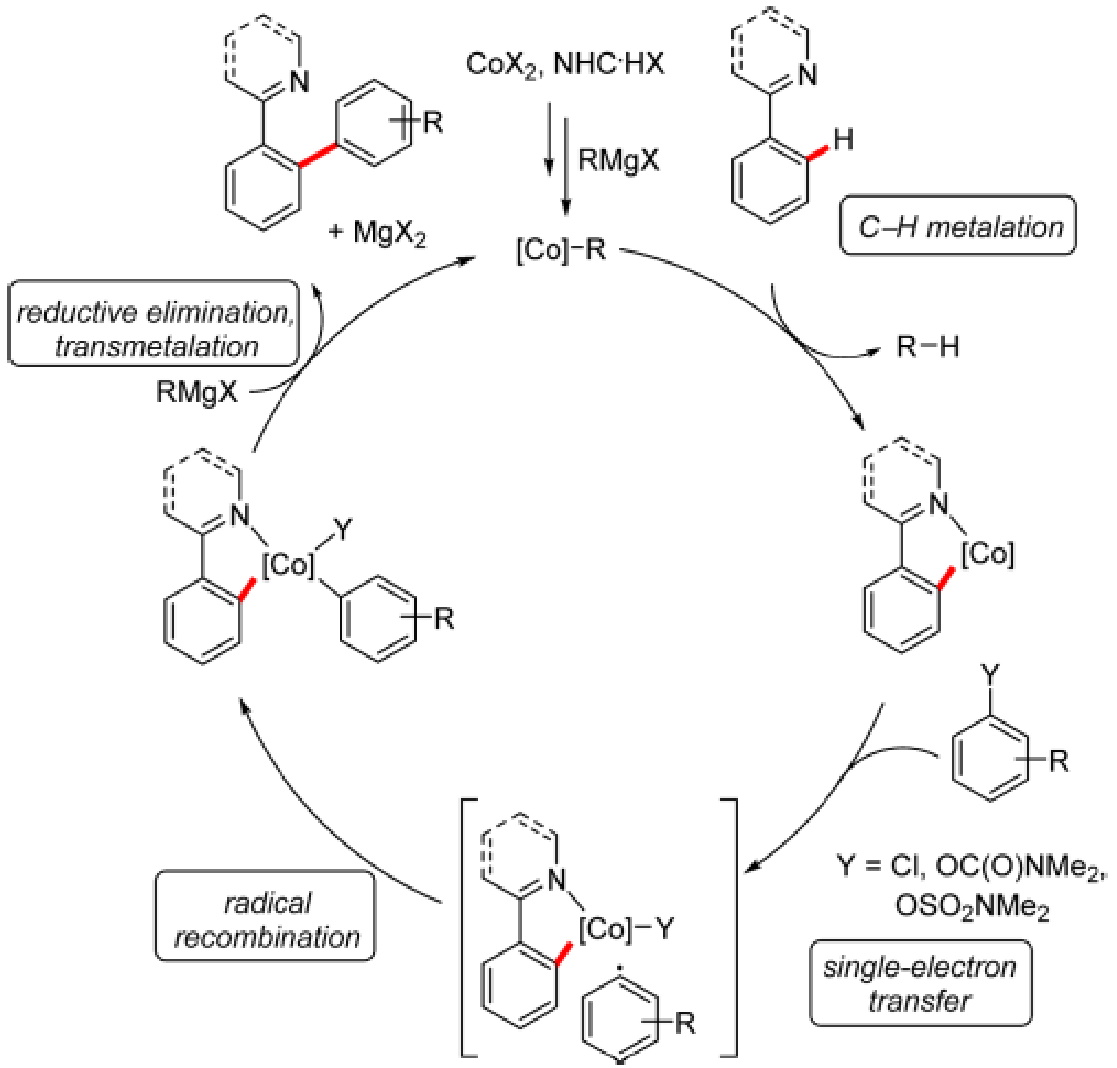


91 85 93

Li, J.; Ackermann, L. *Chem. - Eur. J.* **2015**, *21*, 5718−5722.

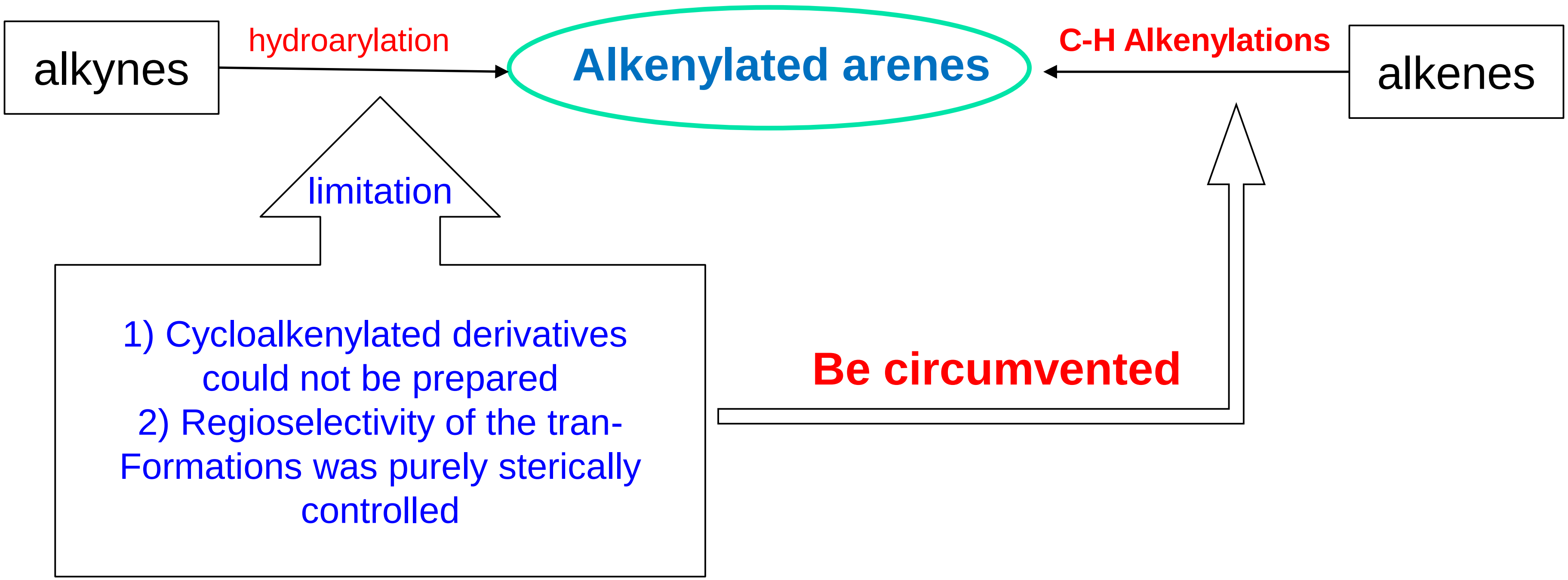
Catalysis with Low-Valent Cobalt Complexes

Scheme 29. Plausible Catalytic Cycle for the Cobalt-Catalyzed C−H Arylation



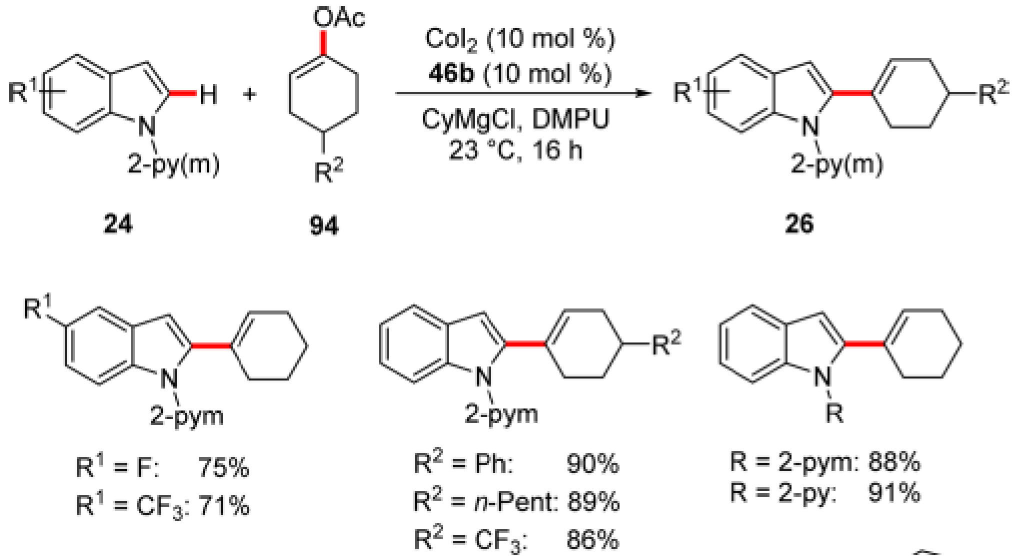
Catalysis with Low-Valent Cobalt Complexes

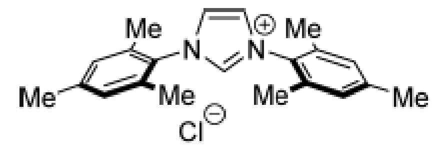
C-H Alkenylations



Catalysis with Low-Valent Cobalt Complexes

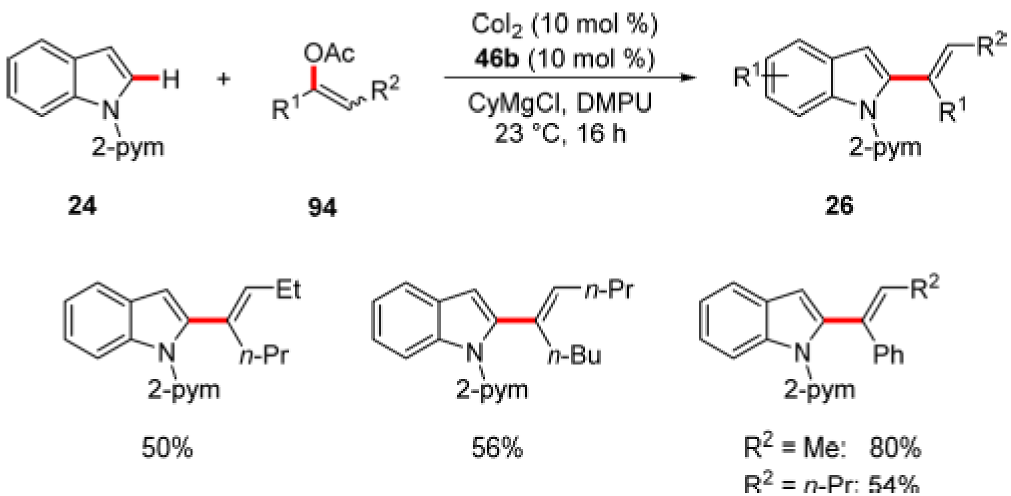
Cyclic Enol Acetates





IMesHCl (**46a**)

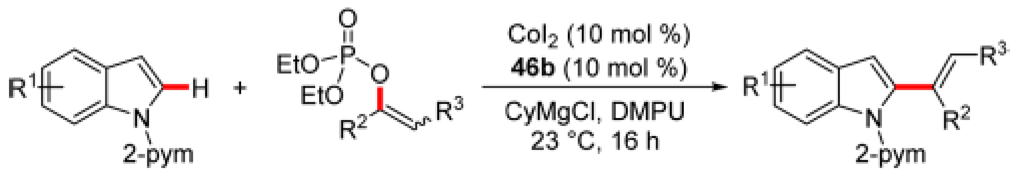
Acyclic Enol Acetates



Moselage, M.; Sauermann, N.; Richter, S. C.; Ackermann, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 6352−6355.

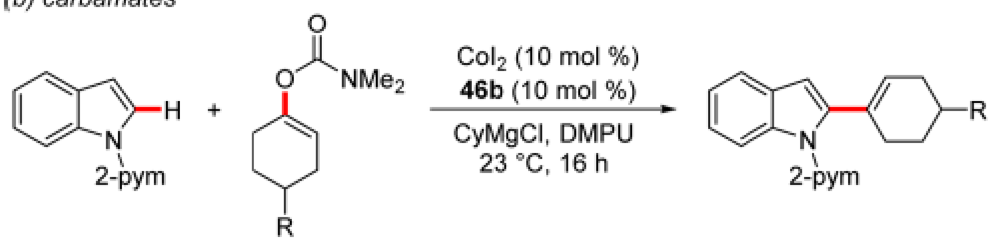
Catalysis with Low-Valent Cobalt Complexes

(a) phosphates



24 **96** **26**

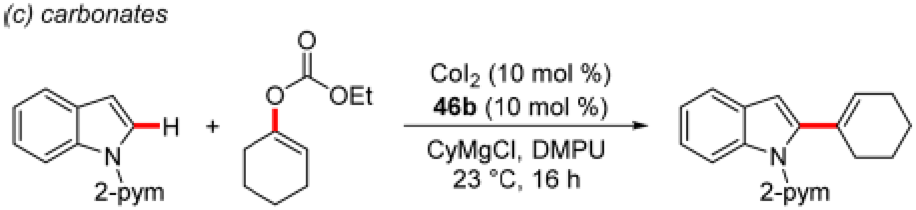
(b) carbamates



24a **97** **26**

R = H: 87%
R = *n*-Pent: 82%
R = O*n*-Pent: 79%

(c) carbonates

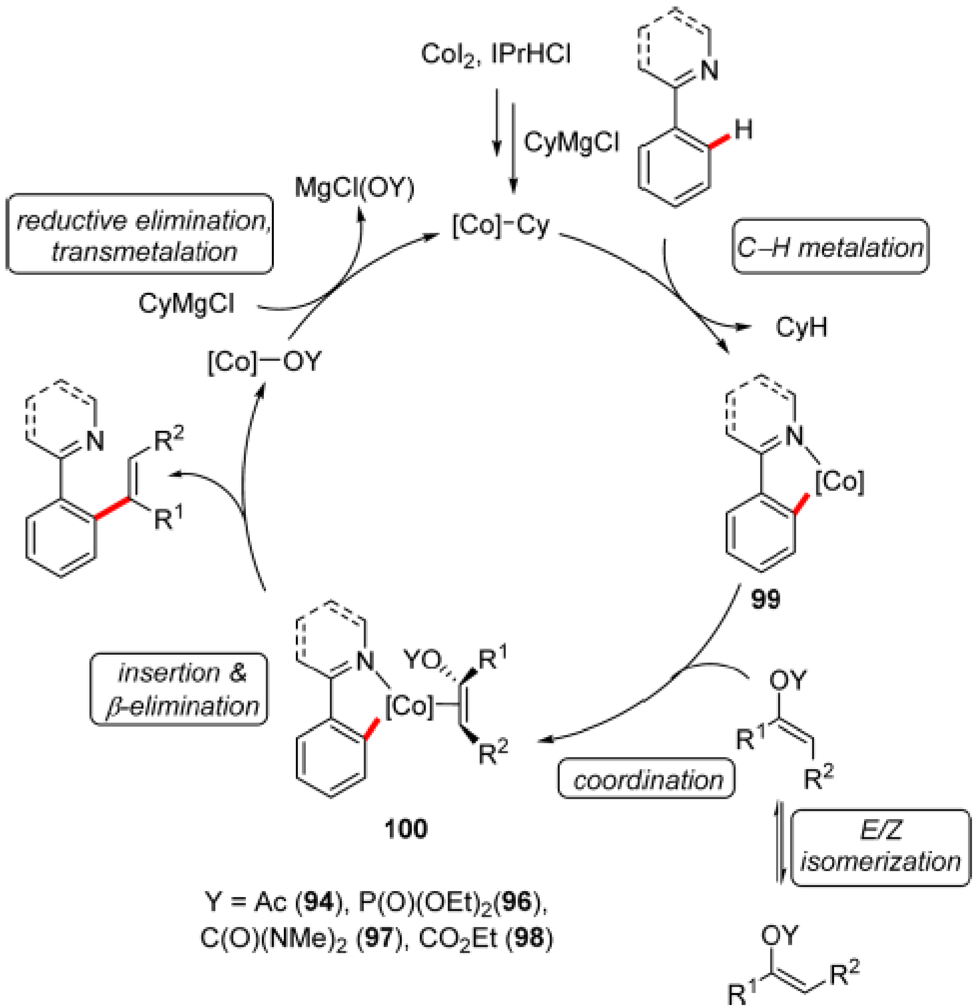


24a **98a**

56%

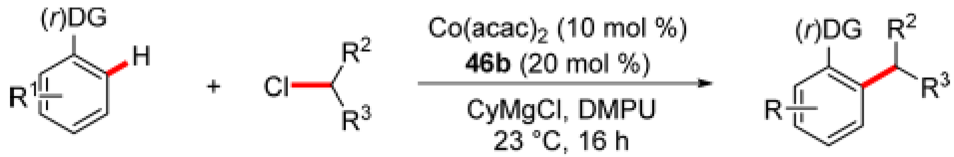
Catalysis with Low-Valent Cobalt Complexes

Scheme 33. Proposed Catalytic Cycle for the Cobalt-Catalyzed C–H Alkenylation with Enol Esters

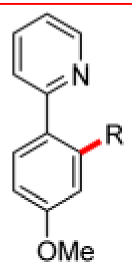


Y = Ac (**94**), $P(O)(OEt)_2$(**96**), $C(O)(NMe)_2$ (**97**), CO_2Et (**98**)

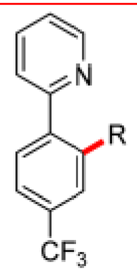
C-H Alkylations



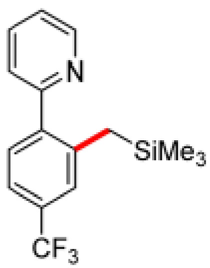
22, **24** + **101** → **47**, **102**



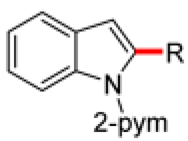
R = *n*-Bu: 79%
R = *n*-Hex: 80%
R = *n*-Oct: 82%



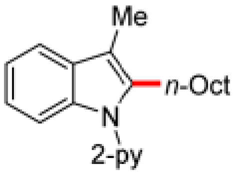
R = *n*-Hex: 91%
R = *n*-Oct: 81%



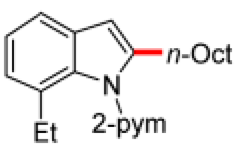
65%



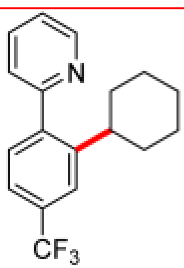
R = *n*-Hex: 82%
R = *n*-Oct: 71%



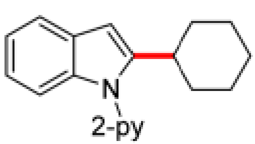
102be: 67%



102ce: 81%

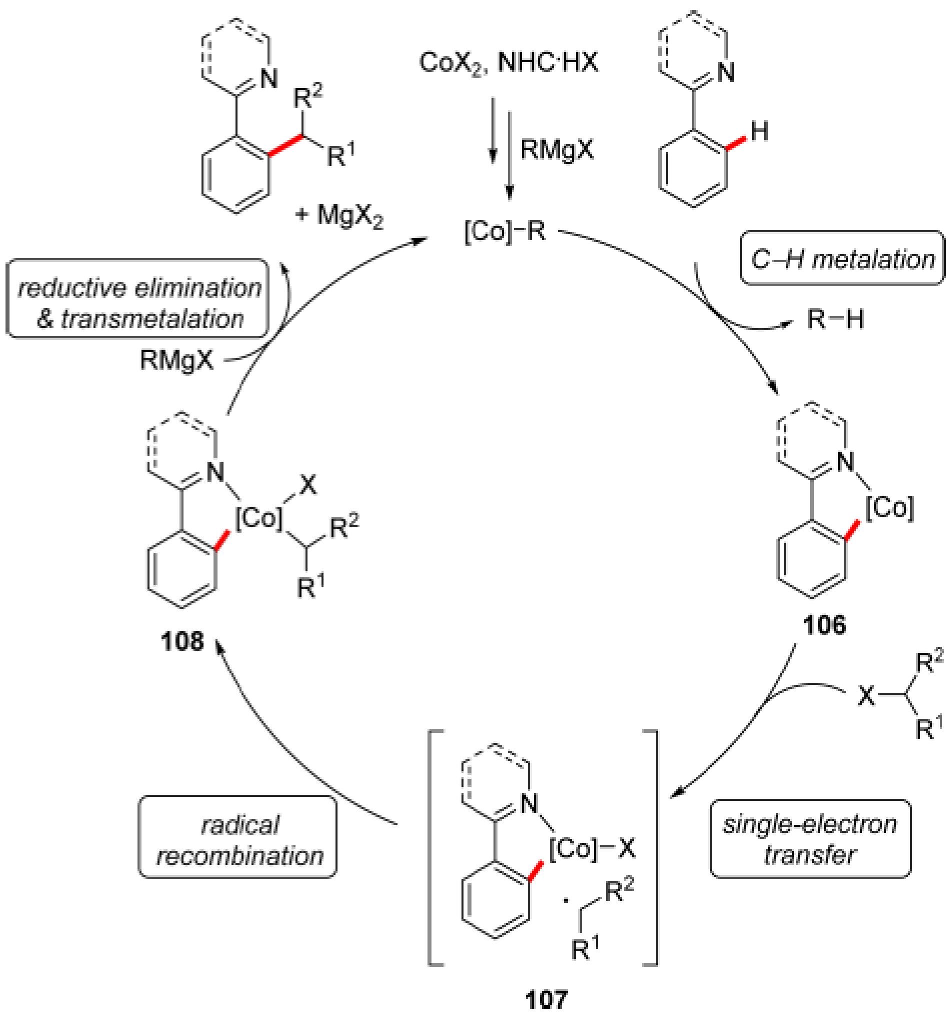


47af: 64%

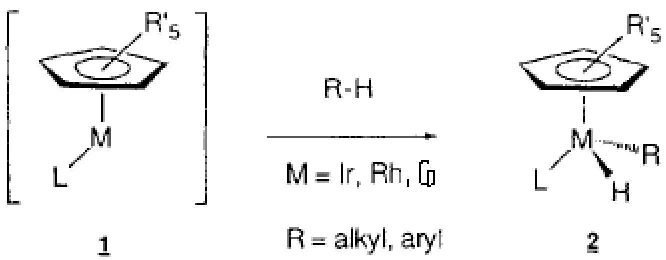


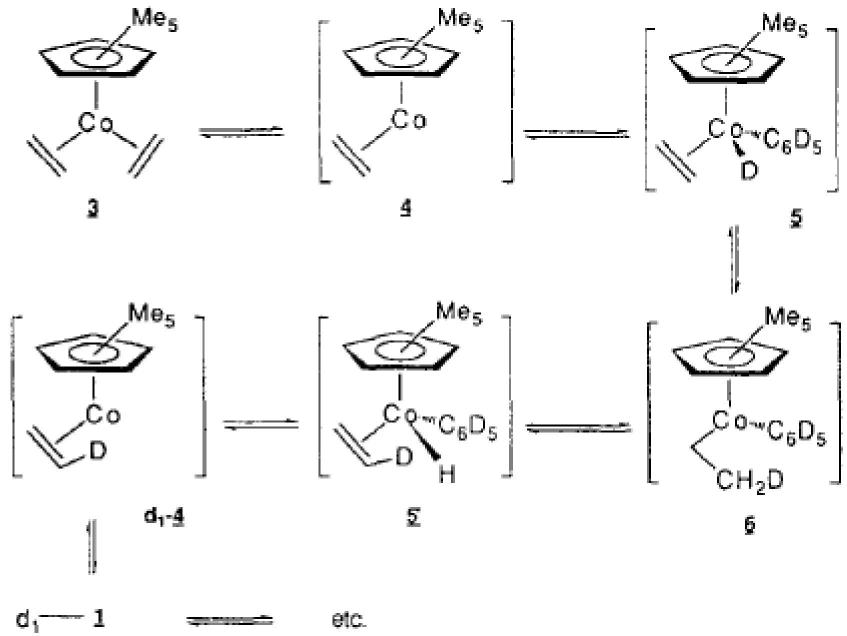
102df: 52%

Scheme 38. Proposed Catalytic Cycle for the Cobalt-Catalyzed C–H Alkylation with Organic Electrophiles



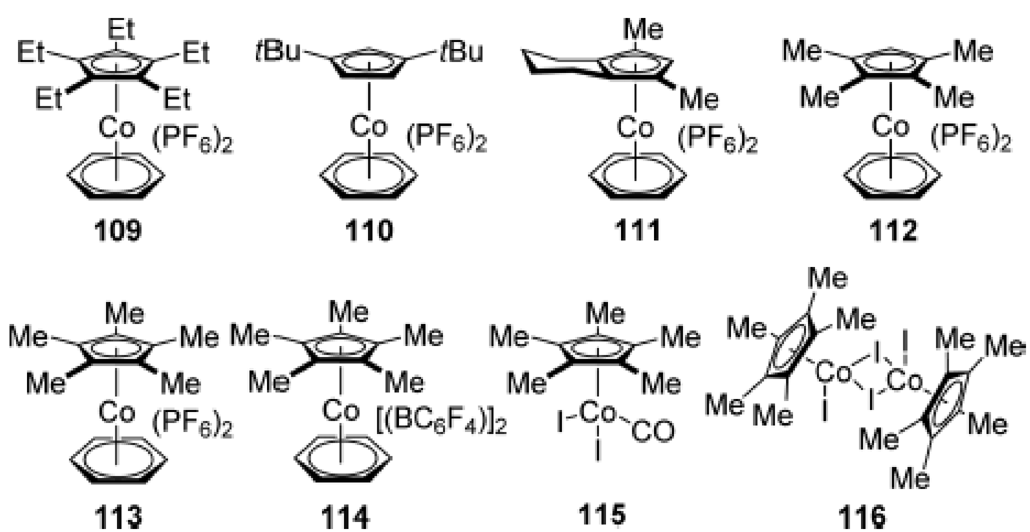
Catalysis with Cp*Co(III) Complexes





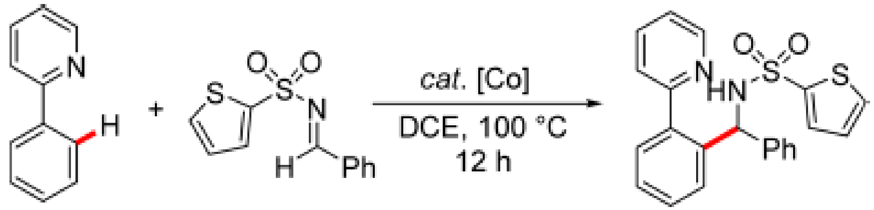
Brookhart, M. *J. Am. Chem. Soc.* 1997, *119*, 3165-3166.
Brookhart, M.; Grant, B. E. *J. Organomet. Chem.* 1997, *528*, 199-203.

Scheme 39. High-Valent Cobalt(III) Complexes



Hydroarylations

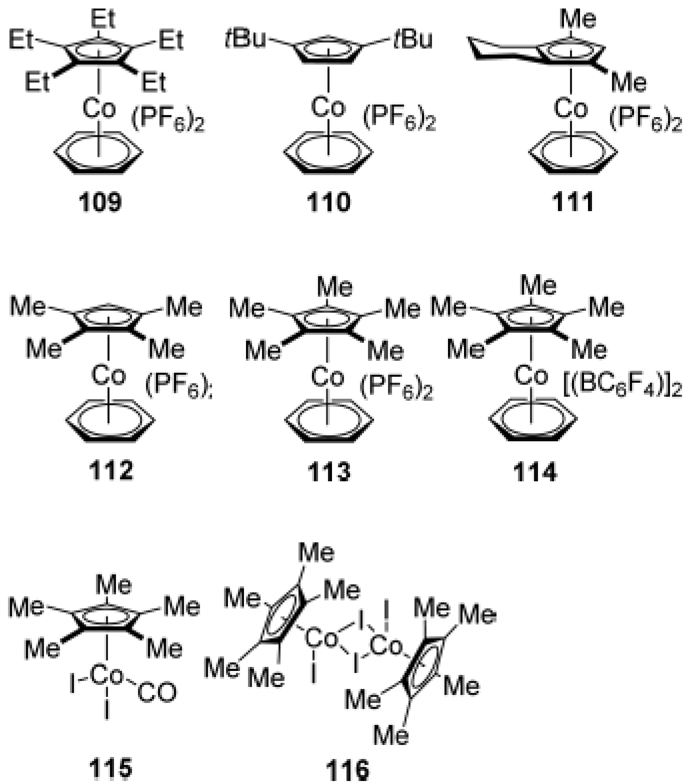
Table 1. Catalytic Activity of Cobalt Complexes



22b + 117a → 118ba

entry	[Co] (mol %)	*t* [h]	yield [%][a]
1	$CoCl_2$ (10)	12	0
2	$CoCl_2$ (10) + $AgPF_6$ (20)	12	0
3	**109** (10)	20	39
4	**110** (10)	20	11
5	**111** (10)	20	traces
6	**112** (10)	20	22
7	**113** (10)	20	80[b]
8	**116**[c] (10) + $AgPF_6$ (20)	20	48

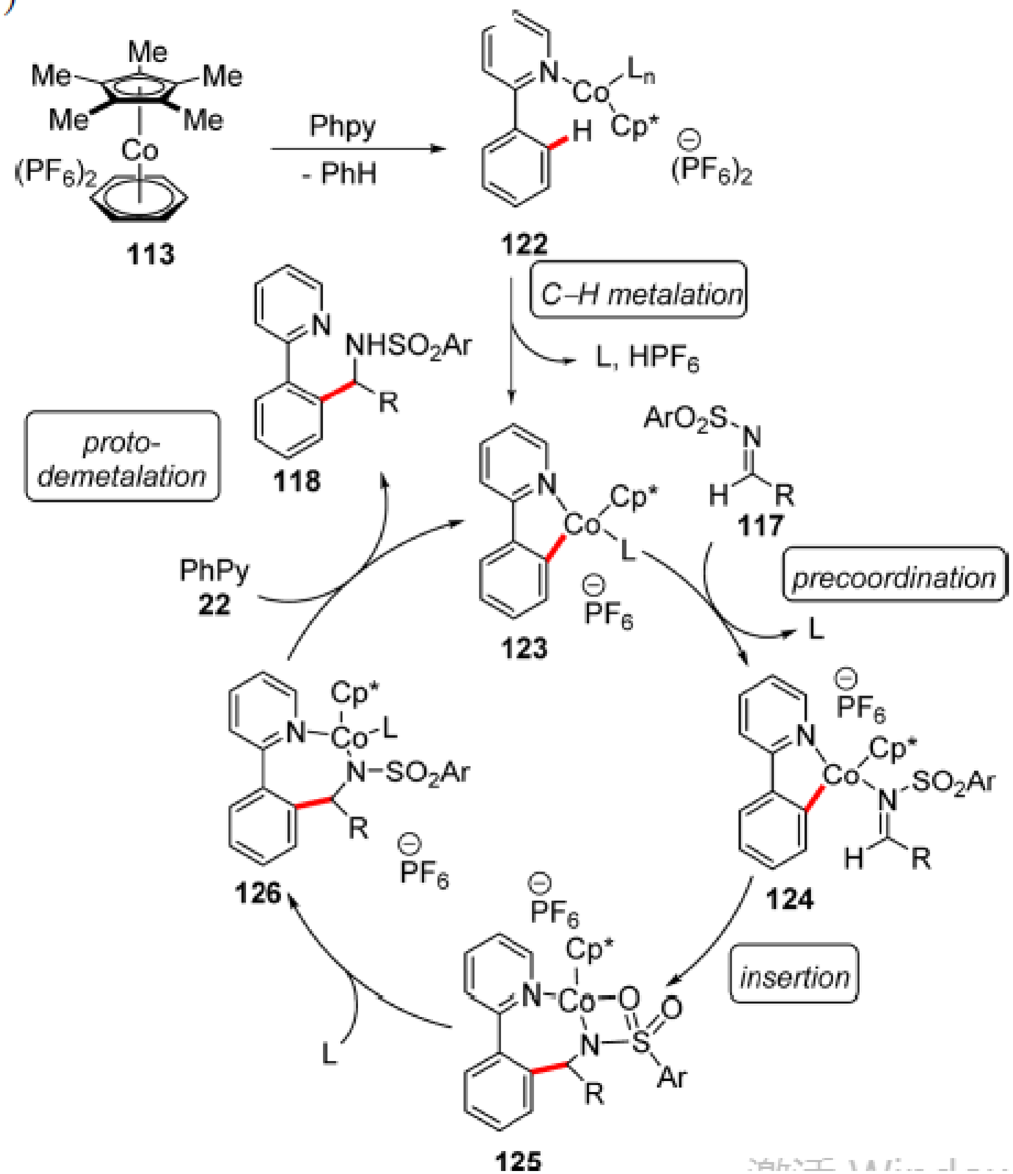
[a]Yield was determined by ^{1}H NMR spectroscopy, [b]Yield of isolated product. [c]The tetra-chloro complex was used.



Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. *Angew. Chem., Int. Ed*. **2013**, *52*, 2207−2211.

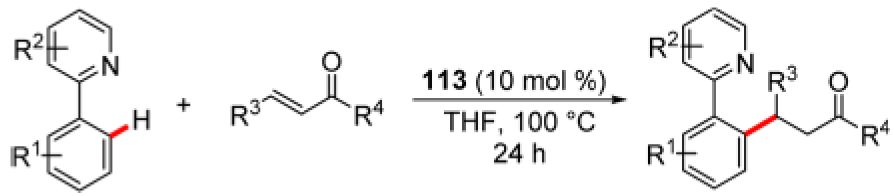
Catalysis with Cp*Co(III) Complexes

Scheme 43. Proposed Catalytic Cycle for the Cobalt(III)-Catalyzed Addition (L = 2-Phpy)



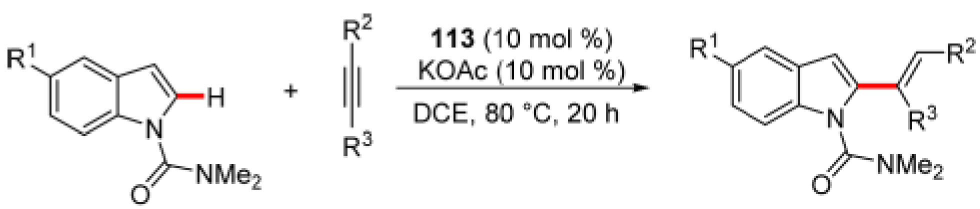
Catalysis with Cp*Co(III) Complexes

Michael Acceptors

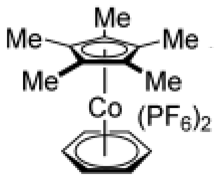


22 120 121

Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 2207−2211.

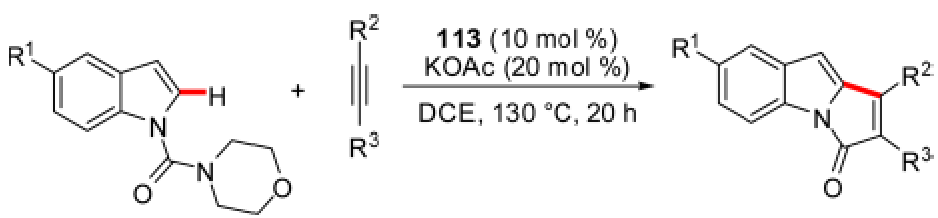


127 20 128



113

Alkynes

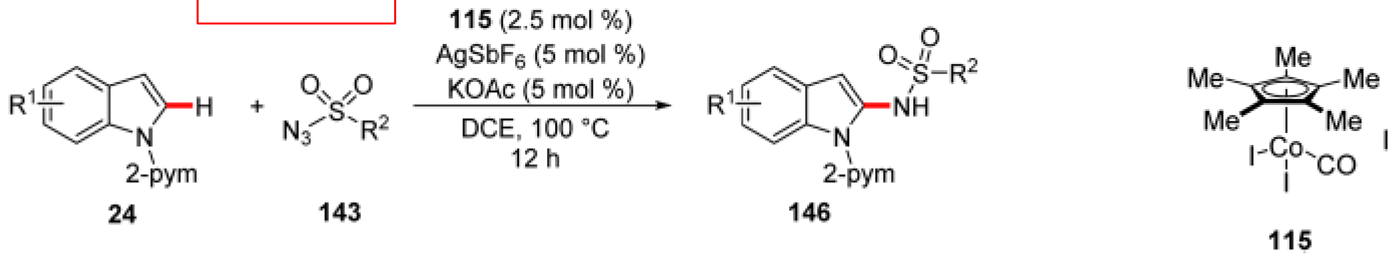


127 20 129

Ikemoto, H.; Yoshino, T.; Sakata, K.; Matsunaga, S.; Kanai, M. *J. Am. Chem. Soc*. **2014**, *136*, 5424−5431.

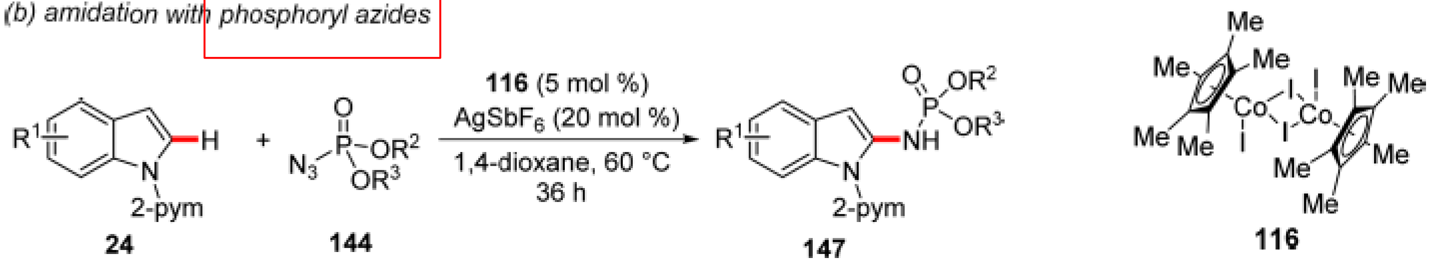
C-H Amidations

(a) amidation with sulfonyl azides



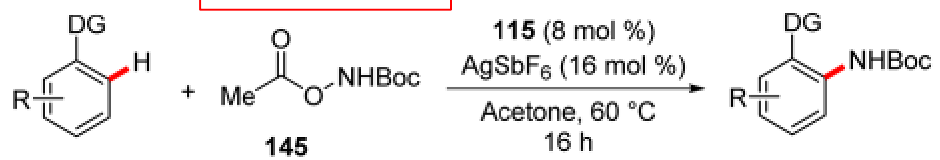
Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Adv. Synth. Catal*. **2014**, *356*, 1491−1495.

(b) amidation with phosphoryl azides



Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Chem. Commun*. **2015**, *51*, 4659−4661.

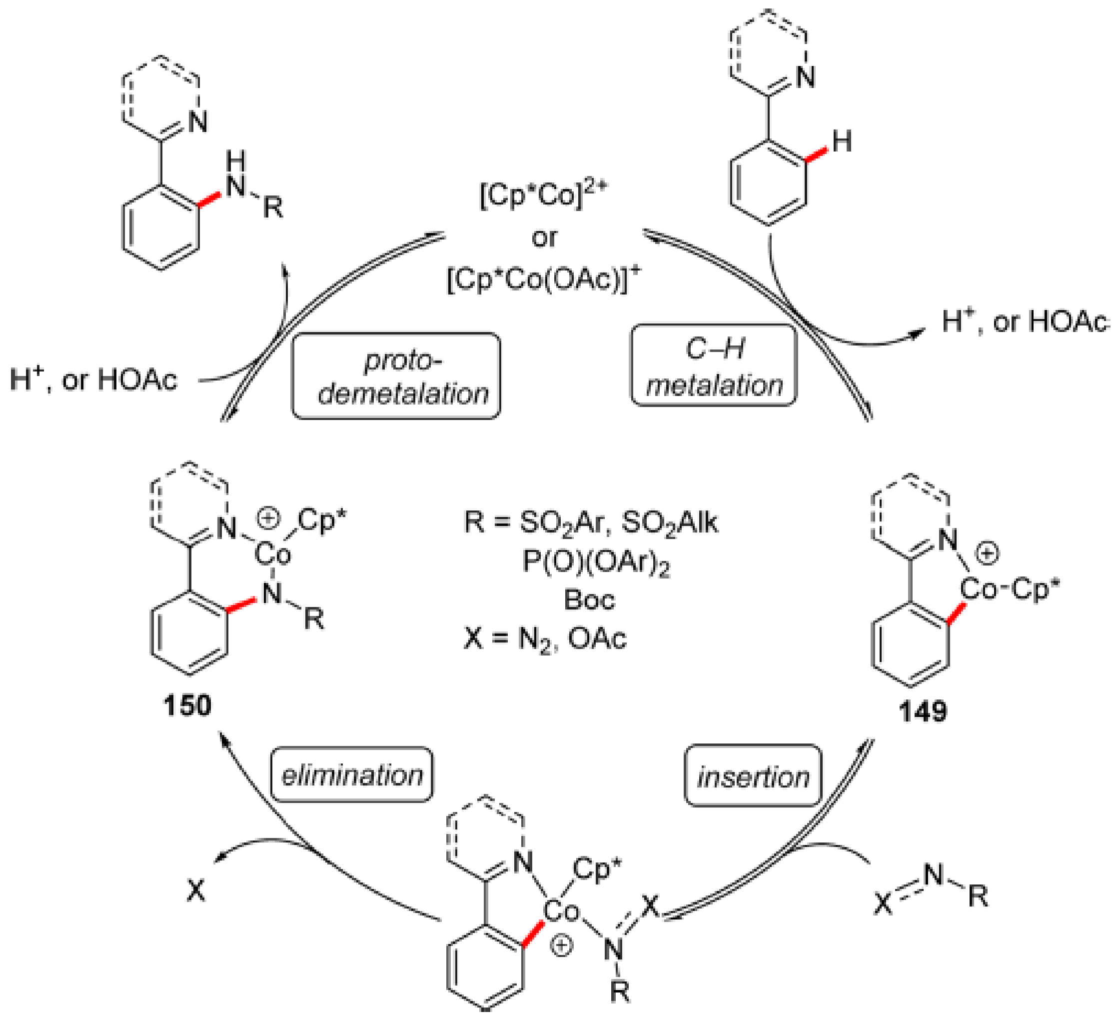
(c) amidation with acetoxycarbamates



Patel, P.; Chang, S. *ACS Catal.* **2015**, *5*, 853−858.

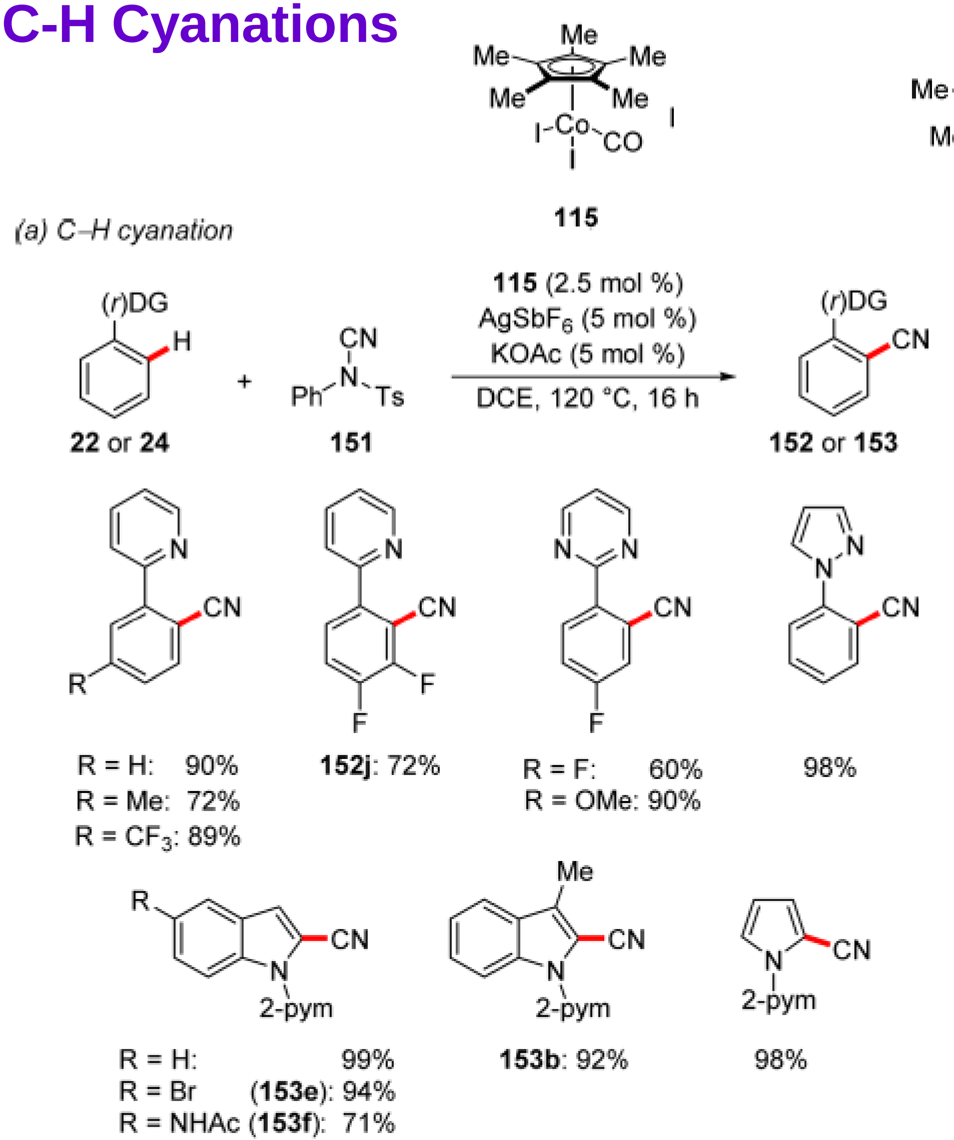
Catalysis with Cp*Co(III) Complexes

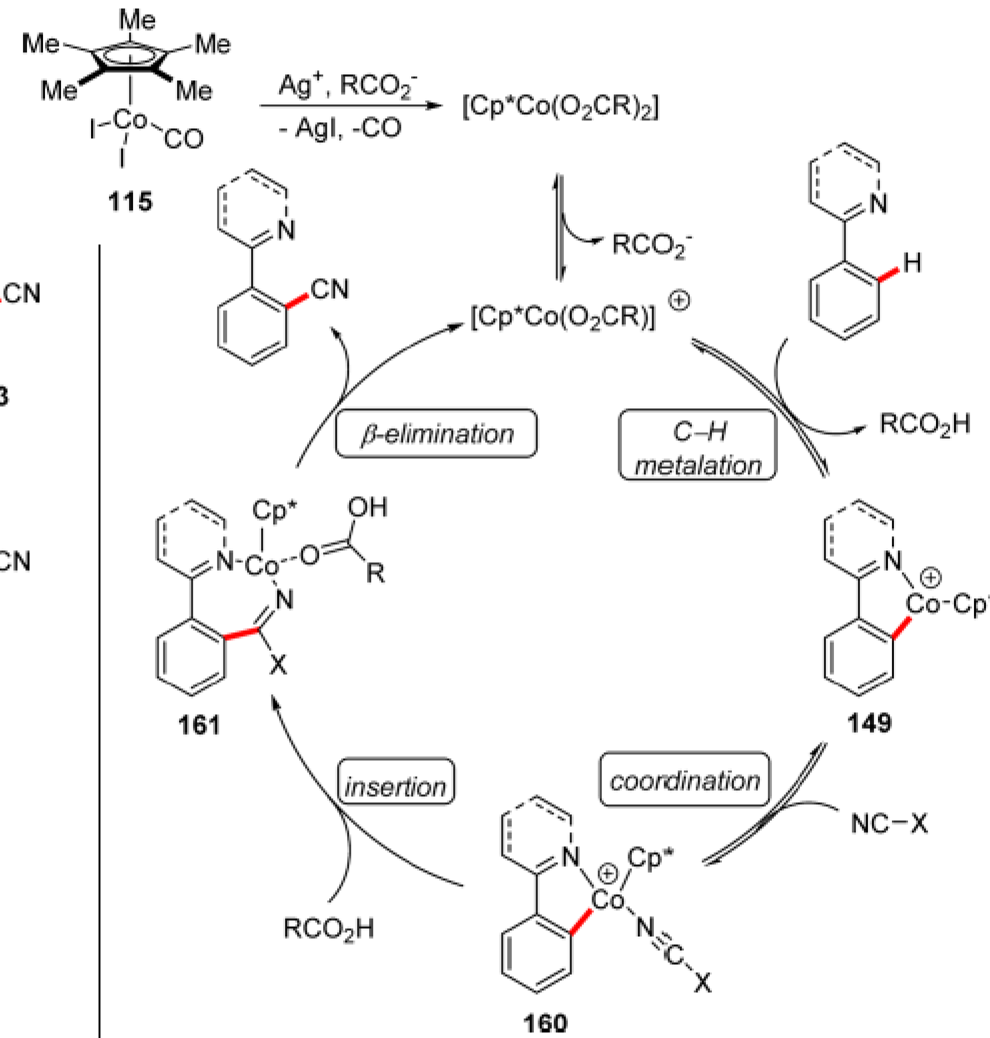
Scheme 51. Proposed Catalytic Cycle for Cp*Co(III)-Catalyzed Amidation



Catalysis with Cp*Co(III) Complexes

C-H Cyanations

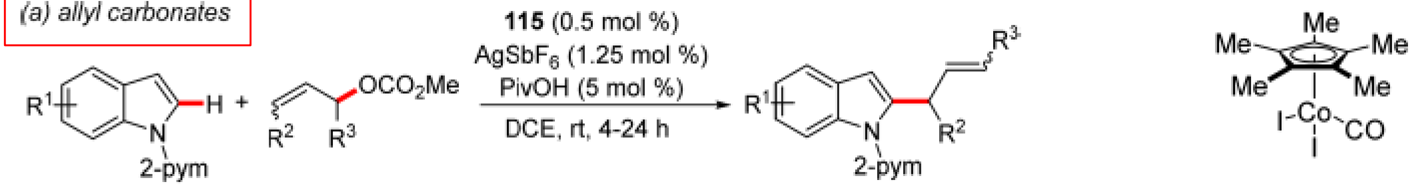




Li, J.; Ackermann, L. *Angew. Chem., Int. Ed*. **2015**, *54*, 3635−3638.

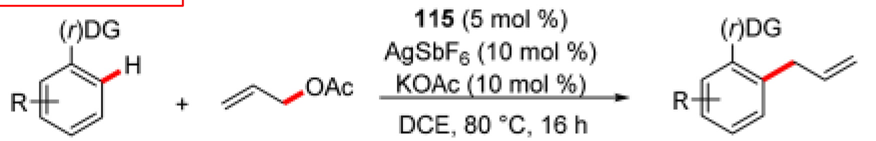
C-H Allylations

(a) allyl carbonates



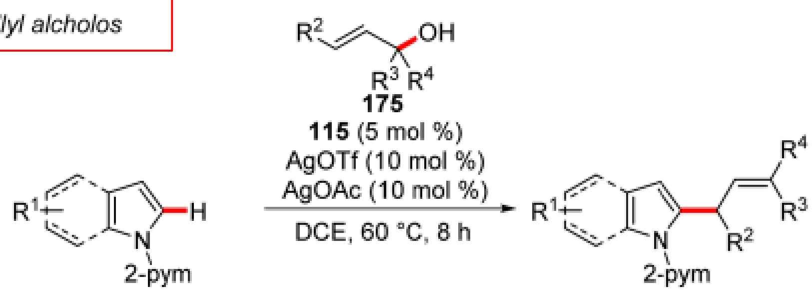
22 171 172 115

(b) allyl acetate



22, 24, 174 173 179, 172, 178

(c) allyl alcholos

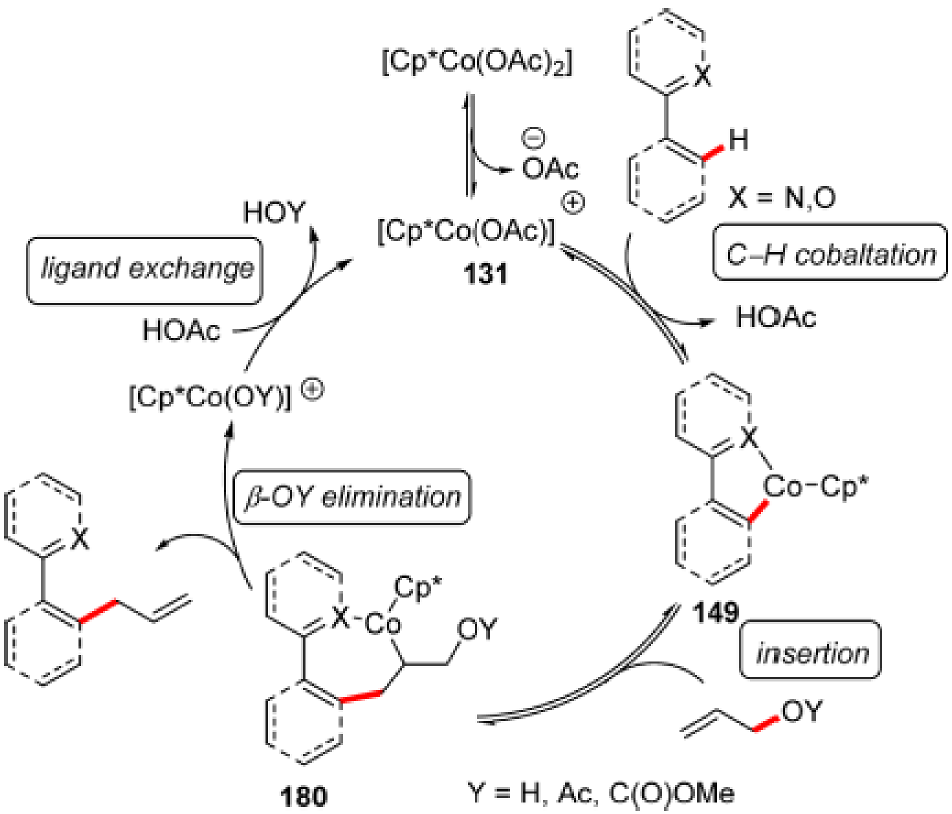


24 or 174 172 or 178

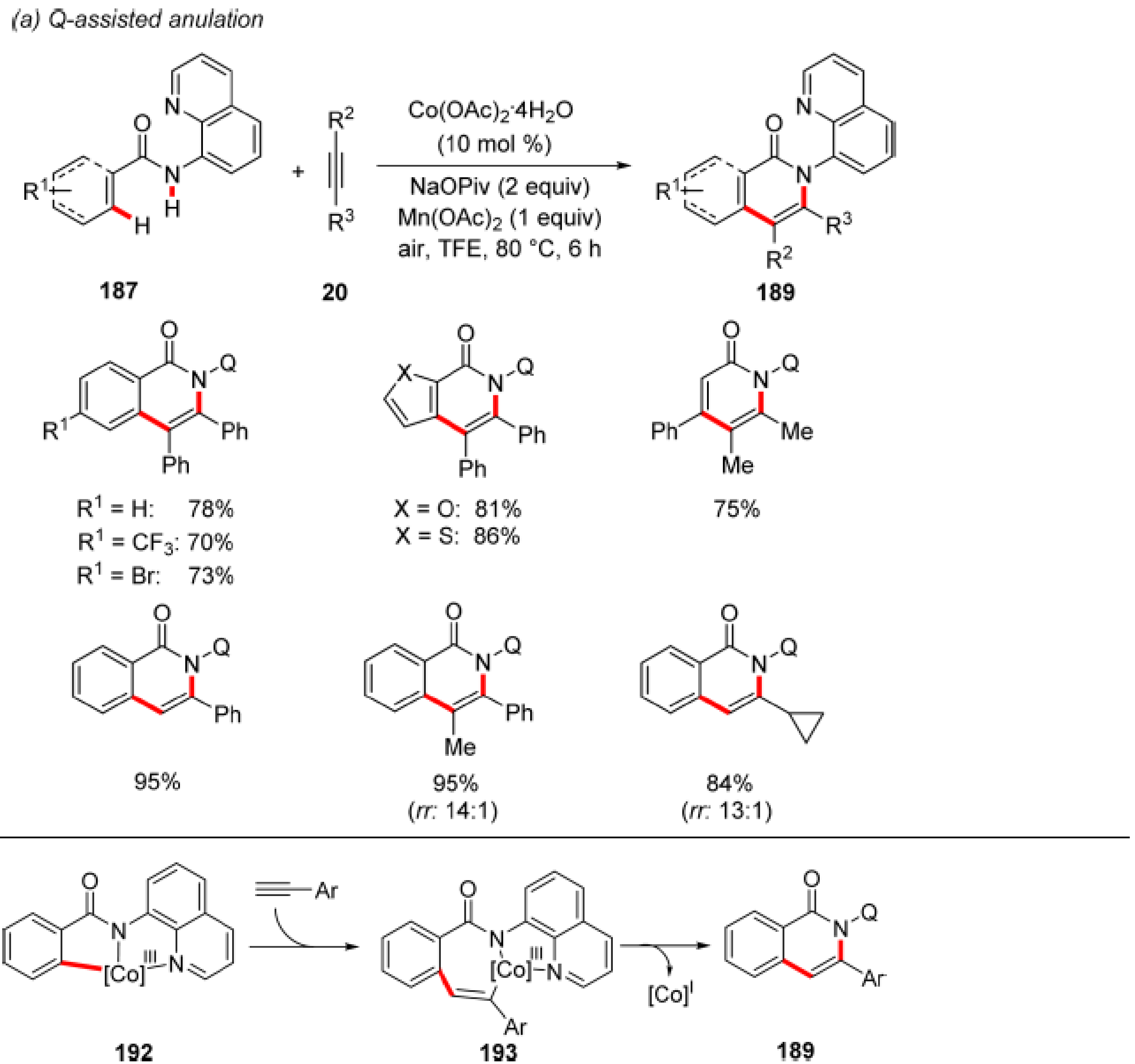
Glorius, F. *J. Am. Chem. Soc*.**2014**, *136*, 17722−17725.
Glorius, F. *Org. Lett*. **2015**, *17*, 3714−3717.
Ackermann, L. *Synlett* **2015**, *26*, 1596−1600.
Kanai, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 9944−9947.

Catalysis with Cp*Co(III) Complexes

Scheme 59. Proposed Catalytic Cycle for the Cobalt-Catalyzed Allylation

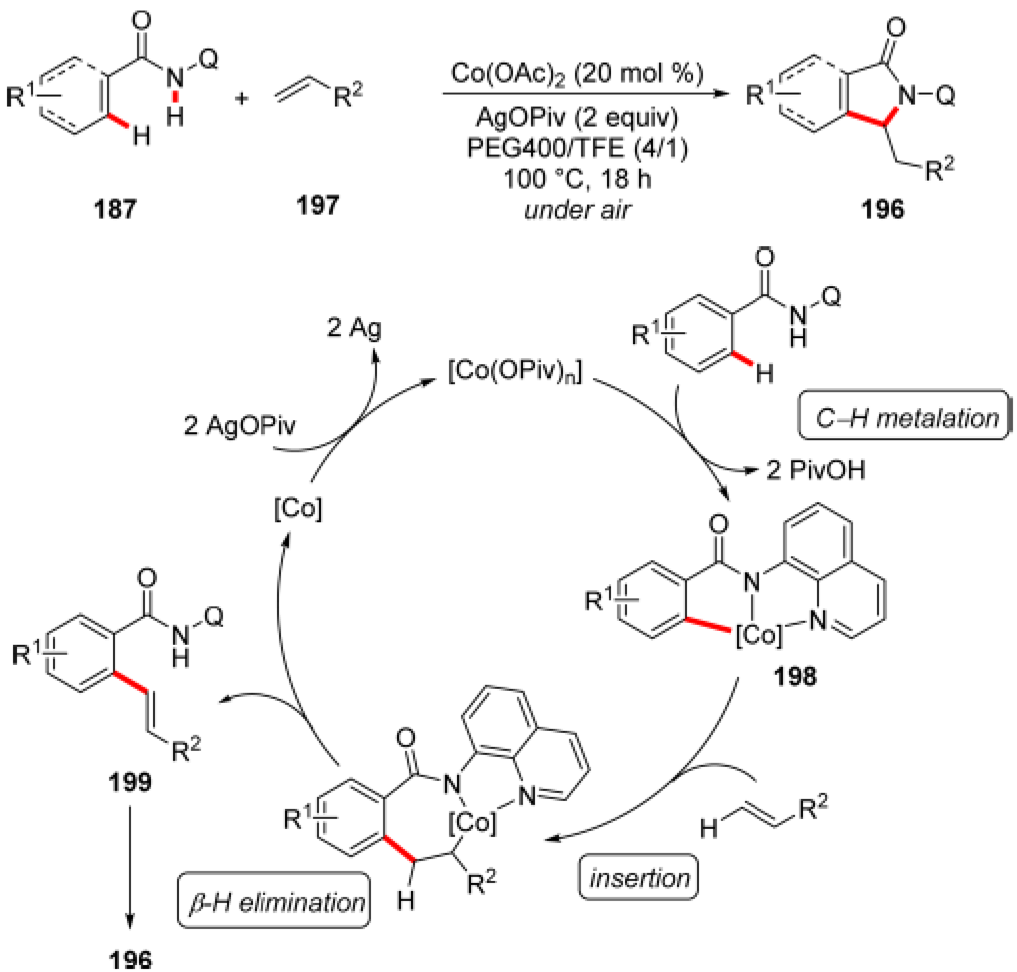


Oxidative C-H Functionalizations and Annulations



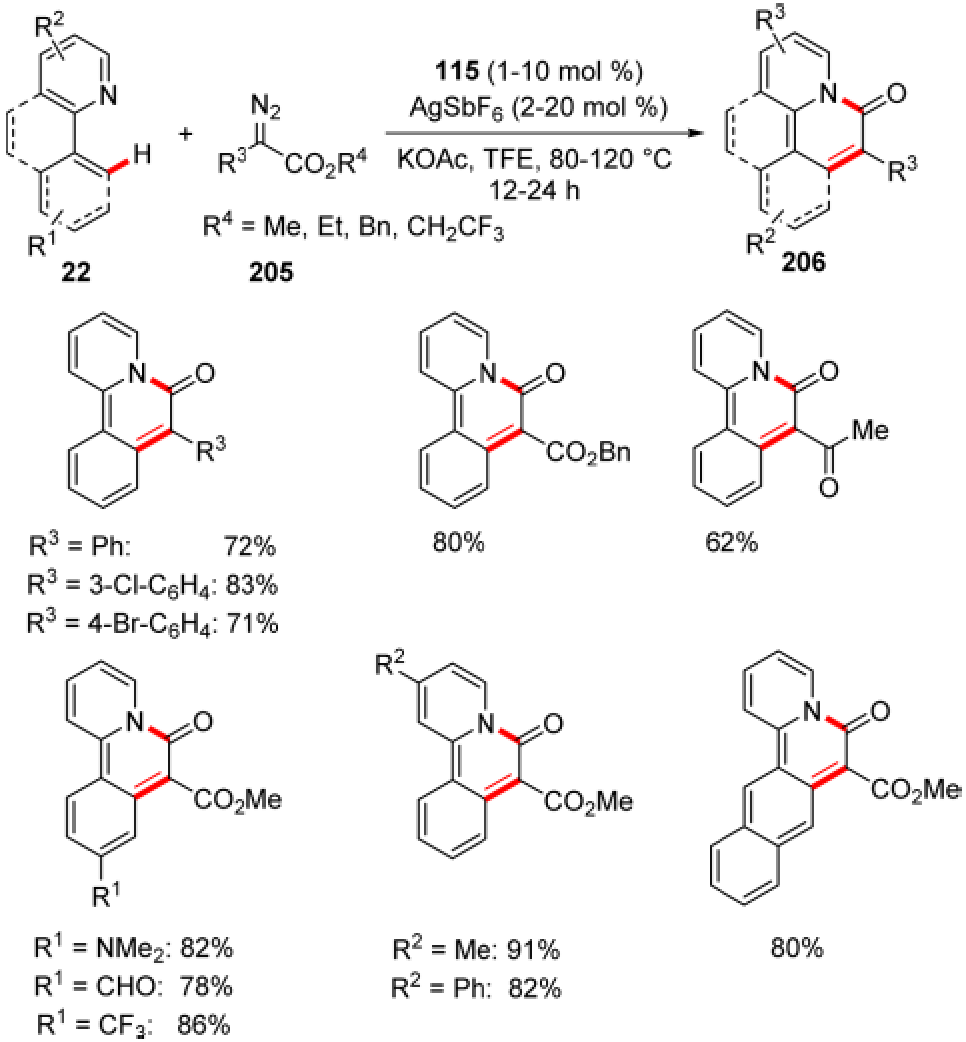
Grigorjeva, L.; Daugulis, O. *Angew. Chem., Int. Ed*. **2014**, *53*, 10209−10212.

Scheme 66. Cobalt-Catalyzed Isoindolinone Synthesis



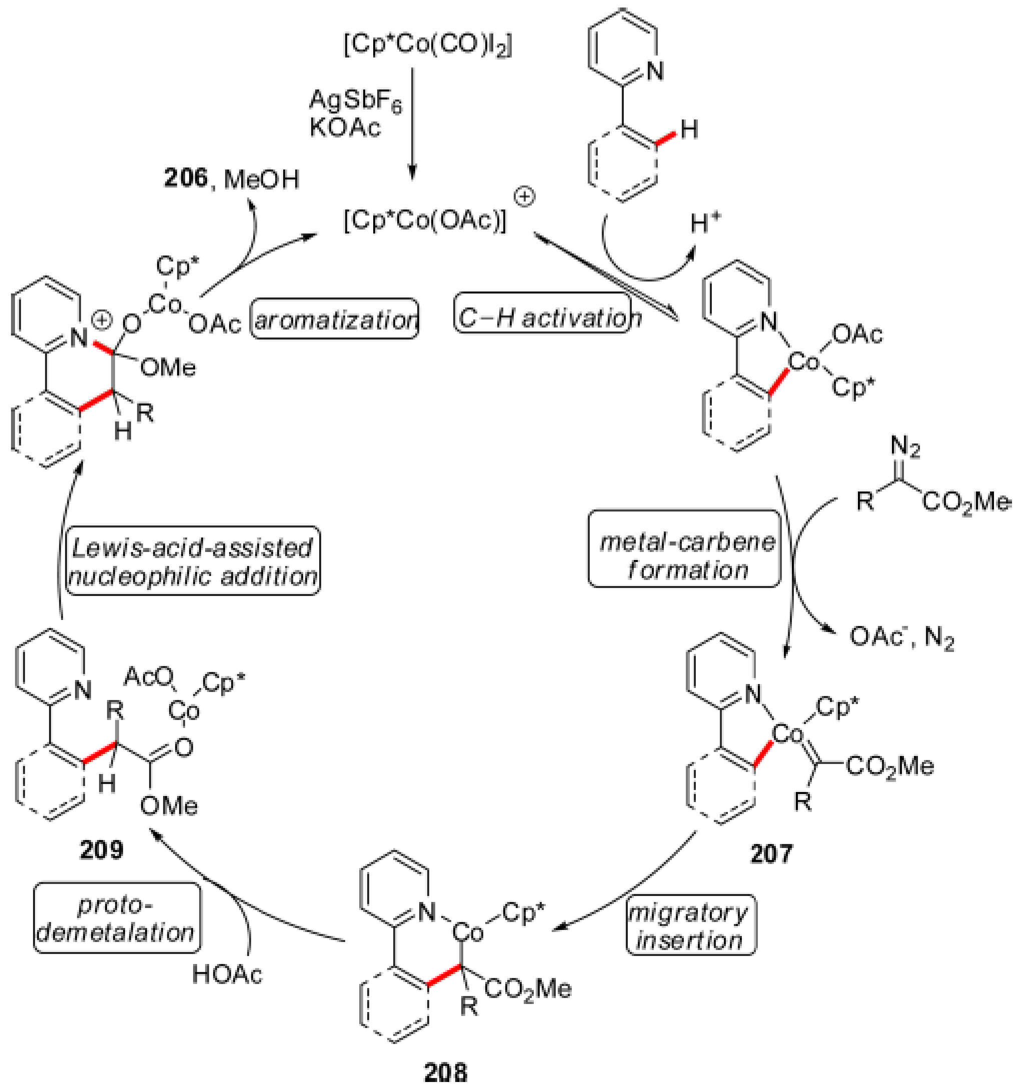
Ma, W.; Ackermann, L. *ACS Catal*. **2015**, *5*, 2822−2825.

Scheme 70. Cobalt(III)-Catalyzed Annulation with Diazocompounds 205



Glorius, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 4508−4511.

Organometallic C-H Activation by Cobalt Carbenoids



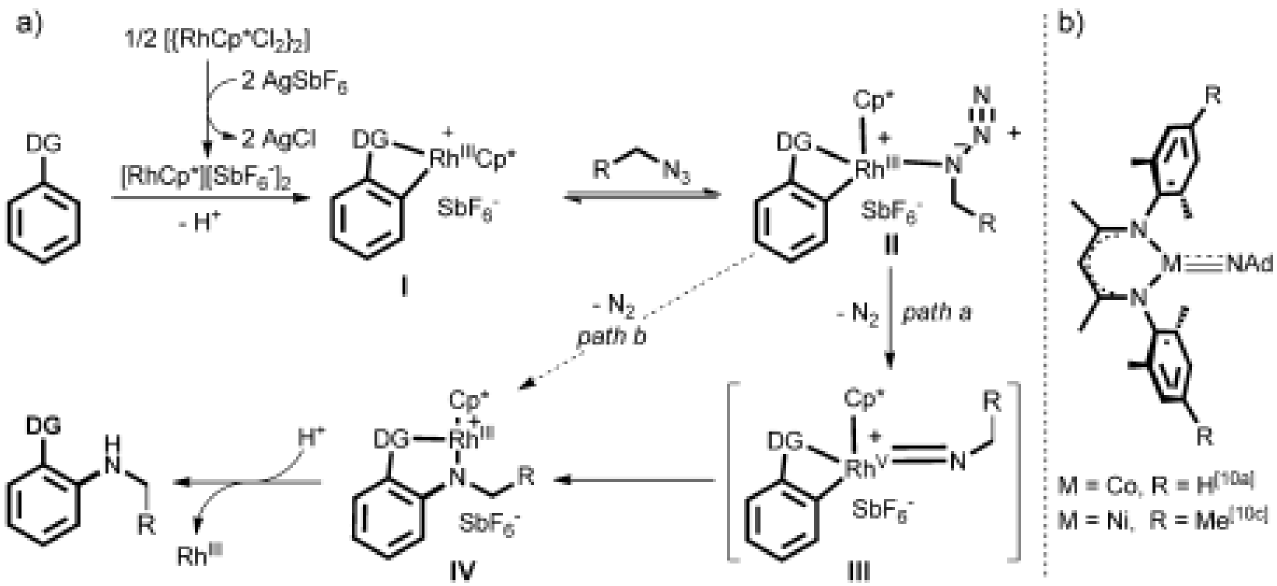
Conclusion & Outlook

- The development of low-valent cobalt-catalysis set the stage for C-H arylations, alkenylations, benzylations and alkylaitons fo arenes as well as alkenes under rather mild reaction conditions. While, the use of Grignard reagent limited the functional group tolerance.
- the discovery of high-valent cobalt(II) and cobalt(III) catalysis recently set the stage for versatile C-H functionalization processes. The higher nucleophilicity of organo-metallic cobalt(III) species enabled improved selectivites and entirely novel chemical transformations.

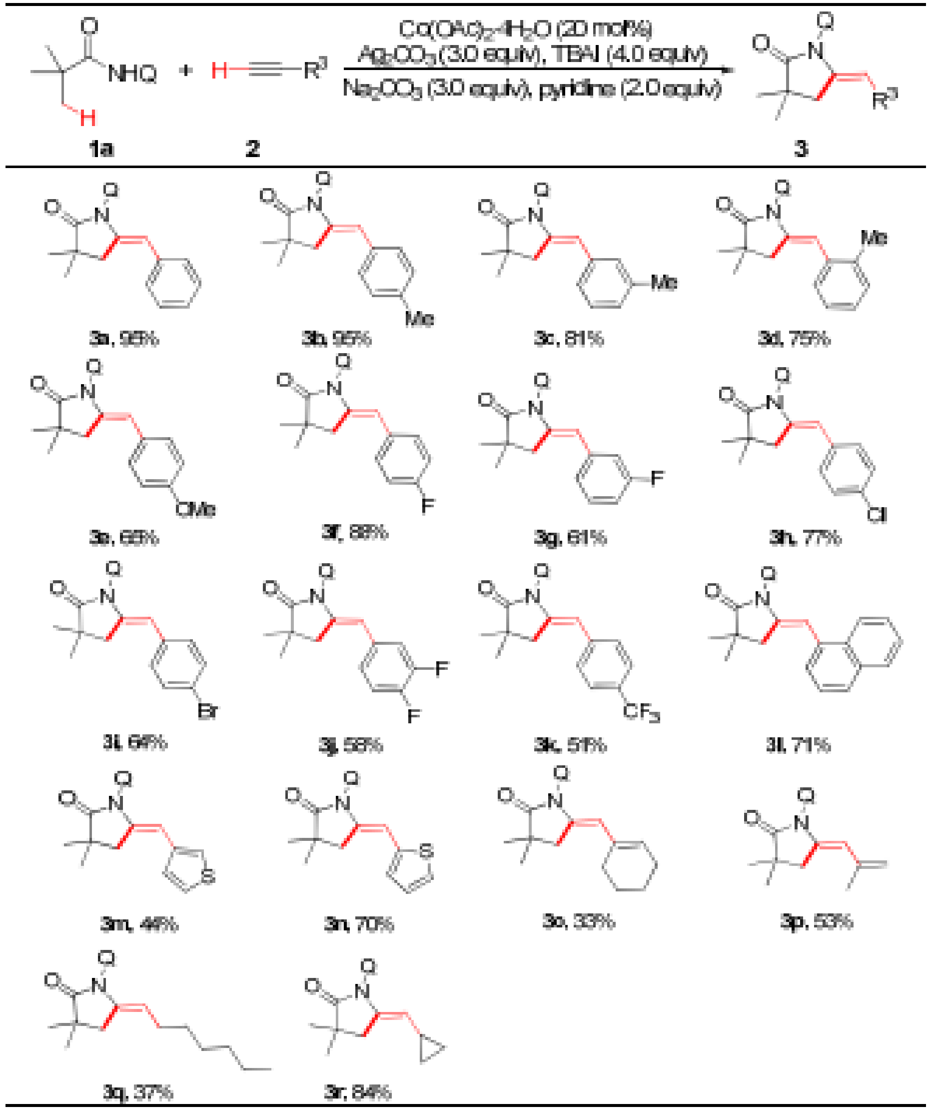
◆ In low-valent cobalt-catalyzed C-H functionalization chemistry it is desirable to establish a generally applicable replacement for the omnipresent Grignard reagents.

◆ The cobalt catalysis is hoped to be applied in C(sp3)-H activation.

THANK YOU!!!



Scheme 8. a) Proposed mechanism of the direct C—H amination. b) Examples of isolated metal alkylimido complexes. Ad = adamantyl.


Co(OAc)2·4H2O (20 mol%)
Ag2CO3 (3.0 equiv), TBAI (4.0 equiv)
Na2CO3 (3.0 equiv), pyridine (2.0 equiv)
NHQ
1a
2
3
3a, 96%
3b, 95%
3c, 81%
3d, 75%
3e, 68%
3f, 88%
3g, 61%
3h, 77%
3i, 64%
3j, 58%
3k, 51%
3l, 71%
3m, 46%
3n, 70%
3o, 33%
3p, 53%
3q, 37%
3r, 84%