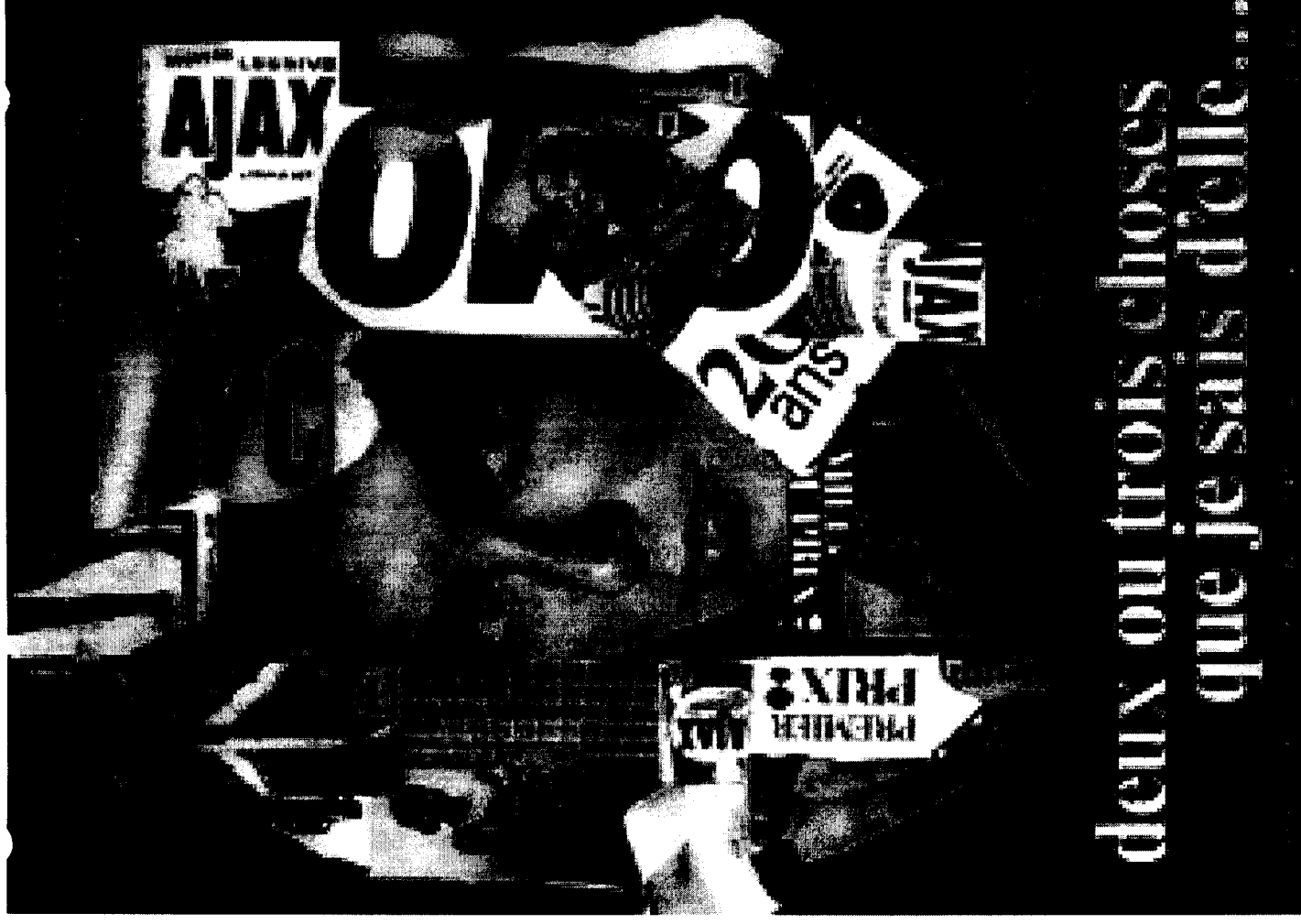


**Group Seminar  
09-20-2005**

**Two or Three Things  
I Know About  
Group 8 Metals**

**Shingo Ito  
Department of Chemistry  
The University of Tokyo  
Japan**

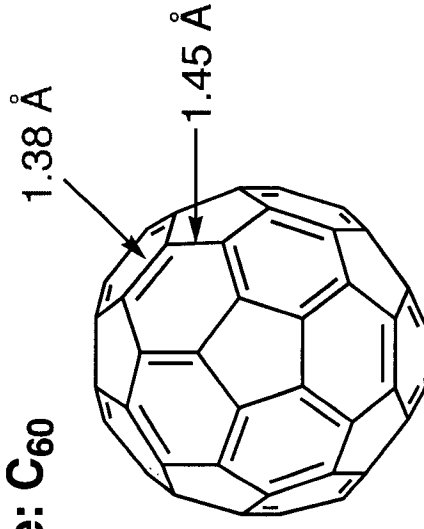


# Contents

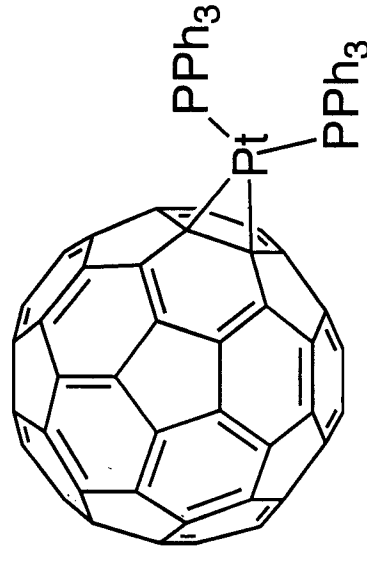
- 1. Backgrounds**
- 2. Synthesis and Properties of Bucky Ruthenocenes**
  - 2-1 Introduction**
  - 2-2 Synthesis of Bucky Ruthenocene**
  - 2-3 Functionalization of Bucky Ruthenocene**
- 3. Iron-Catalyzed Cross-Coupling of Alkyl Halides**
  - 3-1 Introduction**
  - 3-2 Cross-Coupling with Grignard Reagents**
  - 3-3 Cross-Coupling with Organozinc Reagents**
- 4. Acknowledgements**

# Transition Metal Complexes of Fullerene

Fullerene:  $C_{60}$



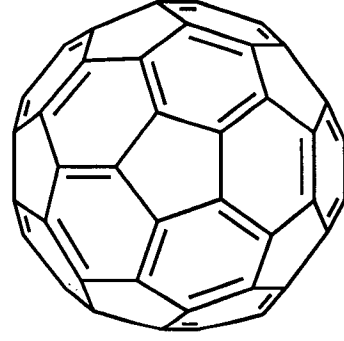
Fullerene-Pt complex



H. W. Kroto et al. *Nature*, 1985, 318, 162.

P. J. Fagan et al. *Science*, 1991, 252, 1160.

Regioselective penta-addition to  $C_{60}$

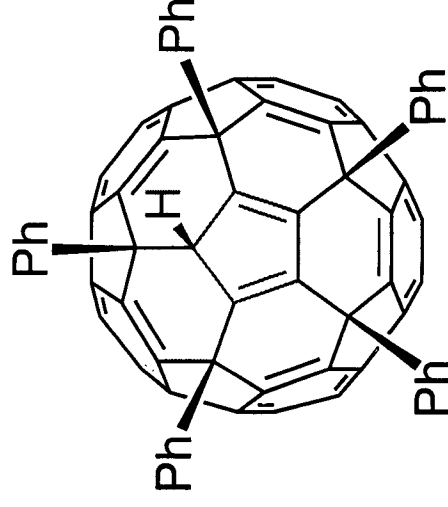


$PhMgBr$  (30 equiv)

$CuBr \cdot SMe_2$  (30 equiv)

$H_2O$

$1,2-Cl_2C_6H_4/THF$

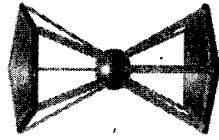


$C_{60}$

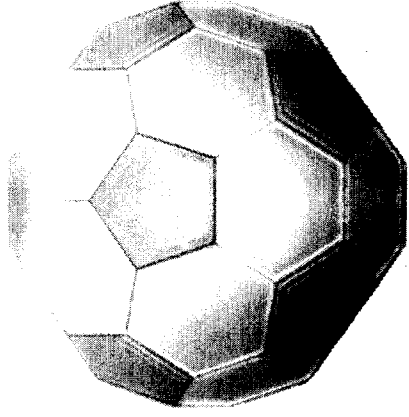
E. Nakamura et al. *JACS*, 1996, 118, 12850.

quant.

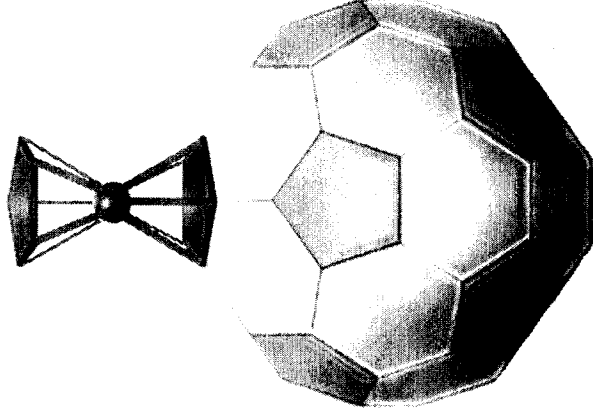
# Ferrocene + Fullerene = ?



+



=



Ferrocene

Fullerene

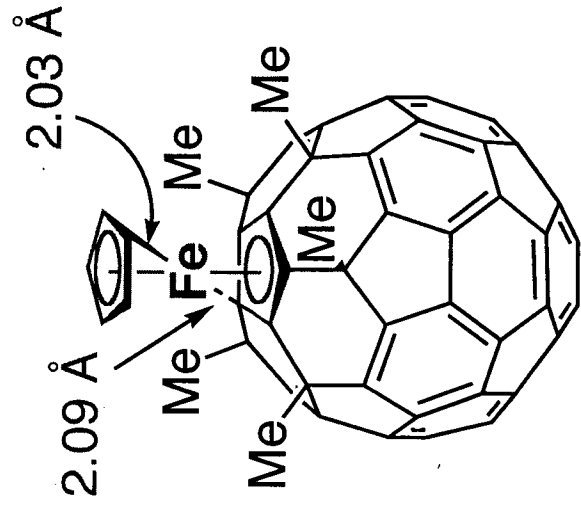
1973 Nobel Prize

1996 Nobel Prize

Nobel Prize?

# Bucky Ruthenocene: $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)$

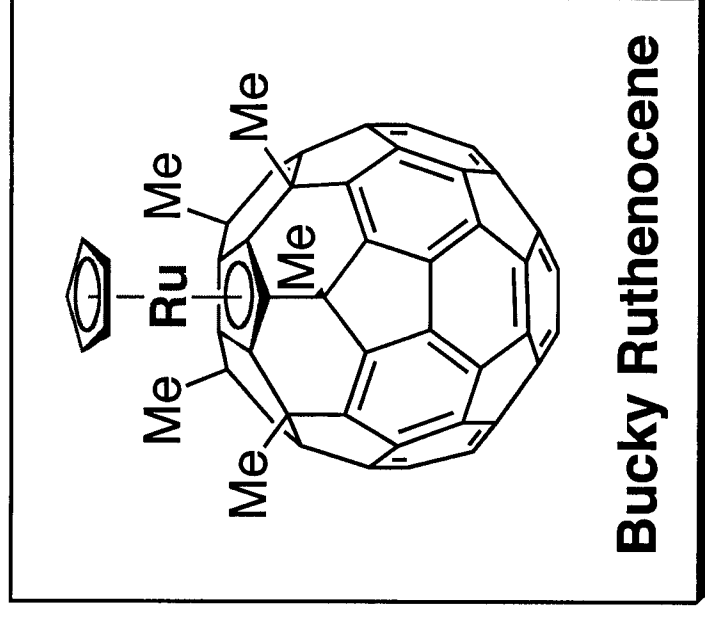
Previous Work



## Bucky Ferrocene

- Sterically hindered ferrocene moiety due to a steric repulsion between Cp ring and five methyl groups

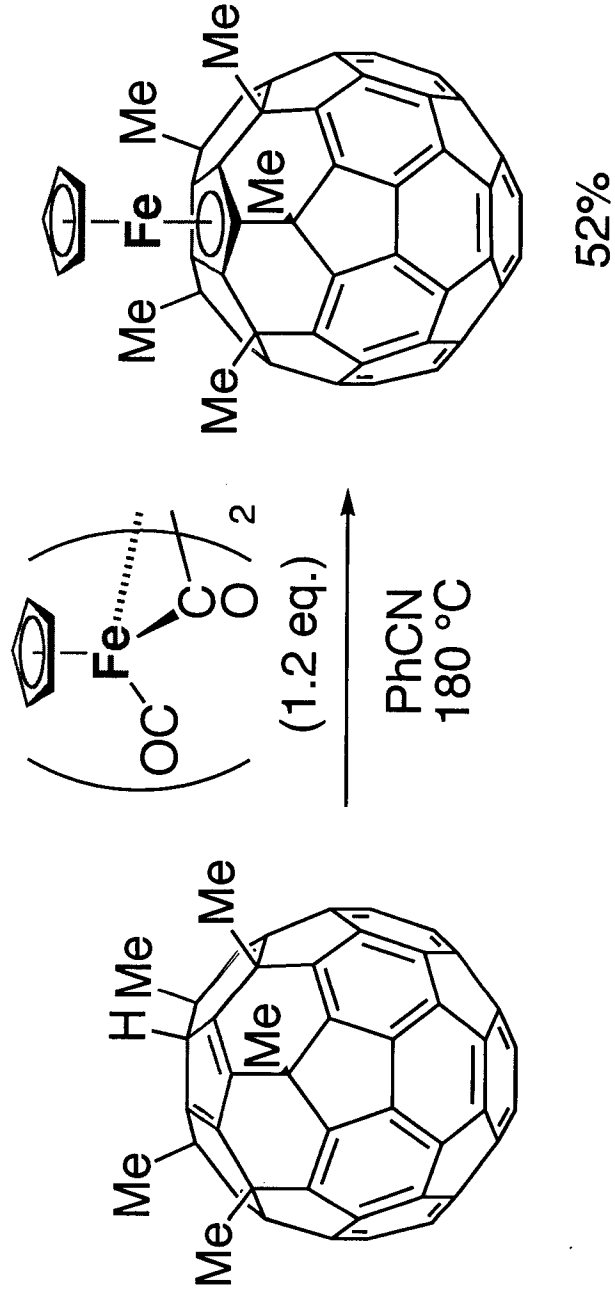
This Work



$$\left[ \begin{array}{l} r(\text{Ru}^{\text{II}}) = 0.68 \text{ \AA} \\ r(\text{Fe}^{\text{II}}) = 0.61 \text{ \AA} \end{array} \right]$$

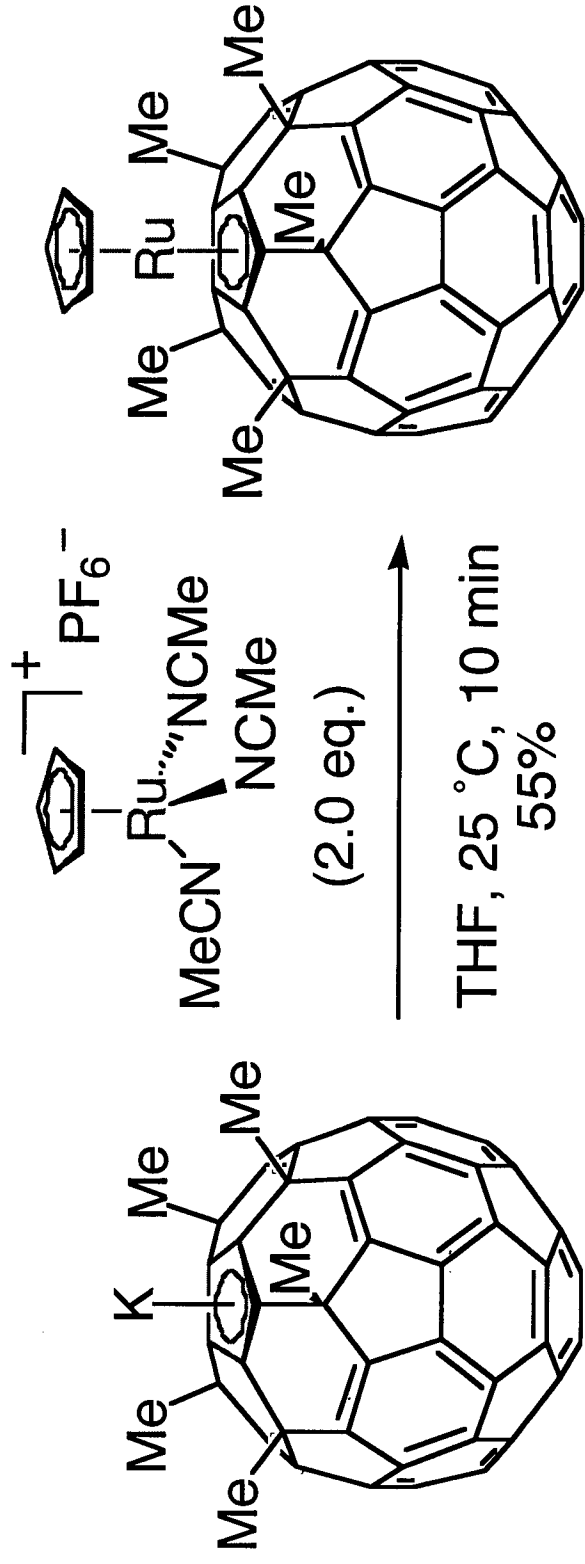
- Large ionic radii reduce the repulsion.  $\implies$  Easy functionalization

# Synthesis of Bucky Ferrocene via C-H Activation



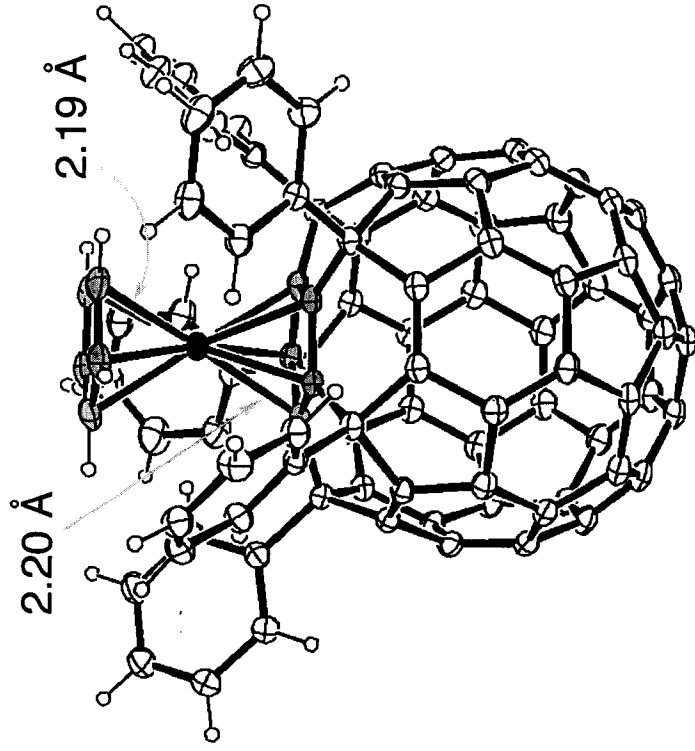
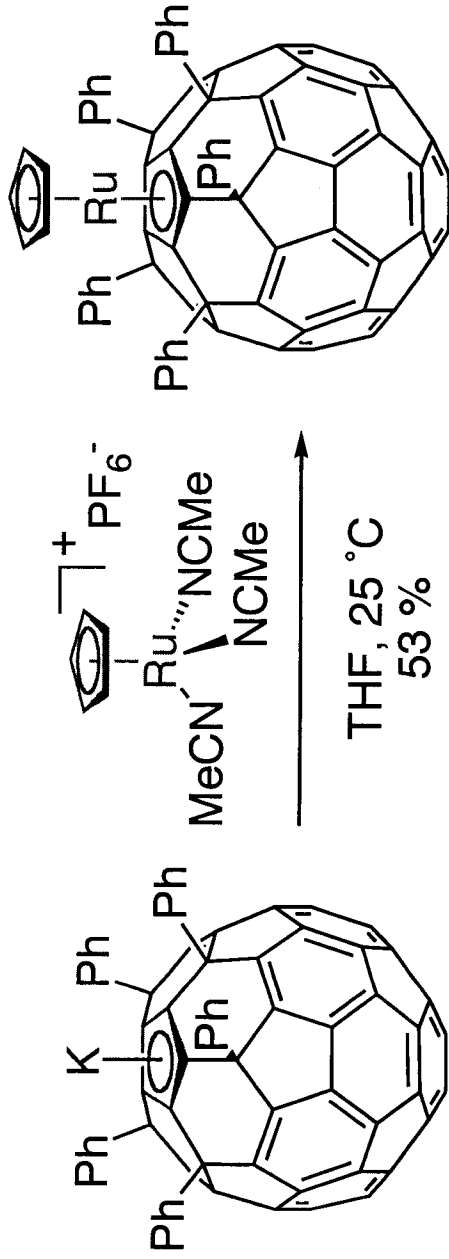
E. Nakamura et al. *J. Am. Chem. Soc.* **2002**, 124, 9354.

# Synthesis of Bucky Ruthenocene via Transmetalation



200 mg scale

# Synthesis of $\text{Ru}(\eta^5\text{-C}_{60}\text{Ph}_5)(\eta^5\text{-C}_5\text{H}_5)$

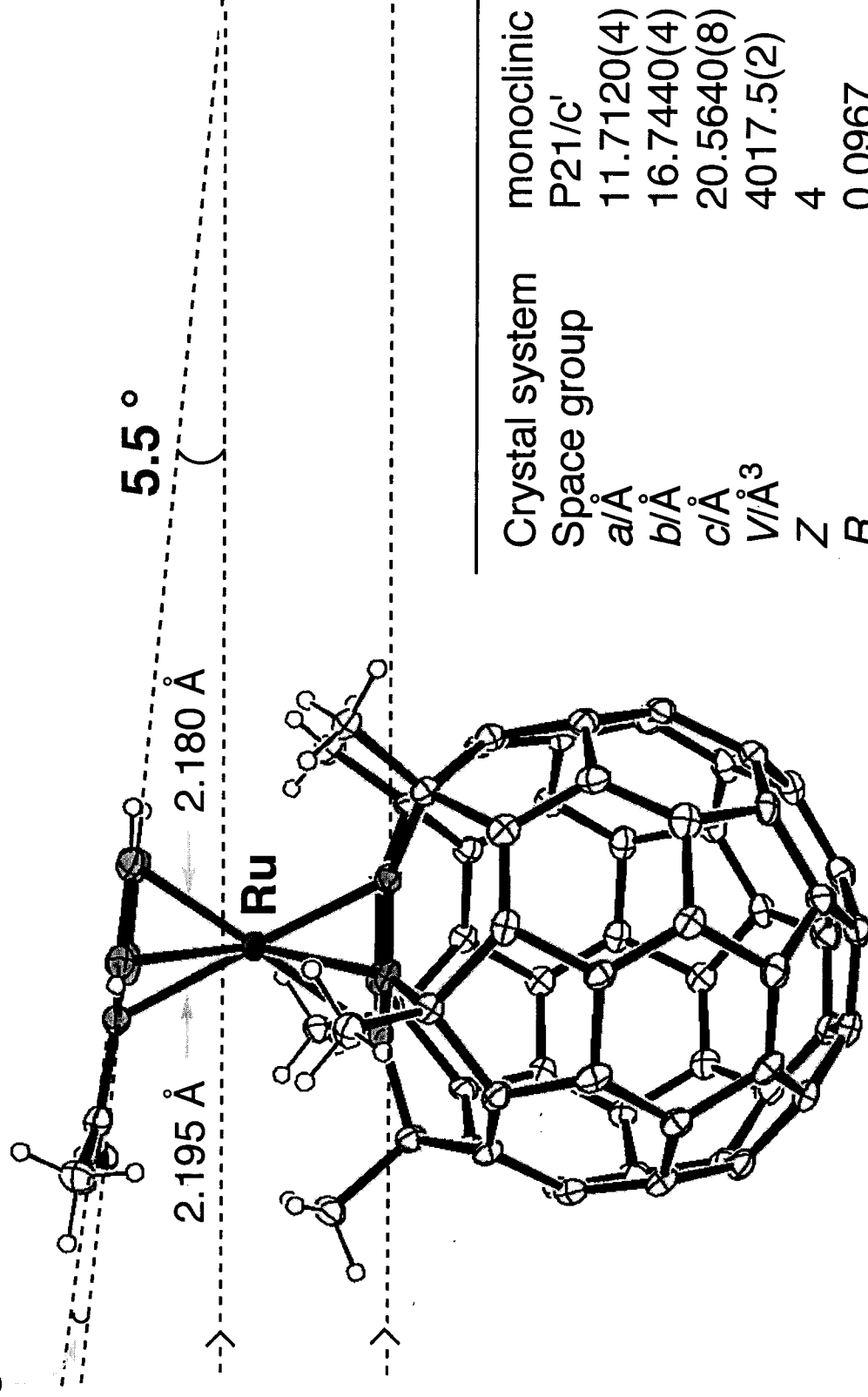


Crystal system	monoclinic
Space group	P 21/n'
a/Å	17.7250(9)
b/Å	14.0460(7)
c/Å	26.1310(7)
V/Å <sup>3</sup>	6234.9(5)
Z	4
R	0.0733
w/R	0.2053



# ORTEP Drawing of $\text{Ru}(\eta^5\text{-C}_{60}\text{Me}_5)(\eta^5\text{-C}_5\text{H}_4\text{COMe})\cdot 1/2\text{CS}_2$

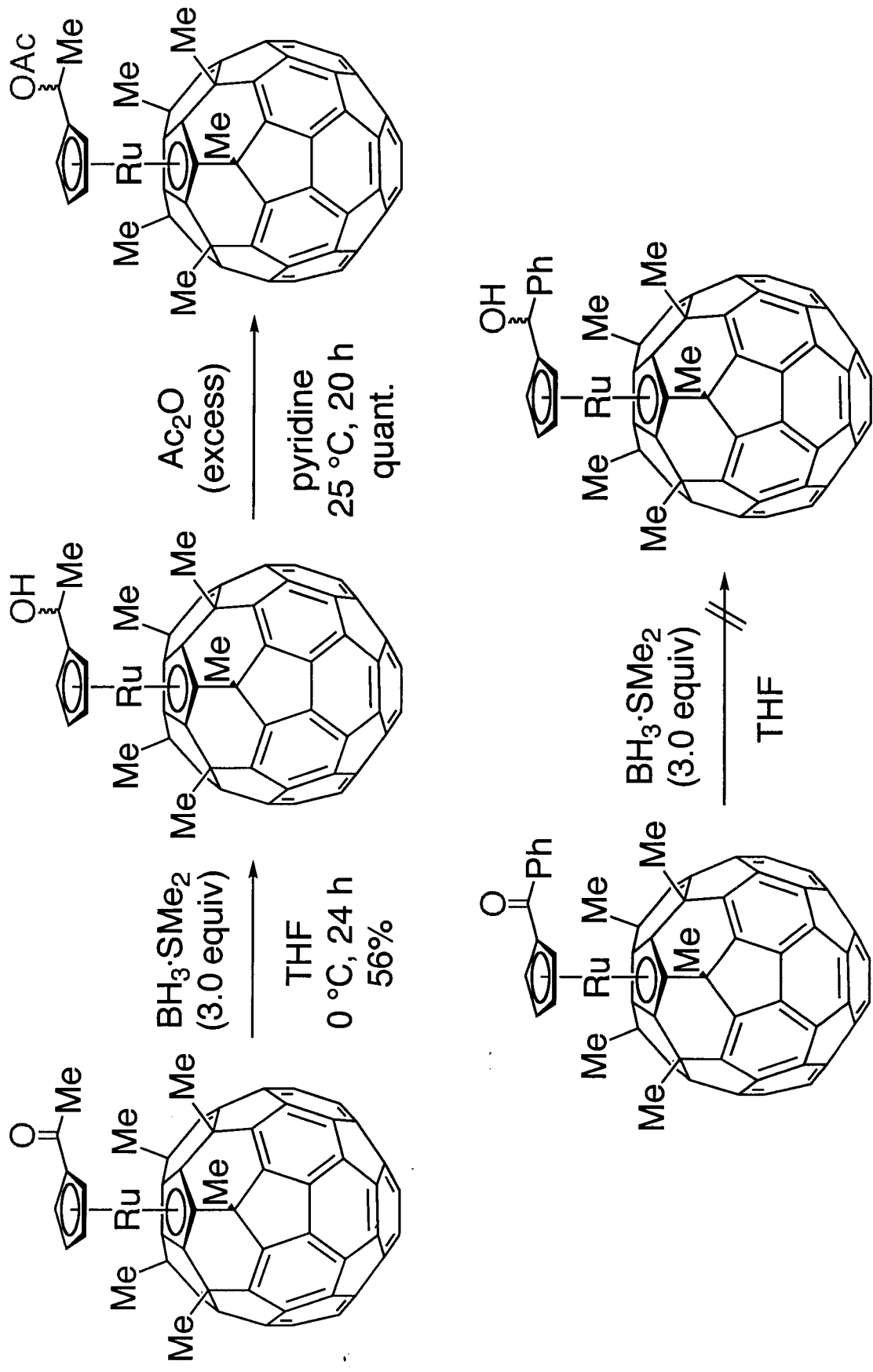
0.5°



The  $\text{CS}_2$  molecules are omitted for clarity  
(30% probability level)

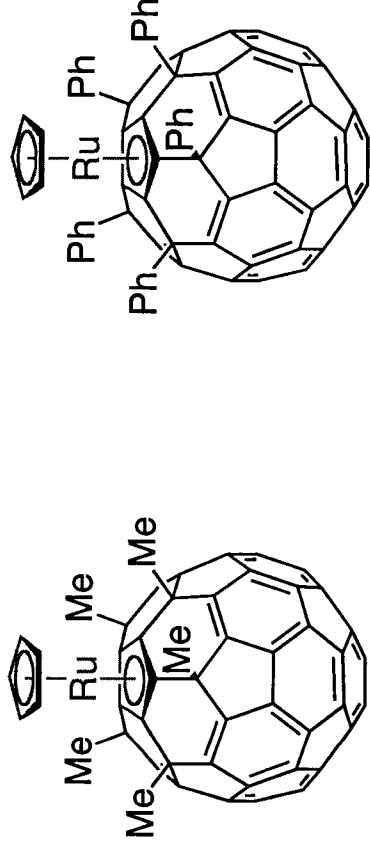
Crystal system	monoclinic
Space group	P21/c
a/Å	11.7120(4)
b/Å	16.7440(4)
c/Å	20.5640(8)
V/Å <sup>3</sup>	4017.5(2)
Z	4
R	0.0967
wR	0.2503

# Further Functionalization of Acetyl Group

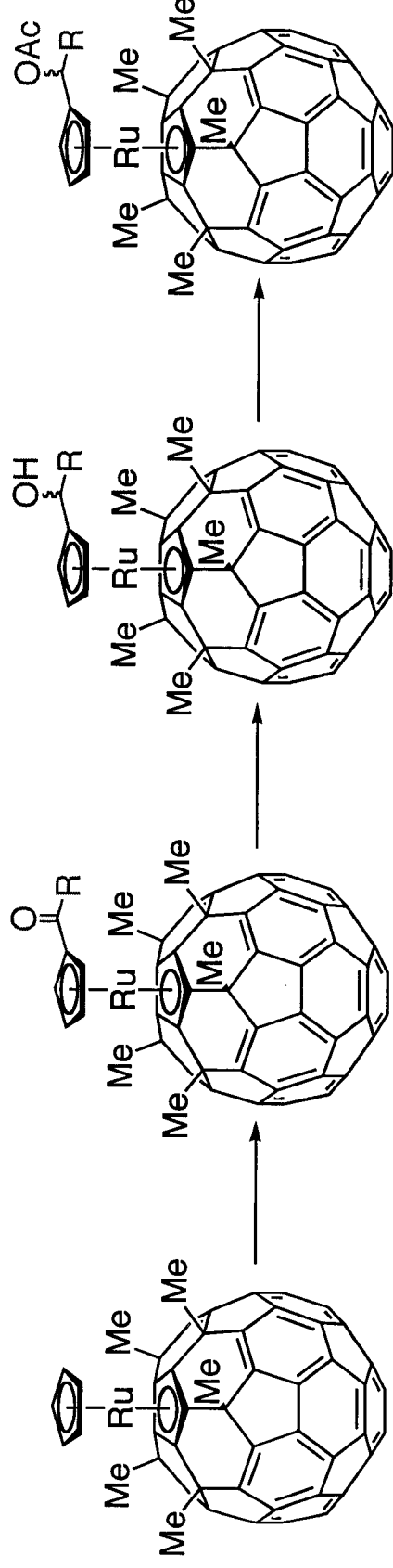


# Summary of Bucky Ruthenocene Chemistry

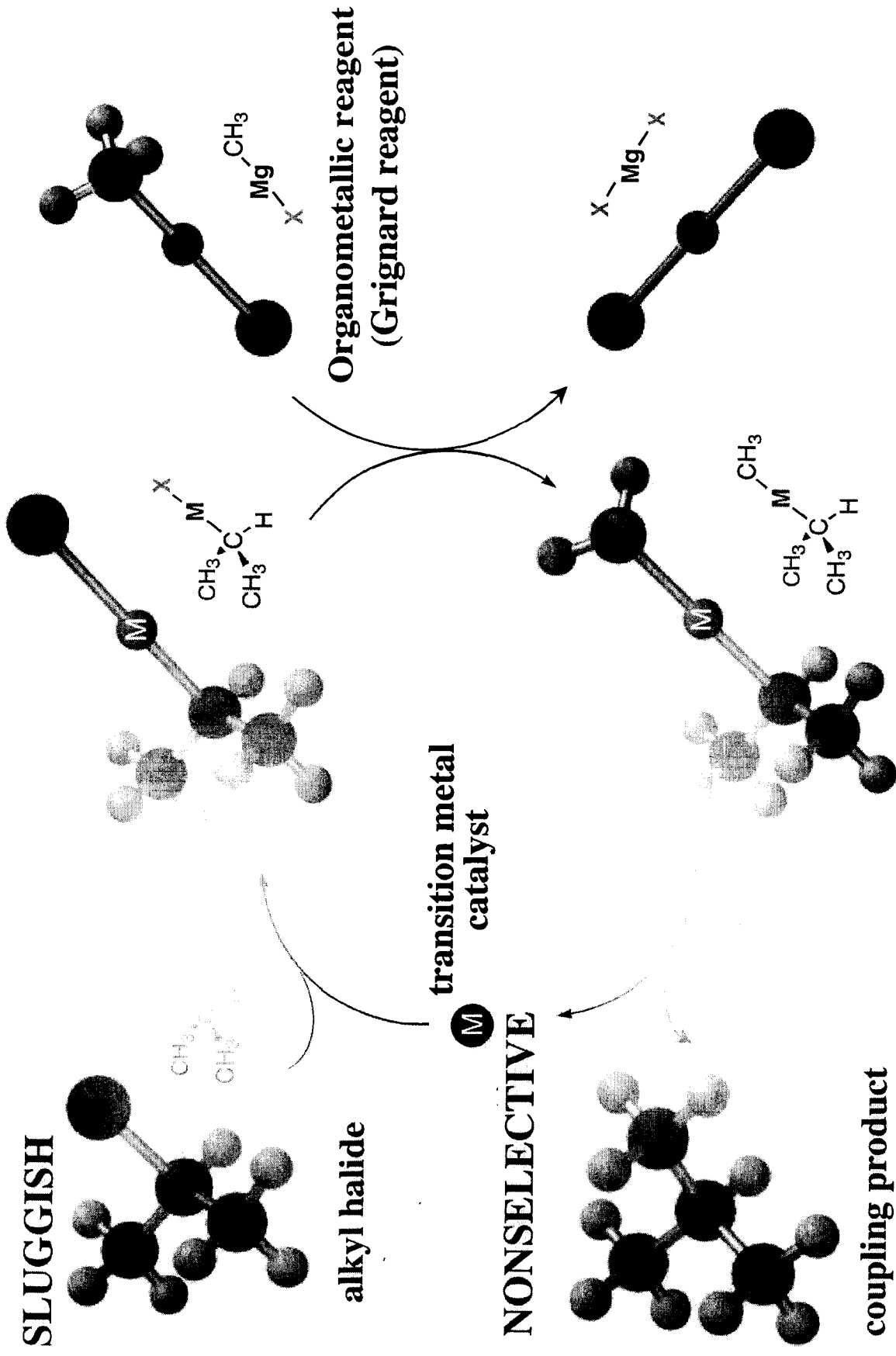
## • Synthesis of Bucky Ruthenocenes



## • Functionalization of Bucky Ruthenocenes



# C(sp<sup>3</sup>)-X Bond Activation and C-C Bond Formation Under Transition Metal Catalysis

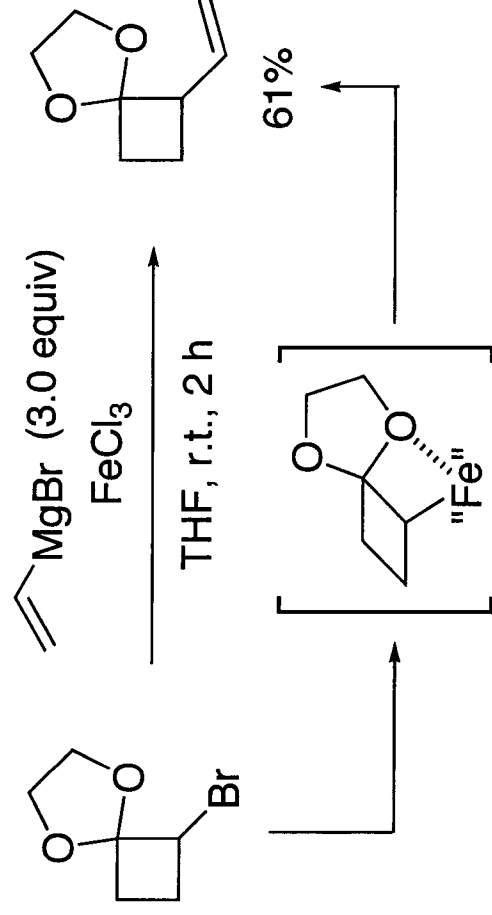


# A Historical Survey of Cross-Coupling Reactions

- 1971 J. K. Kochi, M. Tamura (*J. Am. Chem. Soc.* **1971**, *93*, 1487.)  
Fe(acac)<sub>3</sub>: RMgX + R'X
- 
- 1972 R. J. P. Corriu (*Chem. Commun.* **1972**, 144.)  
Ni(acac)<sub>2</sub>: RMgX + R'X
- 1972 M. Kumada, K. Tamao (*J. Am. Chem. Soc.* **1972**, *94*, 4374.)  
Ni(PR<sub>3</sub>)Cl<sub>2</sub>: RMgX + R'X
- 1975 K. Sonogashira, N. Hagihara (*Tetrahedron Lett.* **1975**, 4464.)  
Pd/Cu/R<sub>2</sub>NH: RC≡CH + R'X
- 1976 E. Negishi (*Chem. Commun.* **1976**, 596. and other 2 papers)  
Pd: R<sub>3</sub>Al, R<sub>2</sub>Zn, RZrCp<sub>2</sub>Cl
- 1977 M. Kosugi, T. Migita (*Chem. Lett.* **1977**, 1423.)  
Pd: R<sub>4</sub>Sn
- 1979 J. K. Stille (*J. Am. Chem. Soc.* **1979**, *101*, 4992.)  
Pd: R<sub>4</sub>Sn
- 1979 N. Miyaura, A. Suzuki (*Tetrahedron Lett.* **1979**, *20*, 3437.)  
Pd: R<sub>3</sub>B
- 1988 T. Hiyama, Y. Hatanaka (*J. Org. Chem.* **1988**, *53*, 918.)  
Pd/F<sup>-</sup>: RSiF<sub>n</sub>R'<sup>3-n</sup>

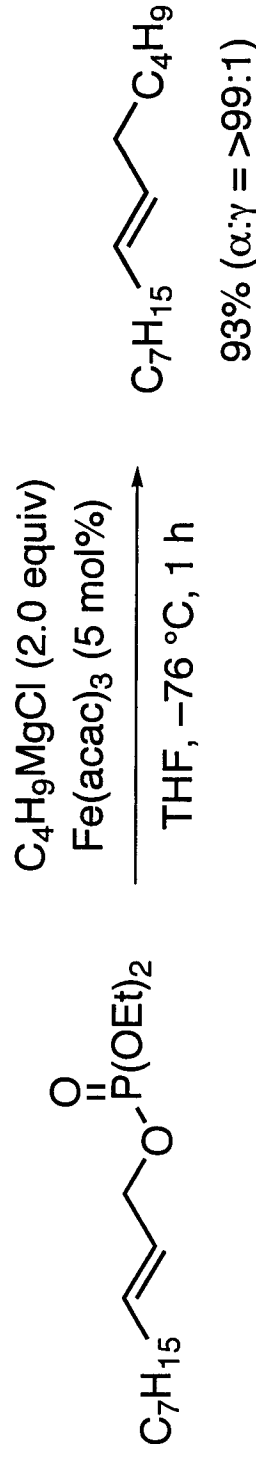
# Iron-Catalyzed Cross-Coupling of $sp^3$ -Electrophiles

## Cyclobutyl Bromides



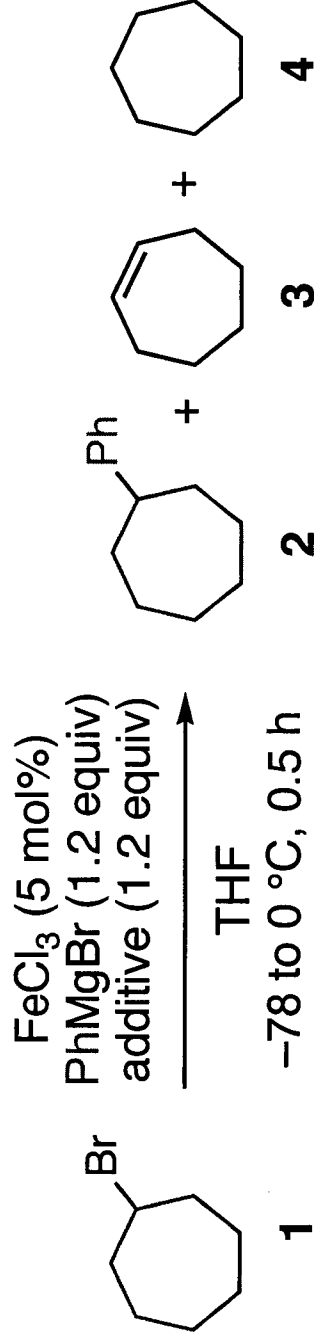
Brinker, H.; König, L. *Chem. Ber.* **1983**, *116*, 882.

## Allyl Phosphates



Yanagisawa, A.; Nomura, N.; Yamamoto, H. *Tetrahedron* **1994**, *50*, 6017.

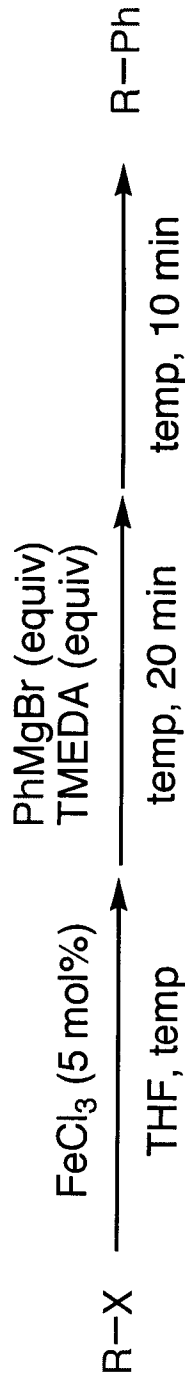
# Cross-Coupling of Alkyl Halides: Effect of Additives

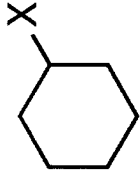
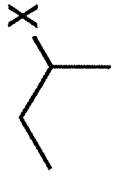



entry	additive	GC yield (%)			
		<b>2</b>	<b>3</b>	<b>4</b>	<b>1</b>
<b>1</b>	none	5	79	0	4
<b>2</b>	$\text{Et}_3\text{N}$	3	78	0	11
<b>3</b>		15	3	1	79
<b>4</b>	$\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$	71	19	3	1
<b>5</b>	$\text{Et}_2\text{NCH}_2\text{CH}_2\text{NEt}_2$	23	48	1	11

*A Serious Problem: Poor Reproducibility!!*

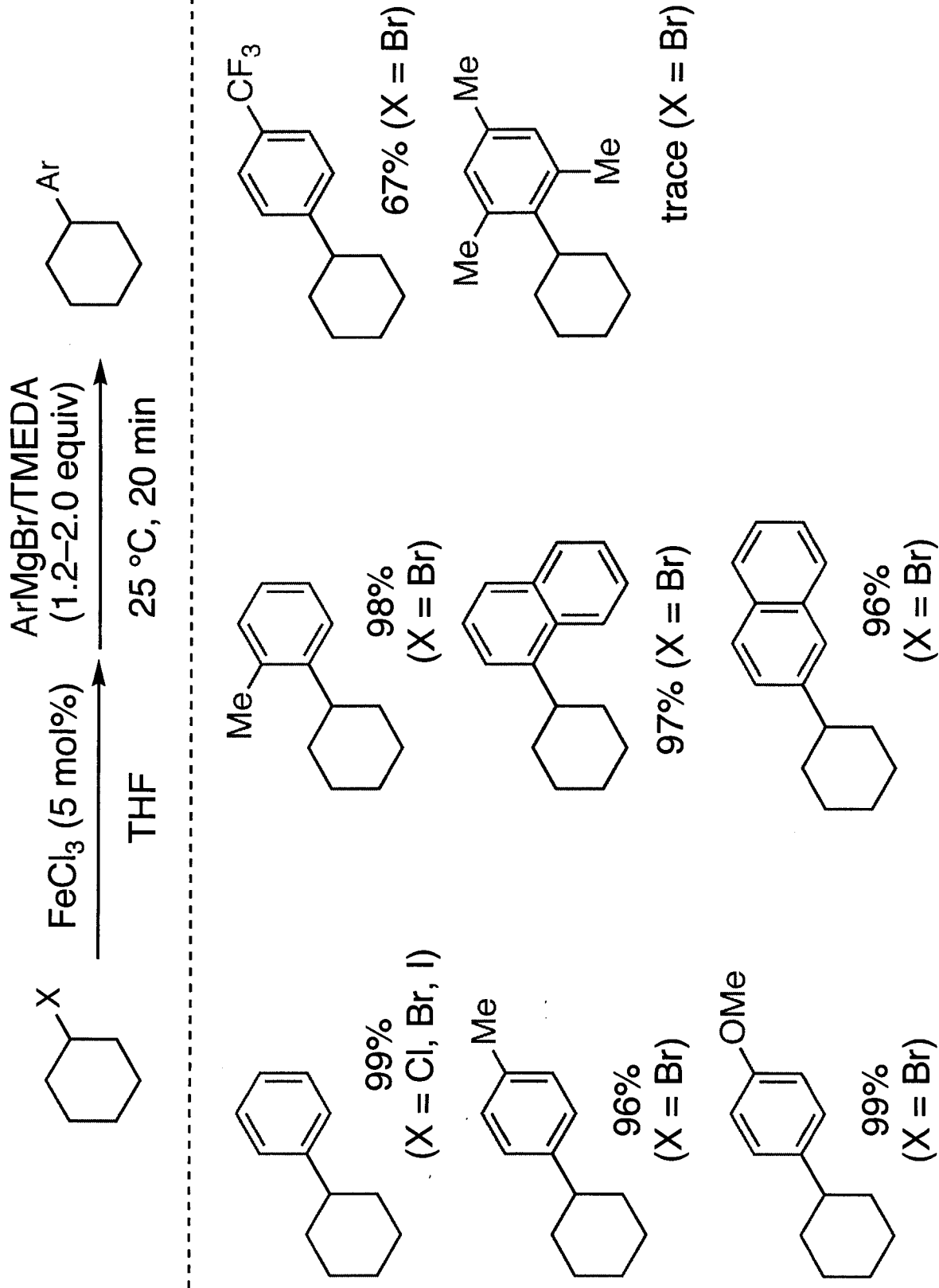
# Scope and Limitations on Alkyl Halides



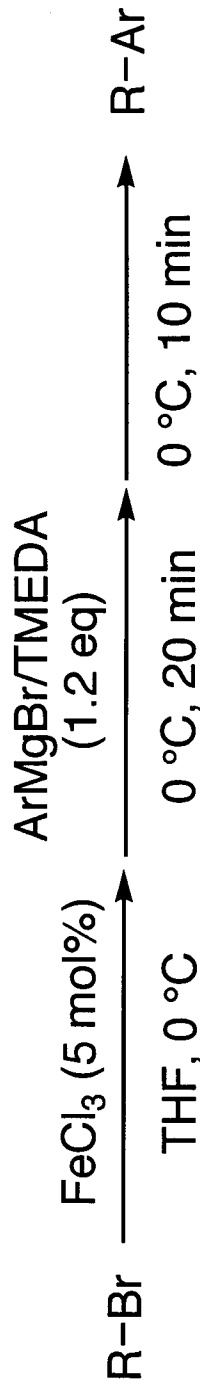
substrate	X	temp	equiv	GC yield (%)
	I	0 °C	1.2	99
	Br	25 °C	1.2	99
	Cl	25 °C	1.5	99
	F	reflux (13 h)	1.5	10
	OTs	25 °C (13 h)	1.5	38
-----				
	I	0 °C	1.2	95
	Br	25 °C	1.2	94
	Cl	40 °C	1.5	84
-----				
	I	0 °C	1.2	97
	Br	25 °C	1.2	91
	Cl	40 °C	1.5	45


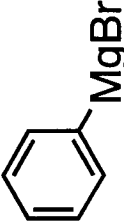
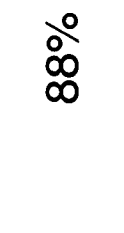
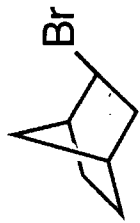
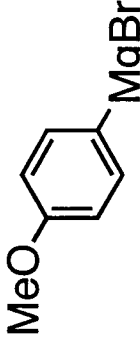
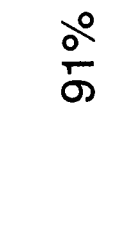

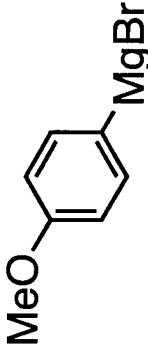


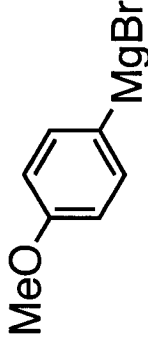



# Scope and Limitations on Grignard Reagents

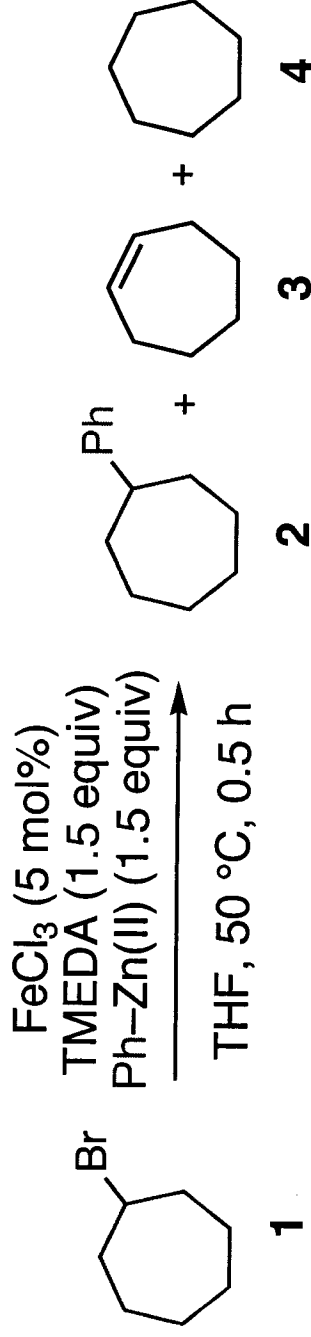


# Stereochemical Course of the Cross-Coupling



entry	substrate	ArMgBr	product	yield
1	 (99.5% ee)			88%
2				91%
3				96%
4				98%

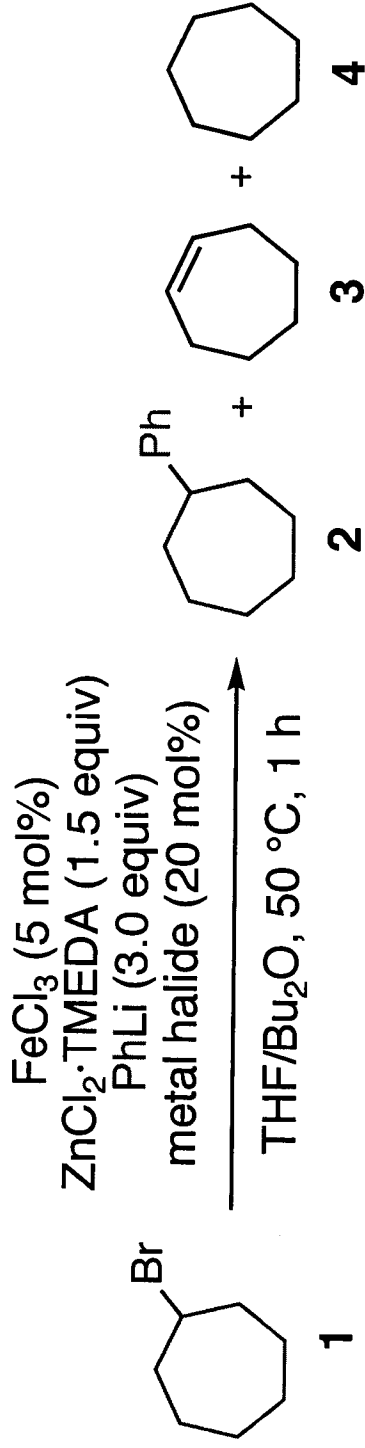
# Screening of Phenylzinc Reagents



entry	Ph-Zn(II)	GC yield (%)			
		2	3	4	1
1	ZnCl <sub>2</sub> + 2PhMgBr	96	3	trace	0
2	ZnCl <sub>2</sub> + PhMgBr	0	trace	trace	>98
3	PhZnBr (Mg free)	0	trace	trace	>98
4	ZnCl <sub>2</sub> + PhLi	0	trace	trace	>98
5	ZnCl <sub>2</sub> + 2PhLi	0	trace	trace	>98
6	ZnCl <sub>2</sub> + PhMgBr + Me <sub>3</sub> SiCH <sub>2</sub> MgCl	95	4	trace	0
7	ZnCl <sub>2</sub> + PhLi + Me <sub>3</sub> SiCH <sub>2</sub> MgCl	92	7	trace	0

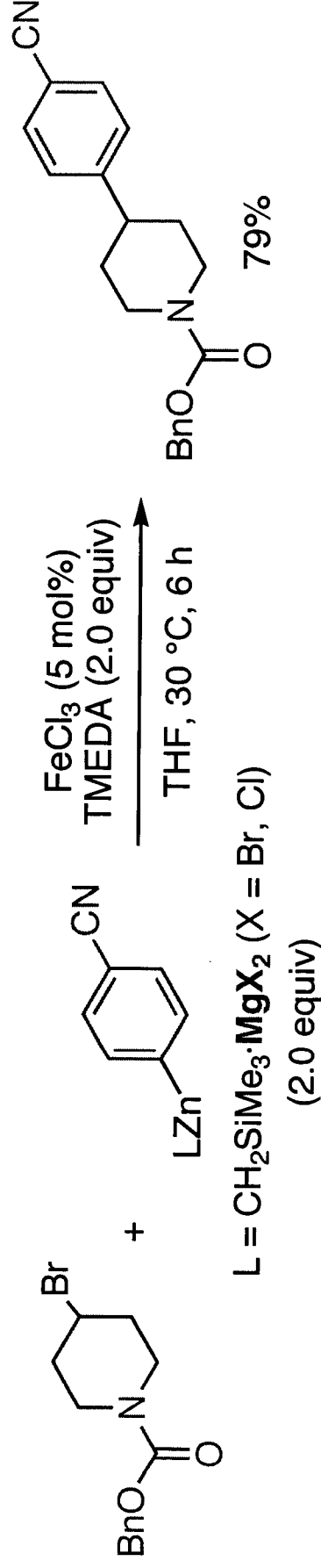
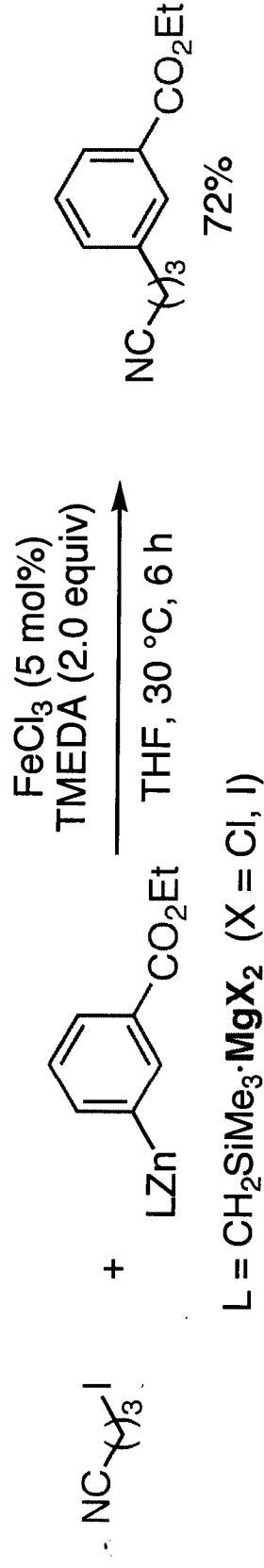
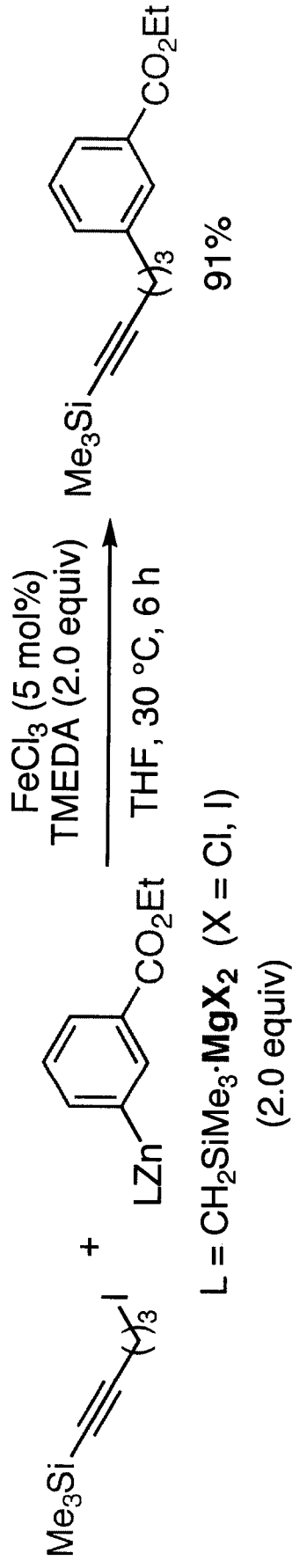
- *The Use of Diarylzinc and Magnesium salts*
- **NO Need of Slow Addition Technique**

# Double Metal Catalysis of Iron and Lewis Acid

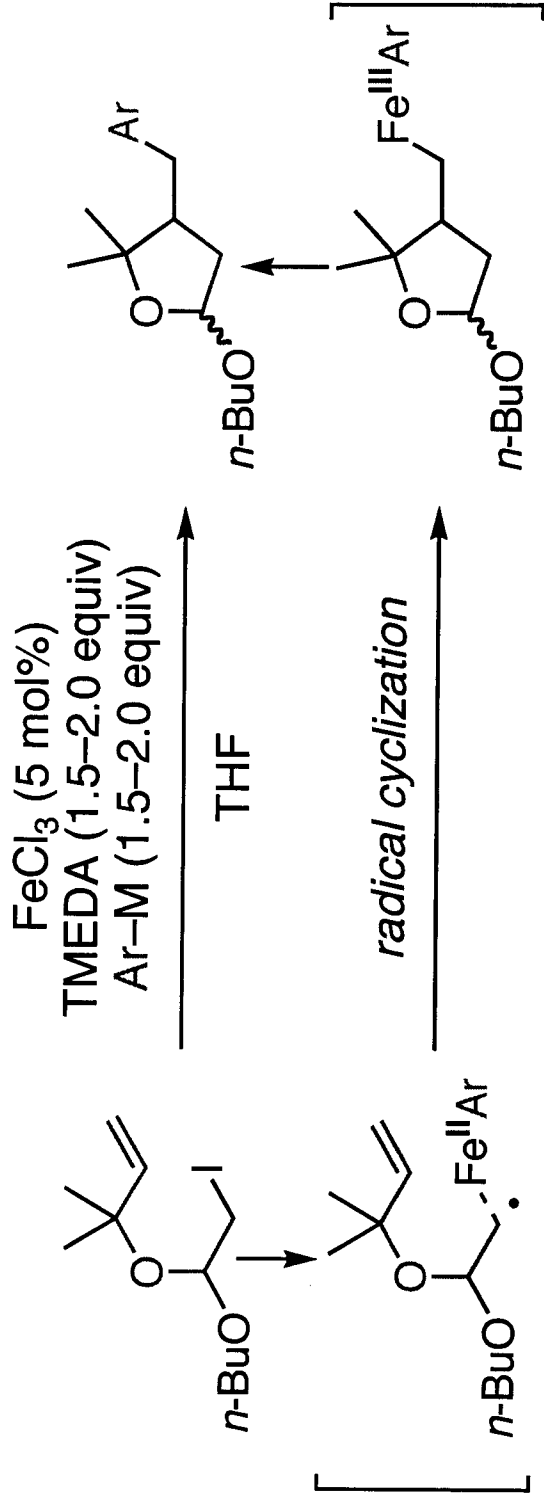


entry	metal halide	GC yield (%)			
		2	3	4	1
1	none	0	trace	trace	>98
2	<b>MgBr<sub>2</sub></b>	>98	trace	trace	0
3	<b>TiCl<sub>4</sub></b>	>98	1	trace	<1
4	ZrCl <sub>4</sub>	90	trace	trace	10
5	HfCl <sub>4</sub>	76	1	1	11
6	AlCl <sub>3</sub>	85	trace	trace	10
7	SnCl <sub>4</sub>	0	2	2	>95
8	CuCl <sub>2</sub>	0	2	3	>95
9	BF <sub>3</sub> ·OEt <sub>2</sub>	6	3	3	<90
10	Me <sub>3</sub> SiCl	3	6	2	<90

# Cross-Coupling between Functional Substrates

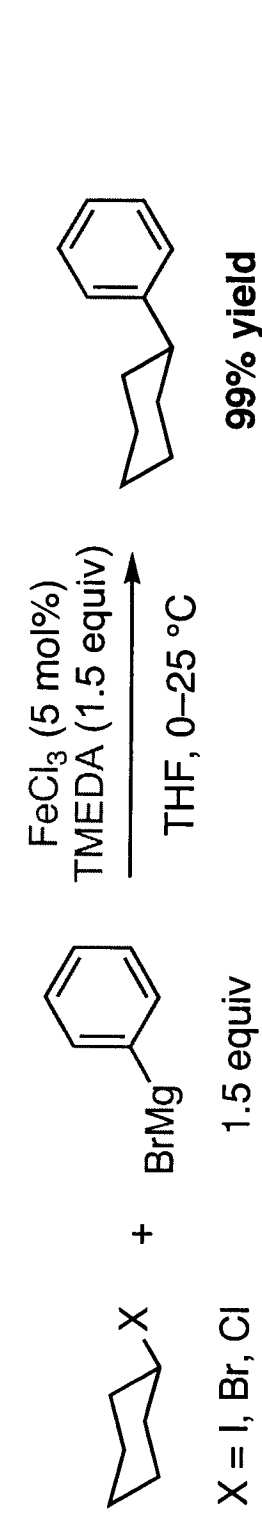


# Tandem Radical Cyclization/Cross-Coupling

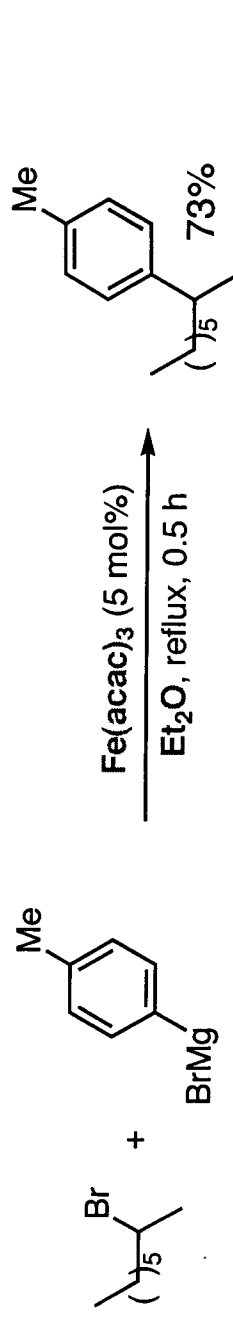


entry	Ar–M	conditions	yield (%)	<i>trans/cis</i>
1		0 °C, 20 min (slow addition)	68	63/37
2		50 °C, 0.5 h	76	63/37
3		50 °C, 0.5 h	86	64/36
4		30 °C, 24 h	73	63/37

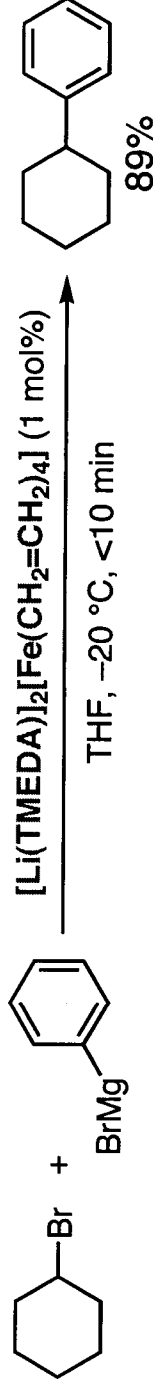
# Recent Development of Cross-Coupling of Alkyl Halides



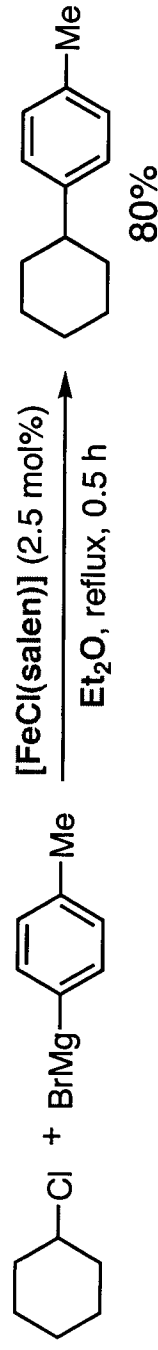
Nakamura, M.; Matsuo, K.; Ito, S.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 3686.



T. Hayashi et al. *Org. Lett.*, **2004**, *6*, 1297.



A. Fürstner et al. *Angew. Chem. Int. Ed.*, **2004**, *43*, 3952.



R.B. Bedford et al. *Chem. Commun.*, **2004**, 2822.