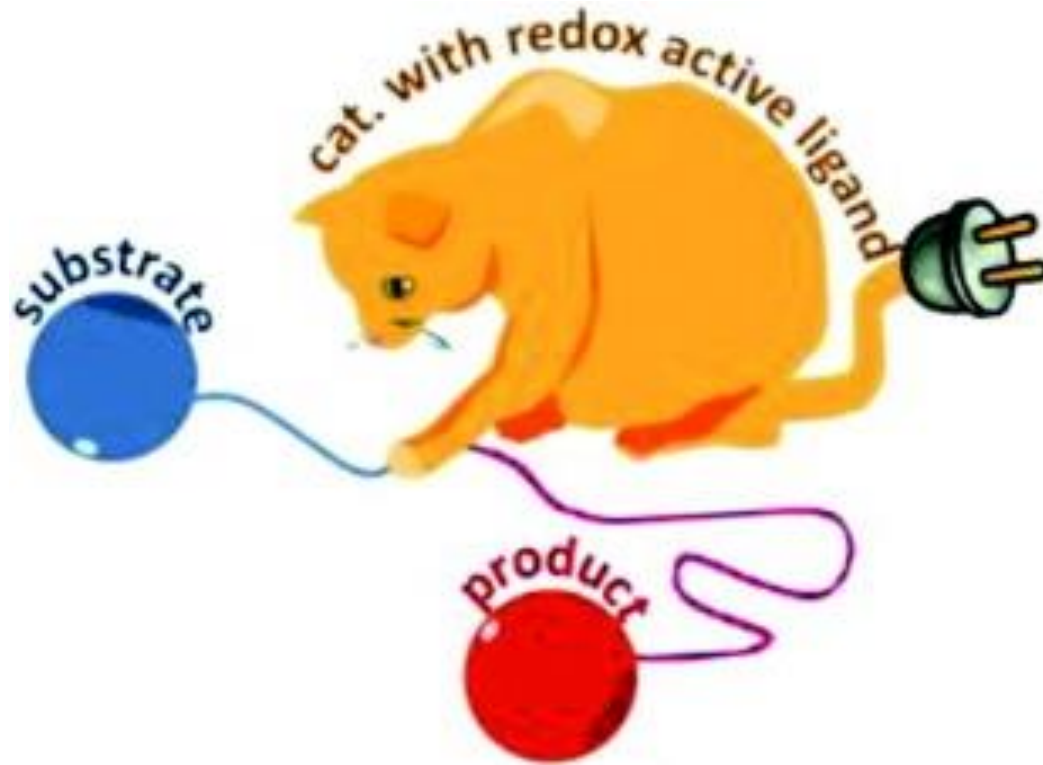


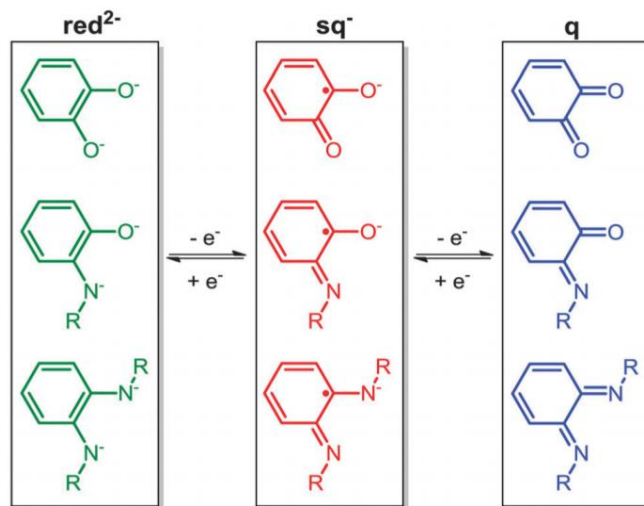
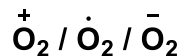
Redox-Active Ligands



Yu Lab Group Meeting
Pritha Verma
August 7, 2017

Introduction

- Classical behavior of a transition metal complex in a redox process involved oxidation or reduction of the metal, leaving the ligand unaffected
- In some cases, however, ligand can also participate in the redox process. Such ligands are referred to as “redox non-innocent” or “redox-active”
- Examples:



Metalloproteins

Definition

The “non-innocent” terminology was introduced in 1966 by Jorgensen:

“ligands are innocent when they allow oxidation states of the central atom to be defined”

Paul Chirik:

“In many cases, the term “noninnocent” has become synonymous with situations where the formal oxidation state, the one determined by a prescribed set of rules, differs from an oxidation state that is determined by experiment.”

H. B. Gray:

“Although we loved these ligands, by the end of the 1960s, we knew that they were **“guilty” as charged.**”

X-Ray crystallography, NMR, EPR, Mossbauer, Computational chemistry

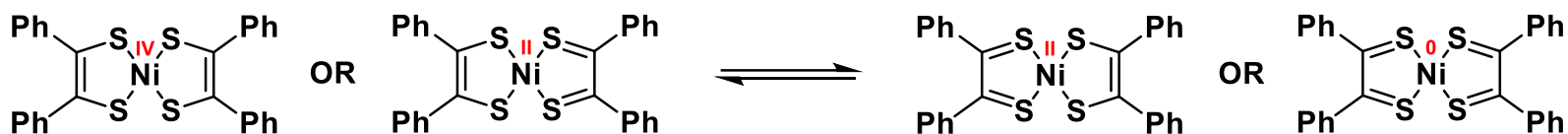
(1) Joergensen, C. K. *Coord. Chem. Rev.* **1966**, *1*, 164. (2) Eisenberg, R.; Gray, H. B. *Inorg. Chem.* **2011**, *50*, 9741.

(3) Chirik, P. J. *Inorg. Chem.*, **2011**, 9737.

Early Examples

Nickel dithiolene complexes (1960s)

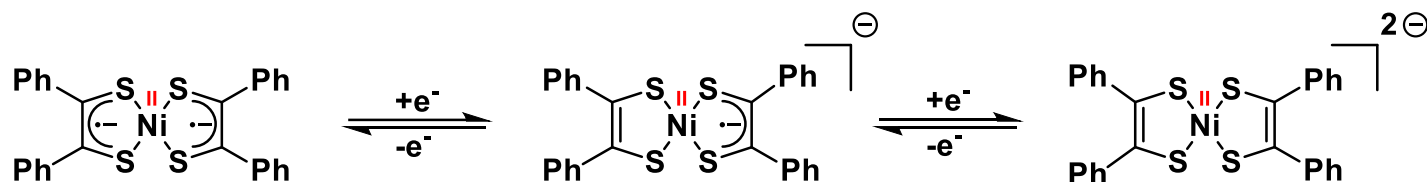
Assignment of Ni oxidation state proved to be problematic



Early Examples

Nickel dithiolene complexes (1960s)

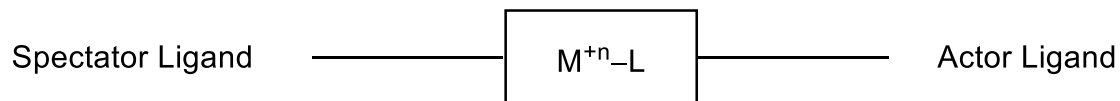
Electronic structure analysis revealed these complexes to be Ni(II) with each ligand bearing a radical



- Facile $1e^-$ transfer suggesting low reorganization energy
- Extensive ligand-metal mixing in the frontier orbitals (LFT was being developed during this time)
- Calculations showed that the frontier orbitals of such complexes are ligand-based rather than metal-based. Therefore, oxidation changes in such complexes occur at the ligand rather than at the metal center.

Redox-Active Ligands: Types of Reactivity

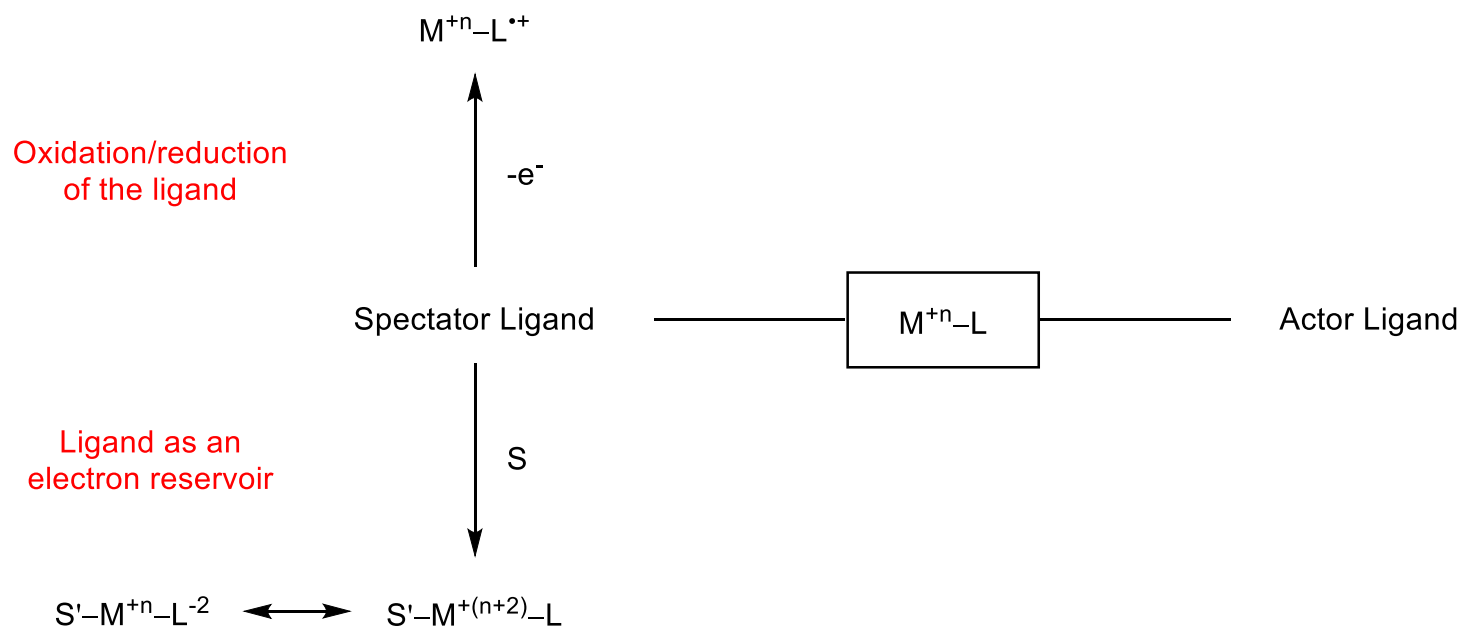
The ligand participates in the catalytic cycle only by accepting/donating electrons



The ligand actively participates in the formation/breaking of substrate covalent bonds

Redox-Active Ligands: Application Strategies

*Increased Lewis
acidity on the metal
(analogous for basicity)*

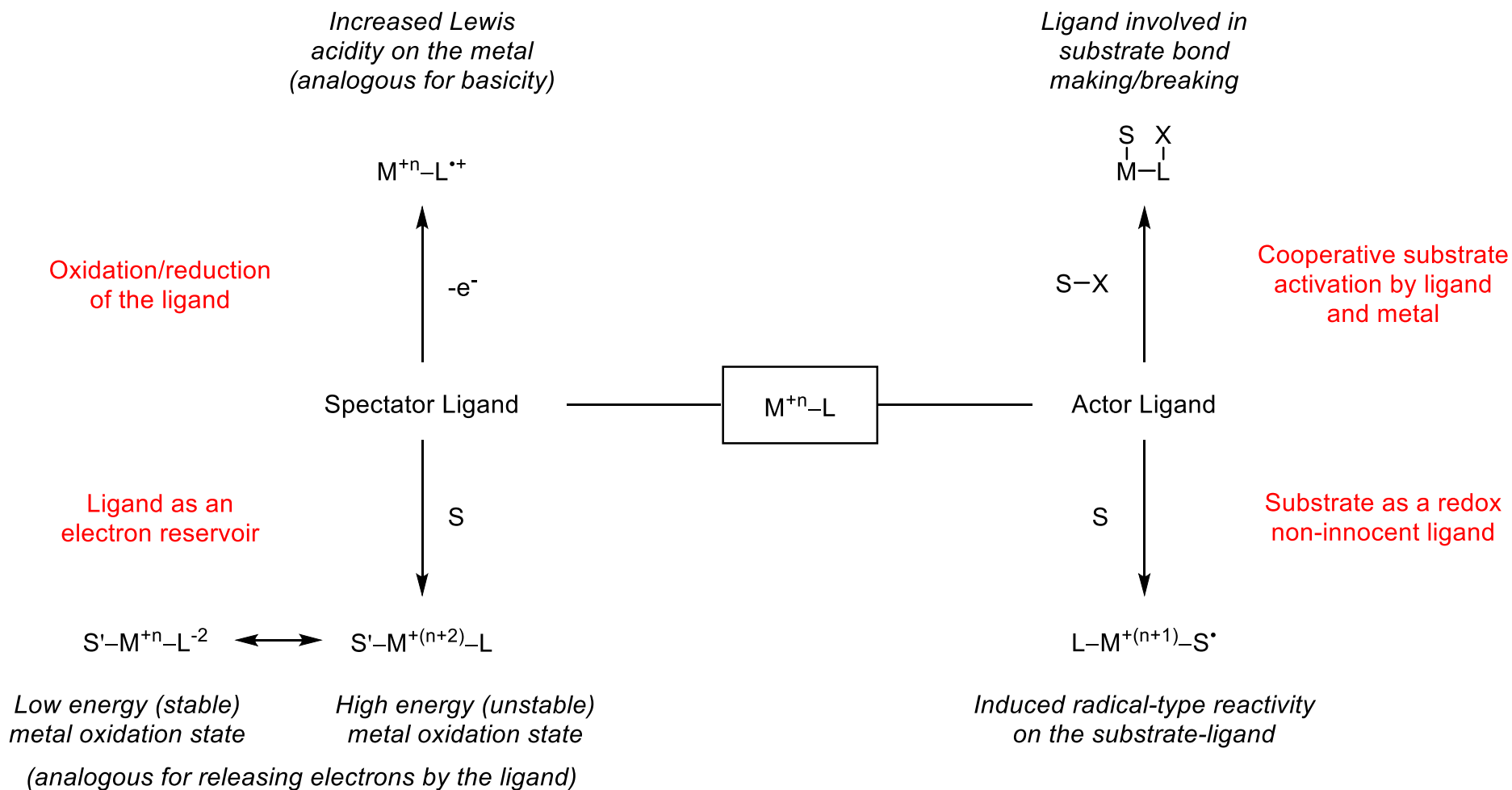


*Low energy (stable)
metal oxidation state*

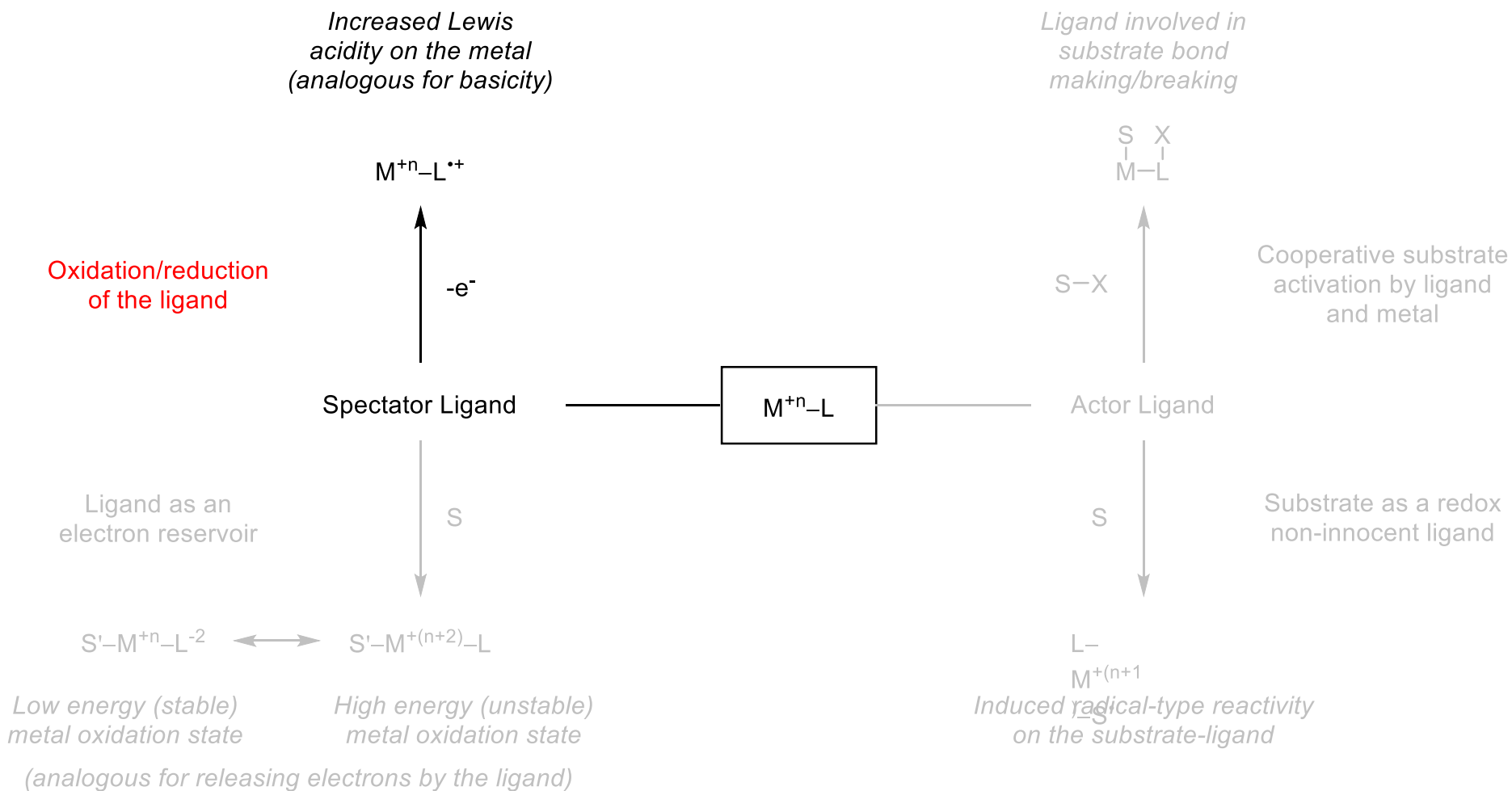
*High energy (unstable)
metal oxidation state*

(analogous for releasing electrons by the ligand)

Redox-Active Ligands: Application Strategies

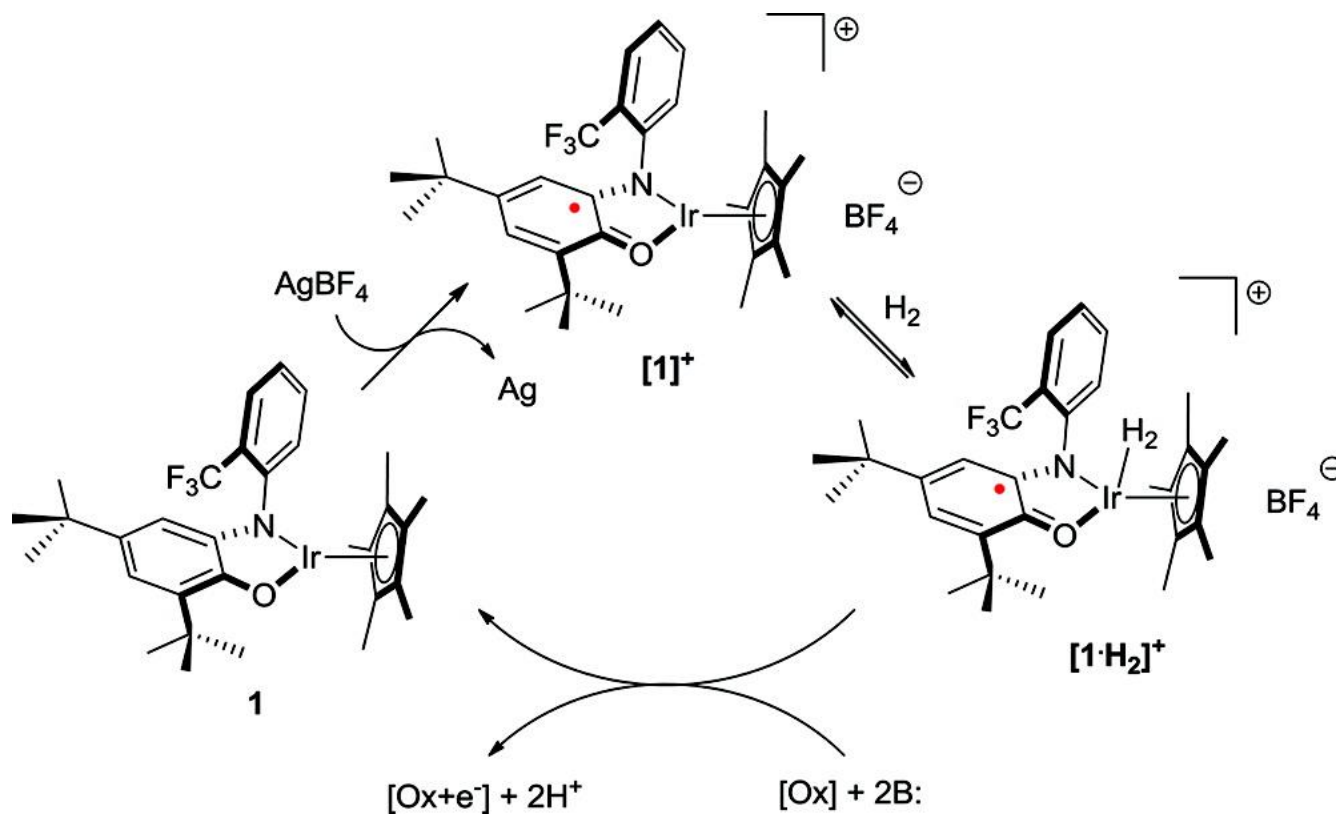


Redox-Active Ligands: Application Strategies



Oxidation of Dihydrogen

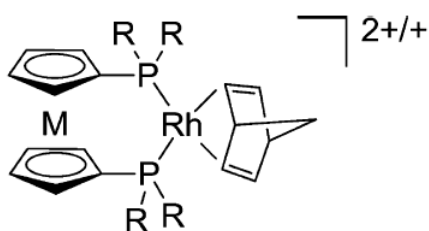
Oxidation of ligand leading to increased Lewis acidity of the metal



- Can uptake 3 eq H₂ in 1.5 hr

Olefin Hydrogenation

Reduction of ligand leading to an electron rich Rh(I)

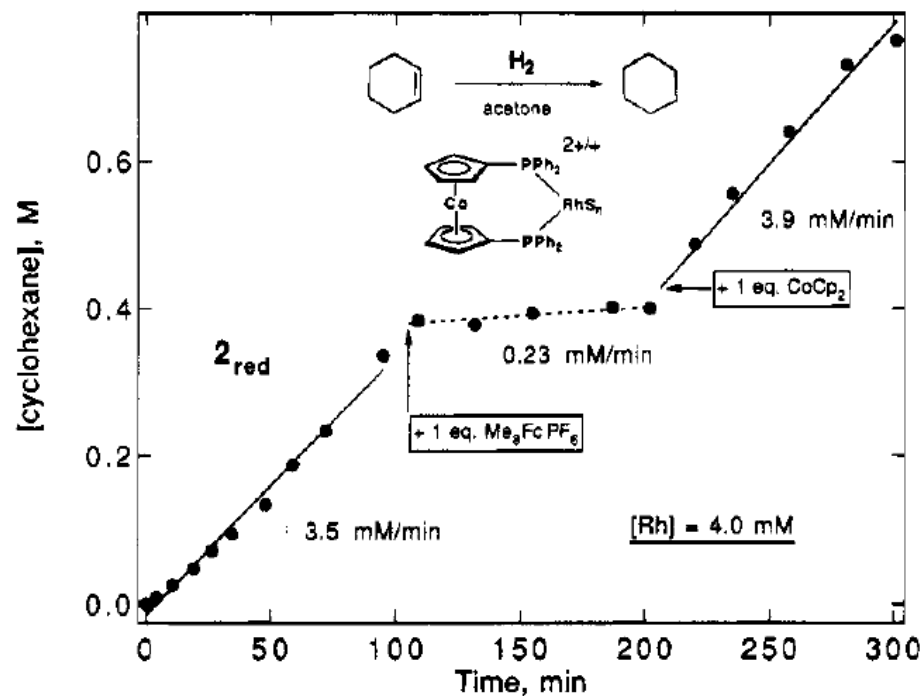


M = Fe; charge = +1

Changing R from Ph to ^tBu increases rate

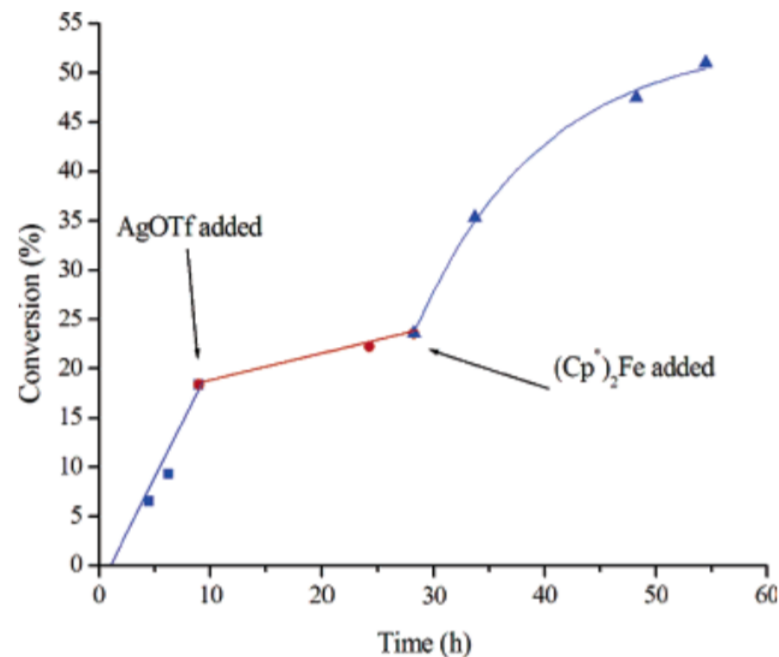
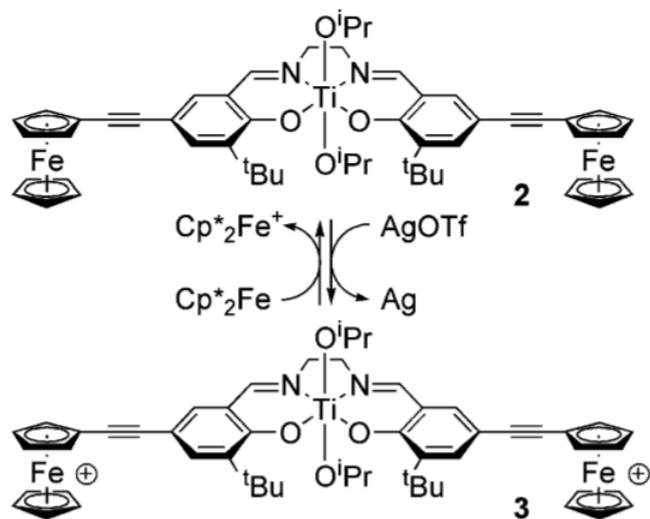
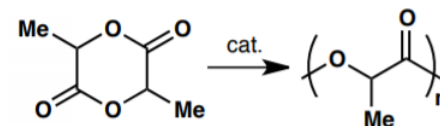
M = Co; charge = +1/+2

Reduced form is 16-times faster than the oxidized form

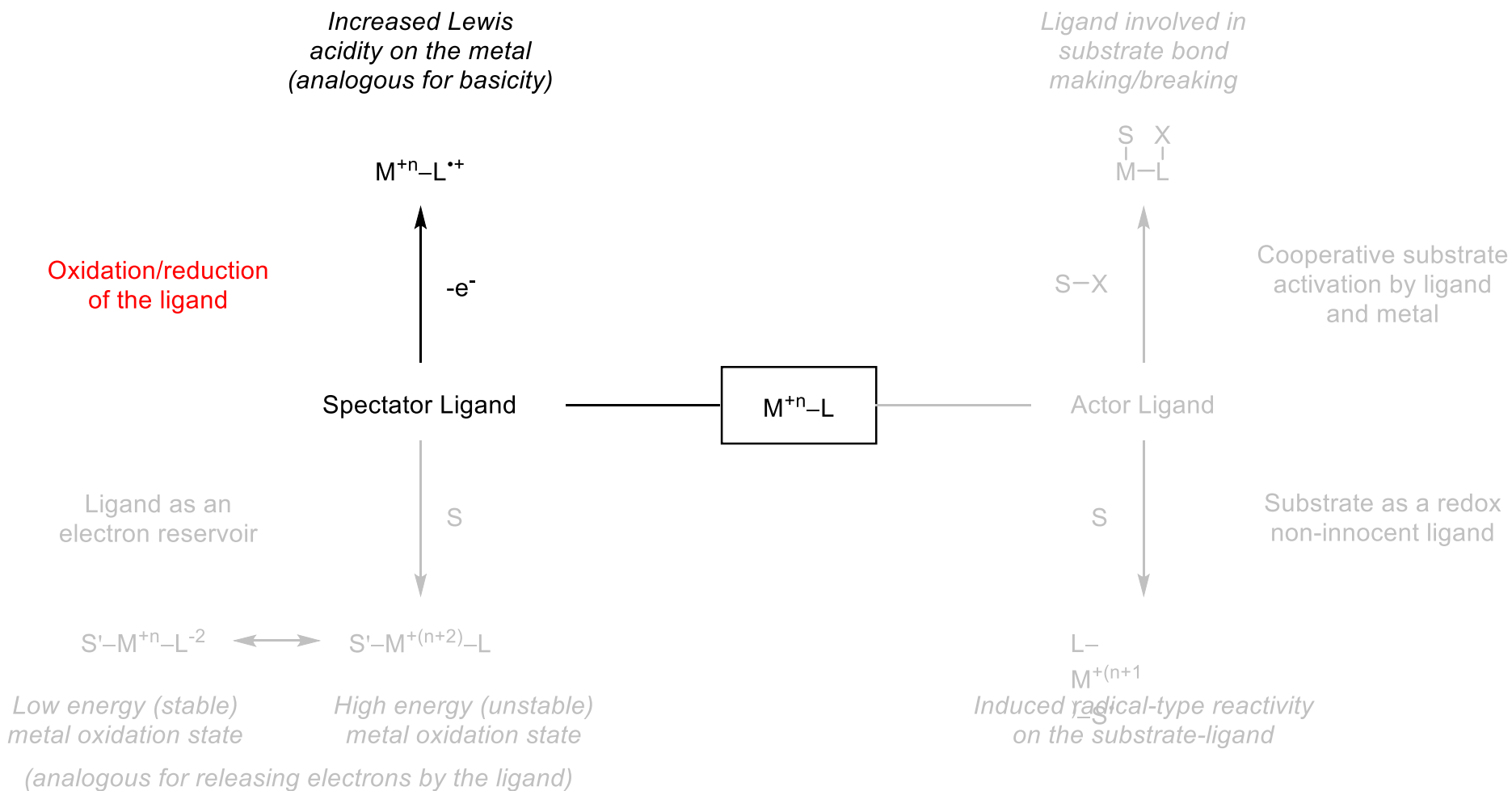


Redox Switch Polymerization

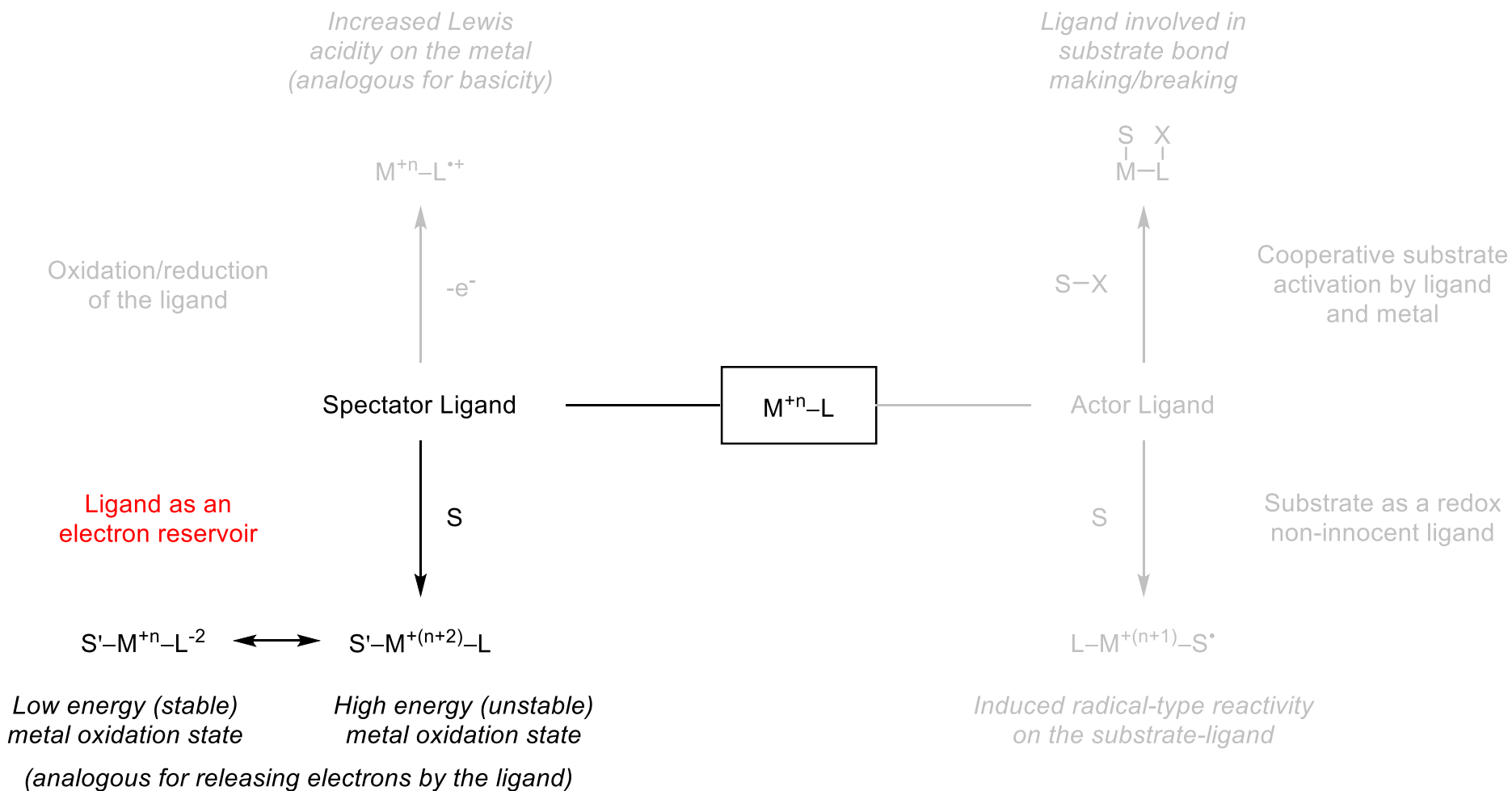
EW properties of the salen ligand slows down polymerization



Redox-Active Ligands: Application Strategies

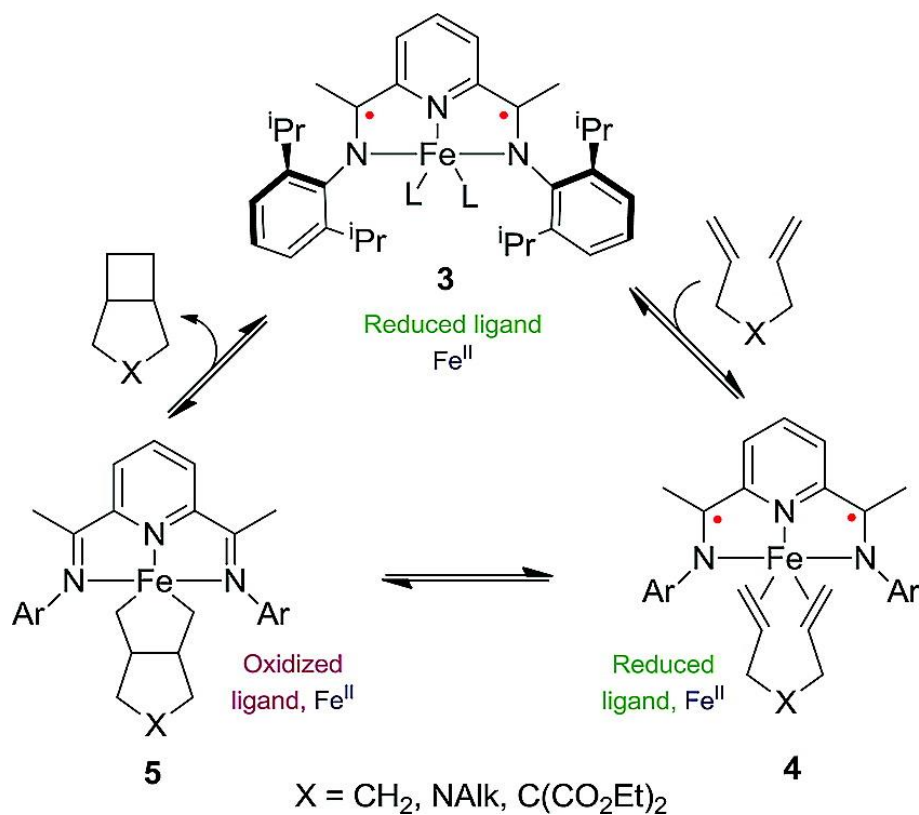


Redox-Active Ligands: Application Strategies

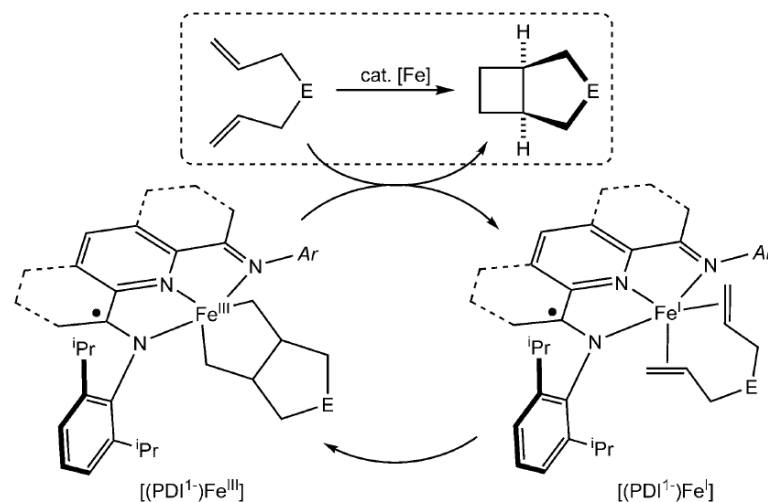


Fe-Catalyzed [2+2] Cycloaddition Ring Closure

2,6-Diiminepyridine ligand as an electron reservoir

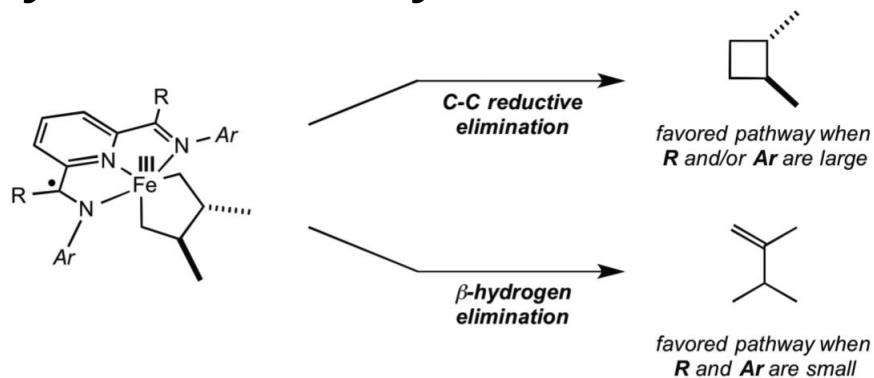
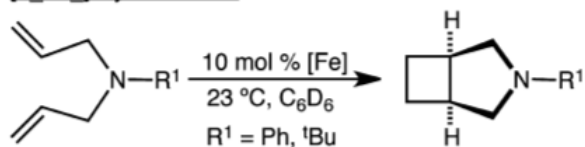


- 10% catalyst
- >90% conversion in 5 h
- Room temperature
- Similar catalytic cycle for Co

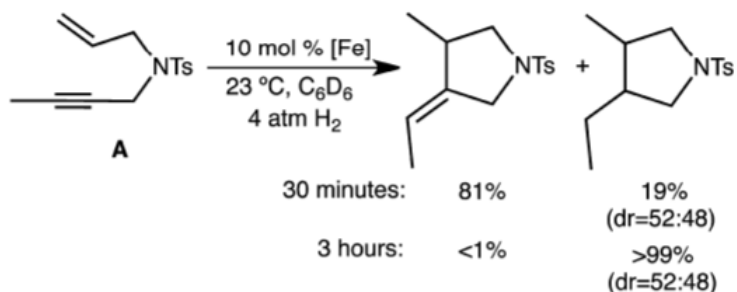


Diiminepyridine Ligands for C-C bond formation

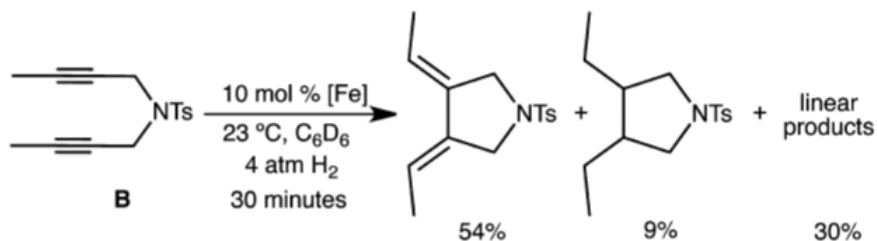
[2π+2π] Cycloaddition



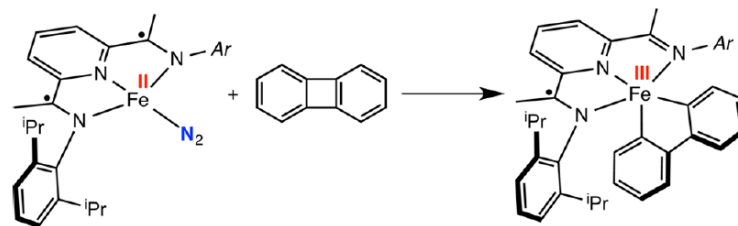
Enyne Hydrogenative Cyclization



Diyne Hydrogenative Cyclization

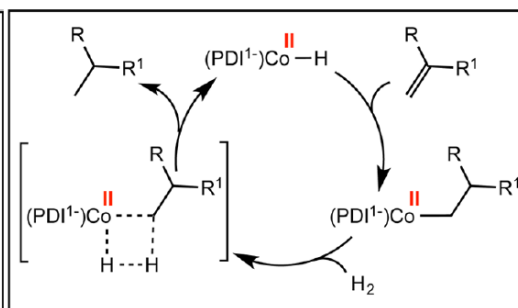
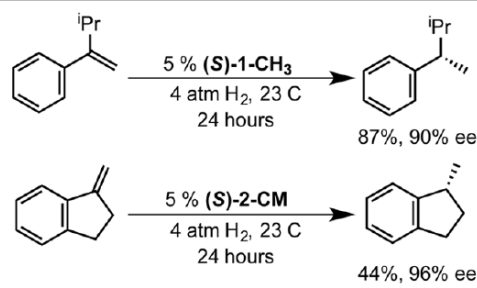
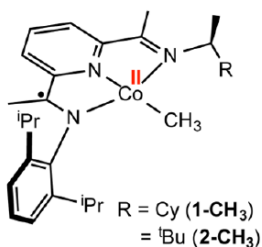


Metal Ligand Cooperativity Enables 2e⁻ Oxidative Addition



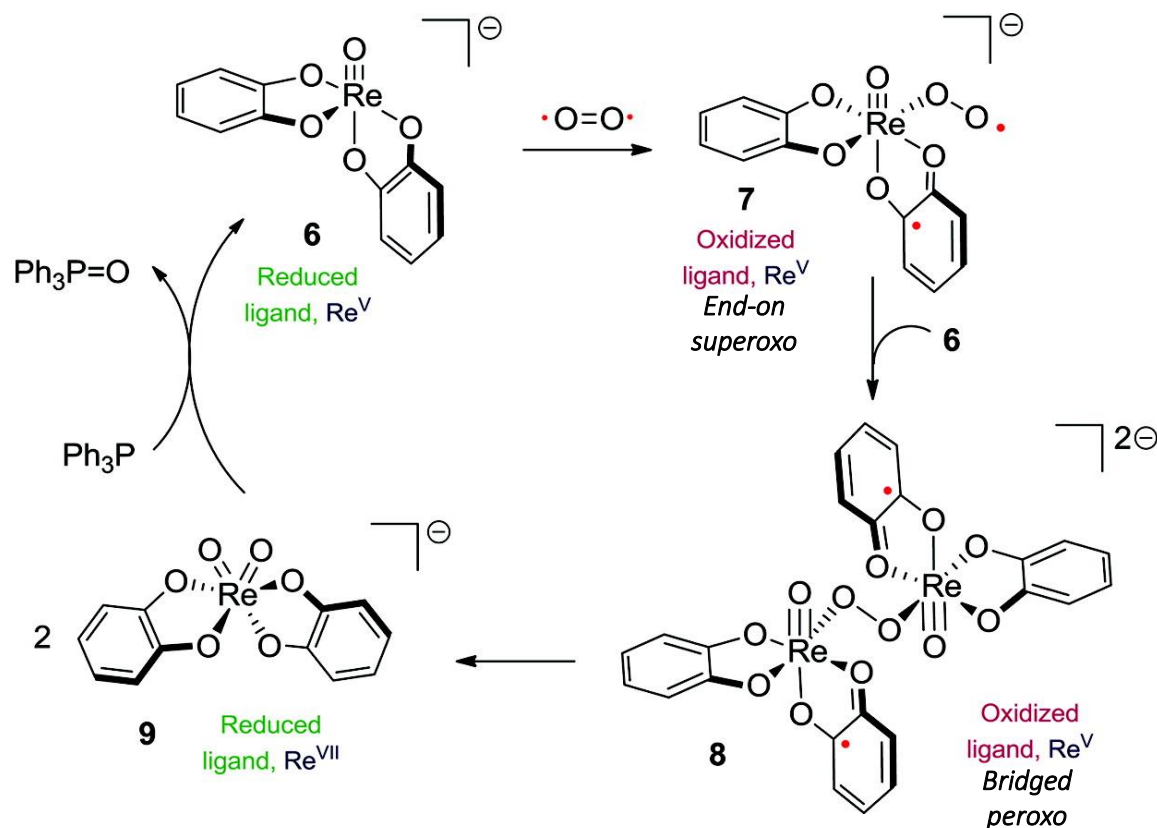
In this case, both ligand and metal give one electron each for the biphenylene OA

C₁ Symmetric Catalysts

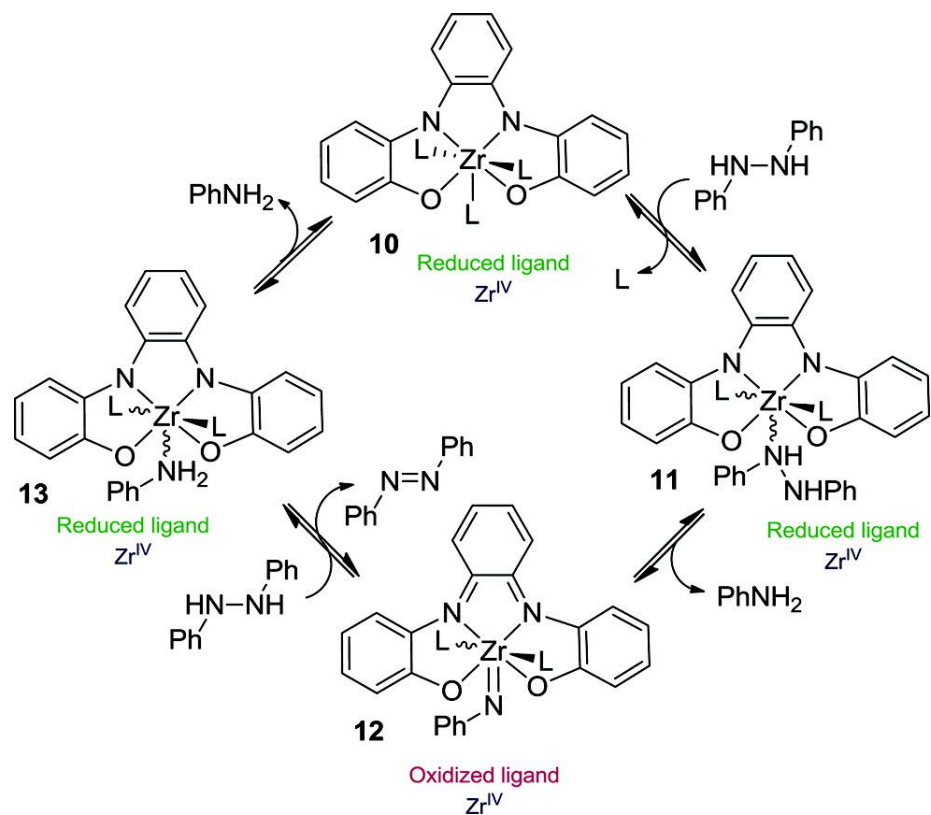
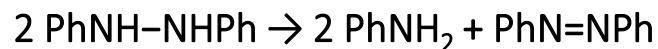


Dioxygen Fixation

The ligand facilitates spin-crossover in the formally “spin-forbidden” reaction between triplet oxygen and the closed-shell (singlet) d^2 rhenium(V)

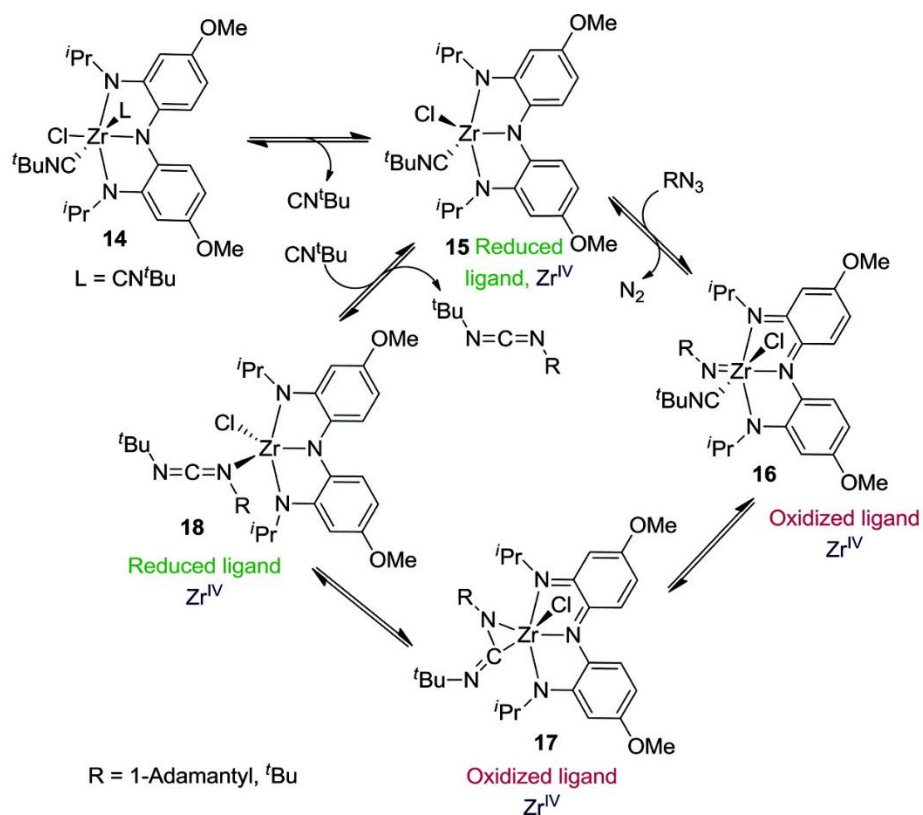


“Oxidative Addition” Reactions at d^0 Zr^{IV} Complexes



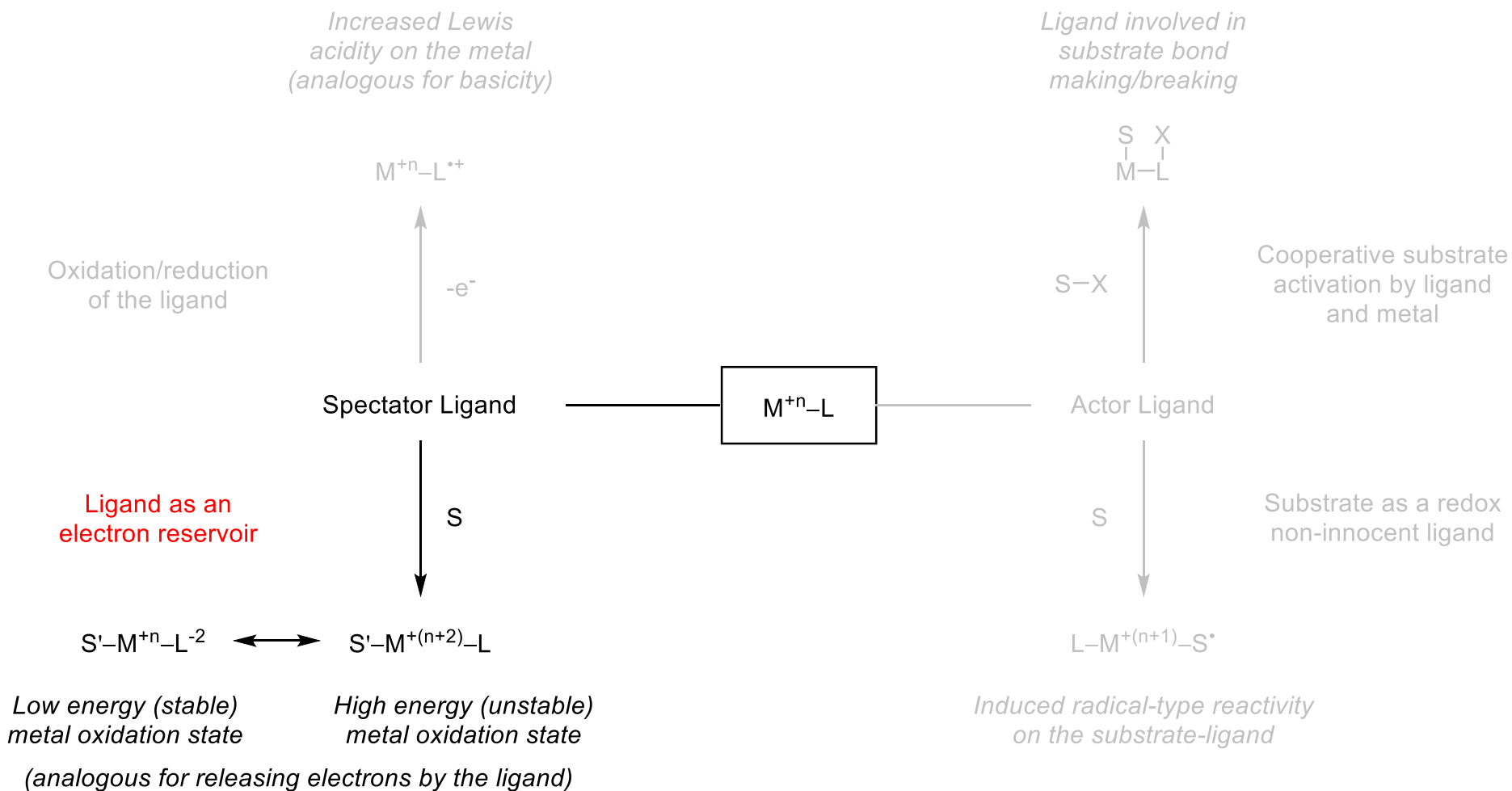
Full conversion with 10 mol% catalyst in one day.

Catalytic Formation of Carbodiimides from Isocyanides and Organic Azides



Full conversion with 10 mol% of the catalyst in 2 h

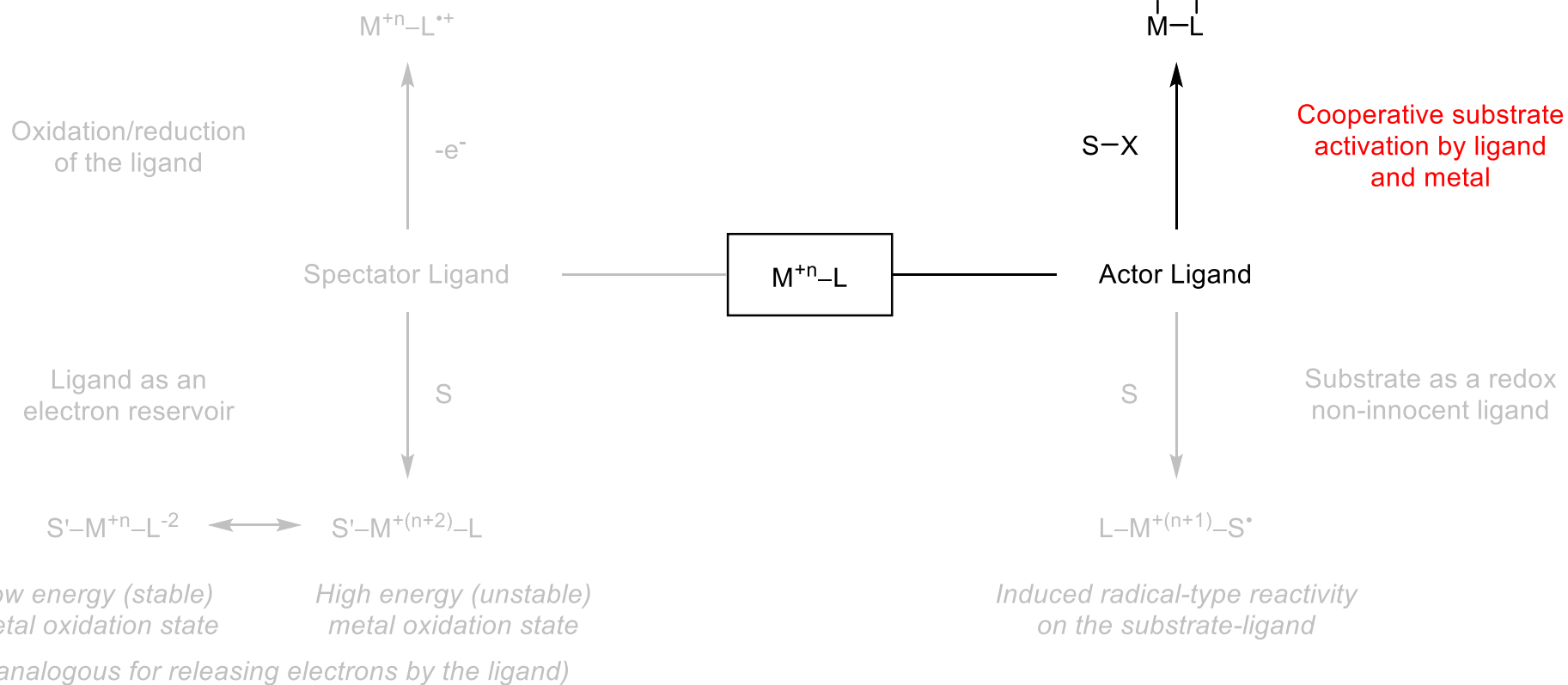
Redox-Active Ligands: Application Strategies



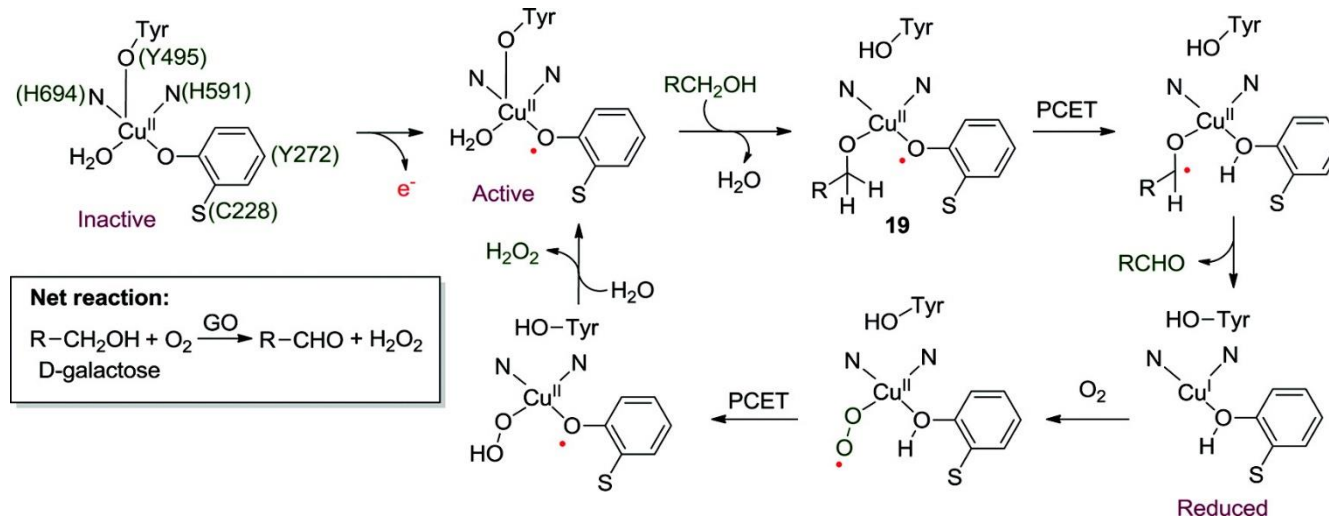
Redox-Active Ligands: Application Strategies

Increased Lewis acidity on the metal (analogous for basicity)

Ligand involved in substrate bond making/breaking



Galacto Oxidase (GOase)

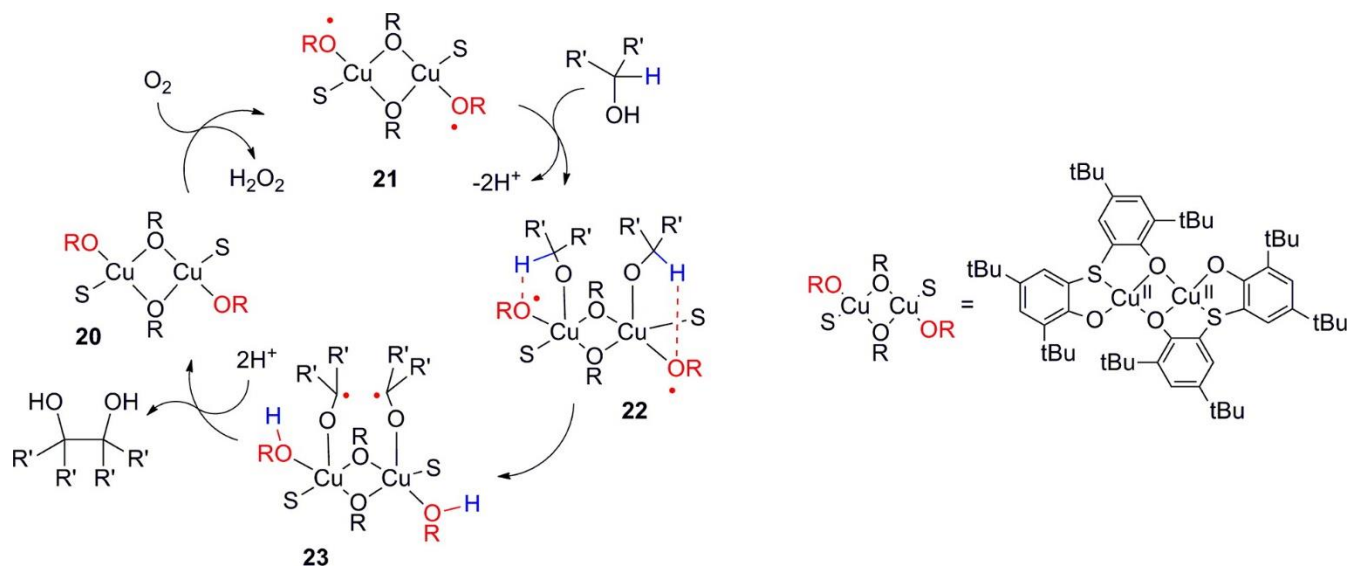
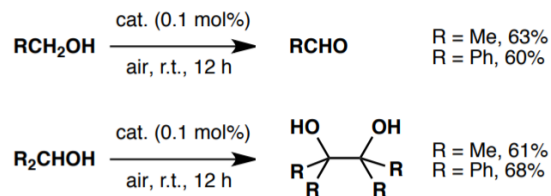


Cooperative substrate activation by metal and ligand:

The substrate binds to the metal, which places it close to the reactive ligand radical, and the actual bond-breaking process takes place between the non-innocent ligand and the substrate

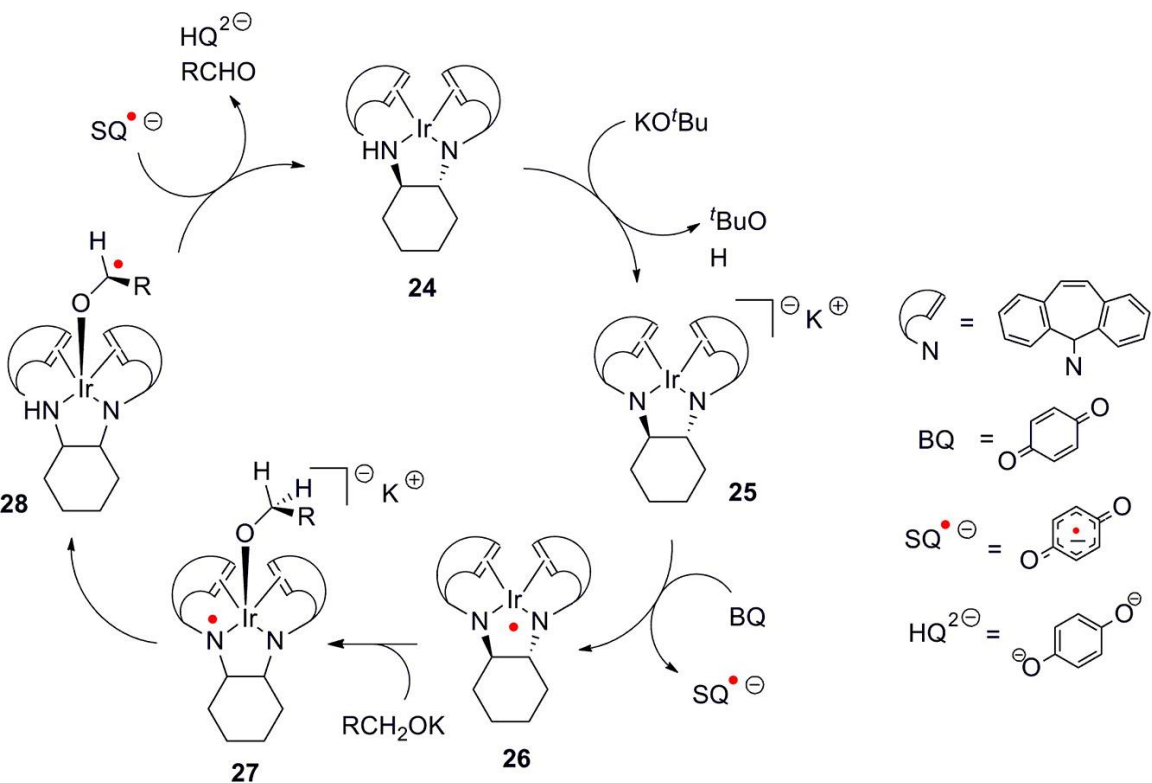
Cu(II) Catalyzed Dimerization of Secondary Alcohols

Bio-inspired



Ir(I) Catalyzed Oxidation of Primary Alcohols

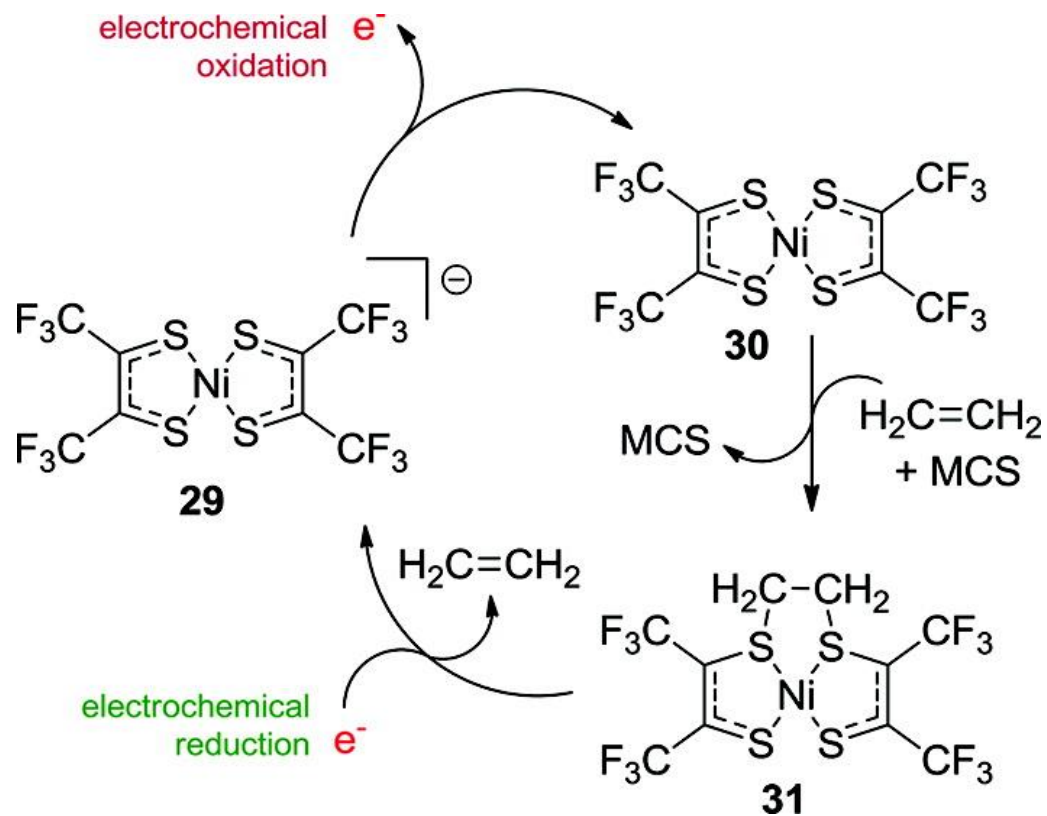
Bio-inspired



Substrate	Product	Yield (Time)	Substrate	Product	Yield (Time)
		94% (3 min)			> 98% (2 h)
		> 98% (3 h)			> 98% (1 h)
CH_3OH	CH_2O	64% (4 h)			> 98% (10 min) BQ (2 equiv.)
$\text{CH}_3\text{CH}_2\text{OH}$	CH_3CHO	94% (4 h)			> 98% (5 min) BQ (2 equiv.)

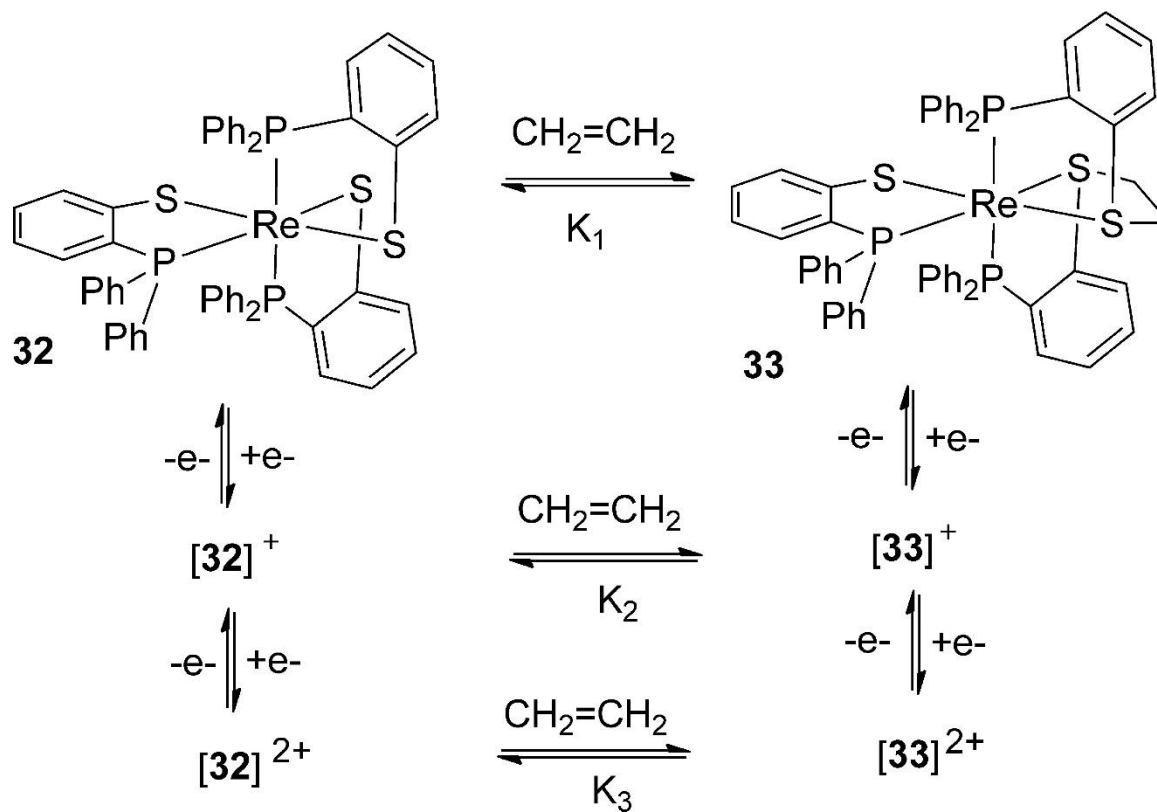
Cat. (0.01 mol%)
 KO^tBu (0.03 mol%)
 BQ (1.2 equiv.)
 PhCl, 80 °C, Ar

Ethylene Purification

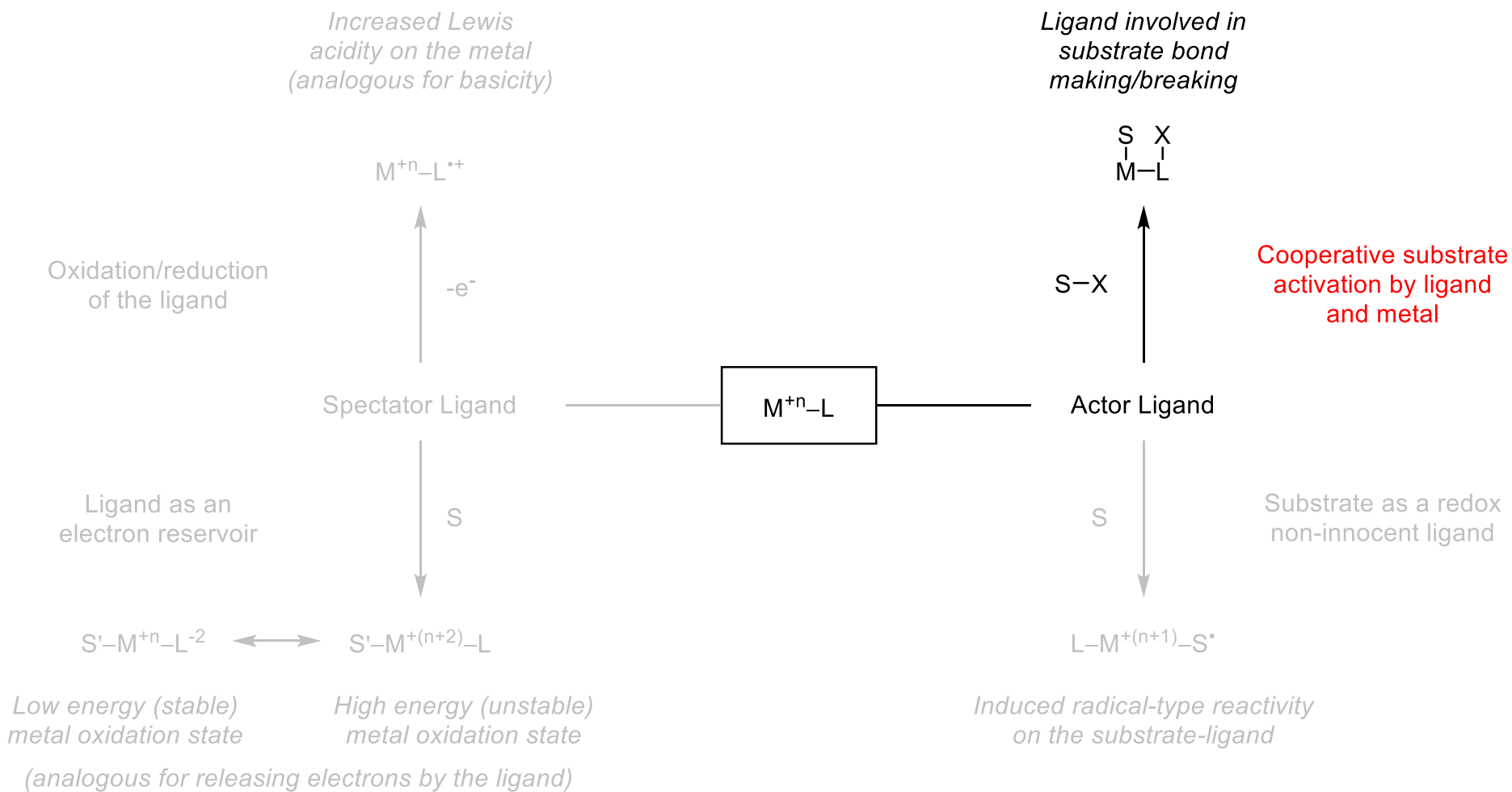


Ethylene Capture by Thiyl-Radical Ligands

$K_3 > K_2 > K_1$



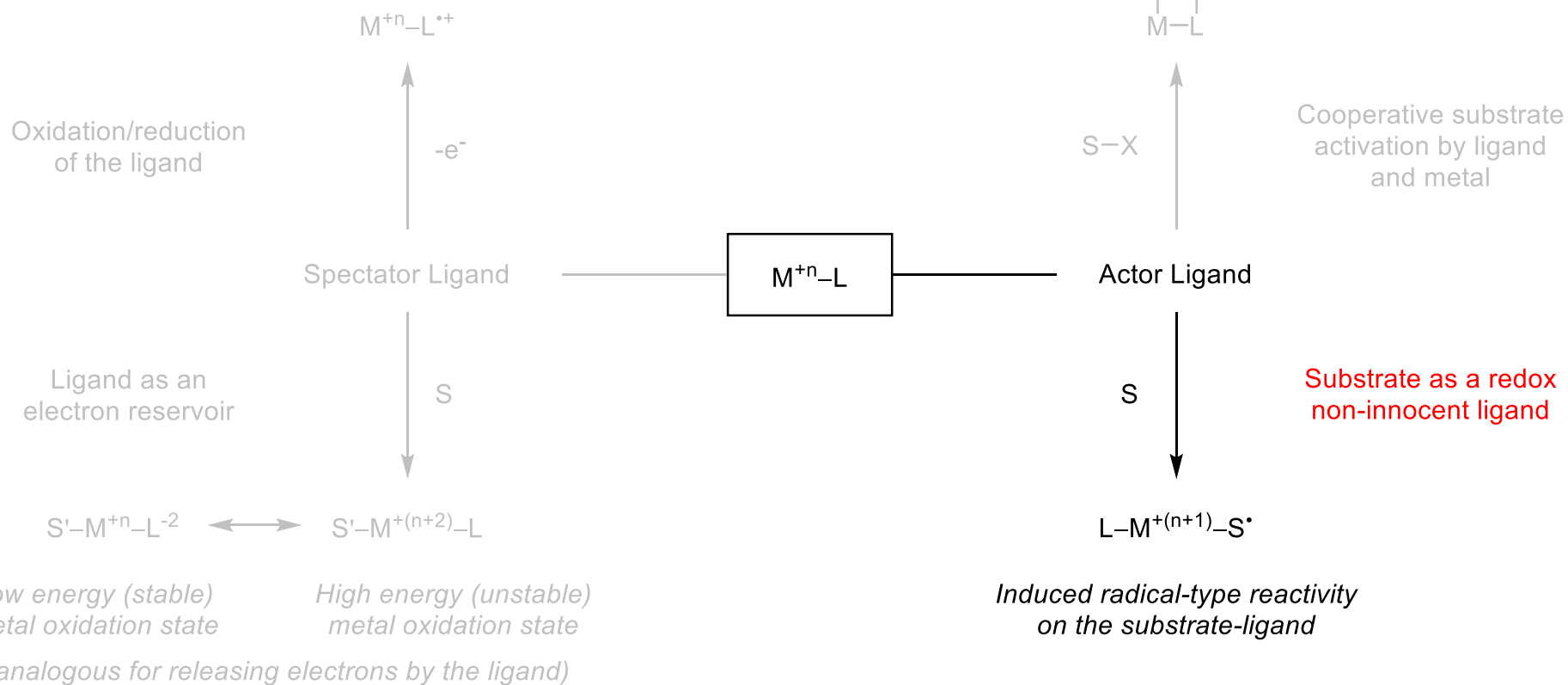
Redox-Active Ligands: Application Strategies



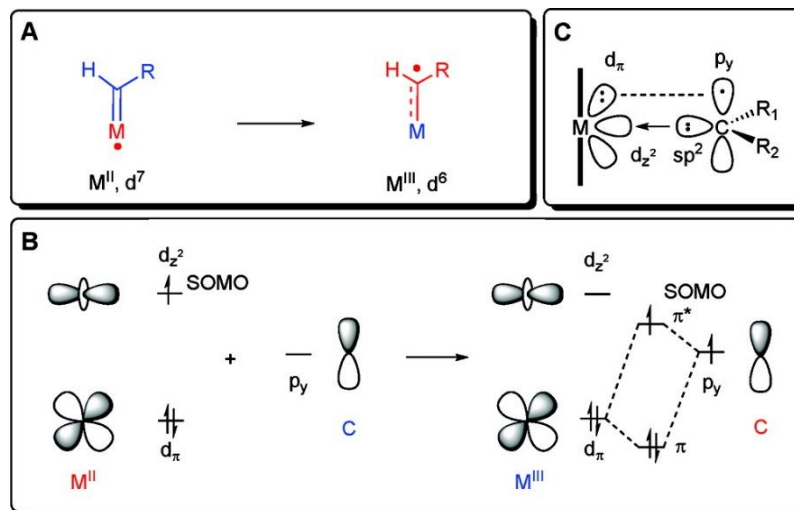
Redox-Active Ligands: Application Strategies

Increased Lewis acidity on the metal (analogous for basicity)

Ligand involved in substrate bond making/breaking



Group 9 M(II) Carbene and Nitrene Ligands

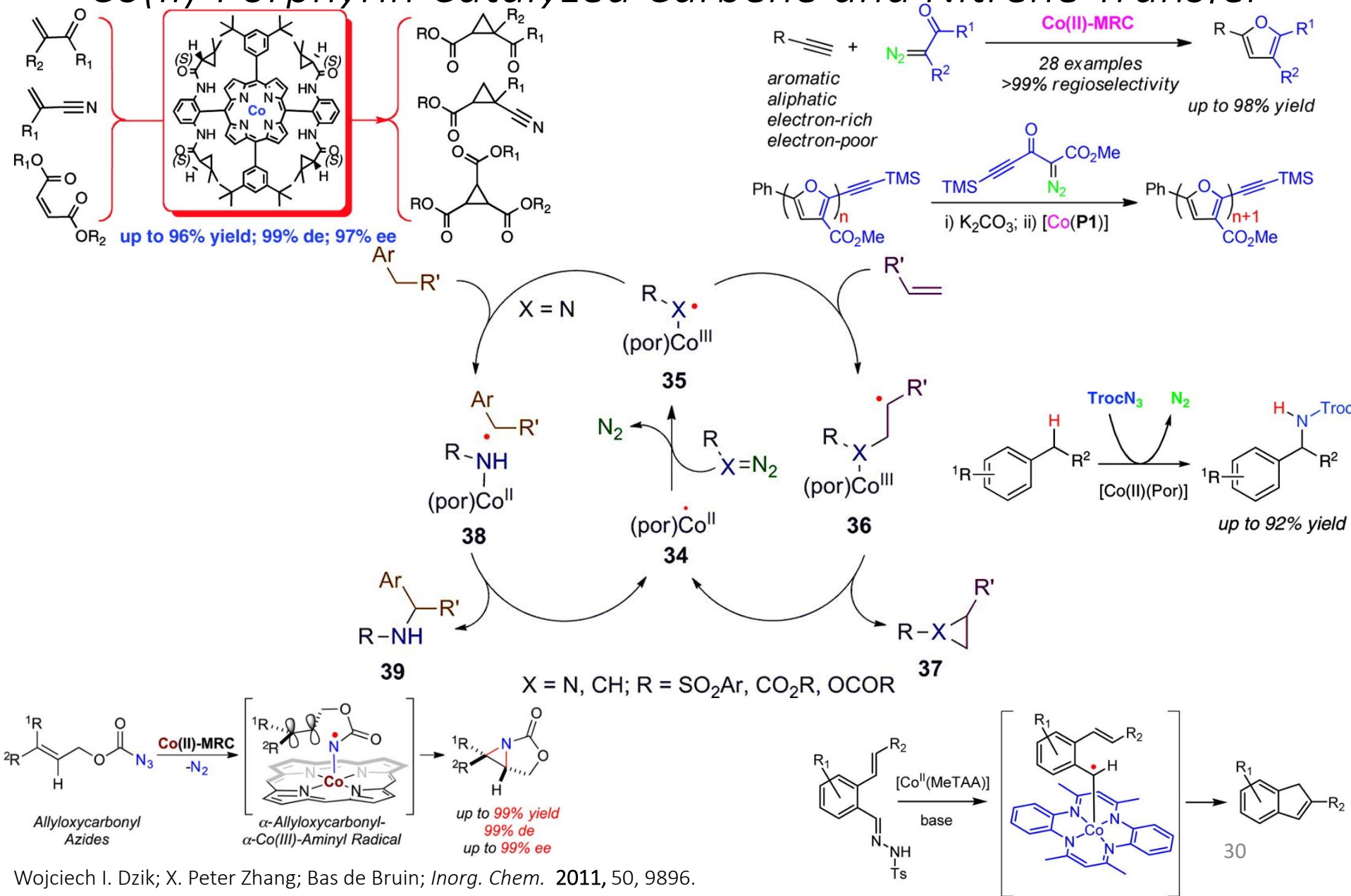


M = Co(II), Rh(II), Ir(II)

Advantages over Fischer-type carbenes:

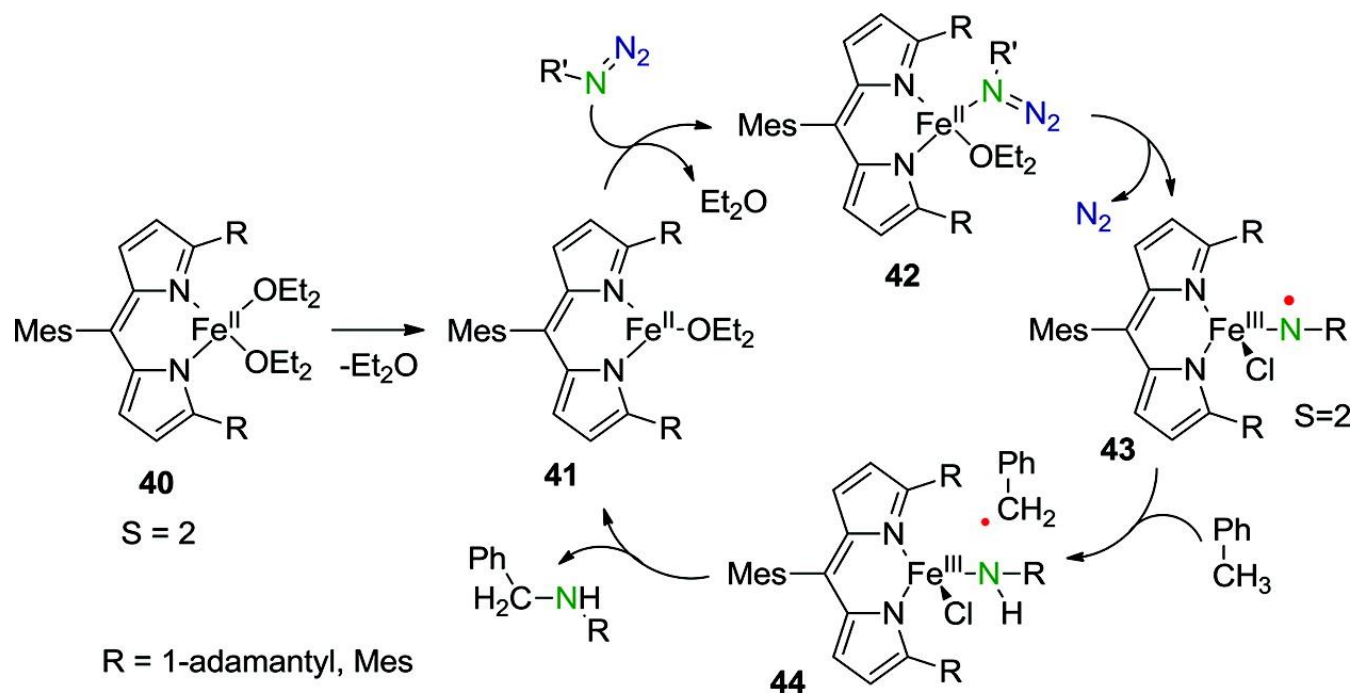
- Nucleophilic character
- Not sensitive to carbene dimerization
- EWGs tolerated

Co(II)-Porphyrin Catalyzed Carbene and Nitrene Transfer



High Spin Fe(II)-Catalyzed C-H Bond Amination

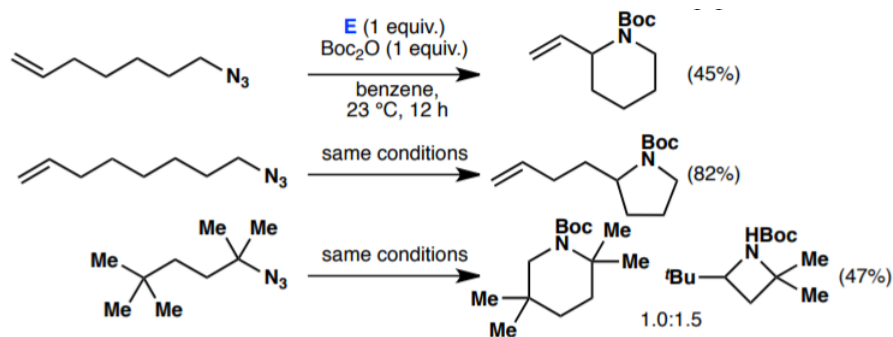
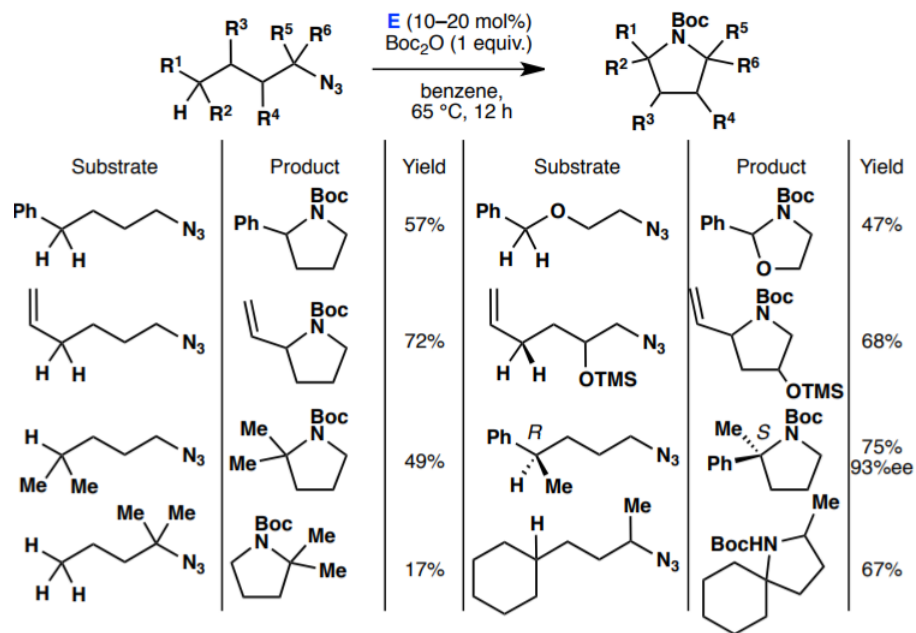
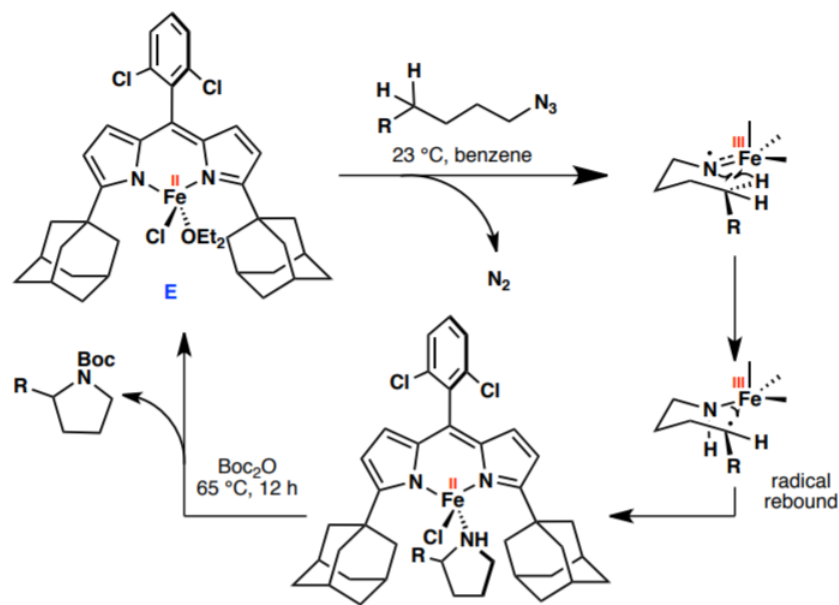
Non-heme Fe(II) complex



- Dipyrromethane ligand with bulky groups
- Forms high spin Fe-imido complex
- Catalytic C-H amination or olefin aziridation
- TON~14

High Spin Fe(II)-Catalyzed C-H Bond Amination

Intramolecular version



Thank you for your attention!

Introduction

The properties of a metal complex as a whole are the result of the interaction of the metal center and its surrounding ligands

Traditional approaches utilize the steric and electronic properties of the ligand to tune catalyst while reactivity takes place at the metal center only

Redox-active ligands: Metal and ligand can cooperate in a synergistic manner, and their interplay facilitates the chemical process. Offers interesting prospects to uncover new catalytic reactions

Definition

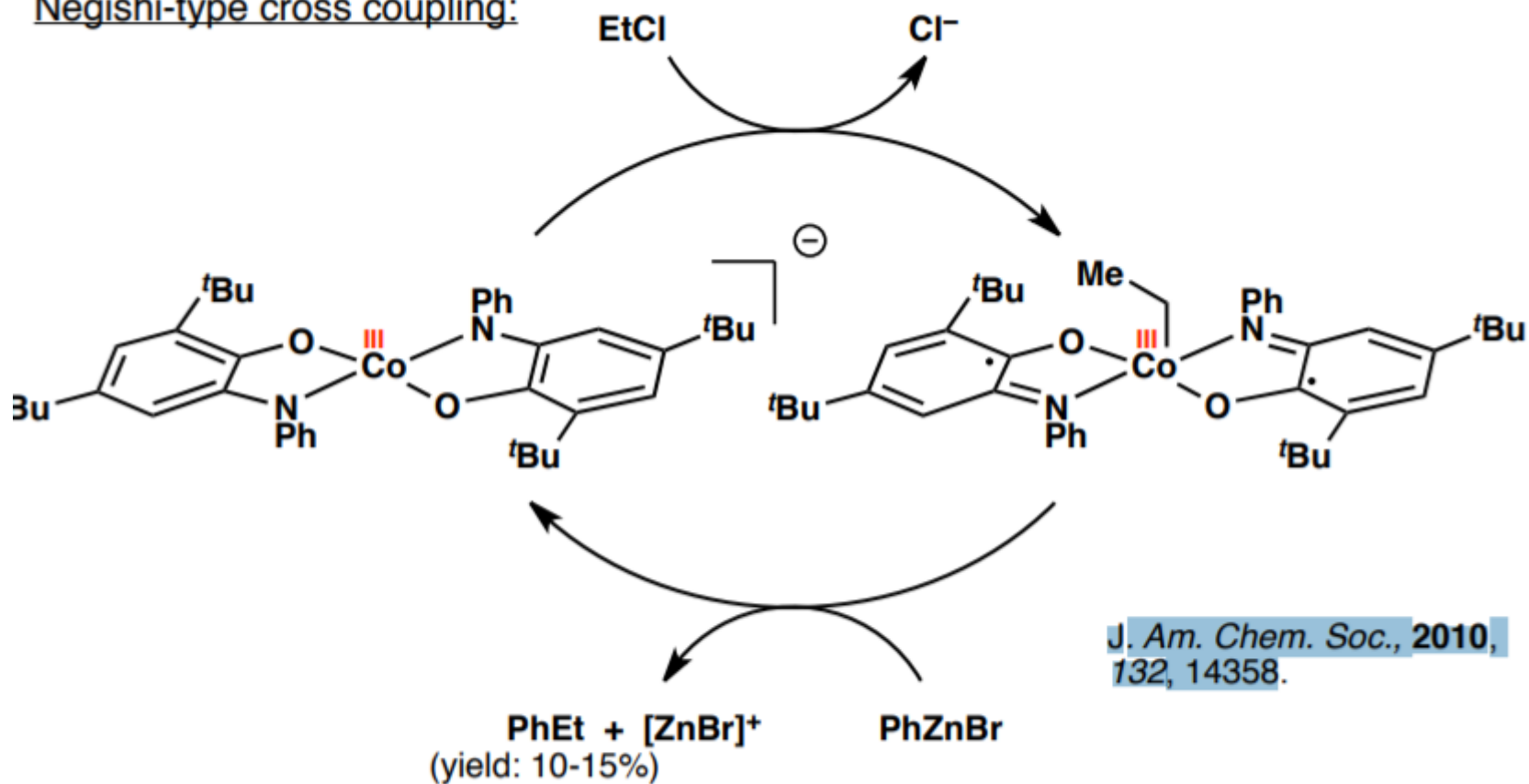
Techniques

high-quality X-ray crystallographic data in a matter of hours has allowed routine characterization of ligand bond distortions, which are often diagnostic of redox activity.

spectroscopic techniques including NMR, electron paramagnetic resonance, and Mössbauer

Perhaps the most significant advance has occurred in computational chemistry. The introduction of the broken-symmetry formalism,¹⁶ whereby the static electron correlation of the singlet diradical state is simulated with a spin-symmetry broken single-determinant wave function, has allowed the prediction of metrical and spectroscopic parameters that are diagnostic of many redox-active ligands. The accuracy of these methods has reached such a high level of success that oftentimes when a discrepancy exists, the experimenter is forced to double check the measurements!

Negishi-type cross coupling:



J. Am. Chem. Soc., **2010**,
132, 14358.

Reaction also works with hexylzinc bromide in similar yields.

Chirk Hydrogenation Chemistry

