



The career and legacy of Jay K. Kochi

Apr 2024
Literature Meeting

Biography



高知 和夫
May 17, 1927 - Aug 9, 2008

- | | |
|------------------|--|
| 1927 | born in Los Angeles, CA |
| 1942 | interned to war relocation camp in AZ |
| 1949 | BSc, UCLA |
| 1952 | PhD, Iowa State University (Hammond, Gilman) |
| 1952-1955 | Instructor, Harvard University |
| 1955-1956 | Fellow, Cambridge University |
| 1956-1962 | Research Scientist, Shell Development Co. |
| 1963-1968 | Assistant Professor, Case Western Reserve University |
| 1969-1983 | Professor, Indiana University |
| 1984-2008 | Professor, University of Houston |

Kochi's career was characterized by broad scope and dogged mechanistic focus

Key questions

1. How do metals interact with organic radicals?
2. How do organic radicals behave?
3. How does the movement of single electrons occur within/between metal and/or organic species?

> 500 papers published

Kochi research philosophy

1. Mechanism over synthetic application
2. Meticulous and rigorous mechanistic chemistry
3. Cutting-edge physical techniques

Moreover, an almost complete ignorance at this juncture of the relative importance of different excited states of the chromophore involved makes further discussion unfruitful.

J. Org. Chem. **1971**, *36*, 3112

Noteworthy contributions

1. Organometallic chemistry
 - Redox chemistry (epoxidation, C-H oxidation)
 - Cross coupling (Cu, Fe, Ag, Ni, etc.)
 - Radicals + metals (especially with Cu)
2. Physical organic chemistry
 - EPR spectroscopy of radicals
 - Transient absorption spectroscopy
 - Photochemistry
 - EDA complexes and processes
3. Inorganic chemistry
 - Synthesis and characterization of novel complexes

Key organometallic references

1. Kochi, J. K. *Organometallic Mechanisms and Catalysis: The Role of Reactive Intermediates in Organic Processes*; Academic Press, 1979
2. Sheldon, R. A. and Kochi, J. K. *Metal-catalyzed Oxidations of Organic Compounds: Mechanistic Principles and Synthetic Methodology Including Biochemical Processes*; Academic Press, 1981

No definitive review of Kochi contributions exists due to the breadth of his contributions

Scope of our survey

1 IA 1A																18 VIIIA 8A			
1 H Hydrogen 1.008	2 IIA 2A														2 He Helium 4.003				
3 Li Lithium 6.941	4 Beryllium 9.012														13 IIIA 3A				
5 IVB 5B	6 VB 5B	7 VIIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A						
11 Sc Scandium 44.956	12 Ti Titanium 47.867	13 V Vanadium 50.942	14 Cr Chromium 51.996	15 Mn Manganese 54.938	16 Fe Iron 55.845	17 Co Cobalt 58.933	18 Ni Nickel 58.693	19 Cu Copper 63.546	20 Zn Zinc 65.38	21 Al Aluminum 26.982	22 Si Silicon 28.086	23 P Phosphorus 30.974	24 S Sulfur 32.066	25 Cl Chlorine 35.453	26 Ar Argon 39.948				
17 K Potassium 39.098	18 Ca Calcium 40.078	19 Sr Strontium 87.62	20 Y Yttrium 88.907	21 Zr Zirconium 89.907	22 Nb Niobium 92.906	23 Ta Tantalum 97.867	24 Mo Molybdenum 95.95	25 Tc Technetium 98.907	26 Ru Ruthenium 101.07	27 Rh Rhodium 102.906	28 Pd Palladium 106.42	29 Ag Silver 107.868	30 Cd Cadmium 112.411	31 Ga Gallium 69.723	32 Ge Germanium 72.610	33 As Arsenic 74.974	34 Se Selenium 78.904	35 Br Bromine 80.904	36 Kr Krypton 83.798
18 Cs Cesium 130.905	19 Ba Barium 137.328	20 Hf Hafnium 178.49	21 Tb Tantalum 180.948	22 W Tungsten 183.84	23 Re Rhenium 186.207	24 Os Osmium 190.23	25 Ir Iridium 192.217	26 Pt Platinum 195.085	27 Au Gold 196.967	28 Hg Mercury 200.592	29 Tl Thallium 204.300	30 Pb Lead 207.2	31 Bi Bismuth 209.000	32 Po Polonium 209.907	33 At Astatine 210.007	34 Rn Radon 222.010			
105 Rf Rutherfordium [261]	106 Db Dubnium [262]	107 Sg Seaborgium [266]	108 Bh Bohrium [264]	109 Hs Hassium [269]	110 Mt Meitnerium [278]	111 Ds Darmstadtium [281]	112 Rg Roentgenium [280]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]						

Covered (*in detail)

Major contributions*

1. epoxidation
2. cross-coupling
3. EDA complexes

Deep but less-cited contributions

1. Cu chemistry*
2. Decarboxylation (Kochi reaction)
3. Organochromium chemistry

Unnoticed contributions

1. amine photolysis
2. HAT from Grignards

Not covered

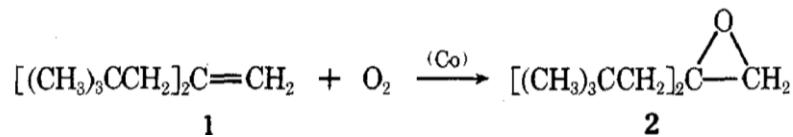
1. Mechanistic details of charge transfer
2. Organogold chemistry
3. EPR of organic radicals
4. NCIs
5. Organomercury chemistry
6. New organometallic complexes
- etc

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Metal-Catalyzed Epoxidation of Olefins

Expoxydation of Olefins with Molecular Oxygen in the Presence of Cobalt Complexes

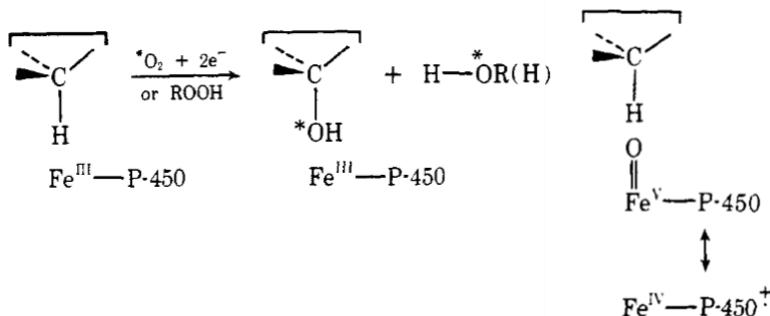
Richard A. Budnik and Jay K. Kochi*



J. Org. Chem. 1976, 41, 1384

Aliphatic Hydroxylation via Oxygen Rebound. Oxygen Transfer Catalyzed by Iron

John T. Groves,* Gary A. McClusky



J. Am. Chem. Soc. 1976, 98, 859

Mechanism of the Chromium-Catalyzed Epoxidation of Olefins. Role of Oxochromium(V) Cations

E. G. Samsel, K. Srinivasan, and J. K. Kochi*

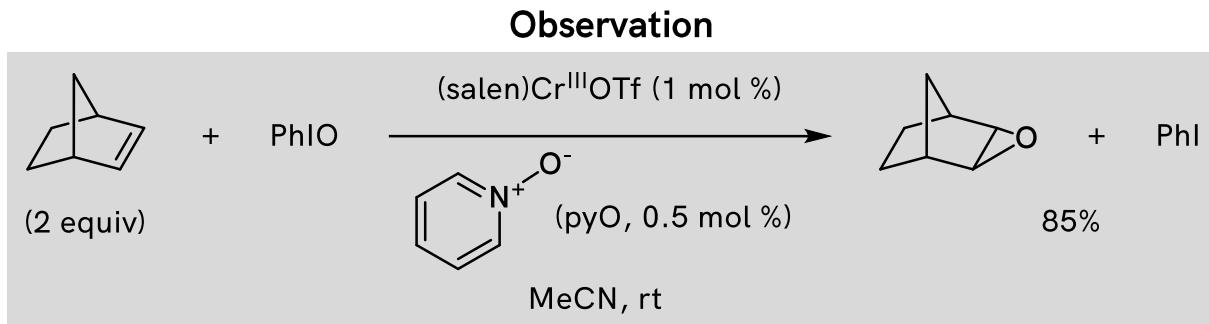
J. Am. Chem. Soc. 1985, 107, 7606

Epoxidation of Olefins with Cationic (salen)Mn^{III} Complexes. The Modulation of Catalytic Activity by Substituents

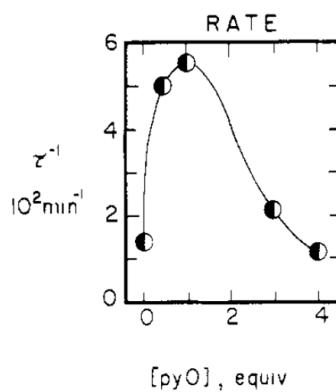
K. Srinivasan, P. Michaud, and J. K. Kochi*

J. Am. Chem. Soc. 1986, 108, 2309

Cr^{III}(salen)-catalyzed epoxidation involves electrophilic O=Cr^V



2. pyO has “dichotomous” effect
on rate



4. With stoichiometric O=Cr^V, k_{obs} saturates and is first-order in olefin

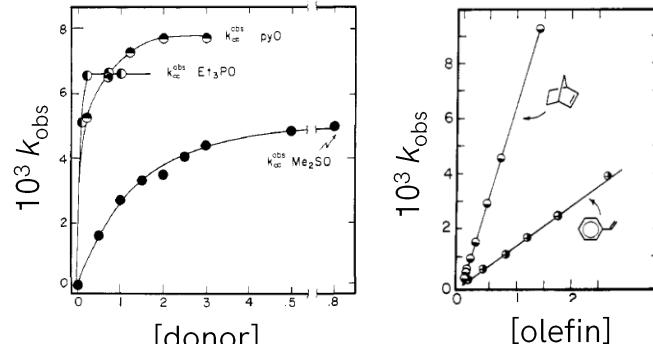


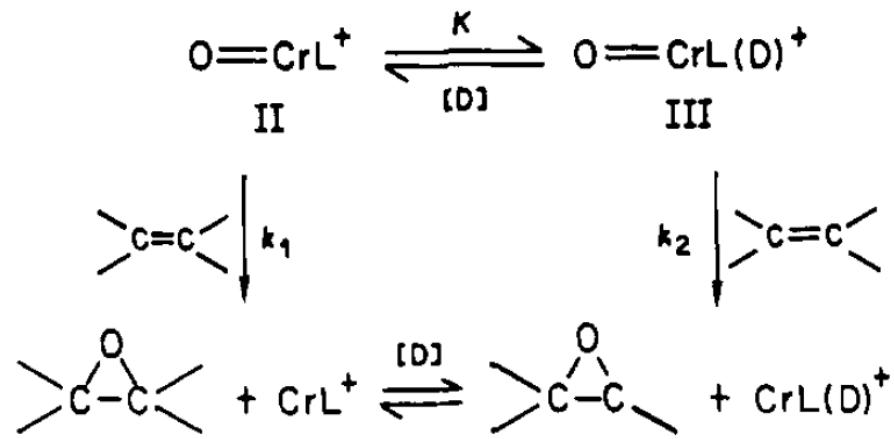
Figure 5. ORTEP diagram of the oxochromium(V) adduct IIIf with pyridine *N*-oxide as the donor ligand.



2. and 3. $O=Cr^V$ and $O=Cr^V(pyO)$ are the reactive intermediates; too much pyO ties up Cr^{III} off-cycle.

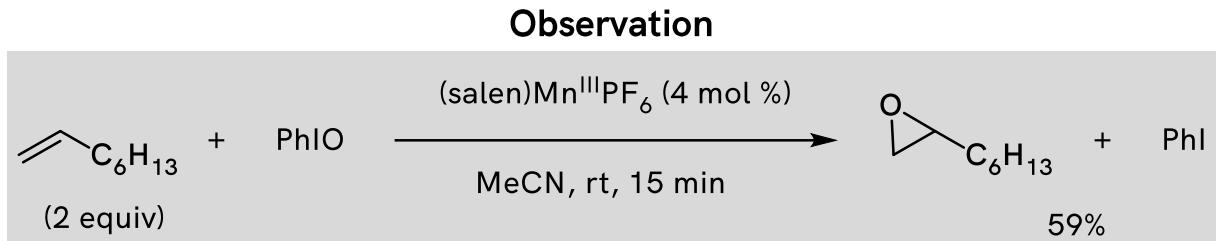
3. Axial ligation of pyO weakens O=Cr^V bond, increasing reactivity

4. $k_{\text{obs}}/[\text{olefin}]$ fits rate law derived from

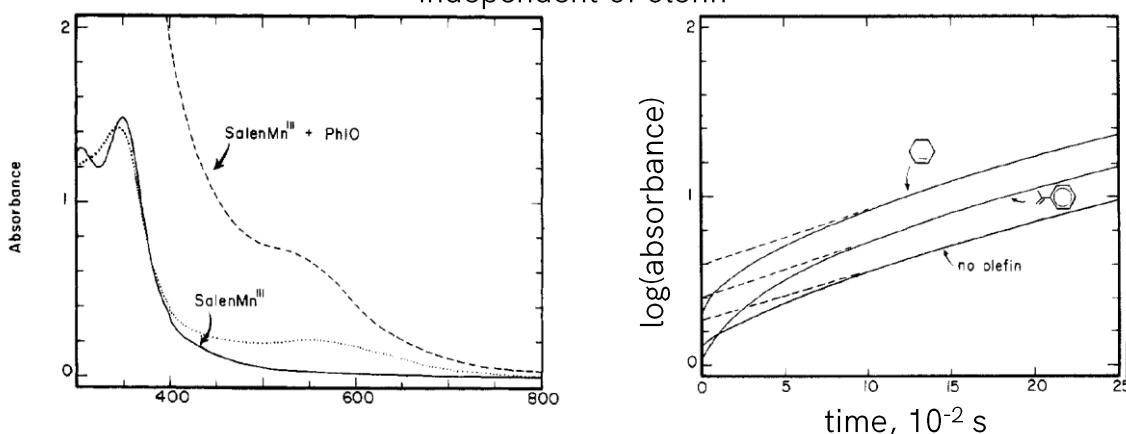


There is an intermediate between $O=Cr^V$ and epoxide; what is it?

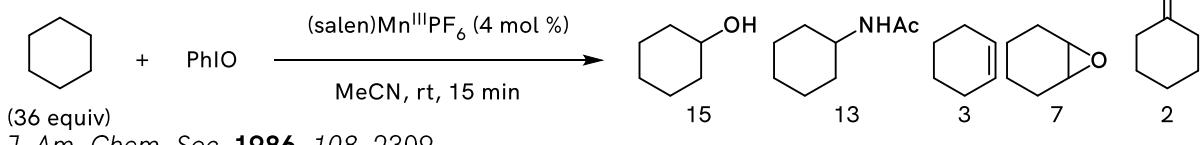
Mn^{III}(salen)-catalyzed epoxidation involves O=Mn^V(salen) but may be single-electron



- When varying salen substituents, activity correlates with reduction potential
 - With EWG on salen, observe:
 - minimal allylic oxidation (for cyclohexene)
 - high but not absolute stereospecificity
 - relative reactivities (styrene to 1-octene) fall within a factor of 10
 - Addition of PhIO leads to short-lived [Mn] intermediate that decomposes independent of olefin



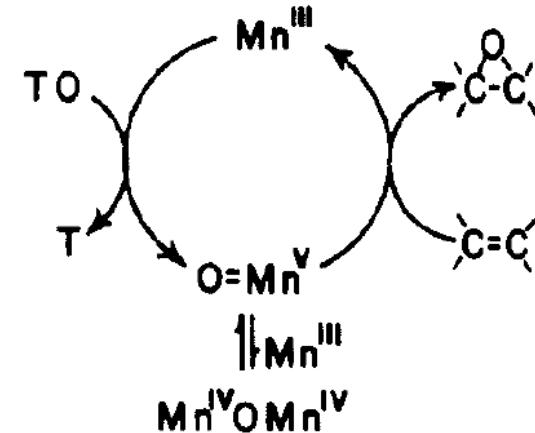
4. Styrene gives Hammett $\rho = -0.3$; 5. cyclohexane is oxidized!



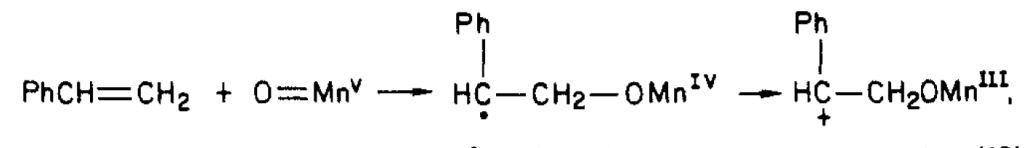
Interpretation

$\text{O}=\text{Mn}^{\text{V}}(\text{salen})$ is the active species but converts to some other species that does not involve olefin.

Propose off-cycle bimetallic complex:



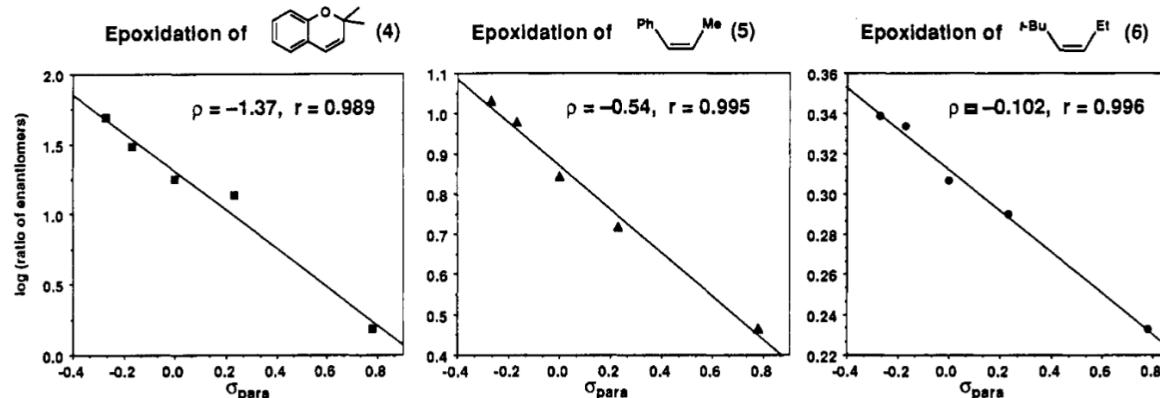
Unlike $O=Cr^V(salen)$, $O=Mn^V(salen)$ activity is weakly dependent on olefin nucleophilicity, and it can oxidize alkanes. Propose single electron transfer:



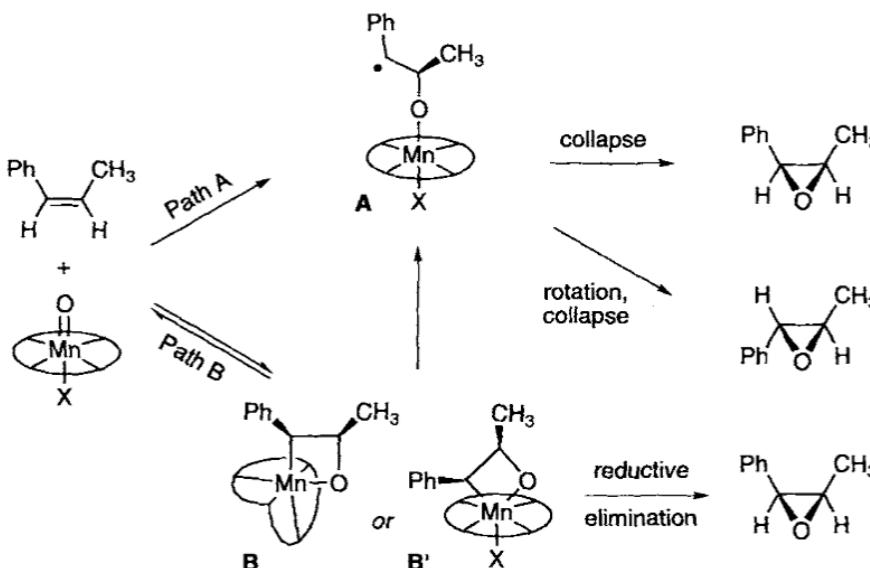
free to rotate,
hence incomplete stereospecificity

Radical species are shown to be viable in (salen)Mn-catalyzed asymmetric epoxidation

Tuning of salen substituents has a noted effect on ee:

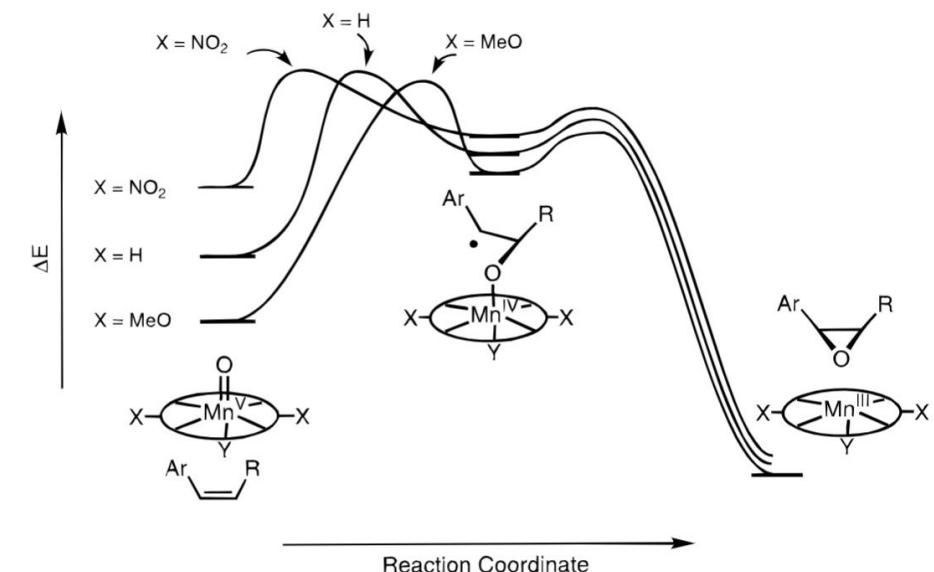


Radical intermediate favored over oxametallacycle:



Studied effect of (salen)Mn substituents on:

1. enantioselectivity
2. SDKIE
3. Eyring analyses



Enantioselectivity is influenced by altering the position of the TS

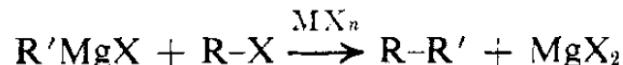
"[Kochi] often reminisced that his careful demonstration of the mechanism of the epoxidation reaction using salen-manganese complexes led to the evolution of a well-known asymmetric epoxidation method of the present day."

ACIE, 2008, 47, 9186

Metal-catalyzed cross coupling

Factors Determining the Course and Mechanisms of Grignard Reactions. IV. The Effect of Metallic Halides on the Reaction of Aryl Grignard Reagents and Organic Halides¹

BY M. S. KHARASCH AND E. K. FIELDS



J. Am. Chem. Soc. 1941, 63, 2316

see also Corriu, Tamao, Kumada, ...

The Mechanism of the Silver-Catalyzed Reaction of Grignard Reagents with Alkyl Halides

Alkylcopper(I) in the Coupling of Grignard Reagents with Alkyl Halides

Vinylation of Grignard Reagents. Catalysis by Iron

M. Tamura, J. Kochi*

Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received November 21, 1970

J. Am. Chem. Soc. 1971, 93, 1483
J. Am. Chem. Soc. 1971, 93, 1485
J. Am. Chem. Soc. 1971, 93, 1487

The Stereochemistry of the Thermal Decomposition of Vinylic Copper(I) and Silver(I) Organometallic Compounds¹

George M. Whitesides, Charles P. Casey

J. Am. Chem. Soc. 1966, 88, 4541

Carbon–Carbon Bond Formation by Selective Coupling of *n*-Alkylcopper Reagents with Organic Halides

E. J. Corey, G. H. Posner

J. Am. Chem. Soc. 1968, 90, 5615

Mechanistic Studies of Nickel Catalysis in the Cross Coupling of Aryl Halides with Alkylmetals. The Role of Arylalkynickel(II) Species as Intermediates

Dennis G. Morrell and Jay K. Kochi*

J. Am. Chem. Soc. 1975, 97, 7262

Mechanism of Biaryl Synthesis with Nickel Complexes

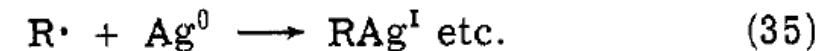
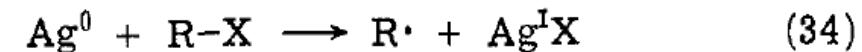
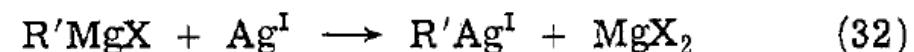
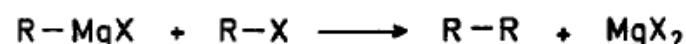
T. T. Tsou and J. K. Kochi*

J. Am. Chem. Soc. 1979, 101, 7547

Ag^{o} , Cu^{l} , Fe^{o} are shown to be efficient catalysts to couple RMgX and RX

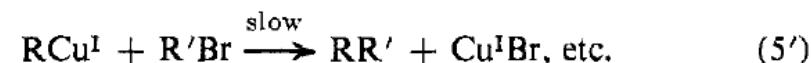
Homo-Coupling

Silver is an effective catalyst for the coupling of Grignard reagents and alkyl halides, and is especially useful when both alkyl groups are the same.



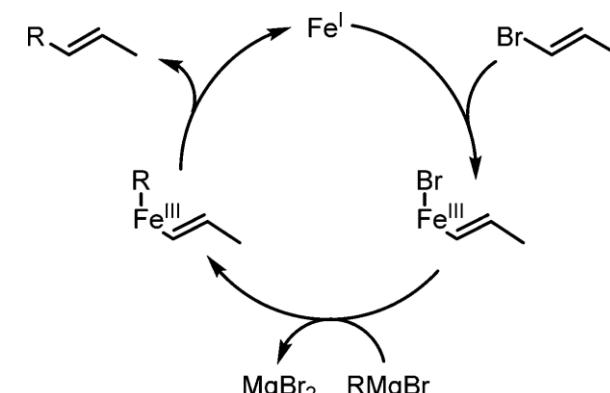
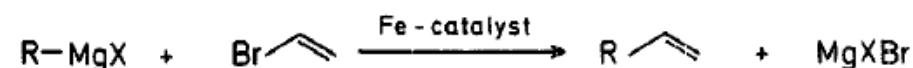
Cross-Coupling

Copper(I) catalyzes the cross-coupling between Grignard reagents and alkyl bromides when carried out in tetrahydrofuran solutions at 0° or lower temperatures (Table 2).



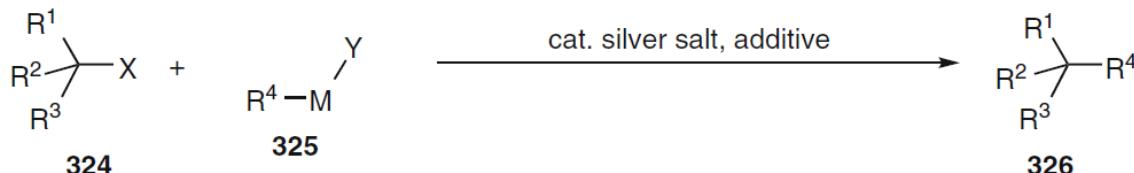
Alkenylation of Grignard Reagents

Facile vinylation of a Grignard reagent can be achieved with vinyl bromide using an iron catalyst (Table 3).



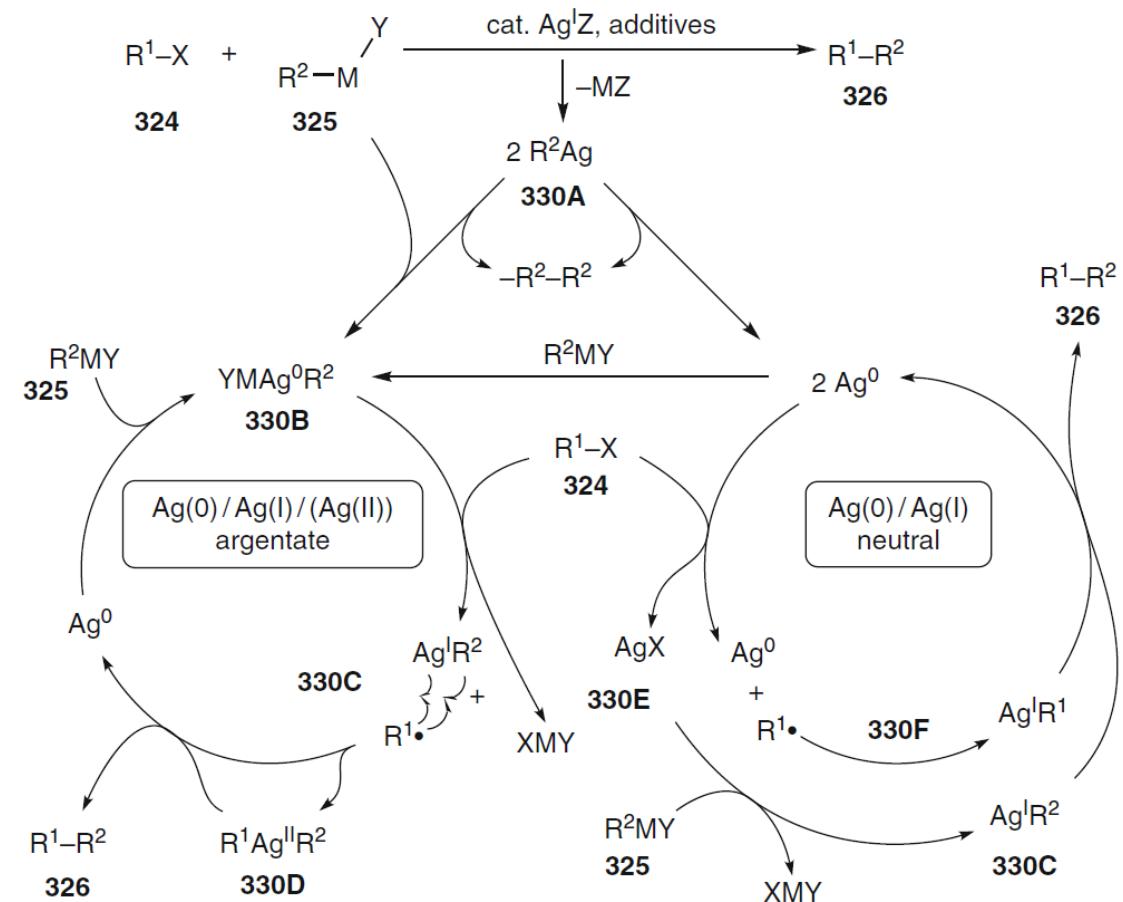
Ag XC scope has been expanded to improve synthetic utility

Oshima and coworkers developed a wide substrate scope:

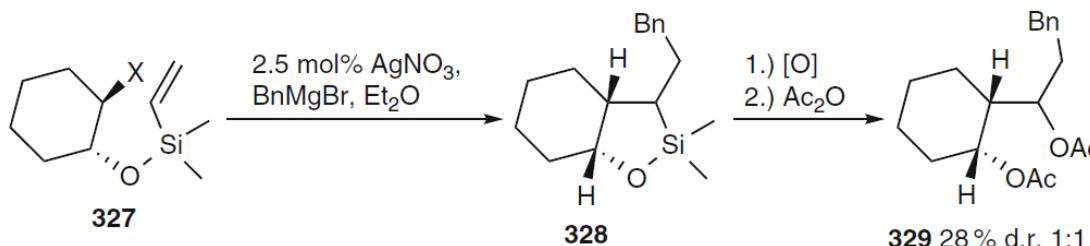


R^1 = Alkyl	R^4	M-Y	Ag salt (mol%)	Additive (mol%)	Yield
R^2 = (H), Alkyl	Bn	MgBr	AgNO ₃ (1-2.5)	-	14-88 %
R^3 = H, Alkyl	Allyl	MgBr	AgNO ₃ (1-2.5)	-	46-83 %
X = (Cl), Br, I	Alkyl	MgBr	AgBr (10)	KF (10)	36-69 %
	Ar	MgBr	AgBr (10)	P(OPh) ₃ (10)	61-88 %
	Indenyl	Li	AgBr (5)	-	61-86 %
	Bn	ZnCl ₂ •LiCl	AgOTf (5)	-	57-90 %
	Allyl	ZnCl ₂ •LiCl	AgOTf (5)	-	42-96 %

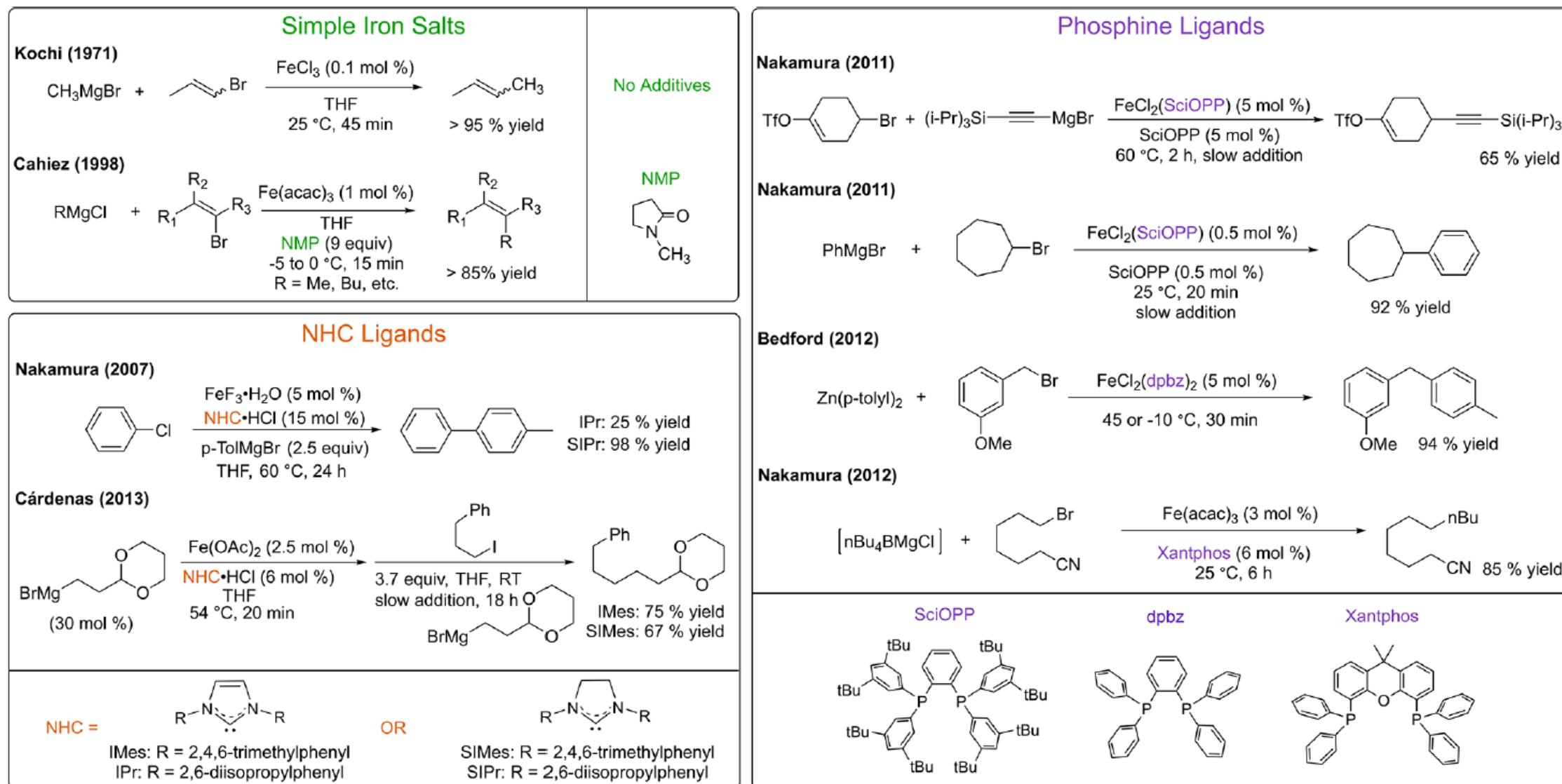
Modern cycle



Cyclizations are possible:



Fe-catalyzed couplings lay dormant until revitalization in early 2000s



Mechanism of Fe-catalyzed couplings remains an active field of study

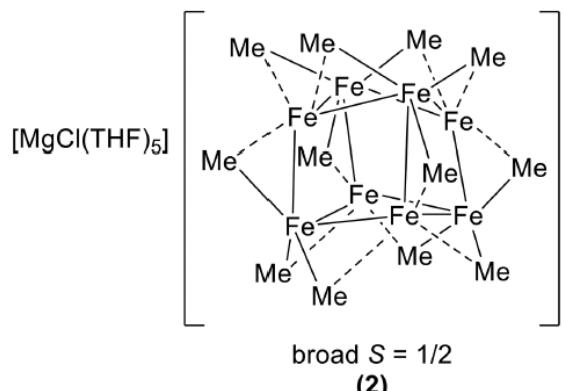
Key players: Neidig, Furstner, Bedford

Challenges

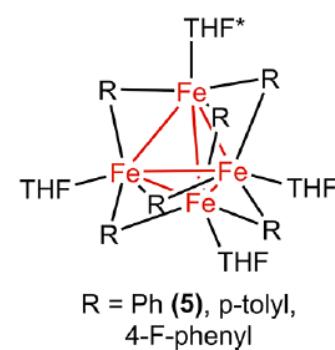
1. Facile interconversion between OS
2. air and thermal instability of organoiron complexes

Fe(-II)/(0), Fe(0)/(II), Fe(I)/(III), Fe(II)/(III) couples have all been proposed!

With MeMgBr:

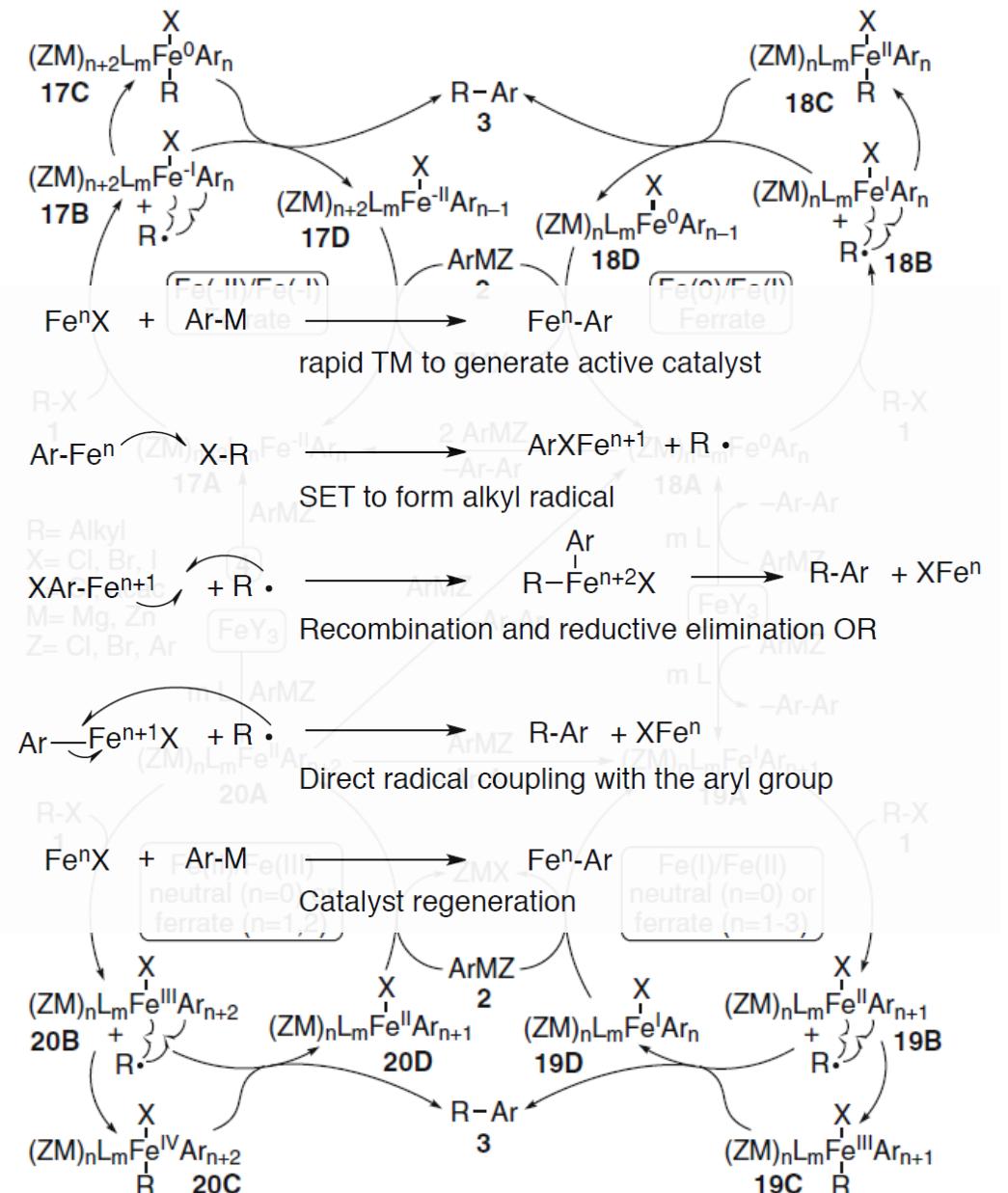


With ArMgBr:



Above species arise from ferric salt catalysts

Mechanistic scenarios differ based on ligand

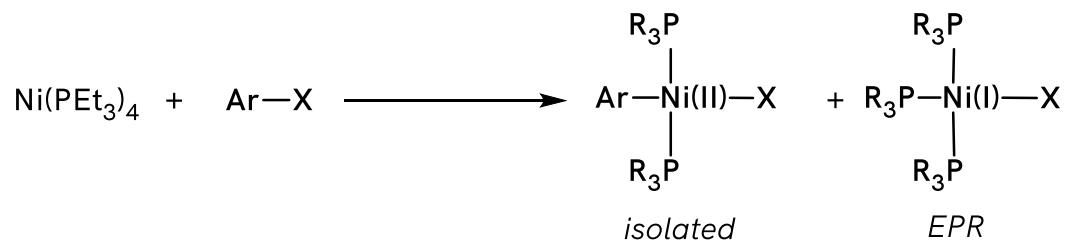


Detailed mechanistic studies reveal intricacies of elementary steps for Ni

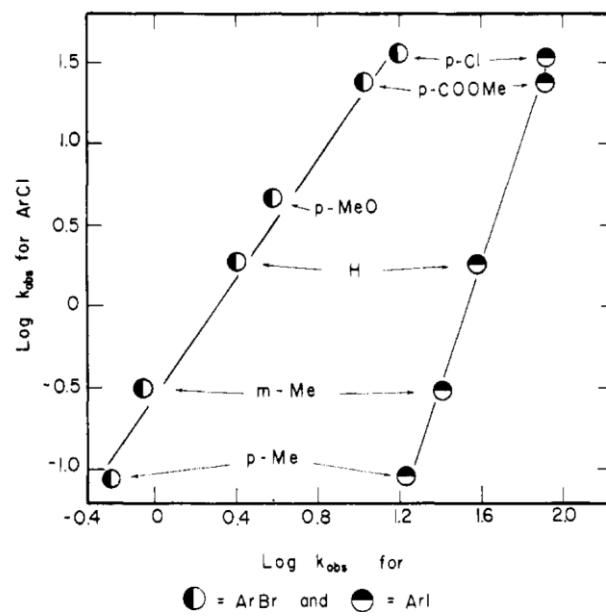


Observation

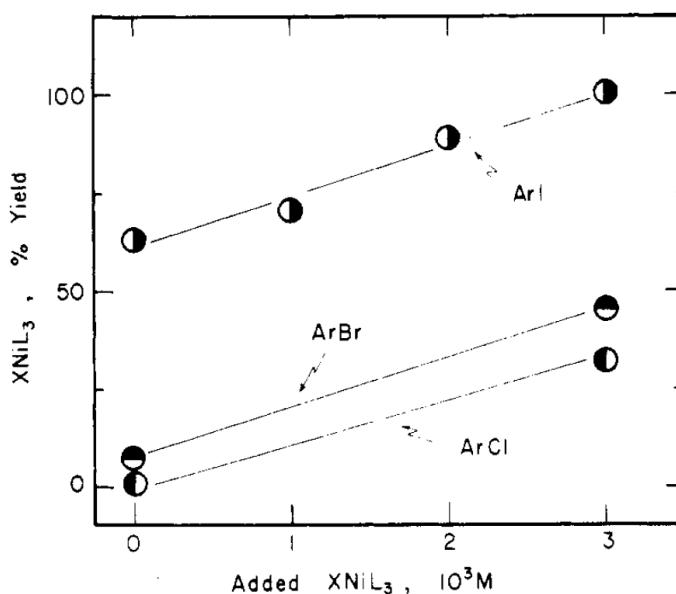
1. Oxidative adduct and Ni(I) are observed



2. ArI, ArBr, ArCl substituents have the same effect on the *rate*, but not the *Ni(II)/Ni(I) distribution*



3. Adding Ni(I) complex leads to increased yields of Ni(I) but no change in rate of Ni(0) consumption



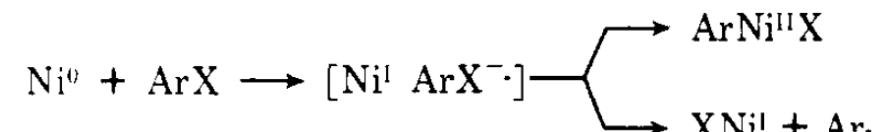
Interpretation

2. Changes to rate-limiting TS is not reflected by product, i.e. there has to be an intermediate

3. Both Ni(I) and Ni(II) products must be formed after rate-limiting step

Both products arise from common intermediate

Ni(0) is known to undergo SEO in CV/with quinones
ArX are known to accept electrons

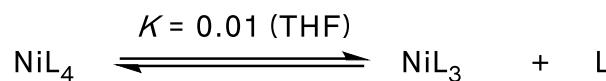


Detailed mechanistic studies reveal intricacies of elementary steps for Ni

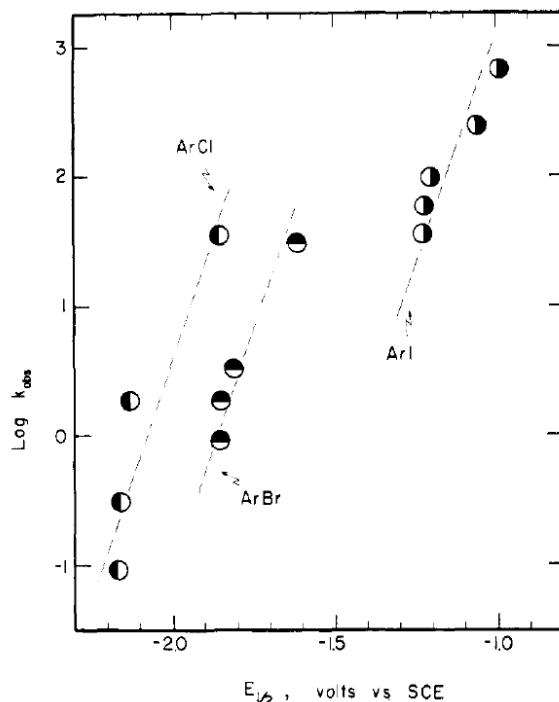


Observation

1. Ligand dissociation equilibrium can be measured



3. E^0 of ArX correlates with rate

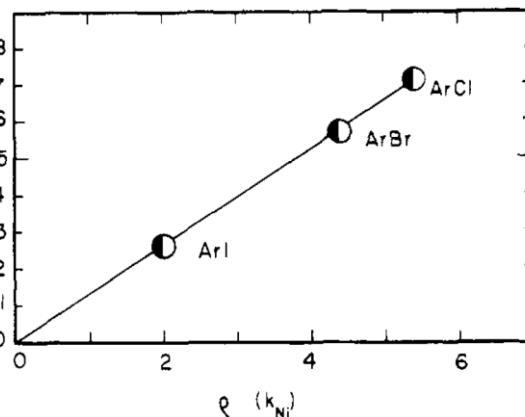


2. Rate law shows inverse [L] dependence

$$-\frac{d(\text{NiL}_3)}{dt} = k_{\text{obsd}}[\text{NiL}_3][\text{ArX}]$$

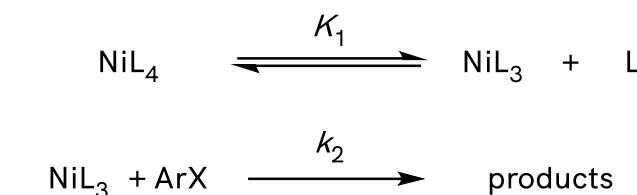
$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k} \left\{ 1 + \frac{[\text{PEt}_3]}{K} \right\}$$

4. E^0 of ArX and reaction rates have correlated Hammett correlations



Interpretation

1. and 2.: the following mechanism is mostly consistent with the rate law



NiL₃ is the key reactive species

3. and 4. SER of ArX is consistent with these trends

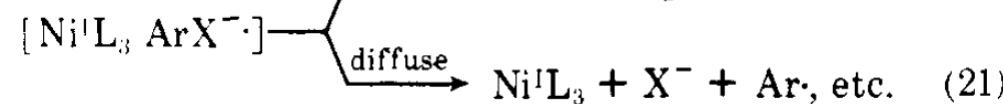


The common intermediate is a cage ion pair from SET.

Detailed mechanistic studies reveal intricacies of elementary steps for Ni



Proposals for partitioning from common intermediate

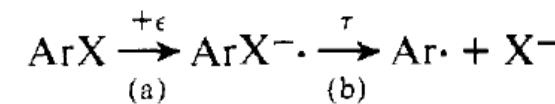


1. Ni(II) product arises from cage collapse of ion pair



Formation of Ni-X bond is driving force

2. Ni(I) product arises from homolysis of anion radical



Halide stability ($\text{I}^- > \text{Cl}^-$) correlates with yields of Ni(I) product

3. Competition is also controlled by phosphine ligation



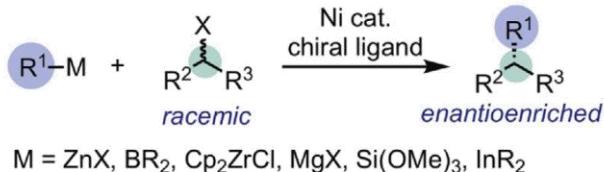
Further questions

1. Does Ni(0) form a π -precomplex with ArX?
2. Why does added Ni(I) affect the reaction?
3. Can Ni(I) be exploited in a related catalytic cycle?

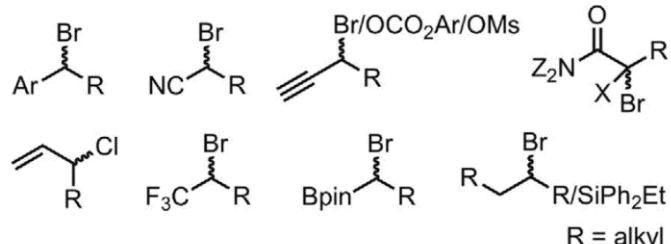
Ni(0) and Ni(I) mechanistic manifolds are intimately related

Ni catalysis of cross coupling reactions is a burgeoning field

(B) Stereoconvergent Coupling of Halides and Pseudohalides

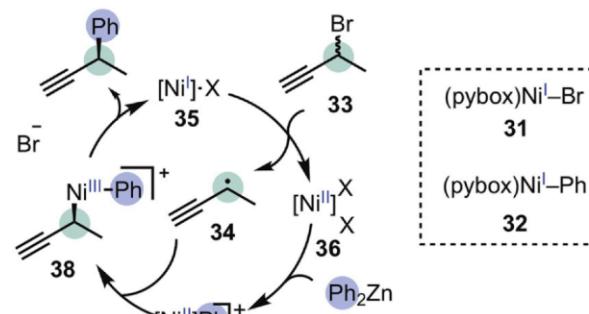
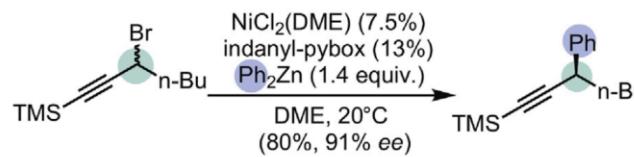


Electrophiles:

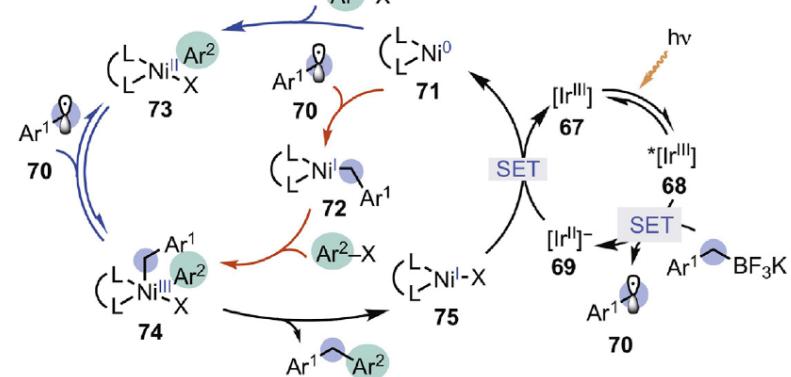


catalysts: $\text{NiX}_2(\text{DME})$ ($\text{X} = \text{Cl}, \text{Br}$) + pybox, box, biOx

'Radical Chain' Mechanism



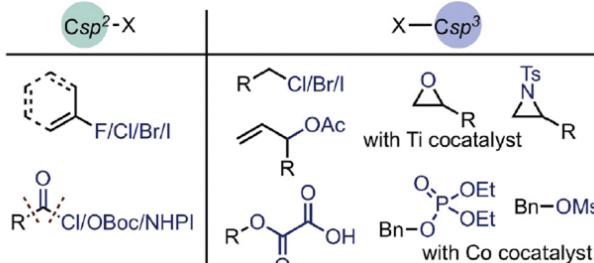
(C) Mechanism involving reduction of Ni by the photosensitizer



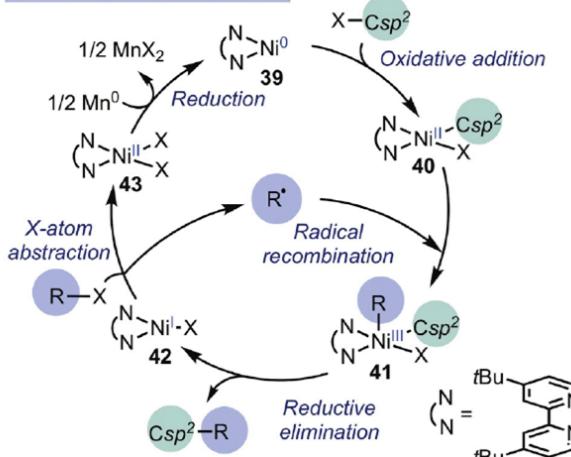
(A) Cross-electrophile coupling



Ni: NiX₂(DME) (X = Cl, Br) Ligands: bpy, phen, box, biOx
 Reductants: Mn⁰, Zn⁰, TDAE Solvents: DMA and DMF



'Radical Chain' Mechanism



Charge-transfer excitation/EDA complexes of organic molecules

Role of Ion Pairs in the Photochemistry of Electron Donor–Acceptor Complexes. Picosecond Spectroscopic Studies of Arene–Tetracyanoethylene Systems

E. F. Hilinski,[†] J. M. Masnovi,[‡] J. K. Kochi,^{*†} and P. M. Rentzepis^{*†}

J. Am. Chem. Soc. **1984**, *106*, 8071

Cycloreversion Induced by Charge-Transfer Excitation of Electron Donor–Acceptor Complexes. Wavelength-Dependent Photochemistry of Dianthracene

J. M. Masnovi and J. K. Kochi*

J. Am. Chem. Soc. **1985**, *107*, 6781

Continuum of Outer- and Inner-Sphere Mechanisms for Organic Electron Transfer. Steric Modulation of the Precursor Complex in Paramagnetic (Ion-Radical) Self-Exchanges

Sergiy V. Rosokha and Jay K. Kochi*

J. Am. Chem. Soc. **2007**, *129*, 3683

A Unified Mechanism for Thermal and Photochemical Activation of Charge-Transfer Processes with Organometals.
Steric Effects in the Insertion of Tetracyanoethylene

S. Fukuzumi, K. Mochida, and J. K. Kochi*

J. Am. Chem. Soc. **1979**, *101*, 5961

Isolation and Oxidation–Reduction of Methylviologen Cation Radicals. Novel Disproportionation in Charge-Transfer Salts by X-ray Crystallography

T. M. Bockman and J. K. Kochi*

J. Org. Chem. **1990**, *55*, 4127 (> 300 citations)

Inner-Sphere Electron Transfer in Organic Chemistry. Relevance to Electrophilic Aromatic Nitration[†]

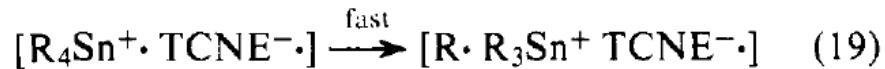
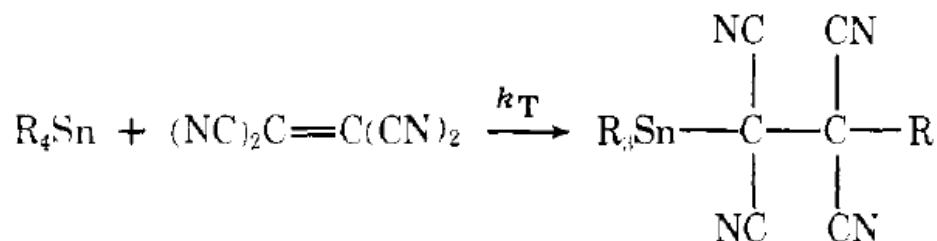
JAY K. KOCHI

Acc. Chem. Res. **1992**, *25*, 39

EDA complexes were implicated and studied as key intermediates in organic reactions



R₄Sn adds across tetracyanoethylene



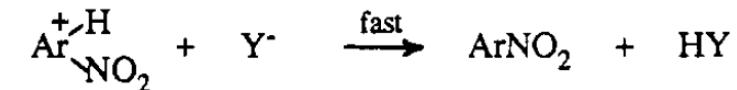
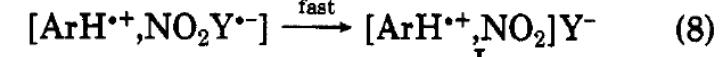
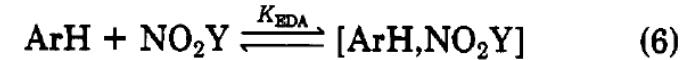
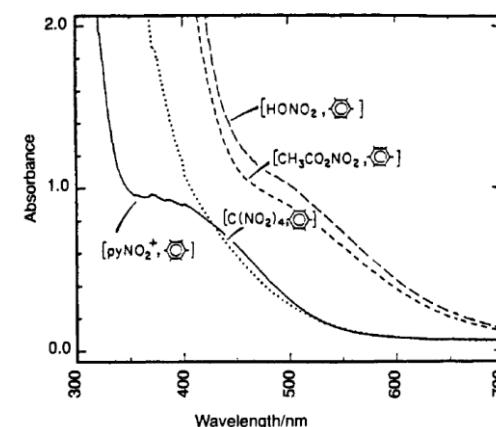
Addition was found to follow separate thermal and photochemical pathways. Caged radical pair observed on frozen matrix by EPR.

Nitration of benzene

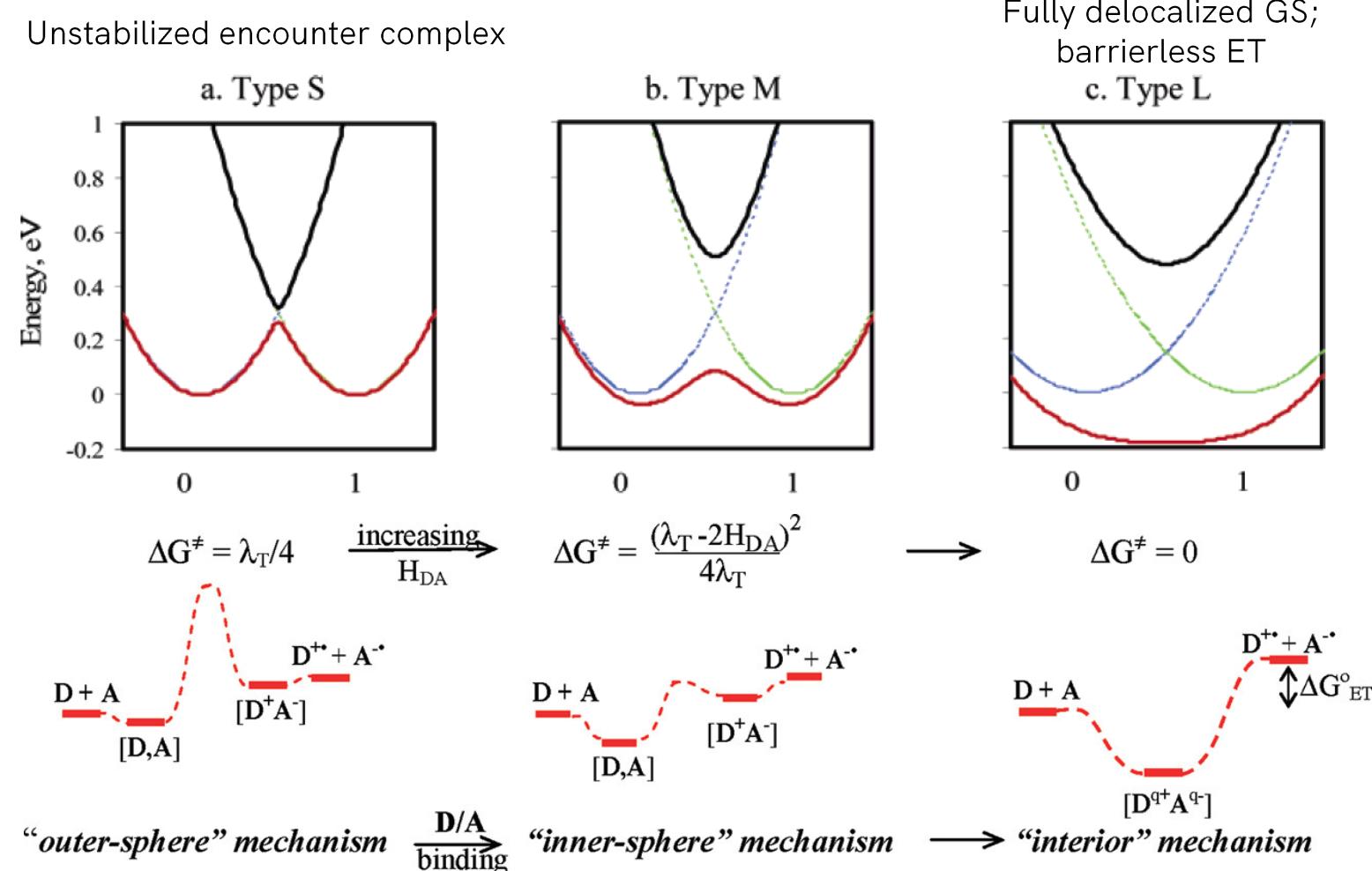
Shown to proceed by single electron transfer before Wheland intermediate

UV Vis and time-resolved absorption spectroscopy show charge transfer complexes to be the *kinetically dominant intermediate*

a. Charge-transfer complexes



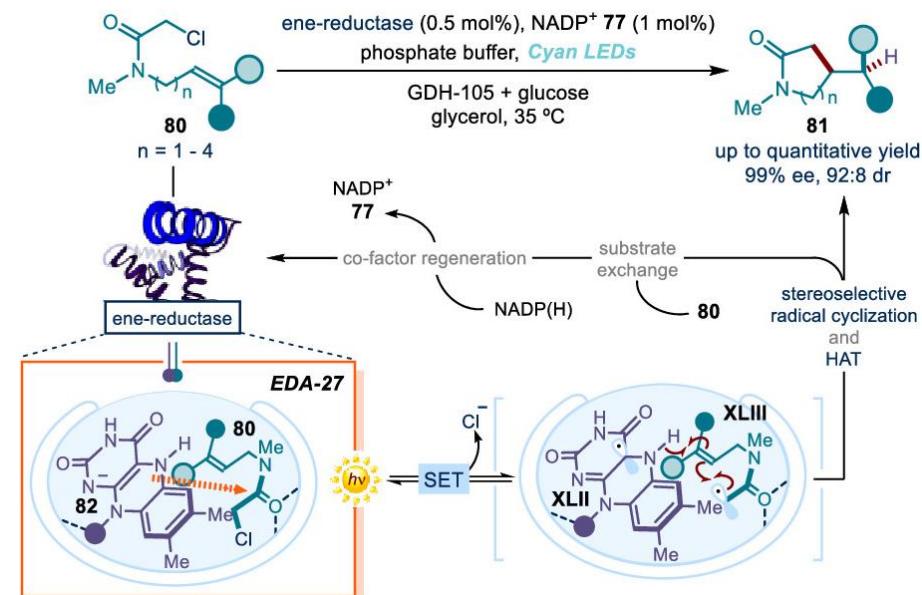
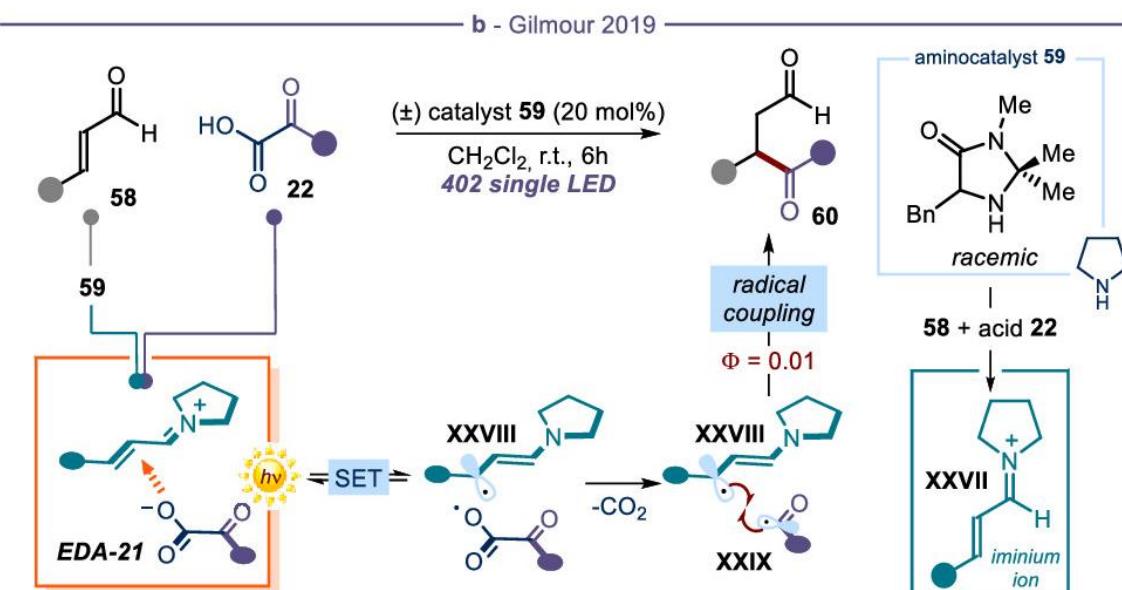
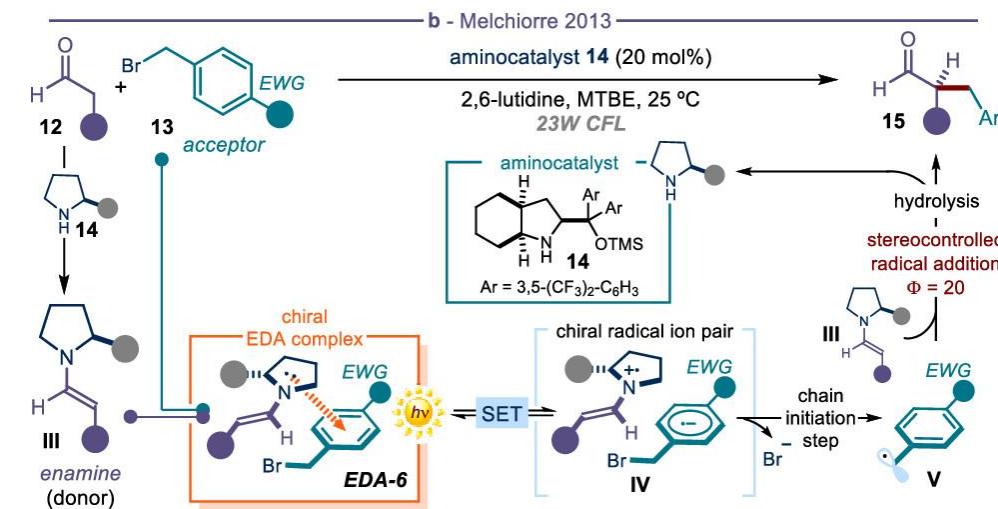
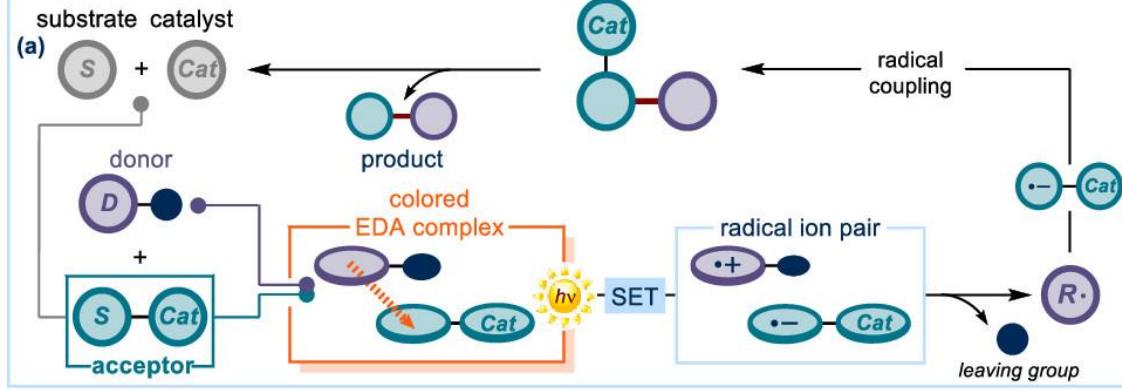
Autumnal work focused on the unification of theories of electron transfer



Crystallographical, analytical, theoretical, and kinetic work to develop a unified theory for ET in EDA complexes.

EDA complexes used in modern synthetic methodology to generate radical pairs

Principle: catalytic unmasking of EDA capabilities



Redox of organic radicals by metal complexes

Mechanisms of Organic Oxidation and Reduction by Metal Complexes

Electron and ligand transfer processes form the basis for redox reactions of radicals and metal species.

Jay K. Kochi

Science **1967**, *155*, 415

Electron-Transfer Mechanisms for Organometallic Intermediates in Catalytic Reactions

Jay K. Kochi

Acc. Chem. Res. **1974**, *7*, 351

Metal-Catalyzed Oxidations of Organic Compounds in the Liquid Phase: A Mechanistic Approach

ROGER A. SHELDON

*Koninklijke/Shell-Laboratorium
Amsterdam, The Netherlands*

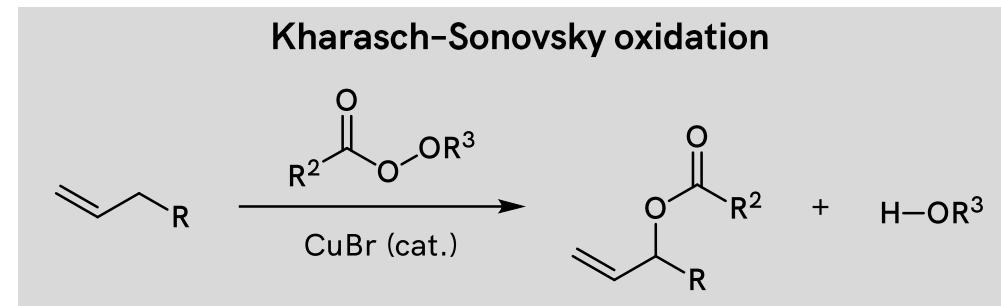
AND

JAY K. KOCHI

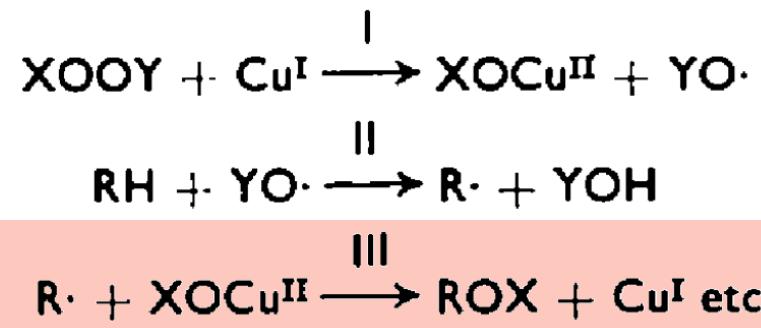
*Department of Chemistry
Indiana University
Bloomington, Indiana*

Adv. Catal. **1976**, *25*, 272

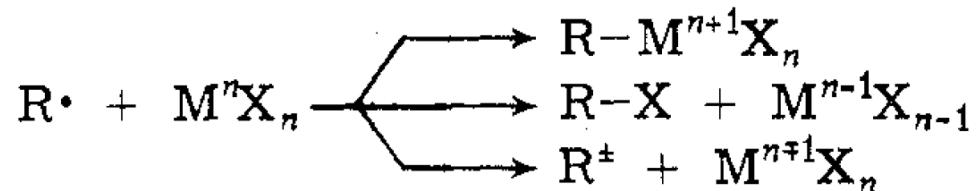
Cu-alkyl radical mechanisms elucidated from studies of C-H oxidation



Mechanistic studies established the following sequence of elementary steps:

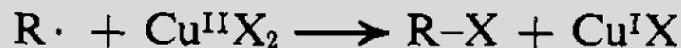


What are the pathways available for reaction between $\text{R}\cdot$ and a metal complex?



Oxidation of R[•] by Cu(II) occurs by ligand transfer or electron transfer

Ligand transfer oxidation



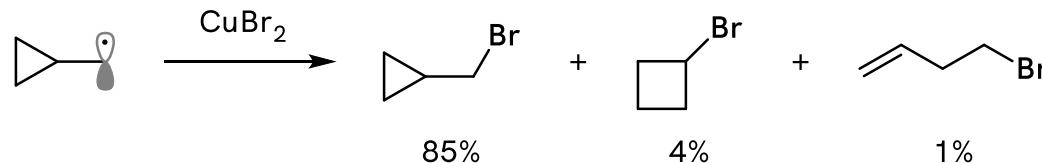
X = Cl, Br, I, SCN, N₃, CN

rate ~ diffusion-control

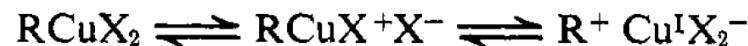
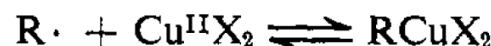
Mode 1: Direct atom transfer



e.g. cyclopropylcarbinyl does not rearrange

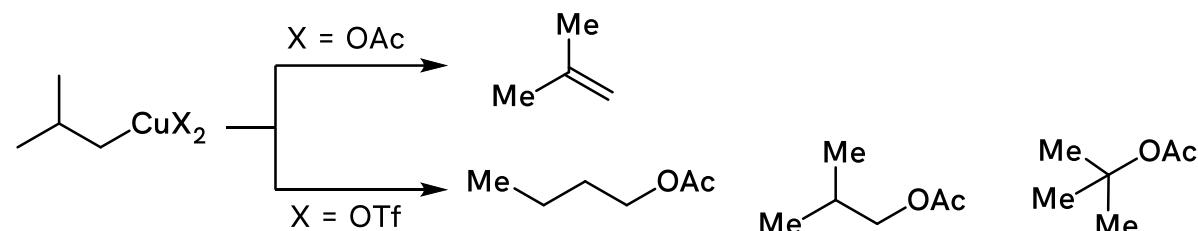


Mode 2: Oxidative substitution



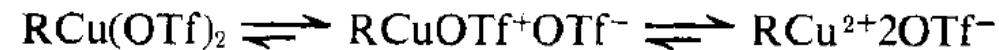
more electron-rich/resonance-stabilized alkyls
e.g. β -(*p*-OMe)phenethyl

Electron transfer oxidation



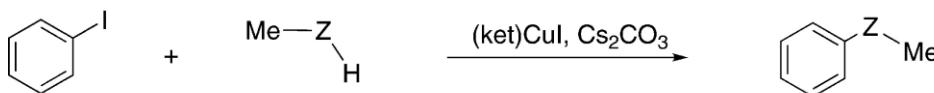
Acetate promotes elimination, triflate promotes solvolysis

Ligand dissociation (triflate) shown to favor ejection of carbocation

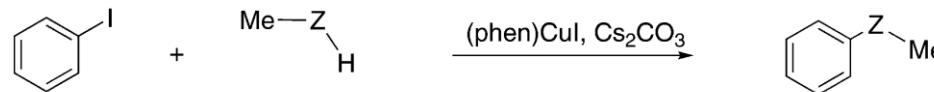


SET oxidation mechanisms underpin important modern synthetic methods

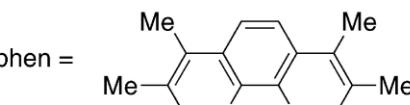
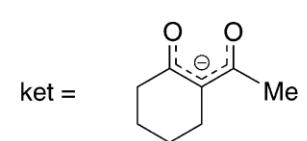
Cu-catalyzed Ullman-type couplings with ligated Cu also proceeds by Kochi-type SET



SET favored over mechanisms involving OA, iodine atom transfer and sigma bond metathesis in both cases.

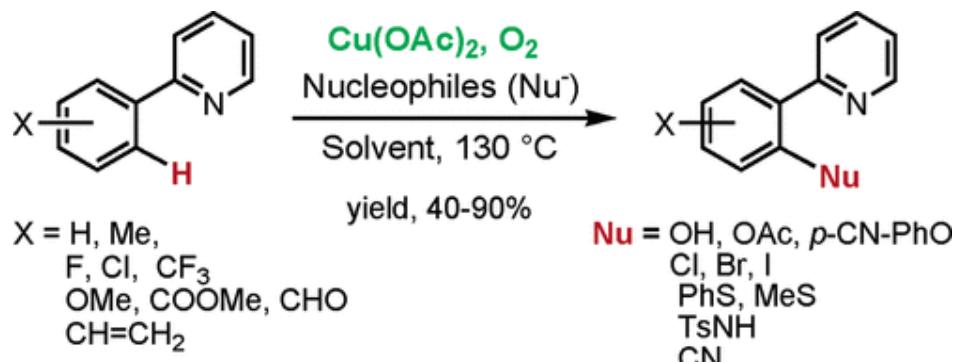


SET favored when Z = O, iodine atom transfer favored when Z = NH.

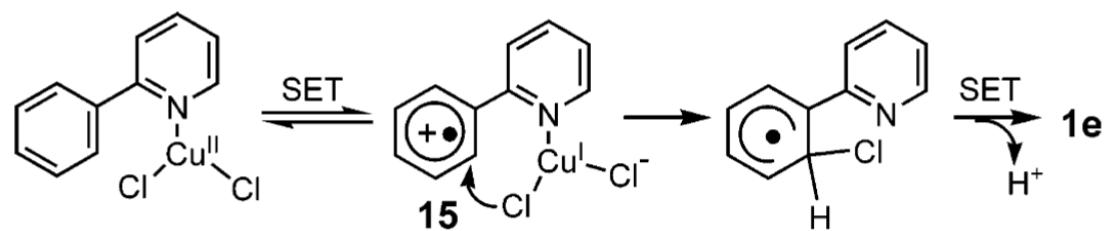


Houk, Buchwald *J. Am. Chem. Soc.* **2010**, 132, 6205

C-H functionalization with O₂



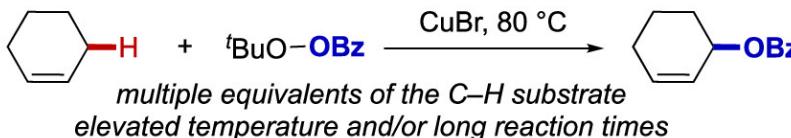
Mechanistic parallels to Kochi's Co(TFA)₃ C-H oxidation



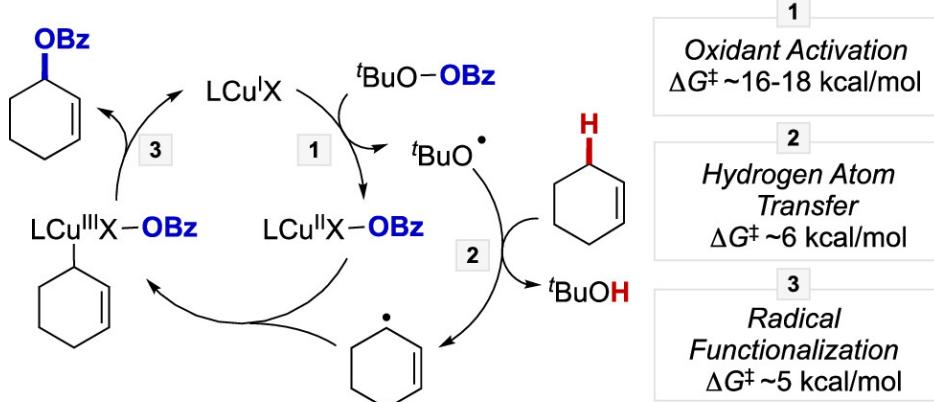
Yu *J. Am. Chem. Soc.* **2006**, 128, 6790

Mechanistic insights used to “modernize” K-S reaction

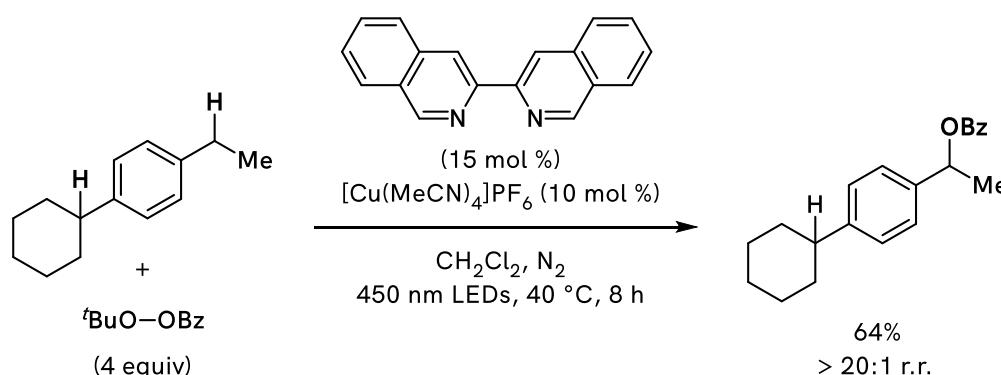
A. Kharasch-Sosnovsky reaction:



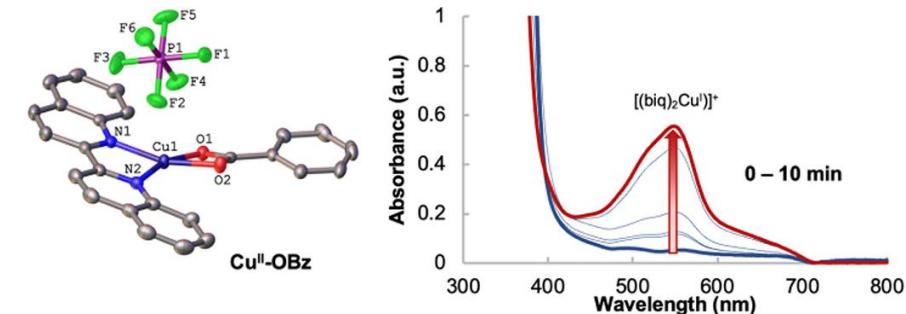
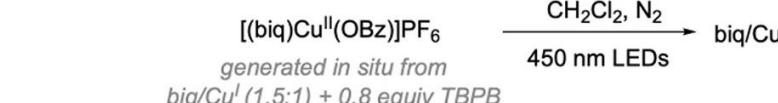
B. Proposed catalytic mechanism:



C. Target: Benzylic C(sp³)-H esterification with limiting C-H substrate

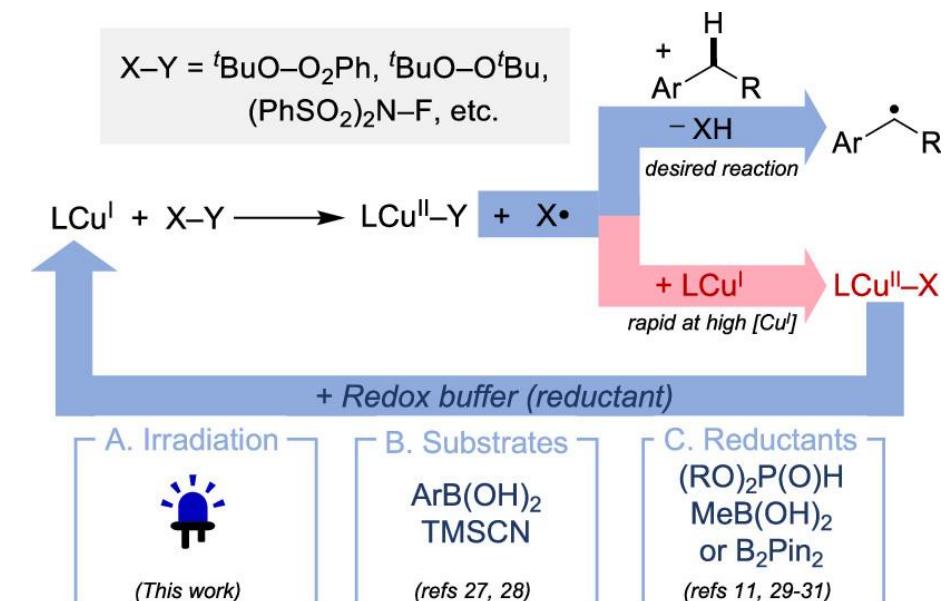


D. Irradiation of [(biq)Cu^{II}(OBz)]PF₆



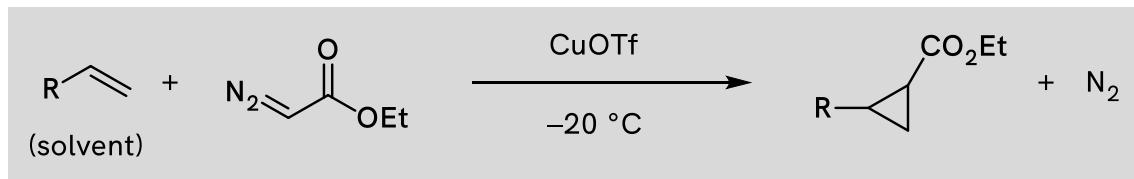
“Photochemical redox buffering”

X-Y = *t*BuO-O₂Ph, *t*BuO-O*t*Bu, (PhSO₂)₂N-F, etc.



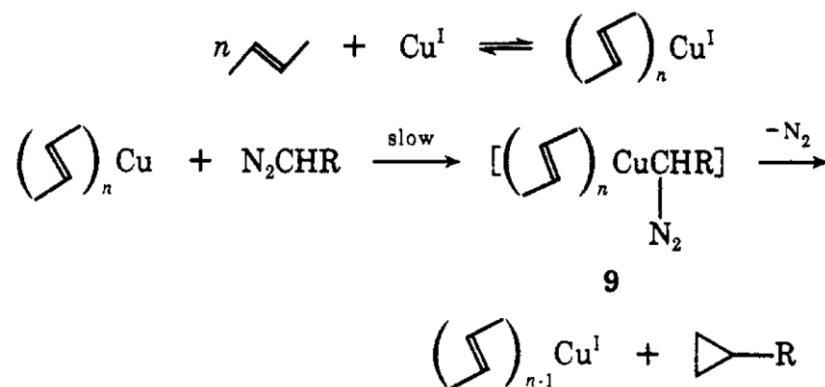
Discovery of Cu cyclopropanation reactivity proves impactful

Original work

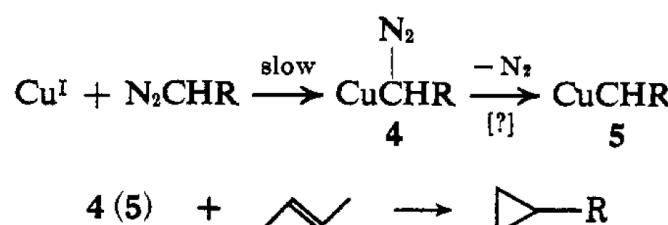


Full mechanistic workup leads to two mechanisms:

Scheme I

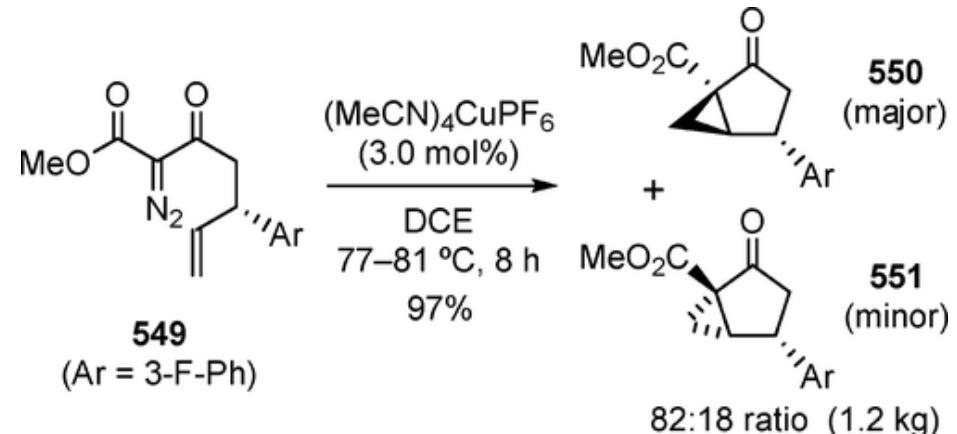


Scheme III

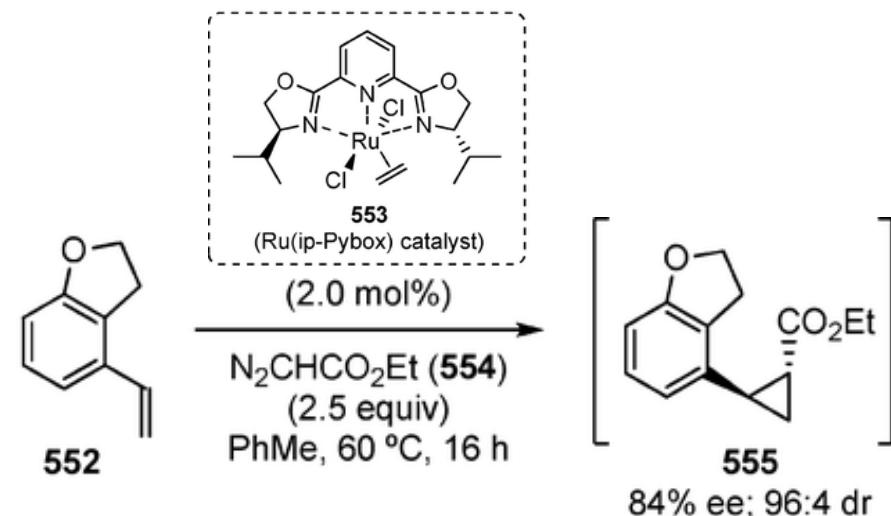


J. Am. Chem. Soc. 1971, 93, 1483

Cyclopropanations are commercially employed

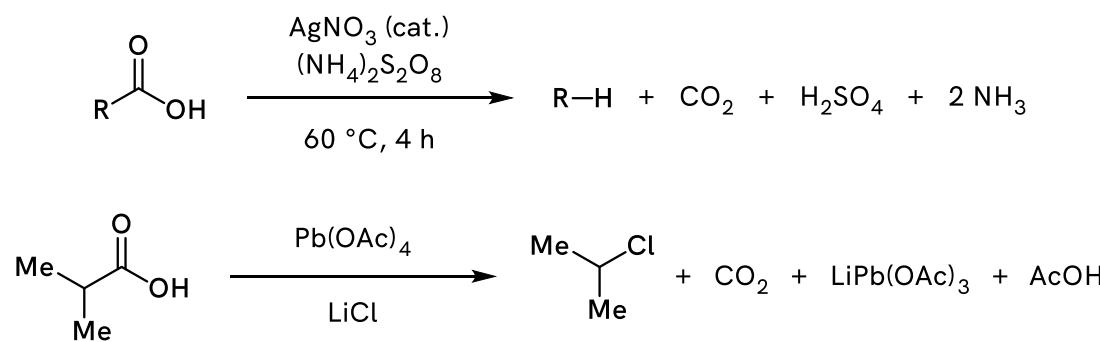


Merck J. Org. Chem. **2002**, **67**, 5508



BMS Tetrahedron: Asymmetry 2003, 14, 3569

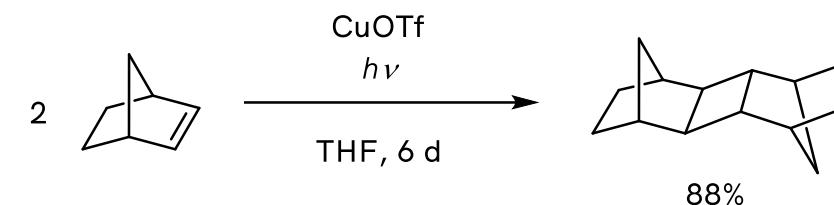
Catalytic decarboxylations with Ag(I) or Pb(IV)



J. Am. Chem. Soc. **1970**, 92, 1652; J. Am. Chem. Soc. **1965**, 87, 3609

Forerunner to modern decarboxylative chemistry

Cu(OTf)-catalyzed photo-[2+2] (Kochi-Salomon reaction)

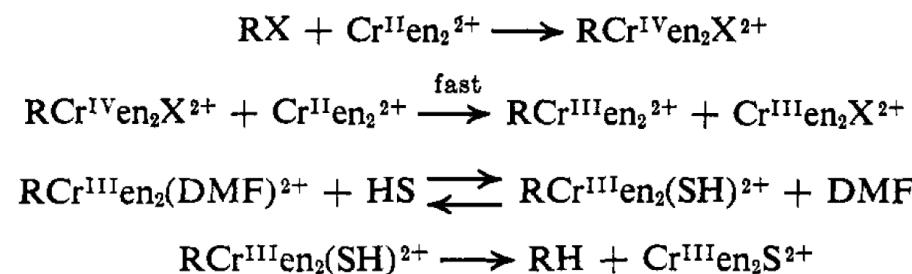


Tet Lett. **1973**, 27, 2529

Modernization and application in total syntheses
(e.g. Yoon, Burns)

Vignettes

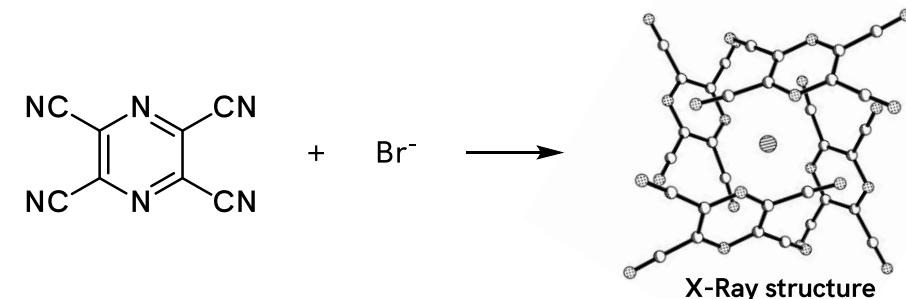
Cr(II) reduction of alkyl halides



J. Am. Chem. Soc. **1970**, 92, 137, etc.

Mechanistic foundation for
Nozaki-Hiyama(-Kishi) reaction and Takai olefination

First observation of anion-π interactions



Angew. Chem. Int. Ed. **2004**, 43, 4650

Supramolecular chemistry, noncovalent interactions

Undiscovered chemistry

Homolytic Reactions of Grignard Reagents and Organomagnesium Compounds by Electron Spin Resonance

Kuang S. Chen, Jean-Paul Battioni, Jay K. Kochi*

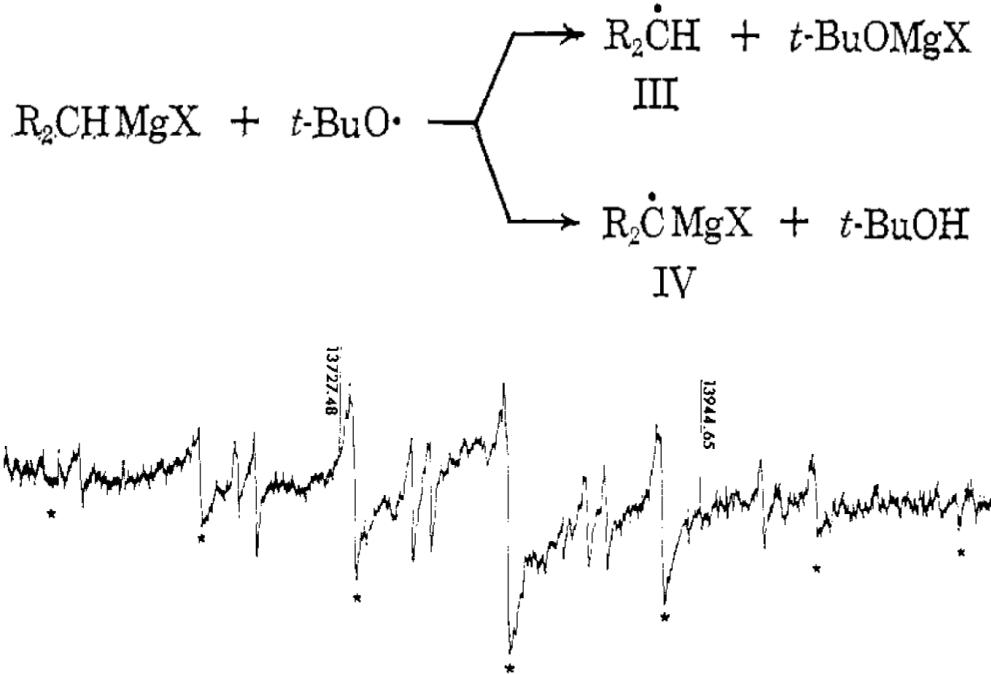


Figure 2. Esr spectrum of the isopropyl radical and α -magnesio-isopropyl radical (starred) from diisopropylmagnesium and the *tert*-butoxy radical in diethyl ether at -115° .

Photolysis of Dibenzylamine. Formation of Benzylamino and Dibenzylamino Radicals

M. A. RATCLIFF, JR., AND J. K. KOCHI*

