Studies on Unusually Reactive Metal Powders. Preparation of New Organometallic and Organic Compounds Including Potential New Catalysts.

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Research Scope and Objectives

We have demonstrated that highly reactive metal powders can be prepared by the reduction of metal salts from ethereal or hydrocarbon solvents. Common reducing agents are potassium, sodium, lithium or other reducing agents of high enough potential. The reduction yields the metal in a finely divided state. Metals studied to date exhibit far superior reactivity towards organic and inorganic substrates to that described in the literature for these metals. We have recently shown that this approach will work with transition metals including the following metals: nickel, cadmium, iron, and uranium. We are proposing to study the chemistry of these highly reactive metals. We wish to examine these metals in a variety of oxidative-insertion reactions, preparation of zerovalent derivatives, and catalytic reactions. New organometallic complexes with potential catalytic activity are proposed. This study is expected to result in several new synthetic techniques as well as several new organic and organometallic compounds.

Recent Results

Nickel: Activitated metallic nickel was prepared in glyme by the reduction of nickel halide with lithium in the presence of a catalytic amount of naphthalene as an electron carrier. A variety of iodobenzenes and bromobenzenes reacted with the nickel at 85°C to give the corresponding biphenyls in good to high yields. Substituents in the para position such as methoxy, chloro, cyano, and acetyl groups were compatible with the reaction conditions employed.

Surprisingly, the homo-coupling reaction of benzylic halides by metallic nickel proceeded at room temperature.

$$2\ ArCH_2X \xrightarrow[\text{glyme, r.t.}]{Ni} ArCH_2CH_2Ar$$

1,2-Diarylethanes having functional groups such as methoxy, trifluoromethyl, chloro, bromo, cyano, and nitro groups could be easily prepared by this method in good to high yields. On the other hand, benzylic polyhalides were converted to the corresponding olefins via vicinal dihalide intermediates.

Cross coupling was tried in the reaction of benzylic halides and acyl halides and the expected ketones were isolated in good to high yields.

$$ArCH_2X^1 + RCOX^2 \xrightarrow[\text{glyme, } 85°C]{Ni} ArCH_2COR$$

When alkyl oxalyl chlorides were employed instead of acyl halides, symmetrical dibenzyl ketones were formed in good yields.

$$2\ ArCH_2X + XCOCO_2R \xrightarrow[\text{glyme, } 85°C]{Ni} ArCH_2COCH_2Ar + 1/2\ RO_2CCO_2R$$

Other new reactions found which were mediated by the highly reactive nickel include the generation of o-xylylene under mild conditions from o-xylylene dibromide.

Cadmium: We have recently discovered that highly reactive cadmium can be generated by this general approach. The cadmium powders react rapidly with α-haloesters to give an organocadmium species which readily adds to ketones and aldehydes to yield β-hydroxy ketones in high yields. We have recently demonstrated that organocadmium species can be prepared directly from the metal and alkyl and aryl halides and these species can be used in a variety of cross coupling reactions.

Iron: Reduction of anhydrous iron(II) and iron(III) salts with lithium and an electron carrier such as naphthalene in ethereal solvents yields a highly reactive iron powder. The iron powder reacts rapidly with alkyl or arylhalides to yield coupled products or the monomeric hydrocarbon. Reaction of α-haloesters with the iron powder in the presence of ketones or aldehydes gives high yields of β-hydroxyesters. Reaction of allylic halides with the iron powder in the presence of aryl aldehydes gives high yields of the cross-coupled alcohol. The iron powders appear to be useful as a general reducing agent.

Uranium: Reduction of UCl_4 with Na/K allay using an electron carrier such as naphthalene yields a highly reactive uranium powder. Reaction of this metal with cycloactatetraene yields uranocene under mild conditions.

Future Research

We are continuing our studies to develop new ways to prepare highly reactive metal powders. We are attempting to understand the high reactivity of these metal powders and to explore their new chemistry. It is expected that several new synthetic techniques will result from this study. We also wish to study the catalytic activities of these new materials.