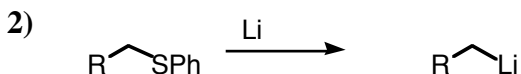
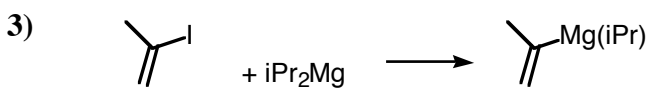


1) Activation of Grignard Reagents: Lai, Y. H. *Synthesis* **1981**, 585.



**Screttas, C. G.**; Micha-Screttas, M. Hydrolithiation of .alpha.-olefins by a regioselective two-step process. Transformation of alkyl phenyl sulfides to alkyllithium reagents. *J. Org. Chem.* **1978**, *43*, 1064-1071



Rottlander, M. B., L.; Cahiez, G.; **Knochel, P.** Stereoselective Preparation of Functionalized Alkenylmagnesium Reagents via an Iodine-Magnesium Exchange Reaction. *J. Org. Chem.* **1999**, *1999*, 1080-1081.

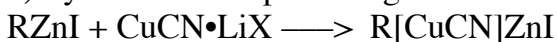


Boymond, L.; Rottländer, M.; Cahiez, G.; **Knochel, P.** Preparation of Highly Functionalized Grignard Reagents by an Iodine-Magnesium Exchange Reaction and its Application in Solid-Phase Synthesis. *Angew. Chem., Int. Ed.* **1998**, *37*, 1701-1703.

5) Directed Metallation: **Snieckus, V.** Directed ortho metalation. Tertiary amide and O-carbamate directors in synthetic strategies for polysubstituted aromatics. *Chem. Rev.* **1990**, *90*, 879.

6)  $\text{Ph}_2\text{CuLi}$  x-ray structure: Nis Peter Lorenzen, **Erwin Weiss.** Synthesis and Structure of a Dimeric Lithium Diphenylcuprate:  $[\{\text{Li}(\text{OEt})_2\}(\text{CuPh}_2)]_2$   
*Angew. Chem. Int. Ed.* **1990**, *29*, 300

7) Synthesis of Cuprate reagents that bear functional groups:



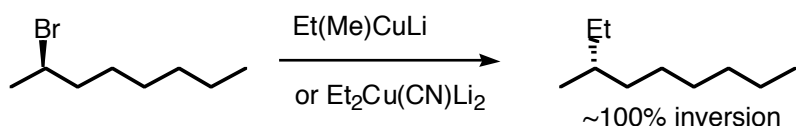
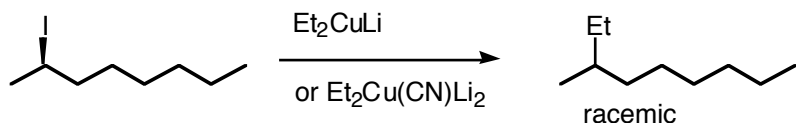
**Knochel, P.**; Yeh, M. C. P.; Berk, S. C.; Talbert, J. Synthesis and reactivity toward acyl chlorides and enones of the new highly functionalized copper reagents  $\text{RCu}(\text{CN})\text{ZnI}$ . *J. Org. Chem.* **1988**, *53*, 2390-2392.

### General References to Cuprate Chemistry

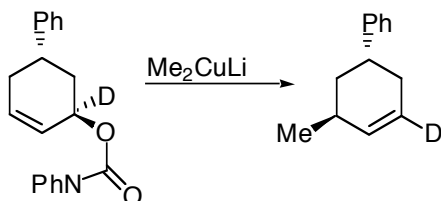
8) **Lipshutz, B. H.**; Sengupta, S. Organocopper reagents: Substitution, conjugate addition, carbo/metallo cupration, and other reactions. *Org. React. (N.Y.)* **1992**, *41*, 136.

9) Lipshutz, B. H. The Evolution of Higher Order Cyanocuprates. *Synlett* **1990**, 119.

10) Lipshutz, B. H.; Wilhelm, R. S. Chemistry of higher order, mixed organocuprates.. The stereochemical outcome of substitution reactions at unactivated secondary centers using organocopper reagents. *J. Am. Chem. Soc.* **1982**, *104*, 4696-4698.



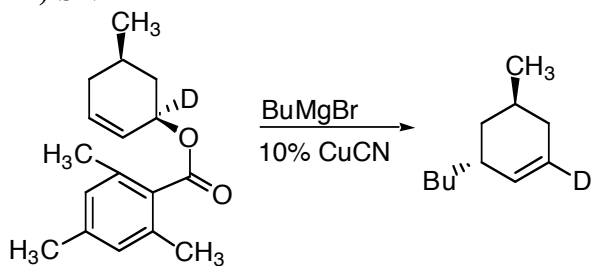
11) Chelation controlled  $\text{SN}2'$



• Gallina, C.; Ciattini, P. G. Conversion of allylic carbamates into olefins with lithium dimethylcuprate. A new formal  $\text{SN}2'$  reaction. *J. Am. Chem. Soc.* **1979**, *101*, 1035-1036.

• Goering, H. L.; Kantner, S. S.; Tseng, C. C. Alkylation of allylic derivatives. 4. On the mechanism of alkylation of allylic N-phenylcarbamates with lithium dialkylcuprates. *J. Org. Chem.* **1983**, *48*, 715-721.

12)  $\text{SN}2'$  w/o chelate



Tseng, C. C.; Paisley, S. D.; Goering, H. L. Alkylation of allylic derivatives. 11. Copper(I)-catalyzed cross coupling of allylic carboxylates with Grignard reagents. *J. Org. Chem.* **1986**, *51*, 2884-2891.

13) For a discussion of the diaxial opening of cyclohexene oxide, see pp 526–531 of Eliel and Wilen, *Stereochemistry of Organic Compounds*

14) 1,4-addition of cyanocuprates to allylic epoxides

- **Marino, J. P.**; Jaen, J. C. Stereospecific umpolung .alpha.' substitution of ketones via reactions of organocuprates with enol ethers of .alpha.,.beta.-epoxycyclohexanones. *J. Am. Chem. Soc.* **1982**, *104*, 3165-3172.
- **Marino, J. P.**; Floyd, D. M. *Tetrahedron Lett.* **1979**, 675
- **Wender, P. A.**; Erhardt, J. M.; Letendre, L. J. Reaction of allylically substituted enolates with organometallic reagents: a convenient source of enolonium ion equivalents. *J. Am. Chem. Soc.* **1981**, *103*, 2114-2116.

15) Pd-catalyzed Cross coupling Reactions

• Couplings of Aryl Chlorides

-Littke, A. F.; **Fu, G. C.** Palladium-catalyzed coupling reactions of aryl chlorides. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 4176-4211.

• Heck Reaction

- Whitcombe, N. J.; Hii, K. K.; Gibson, S. E. Advances in the Heck chemistry of aryl bromides and chlorides. *Tetrahedron* **2001**, *57*, 7449-7476.
- **Heck, R. F.** Palladium-Catalysed Vinylation of Organic Halides. *Org. React. (N.Y.)* **1982**, *27*, 345.

• Suzuki

- **Suzuki, A.** Cross-coupling reactions via organoboranes. *J. Organomet. Chem.* **2002**, *653*, 83-90.
- Kotha, S.; Lahiri, K.; Kashinath, D. Recent applications of the Suzuki-Miyaura cross-coupling reaction in organic synthesis. *Tetrahedron* **2002**, *58*, 9633-9695.
- **Suzuki, A.**; Brown, H. C. Organic Synthesis via Boranes, Vol 3. Aldrich/Milwaukee, WI, 2003

• Stille

- Farina, V.**; Krishnamurthy, V.; Scott, W. J. The Stille Reaction. *Org. React. (N.Y.)* **1997**, *50*, 1-652.
- **Kosugi, M.**; Fugami, K. *Overview of the Stille Protocol with Sn In Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-i., de Meijere, A., Eds.; Wiley-Interscience, 2002; Vol. 1, pp 263-285.

• Sonogashira Reaction

- Sonogashira, K.** Development of Pd-Cu catalyzed cross-coupling of terminal acetylenes with sp<sup>2</sup>-carbon halides. *J. Organomet. Chem.* **2002**, *653*, 46-49.
- **Sonogashira, K.** *Cross-coupling reactions to sp carbon atoms.* In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH, Inc: 605 Third Ave/New York/NY 10158-0012, 1998, pp 203-229.
- Axel Köllhofer, T. P., Herbert Plenio A Versatile Catalyst for the Sonogashira Coupling of Aryl Chlorides. *Angew. Chem., Int. Ed.* **2003**, *42*, 1056-1058.

• Amination and C-O bond formation

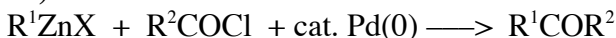
- Muci, A. R.; **Buchwald, S. L.** Cross-Coupling Reactions: Practical palladium catalysts for C-N and C-O bond formation. *Top. Curr. Chem.* **2002**, 219, 131-209.

- **Hartwig, J. F.** *Palladium-catalyzed amination of aryl halides and related reactions* In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-i., de Meijere, A., Eds.; Wiley-Interscience, 2002; Vol. 1, pp 1051-1096.

Ketone arylation

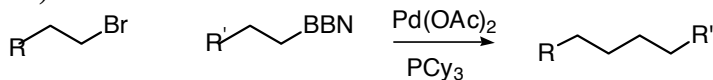
-Fox, J. M.; Huang, X.; Chieffi, A.; **Buchwald, S. L.** Highly Active and Selective Catalysts for the Formation of  $\alpha$ -Aryl Ketones *J. Am. Chem. Soc.* **2000**; 122(7); 1360-1370.

16)



**Negishi, E-i.** et al Palladium Catalyzed Acylation of Organozincs and other Organometallics as a Convenient Route to Ketone *Tetrahedron Lett.* **1983**, 24, 5181

17)



Netherton, M. R.; Dai, C.; Neuschutz, K.; **Fu, G. C.** Room-Temperature Alkyl-Alkyl Suzuki Cross-Coupling of Alkyl Bromides that Possess Hydrogens. *J. Am. Chem. Soc.* **2001**, 123, 10099-10100.

18) Review of Collman's Reagent:  $Na_2Fe(CO)_4$

**Collman, J. P.** Disodium Tetracarbonylferrate - a Transition Metal Analog of a Grignard Reagent. *Acc. Chem. Res.* **1975**, 8, 342.

19) Cyanation of Arylhalides and aryldiazonium salts:

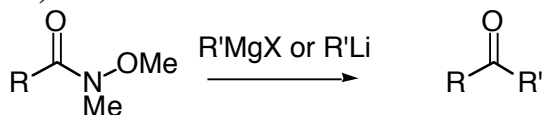
- Review: **Lindley, J. A.** Copper Assisted Nucleophilic Substitution of Aryl Halogen. *Tetrahedron* **1984**, 40, 1433.

-Mark Sundermeier, A. Z., **Matthias Beller** Palladium-Catalyzed Cyanation of Aryl Halides: Recent Developments and Perspectives. *European Journal of Inorganic Chemistry* **2003**, 19, 3513-3526.

-**Jin, F.**; Confalone, P. N. Palladium-catalyzed cyanation reactions of aryl chlorides. *Tetrahedron Lett.* **2000**, 41, 3271-3273.

- **S.L. Buchwald** Copper-Catalyzed Domino Halide Exchange Cyanation of Aryl Bromides *J. Am. Chem. Soc.* **2003**, 125, 2890

20) Weinreb's Amide



• Nahm and Weinreb *Tetrahedron Lett.* **1981**, 22, 3815

• Review: Sibi, M. P. Chemistry of N-methoxy-N-methylamides. Applications in synthesis. *Org. Prep. Proced. Int.* **1993**, 25, 15.

21)  $\text{R}'\text{COOH} + 2 \text{RLi} \longrightarrow \text{R}'\text{COR}$

Jorgenson, M. J. The Preparation of Ketones from the Reaction of Organolithium Reagents with Carboxylic Acids. *Org. React. (N.Y.)* **1970**, 18, 1.

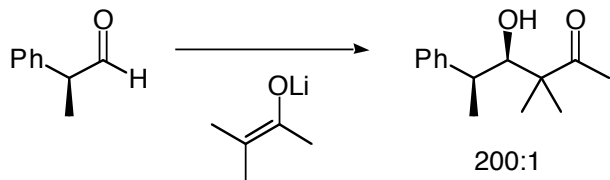
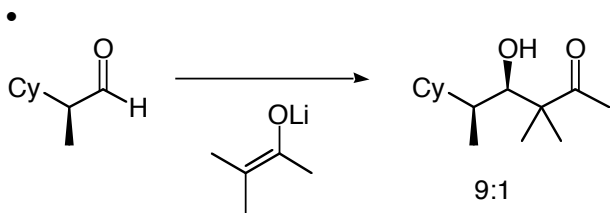
22) Felkin Selectivity in 1,2 additions: selected examples

• Nakada, M.; Urano, Y.; Kobayashi, S.; Ohno, M. High diastereofacial selectivity in nucleophilic additions to chiral acylsilanes. *J. Am. Chem. Soc.* **1988**, 110, 4826-4827.



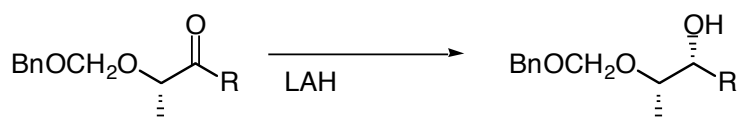
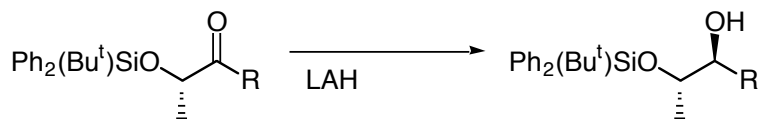
LAH: 74:26 dr  
L-selectride: 99:1 dr

-Yamamoto, Y.; Matsuoka, K.; Nemoto, H. Anti-Cram selective reduction of acyclic ketones via electron transfer initiated processes. *J. Am. Chem. Soc.* **1988**, 110, 4475-4476.



Flippin, L. A.; Onan, K. D. *Tetrahedron Lett.* **1985** 973

**23) Chelate vs Steric controlled selectivity in 1,2-additions**



**Overman** and McCready *Tetrahedron Lett.* **1982**, 23, 2355

**24) Stereochemistry of 1,2 additions to cyclic ketones: Review**

**Ashby, E. C.**; Laemmle, J. T. Stereochemistry of Organometallic Compound Addition to Ketones. *Chem. Rev.* **1975**, 75, 521.