

Nickel Catalyzed Cross-Couplings involving Carbon – Oxygen Bonds

By Zhi Ren

2014/2/5

Reference

- Mainly from the Chemical Review, 2011, 111, 1346 - 1416. Up until late July 2010.

**CHEMICAL
REVIEWS**

REVIEW

pubs.acs.org/CR

Nickel-Catalyzed Cross-Couplings Involving Carbon–Oxygen Bonds

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- Some are directly from the reference

Contents of the review

- 1. Introduction
- 2. Nickel-Catalyzed Reaction of Aryl and Vinyl sulfonates and sulfates
- 3. Nickel-Catalyzed Cross-Coupling of Aryl Sulfamates
- 4. Nickel-Catalyzed Cross-Coupling of Aryl Ethers
- 5. Nickel-Catalyzed Cross-Coupling of Aryl and Vinyl phosphates
- 6. Nickel-Catalyzed Cross-Coupling of Aryl and Vinyl Esters
- 7. Nickel-Catalyzed Cross-Coupling of Aryl and Vinyl Carbamates and Carbonates
- 8. Nickel-Catalyzed Cross-Coupling of Phenols
- 9. Nickel-Catalyzed Activation of Other Inert Bonds

Outline of this presentation

- 1. Introduction
- 2. Background for Homocoupling
- 3. Nickel-Catalyzed Cross-Coupling focus on C-O bond
- 4. Nickel-Catalyzed Activation of Other Inert Bonds focus on C-F Bond
- 5. Conclusions

1. Introduction

- 1. Early TM vs. Late TM

Ni \$1.2/mol, Pd \$1,500/mol, Pt \$10,000/mol

Jul 23/2010. Pd \$2380/mol Feb 4/2014!

- 2. Coupling partner

Most of Pd/Pt using halides(I, Br)

Ni can use phenol- and enol and halides (even: Cl, F)

- 3. Economics and versatility

Ni catalyzed reaction is more economical and more versatile.

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2. Background for Homocoupling

- 2.1 Ni(0) catalyst or reagent
- 2.2 Reaction system and mechanism studies
- 2.3 Summary

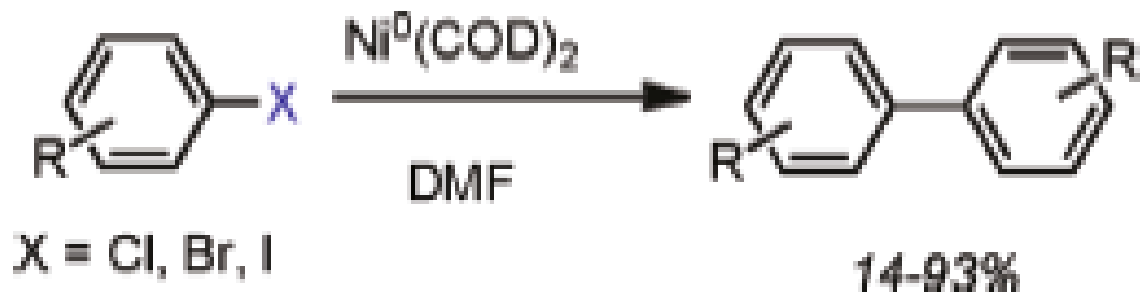
2.1 Ni(0) catalyst or reagent

- In 1963, Wilke realized cyclooligomerization of butadiene which was the first time using Ni(0) complexes as reagent for homocoupling reaction.

Angew. Chem. **1963**, 75, 10.

2.1 Ni(0) catalyst or reagent

- In 1971 Semmelhack's group found that $\text{Ni}(\text{COD})_2$ could mediate homocoupling of aryl halides in DMF.



2.1 Ni(0) catalyst or reagent

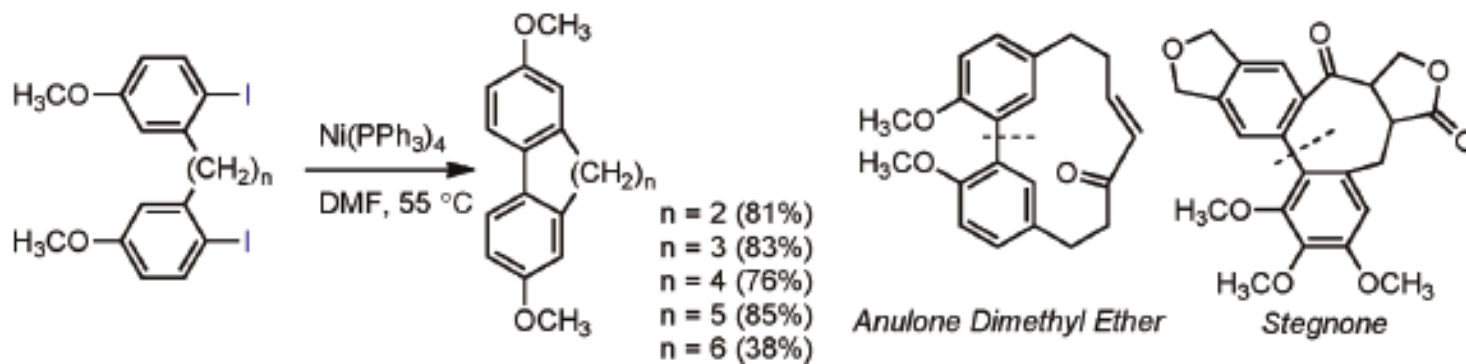
- Compare to Ullmann coupling (state-of-the-art), this approach is very mild, robust, selective to the synthesis of biaryls and heterobiaryls.
- The proposed mechanism was:
 - 1). Ar-X oxidative addition to Ni(0)
 - 2). Ar-X oxidative addition to Ni(II)ArX
 - 3). Reductive elimination to generate biaryl

2.1 Ni(0) catalyst or reagent

- Three limitations:
 - 1). Poor reactivity with ortho-substituted aryl halides
 - 2). Rapid decomposition of the Ni(0) reagent at higher temperature or in different solvent
 - 3). Reduction of the C-X bond to C-H bond when protic substrates were used

2.1 Ni(0) catalyst or reagent

- In 1975, Kende using $\text{Ni}(\text{PPh}_3)_4$ as reagent to form cyclic biphenyls.
- Application to natural product Anulone, but cannot synthesize Stegnone.

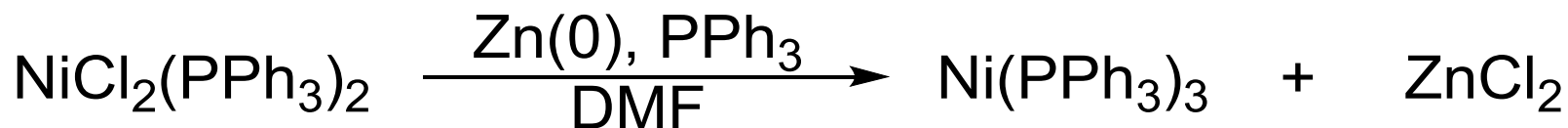


JACS 1975, 97, 3874

JACS 1981, 103, 6460

2.1 Ni(0) catalyst or reagent

- In 1972, Tolman, first reported the $\text{Ni}(\text{PPh}_3)_4$ can dissociate to form $\text{Ni}(\text{PPh}_3)_3$ due to steric bulk of PPh_3 .
- In 1975, Kende realized the $\text{Ni}(\text{PPh}_3)_3$ is likely to be the active catalyst and prepared this reagent in situ to successfully mediate homocoupling reaction.



JACS **1972**, 94, 2669
TL **1975**, 3375

2.1 Ni(0) catalyst or reagent

- In 1977, “Rieke nickel”, which was generated by reduction of NiI_2 with K or Li metal in the presence of PEt_3 , was reported.
- This new complex can also mediate the Ni homocoupling reaction.
- But the presence of a nitro group completely inhibited the reaction.

2.1 Ni(0) catalyst or reagent

- In 1983, Caubere using NiCRA (CRA = complex reducing reagents), a 4:2:1 mixture of NaH, t-AmONa, and Ni(OAc)₂ to mediate the homocoupling reaction.
- Aryl Fluorides can be reduced under this condition.
- The Ni(0) was generated by hydridic reduction to give hydrogen gas.

2.1 Ni(0) catalyst or reagent

- Other preparations of Ni(PPh₃)₃ were done by Jennings(1976), Ban(1980).

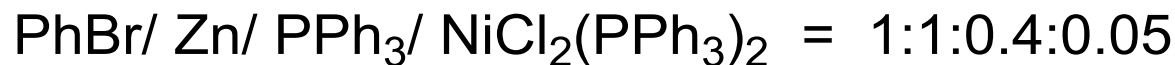


JOC **1976**, 41, 719

TL **1980**, 21, 631

2.2 Reaction system and mechanism studies

- Finally in 1977, Kumada and co-worker demonstrated that the homocoupling reaction could be made catalytic in Ni when 1 eq. Zn(0) were used.
- The optimized ratio of reaction was:



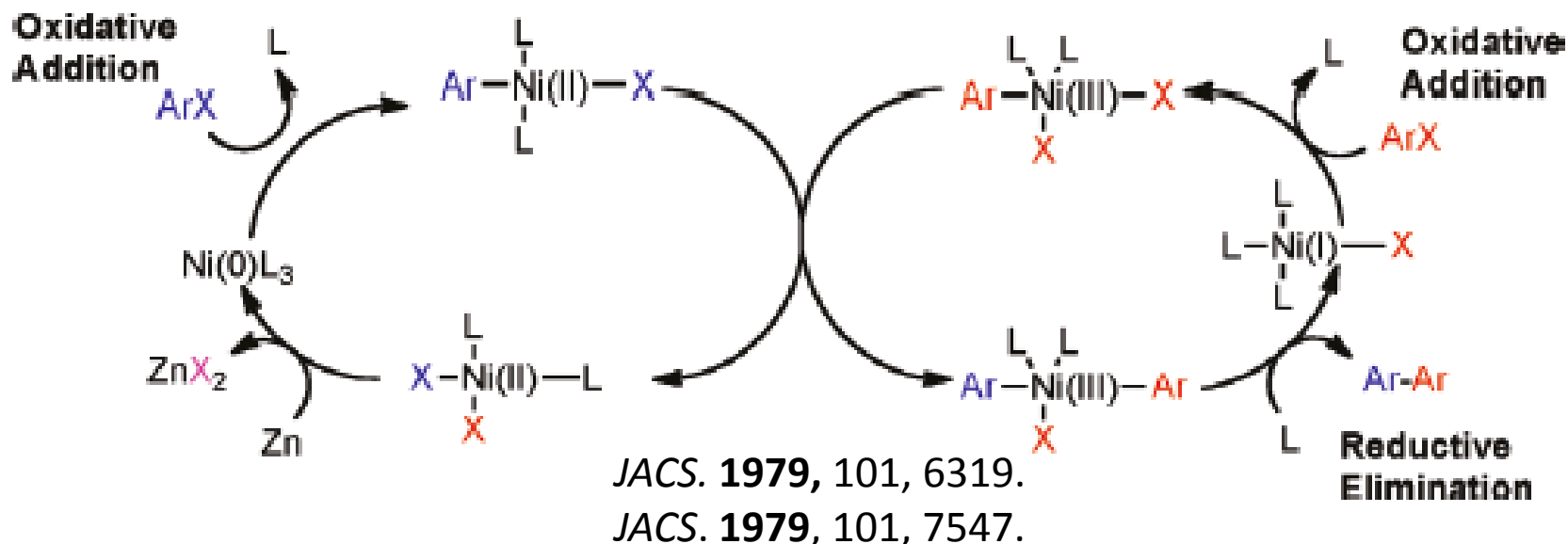
The yield is 89%

- Add KI accelerates the rate of the reaction

TL 1977, 4089

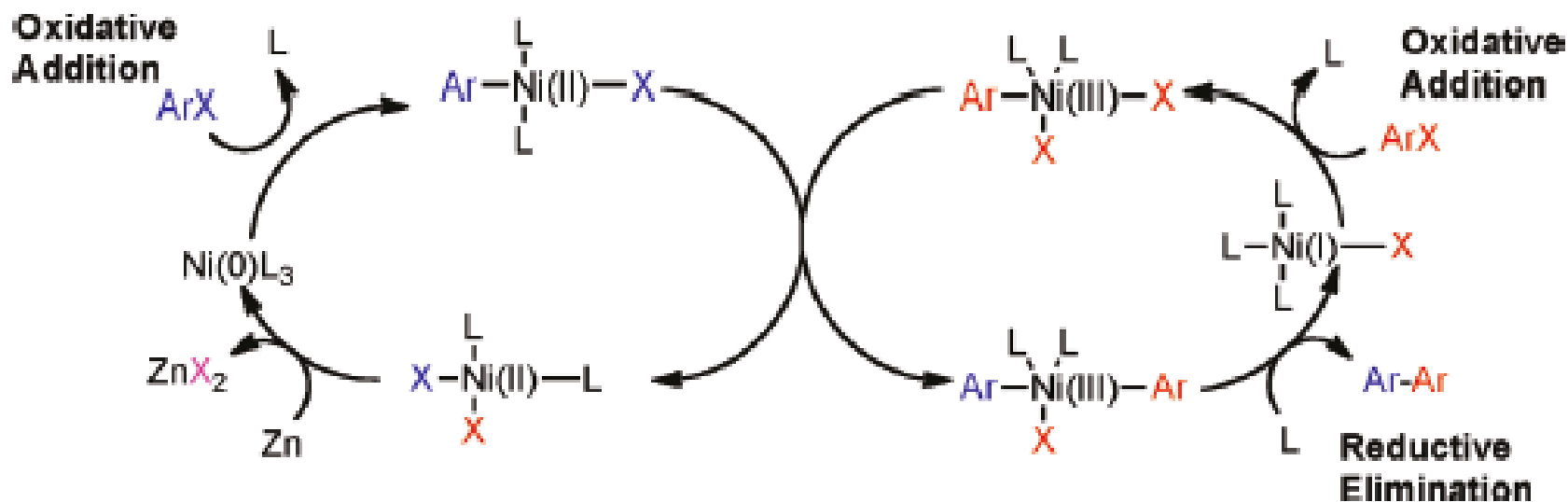
2.2 Reaction system and mechanism studies

- In 1971 Semmelhack's work, the proposed mechanism involving Ni(0), Ni(II) and Ni(IV).
- In 1979, Tsou and Kochi suggested a Ni(I)/Ni(III) radical-chain pathway.



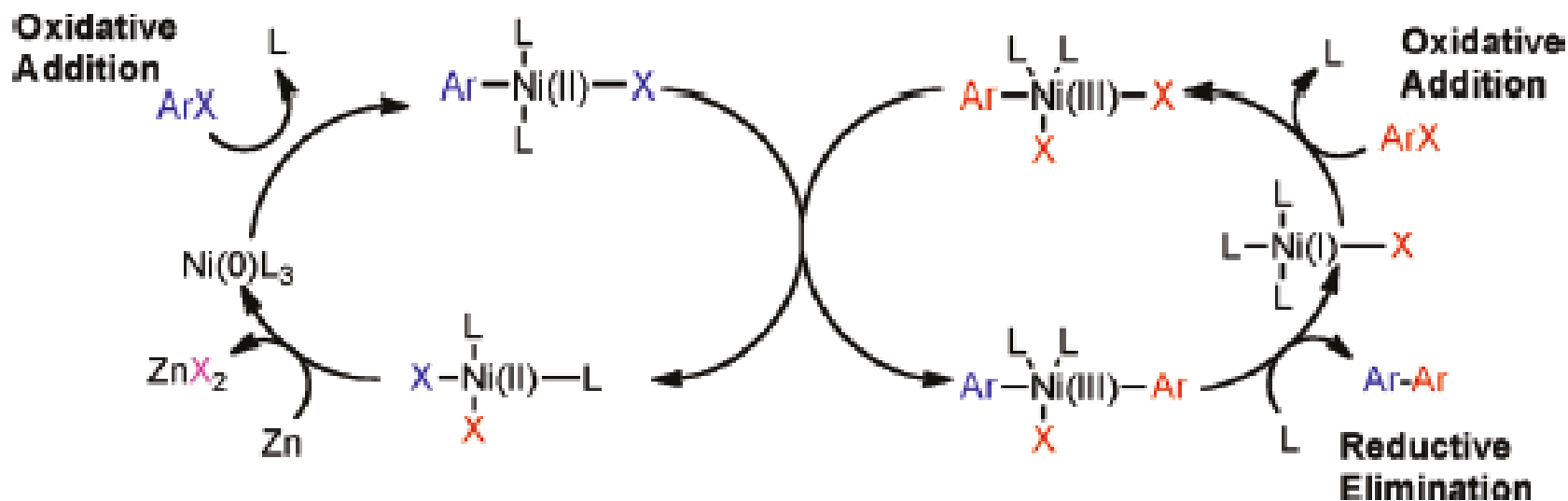
2.2 Reaction system and mechanism studies

- However, the treatment of $\text{Ni}(\text{PPh}_3)_3$ with Ar-I produces barely any biaryl product.



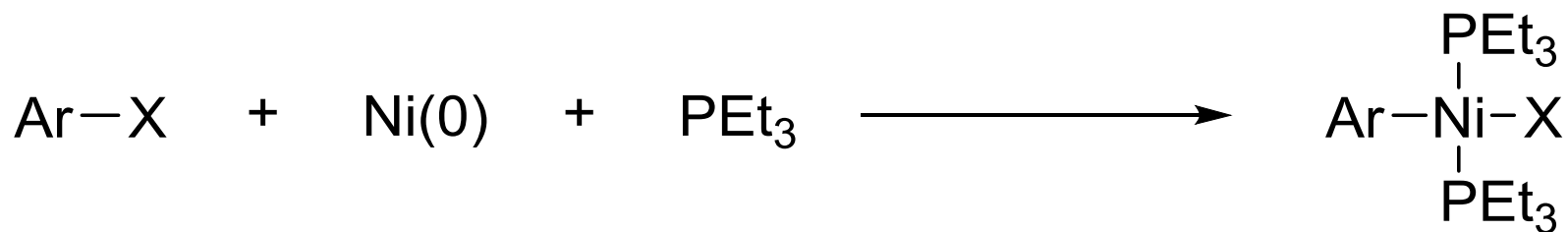
2.2 Reaction system and mechanism studies

- Also later work done by T. Yamamoto suggested that oxidative addition is not the rate determining step.



2.2 Reaction system and mechanism studies

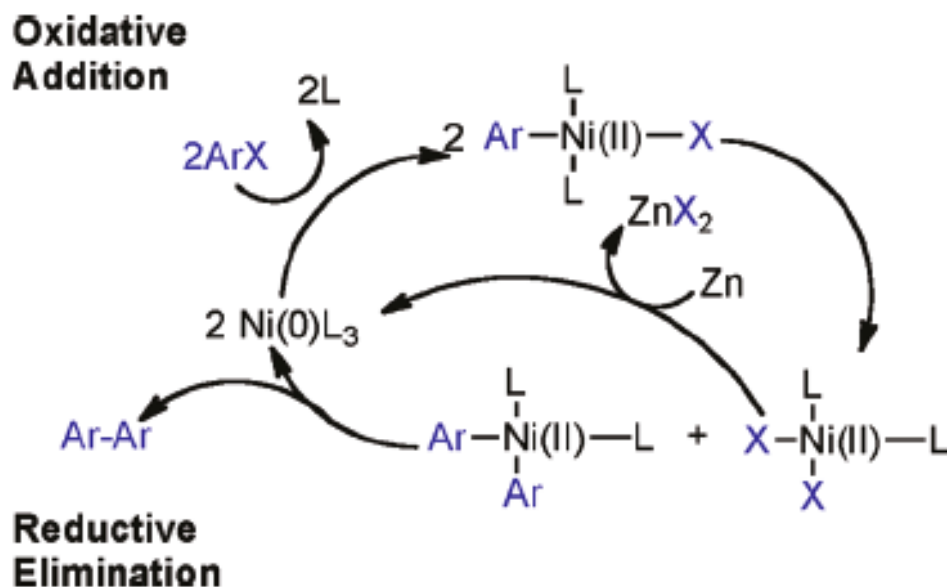
- In 1983, Rieke concluded that the oxidative addition must represent the first step of the reaction, based on the isolated trans-haloaryl Ni complex in 1977.



JOC. **1983**, 48,840.

2.2 Reaction system and mechanism studies

- An alternative mechanism was suggested in this paper, wherein the metathesis/disproportionation was involved.



JOC. **1983**, 48,840.

2.2 Reaction system and mechanism studies

- In 1981 patent and in 1986 paper, Colon's group reported other methods to generate the Ni(0) complex in situ.

Table II. Coupling of Chlorobenzene with Nickel Chloride and Various Metals^a

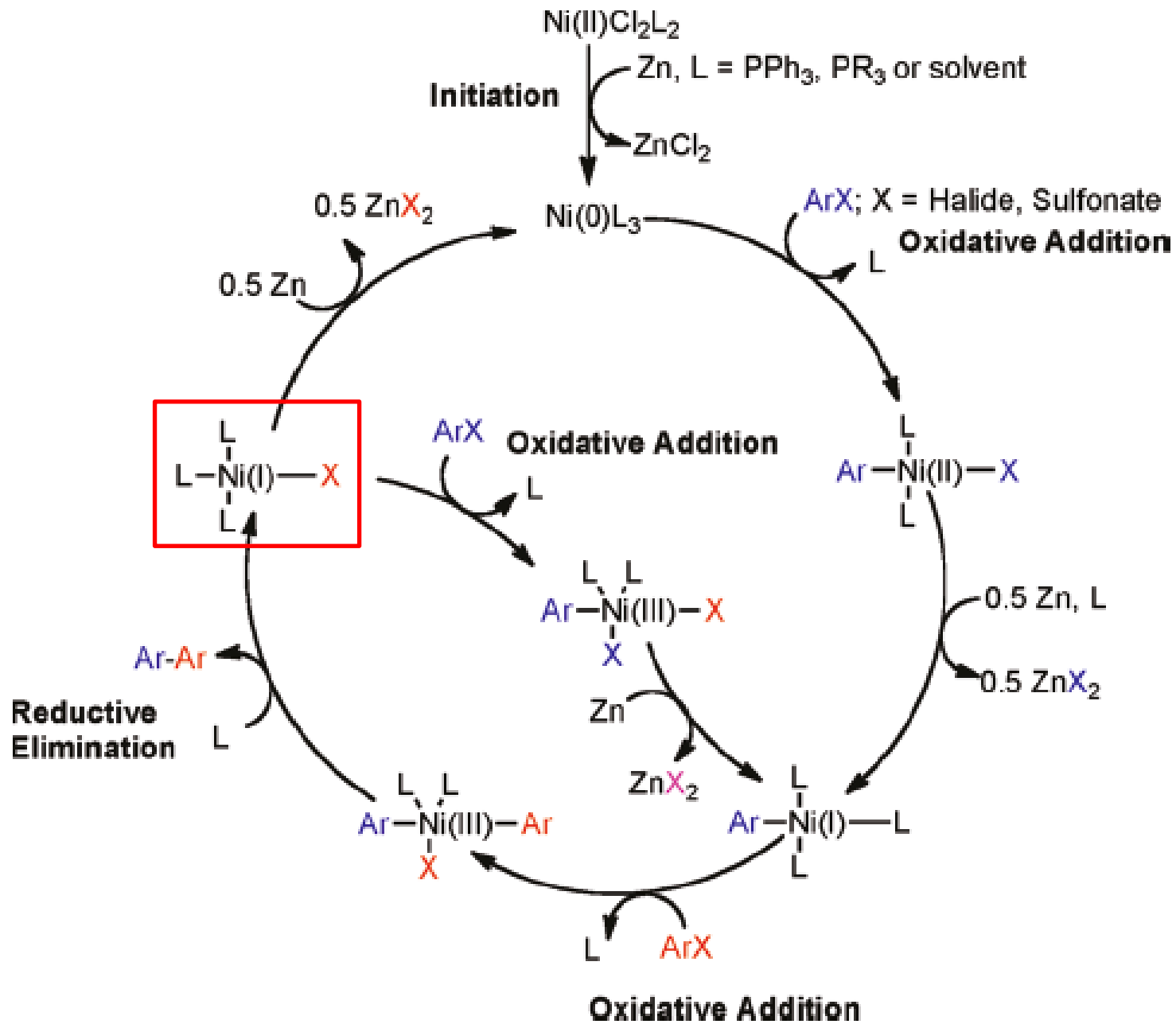
metal	time (h)	yield (%)	
		benzene	biphenyl
Fe	24	0	0
Zn	2	1	99
Mn	24	0	>99
Al	5	76	22
Mg	2	4	96
Na	24	6	5
Ca	6	77	22 (65 ^b)

^a At 65–80 °C in DMAc (see Experimental Section) yields by GC analysis. ^b Calcium oxide layer removed and 2,2'-bipyridine added (see Experimental Section).

U.S. Patent
4,263,466, 1981.
JOC. **1986**, 51,2627.

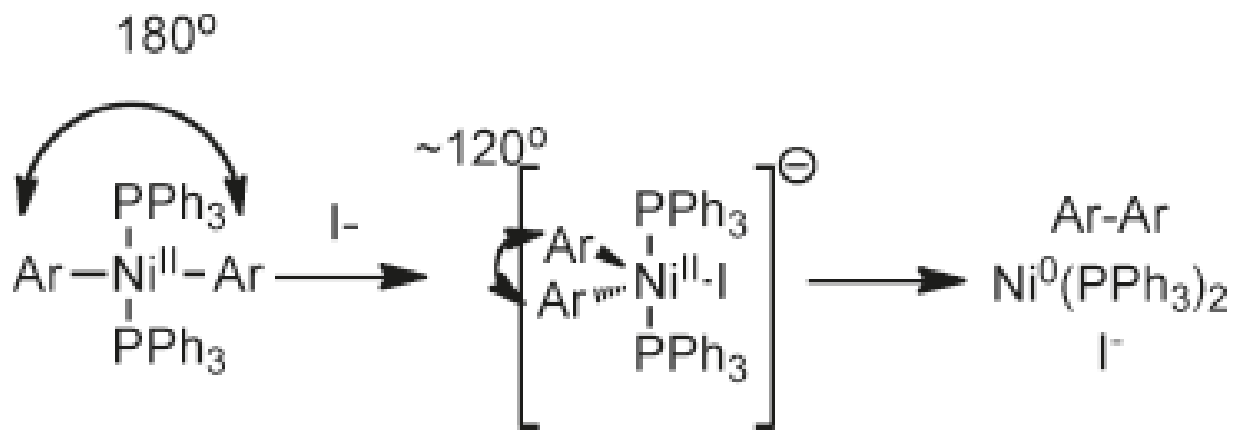
2.2 Reaction system and mechanism studies

- Based on the observation of the excess Zn greatly improved the yield, Colon and co-workers modified the mechanism that Bontempelli and co-workers proposed in 1981.
- The mechanism is on the next slide.



2.2 Reaction system and mechanism studies

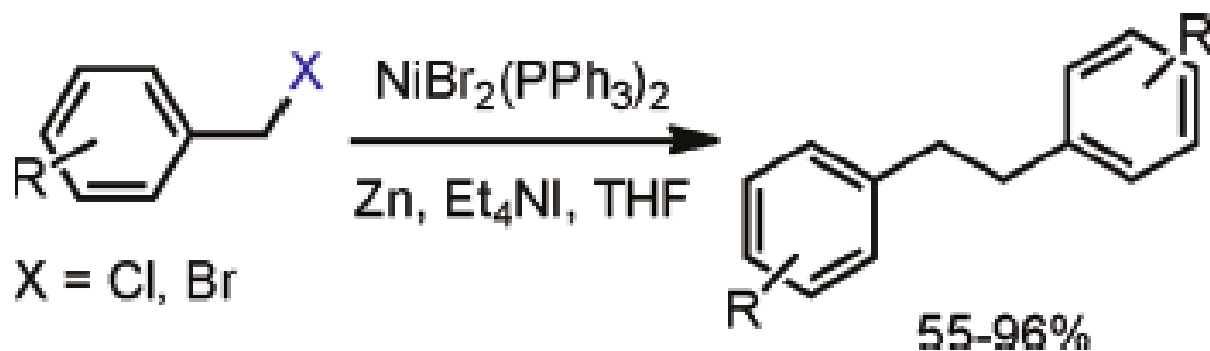
- The explanation of the acceleration by halide ion was caused by the geometry change from square planar to trigonal-bipyramidal structure that would enhance reductive elimination.



JOC. **1986**, 51,2627.

2.2 Reaction system and mechanism studies

- The final step forward in Ni(0) based homocoupling aryl halides was the use of iodide source, e.g. Et₄Ni. In 1985, Iyoda reported the homocoupling of benzyl chlorides and benzyl bromides.



2.3 Summary

- To prevent all of you fall into sleep. I decide to summarize this part here.
- I will not talk more about the homocoupling reactions after the summary. If you are interested, please read the section of this review.

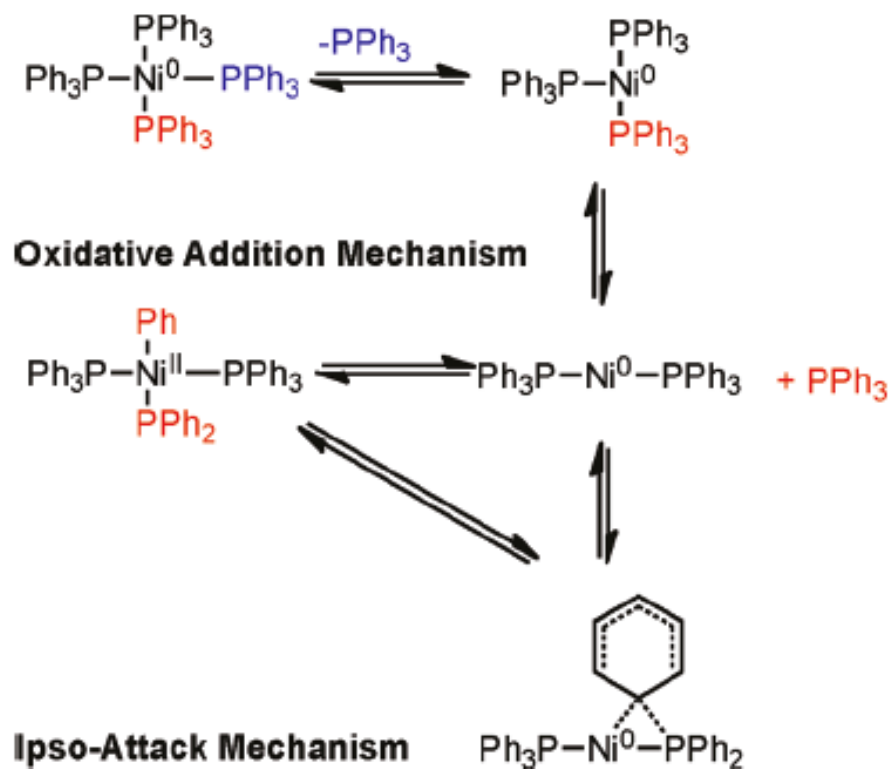
2.3 Summary

- 1. There are many systems that have been developed, the best one for homocoupling is $\text{NiBr}_2(\text{PPh}_3)_2$ / Zn / Et_4NI / THF.
- 2. The initial step of the reaction cycle is oxidative addition of Ar-X to Ni(0).
- 3. The Zn is crucial for the catalytic system, and Zn-free conditions may go through a different mechanism.
- 4. The rds is not clear, and depends on the substrates.

2.3 Summary

General problems for these reactions:

1. Aryl exchange with PAr_3 ligands.



2.3 Summary

General problems for these reactions:

1. Aryl exchange with PAr_3 ligands.
2. Cannot tolerate the nitro group.
3. For protic substrate, the reduction of Aryl halides occurs.

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- 5. Conclusions

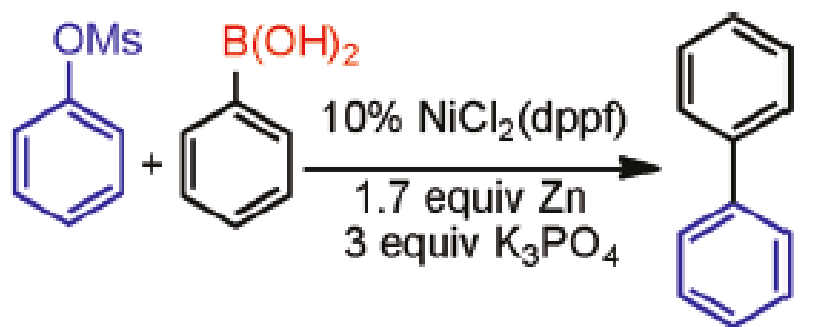
3. Nickel-Catalyzed Cross-Coupling

focus on C-O bond

- 3.1 Cross-Coupling of aryl and vinyl mesylates and Tosylates
- 3.2 Cross-Coupling of aryl sulfamates
- 3.3 Cross-Coupling of aryl ethers
- 3.4 Cross-Coupling of aryl and vinyl phosphates
- 3.5 Cross-Coupling of aryl and vinyl esters
- 3.6 Cross-Coupling of aryl and vinyl carbamates and carbonates
- 3.7 Cross-Coupling of phenols

3.1 Cross-Coupling of aryl and vinyl mesylates and Tosylates

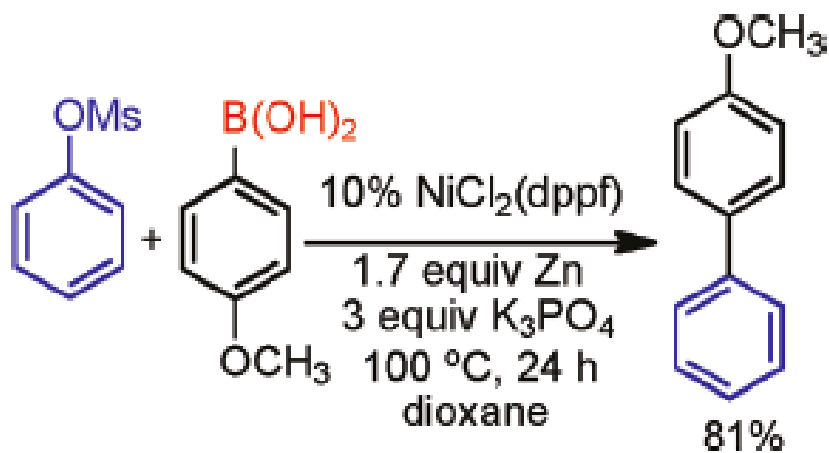
- In 1995, Percec's group reported the first Ni-catalyzed Suzuki-Miyaura cross-coupling of aryl boronic acids with aryl mesylates.



95 °C, 24 h	dioxane		67%
67 °C, 24 h	THF		54%
67 °C, 24 h	THF	no Zn	0%

3.1 Cross-Coupling of aryl and vinyl mesylates and Tosylates

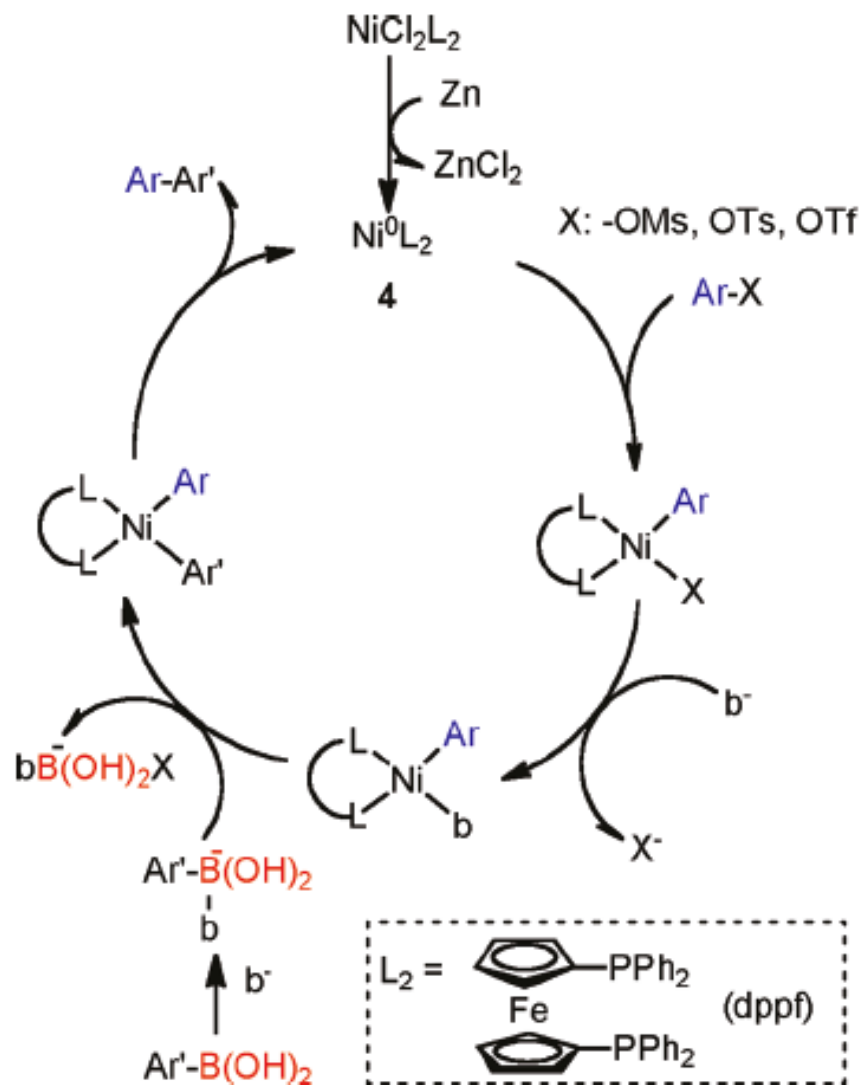
- 1. the use of dioxane as solvent at higher temperature provide higher yield
- 2. Other catalysts are not as effective as $\text{NiCl}_2(\text{dppf})$



JOC. 1995, 60, 1060

3.1 Cross-Coupling of aryl and vinyl mesylates and Tosylates

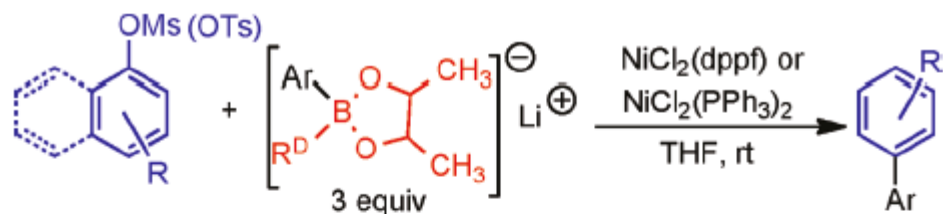
- Possible mechanism



JACS. 1985, 107, 972

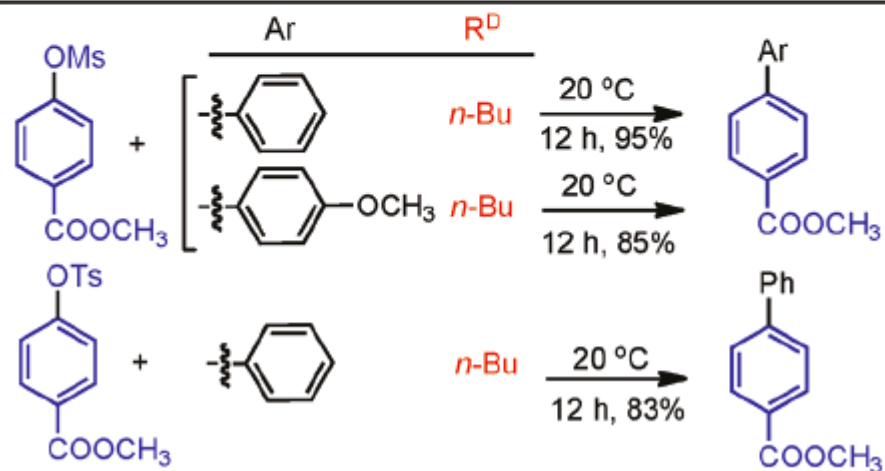
3.1 Cross-Coupling of aryl and vinyl mesylates and Tosylates

- In 1996, Kobayashi's group reported using lithium aryl boronates as coupling partner.



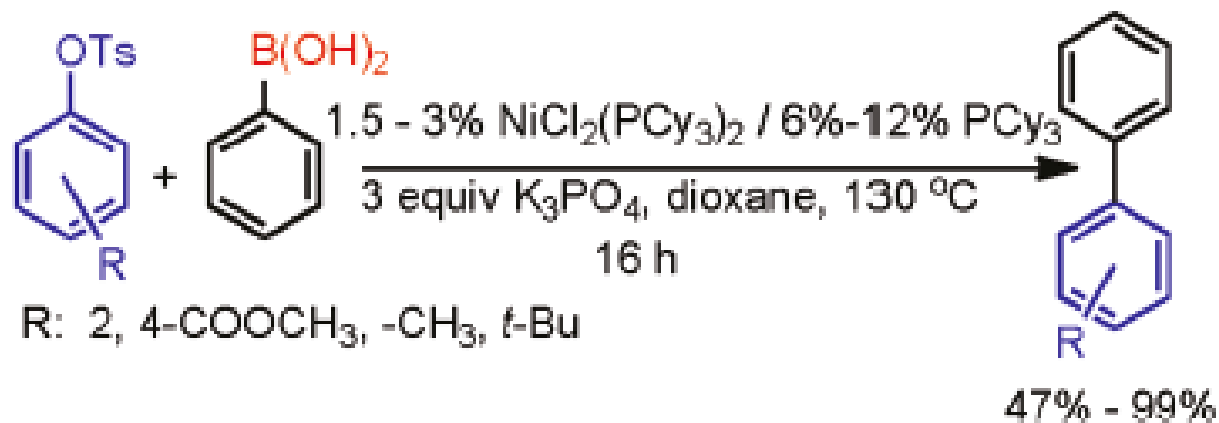
R: -CN, -F, -Ac, -OCH₃ Ar: -C₆H₅, -C₆H₄(p-OMe), -C₆H₄(p-Me)

R^D: -Me, -*n*-Bu; -*t*-Bu, -CH₂-TMS



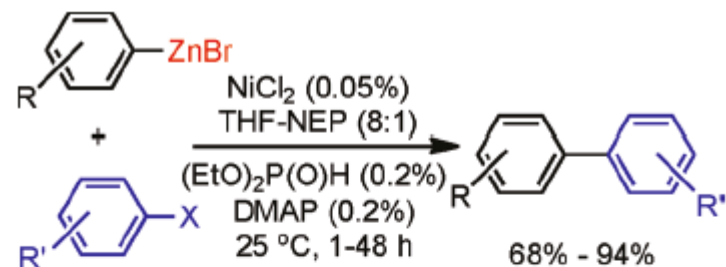
3.1 Cross-Coupling of aryl and vinyl mesylates and Tosylates

- In 2001, Zim and Monteiro expanded the use of $\text{NiCl}_2(\text{PCy}_3)_2 / 2 \text{PCy}_3$ as an efficient reducing-agent free system to aryl tosylates.

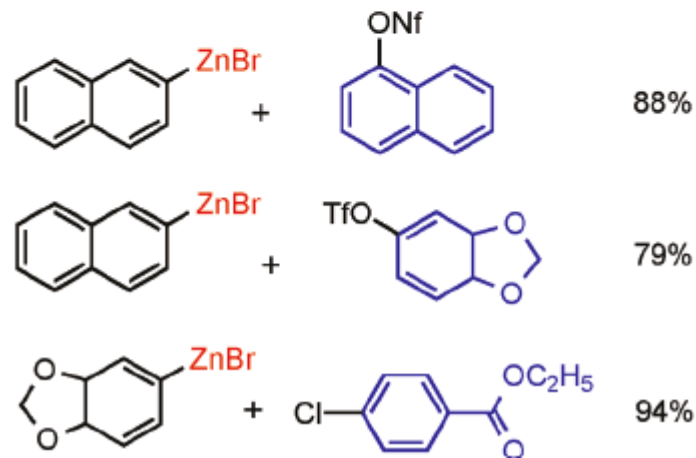


3.1 Cross-Coupling of aryl and vinyl mesylates and Tosylates

- In 2006, Knochel's group reported the Ni-catalyzed Negishi reaction with aryl or alkenyl triflates and Nonaflates.



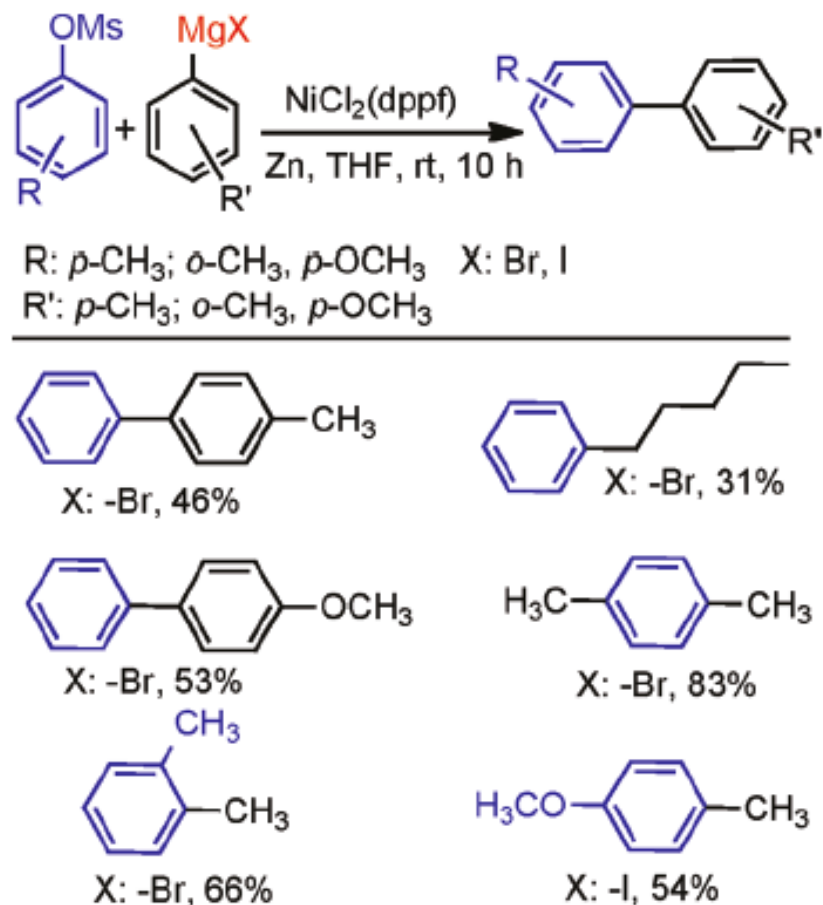
X: -Br, Cl, OTf, ONf R: p-OCH₃, m-OCH₃, -F, -CF₃
R': o-COOCH₃, m-F, p-CO-R, p-COOC₂H₅



Tetrahedron **2006**, 62, 7521

3.1 Cross-Coupling of aryl and vinyl mesylates and Tosylates

- In 1995, Percec's group reported a Ni catalyzed Kumada reaction with aryl mesylates.



JOC. 1995, 60, 6895

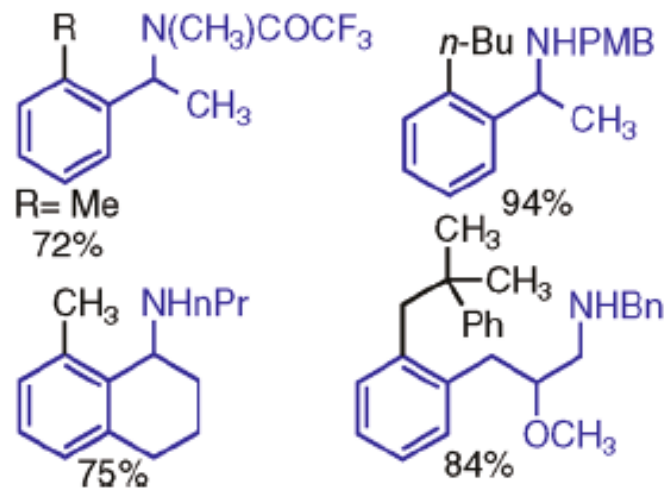
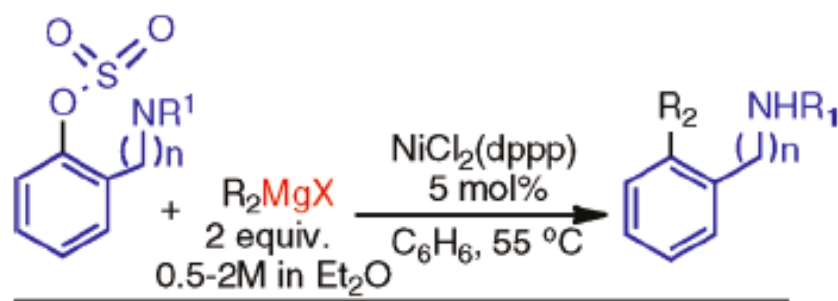
3. Nickel-Catalyzed Cross-Coupling

focus on C-O bond

- 3.1 Cross-Coupling of aryl and vinyl mesylates and Tosylates
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- 3.4 Cross-Coupling of aryl and vinyl phosphates
- 3.5 Cross-Coupling of aryl and vinyl esters
- 3.6 Cross-Coupling of aryl and vinyl carbamates and carbonates
- 3.7 Cross-Coupling of phenols

3.2 Cross-Coupling of aryl sulfamates

- In 2005, Du Bois' group reported a benzene-fused cyclic sulfamates as coupling partner for a Kumada type reaction.



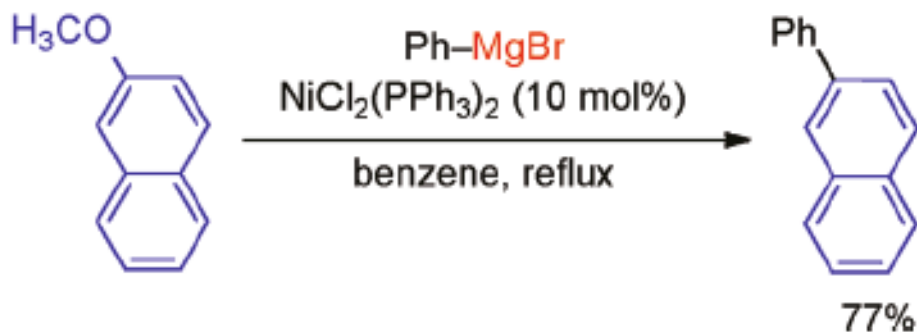
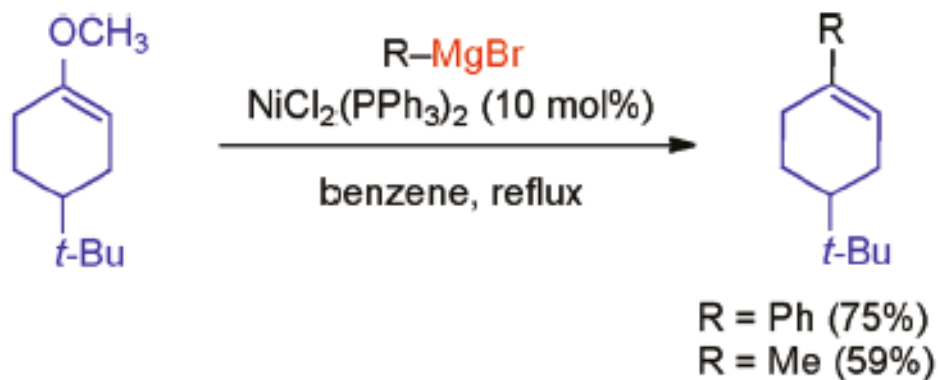
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3.3 Cross-Coupling of aryl ethers

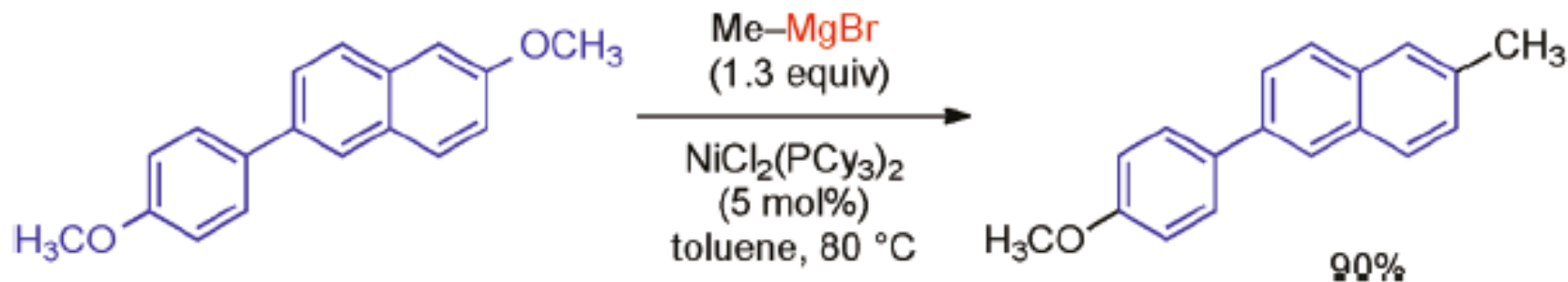
- In 1979, Wenkert's group reported the first example of ether Kumada type coupling reaction.



JACS. 1979, 101, 2246

3.3 Cross-Coupling of aryl ethers

- In 2008, Shi's group enabled the formation of sp^3 - sp^2 C-C bonds via methyl magnesium bromide and aryl ether coupling reaction.



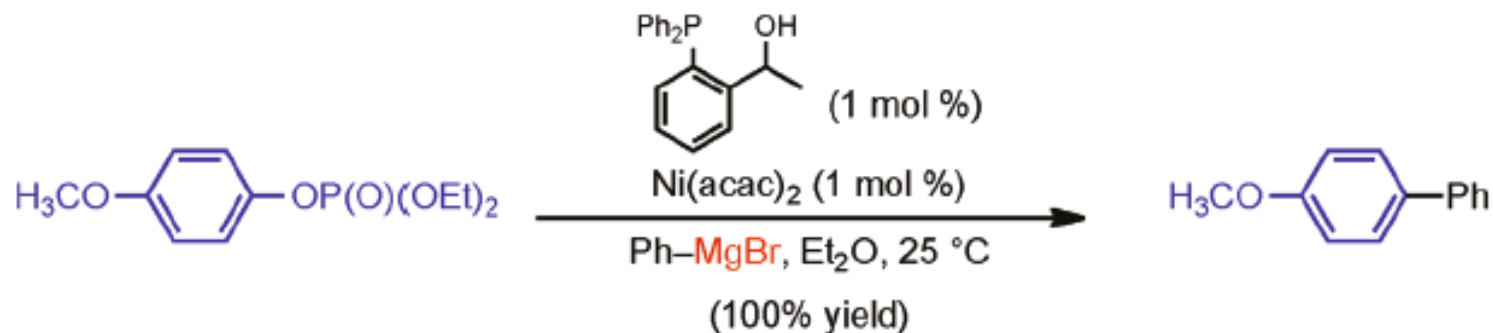
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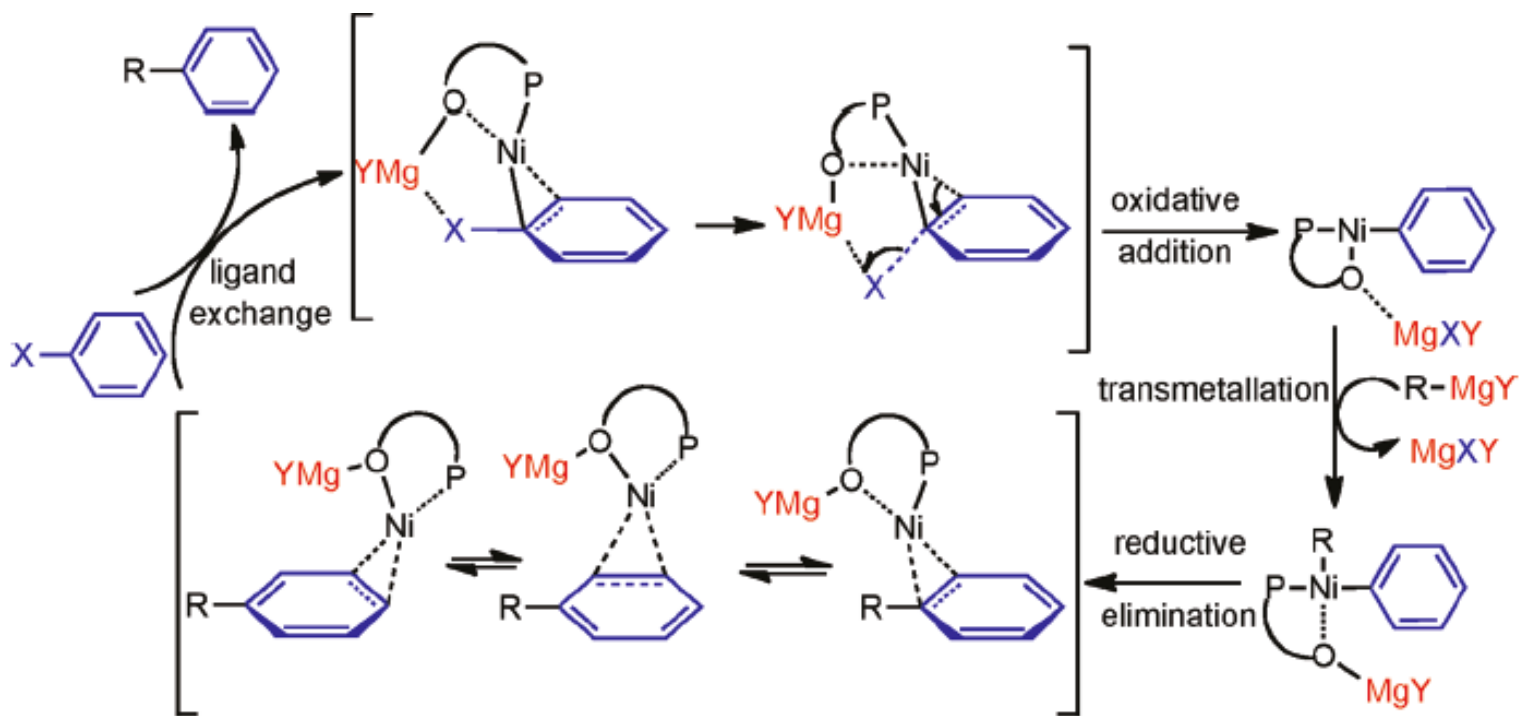
3.4 Cross-Coupling of aryl and vinyl phosphates

- In 2009, Nakamura's group reported the kumada coupling of aryl phosphates using a versatile hydroxyphosphine ligand.



3.4 Cross-Coupling of aryl and vinyl phosphates

- The mechanism of bimetallic species can provide high reactivity.



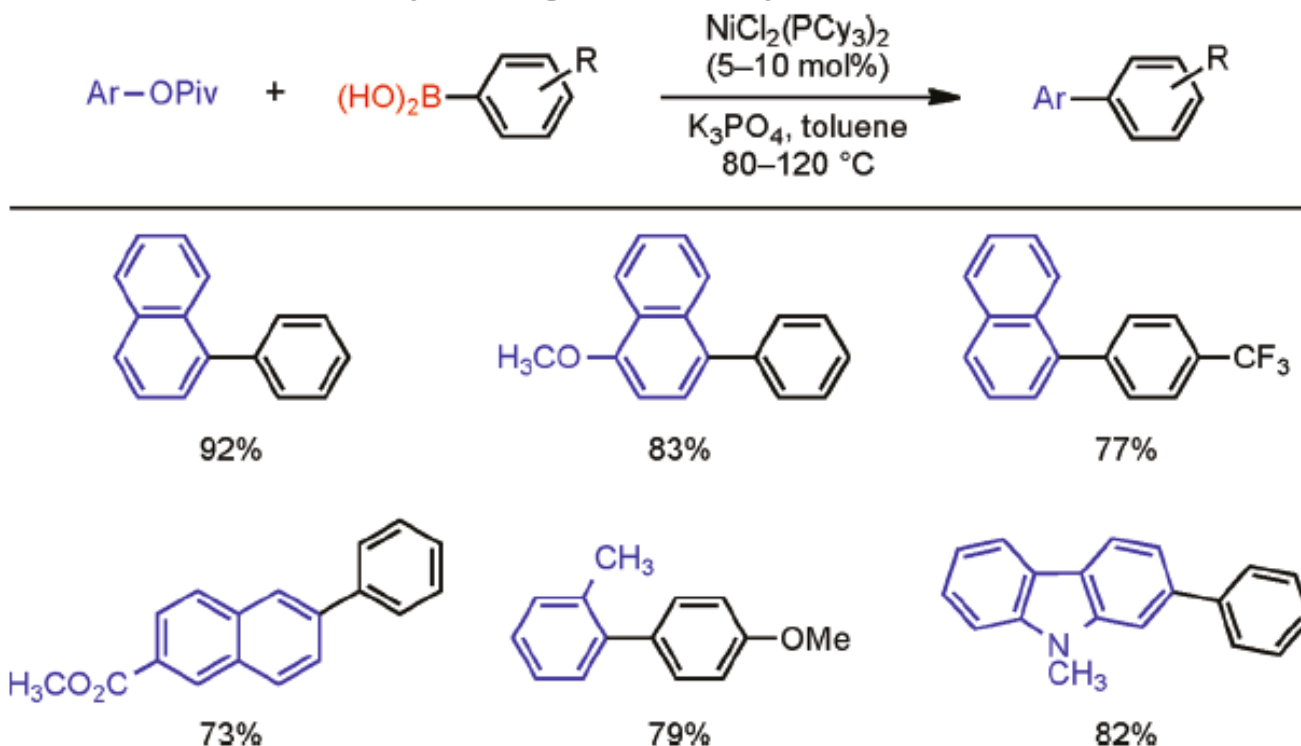
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- 3.7 Cross-Coupling of phenols

3.4 Cross-Coupling of aryl and vinyl phosphates

- In 2008, Garg and Shi independently reported the Suzuki coupling of aryl esters.

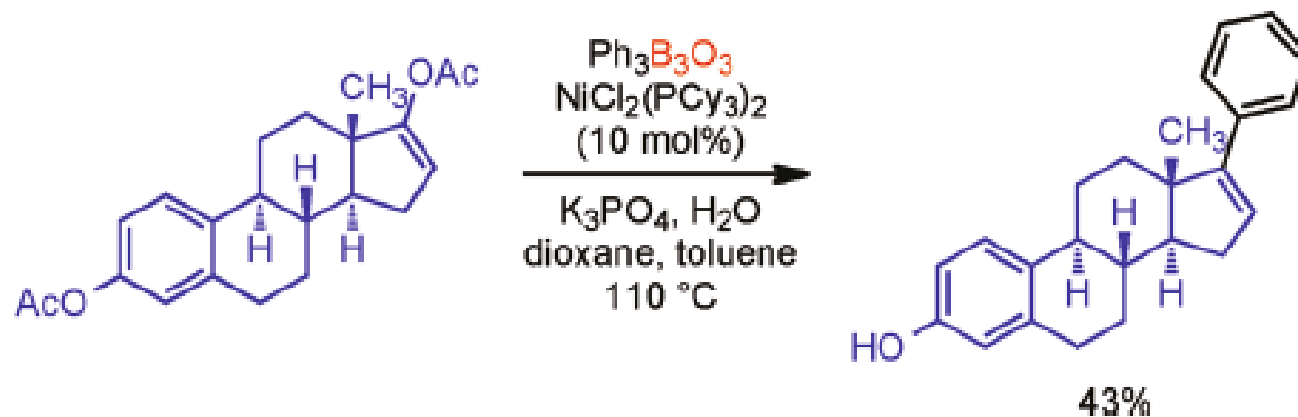
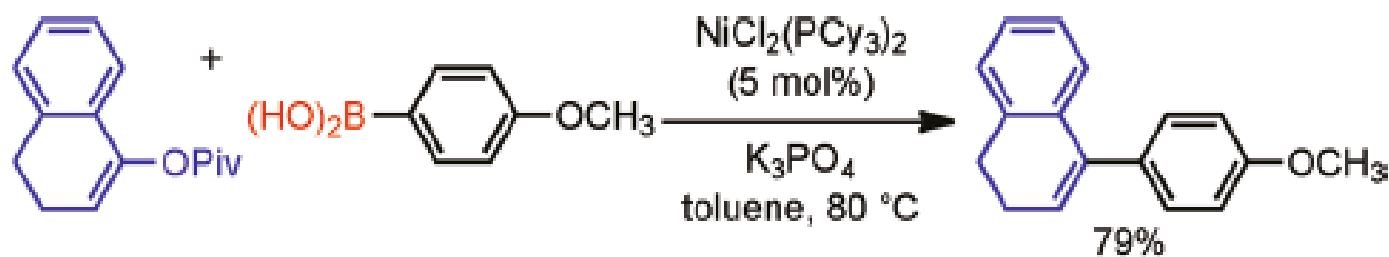


Garg: *JACS*. **2008**, 130, 14422.

Shi: *JACS*. **2008**, 130, 14468.

3.4 Cross-Coupling of aryl and vinyl phosphates

- In 2010, Shi reported the Suzuki coupling of vinyl esters.



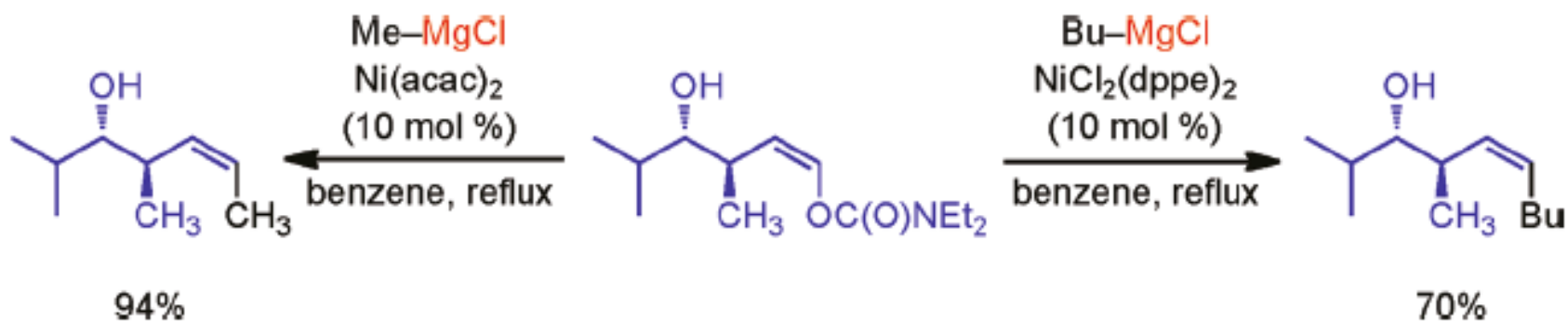
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- 3.7 Cross-Coupling of phenols

3.6 Cross-Coupling of aryl and vinyl carbamates and carbonates

- In 1989, Kocienski's group reported the first Kumada coupling of vinyl carbamate.



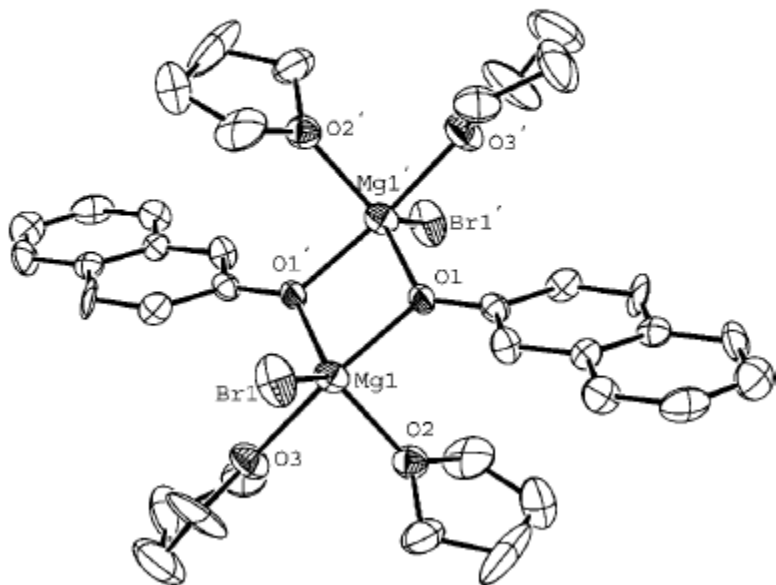
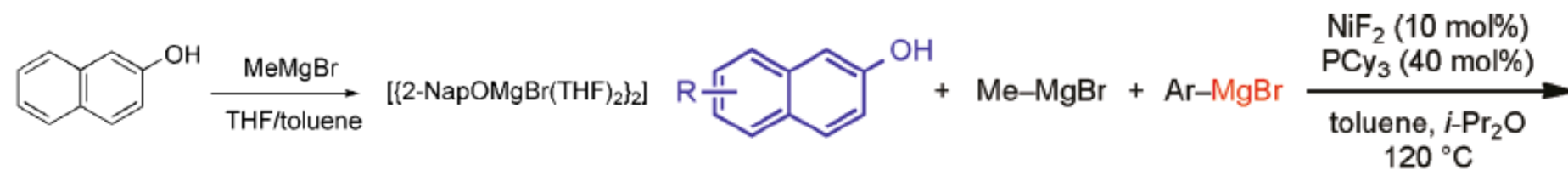
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- **3.7 Cross-Coupling of phenols**

3.7 Cross-Coupling of phenols

- In 2010, Shi's group reported the cross-coupling of 2-naphthol derivatives.



Angew. Chem., Int. Ed. **2010**, 49, 4566

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4. Nickel-Catalyzed Activation of Other Inert Bonds focus on C-F Bond

- 1. Bond Strength (Bond Dissociation Energy)

C-O BDE = 85.5 kcal/mol

C-C BDE = 83 kcal/mol

C-F BDE = 116 kcal/mol

C-H BDE = 95 kcal/mol

C-Cl BDE = 81 kcal/mol

C-Br BDE = 68 kcal/mol

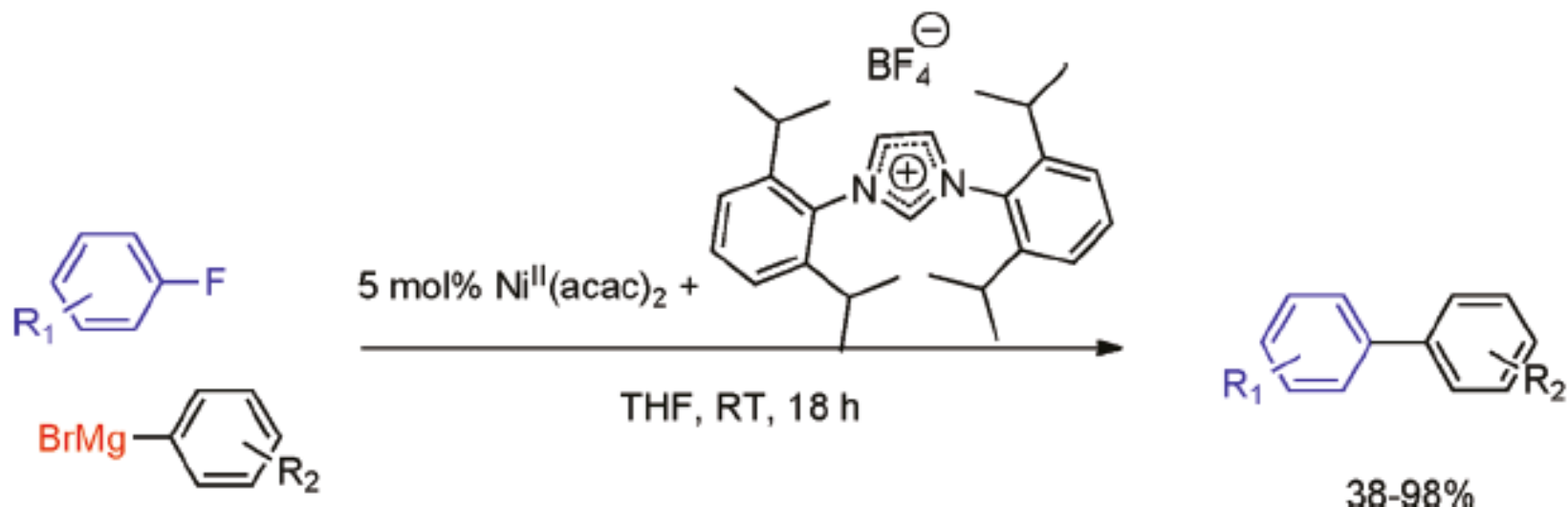
C-I BDE = 51 kcal/mol

4. Nickel-Catalyzed Activation of Other Inert Bonds focus on C-F Bond

- 1. Bond Strength
- 2. C-F bond coupling provide an orthogonal functional group for synthesis of complex organic frameworks.

4. Nickel-Catalyzed Activation of Other Inert Bonds focus on C-F Bond

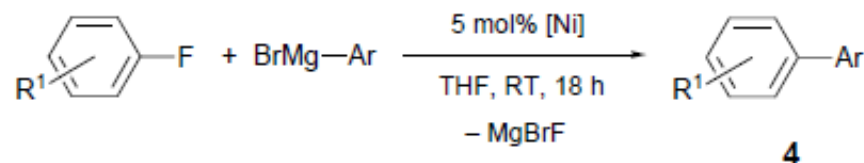
- 3. The first successful cross-coupling of C-F electrophile was done by Herrmann's group in 2001.



ACHIE. **2001**, 40, 3387

4. Nickel-Catalyzed Activation of Other Inert Bonds focus on C-F Bond

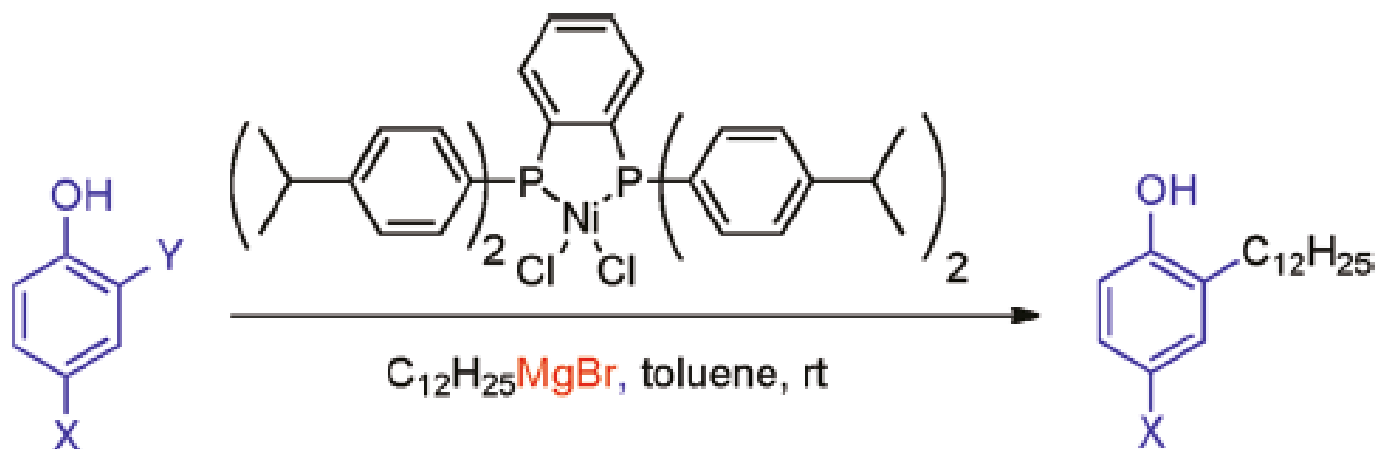
- Substrate Scope



Entry	R ¹	Ar	[Ni] ^[b]	Yield 4 [%] ^[c]
1	4-CF ₃	C ₆ H ₅	1	95
2	4-CF ₃	C ₆ H ₅	in situ	98
3	4-CH ₃	C ₆ H ₅	1	82
4	4-CH ₃	C ₆ H ₅	in situ	92
5	2-CH ₃	C ₆ H ₅	1	38
6	2-CH ₃	C ₆ H ₅	in situ	53
7	4-OCH ₃	C ₆ H ₅	in situ	58 ^[a]
8	4-CF ₃	4- <i>t</i> BuC ₆ H ₄	1	95
9	4-CF ₃	4- <i>t</i> BuC ₆ H ₄	in situ	97
10	H	4- <i>t</i> BuC ₆ H ₄	1	83
11	H	4- <i>t</i> BuC ₆ H ₄	in situ	86
12	4-CH ₃	4- <i>t</i> BuC ₆ H ₄	in situ	95
13	2-CH ₃	4- <i>t</i> BuC ₆ H ₄	in situ	69
14	4-OCH ₃	4- <i>t</i> BuC ₆ H ₄	1	59 ^[d]
15	4-OCH ₃	4- <i>t</i> BuC ₆ H ₄	in situ	73 ^[d]
16	4-CF ₃	2,4,6-Me ₃ C ₆ H ₂	in situ	75

4. Nickel-Catalyzed Activation of Other Inert Bonds focus on C-F Bond

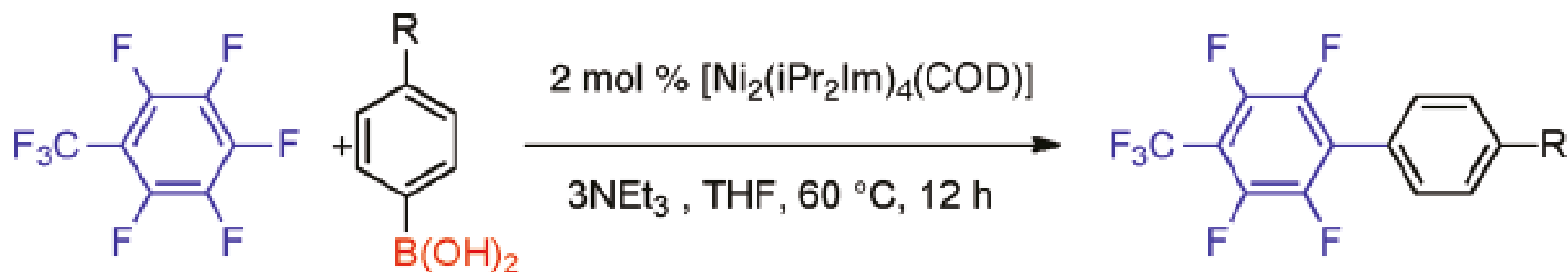
- 4. In 2009, Manabe's group reported a ortho-selective cross-coupling of Halophenols.



X = Br, Y = F: 65% vs X = Br, Y = Cl: 61%
X = Cl, Y = F: 60% vs X = Cl, Y = Br: 43%
X = F, Y = F: 75% vs X = Br, Y = Br: 36%

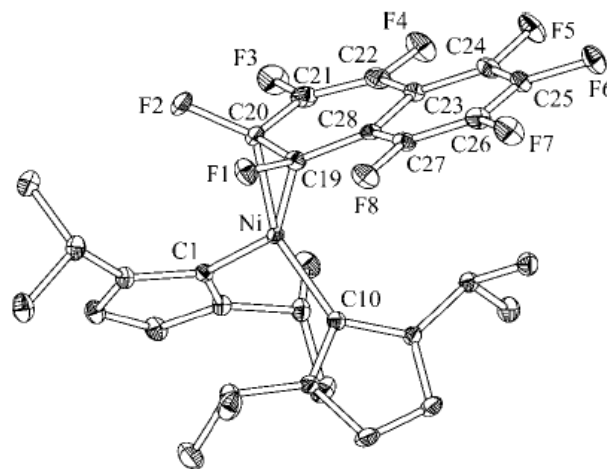
4. Nickel-Catalyzed Activation of Other Inert Bonds focus on C-F Bond

- 5. In 2006, Radius' group reported a selective para C-F bond cross-coupling reaction.



R = H, OCH₃, CH₃, Ph

JACS. 2006, 128, 15964



Outline of this presentation

- 1. Introduction
- 2. Background for Homocoupling
- 3. Nickel-Catalyzed Cross-Coupling focus on C-O bond
- 4. Nickel-Catalyzed Activation of Other Inert Bonds focus on C-F Bond
- 5. Conclusions

5. Conclusion

- 1. Ni is an extraordinarily versatile catalyst for homocoupling, cross-coupling, functionalization and defunctionalization reactions.
- 2. Ni is particularly effective for reactions involving C-O derived electrophiles.
- 3. In cross-coupling reactions, a vast assortment of coupling partners have been explored.
- 4. Ni reaction involving less reactive electrophiles are typically achieved using less-expensive catalytic systems.

Not covered materials

- 1. Homocoupling reaction and polymerization
- 2. Functionalization of sulfonates
- 3. C-N or C-B or C-H bond formation

Thanks for your attention!

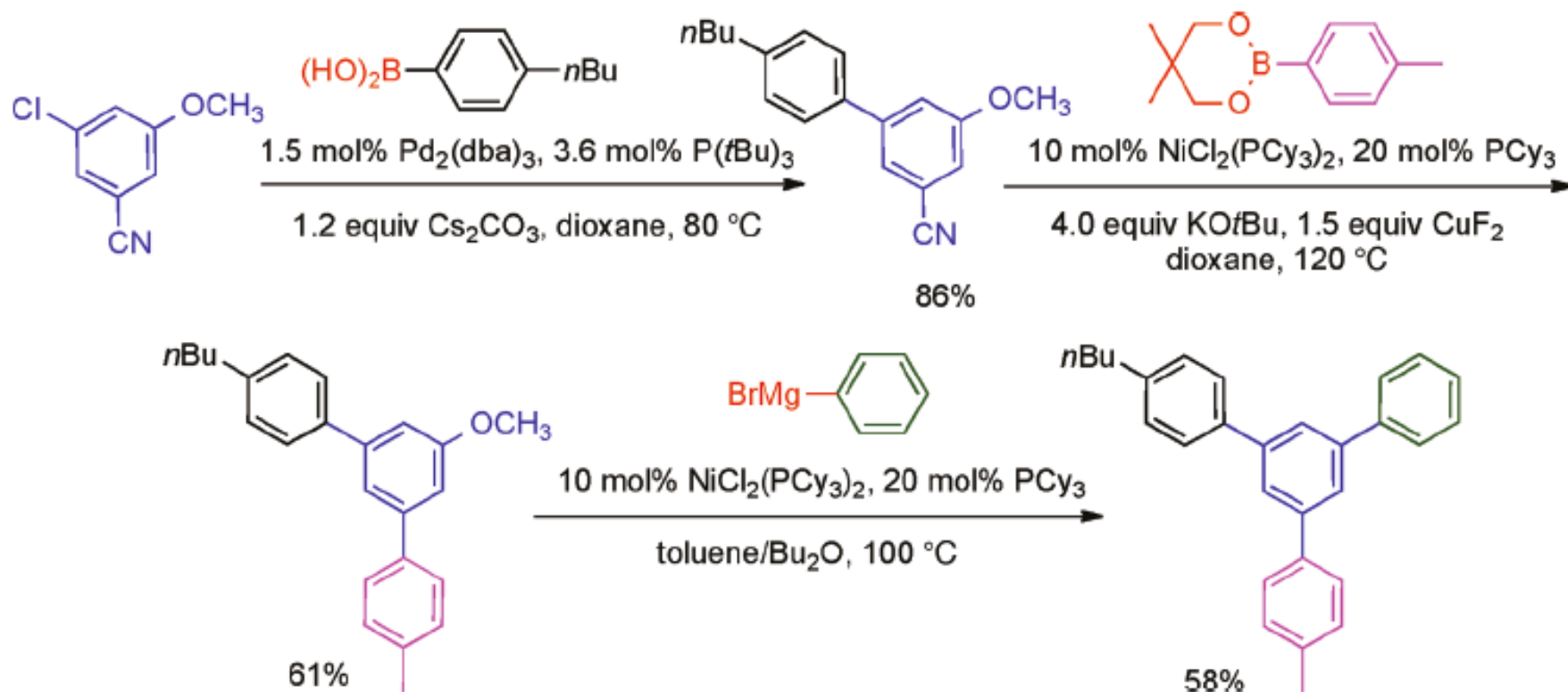


Answers to the Questions!

- Q1, too simple to get it wrong.

Answers to the Questions!

- Q2



Answers to the Questions!

- Q3

