Redox Non-Innocent Ligands in Catalysis
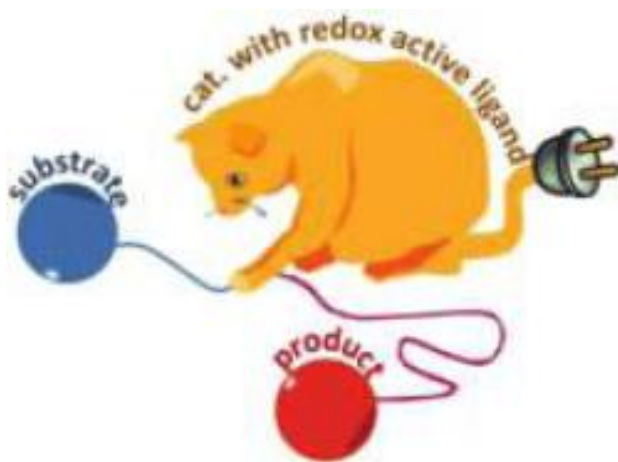
Literature Seminar
Hideya Ikemoto (B4)
2012/12/22

Today's Contents

<u>Today's</u> <u>Contents</u>

1. What is redox non-innocent ligands?
 1.1 Definition of "non-innocent"
 1.2 4 strategies of redox-active ligands in catalysis

2. Reactions using redox non-innocent ligands
 2.1 Oxidative addition of C-C bond with iron complex
 2.2 Oxidative addition and reductive Elimination with cobalt complex
 2.3 Oxidation of benzylic alcohol with copper complex

3. Summary

Definition of "non-innocent" ligands

C.K.Jørgensen:
   "Ligands are innocent when they allow oxidation states
                              of the central atoms to be defined"

Coor. Chem. Rev **1966**, *1*, 164

The *formal* oxidation number:
   the charge left on the metal after all ligands have been removed
   in their normal, closed-shell configuration that is with their
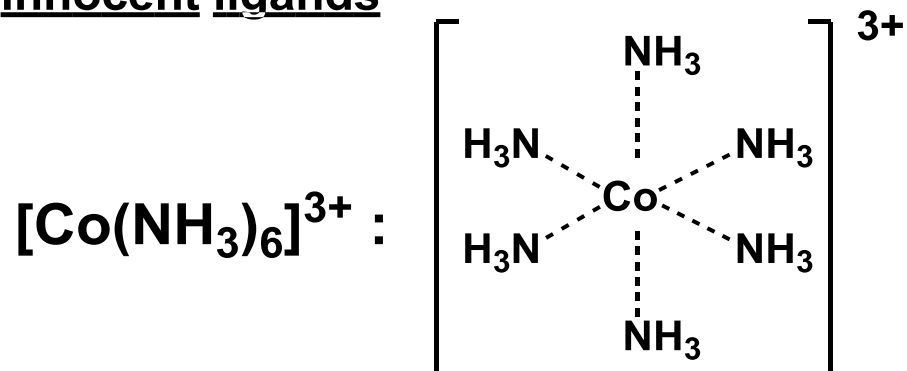   **electron pair**

The *physical* oxidation number:
   an oxidation number which is derived from a known d^n

   configuration

   (n for d^n electronic configuration is a measurable quantity)

Definition of "non-innocent"
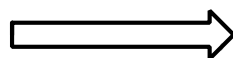
Examples of innocent ligands

$[Co(NH_3)_6]^{3+}$:

remove NH_3 ligands in their closed-shell configuration,

then Co is left as Co^{+3}

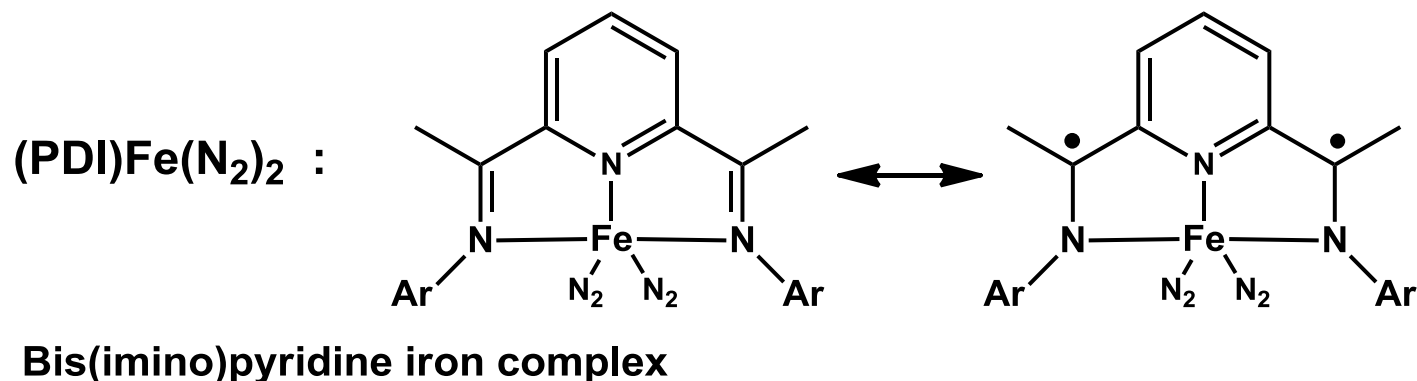⟶ *formal* oxidation number is +3

Co is the low spin d^6 ion

⟶ *physical* oxidation number is +3

⟹ **NH₃ is innocent ligand**

Definition of "non-innocent"

Examples of non-innocent ligands

(PDI)Fe(N$_2$)$_2$:

Bis(imino)pyridine iron complex

remove PDI(bis(imino)pyridine) ligands and N$_2$ in their closed-shell configuration, then Fe is left as Fe^0

$\longrightarrow$ *formal* **oxidation number is 0**

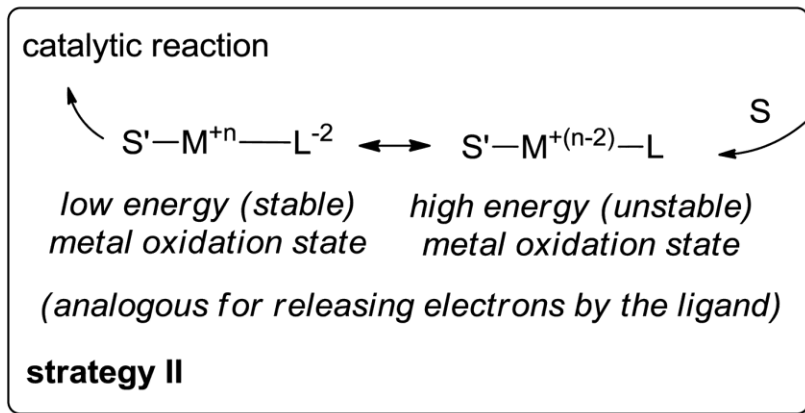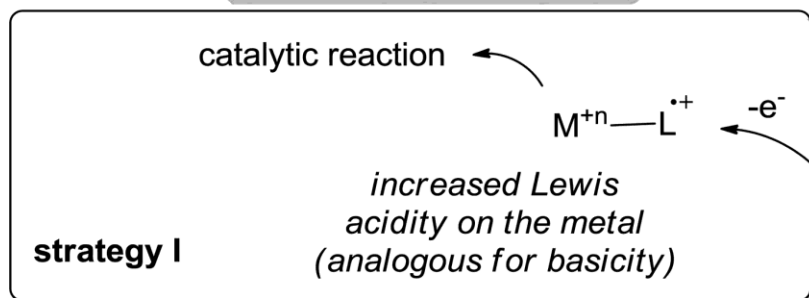**Fe is intermediate spin d^6 ion**

$\longrightarrow$ *physical* **oxidation number is +2**

$\Longrightarrow$ **PDI ligand is non-innocent ligand**
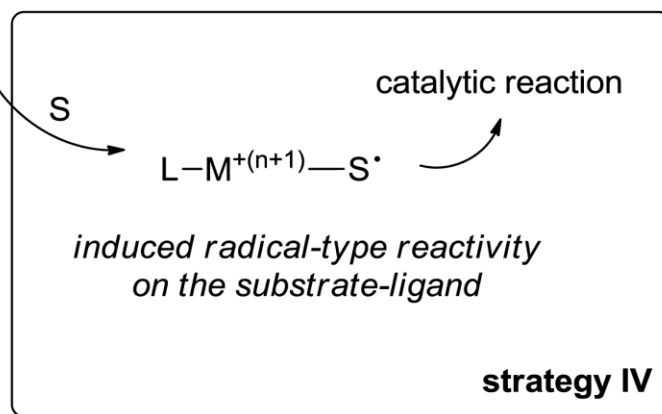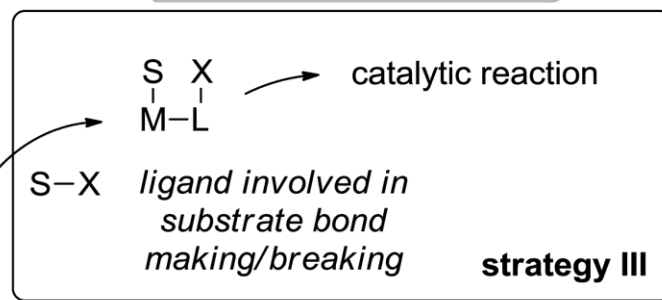
4 strategies of redox-active ligands in catalysis

Approach A:
ligands participate in catalytic cycle
by accepting/donating electrons

Approach B:
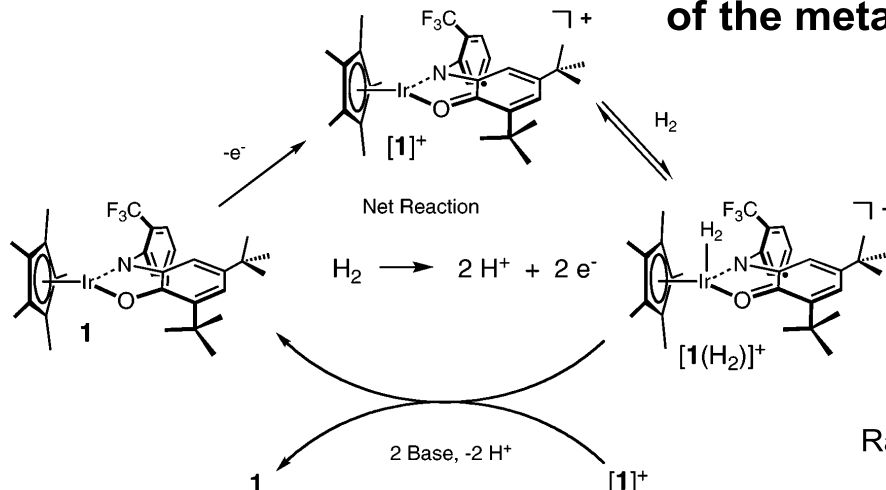**ligands participate in the formation/breaking**
of substrate covalent bond.

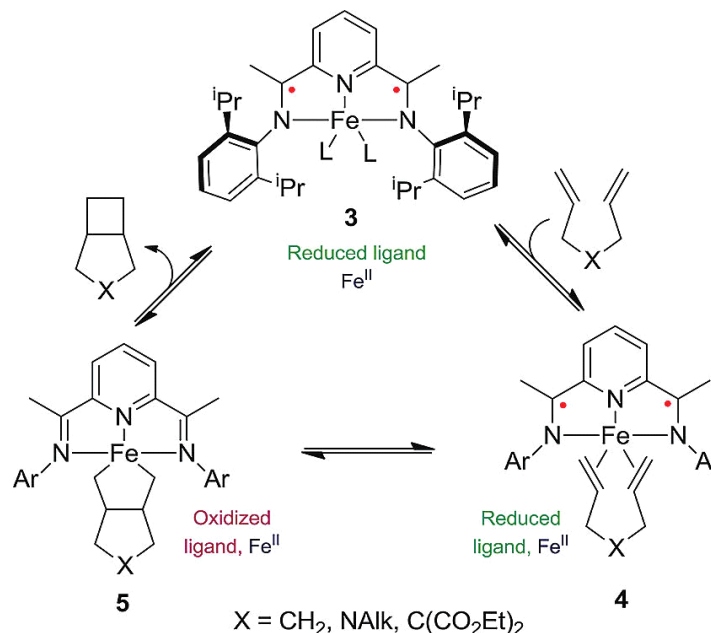S = substrate

de Bruin, B. *ACS Catal.* **2012**, 2, 270

4 strategies of redox-active ligands in catalysis

**Strategy I: Oxidation/Reduction of ligands to tune electronic properties
of the metal (Lewis acidity/basicity)**

Net Reaction

$$H_2 \longrightarrow 2 H^+ + 2 e^-$$

Rauchfuss, T. B. *et al. JACS,* **2008**, *130*, 788

Strategy II: Ligand acts as an electron reservoir to maintain the metal's oxidation state
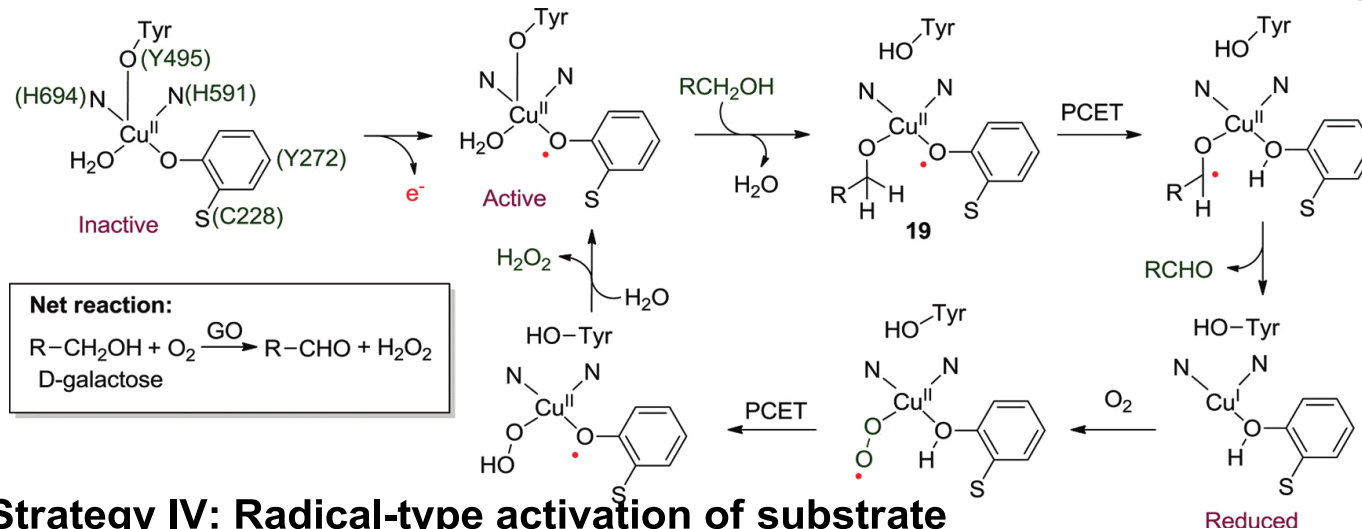

X = CH₂, NAlk, C(CO₂Et)₂

Chirik, P. J. *et al. JACS,* **2006**, *128*, 13340

Ref.) Mr.Kimura's Lit.Seminar (2010)
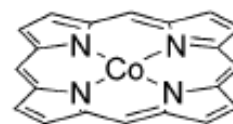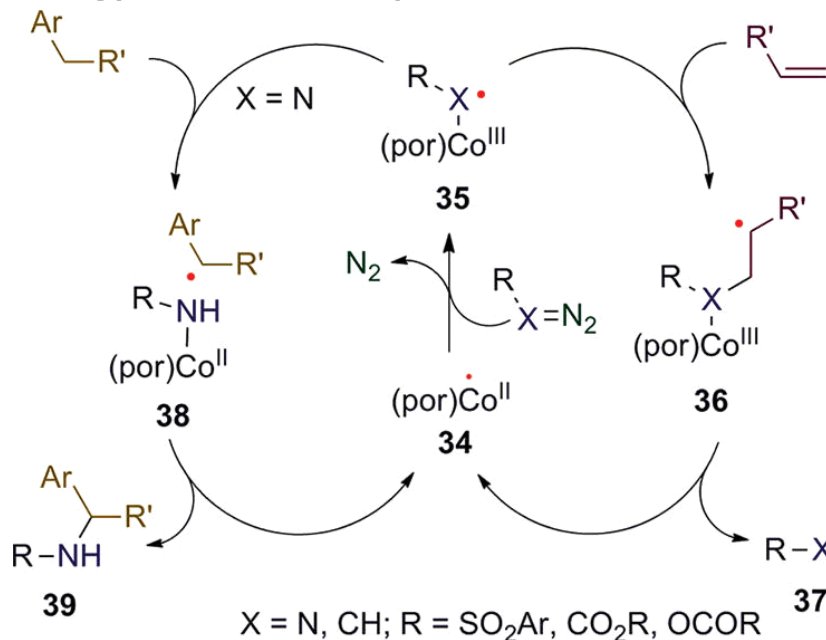
4 strategies of redox-active ligands in catalysis

Strategy III: Ligand-radicals to make/break chemical bonds

Tolman. W. B. *et al.*
Nature, **2008**, *455*, 333

Net reaction:

$$R-CH_2OH + O_2 \xrightarrow{GO} R-CHO + H_2O_2$$
D-galactose

Strategy IV: Radical-type activation of substrate

X = N, CH; R = SO₂Ar, CO₂R, OCOR

de Bruin, B. *et al. JACS,* **2010**, *132*, 10891

Ref.) Mr.Kato's Lit. Seminar (2012)

Today's Contents

metal

ligand

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Oxidative addition of C-C bond

Chirik, P. J. *et al. JACS,* **2012,** *134*, 17125

Oxidative addition of C-C bond

Chirik, P. J. *et al. JACS,* **2012,** *134*, 17125

Concept

Scheme 1. Oxidative Addition Reactions

Traditional Oxidative Addition

$$L_xM^{n+} + X-Y \longrightarrow L_xM^{n+2}{-}X$$

$d^n \qquad\qquad d^{n-2}$

M= Pd, Rh,
or other expensive noble metals

In A Redox-Active Metal-Ligand Complex

$$\overset{z+}{L_x}M^{n+} + X-Y \longrightarrow \overset{z+2}{L_x}M^{n+}{-}X$$
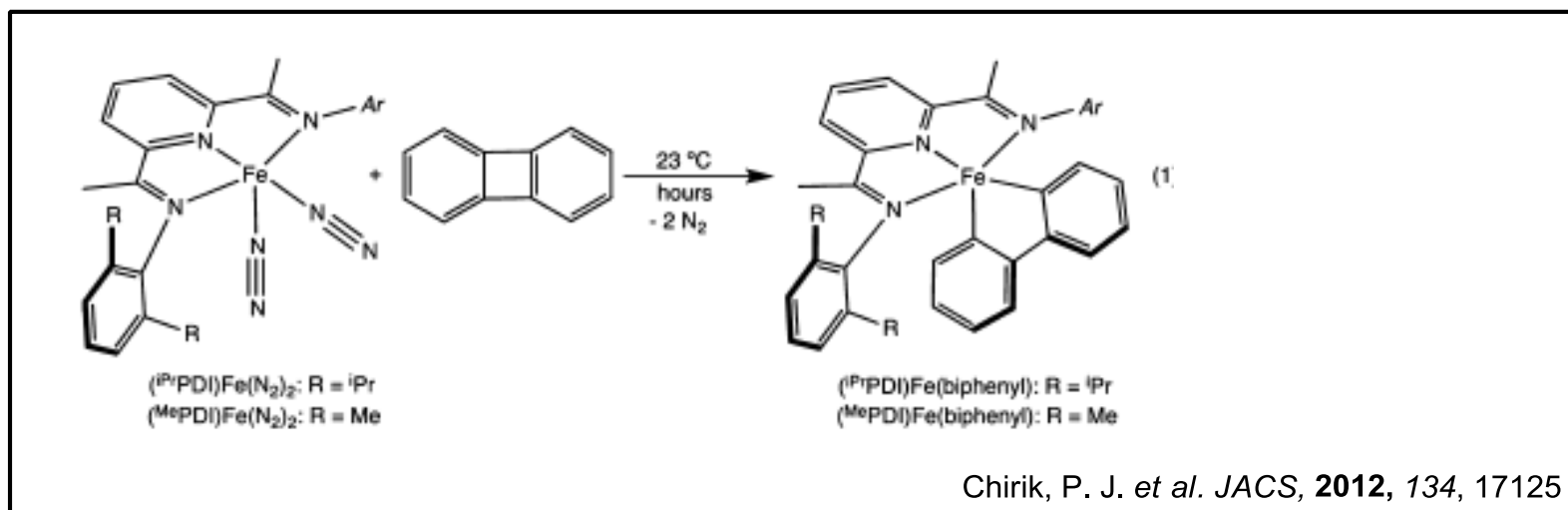
$d^n \qquad\qquad d^n$

M= Fe, Co, etc.
More abundant first-row transition metals

Ligands act as electron reservoirs

Redox non-innocent ligands allow first-row transition metals to mimic some of the catalytic properties of noble metals.

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Bis(imino)pyridine Iron Complex

Chirik, P. J. *et al. JACS,* **2012,** *134,* 17125

Synthesis of (PDI)FeCl$_2$

+ FeCl$_2$ $\xrightarrow{\text{n-BuOH}}$

Reduction of complex

1-Cl$_2$	1-Cl	1-(N$_2$)$_2$
[PDI]^0	[PDI]$^{1\cdot}$	[PDI]$^{2-}$
high spin Fe(II), d^6	high spin Fe(II), d^6	intermediate spin Fe(II), d^6

Ar =
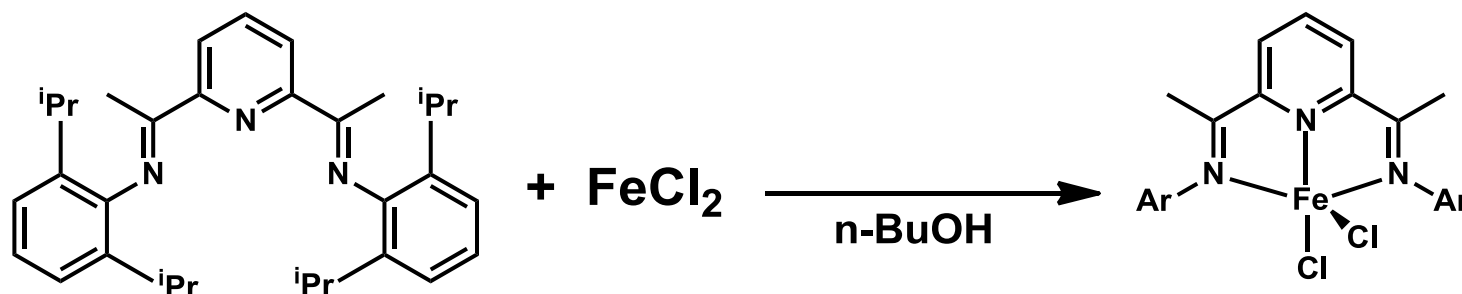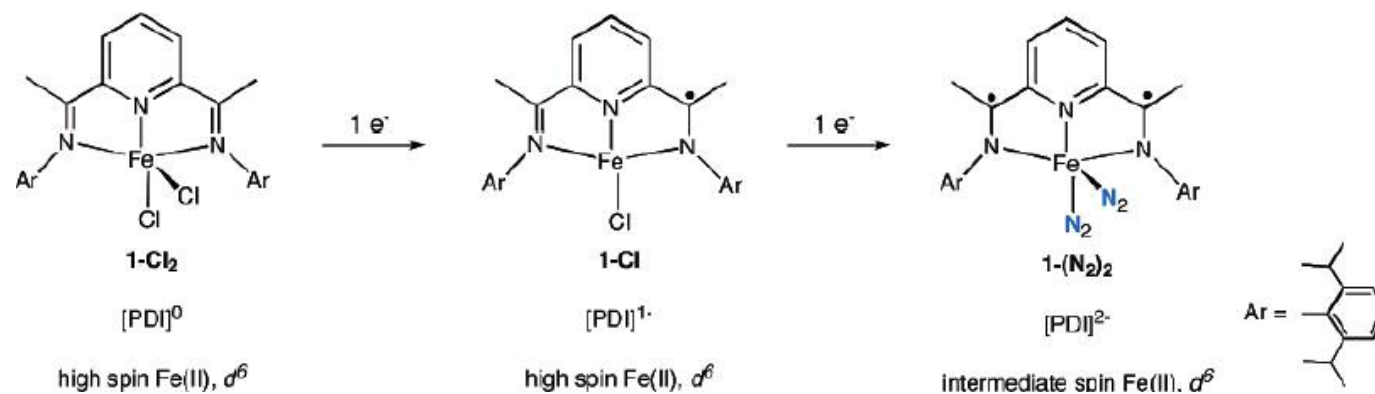
reductant : Na/Hg (under N$_2$)

Bis(imino)pyridine Iron Complex

Chirik, P. J. *et al. JACS* **2006**, *128*, 13901

Evidence for Fe(II) (Calculations and Mössbaur spectra)

a)

$S = 0.34$

$S = 0.48$

x

y

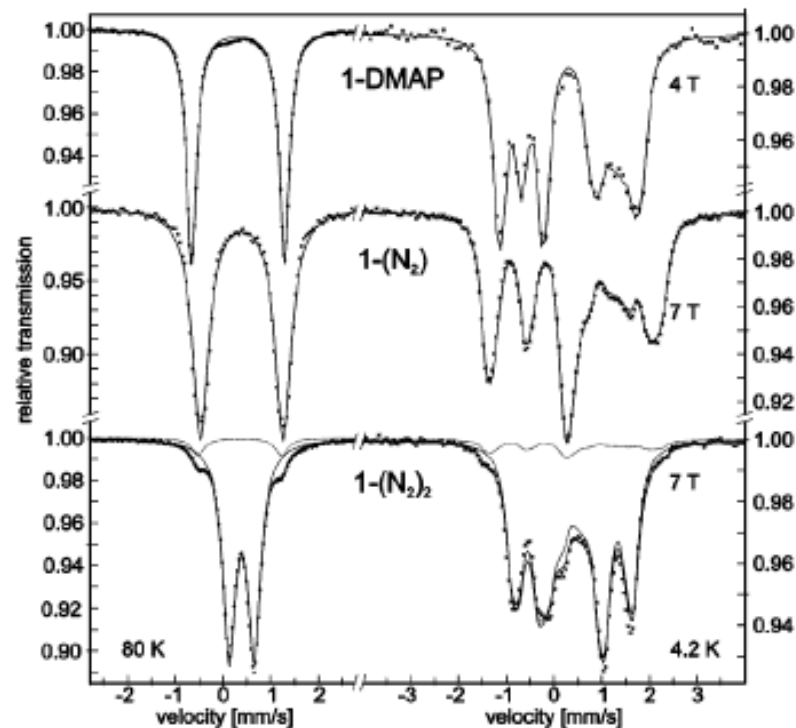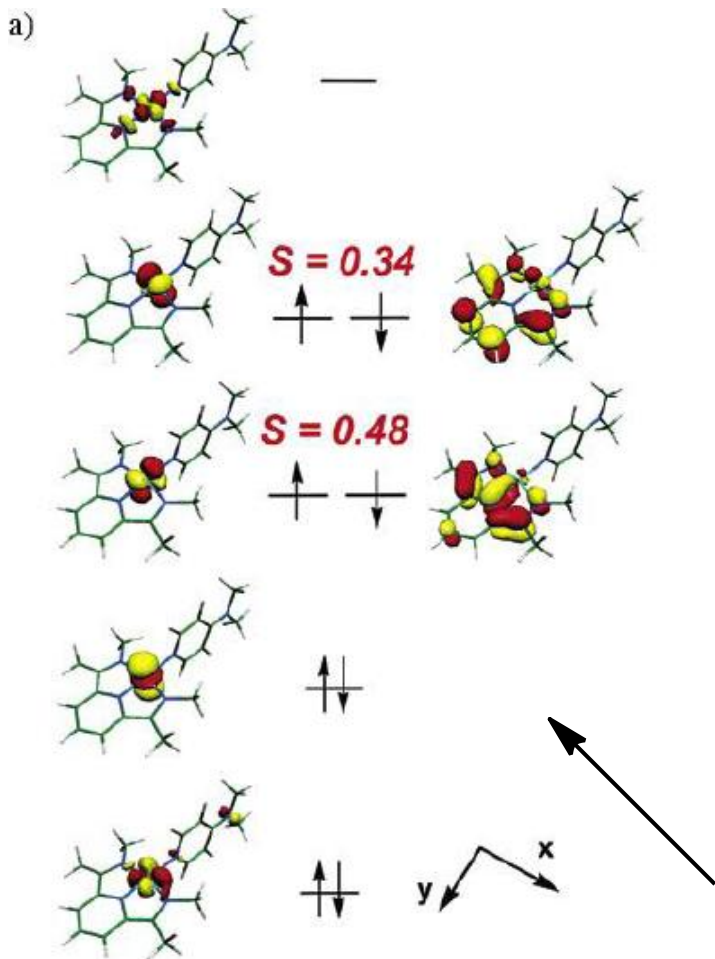Figure 11. Mössbauer spectra of **1-DMAP**, **1-(N$_2$)**, and **1-(N$_2$)$_2$** recorded at 80 K in zero-field (left column) and at 4.2 K with applied fields as indicated (right column). The lines are fits with Lorentzian doublets for the zero-field spectra and magnetic simulations for $S = 0$ with the usual nuclear Hamiltonian for the magnetic spectra. The Mössbauer parameters are given in the text or in Table 6. The dotted lines in the spectra from **1-(N$_2$)$_2$** represent a 7.5% contamination with **1-(N$_2$)**.

Evidences of Fe(II) oxidation state and the triplet diradical bis(imino)pyridine ligands

Figure 12. Qualitative molecular orbital diagram for (^{Me}pdi)Fe(DMAP) derived from BS(2,2)

Ref.) Mr.Kimura's Lit.Seminar (2010)

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X-ray diffraction of metallacycle Chirik, P. J. *et al. JACS*, **2012**, *134*, 17125
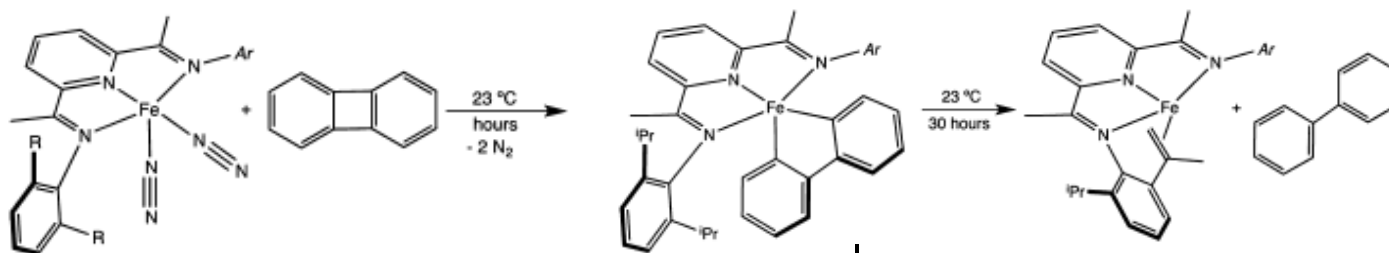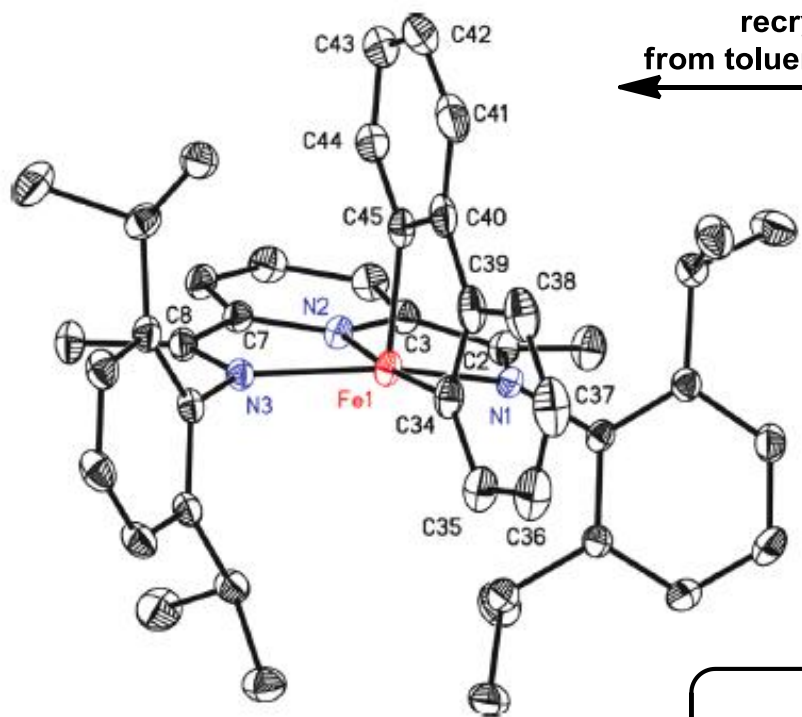
**recrystallized
from toluene/Et₂O at -35 °C**

Table 1. Selected Bond Distances (Å) and Angles (deg) for (ᶦᴾʳPDI)Fe(biphenyl) and (ᴹᵉPDI)Fe(biphenyl)

	(ᶦᴾʳPDI)Fe(biphenyl)	(ᴹᵉPDI)Fe(biphenyl)
Fe(1)−N(1)	1.959(2)	1.9402(18)
Fe(1)−N(2)	1.852(2)	1.8569(16)
Fe(1)−N(3)	1.988(2)	1.9503(18)
Fe(1)−C$_{basal}$	1.965(3)	1.9656(19)
Fe(1)−C$_{apical}$	1.943(3)	1.9436(19)
N(1)−C(2)	1.315(4)	1.318(2)
N(3)−C(8)	1.317(4)	1.320(2)
C(2)−C(3)	1.438(4)	1.452(3)
C(7)−C(8)	1.433(4)	1.447(3)

: ᶦᴾʳPDI ligand

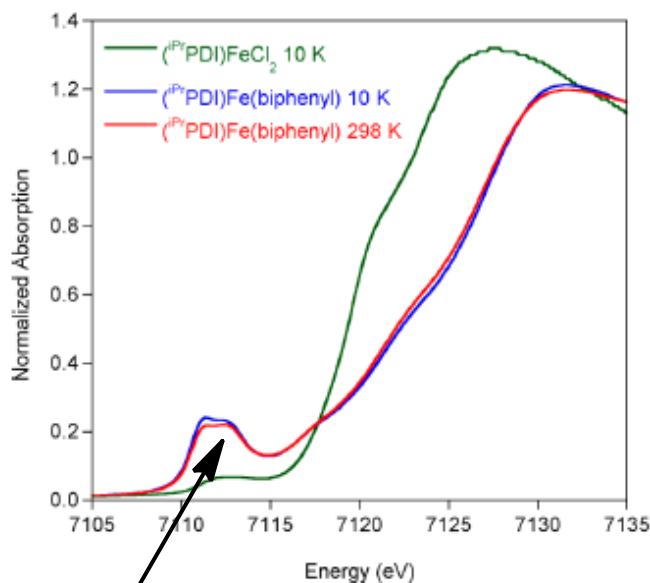| N$_{imine}$−C$_{imine}$	C$_{imine}$−C$_{ipso}$
1.274(3)	1.489(3)

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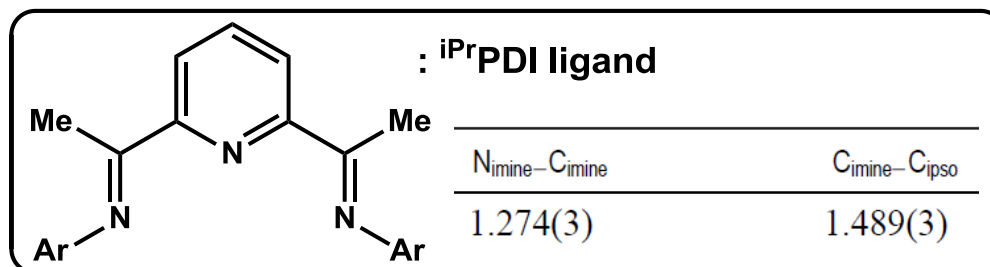
What is the oxidation state of iron?
Chirik, P. J. *et al. JACS,* **2012,** *134*, 17125

Figure 5. Comparison of the normalized Fe K-edge XAS spectra for (^{iPr}PDI)FeCl$_2$ and (^{iPr}PDI)Fe(biphenyl).
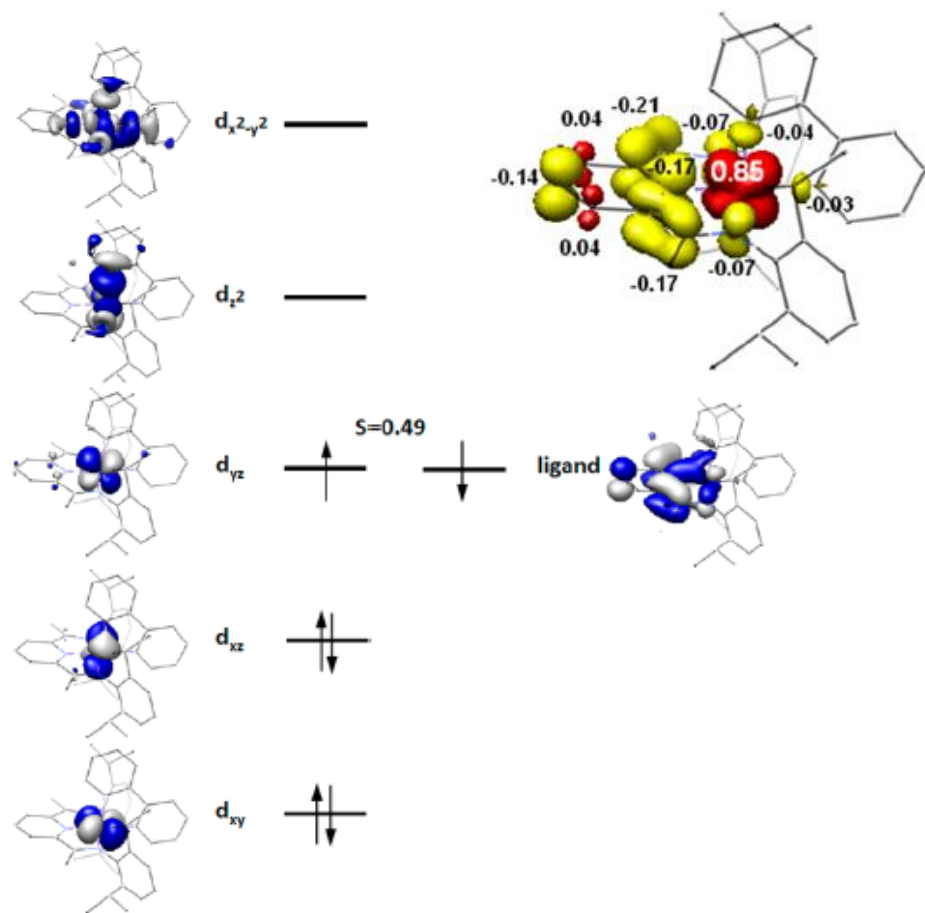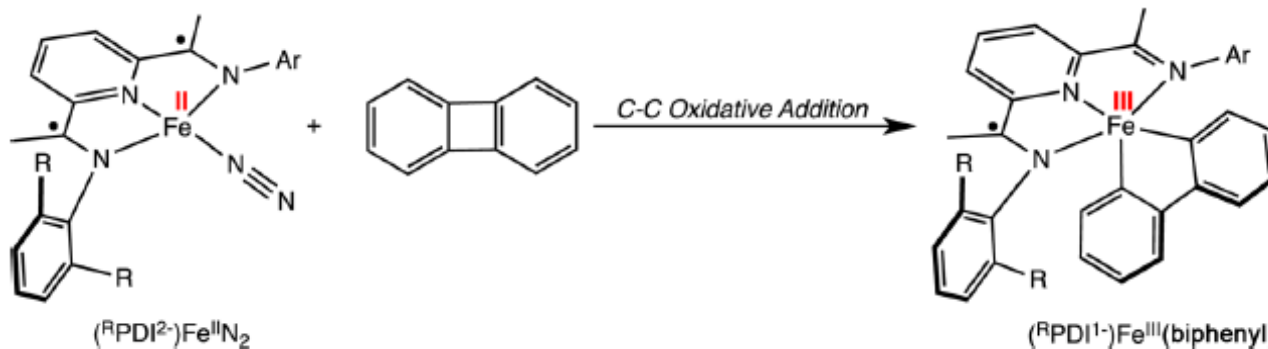
Indication of Fe(III) oxidation state

Figure 7. Qualitative molecular orbital diagram (left) and spin density plot (right) obtained from the BS(1,1) solution for (^{iPr}PDI)Fe(biphenyl).

Both the iron and bis(imino)pyridine ligand undergo concomitant one-electron oxidations resulting overall two-electron cleavage of the C-C bond, whithout high energy Fe(IV) oxidation state.

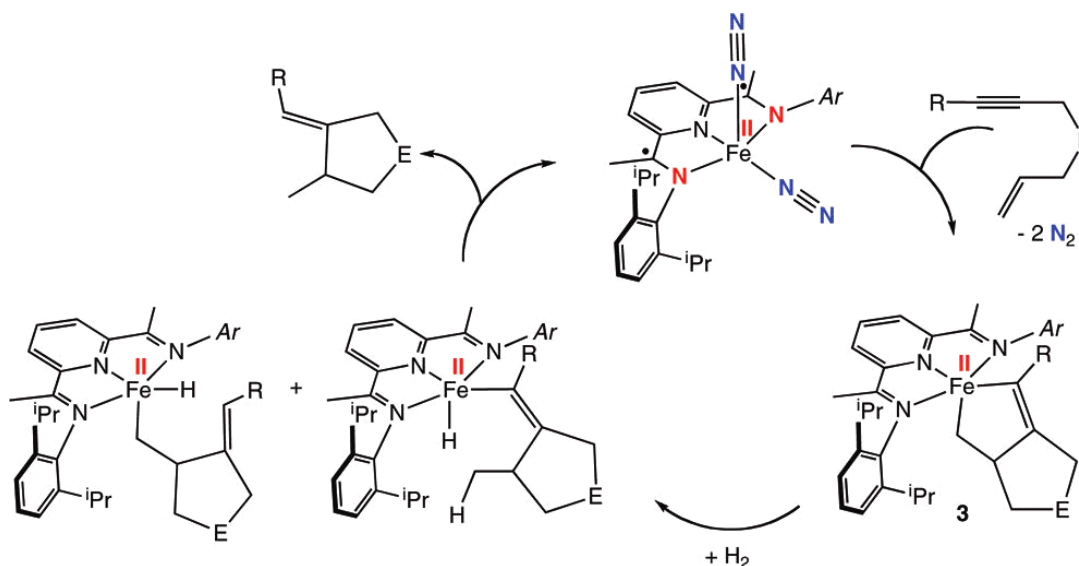16

Conclusion

$(^RPDI^{2-})Fe^{II}N_2$

C-C Oxidative Addition

$(^RPDI^{1-})Fe^{III}(biphenyl)$

Cooperative one-electron oxidation at both the metal and ligand

Example of catalytic reaction

$- 2 N_2$

$+ H_2$

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Today's Contents

Redox-active cobalt mediated reaction

Scheme 1

a.

$[Co^{III}(ap^{Ph})_2]^-$ CH_2Cl_2 → $ClCH_2$ Cl^- $Co^{III}(CH_2Cl)(isq^{Ph})_2$

Also in this reaction, ligands(amidophenolate) work as reservoirs of electorons.

b.

$Co^{III}(Et)(isq^{Ph})_2$ ZnBr → $[ZnBr]^+[Co^{III}(ap^{Ph})_2]^-$

R–X   X⁻

(a) → $Co^{III}(R)(isq^{Ar})_2$ — R'M

$[Co^{III}(ap^{Ar})_2]^-$ (b)

(c) — $[Co^{III}(R)(R')(isq^{Ar})_2]^-$ ← $[M]^+$

R–R'

Theoretical cycle

X-ray diffraction of alkyl complex

Soper, J. D. *et al. JACS,* **2010,** *132*, 14358

a.

C42
C41
O1
N2
N1
Co
O2

b.

H₃C
1.507(4)
'Bu
CH₂
Ph
2.021(3)
1.442(3)
1.390(3) 1.436(3)
O
1.867(2)
N
1.425(3) 1.383(3)
'Bu
1.321(3)
1.378(3)
1.436(4)
1.435(3)
1.859(2)
1.431(3)
1.442(4)
1.372(3)
'Bu
1.382(3) 1.433(3)
N
1.859(2) 1.870(2)
O
1.323(3)
1.439(3) 1.386(3)
1.444(3)
Ph
'Bu

d (C-C) ~ 1.39 Å

Pd^{ll}
O 1.43 1.38
1.30
1.35 1.44 1.43
N 1.42 1.37

Pd^{ll}
O 1.35
1.37

Ni^{ll}
O 1.46 1.36
1.24
1.30 1.52 1.46
N 1.44 1.36

Wieghardt, K. *Chem. -Eur. J.* **2005,** *11*, 204

•**Four long and two short C-C**
**Semiquinonate form** ⟹

Ar 'Bu
'Bu N O
Co^{lll}
O N 'Bu
'Bu Ar

Mechanism of alkylation

Soper, J. D. *et al. JACS,* **2010,** *132*, 14358

Table S1. Relative Rates of Organohalide Addition to $[Co^{III}(ap^{Ph})_2]^{-}$.[a]

entry	R–X	reaction time
1	CH_3I	<30 s
2	CH_3OTf	<30 s
3	CH_2ClBr	30 min[b]
4	CH_2Cl_2	12 h
5	EtI	<1 min
6	EtBr	1 h
7	$PhCH_2Cl$	24 h
8	$PhCH_2Br$	>2 d
9	PhI	—
10	C_2H_3Br	—

[a]All reactions performed under N_2 using 0.010 M $Na[Co^{III}(ap^{Ph})_2]$ and 0.050 M R–X in CH_3CN.
[b]Gives exclusively $Co^{III}(CH_2Cl)(isq^{Ph})_2$, as determined by ESI–MS.
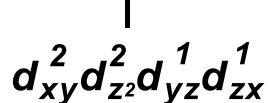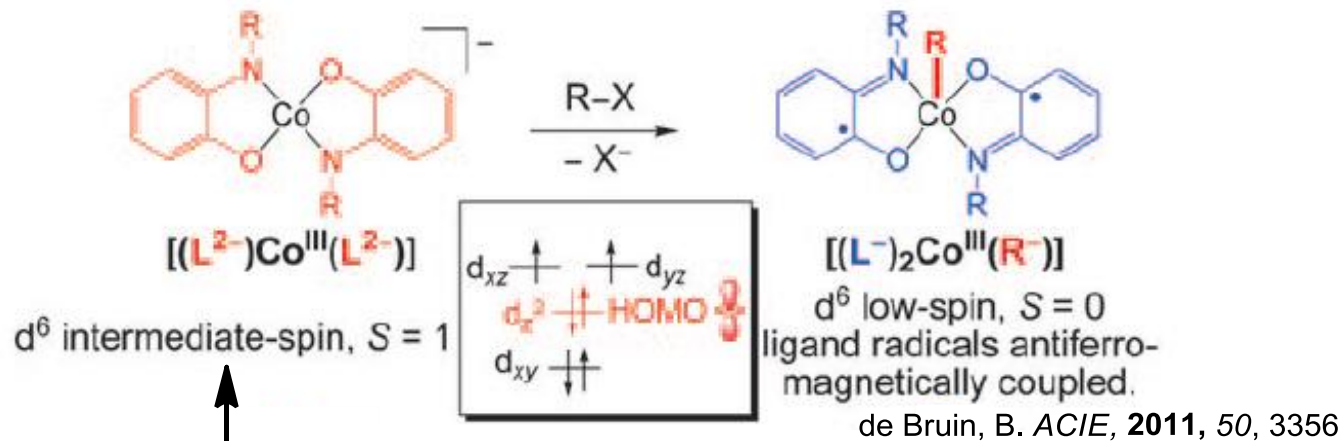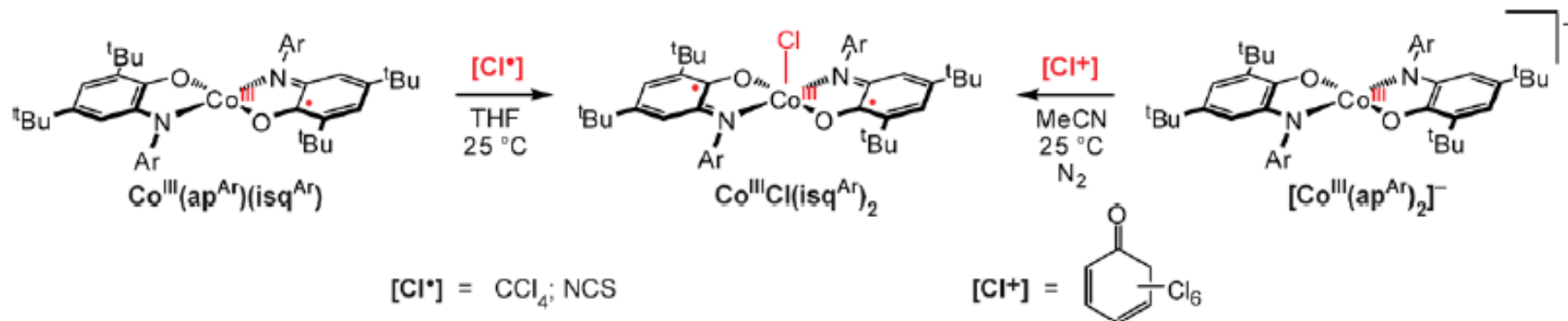
(1) Parallel to the lability of halides

(2) Steric factor of haloalkane

(3) No addition to *sp²* carbon

(4) Steric factor of cobalt center

Mechanism of alkylation

Soper, J. D. *et al. JACS,* **2010,** *132*, 14358
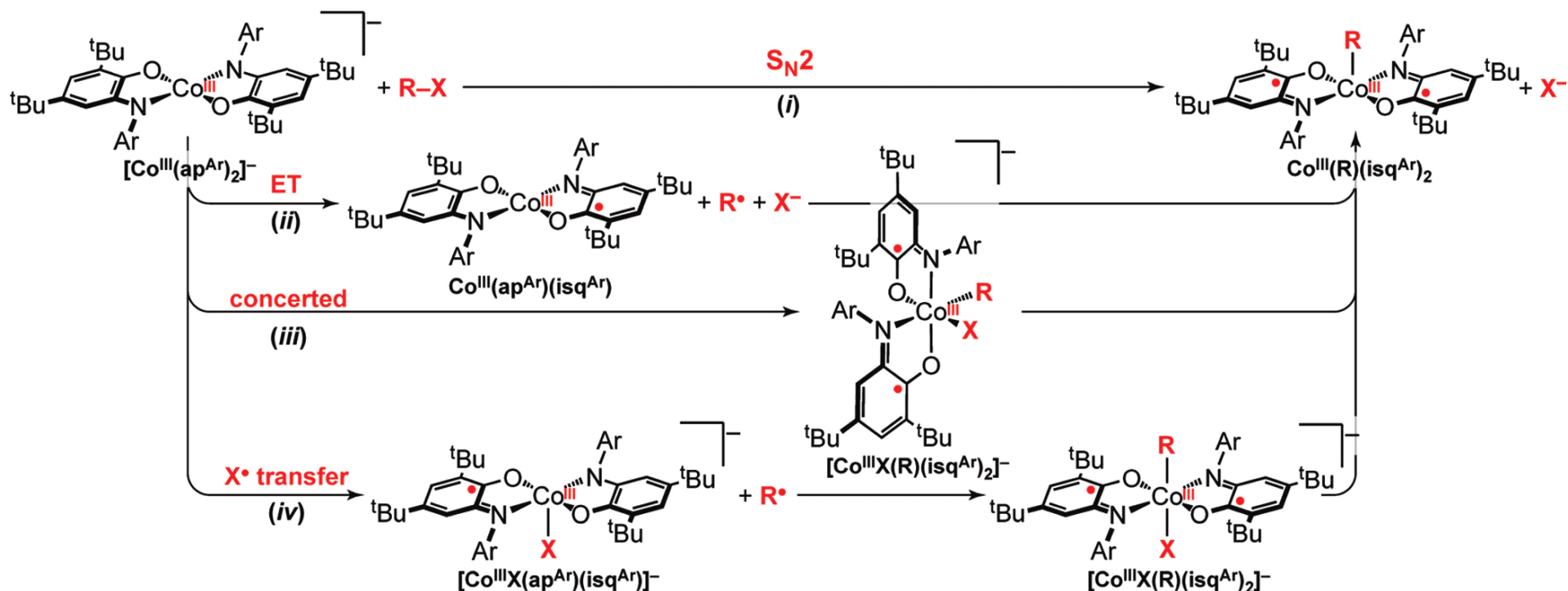
Pass (*i*) is likely to match the experimental observations.
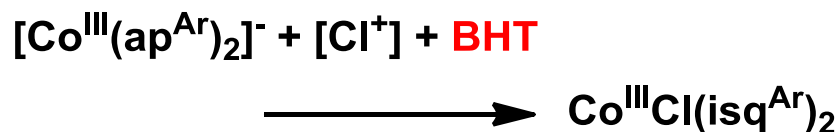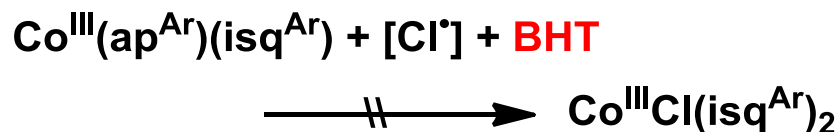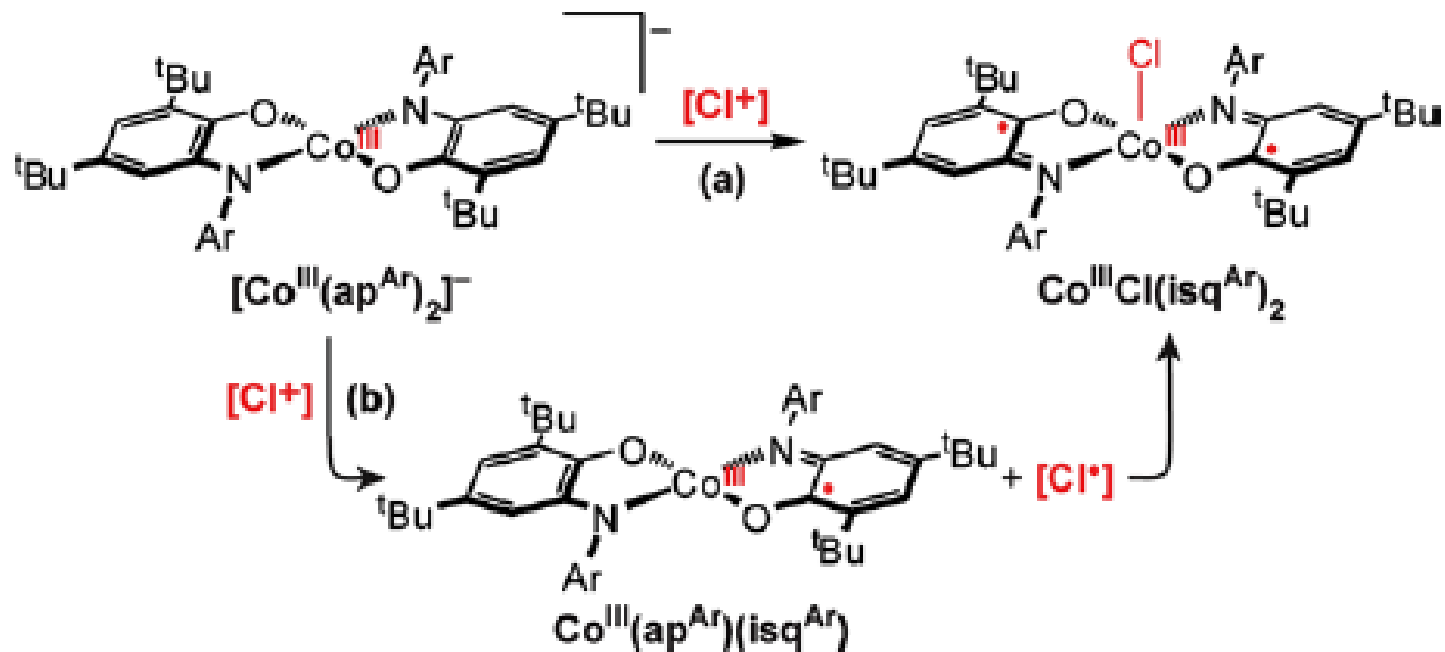
Nucleophilic attack of cobalt

Soper, J. D. *et al. Polyhedron,* **2010,** *29*, 164

$Co^{III}(ap^{Ar})(isq^{Ar})$ [Cl•] / THF 25 °C $Co^{III}Cl(isq^{Ar})_2$ [Cl+] / MeCN 25 °C N₂ $[Co^{III}(ap^{Ar})_2]^-$

[Cl•] = CCl₄; NCS   [Cl+] = ⬡—Cl₆

$[(L^{2-})Co^{III}(L^{2-})]$ R–X / – X⁻ $[(L^-)_2Co^{III}(R^-)]$

d^6 intermediate-spin, $S = 1$

d_{xz} d_{yz}
d_{z^2} HOMO
d_{xy}

d^6 low-spin, $S = 0$
ligand radicals antiferro-
magnetically coupled.

de Bruin, B. *ACIE,* **2011,** *50*, 3356

$d_{xy}^2 d_{z^2}^2 d_{yz}^1 d_{zx}^1$

d_{z^2} HOMO explains the nucleophilic character of the metal

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Nucleophilic attack of cobalt

2 possible mechanism

$Co^{III}(ap^{Ar})(isq^{Ar}) + [Cl^{\bullet}] + BHT$

$\xrightarrow{\quad\quad \|\!\| \quad\quad} Co^{III}Cl(isq^{Ar})_2$

$[Co^{III}(ap^{Ar})_2]^- + [Cl^+] + BHT$

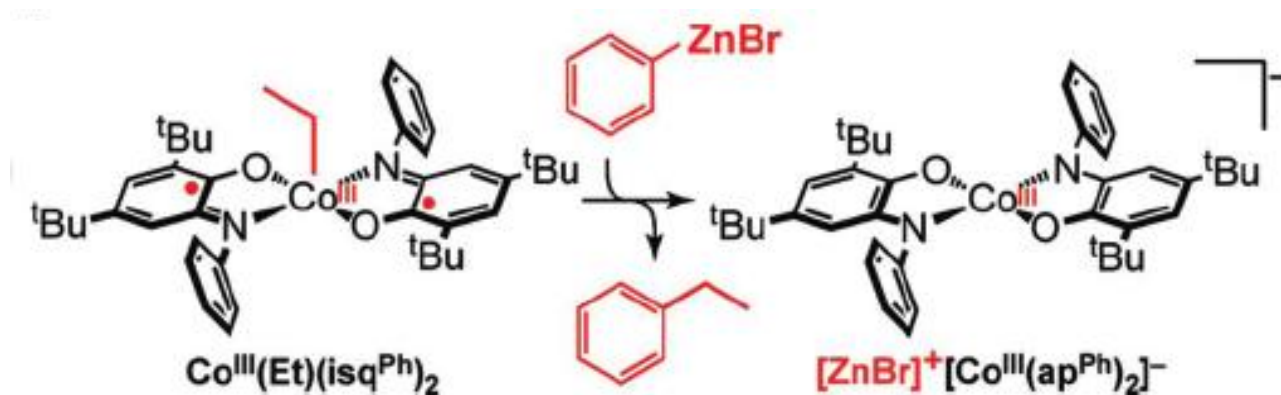$\xrightarrow{\quad\quad\quad\quad} Co^{III}Cl(isq^{Ar})_2$

Pass (a) is possible*!!*

Reaction with zinc reagent

Soper, J. D. *et al. JACS,* **2010,** *132*, 14358

entry	PhZnBr (equiv)	$Co^{III}(Et)(isq^{Ph})_2$ consumed (%)[b]	Ph–Et yield (%)[c]	Ph–Ph yield (%)[d]
1	2	80	11	1.6
2	4	93	15	2.4
3	6	97	15	1.7
4	10	98	15	1.8

But...

{ **low yield**
amount of zinc reagent
unidentified mechanism of reductive elimination

are ploblematic point.

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Today's Contents

Oxidation of benzylalcohol
Chaudhuri, P. *et al. Inorg. Chem.*, **2008**, *47*, 11620

CH₂Cl₂, Air
ⁿBu₄NOMe

TON ~ 60

Figure 2. Molecular structure of complex 1, [Cu^{II}(L$^{••}$)].

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 1, [Cu^{II}(L$^{••}$)]

Distances			
C(2)−C(7)	1.452(5)	C(4)−C(5)	1.434(5)
C(2)−C(3)	1.436(5)	C(5)−C(6)	1.368(5)
C(3)−C(4)	1.377(5)	C(6)−C(7)	1.417(5)

angles	
C(7)−N(8)−C(9)	122.8(3)
C(9)−N(8)−Cu(1)	124.5(3)
C(7)−N(8)−Cu(1)	112.3(2)

Ligand is semiquinonato diradical

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Kinetics of the reaction

Chaudhuri, P. *et al. Inorg. Chem.*, **2008**, *47*, 11620

Initial rate method

[catalyst]
2.5 x 10^{-4} M ~ 10 x 10^{-4} M

[substrate]
5 x 10^{-4} M ~ 5 x 10^{-2} M

absorbance at 290 nm (benzaldehyde)

k_{sub} = 2.3 min^{-1}

k_{cat} = 2.2 x 10^2 min^{-1}

(first order)
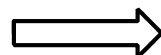
$\Rightarrow$ **Rate = k [catalyst][substrate]**

Deuterated substrate
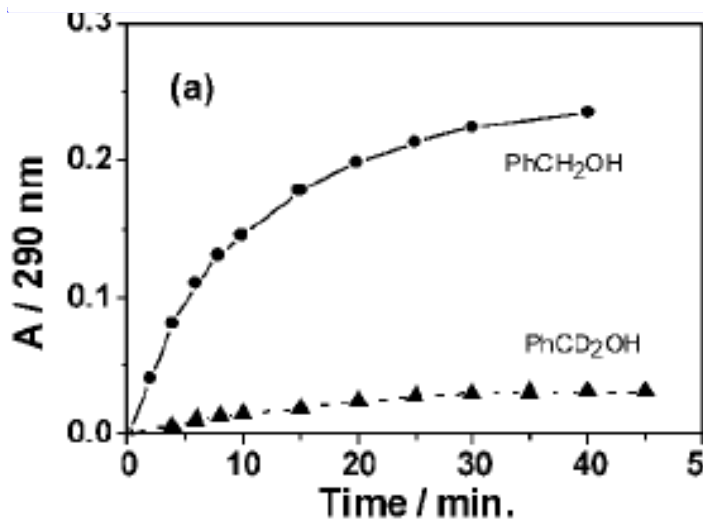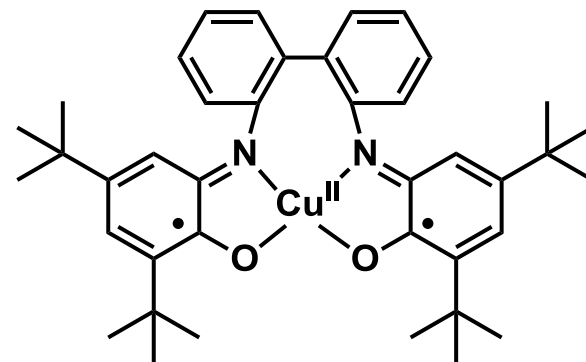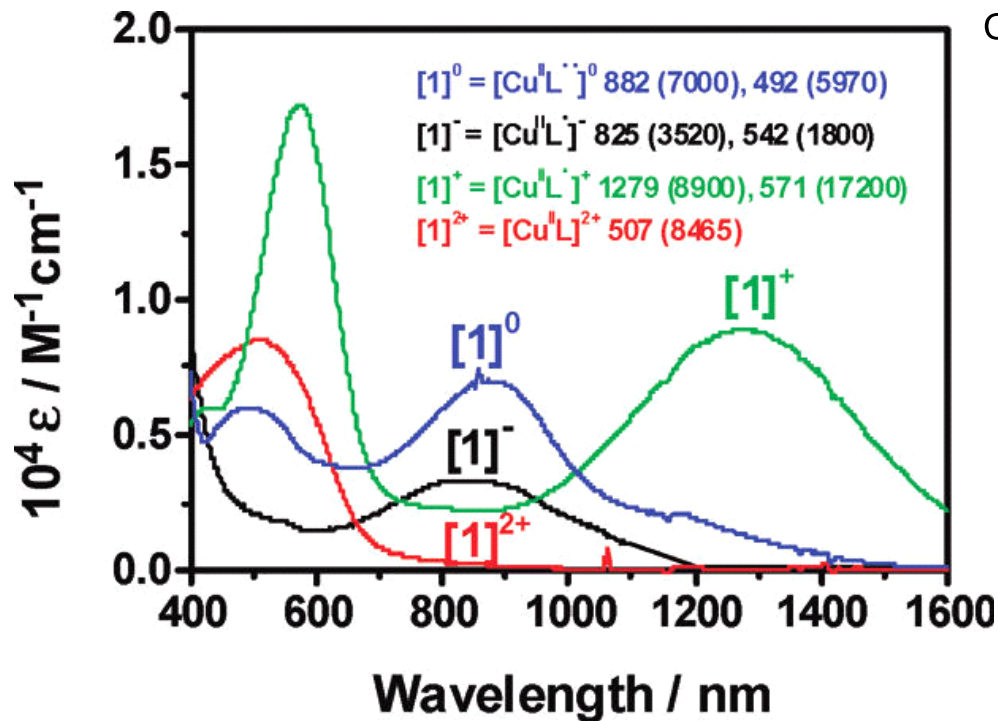

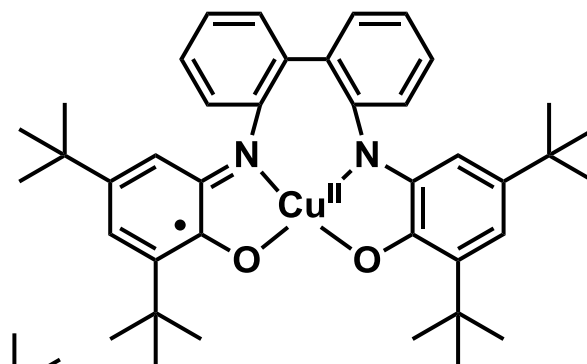k_H / k_D = 14

H-atom abstraction is r.d.s.

Figure 11. (a) Plots of change in absorption (i.e., [Benzaldehyde]) with time to evaluate the primary KIE.

Active species of the reaction

Chaudhuri, P. *et al. Inorg. Chem.*, **2008**, *47*, 11620

$[1]^0 = [Cu^{II}L^{\bullet\bullet}]^0$ 882 (7000), 492 (5970)
$[1]^- = [Cu^{II}L^{\bullet}]^-$ 825 (3520), 542 (1800)
$[1]^+ = [Cu^{II}L^{\bullet}]^+$ 1279 (8900), 571 (17200)
$[1]^{2+} = [Cu^{II}L]^{2+}$ 507 (8465)
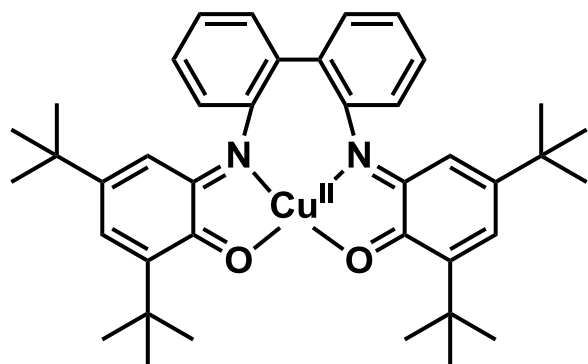
$[Cu^{II}L^{\bullet\bullet}]^0$
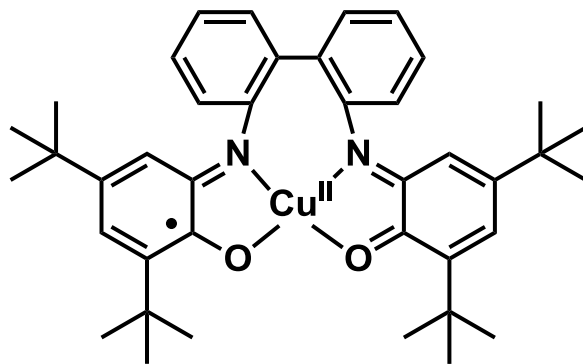
$[Cu^{II}L^{\bullet}]^-$

$[Cu^{II}L]^{2+}$

$[Cu^{II}L^{\bullet}]^+$

Active species of the reaction

Chaudhuri, P. *et al. Inorg. Chem.*, **2008**, *47*, 11620
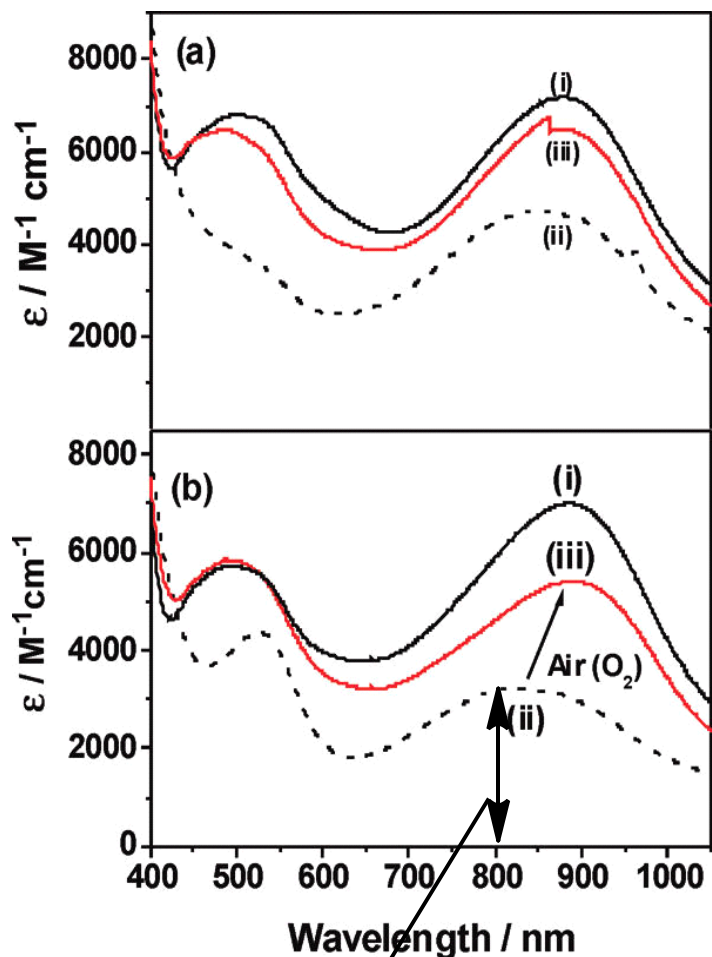
(a) indicates that during catalysis, there are [Cu^{II}L$^•$]$^-$ spesies.
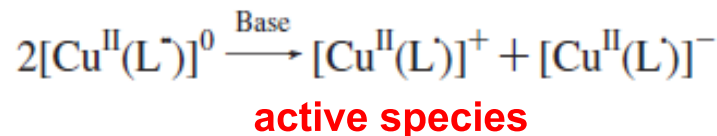
(b) indicates that addition of base, leads to disproportionation.

$$2[Cu^{II}(L^•)]^0 \xrightarrow{\text{Base}} [Cu^{II}(L)]^+ + [Cu^{II}(L)]^-$$

active species

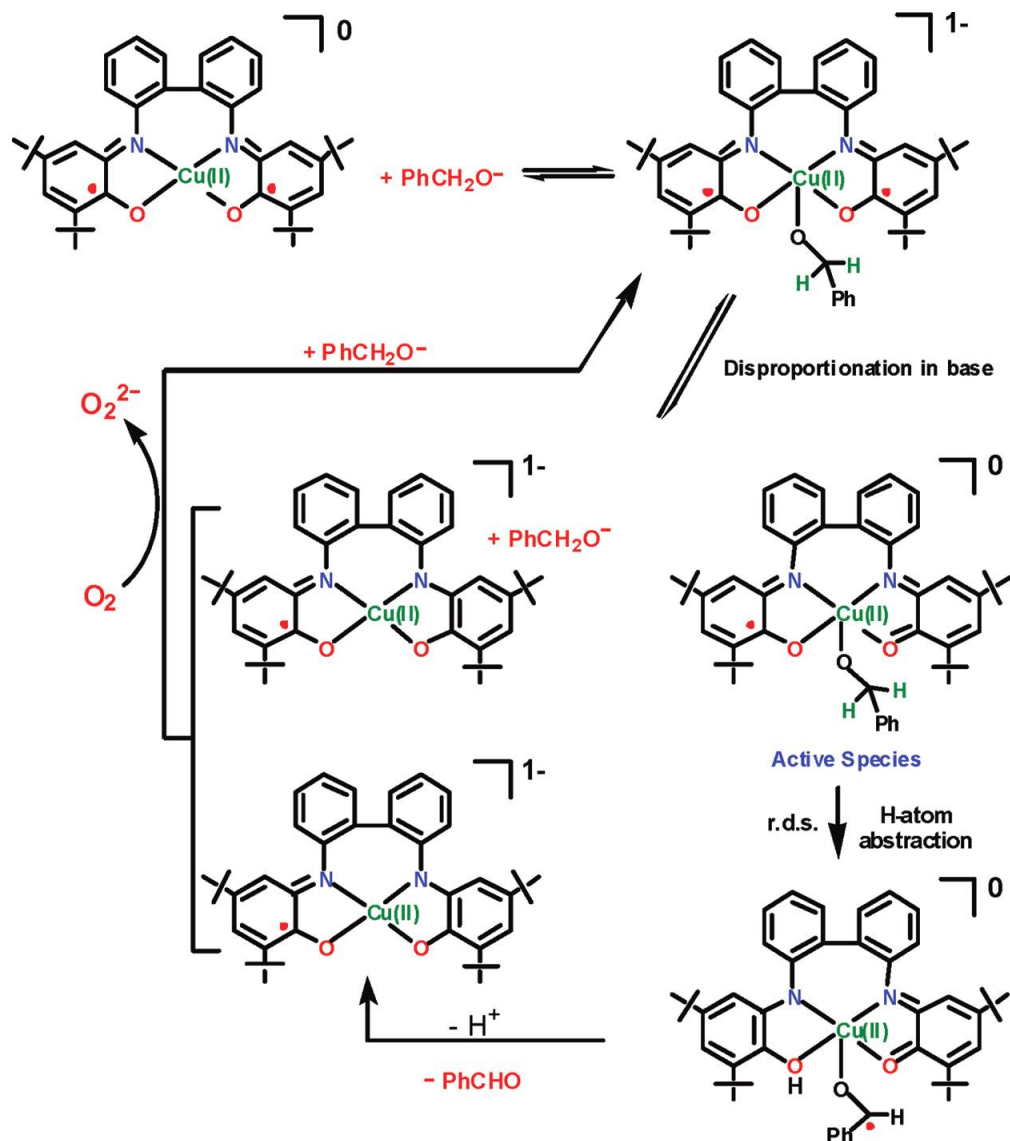**Figure 12.** (a) Change in electronic spectra during and after the catalysis: (i) complex 1 before addition of benzylalcohol and [*n*-Bu$_4$]NOMe; (ii) during the catalysis in the presence of air; (iii) after 16 h of the catalytic reaction. (b) Effect of base on the electronic spectra of catalyst, complex **1**: (i) complex 1 under argon; (ii) complex 1 on addition of base under argon; (iii) after exposure of solution ii to air. The electronic spectrum changes from (i) → (ii) → (iii).

equal to the sum of [Cu^{II}L$^•$]$^-$, [Cu^{II}L$^•$]$^+$,50 % each relative to the total amount of complex.

Mechanism of the reaction Chaudhuri, P. *et al. Inorg. Chem.*, **2008**, *47*, 11620

Cu complex 1 eq.

$PhCH_2OH$ 10 eq.

$^nBu_4OME$ 9 eq.

under Ar | CH_2Cl_2

benzaldehyde 0.5 eq.

$[Cu^{II}L^\bullet]^{-1}$

Ligand participates in the reaction in radicalic way.

+ $PhCH_2O^-$

Disproportionation in base

+ $PhCH_2O^-$

+ $PhCH_2O^-$

O_2^{2-}

O_2

Active Species

r.d.s.   H-atom abstraction

- H^+

- PhCHO

Today's Contents

3. Summary

<u>Summary(1)</u>

· **Redox non-inocent ligand works as electron reservoir.**

⟶ **oxidative addition/reductive elimination**
   replacement to noble metals

· **Redox non-inocent ligand perticipate in reaction by making/breaking bonds in radicalic manner.**

⟶ **oxidation of alcohol**
   cyclo propanation, amination

Ref.) Mr.Kato's Lit.seminar (2012)

<u>Redox non-innocent ligands are versatile new tools</u>

<u>to control catalytic reactions.</u>

<u>Summary(2)</u>

But...
- **mechanism of reaction is a little unclear**
- **applicated to stoichiometric reaction,**
  a few example of catalytic reactions

- **applicated to simple reactions**

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Refference

Review: de Bruin, B. *ACS Catal.* **2012**, *2*, 270
Ward, T.R. *ACIE.* **2012**, *51*, 2