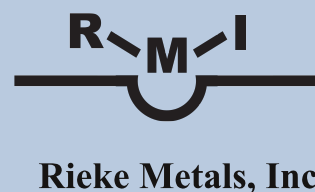


The Utility of Rieke® Highly Reactive Zinc and Organozinc Reagents



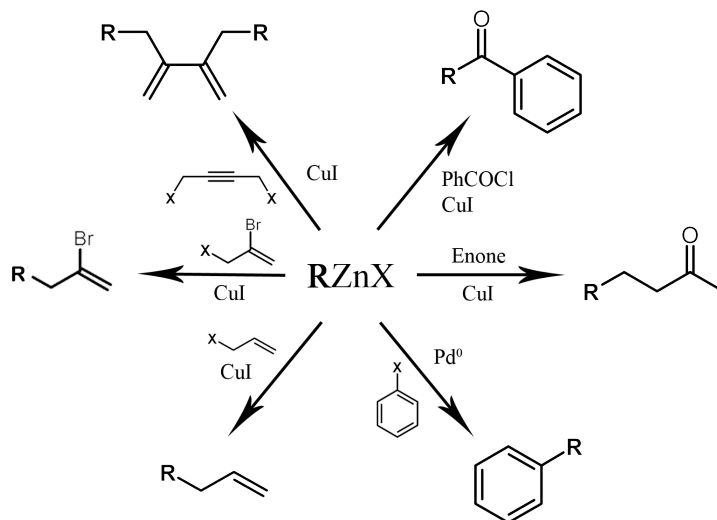
Rieke® Highly Reactive Zinc (Zn*) readily undergoes oxidative addition to alkyl, aryl and vinyl halides under mild conditions to generate the corresponding organozinc reagents.

Significantly, unlike the formation of Grignard or organolithium reagents, organozinc halides will tolerate a variety of functional groups such as chlorides, nitriles, esters and olefins.



As seen here, highly reactive zinc has become a powerful tool in both the generation of heteroaromatic organometallics and in the oxidative addition to difficult halides to form the organozinc reagent by inserting into the carbon-halogen bond.

Rieke organozinc reagents react with a variety of electrophiles in the presence of Cu(I) or Pd(0). For example, organozinc reagents can be employed for cross coupling with acid chlorides, aryl halides and substituted or non-substituted allyl halides. They may also undergo Michael additions to saturated ketones or additions to alkynes to give substituted dienes.



For a full paper on the direct formation of functionalized Organozinc reagents and their reactions with acid chlorides, alpha, beta-unsaturated ketones and allylic, aryl and vinyl halides, see: L. Zhu, R. Wehmeyer and R. Rieke. *Journal of Organic Chemistry*, 56 (1991) 1445.

For experimental details see: Reuben D. Rieke and Mark V. Hanson, Chapter 2, "Practical Approach in Organozinc Reagents" Edited by Paul Knochel and Philip Jones (Oxford University Press).

For detailed mechanistic studies and relative rates of reactions, see: A. Guijarro, D.M. Rosenberg and R.D. Rieke, *J. of the American Chemical Society* 121 (1999) 4155.

For a review of Rieke® Highly Reactive Zinc chemistry, see: Reuben D. Rieke and Mark V. Hanson, *Tetrahedron*, 53 (1997) 1925 and leading references.

"Coupling reactions with haloaromatic amines and alcohols for a practical synthetic route to 2-substituted aminophenyl and hydroxyphenyl pyridines." S. Kim and R.D. Rieke, *Tetrahedron Letters*, 50 (2009) 6985.

"A convenient synthesis of 5-aryl- and 5-heteroaryl-2-furaldehydes by the cross-coupling reaction of organozincs." S. Kim and R.D. Rieke, *Tetrahedron Letters*, 51 (2010) 2657.

"5-Bromo-2-pyridylzinc reagent; direct preparation and its coupling reactions." R.D. Rieke and S. Kim, *Tetrahedron Letters*, 52 (2011) 244.

"A novel organozinc reagent 4-coumarinylzinc bromide; preparation and application in the synthesis of 4-substituted coumarin derivatives." R.D. Rieke and S. Kim, *Tetrahedron Letters*, 52 (2011) 3094.