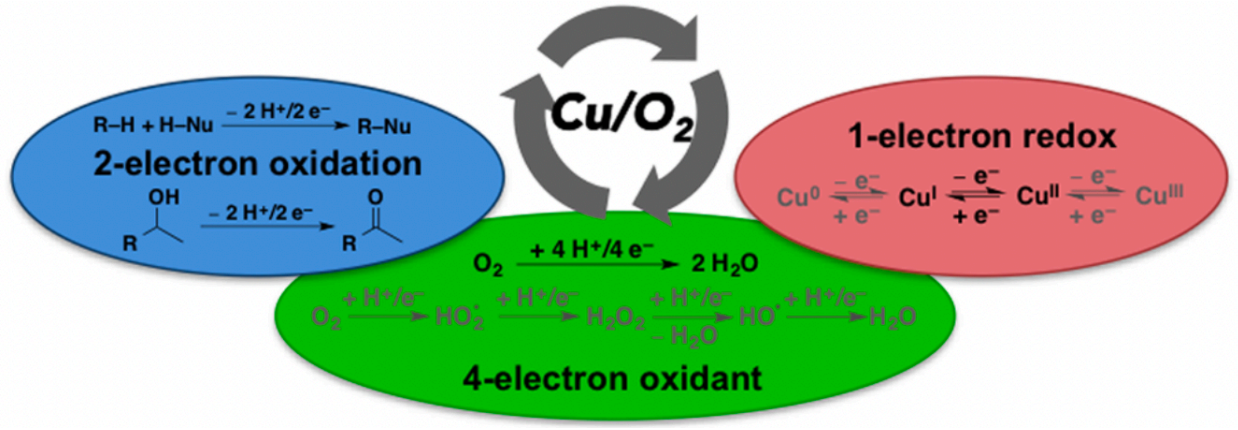
Copper–Catalyzed Aerobic Oxidative Reaction



2023/10/28 (Sat)
SHUNKI Matsuyama

Contents

1. Introduction

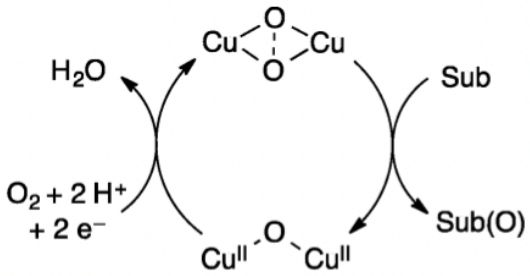
1-1) Aerobic Oxidation

Features

O_2 Low Toxicity Low Cost Natural Abundance

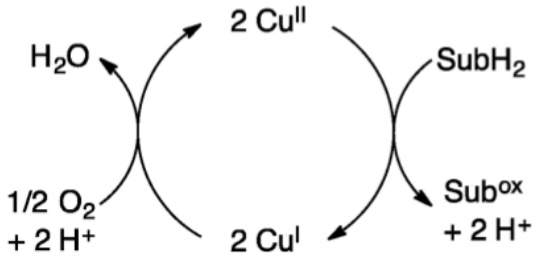
Reaction Types[a]

oxygenase-type



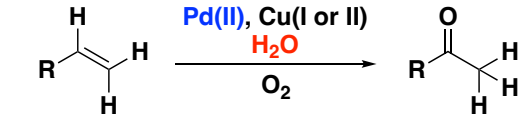
directly incorporate oxygen atoms into the organic molecule

oxidase-type



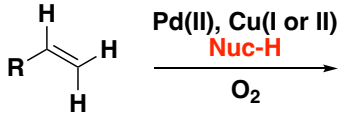
couple diverse oxidation reactions to the reduction of O_2 to water or hydrogen peroxide

Wacker Oxidation[b]

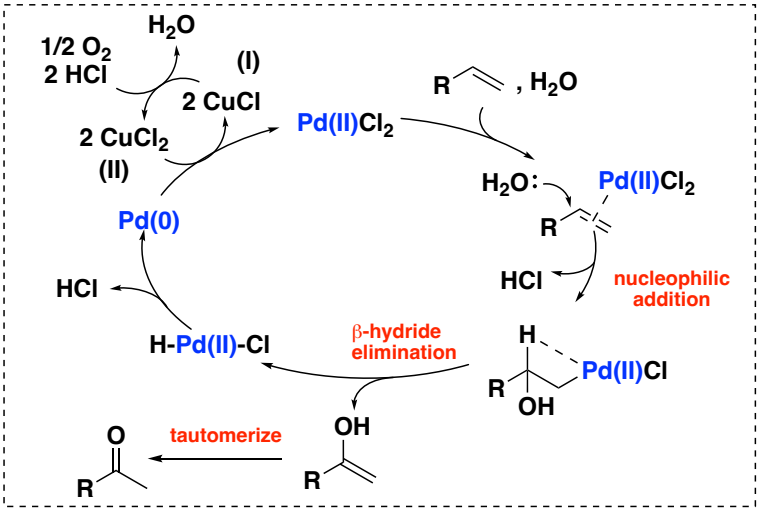


terminal alkene

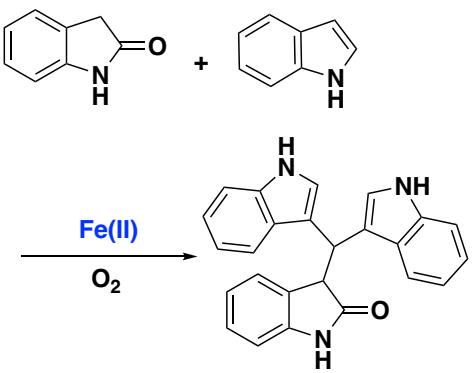
Wacker-type oxidation

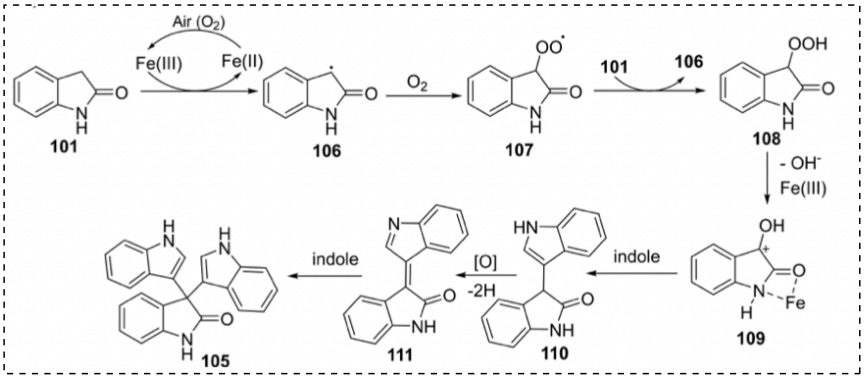


terminal alkene



Aerobic Oxidative Alkylation with Fe Catalysis[c]





(a) Hayaishi, O. et al. *J. Am. Chem. Soc.* **1955**, 77, 5450-5451.
(b) Smidt, J.; Sieber, R. *Angew. Chem.* **1959**, 1, 176.
(c) Xu, D-Z. at al. *Angew. Chem.* **2020**, *132*, 3904–3908.

1. Introduction

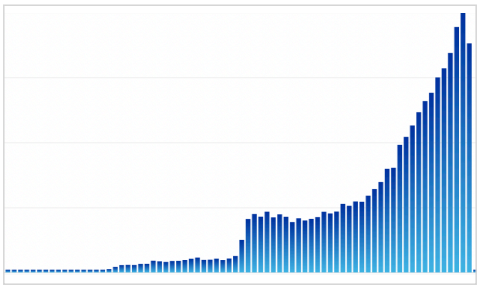
1-2) Copper Catalysis

29
Cu
copper
63.546

Electron confiduration: [Ar] $3d^{10}$ $4s^1$

Period numver: 4 **Group number: 11**

Group name: transition metal



reports about Cu and molecular oxygen (1950-2023)

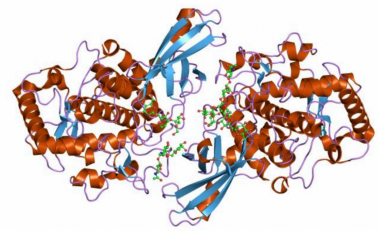
Superiority (compared to other 4d, 5d metal)

Low cost Low toxicity High occurrence in the earth's crust

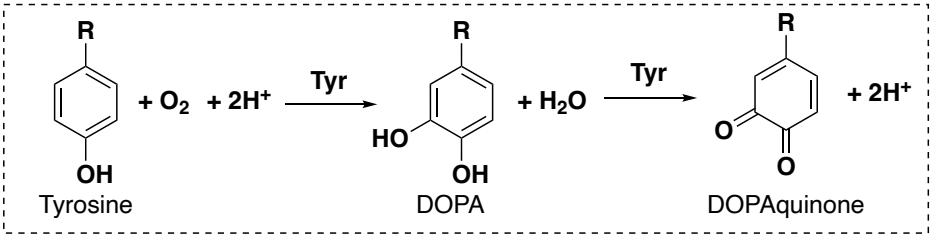
Features

Cu(0), Cu(I), Cu(II), Cu(III) Lewis acid interactions π-coordination

Copper-Containing Enzymes[1]



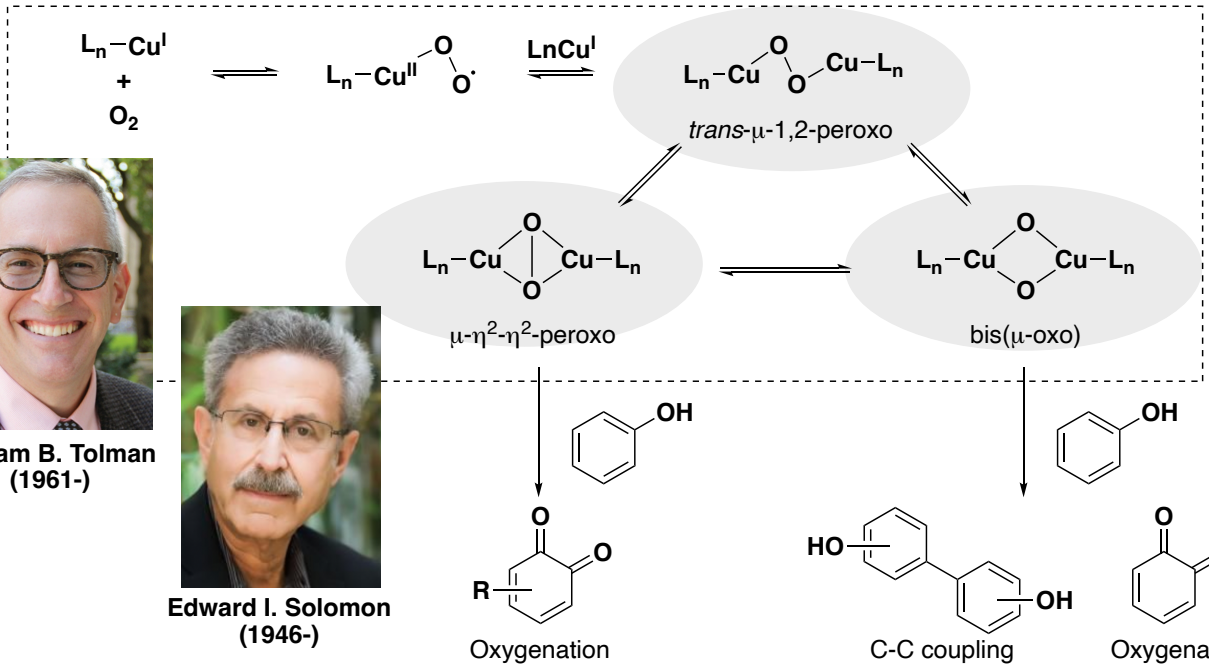
Tyrosinase



Diverse Biochemical Processes

Melanin production, protection from pathogens, hydrocarbon metabolism, etc.

1-3) Cu_2-O_2 Complex[2]

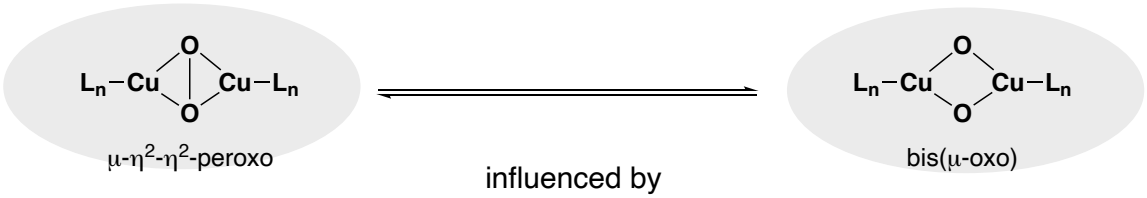


William B. Tolman (1961-)

Edward I. Solomon (1946-)

1) Fujieda, N.; Ito, S. *J. Jpn. Biochem. Soc.* **2021**, 93, 4, 521-525.
2) (a)*Chem. Rev.* **2004**, 104, 2, 1047–1076. (b)Ch*em. Rev.* **2014**, 114, 7, 3659–3853.

1. Introduction



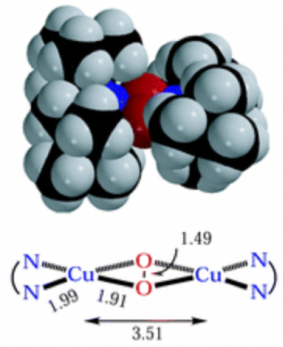
influenced by

the steric and electronics effects of the ligands,
the counter-ion on copper,
solvent, temperature

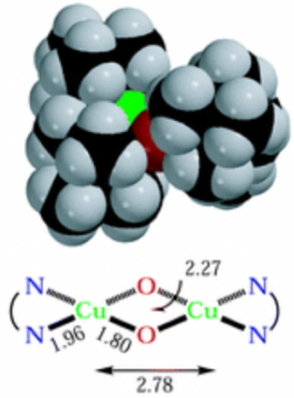
Ligand Steric Effects[a]

T. Daniel P. Stack
(1959-)

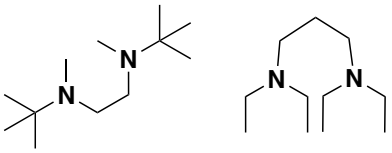
μ-η²-η²-peroxo

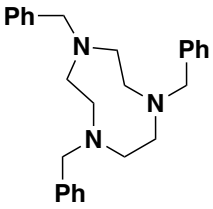


bis(μ-oxo)

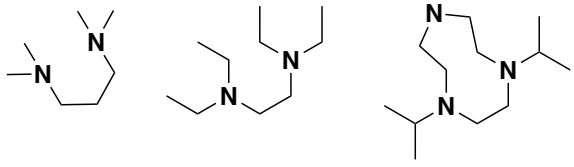


μ-η²-η²-peroxo

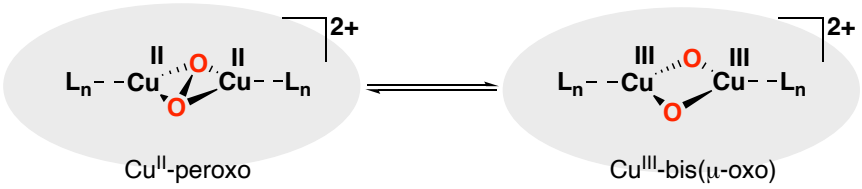


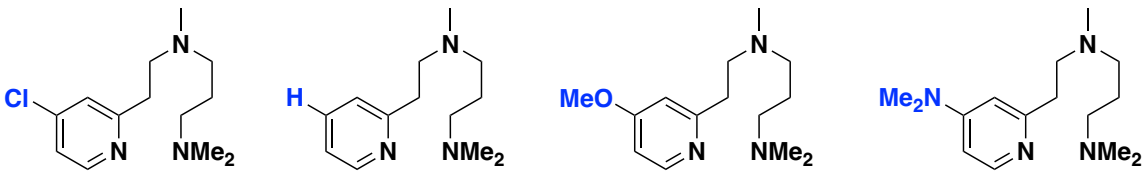


bis(μ-oxo)



Ligand Electronic Effects[b]

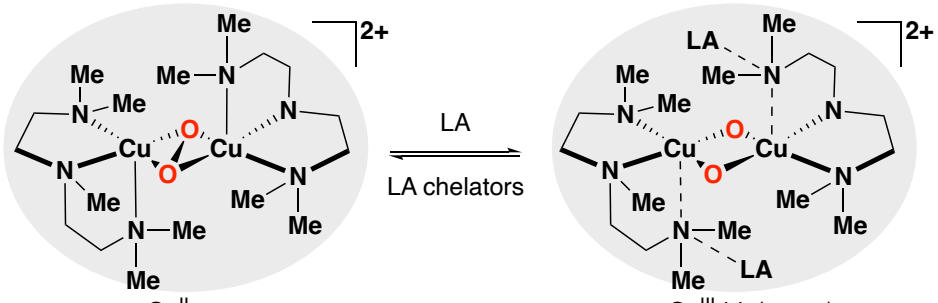


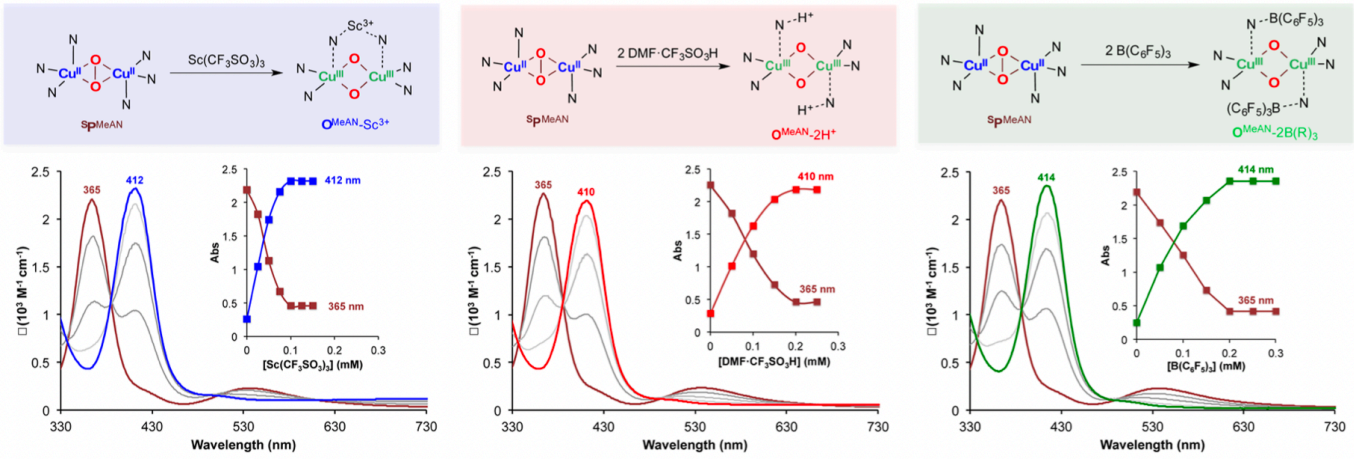


(a) (1) Stack, T. D. *Dalton Trans.* **2003**, *10*, 1881. (2) Tolman, W. B. *Acc. Chem. Res.* **1997**, 30, *6*, 227–237
(b) (1) Stack, T. D. et al. *J. Am. Chem. Soc.* **2006**, *128*, 2654. (2) Stack, T. D. et al. *J. Am. Chem. Soc.* **2006**, *128*, 9268.

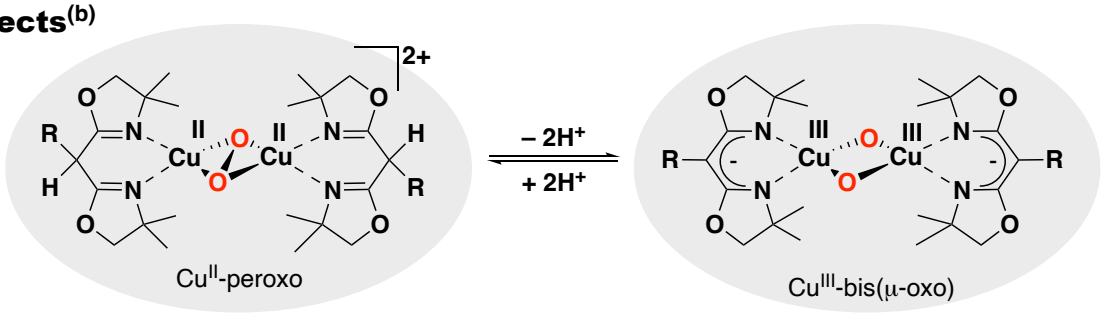
1. Introduction

Lewis Acid Additive Effects[a]

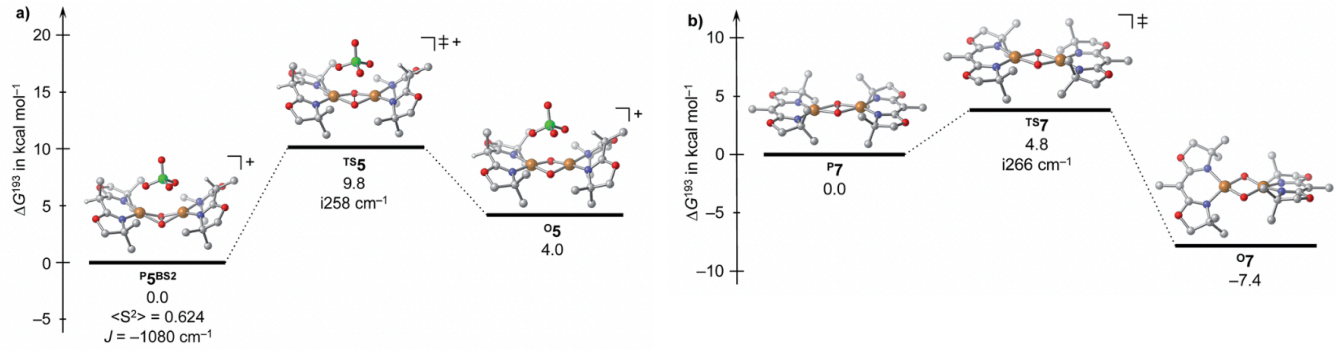




pH Effects[b]



(a) acidic condition **(b) neutrality condition**



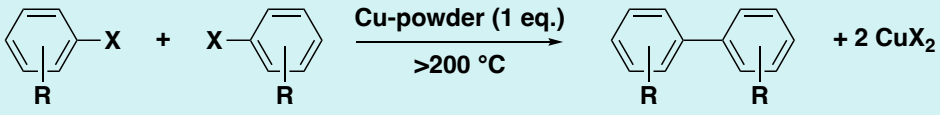
(a) Karlin, K. D. et al. *J. Am. Chem. Soc.* **2017**, *139*, 3186.
(b) Meyer, F. et al. *Chem. Sci.* **2017**, *8*, 3031.

2. Copper

2-1) Cu Catalyzed Reaction –Mechanism

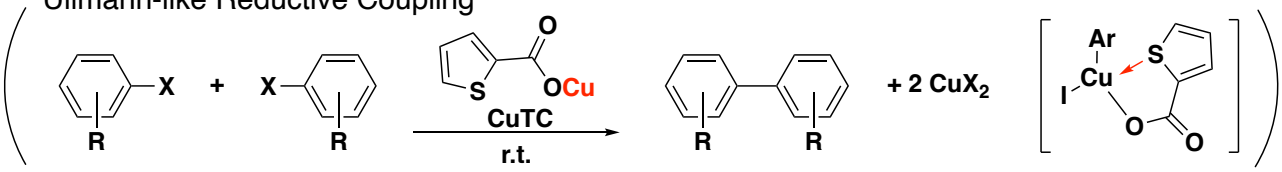
(a) Cu^{I} / Cu^{III} Catalytic Cycle
(b) Cu^{I} / Cu^{II} / Cu^{III} Catalytic Cycle
(c) Single Electron Transfer (Cu^{II} / Cu^{I})

Ullmann Coupling[a]

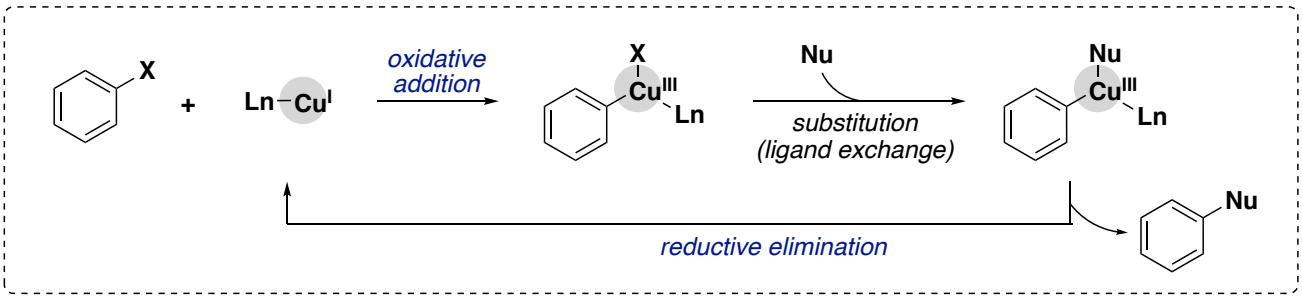


Fritz Ullman
(1875-1939)

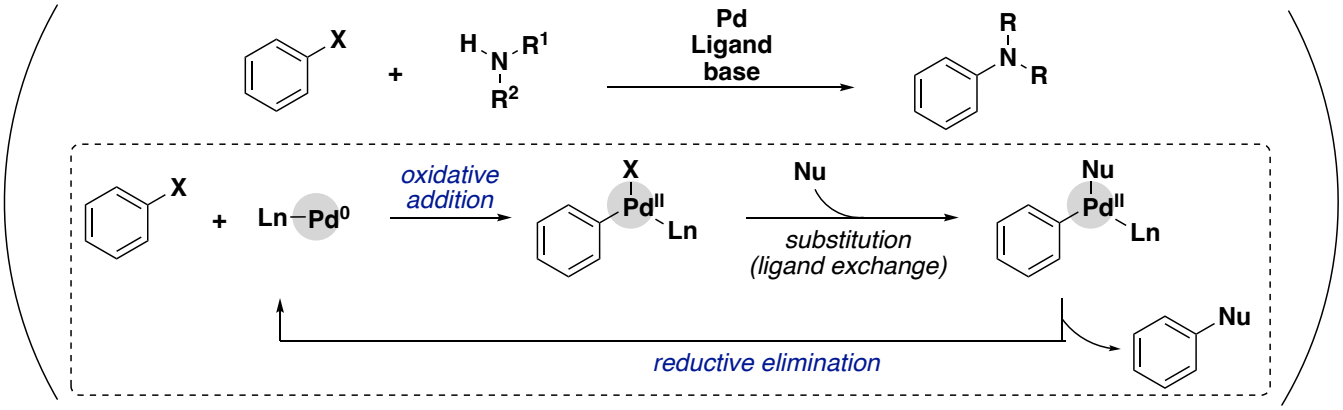
Ullmann-like Reductive Coupling



(a) Cu^{I} / Cu^{III} Catalytic Cycle[c]



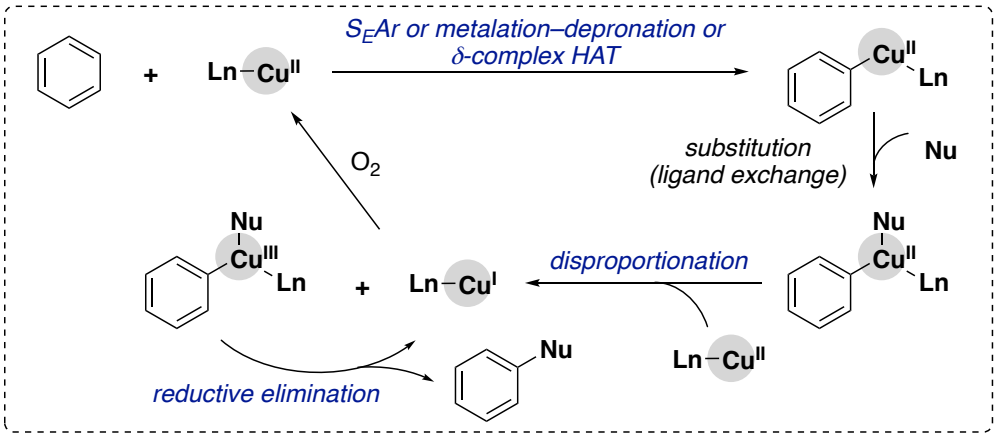
Buchwald–Hartwig reactions mediated by Pd

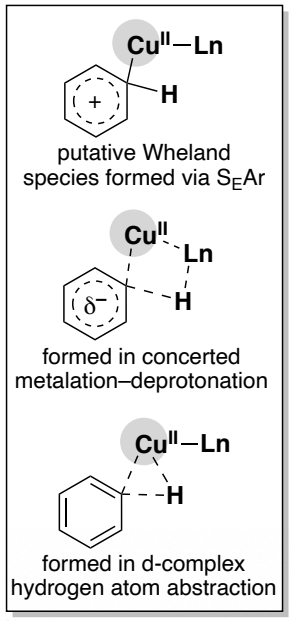


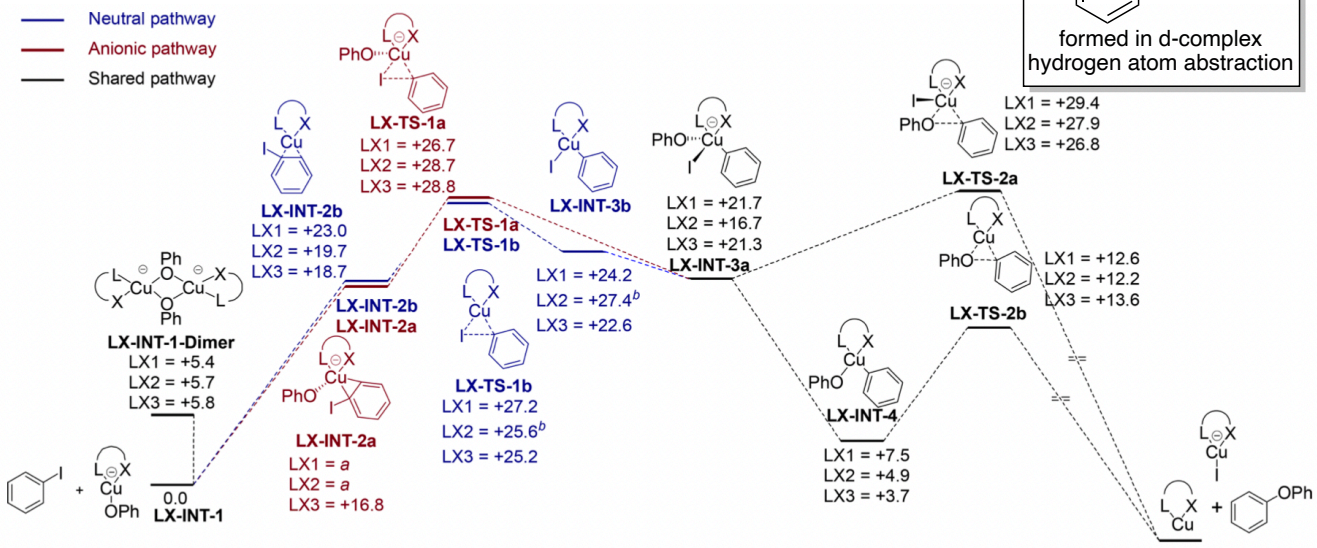
(a) Ullmann, F.; Bielecki, J. *Chem. Ber.* **1901**, *34*, 2174.
(b) Zheng, S.; Zhang, D.; Liebeskind, L. S. *J. Org. Chem.* **1997**, *62*, 2312.
(c) (1)Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994**. *116*, 5969. (2)Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**. *116*, 7901.

2. Copper

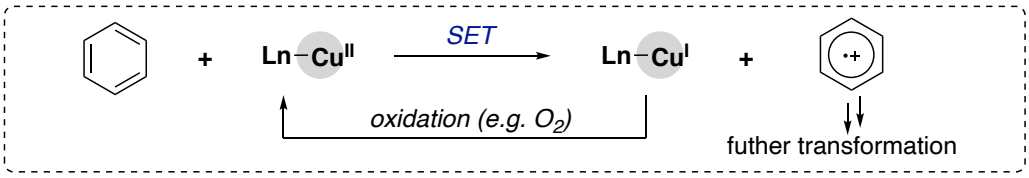
(b) Cu^{I} / Cu^{II} / Cu^{III} Catalytic Cycle[(a)]





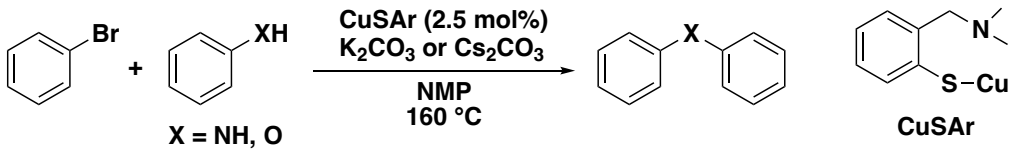


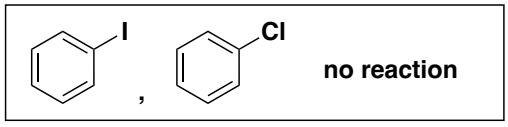
(c) Single Electron Transfer (Cu^{II} / Cu^{I})[(b)]



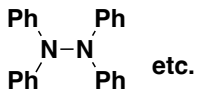
William A. Waters (1869-1948)

Coupling reaction of bromobenzene with nitrogen and oxygen nucleophiles[(c)]





radical scavenger



reaction: slowed down / stopped

a) (1)Mondal, S.* *ChemTexts* **2016**, *2*, 17. (2)Giri, R.; Brusoe, A.; Troshin, K.; Wang, J. Y.; Font, M.; Hartwig, J. F.* *J. Am. Chem. Soc.* **2018**, *140*, 793-806.
b) Casitas, A.; Ribas, X.* *Chem. Sci.* **2013**, *4*, 2301-2318.
c)Sperotto, E.; Klink, G. P. M.; Koten, G.*, Vries, J. G.* *Dalton Trans.*, **2010**, 39, 10338–10351.