Organometallic Chemistry Involving Radical –Forming Noninnocent Ligands

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Fonds der Chemischen Industrie (FCI)
COST (EU)

stable radicals, „trivalent carbon“

Wilhelm Schlenk (*1879): ketyls, Mg alkyls

Karl Ziegler (*1898): C radicals, Al alkyls

Eugen Müller (*1905): phenoxyls, semiquinones

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G.M. Whitesides, R.H. Grubbs, T.L. Brown, F. Basolo, ….

J.K. Kochi (*1927)[1]

D. Astruc (*1946)[2]

organo-metallic chemistry

[1] „Organometallic mechanisms and catalysis“ 1978
[2] „Electron transfer and radical processes in transition metal chemistry“ 1995

Innocent Ligands

- H_2O, NH_3, …
- Cl^-, OH^-,…
- CH_3^-, O^{2-} (?)

“The Shrinking World of Innocent Ligands: Conventional and Non-conventional Redox-active Ligands (Essay)”
W. Kaim, *Eur. J. Inorg. Chem.* 2012, 343-348

Proof of Innocence ?

- non-innocent ligands
(Jørgensen 1966, 1969; $O_2^{0/\bullet-/2-}$, $NO^{+/\bullet/-}$, $Q^{0/\bullet-/2-}$, etc)

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

„Ligands are innocent when they allow oxidation states of the central atoms to be defined. The simplest case of a suspect ligand is NO.“

- non-innocent behaviour in complexes
(Ward, McCleverty **2002**)

- physical vs. formal oxidation states
(Chaudhuri, Wieghardt et al. **2001**)

NO_x^- + Fe^{2+} + H_2SO_4 (conc.) →

$[Fe^{I}(H_2O)_5(NO^+)]^{2+}$

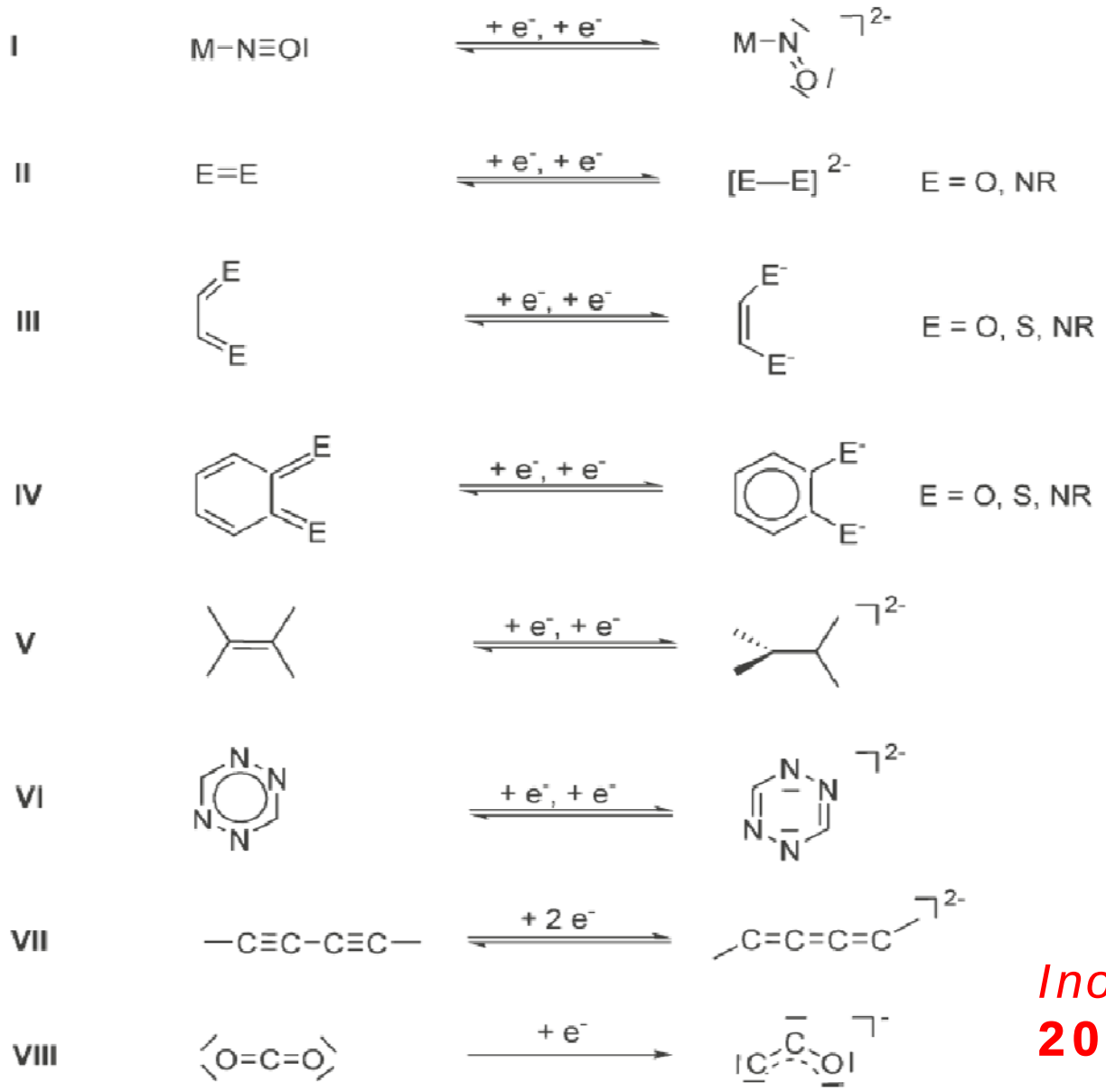
or $[Fe^{II}(H_2O)_5(NO^{\bullet})]^{2+}$

or $[Fe^{III}(H_2O)_5(NO^-)]^{2+}$

brown ring probe

Inorg. Chem. **2002,** *41*, 4

Potentially redox-active ligands



Inorg. Chem
2011, *50*, 9752

Oxidation State Ambivalence I

metal/ligand: e.g. M^{n}-(L^{-}) or M^{n+1}-(L^{2-})

→ redox isomerism (valence tautomerism)

metal/metal: M^{n}-(μ-L)-$M'^{\,n+1}$ or M^{n+1}-(μ-L)-$M'^{\,n}$

→ mixed-valency (if degenerate),

inner-sphere electron transfer (inorganic)

metal/ligand/metal:

M^{n}-(μ-L^{2-})- $M'^{\,n+1}$ or M^{n}-(μ-$L^{\bullet-}$)- $M'^{\,n}$

Oxidation State Ambivalence II

ligand/ligand: L^{n}-(M)-L'^{n+1} or L^{n+1}-(M)-L'^{n}

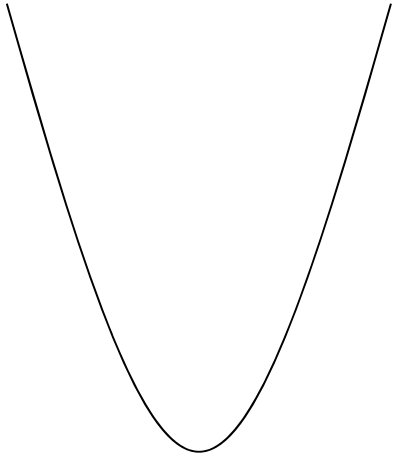
→ electron hopping (if degenerate),

inner-sphere electron transfer (organic)

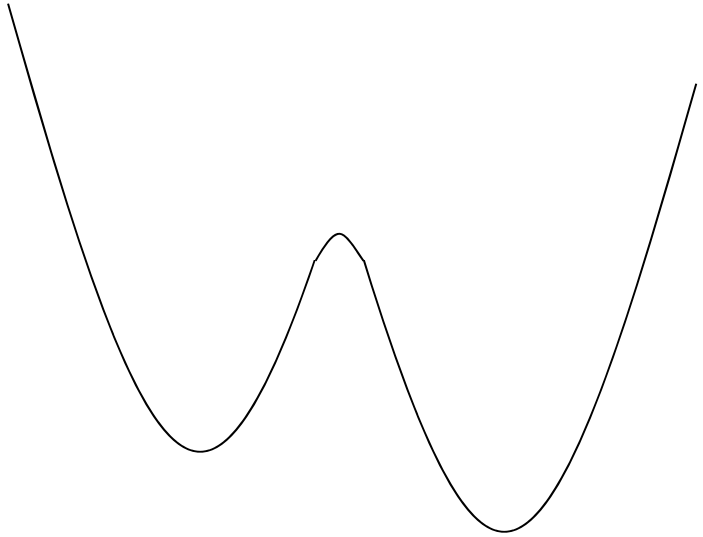
ligand/metal/ligand:

L^{n}-(M)-L'^{n+1} or L^{n}-(M^{+})-L'^{n}

$M^{x}(NIL^{y}) \longleftrightarrow M^{x+1}(NIL^{y-1})$



$M^{x}(NIL^{y}) \rightleftharpoons M^{x+1}(NIL^{y-1})$



Recent Overviews

„Non-innocent ligands in bioinorganic chemistry – an overview“
W. Kaim, B. Schwederski, *Coord. Chem. Rev.* **2010**, *254*, 1580-1588

„Manifestations of non-innocent ligand behavior (Forum article)“
W. Kaim, *Inorg. Chem.* **2011**, *50*, 9752-9765

„The shrinking world of innocent ligands: Conventional and non-conventional
redox-active ligands (Essay)“
W. Kaim, *Eur. J. Inorg. Chem.* **2012**, 343-348

„Redox-active ligands in catalysis“
V. K. K. Praneeth, M.R. Ringenberg, T.R. Ward, *Angew. Chem. Int. Ed.* **2012**, *51*, 10228-10234

„Redox-active ligands in catalysis“
O.R. Luca, R.H. Crabtree, *Chem. Soc. Rev.* **2013**, *42*, 1440-1459

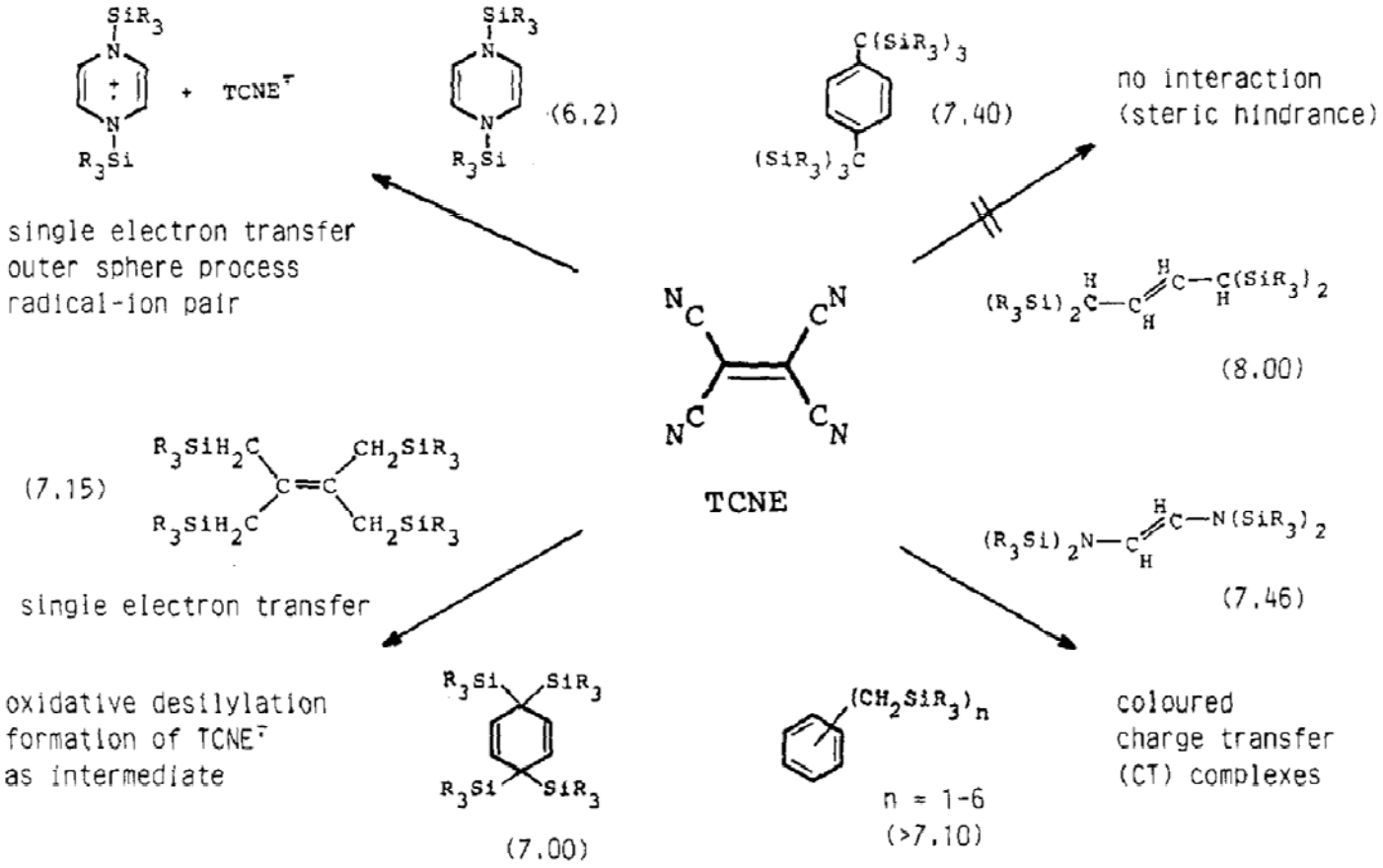
„Electron Transfer Reactivity of Organometallic Compounds Involving Radical-Forming Noninnocent Ligands“
W. Kaim, *Proc. Natl. Acad. Sci., India, Sect. A. Phys. Sci.* **2016**, *86*, 445-457

Radical Ligands Confer Nobility on Base-Metal Catalysts

Redox-active metal-ligand combinations, once the domain of coordination chemists and spectroscopists interested in structures, are undergoing a rebirth and entering the realm of catalysis. Performing metal-mediated redox chemistry where oxidation state changes occur at the ligand while the metal´s electronic configuration is maintained is a much broader concept that is likely to inspire new transformations and, ultimately, new applications.

P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794

Molecular and Electronic Structure of Electron-Transfer Active Main Group Organometallics



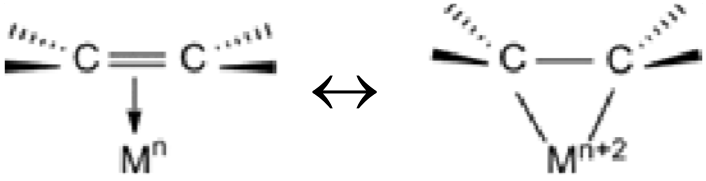
J. Baumgarten, C. Bessenbacher, W. Kaim, T. Stahl, *J. Am. Chem. Soc.* **1989**, *111*, 2126

Potentially Noninnocent Organic Ligands

$^{-}CR_3$, ^{-}H ($^{\bullet}CR_3$, $^{\bullet}H$, $^{+}CR_3$, ^{+}H)

CR_2 ↔ $^{2-}CR_2$

Fischer Schrock



$(C_n)^x$

$[cyclo\text{-}C_nR_n]^x$ n=5, x=1-: Cp^- donor
n=6, x=0: arene, π acceptor

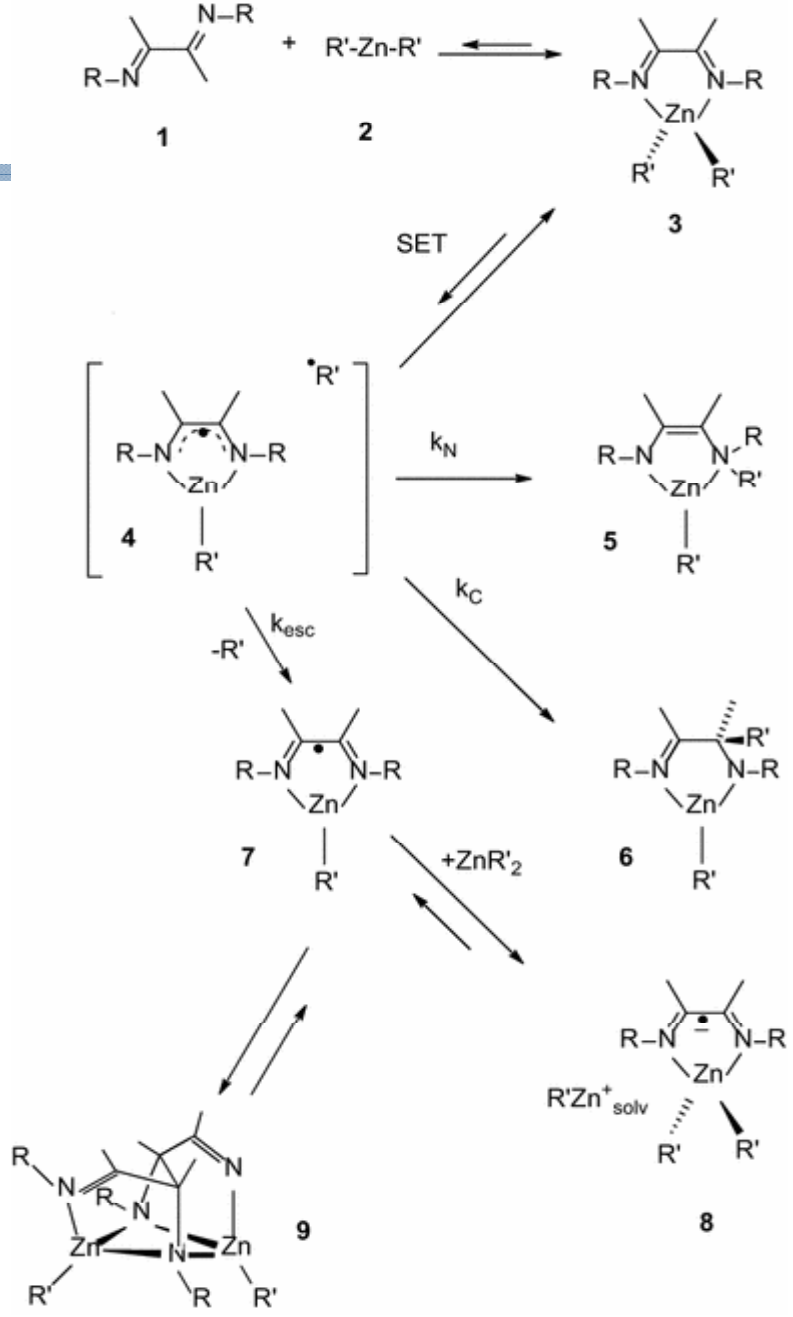
CO, CNR ($\rightarrow$ CO^-, $^{-}O\text{-}C{\equiv}C\text{-}O^-$)

Metal Alkyls

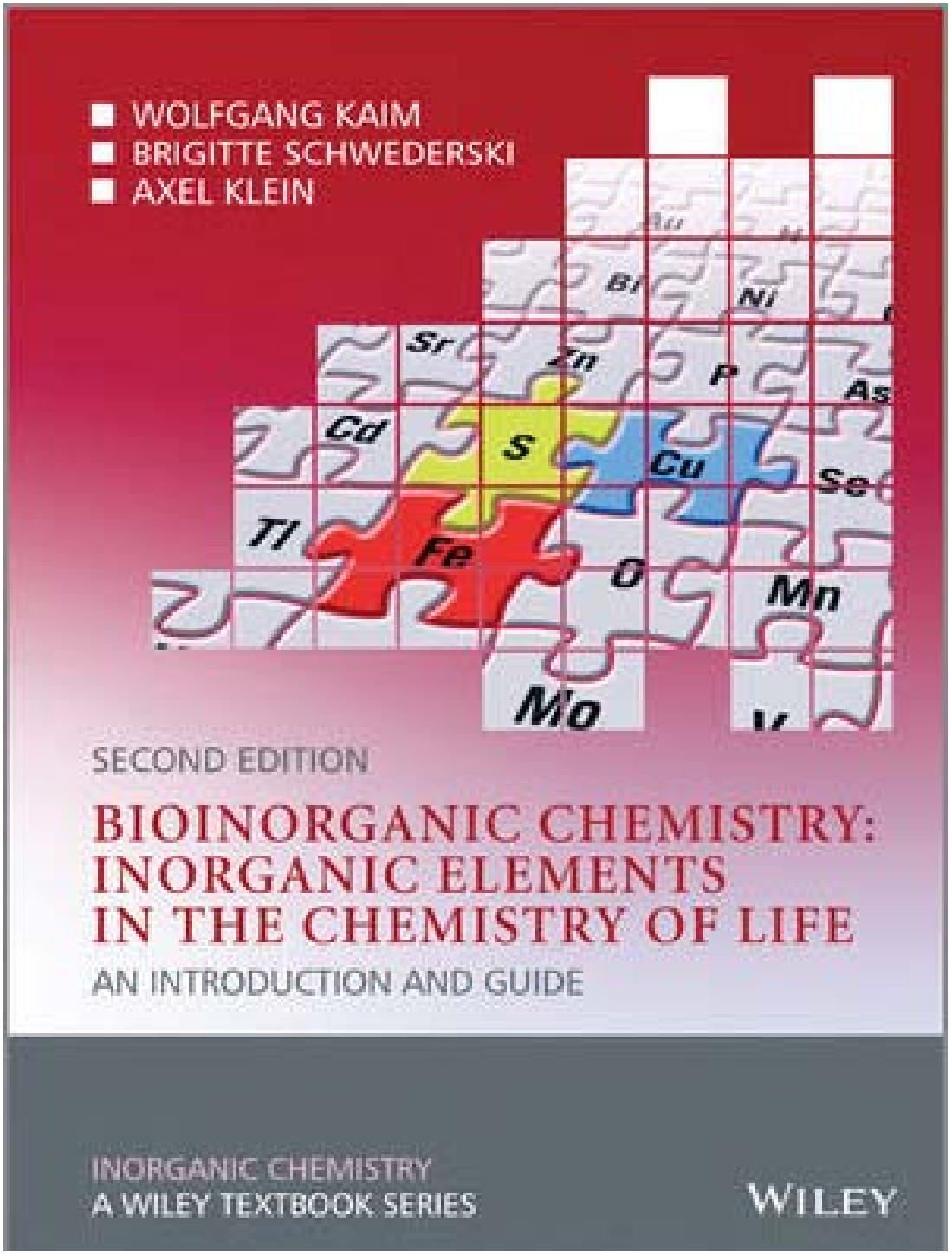
Mechanistic Alternatives

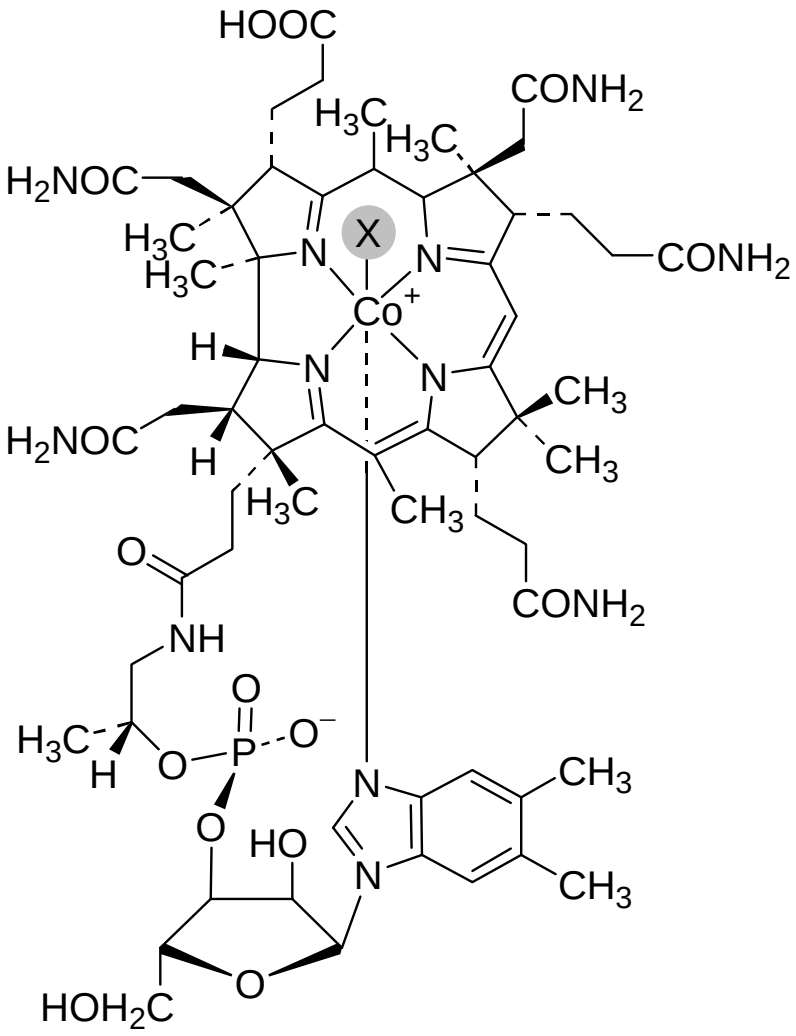
derived from experimal and computalional studies

(R = *tert*-Bu, R´= Me, Et, *iso*-Pr, *tert*-Bu)



J. Am. Chem. Soc.
1991, *113*, 5606


WOLFGANG KAIM
BRIGITTE SCHWEDERSKI
AXEL KLEIN
Au
Bi
Ni
Sr
Zn
P
As
Cd
S
Cu
Se
Tl
Fe
O
Mn
Mo
V
SECOND EDITION
BIOINORGANIC CHEMISTRY:
INORGANIC ELEMENTS
IN THE CHEMISTRY OF LIFE
AN INTRODUCTION AND GUIDE
INORGANIC CHEMISTRY
A WILEY TEXTBOOK SERIES
WILEY



Vitamin B_{12} (X = CN)

X = CH_3: Methylcobalamin (MeCbl oder MeB_{12})

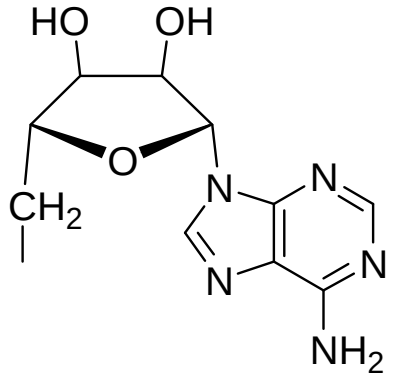
CN: Cyanocobalamin (Vitamin B_{12})

OH: Hydroxycobalamin (Vitamin B_{12a})

H_2O: Aquocobalamin

R: 5´-Desoxyadenosyl-cobalamin (Coenzym B_{12} oder AdoCbl)

R = 5´-Desoxyadenosyl



Tetrapyrrole Macrocycles

(a) stability

(b) chelate effect (thermodynamic and kinetic !)

(c) macrocyclic („size“) effect

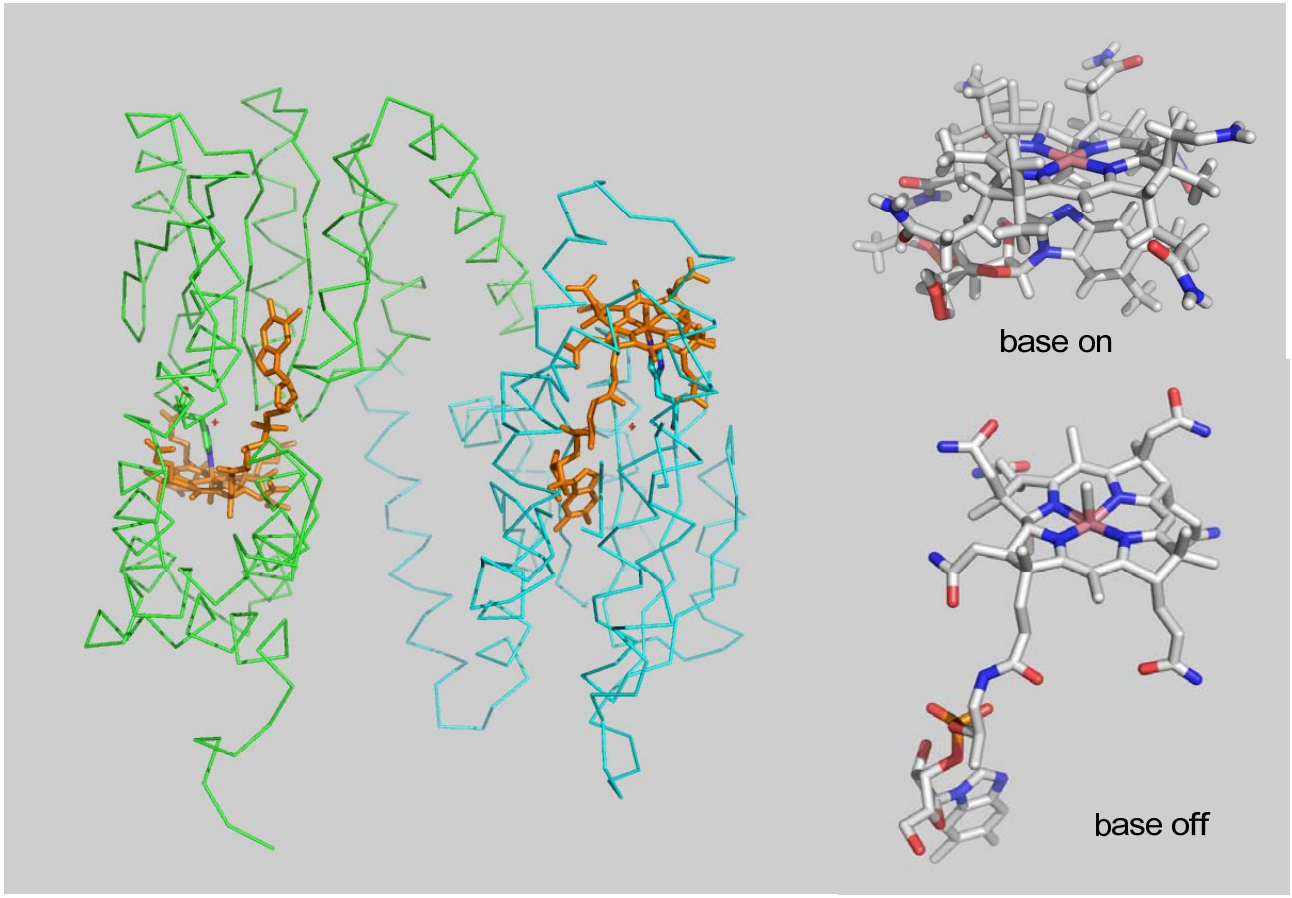
(d) π system (colour, electron transfer reactivity)

(e) axial ligation (substrate, control)

(f) distortion potential

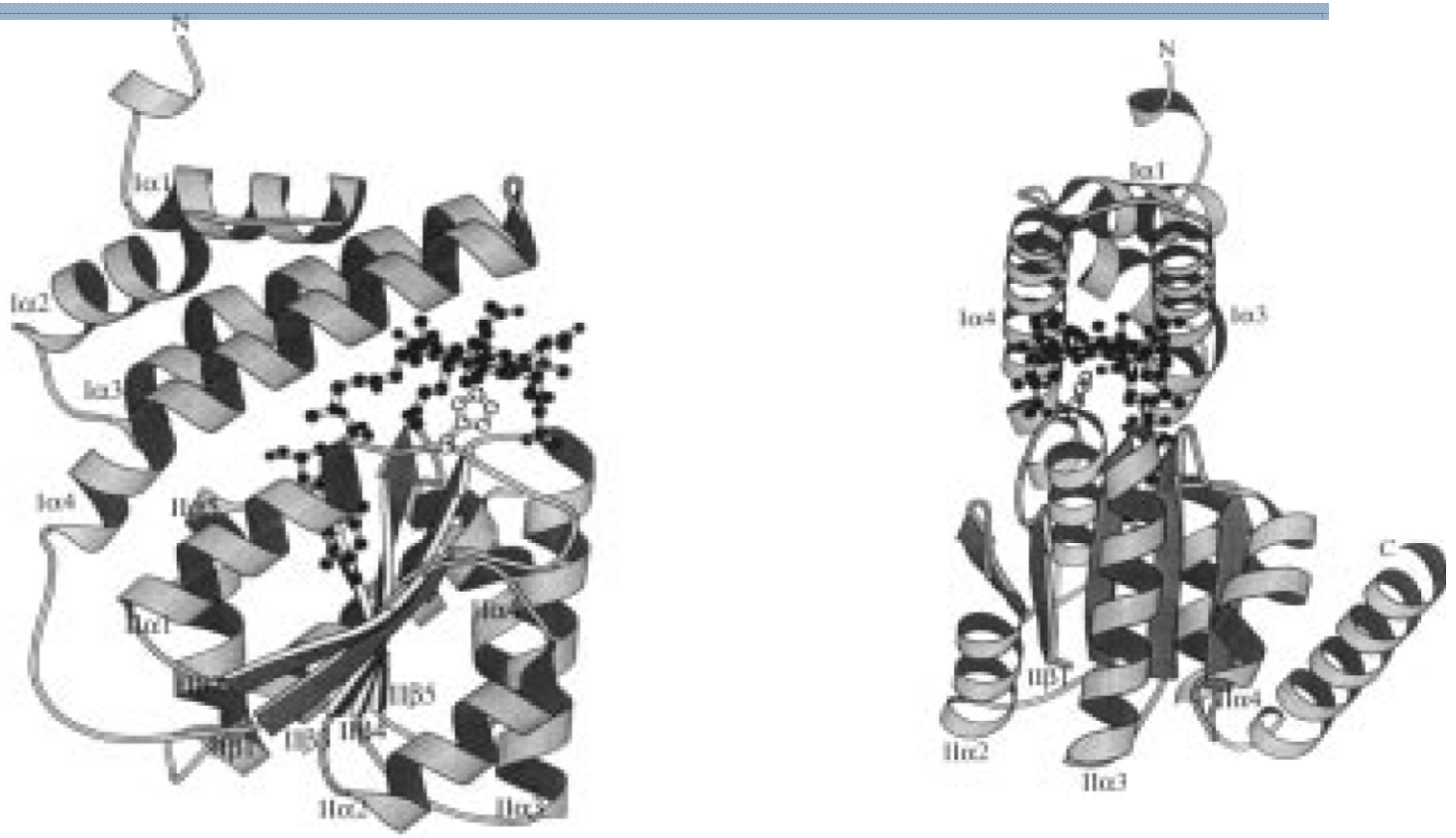
(g) ligand field effects

Methionine Synthase



Structure of B_{12}-binding domains of methionine synthase (PDB code 1BMT); base on/base off configurations of the coenzyme

Cobalamine-binding Fragment



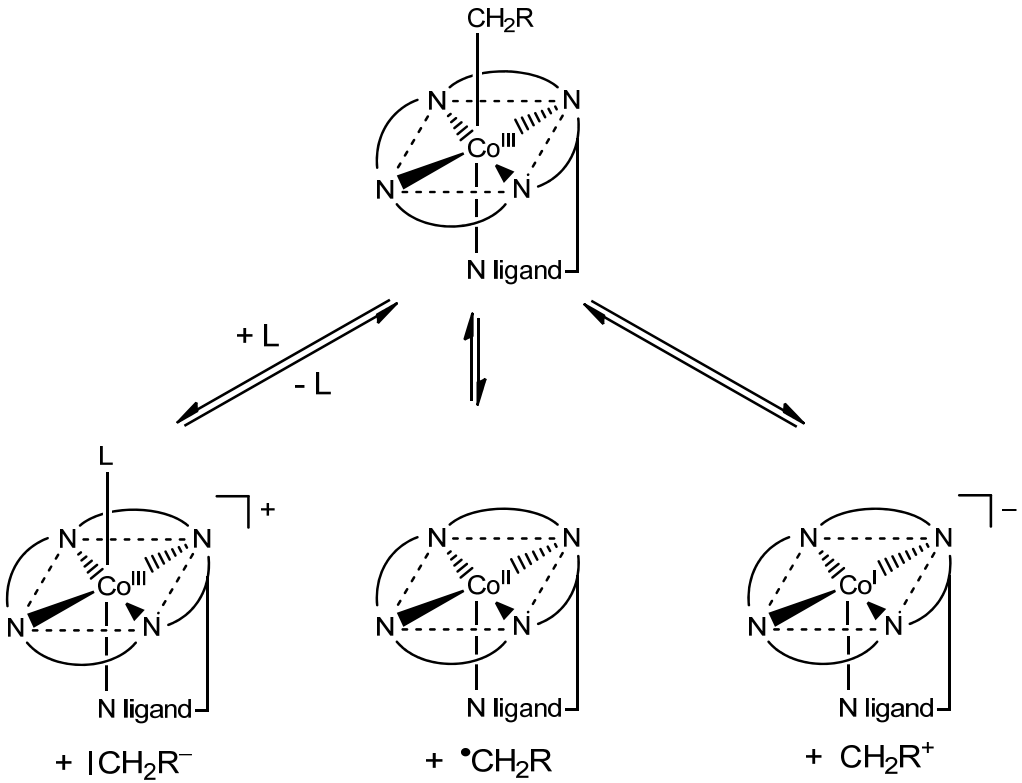
Drawings of the structure of the cobalamin-binding fragment. In the view on the left, the N-terminal four-helix bundle constituting domain I is at the upper left, and the α/β fold constituting domain II is at the lower right. The dimethylbenzimidazole side chain protrudes into the center of domain II, and the loop carrying the Co ligand, His-759, can be seen emerging from strand IIβ1. Association of the upper face of the corrin ring with domain I and of the lower face with domain II is evident in this view. The view on the right is rotated 90° about the vertical axis.

coenzyme	**+**	**apoenzyme**	**=**	**holoenzyme**
low molecular weight, determines the type of reactivity		high molecular weight (protein), determines substrate specificity and reaction rate		complete enzyme, fully functional

- cobalt — rarest first row transition metal
  - very special functionality
- corrin — smaller macrocycle than porphins
- primary alkyl — “natural” organometallic
- Co – CH_2R — hydrolysis-resistent

special reactivities:

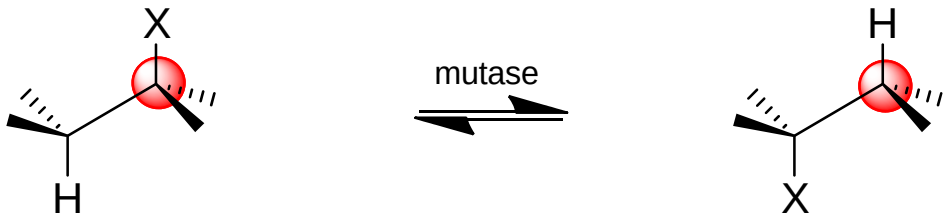
- methylation (R = H)
- *enzymatically controlled formation of reactive carbon radicals*



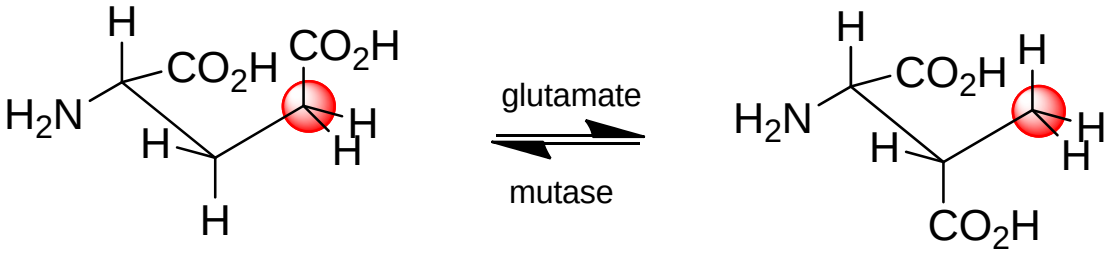
type of reaction:	heterolysis	homolysis	heterolysis
metal configuration in the product	d^6 low-spin, stable, inert	d^7 low-spin, 1 unpaired electron $(d_{z^2})^1$	d^8, "super-nucleophilic" $(d_{z^2})^2$
alkyl ligand, eliminated as:	"carbanion", nucleophilic	1° alkyl radical, very reactive	"carbocation", electrophilic
app. electrochemical potential equivalent[a]:	> 0 V		< -0.9 V

[a] In biochemistry, all redox potentials are generally referenced to the normal hydrogen electrode (NHE)

in general:



example:

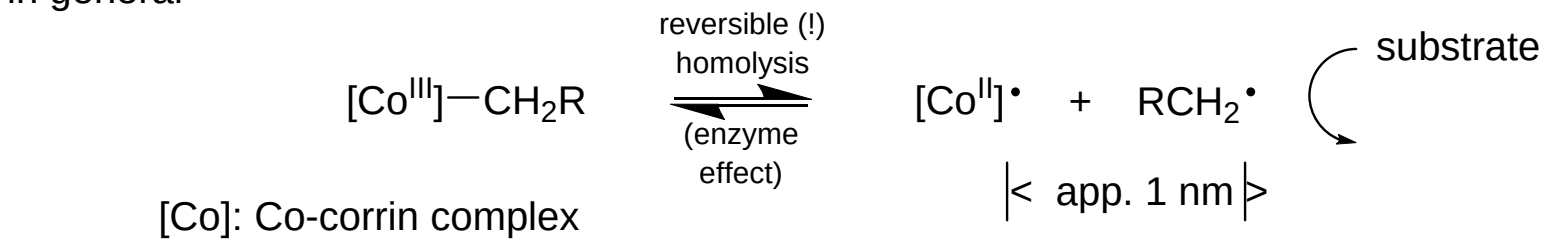


glutamic acid

β-methylaspartic acid

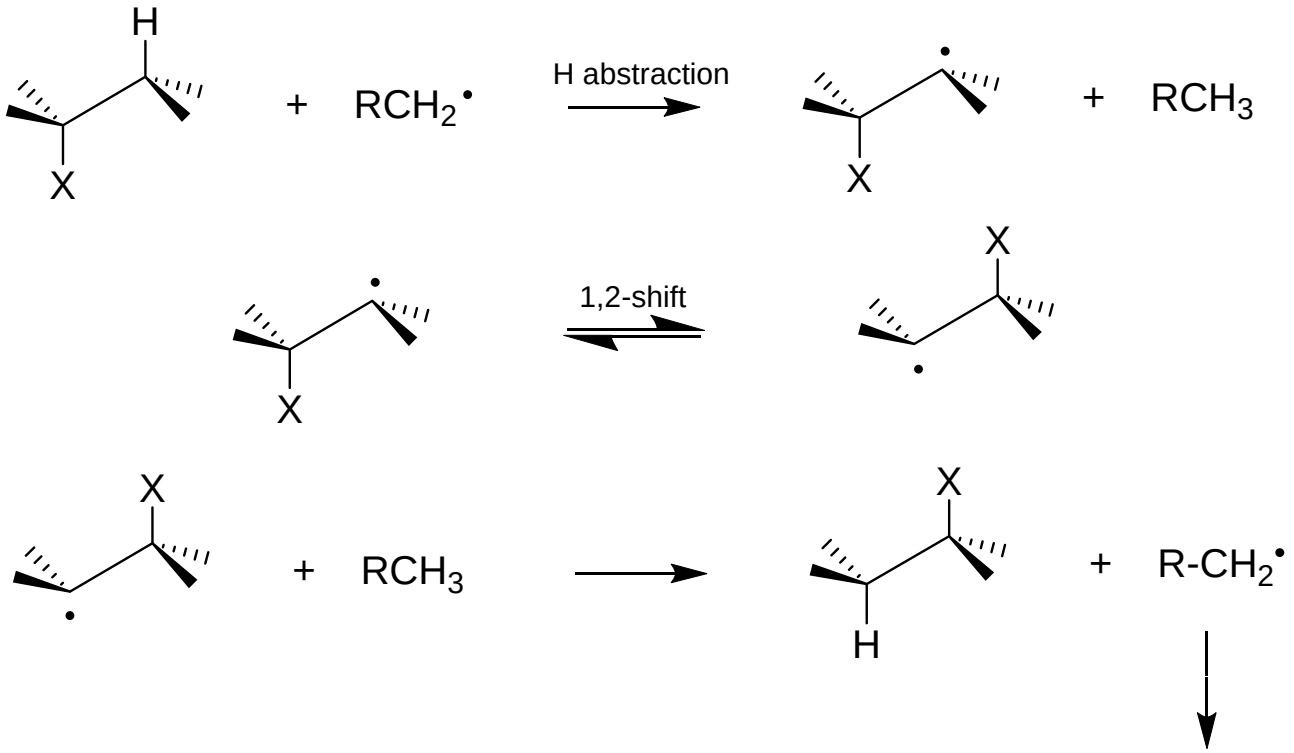
X = O, NH

in general



[Co]: Co-corrin complex

reaction steps:



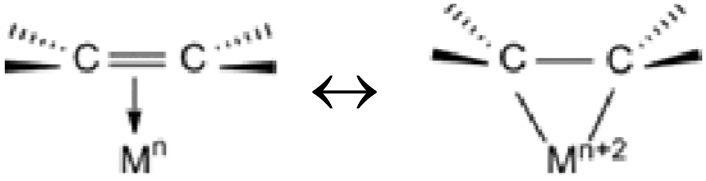
Polycarbon Ligands

Potentially Noninnocent Organic Ligands

$^{-}CR_3$, ^{-}H ($^{\bullet}CR_3$, $^{\bullet}H$, $^{+}CR_3$, ^{+}H)

CR_2 ↔ $^{2-}CR_2$

Fischer Schrock

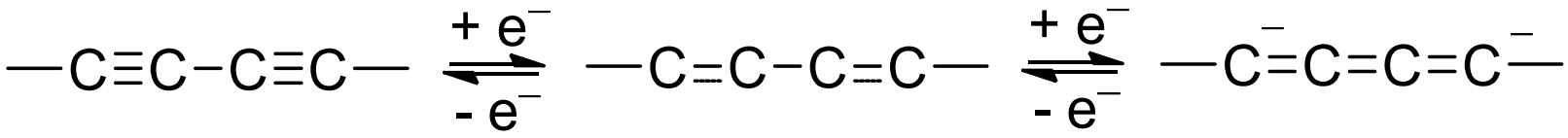


$(C_n)^x$

$[cyclo\text{-}C_nR_n]^x$ n=5, x=1-: Cp^- donor
n=6, x=0: arene, π acceptor

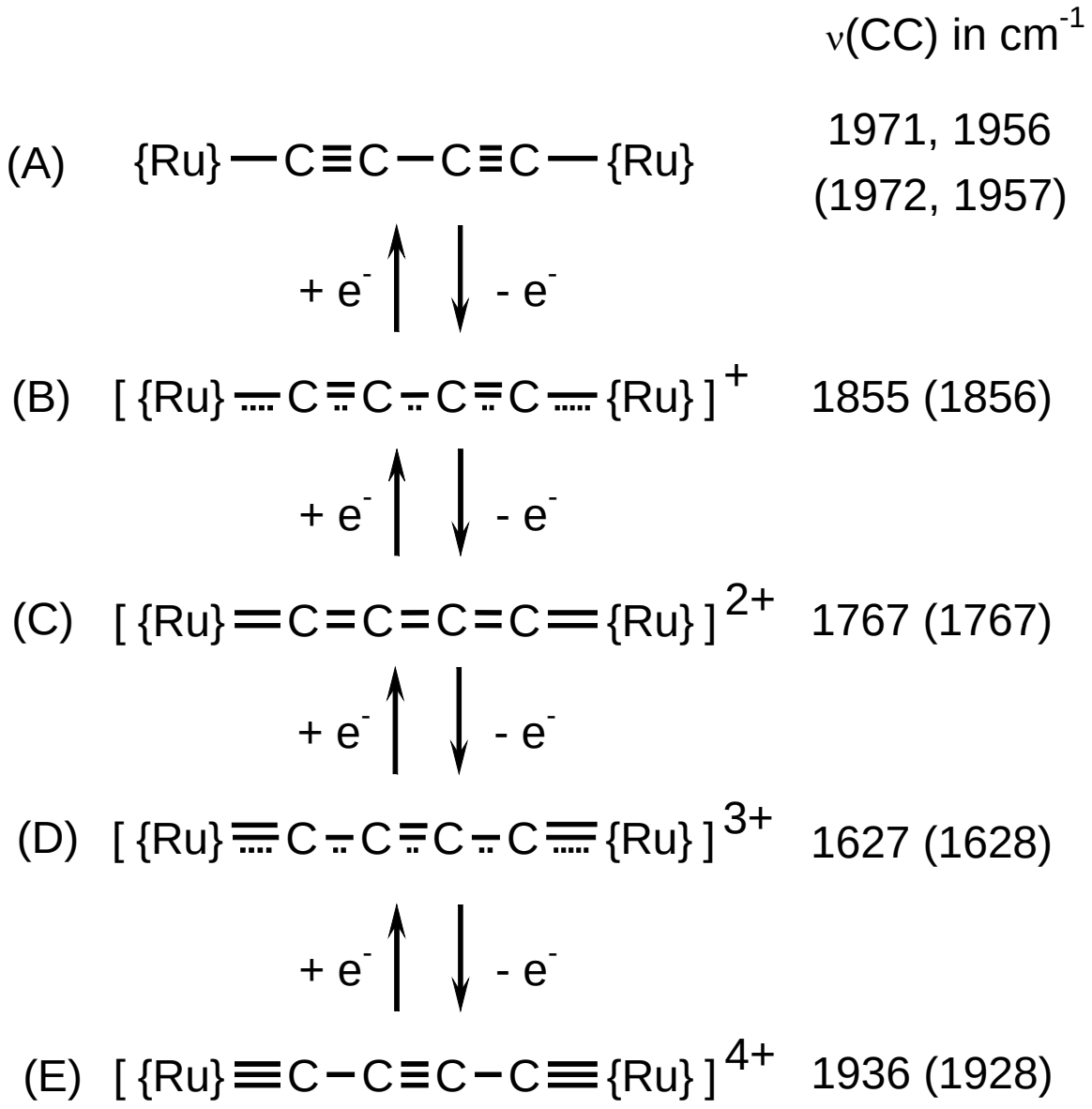
CO, CNR ($\rightarrow$ CO^-, $^{-}O\text{-}C{\equiv}C\text{-}O^-$)

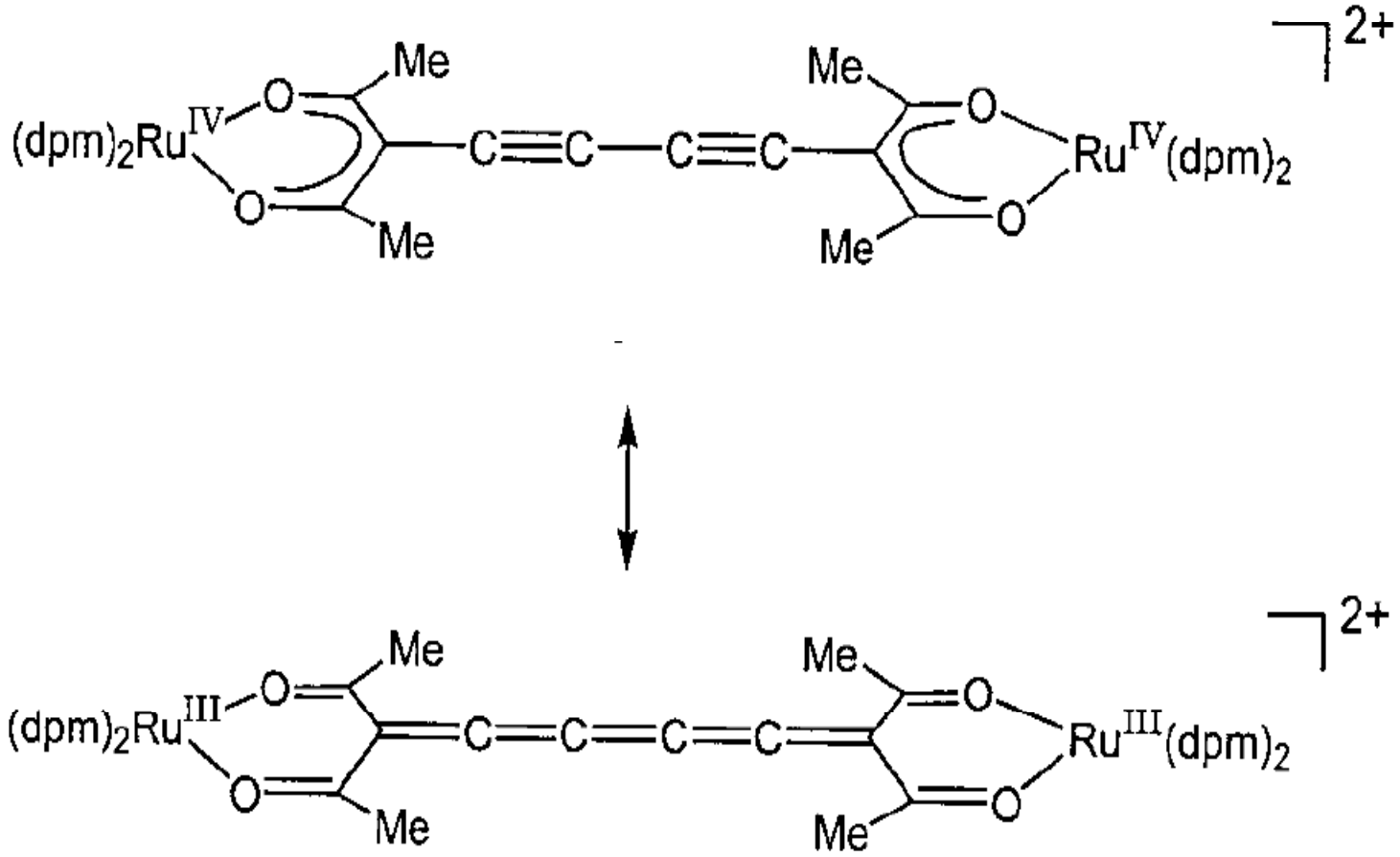
$[C_n]^x$ Systems



1,3-diyine

butatrienyl dianion


ν(CC) in cm-1
(A) {Ru}—C≡C—C≡C—{Ru}
1971, 1956
(1972, 1957)
+ e-
- e-
(B) [{Ru}=C=C=C=C=C=C=C=C={Ru}]+
1855 (1856)
+ e-
- e-
(C) [{Ru}=C=C=C=C=C=C=C=C={Ru}]2+
1767 (1767)
+ e-
- e-
(D) [{Ru}≡C-C≡C-C≡C-C≡C-{Ru}]3+
1627 (1628)
+ e-
- e-
(E) [{Ru}≡C-C≡C-C≡C-C≡C-{Ru}]4+
1936 (1928)
{Ru} = (η5-C5R5)(L)2Ru



Angew. Chem. Int. Ed. **2003**, *42*, 674

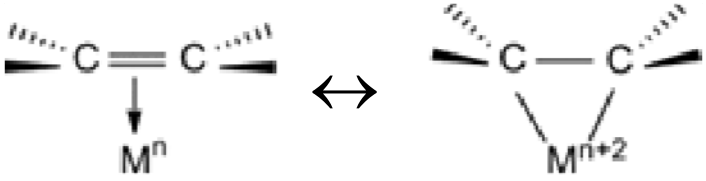
Half-Sandwich Compounds

Potentially Noninnocent Organic Ligands

$^{-}CR_3$, ^{-}H ($^{\bullet}CR_3$, $^{\bullet}H$, $^{+}CR_3$, ^{+}H)

CR_2 ↔ $^{2-}CR_2$

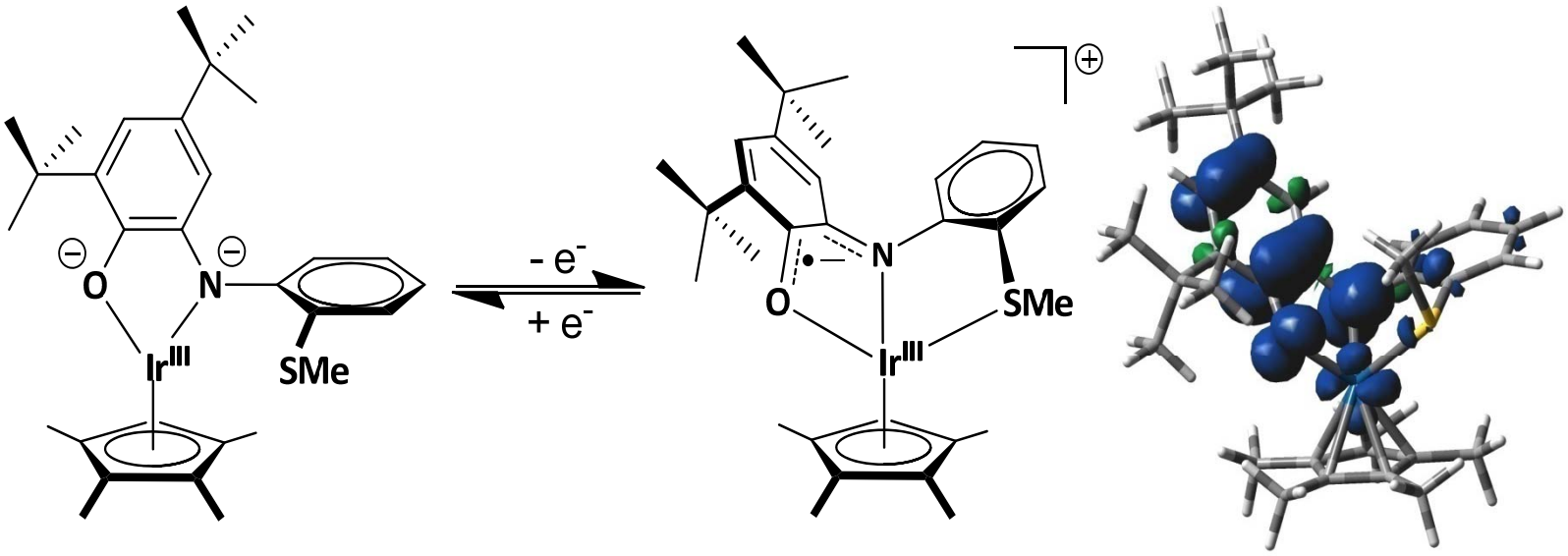
Fischer Schrock



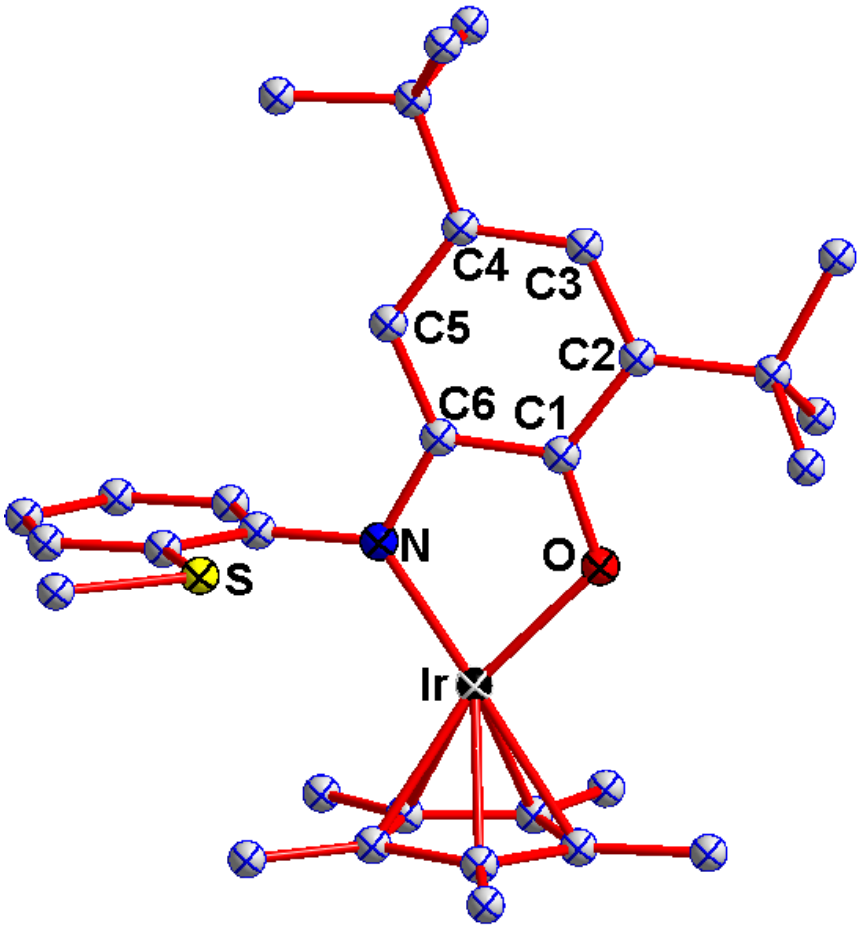
$(C_n)^x$

[*cyclo*-C_nR_n]^x n=5, x=1-: Cp^- donor
n=6, x=0: arene, π acceptor

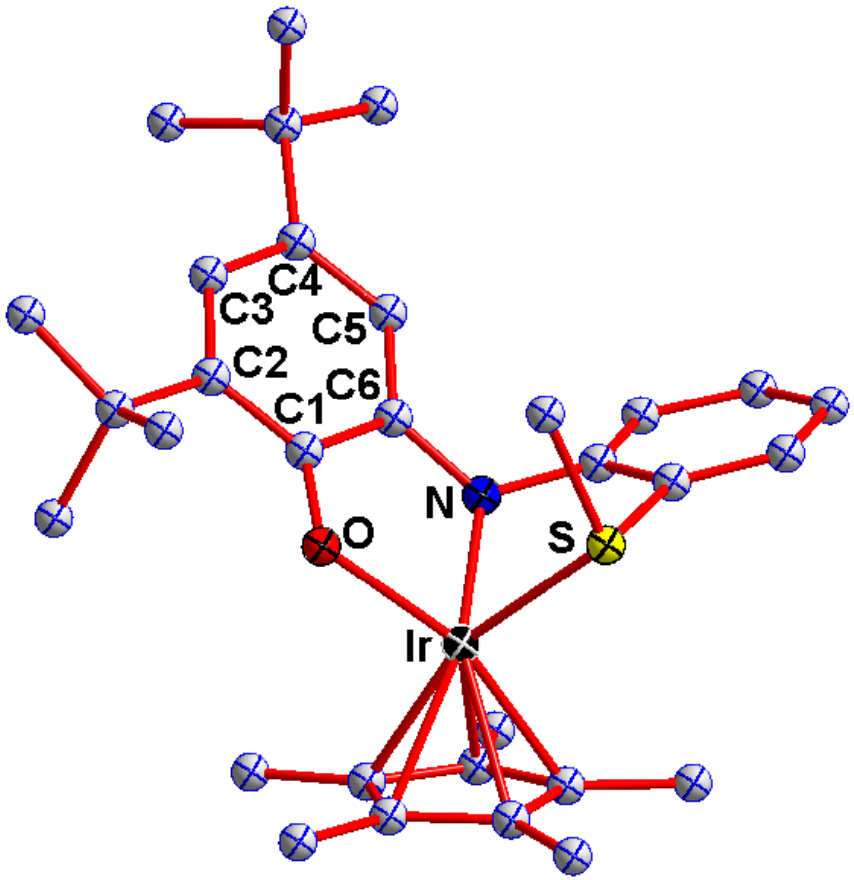
CO, CNR ($\rightarrow$ CO^-, ^{-}O-C≡C-O^-)



R. Hübner, S. Weber, S. Strobel, B. Sarkar, S. Zalis and W. Kaim, *Organometallics* **2011**, *30*, 1414



neutral



cation

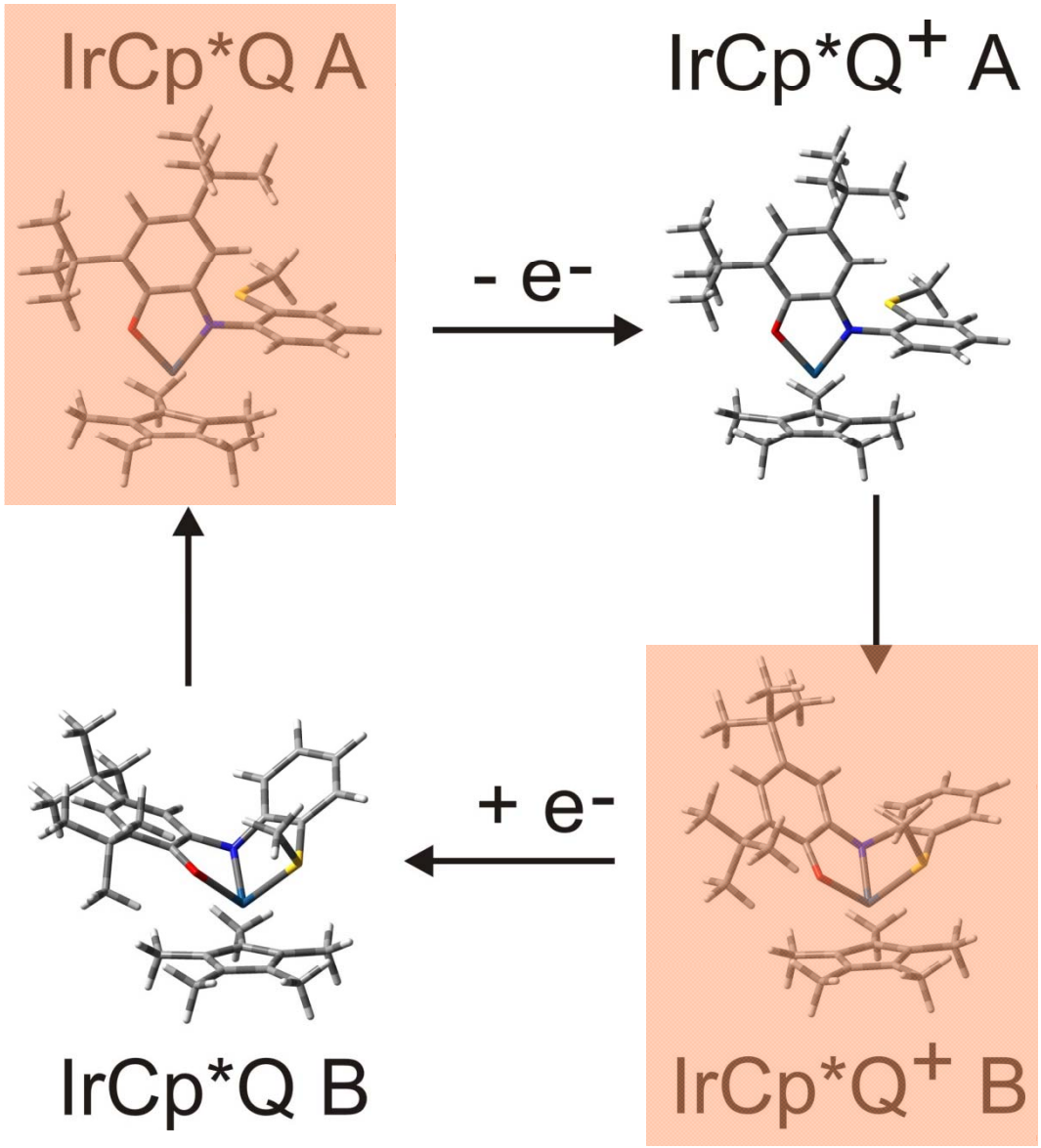
[IrCp*Q](PF_6)

- EPR (1.996, 1.985, 1.951; A_3 1.7 mT)
- Vis/NIR (800, 470 nm)
- DFT (8% Ir)

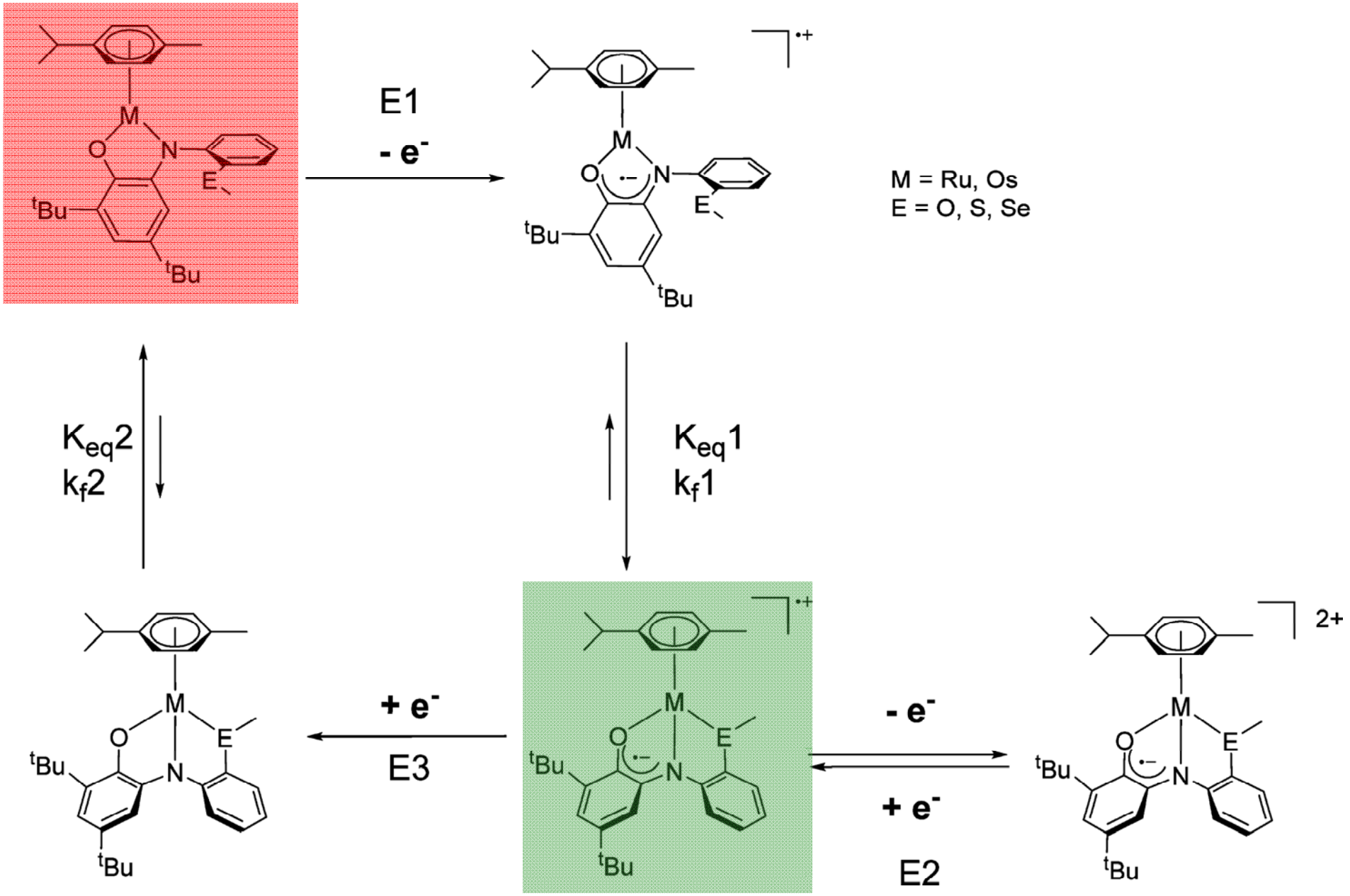
$Ir^{III}(\eta^3\text{-}Q^{o})$ / $Ir^{III}(\eta^3\text{-}Q^{\bullet -})$ / $Ir^{III}(\eta^2\text{-}Q^{2-})$

2+ / + / o

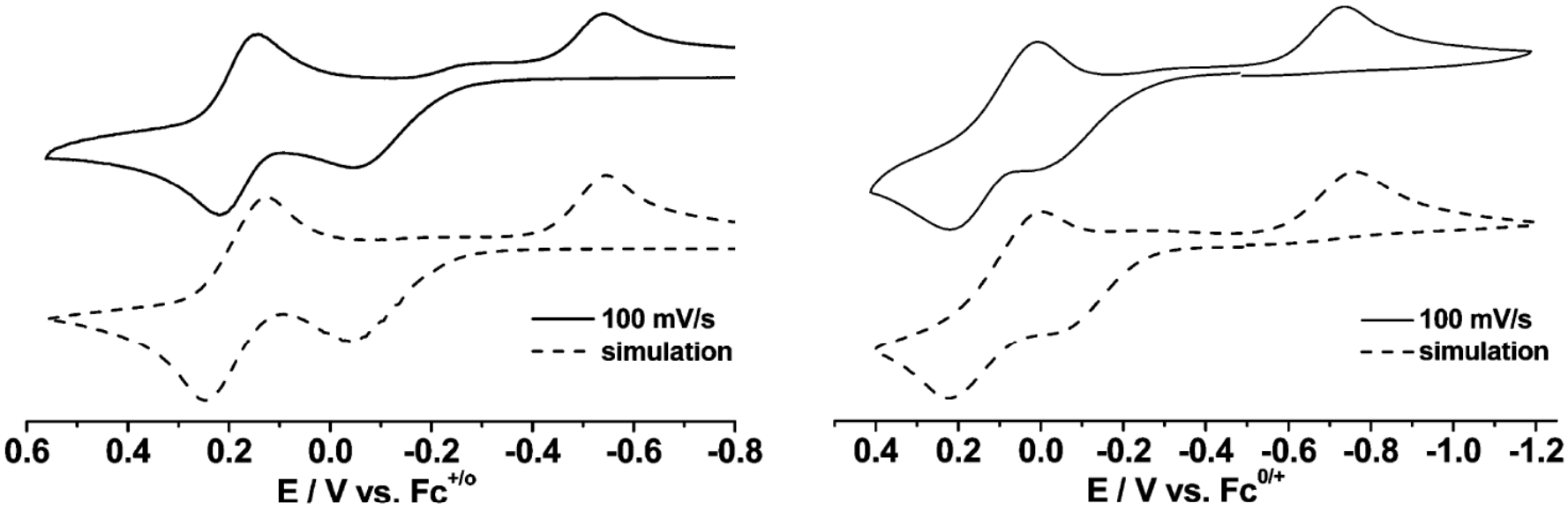
DFT:



W. Kaim, M. Bubrin, R. Hübner in *Advances in Organometallic Chemistry and Catalysis* (A.J.L. Pombeiro, ed.), *John Wiley & Sons* **2014,** p. 667-675.



M. Bubrin, D. Schweinfurth, F. Ehret, S. Zalis, H. Kvapilova, J. Fiedler, Q. Zeng, F. Hartl, W. Kaim *Organometallics* **2014,** *33***,** 4973-4985.



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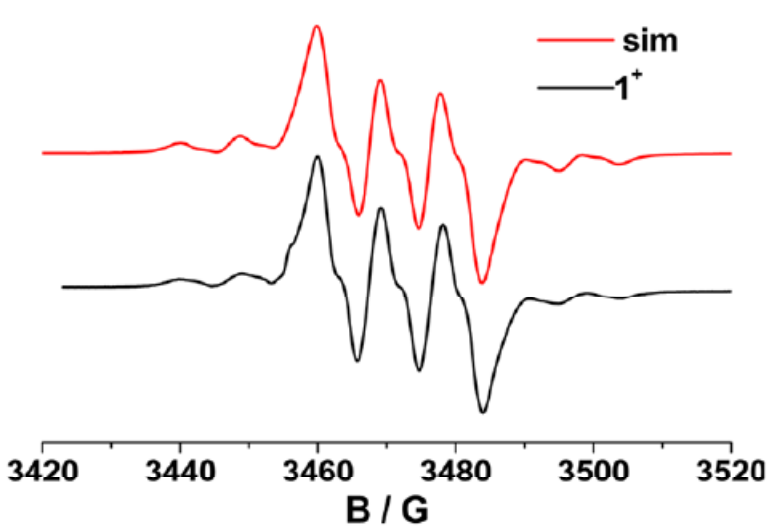

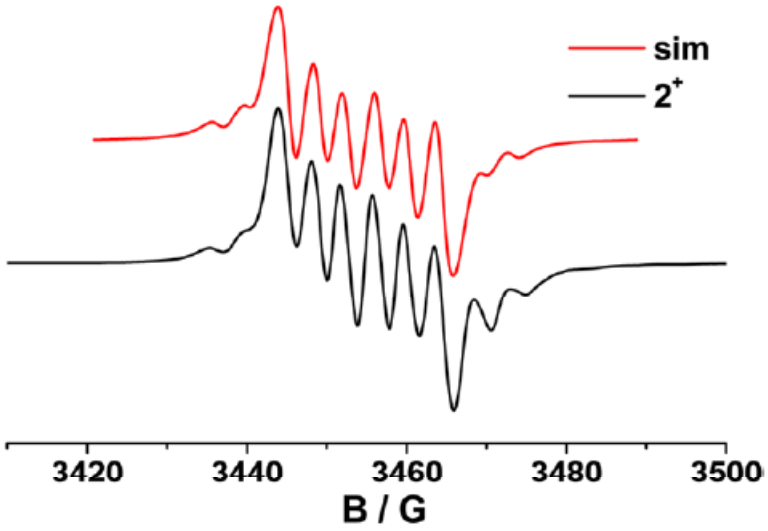

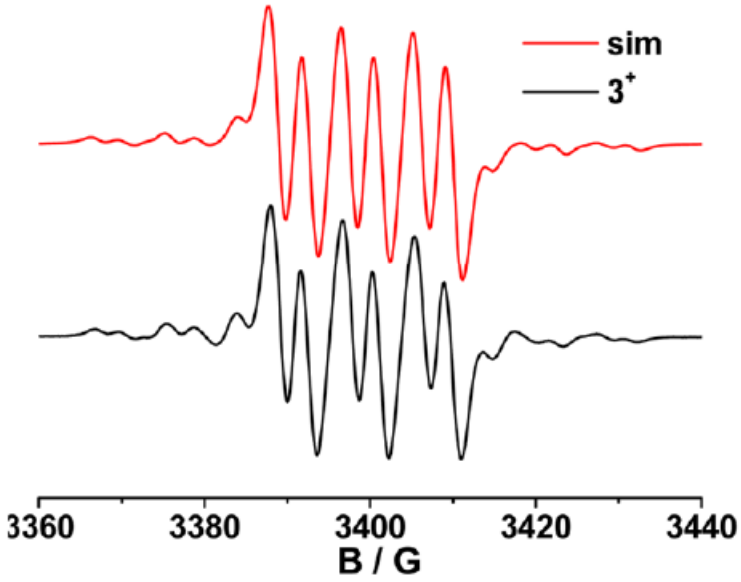

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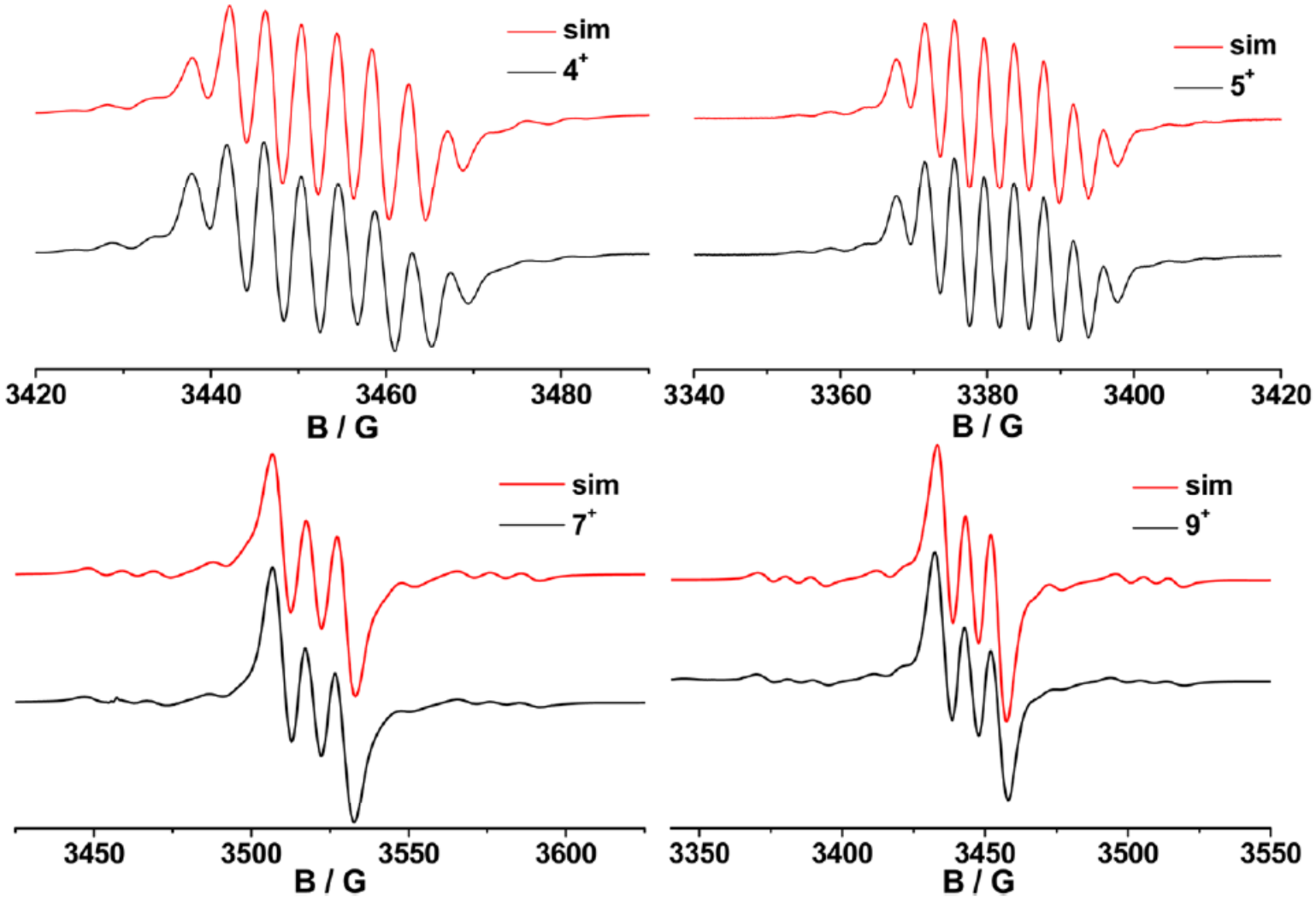

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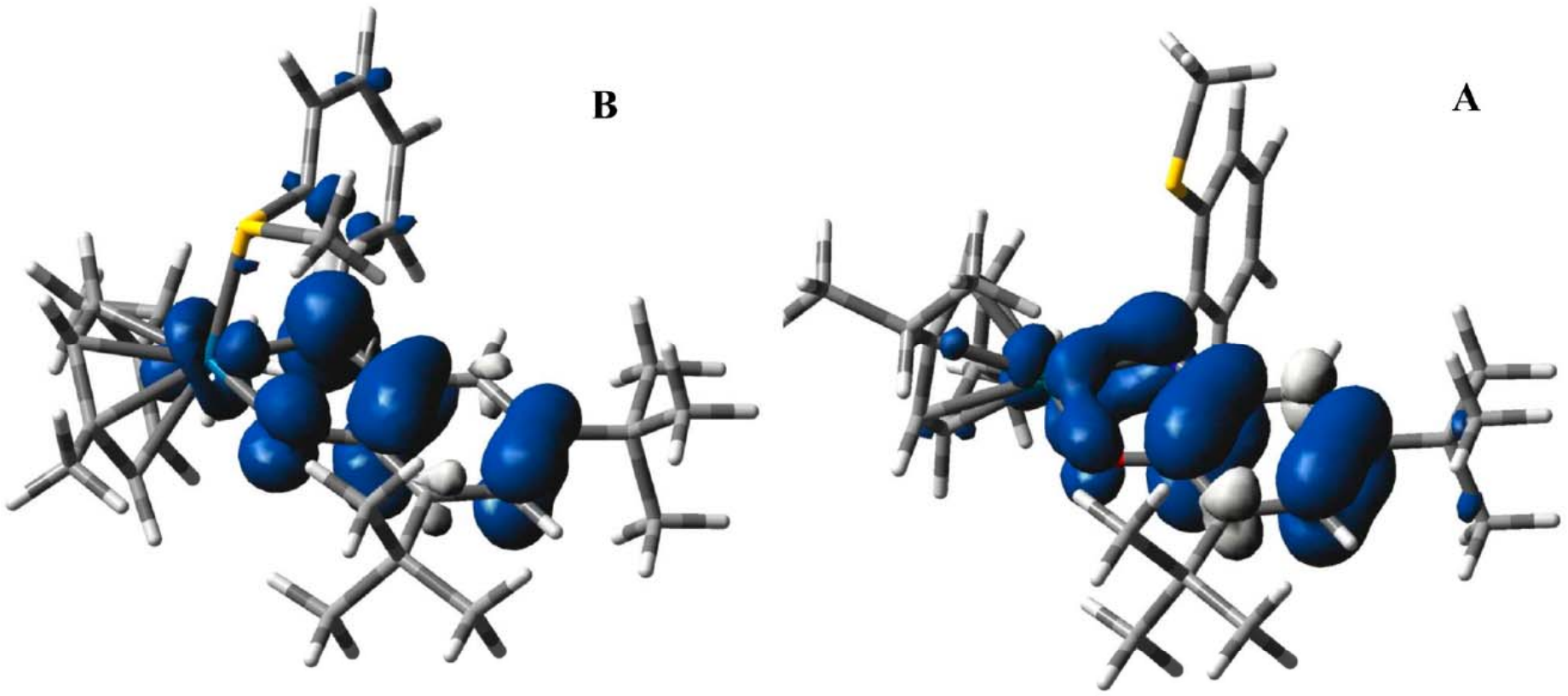
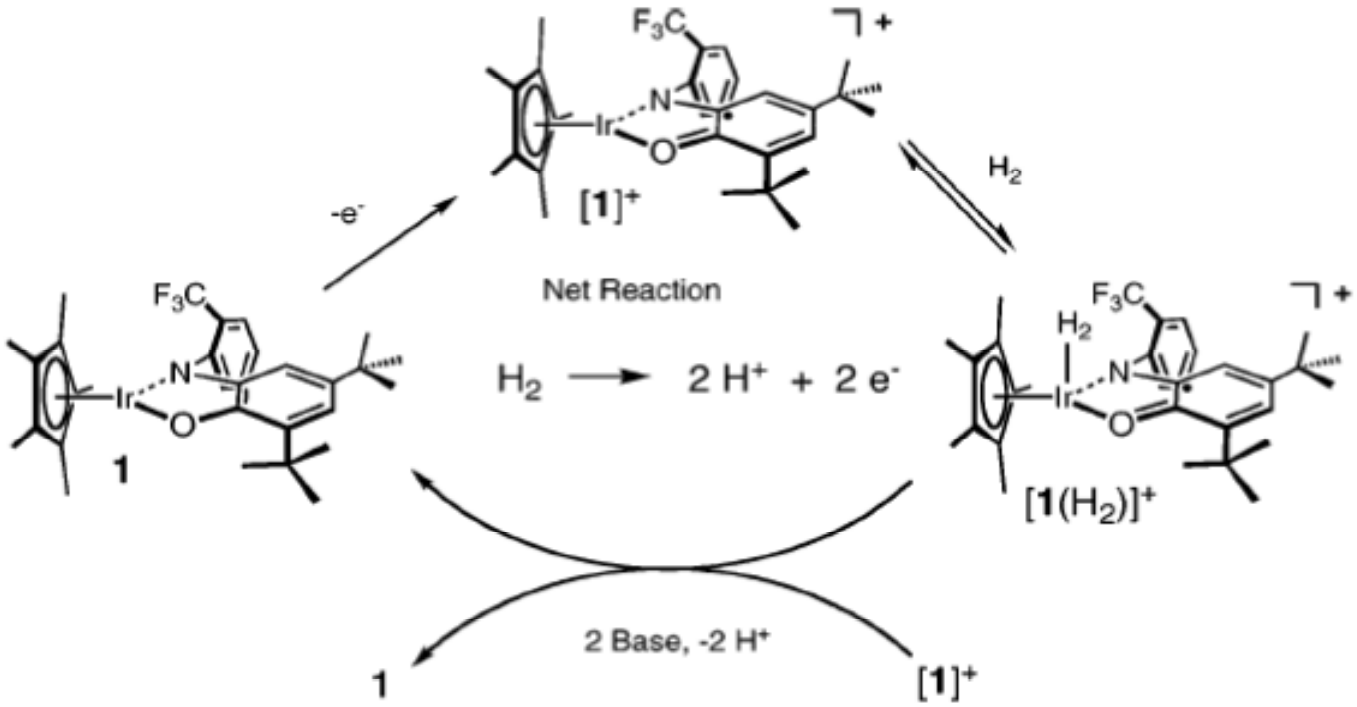


M. Bubrin, D. Schweinfurth, F. Ehret, S. Zalis, H. Kvapilova, J. Fiedler, Q. Zeng, F. Hartl, W. Kaim *Organometallics* **2014,** *33***,** 4973-4985.

Redox-Switched Oxidation of Dihydrogen Using a Non-Innocent Ligand

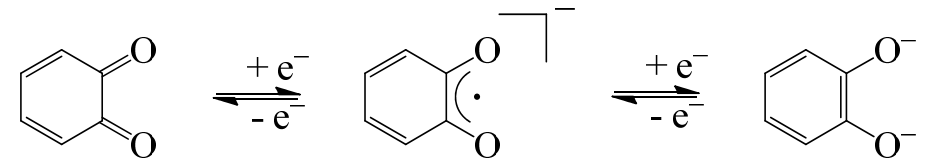
M.R. Ringenberg, S.L. Kokatam, Z.M. Heiden, T.B. Rauchfuss, *J. Am. Chem. Soc.* **2008**, *130*, 788

Proposed H_2 Oxidation Cycle:



Quinones

Quinones



o-quinone *o*-semiquinone catecholate

- three oxidation states (non-aromatic, radical intermediates, aromatic)

- natural products (photosynthesis, respiration, vitamins, antioxidants, neurotransmitters, pigments)

- toxicity (effect on metabolism)

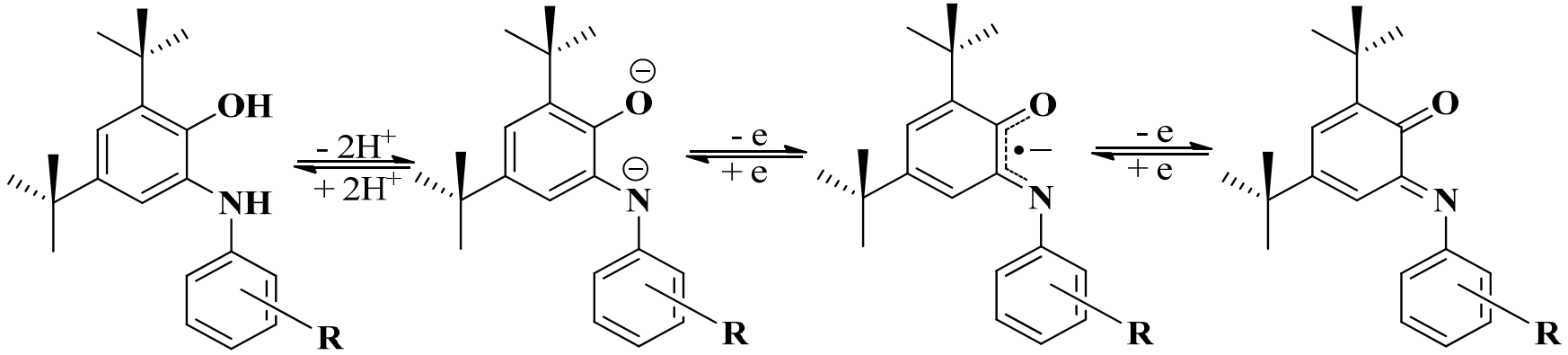
- metal chelators (→analytical reagents)

- variable electronic structure (*o,p*-tautomerism, non-innocent ligands)

- electron transfer reagents (organic synthesis, AO process of H_2O_2 production)

Complexes ML_2

L:



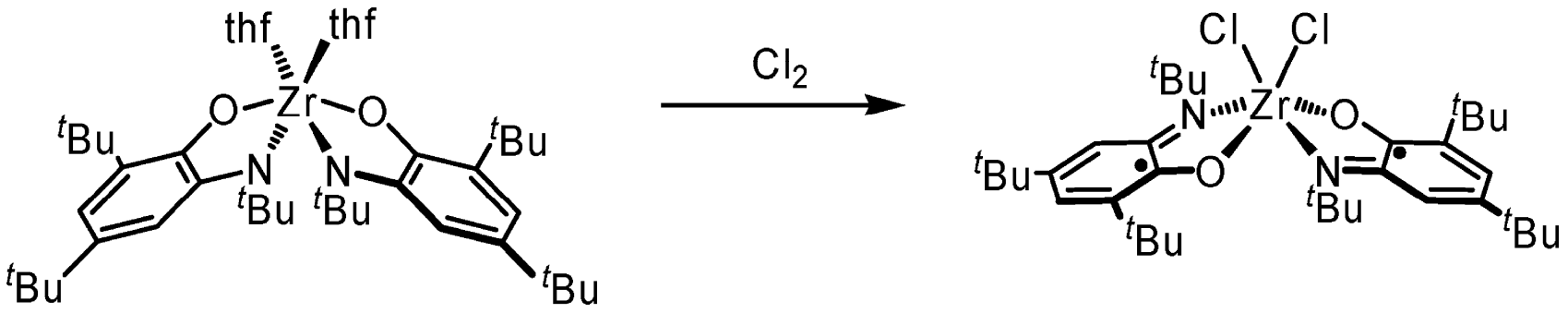
o-aminophenol *o*-amidophenolate *o*-iminosemiquinone *o*-iminoquinone

A.I. Poddel´sky, V.K. Cherkasov, G.A. Abakumov, *Coord. Chem. Rev.* **2009**, *253*, 291

S.N. Brown, *Inorg. Chem.* **2012**, *51*, 1251

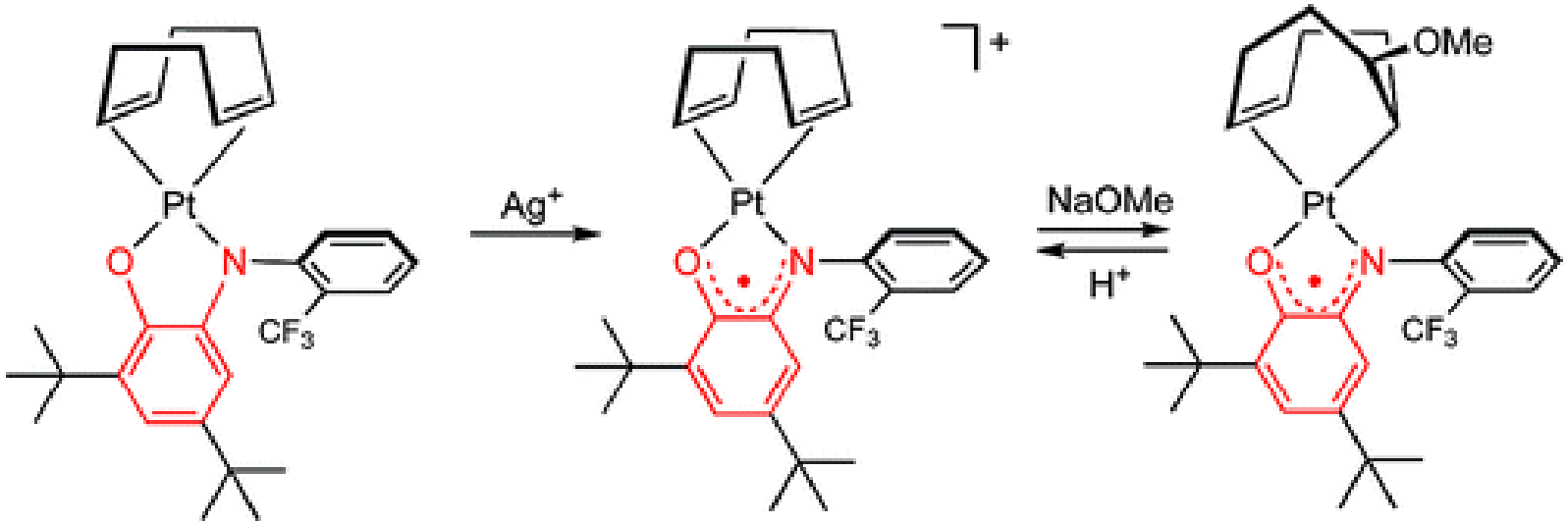
“Oxidative Addition” to a Zirconium(IV) Redox-Active Ligand Complex

Karen J. Blackmore, Joseph W. Ziller, and Alan F. Heyduk,
Inorg. Chem., **2005**, *44*, 5559



Redox Activation of Alkene Ligands in Platinum Complexes with Non-innocent Ligands

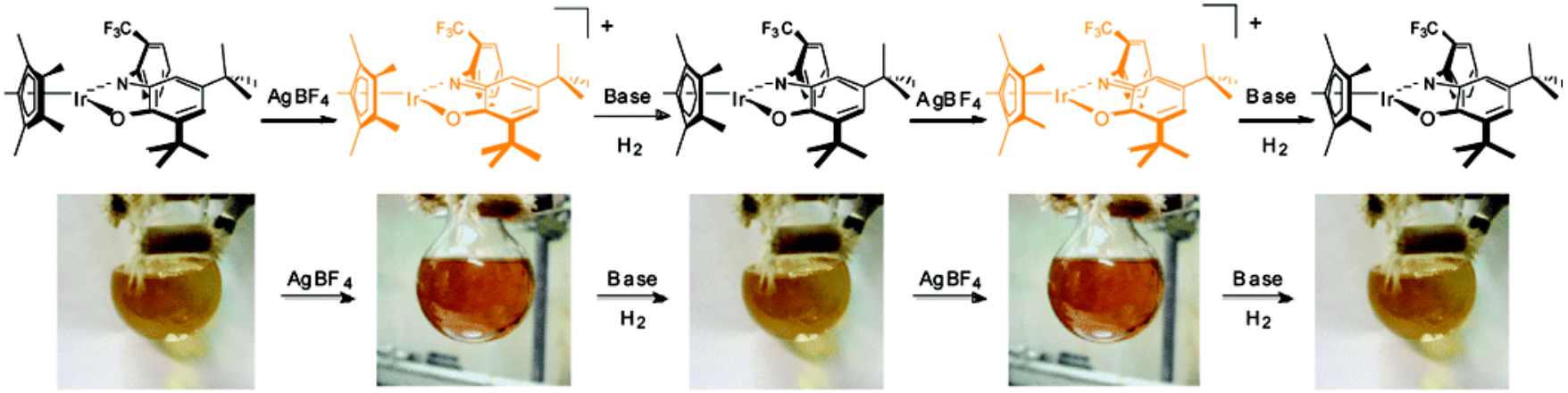
Julie L. Boyer[‡], Thomas R. Cundari, Nathan J. DeYonker, Thomas B. Rauchfuss and Scott R. Wilson,
Inorg. Chem., **2009**, *48*, 638

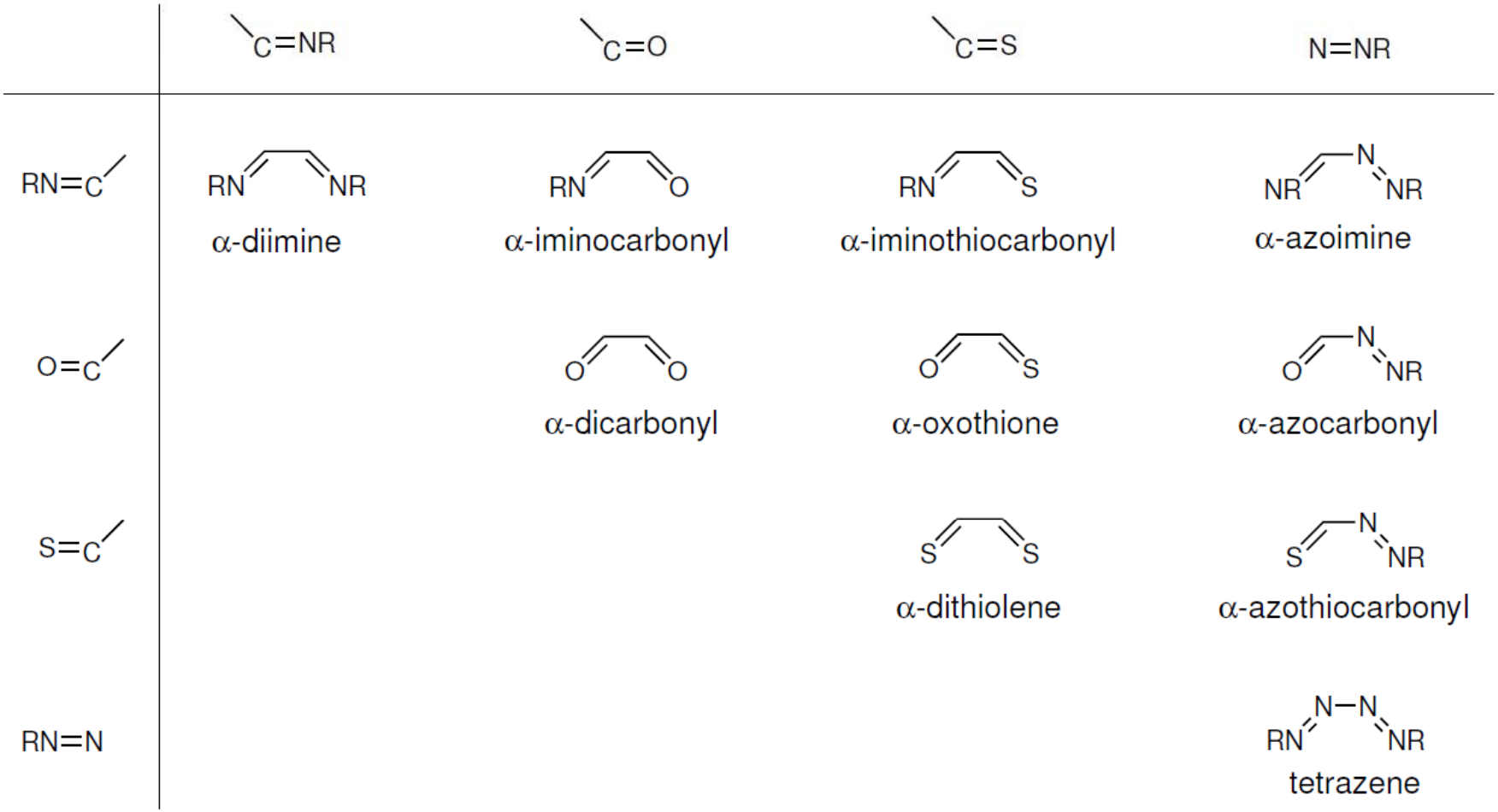


Redox-Switched Oxidation of Dihydrogen Using a Non-Innocent Ligand

Mark R. Ringenberg, Swarna Latha Kokatam, Zachariah M. Heiden, and Thomas B. Rauchfuss,

J. Am. Chem. Soc., **2008**, *130, 788*

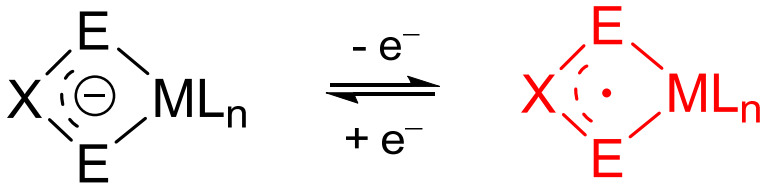




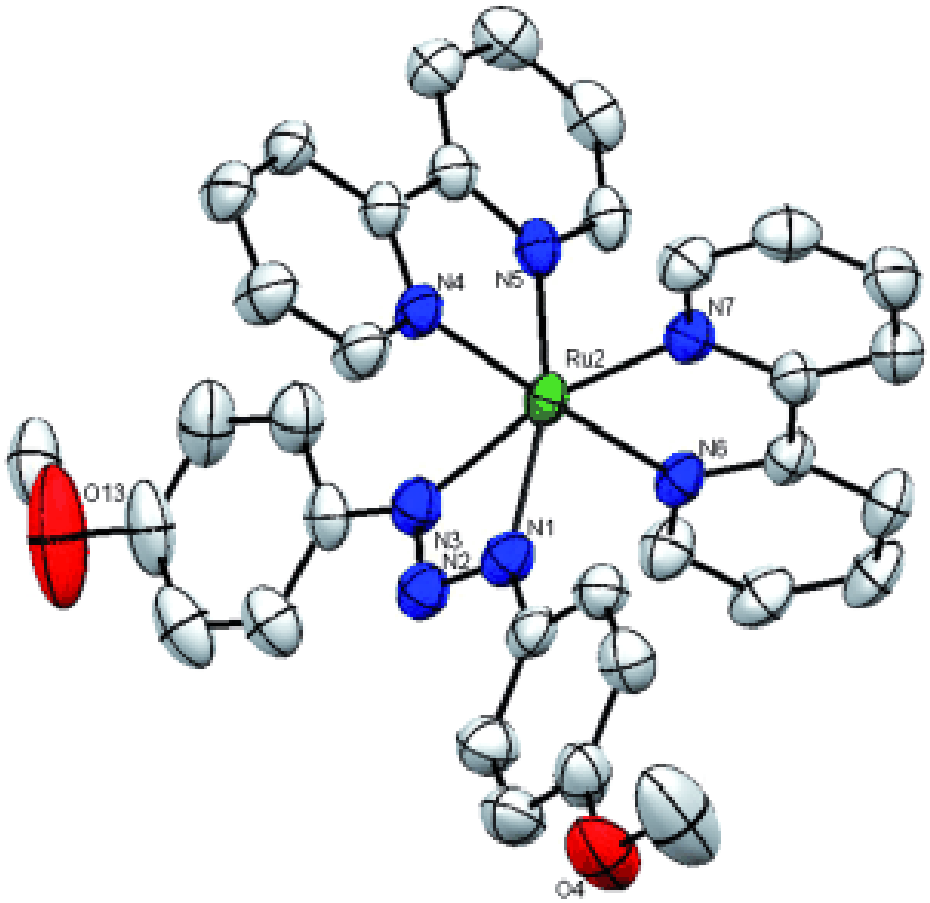
"Filling gaps in the series of noninnocent hetero-1,3-diene chelate ligands: Ruthenium complexes of redox-active α-azocarbonyl and α-azothiocarbonyl ligands RNNC(R´)E, E = O or S"

F. Ehret, M. Bubrin, R. Hübner, D. Schweinfurth, I. Hartenbach, S. Zalis, W. Kaim, *Inorg. Chem.* **2012**, *51*, 6237-6244

Four-membered Chelate Rings with Redox-Active Ligands ?

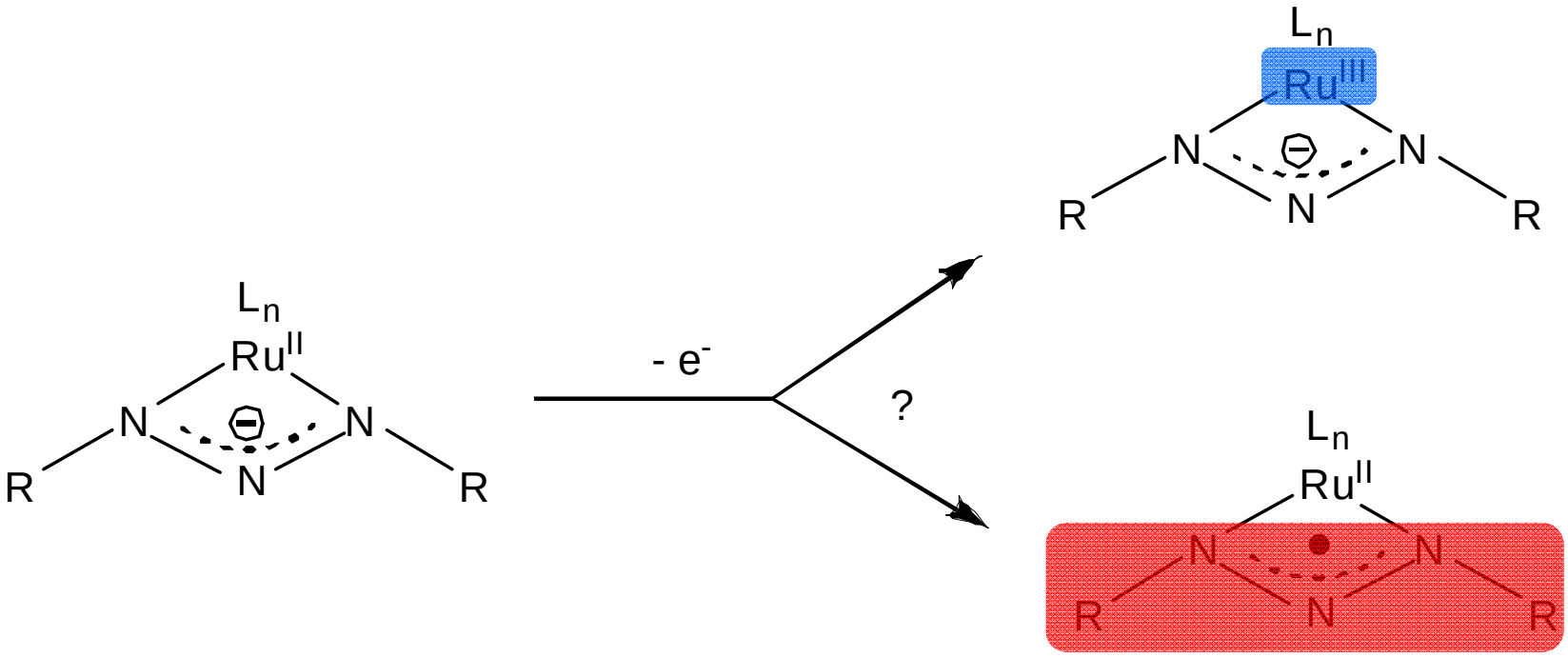


X	E	
CR	O	carboxylato
CR	NR	amidinato
CNR_2	NR	guanidinato
N	NR	triazenido
N	O	nitrito



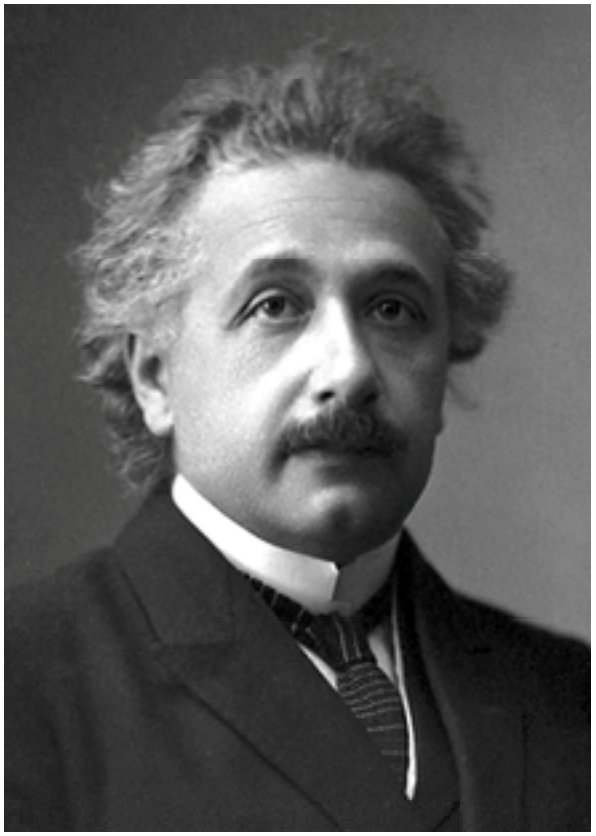
Molecular structure of the cation $[Ru(bpy)_2(RNNNR)]^+$, R=4-C_6H_4OMe

F. Ehret, M. Bubrin, S. Zalis, W. Kaim, *Angew. Chem.* **2013**, *125*, 4771; *Angew. Chem. Int. Ed.* **2013**, *52*, 4673



Discovering More Non-Innocence: Triazenido versus Triazenyl Radical Ligand Function, and a Comment on $[NO_2]^n$ as a „Suspect“ Ligand

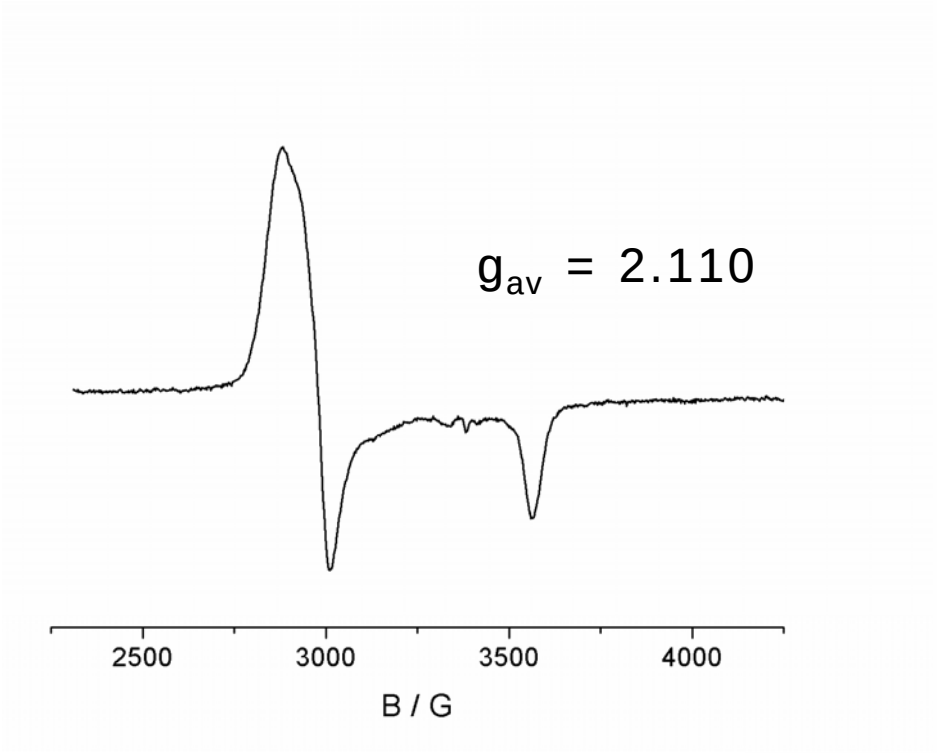
F. Ehret, M. Bubrin, S. Zalis, W. Kaim, *Angew. Chem.* **2013**, *125*, 4771; *Angew. Chem. Int. Ed.* **2013**, *52*, 4673



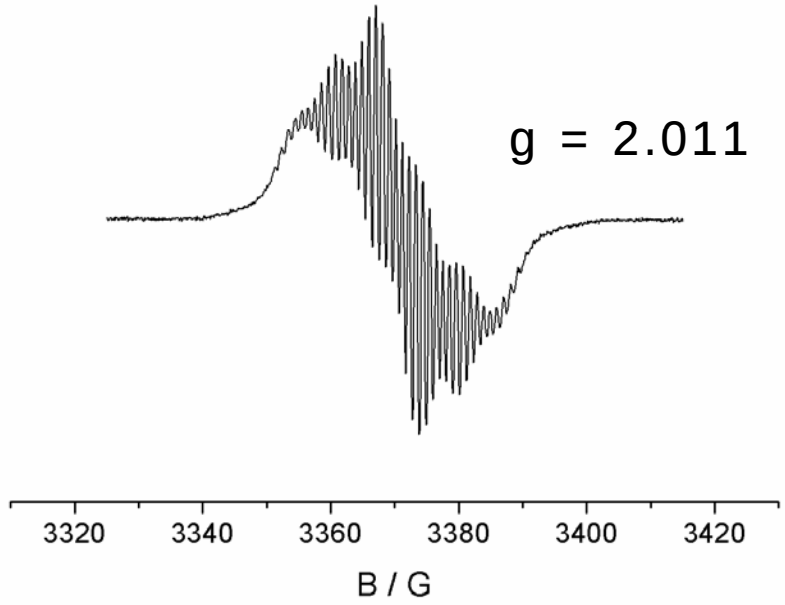
„The deviations of atomic and molecular electronic *g*-factors from the free electron value $g_e \approx 2.0023$ … represent directly observable relativistic effects.“

J. Autschbach, *J. Chem. Phys.* ***2012***, *136*, 150902

EPR Spectra of Paramagnetic Complexes after One-electron Oxidation

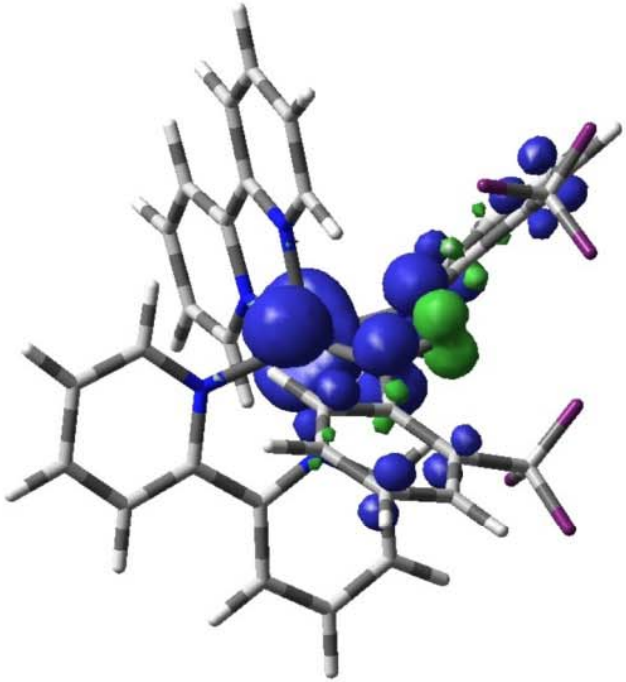


$[Ru(bpy)_2(RNNNR)](X)$,
R = 2-$C_6H_4CF_3$, X = BF_4
($[1(BF_4)]$)
110 K, in CH_2Cl_2/0.1 M Bu_4NPF_6

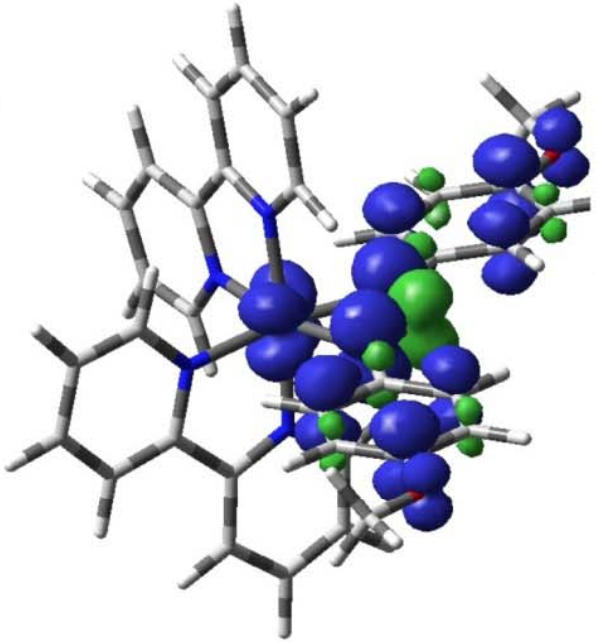


$[Ru(Cym)(NCCH_3)(RNNNR)](SbF_6)$,
R = 4-C_6H_4OMe
($[3(SbF_6)]$)
298 K in CH_2Cl_2/0.1 M Bu_4NPF_6

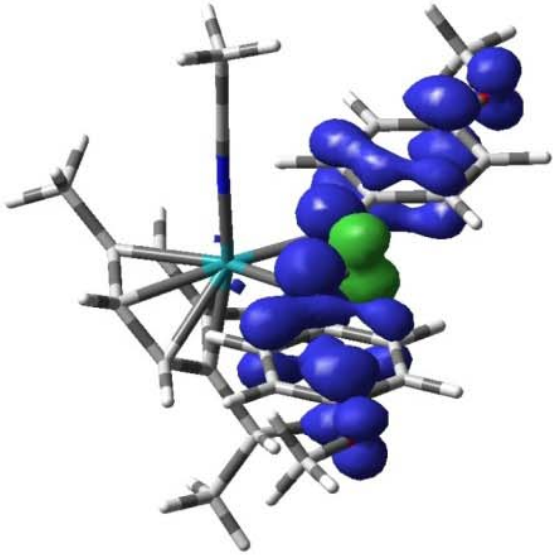
DFT (G09/PBE0/PCM-CH_2Cl_2) Calculated Spin Densities



$[Ru(bpy)_2(RNNNR)]^{2+}$,
R = 2-$C_6H_4CF_3$

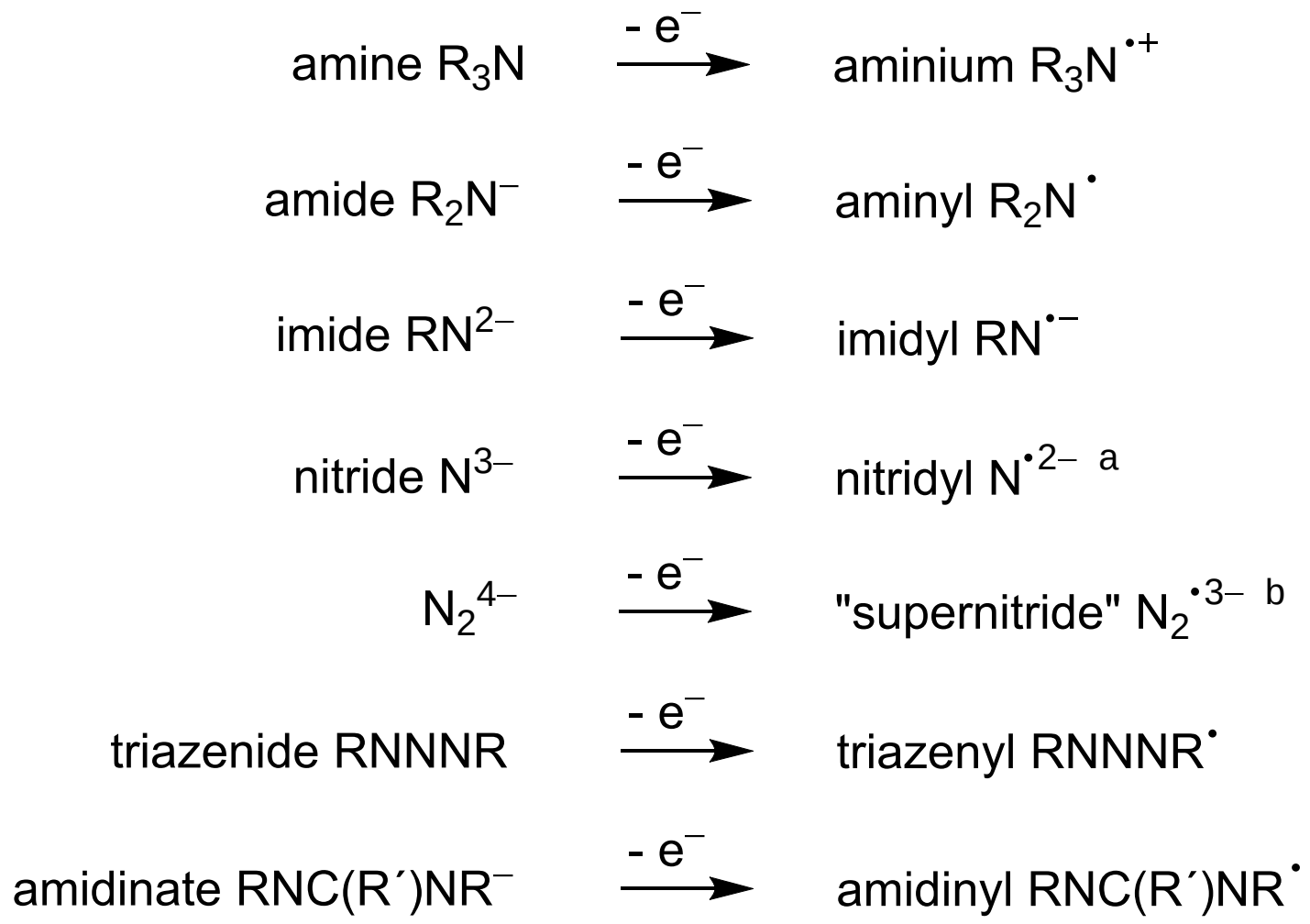


$[Ru(bpy)_2(RNNNR)]^{2+}$,
R = 4-C_6H_4OMe

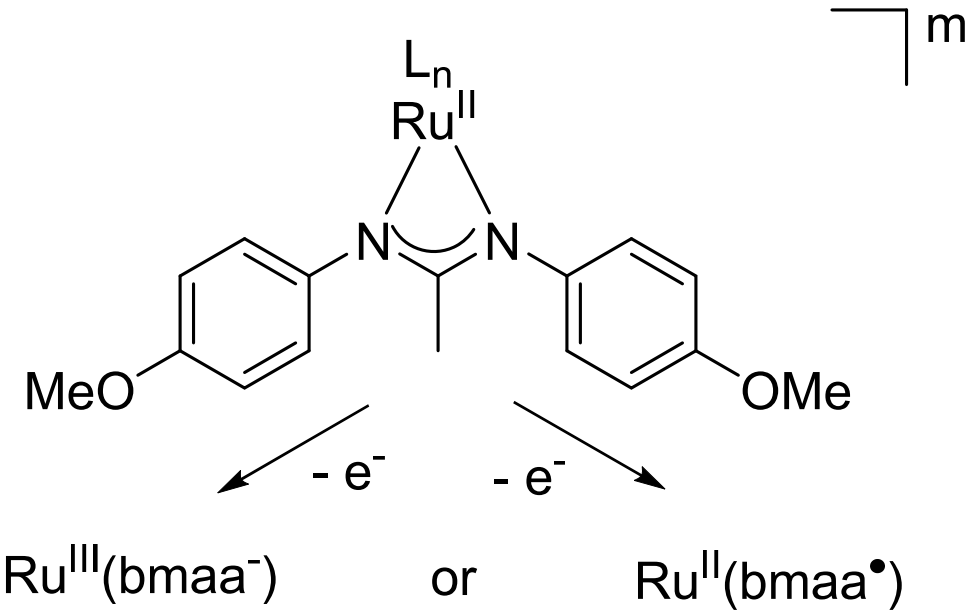


$[Ru(Cym)(NCCH_3)(RNNNR)]^{2+}$

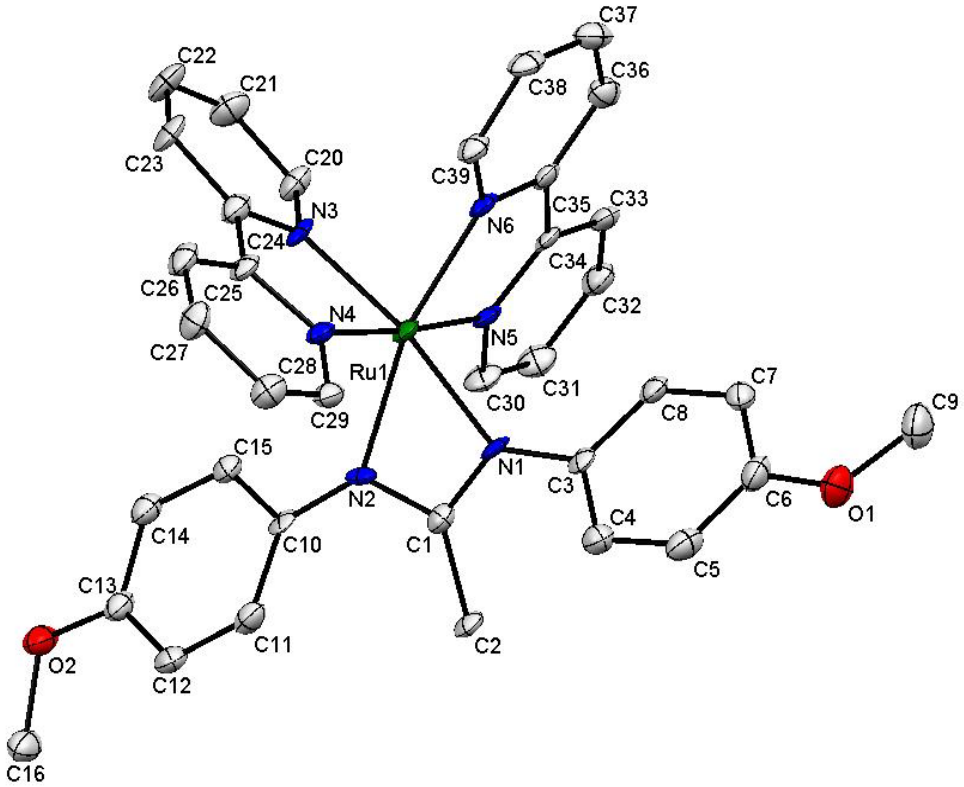
Nitrogen-Based Radicals from Oxidation



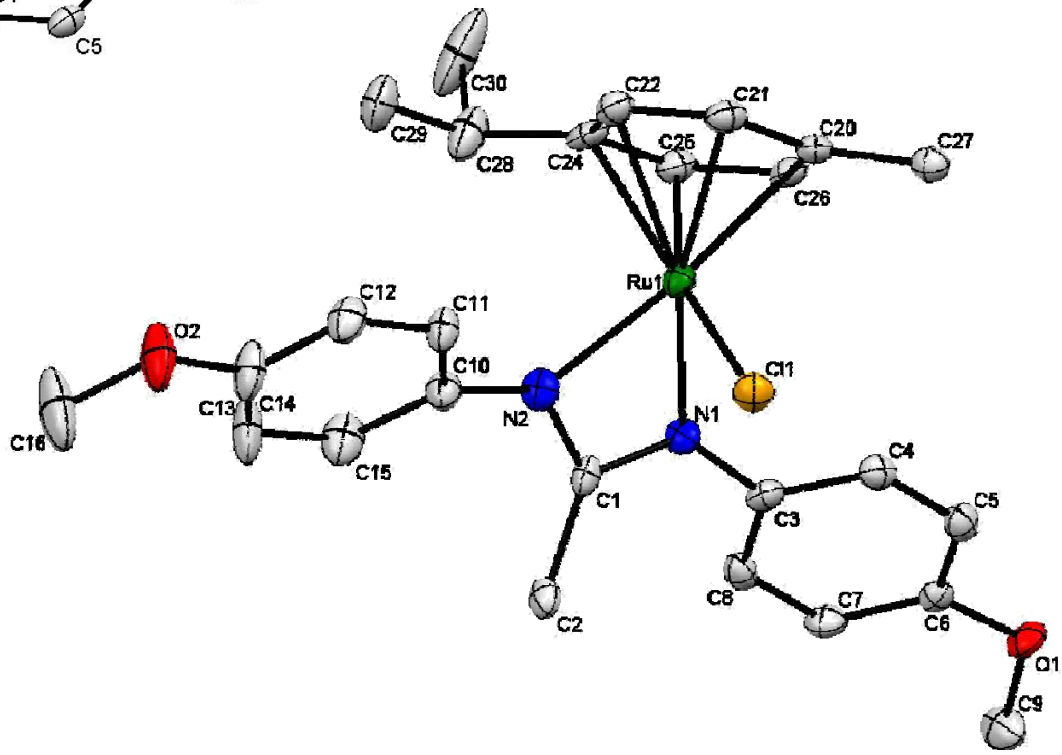
[a] S. Schneider et al. **2014**
[b] W.J. Evans et al. **2009**



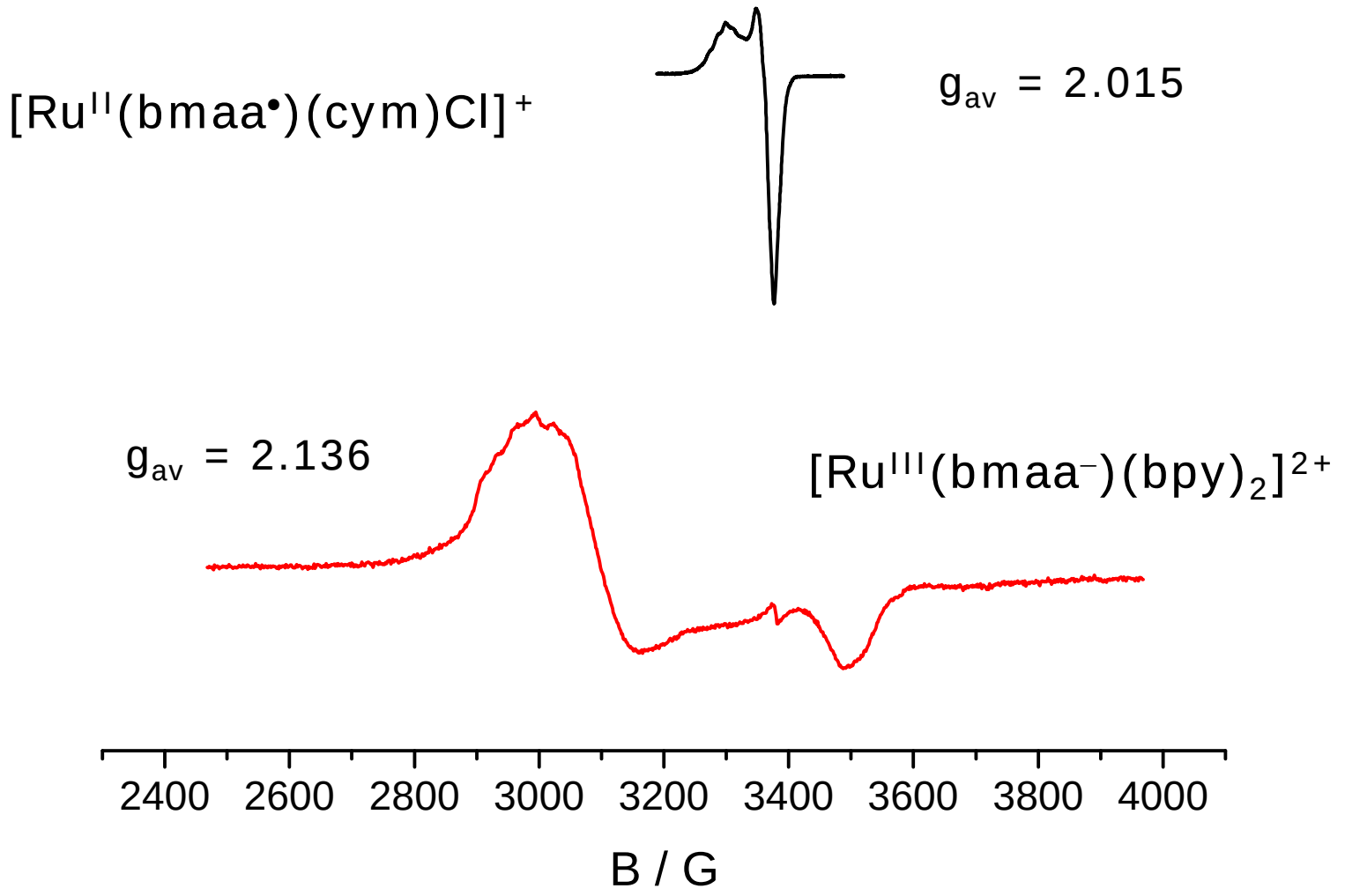
depending on L_n



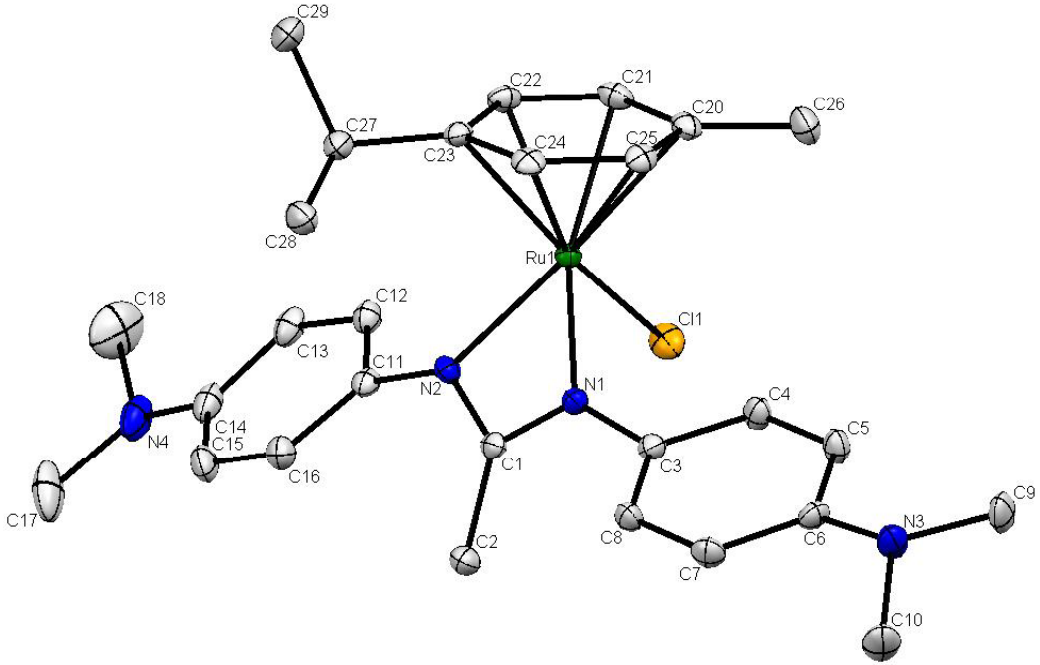
$[Ru(bmaa)(bpy)_2]^+$



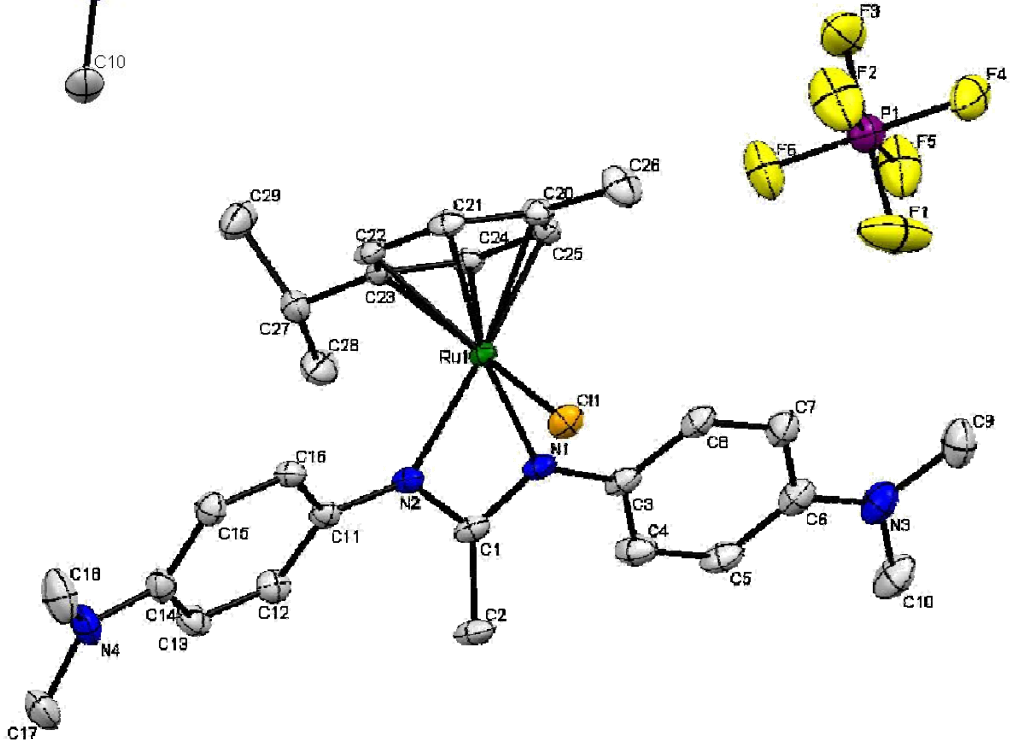
$[Ru(bmaa)(cym)Cl]$



F. Ehret, M. Bubrin, S. Záliš, W. Kaim, *Z. Anorg. Allg. Chem.*, in print



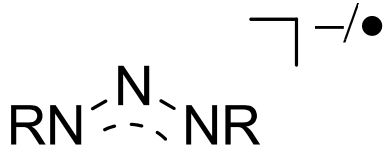
$[Ru^{II}(L^{-})(cym)Cl]$



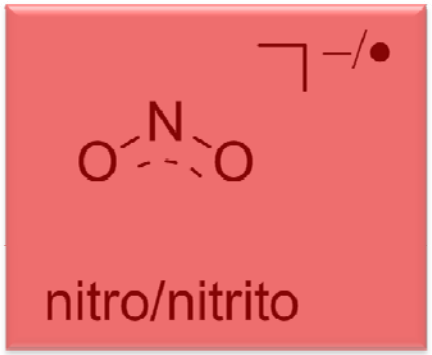
$[Ru^{II}(L^{\bullet})(cym)Cl](PF_6)$

Non-innocent ?

✓

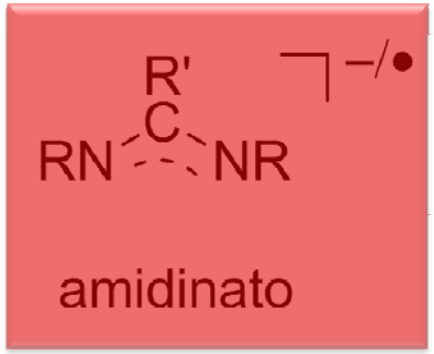


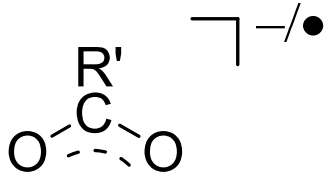
triazenido



?

✓



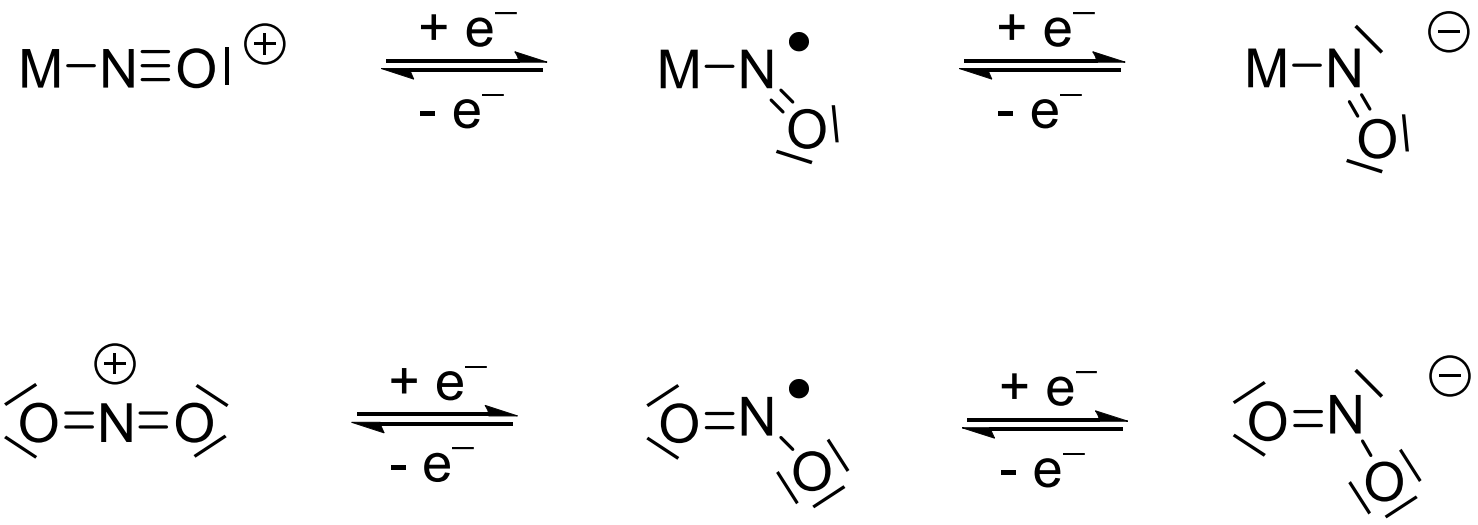


carboxylato

??

C/O and N/O Ligands

CO	**CO_2**
π acceptors	
$NO^{\bullet}$	**$NO_2^{\bullet}$ (?)**
(NO^{+}, $^{\bullet,-}$, $^{\bullet 2-}$)	(NO_2^{+}, $^{\bullet,-}$)



nitronium

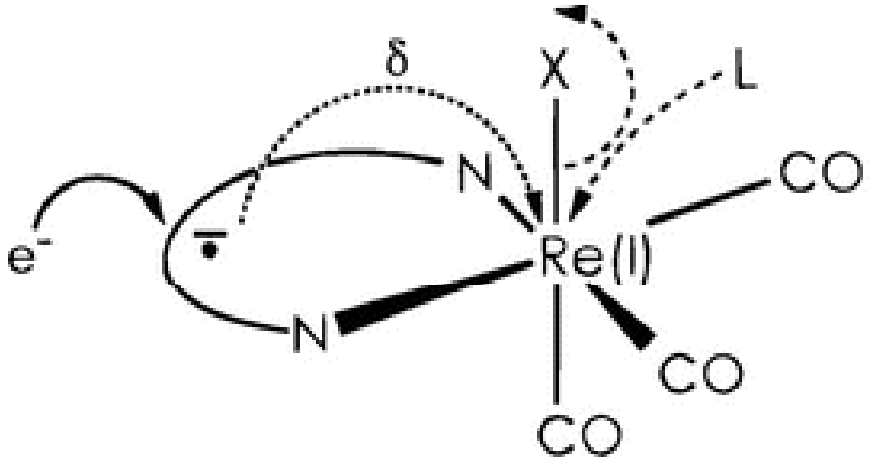
nitrogen dioxide

nitrite

(A. Werner)

The δ in $18+\delta$ Electron Complexes: Importance of the Metal/Ligand Interface for the Substitutional Reactivity of "Re(0)" Complexes (α-Diimine^{-I})Re^{+I}(CO)$_3$(X)

A. Klein, C. Vogler, W. Kaim, *Organometallics* **15** (1996) 236-244



X = Cl^-, Br^-

L = CH_3CN, PPh_3, CN^-, CO_2