LABORATOIRE DE SYNTHESE ET PRODUITS NATURELS

Reactivities of Square-Planer Cobalt (I), (II), (III) Complexes

Takuji Fujii

Group Seminar 21/01/2022

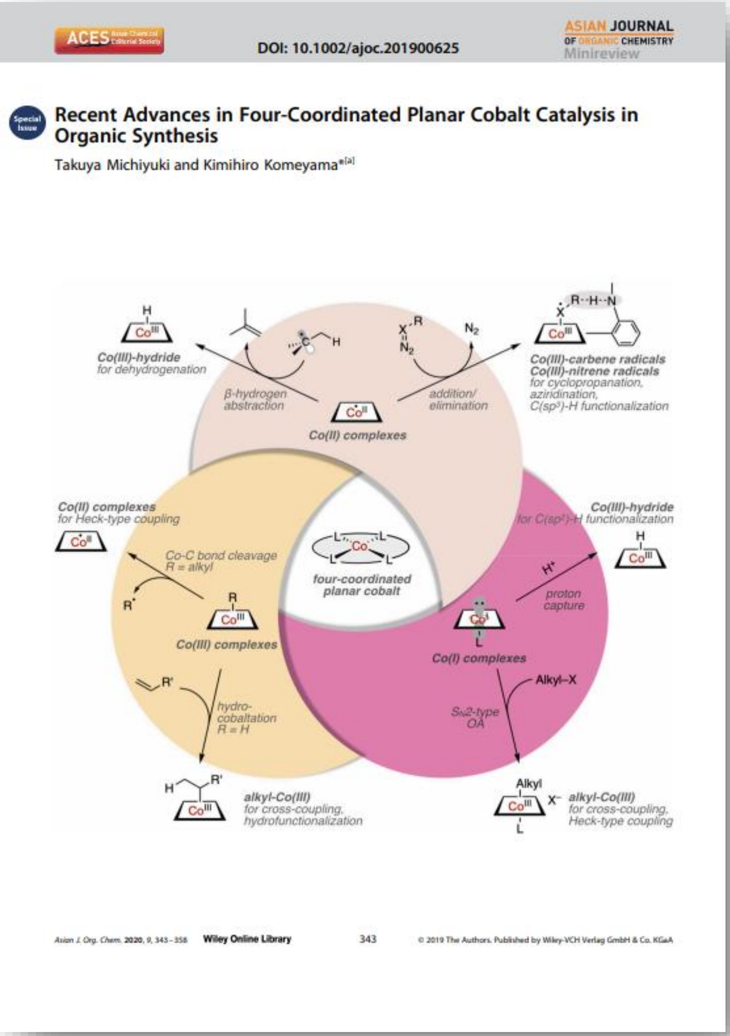
EPFL-ISIC-LSPN

Jieping Zhu Group

Outline

1. Generalities of cobalt
2. β-Hydrogen abstraction
3. Co(III)-carbene or nitrene radicals
4. Hydrocobaltation
5. Co(I) bases
6. S_N2-type oxidative addition
7. Conclusion

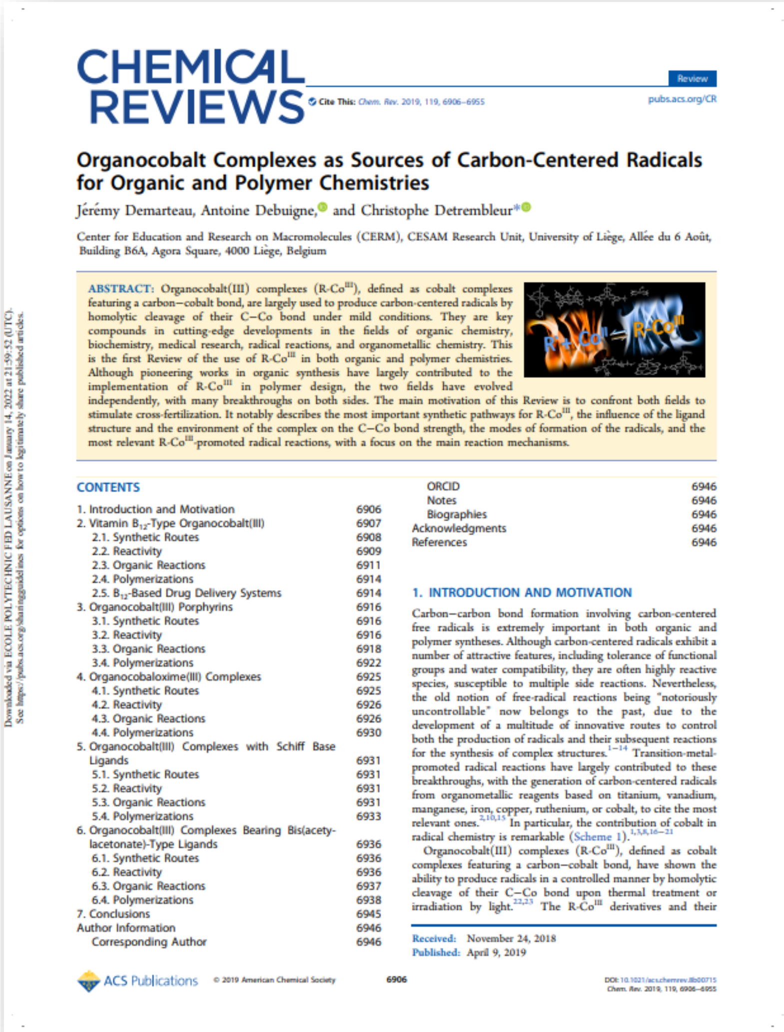
Literature references (Reviews)


ACES
DOI: 10.1002/ajoc.201900625
ASIAN JOURNAL OF ORGANIC CHEMISTRY
Minireview

Special Issue

Recent Advances in Four-Coordinated Planar Cobalt Catalysis in Organic Synthesis

Takuya Michiyuki and Kimihiro Komeyama*[a]


CHEMICAL REVIEWS
Review
Cite This: Chem. Rev. 2019, 119, 6906–6955
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Organocobalt Complexes as Sources of Carbon-Centered Radicals for Organic and Polymer Chemistries

Jérémy Demarteau, Antoine Debuigne, and Christophe Detrembleur*

Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liège, Allée du 6 Août, Building B6A, Agora Square, 4000 Liège, Belgium

ABSTRACT: Organocobalt(III) complexes (R-Co^{III}), defined as cobalt complexes featuring a carbon–cobalt bond, are largely used to produce carbon-centered radicals by homolytic cleavage of their C–Co bond under mild conditions. They are key compounds in cutting-edge developments in the fields of organic chemistry, biochemistry, medical research, radical reactions, and organometallic chemistry. This is the first Review of the use of R-Co^{III} in both organic and polymer chemistries. Although pioneering works in organic synthesis have largely contributed to the implementation of R-Co^{III} in polymer design, the two fields have evolved independently, with many breakthroughs on both sides. The main motivation of this Review is to confront both fields to stimulate cross-fertilization. It notably describes the most important synthetic pathways for R-Co^{III}, the influence of the ligand structure and the environment of the complex on the C–Co bond strength, the modes of formation of the radicals, and the most relevant R-Co^{III}-promoted radical reactions, with a focus on the main reaction mechanisms.

CONTENTS

1. INTRODUCTION AND MOTIVATION

Carbon–carbon bond formation involving carbon-centered free radicals is extremely important in both organic and polymer syntheses. Although carbon-centered radicals exhibit a number of attractive features, including tolerance of functional groups and water compatibility, they are often highly reactive species, susceptible to multiple side reactions. Nevertheless, the old notion of free-radical reactions being "notoriously uncontrollable" now belongs to the past, due to the development of a multitude of innovative routes to control both the production of radicals and their subsequent reactions for the synthesis of complex structures.[1−14] Transition-metal-promoted radical reactions have largely contributed to these breakthroughs, with the generation of carbon-centered radicals from organometallic reagents based on titanium, vanadium, manganese, iron, copper, ruthenium, or cobalt, to cite the most relevant ones.[2,10,15] In particular, the contribution of cobalt in radical chemistry is remarkable (Scheme 1).[1,3,8,16−21]

Organocobalt(III) complexes (R-Co^{III}), defined as cobalt complexes featuring a carbon–cobalt bond, have shown the ability to produce radicals in a controlled manner by homolytic cleavage of their C–Co bond upon thermal treatment or irradiation by light.[22,23] The R-Co^{III} derivatives and their

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Chem. Rev. 2019, 119, 6906–6955

[1] Komeyama, K. et al, *Asian. J. Org. Chem.* **2020**, *9*, 343. [2] Detrembleur, C. et al, *Chem. Rev.* **2019**, *119*, 6906.
[3] Hisaeda, Y. et al, *Beilstein. J. Org. Chem.* **2018**, *14*, 2553. [4] Hilt, G. et al, *Synthesis.* **2008**, *22*, 3537.

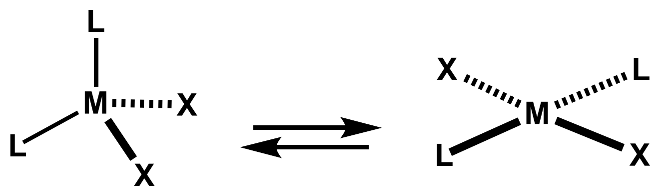
1. Generalities of cobalt

27
Co
Cobalt
58.933

- Discovered in 1735
- Group: 9 (Rh, Ir), Period: 4 (Fe, Ni, Cu)
- Cheap (er than Ru, Rh, Ir, Pd, Ag, Au, Pt)
- Abundant (Congo, Canada, Zambia, Russia)
- Common oxidation states: I, II, III
- Used for Pauson-Khand reaction, Nicholas reaction, [2+2+2] cycloaddition, Wakamatsu reaction…

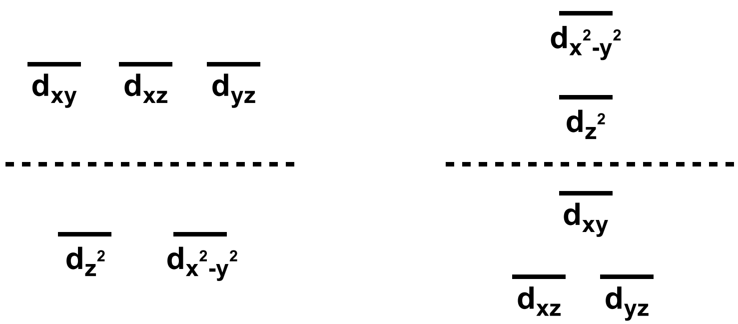
[5] Omae, I., *Appl. Organometal. Chem.* **2007**, *21*, 318.

1. Generalities of cobalt



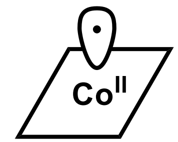
tetrahedral

square-planar



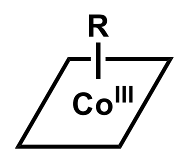
Sterically favored
Small LFSE
(Ligand Field Stabilization Energy)

Sterically disfavored
Big LFSE



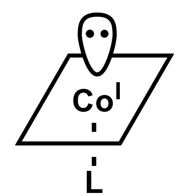
Open-shell and an unpaired electron
Acting as metalloradical catalysts

d^7 Co(II) metalloradicals



Planar geometry
Stabilizing alkyl and hydro Co(III) species

d^6 Alkyl and Hydro Co(III) complexes



Axial coordination
Resulting in an increase of basicity and nucleophilicity (HOMO)

d^8 Co(I) bases and nucleophiles

[6] Chirik, P. J. et al, *Inorg. Chem.* **2005**, *44*, 3103.

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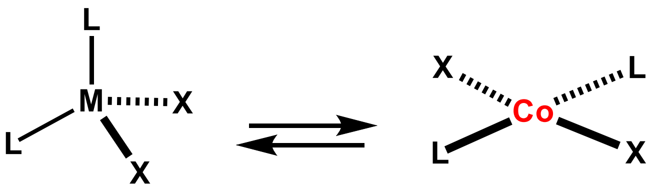

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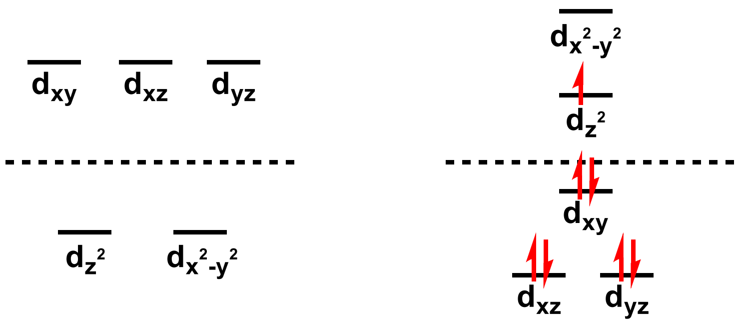
square-planar



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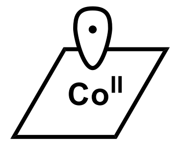

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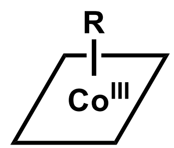

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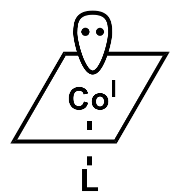

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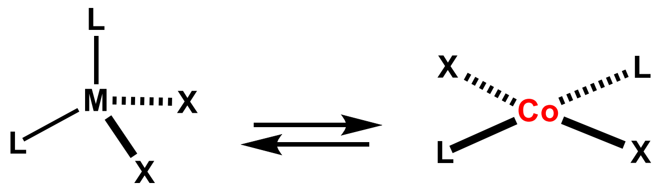
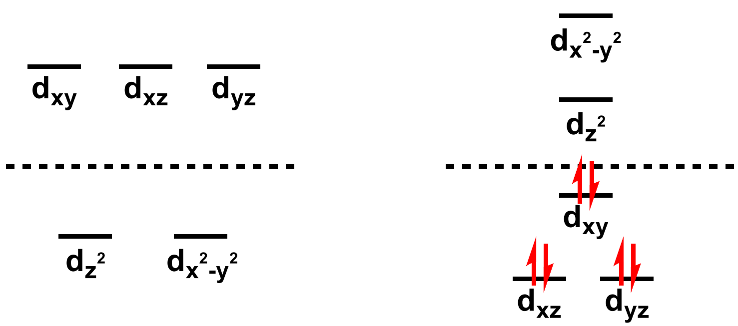


tetrahedral square-planar



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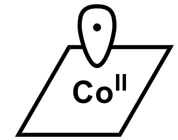

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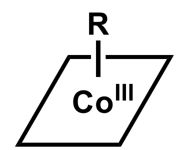

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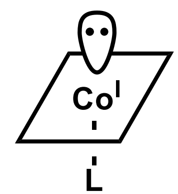

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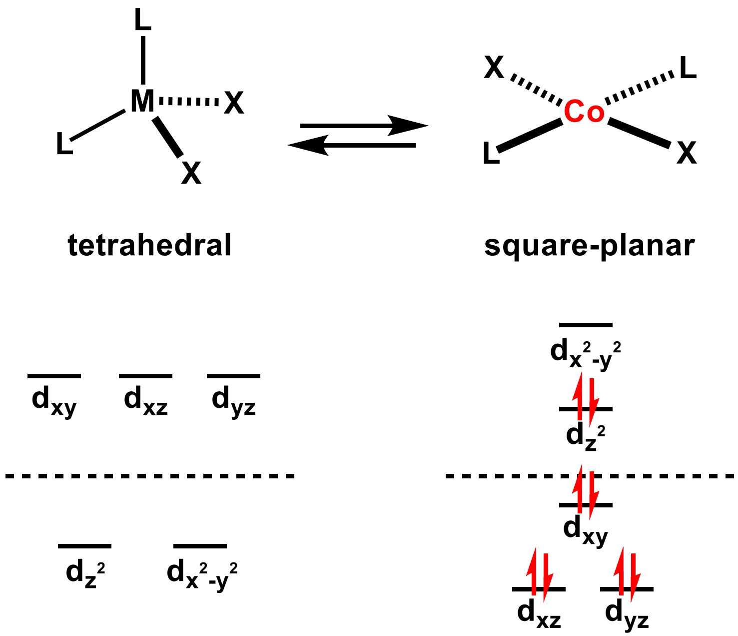

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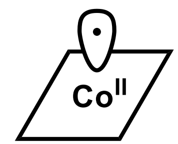

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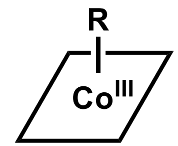

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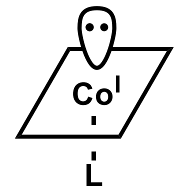

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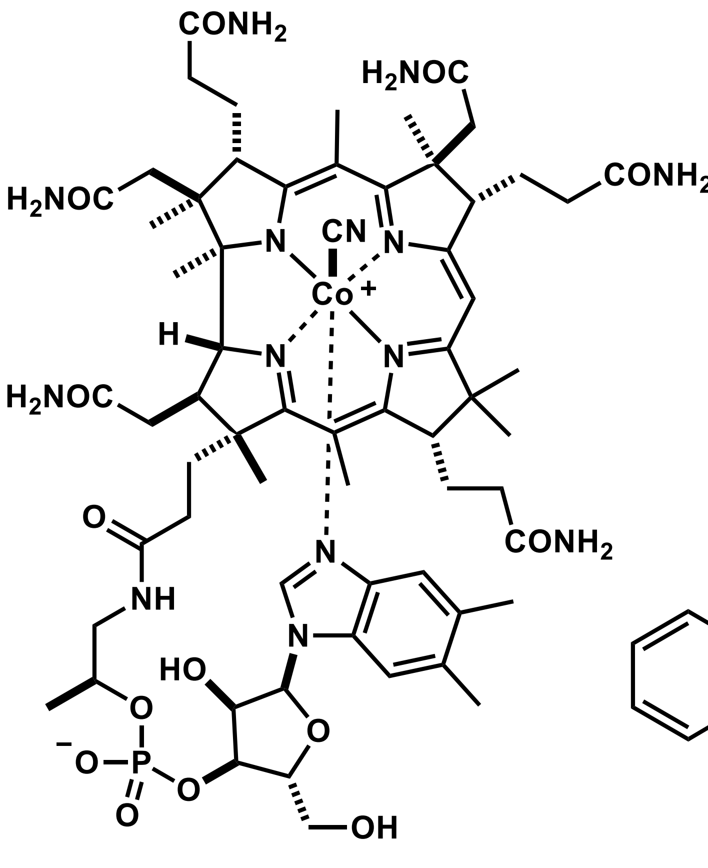
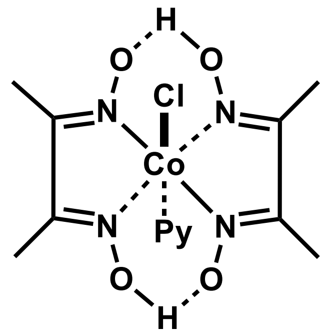
1. Generalities of cobalt

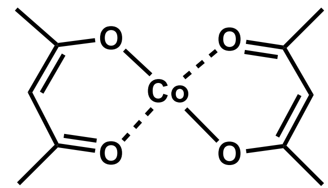
Representative Square-Planner Cobalt Catalysts (Ligands)



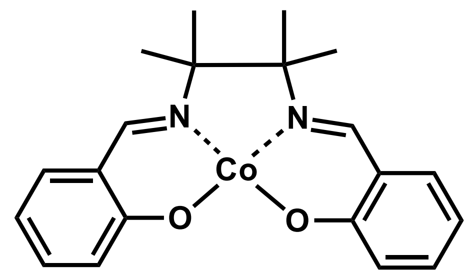
Vitamin B_{12}



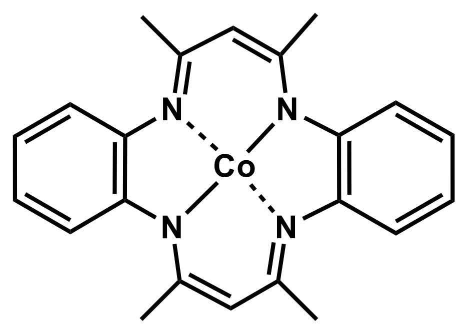
$Co^{III}Cl(dmgH)_2py$



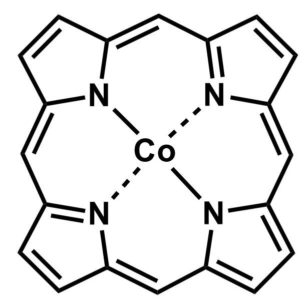
$Co^{III}(acac)_2$



$Co^{II}(salen)$



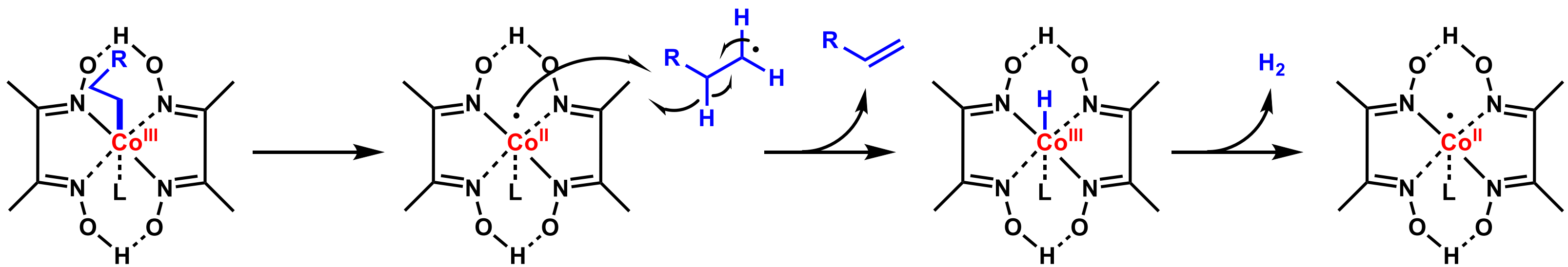
Co^{II} (MeTAA)



Co^{II} porphyrin

2. β-Hydrogen abstraction

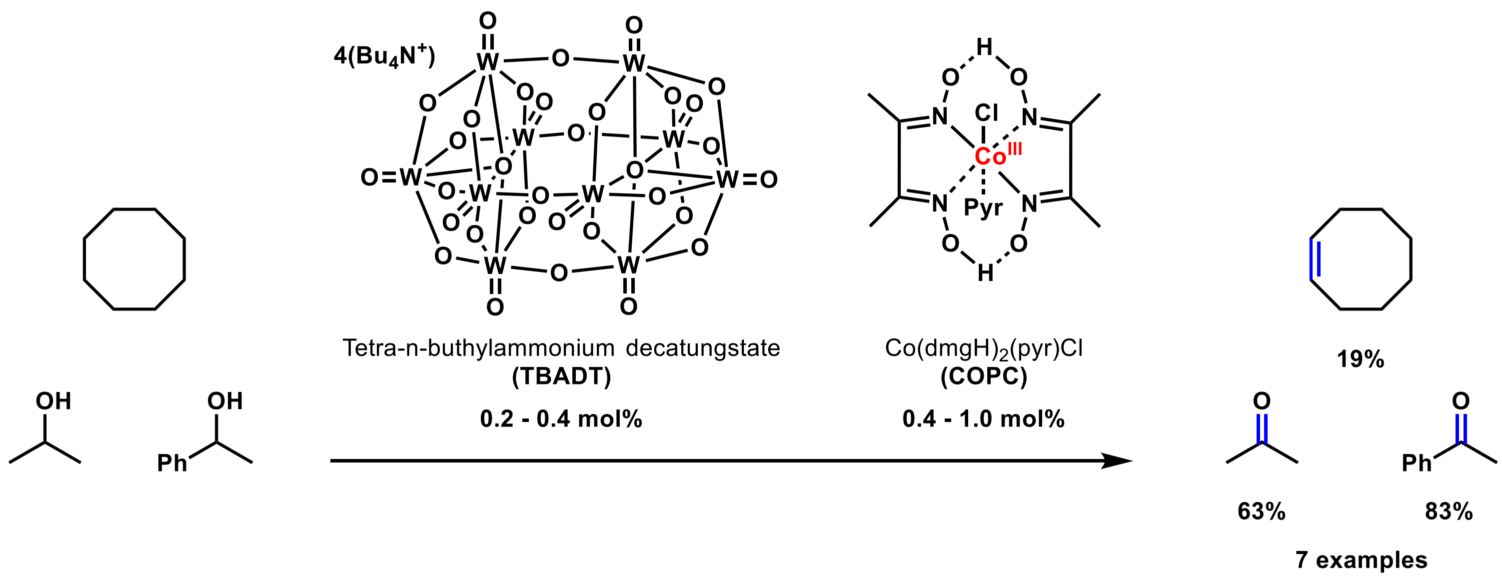
β-hydrogen abstraction (Rampel, Ng, and Halpern, 1982)



$Co^{III}R(dmgH)_2L$

[7] Ng, F. T. T. et al, *J. Am. Chem. Soc.* **1982**, *104*, 621.

Seminal work for hydrogenative transformation combing Cobalt and other catalysts (Sorensen, 2015)



[8] Sorensen, E. J. et al, *Nat. Commun.* **2015**, *6*, 10093.

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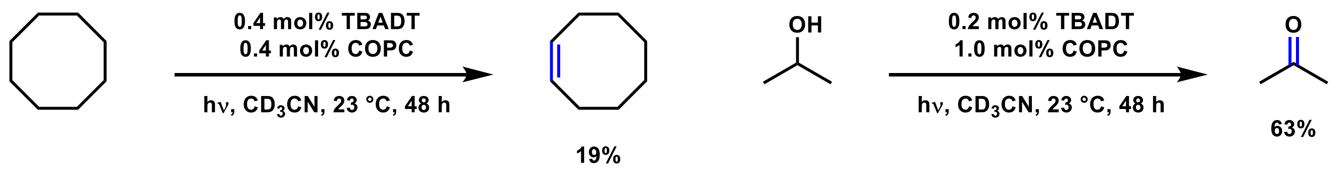
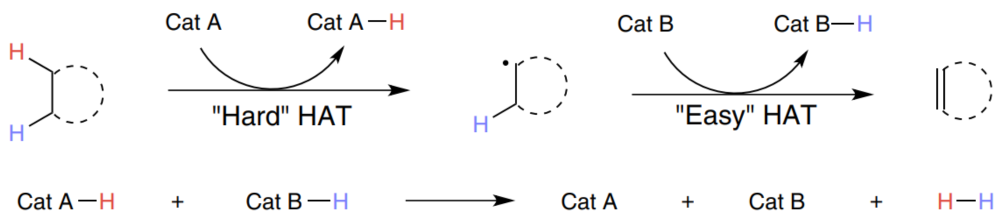
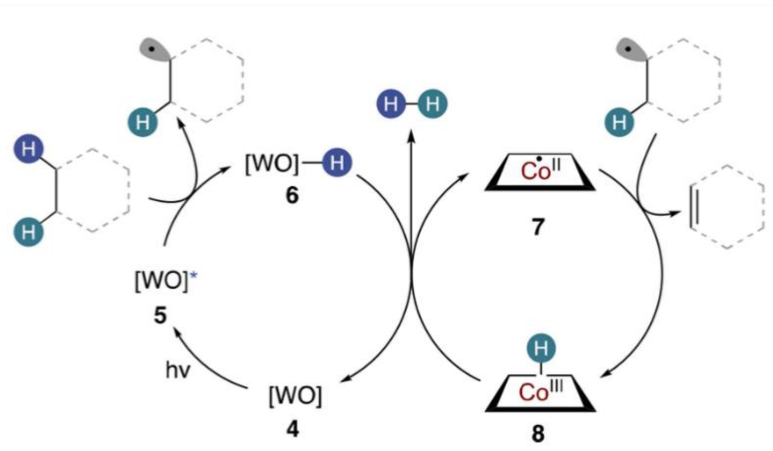


Cooperative hydrogen atom transfer (cHAT)

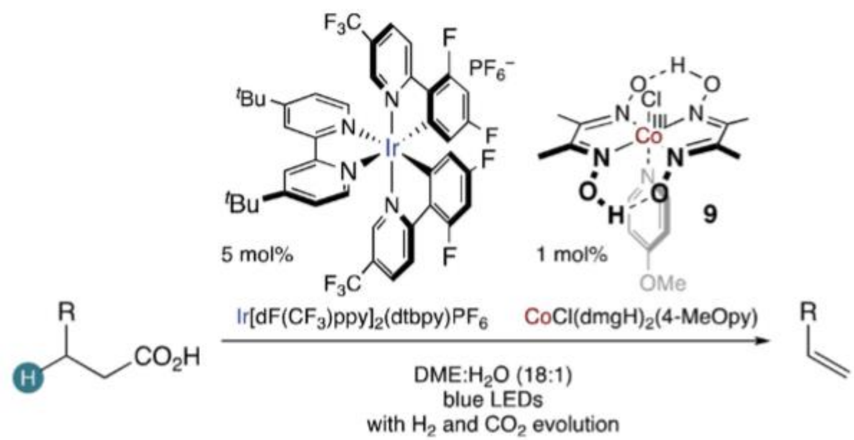


Plausible mechanism for the TBADT/COPC-catalyzed dehydrogenation of alkanes.

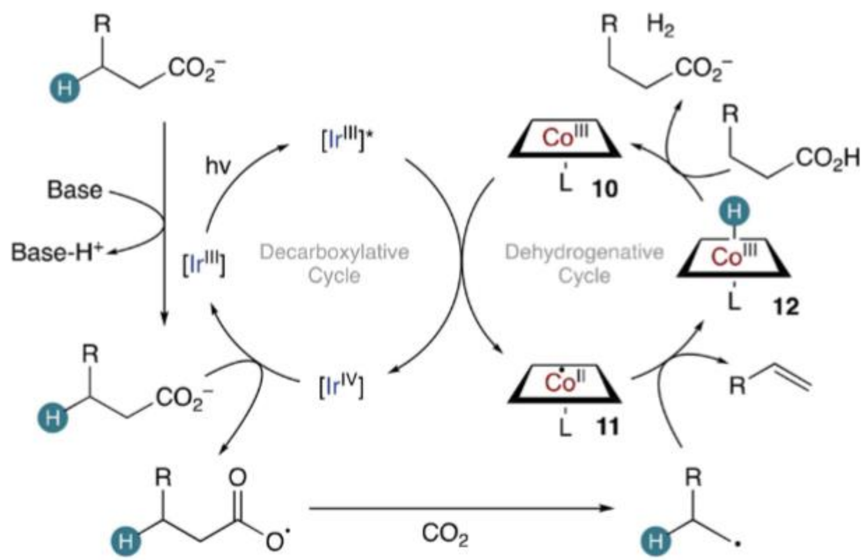


2. β-Hydrogen abstraction

Catalytic dehydrogenative decarboxylativeolefination of carboxylic acids (Ritter, 2018)

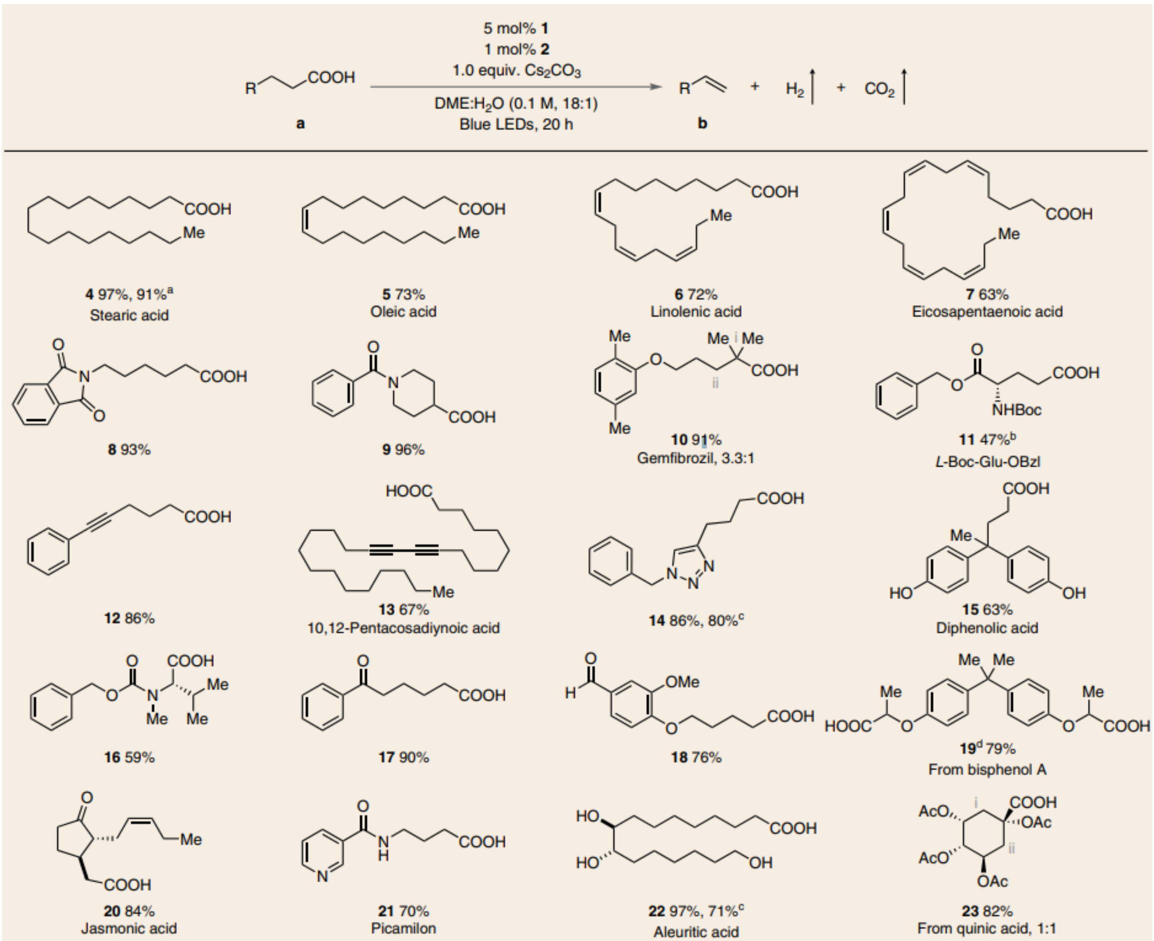


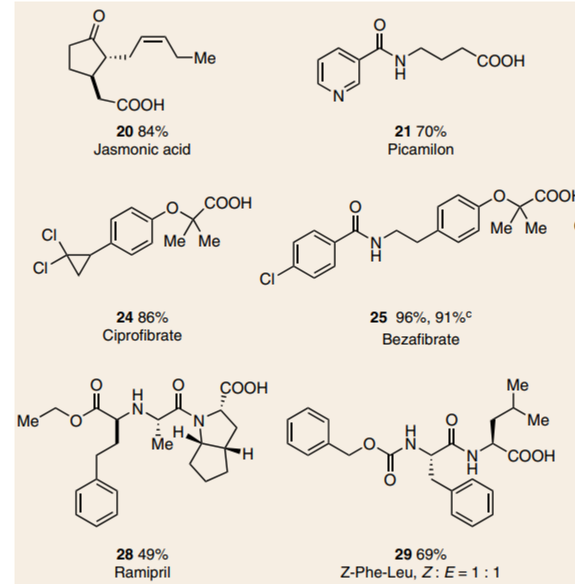
Plausible mechanism

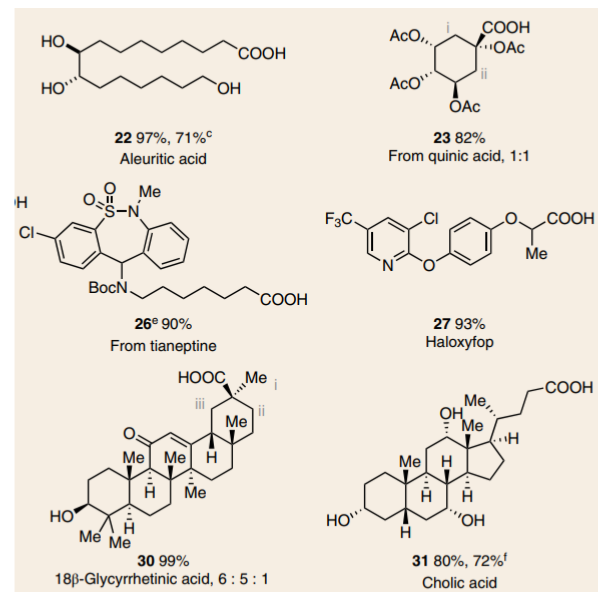


[9] Ritter, T. et al, *Nat. Chem.* **2018**, *10*, 1229.

2. β-Hydrogen abstraction

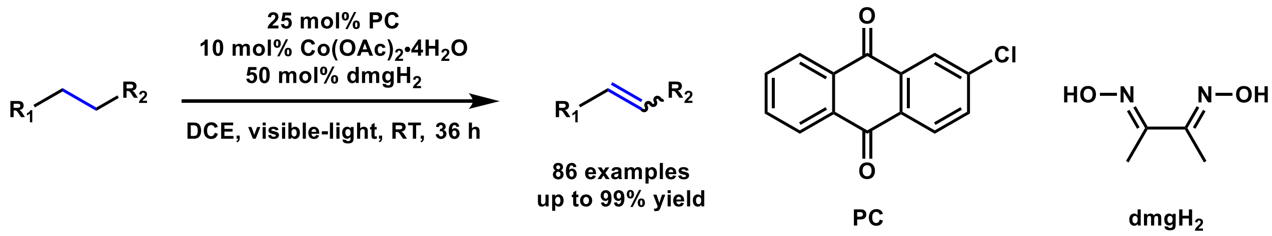




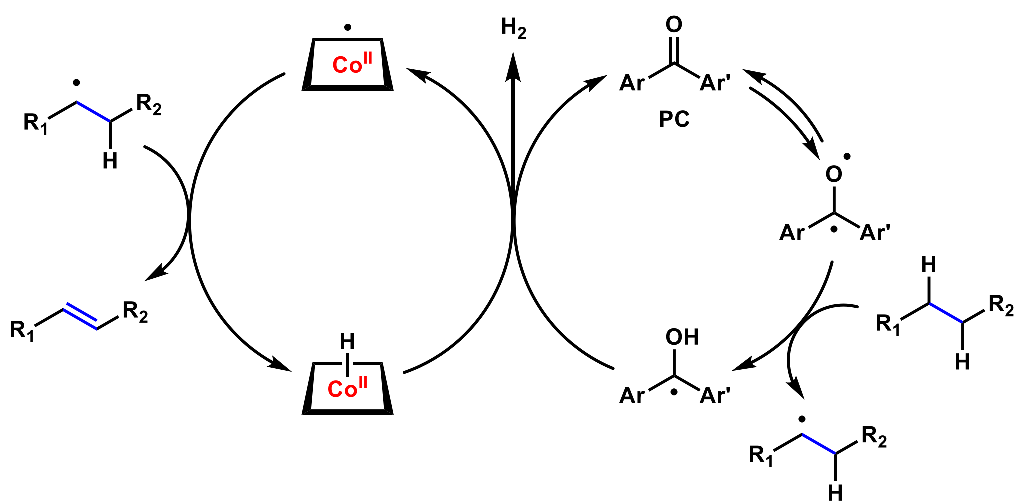


2. β-Hydrogen abstraction

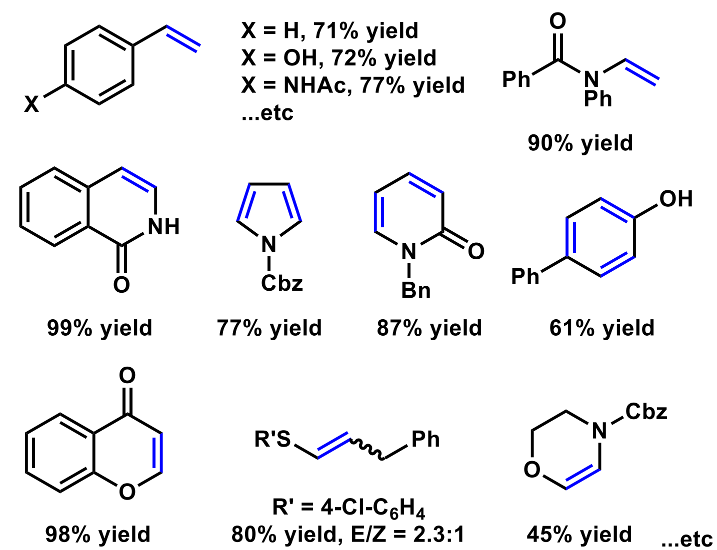
Dehydrogenation of aliphatics by photoredox/cobalt catalysts (Xu and Huang, 2021)



Plausible mechanism



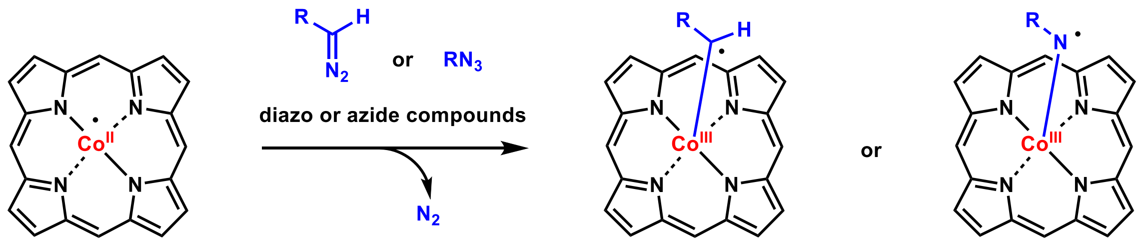
Selected examples



[10] Xu, C. et al, *J. Am. Chem. Soc.* **2021**, *143*, 40.

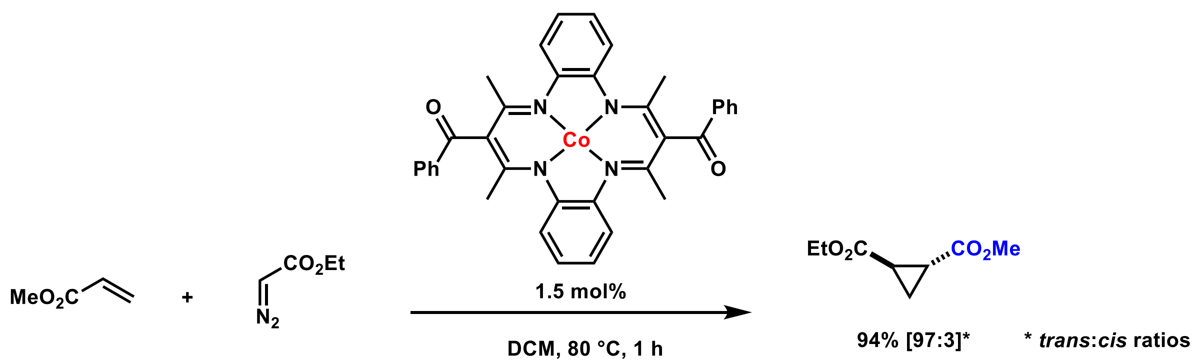
3. Co(III)-carbene or nitrene radicals

Co(III) Carbene (or Nitrene)-radical complexes

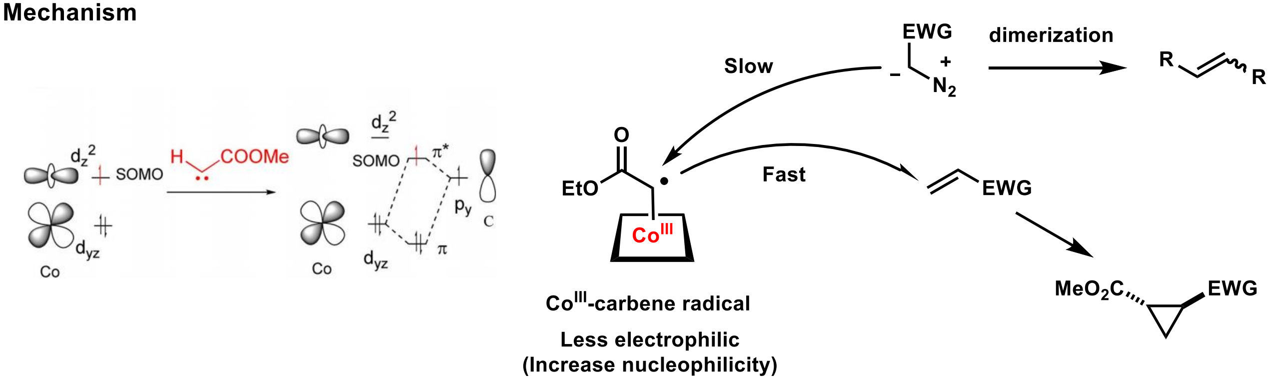


Behave as radicals rather than metallocarbenes or nitrenes

Cyclopropanation catalyzed by Co-porphyrin complexes (de Bruin, 2017)



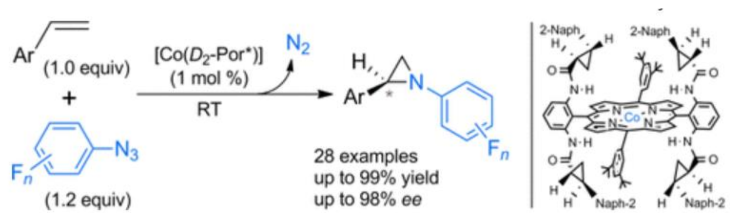
Mechanism



[11] de Bruin, B. et al, *ChemCatChem* **2017**, *9*, 1413.

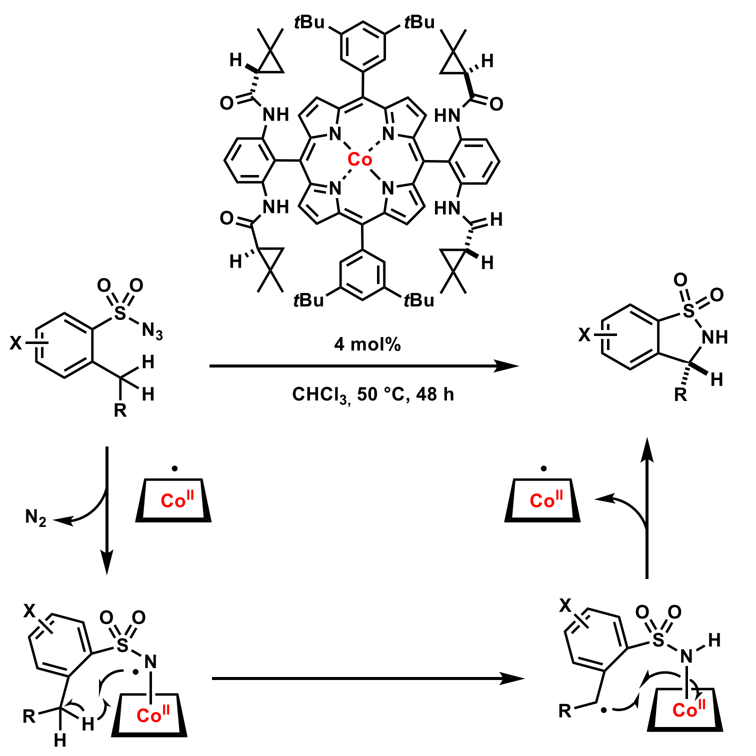
3. Co(III)-carbene or nitrene radicals

Asymmetric aziridination catalyzed by Co-porphyrin complexes (Zhang, 2013)

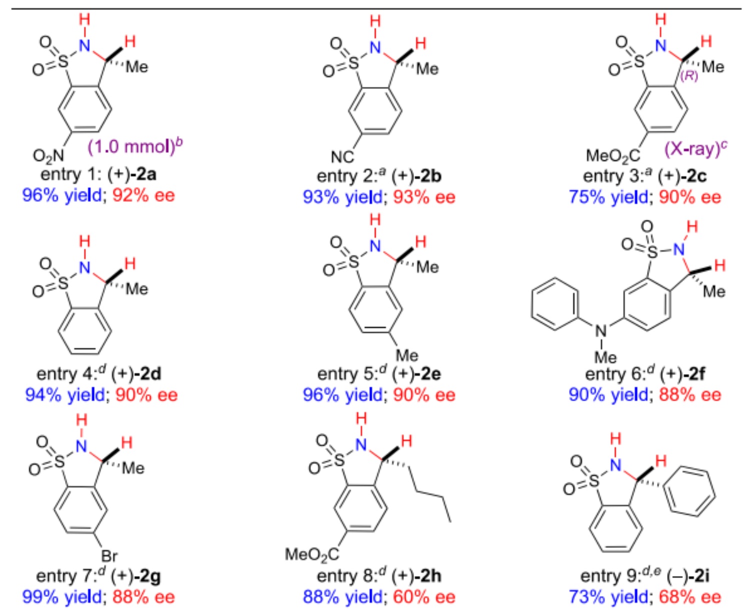


[12] Zhang, X. P. et al, *Angew. Chem. Int. Ed.* **2013**, *52*, 5309.

Asymmetric C-H amination catalyzed by Co-porphyrin complexes (Zhang, 2019)



Co^II nitrene radical

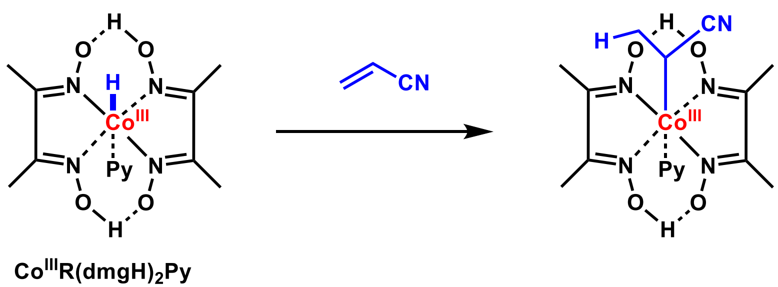


[a]Reactions were carried out in chloroform at 50 °C for 48 h on 0.10 mmol scale under N_2; [**1**] = 0.25 M. Isolated yields enantiomeric excess determined by chiral HPLC. [b]At 1.0 mmol scale. [c]Absolute configuration determined by X-ray analysis. [d]At 80 °C. [e]In chlorobenzene.

[13] Zhang, X. P. et al, *J. Am. Chem. Soc.* **2019**, *141*, 18160.

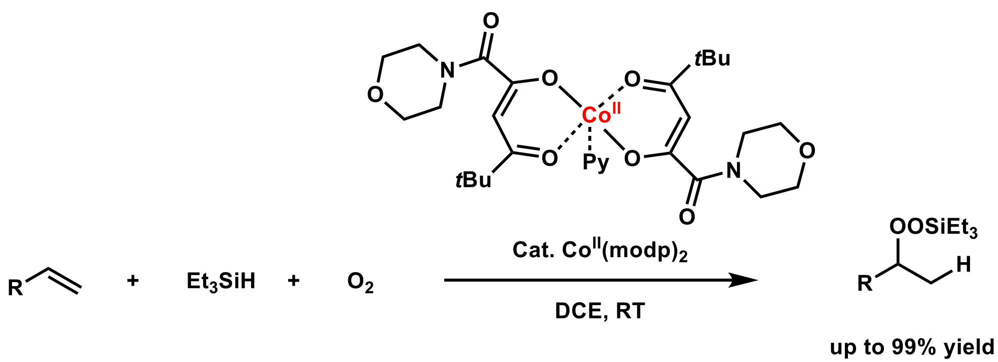
4. Hydrocobaltation

Hydrocobaltation (Schrauzer, 1967)



[14] Schrauzer, G. N. et al, *J. Am. Chem. Soc.* **1967**, *89*, 1999.

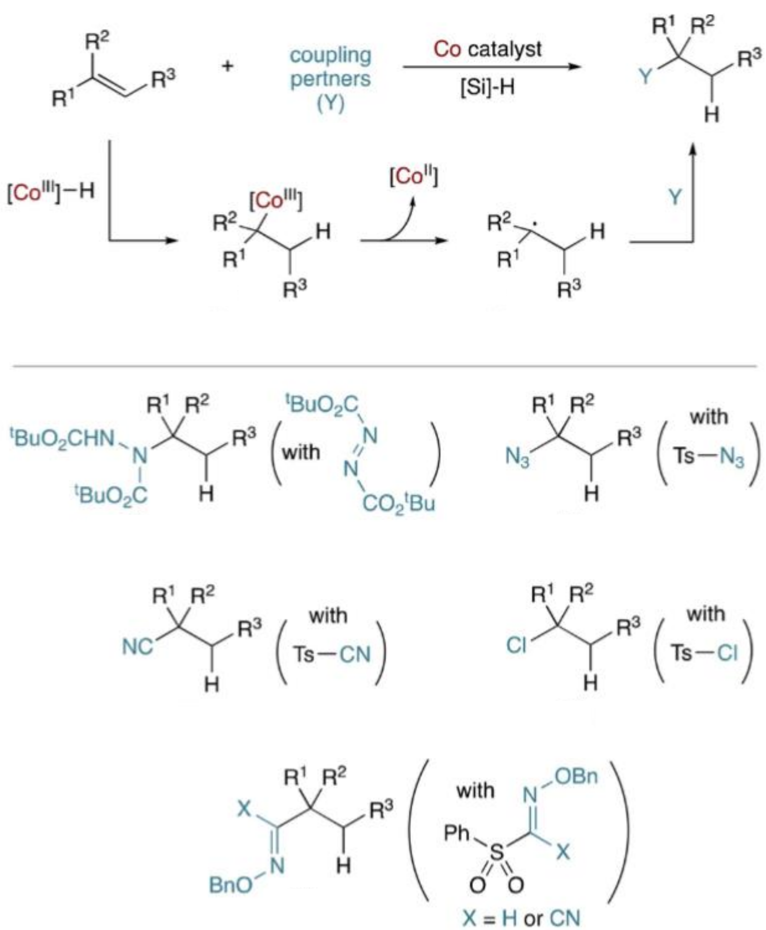
Seminal work for hydrofunctionalization *via* hydrocobaltation (Isayama and Mukaiyama, 1989)



[15] Isayama, S. et al, *Chem. Lett.* **1989**, *18*, 573.

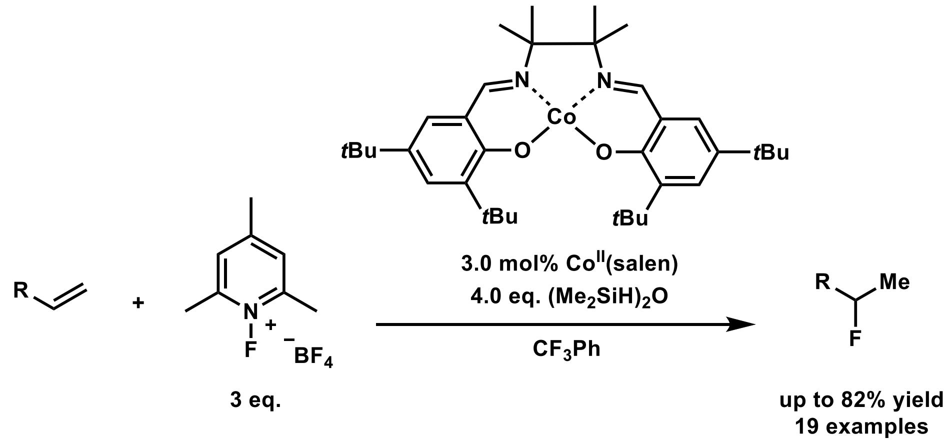
4. Hydrocobaltation

Hydrofunctionalizations (Carreira)



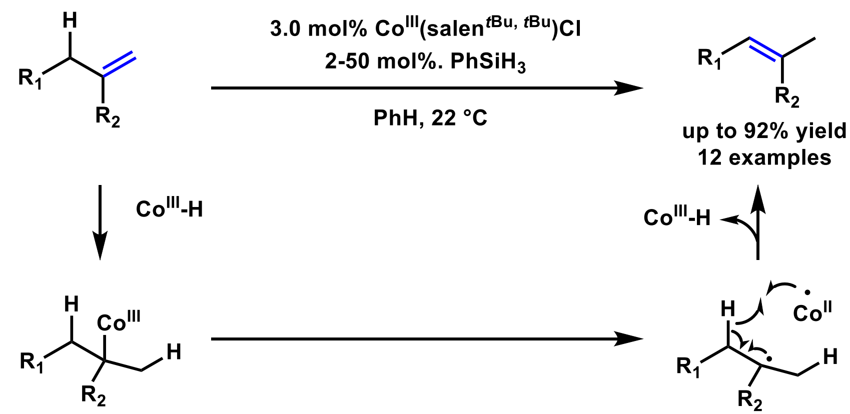
[16] a) Carreira, E. M. et al, *J.* Am. *Chem. Soc.* **2004**, 126, 5676. b) Carreira, E. M. et al, *J.* Am. *Chem. Soc.* **2005**, 127, 8294. c) Carreira, E. M. et al, *Angew. Chem. Int.* Ed. **2007**, 46, 4519. d) Carreira, E. M. et al, *Angew. Chem. Int. Ed.* **2008**, 47, 5758. e) Carreira, E. M. et al, *J.* Am. *Chem. Soc.* **2009**, 131, 13214.

Hydrofluorination (Shigehisa and Hiroya, 2013)



[17] Shigehisa, H. et al, *Org. Lett.* **2013**, 15, 5158.

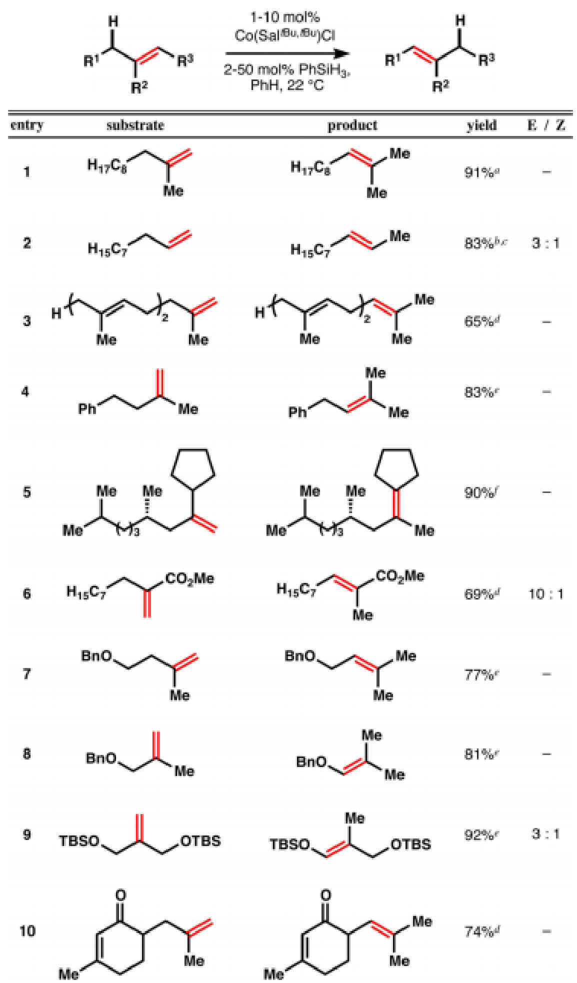
Isomerization of alkenes (Shenvi, 2014)



[18] Shenvi, R. A. et al, *J.* Am. *Chem. Soc.* **2014**, 136, 16788.

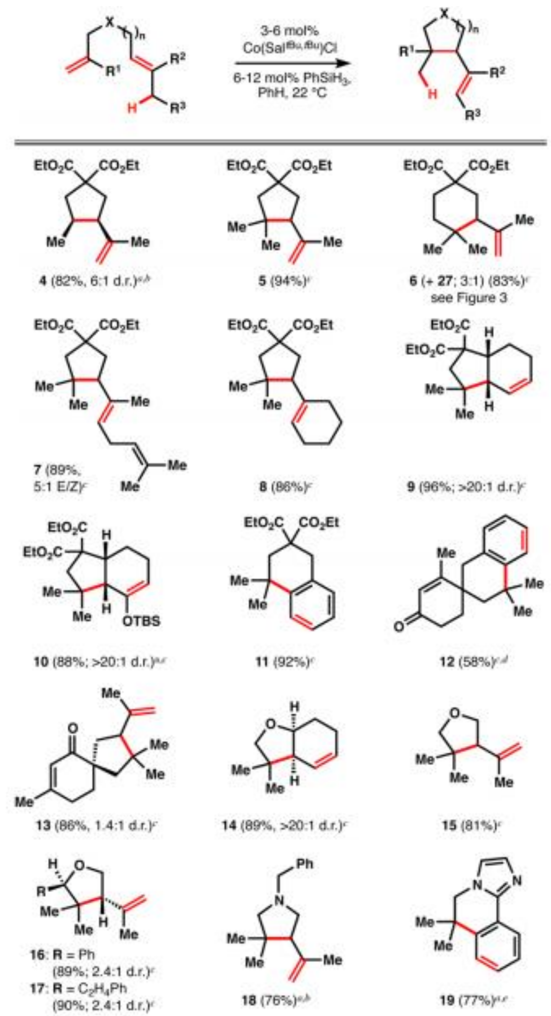
4. Hydrocobaltation

Isomerization of alkenes (Shenvi, 2014)



[a]2 mol% [Co], 2 mol% [Si]. [b]10 mol% [Co], 50 mol% [Si] at 60 °C. [c]86:14 2-decene:decenes. [d]5 mol% [Co], 10 mol% [Si]. [e]3 mol% [Co], 6 mol% [Si]. [f]1 mol% [Co], 2 mol% [Si].

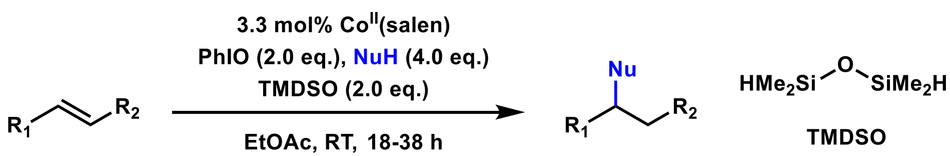
Diene cycloisomerization

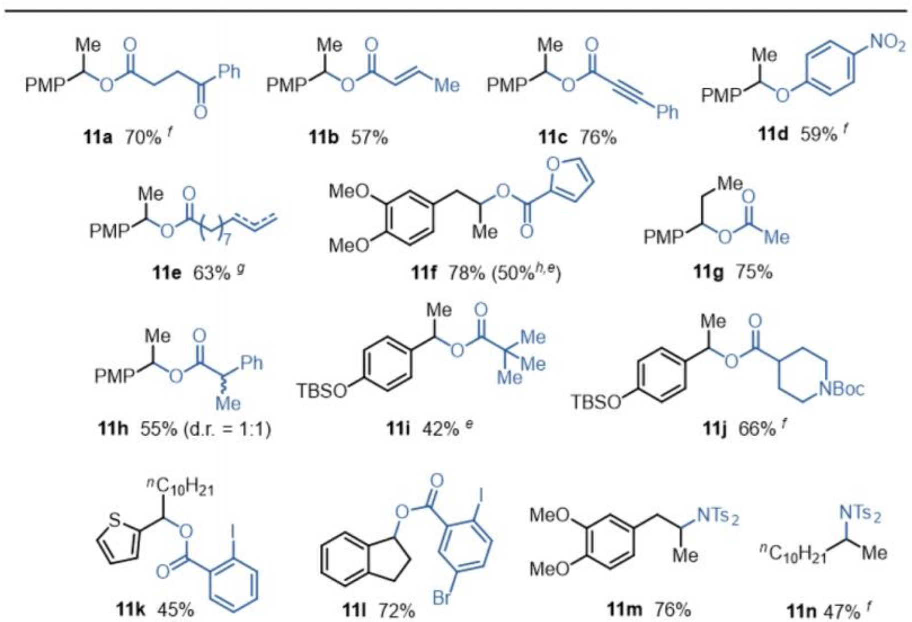


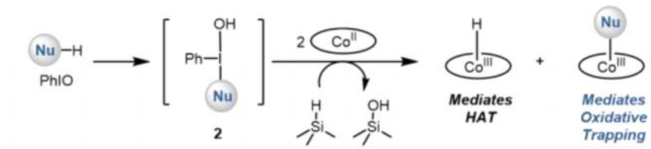
[a]At 60 °C. [b]5 mol% [Co], 10 mol% [Si]. [c]3 mol% [Co], 6 mol% [Si]. [d]at 100 °C. [e]6 mol% [Co], 12 mol% [Si]. [f]Stereoisomer tentatively assigned by NOE.

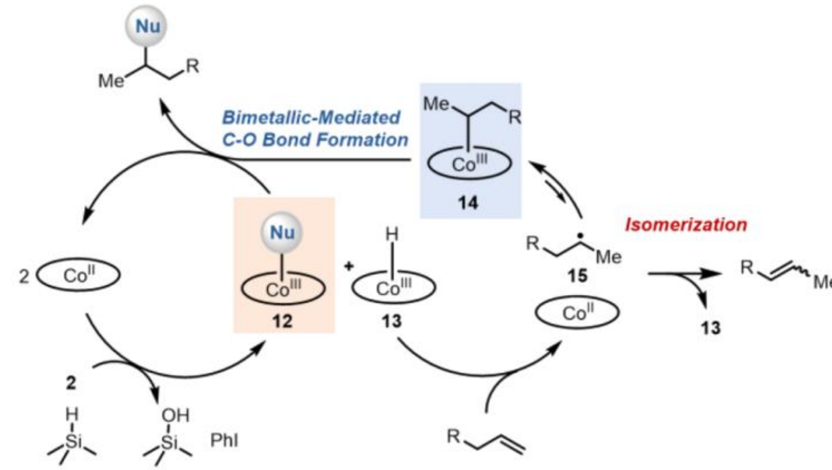
4. Hydrocobaltation

Hydrofunctionalization of alkenes trapping Co-Nu intermediates (Zhu, 2019)





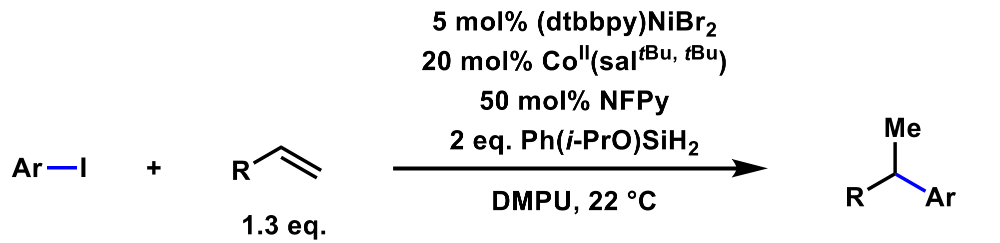




[19] Zhu, R. et al, *J.* Am. *Chem. Soc.* **2019**, *141*, 7250.

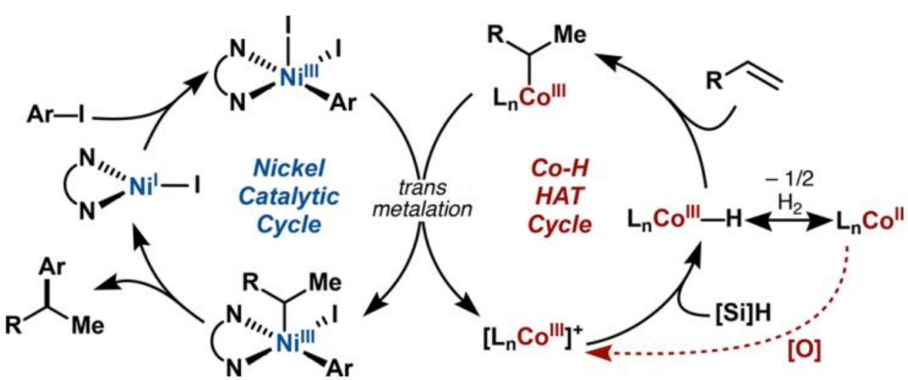
4. Hydrocobaltation

Hydroarylation catalyzed by Ni/Co complexes (Shenvi, 2016)

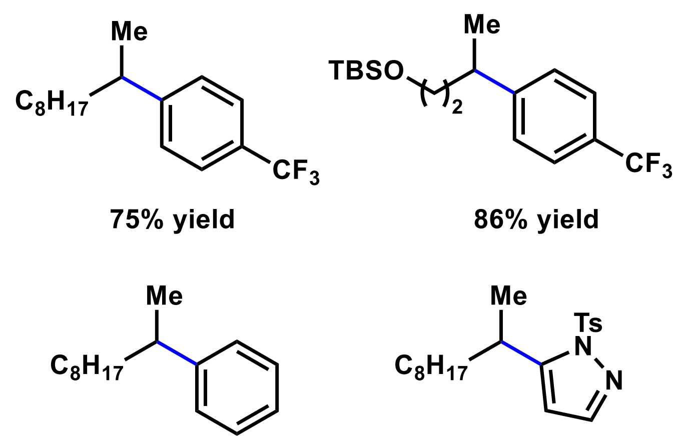


up to 86% yield
34 examples

Plausible mechanism



Selected examples



75% yield

86% yield

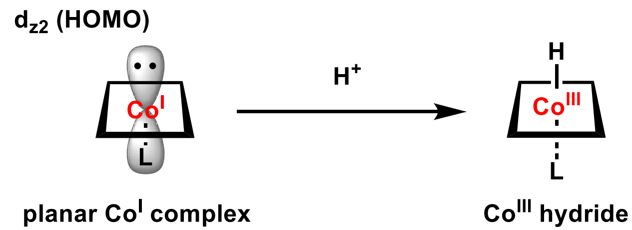
55% yield

67% yield ...etc

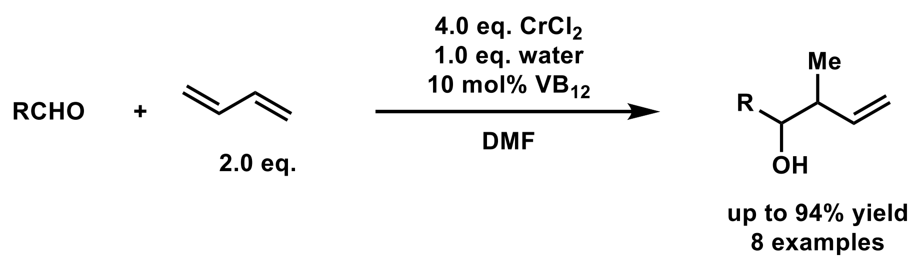
[20] Shenvi, R. A. et al, *J.* Am. *Chem. Soc.* **2016**, *138*, 12779.

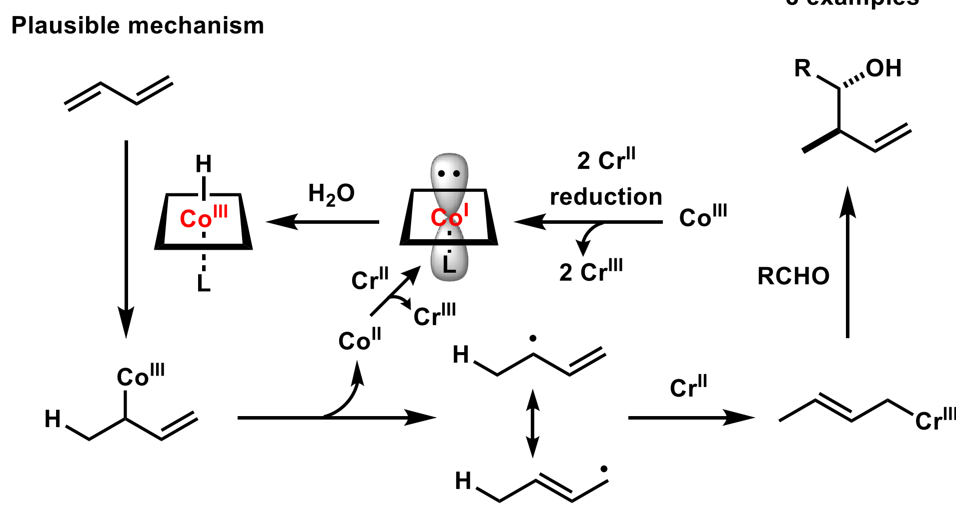
5. Co(I) bases

Co^{III}-Hydride from Co^{I} bases



Three-component coupling using Co^{III}-hydride (Takai, 1998)

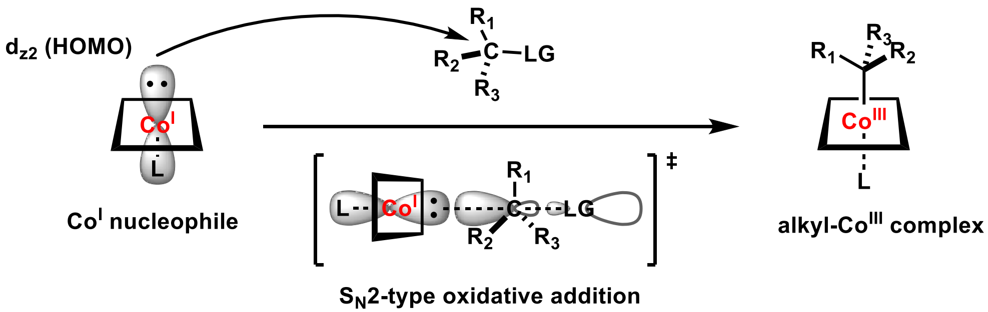


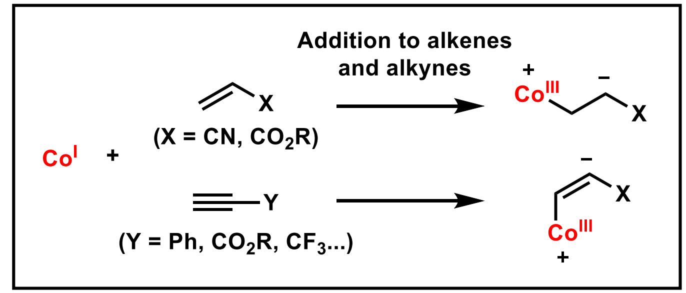


[21] Takai, K. et al, *J. Org. Chem.* **1998**, *63*, 6450.

6. S_N2-type oxidative addition

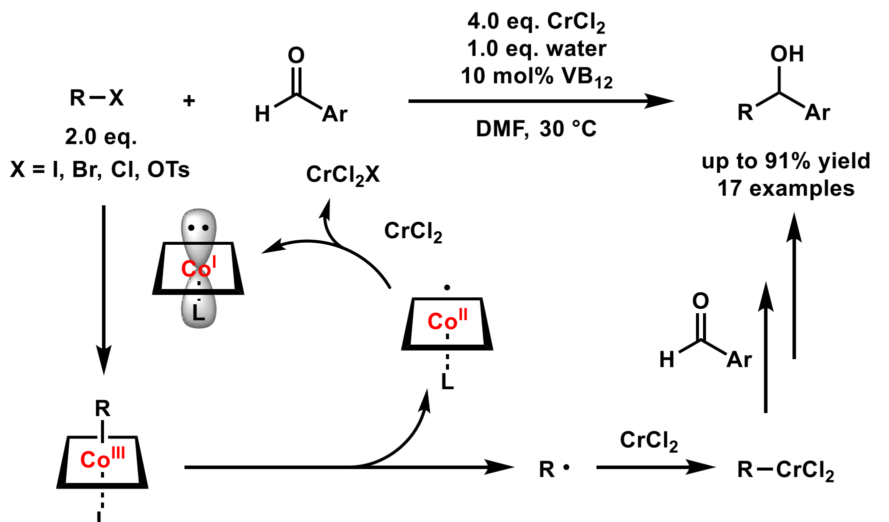
Co^I nucleophile





[22] Gupta, B. D. et al, *Inorg. Chim. Acta.* **1988**, *146*, 209.

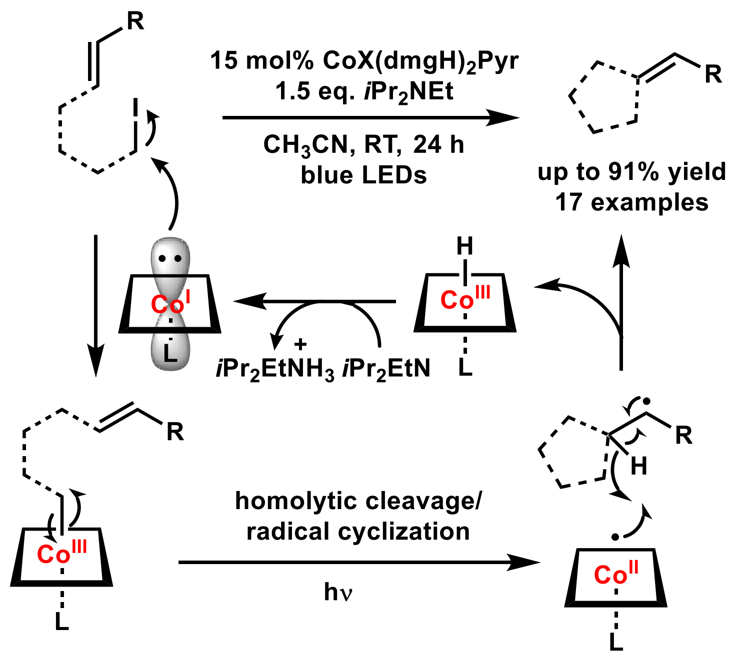
Seminal work for the use of nucleophilic Co^I catalyst (Takai and Utimoto, 1989)



[23] Takai, K. et al, *J. Org. Chem.* **1989**, *54*, 4732.

6. S_N2-type oxidative addition

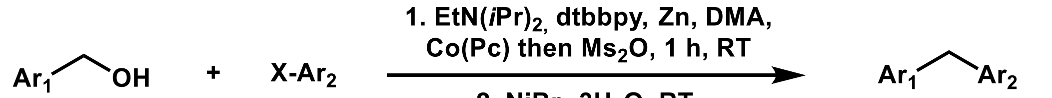
Intramolecular Heck reaction of alkenes using nucleophilic Co^{I} catalyst (Carreira, 2011)



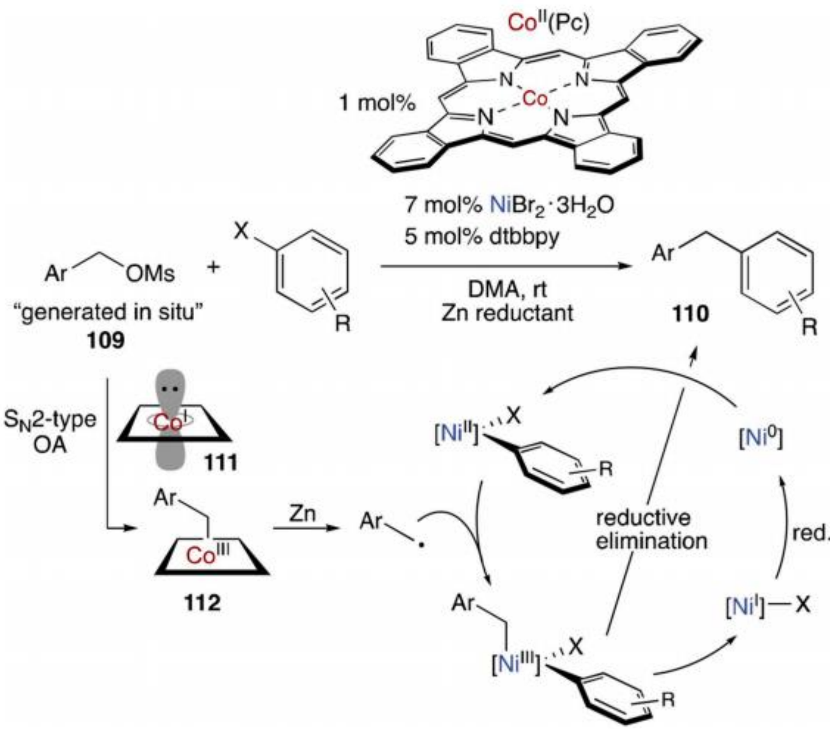
[24] Carreira, E. M. et al, *Angew. Chem. Int. Ed*. **2011**, *50*, 11125.

6. S_N2-type oxidative addition

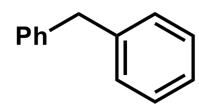
Cross-coupling using nucleophilic Co^{I} catalyst (Weix, 2015)



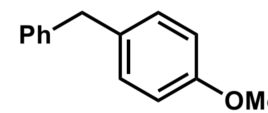
up to 88% yield
17 examples



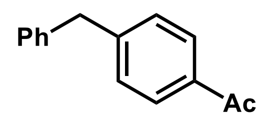
Selected examples



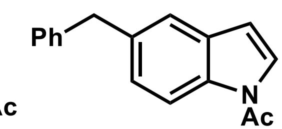
X = Br, 80% yield
X = I, 73% yield



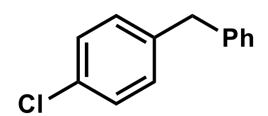
X = Br, 50% yield
X = I, 70% yield



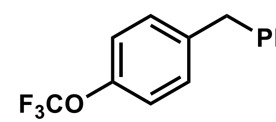
X = I, 71% yield



X = Br, 52% yield



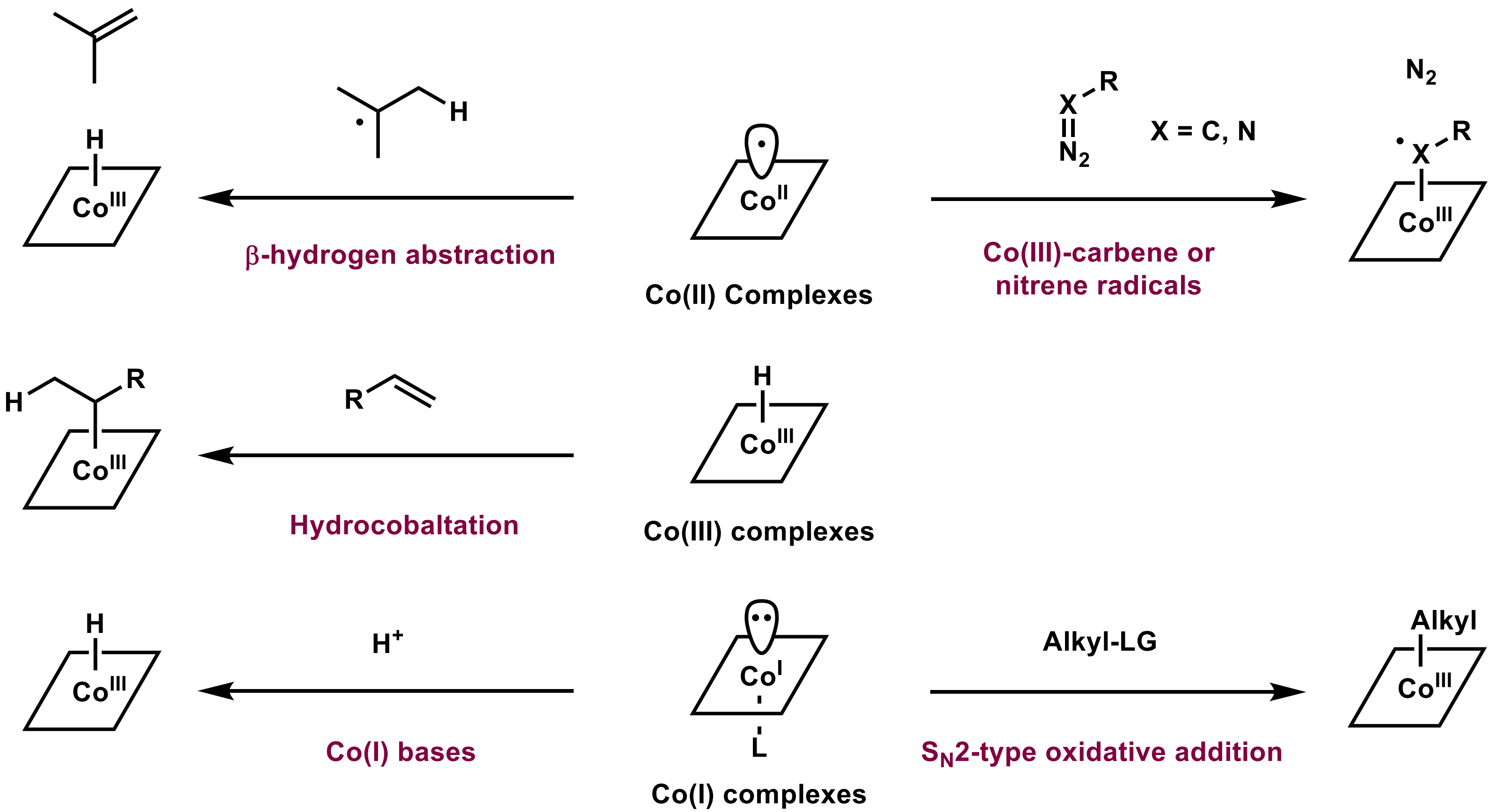
X = Br, 81% yield



X = Br, 78% yield

[25] Weix, L. et al, *Chem. Sci.* **2015**, *6*, 1115.

7. Conclusion



EPFL

(LSPN)
LABORATOIRE DE SYNTHESE
ET PRODUITS NATURELS

Thank you for your time and attention.

Takuji Fujii
Group Seminar 21/01/2022
EPFL-ISIC-LSPN
Jieping Zhu Group

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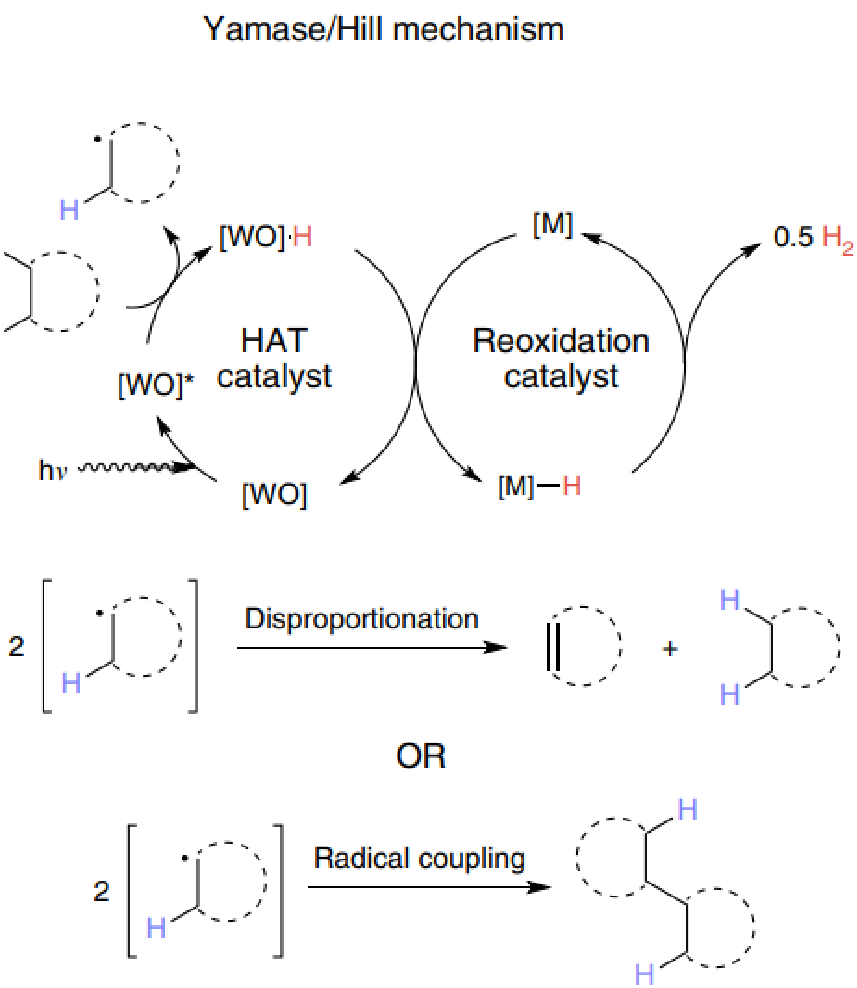
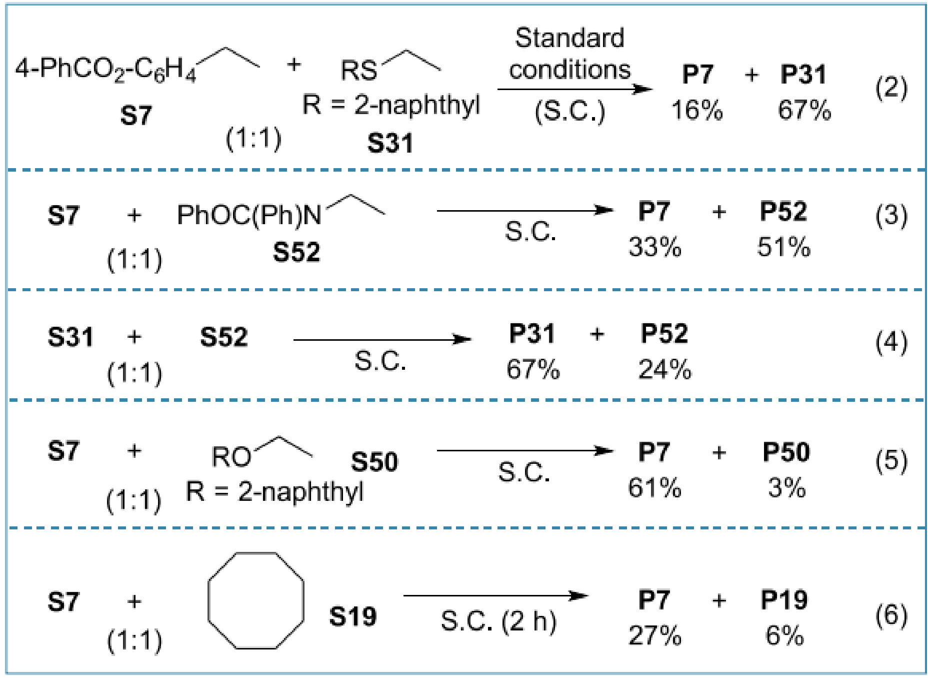
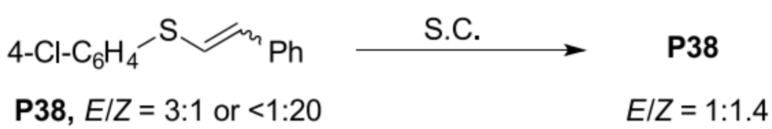

Yamase/Hill mechanism
H
H
H
[WO]·H
[M]
0.5 H2
HAT
catalyst
Reoxidation
catalyst
[WO]*
hν
[WO]
[M]—H
2
H
Disproportionation
+
H
H
OR
2
H
Radical coupling
H
H



Reactivity order: thioether, amide, acryl alkane, ether, cycloalkane



Photoisomerization under the reaction condition