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PREPARATION AND STUDY OF HIGHLY REACTIVE METAL POWDERS

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FINAL REPORT

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2. STATEMENT OF PROBLEM

We recently discovered 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 recently have shown that this approach will work with transition metals including nickel, palladium, platinum, cobalt, iron, and uranium. We proposed to study the chemistry of these highly reactive metals. We wished to examine these metals in a variety of oxidative-insertion reactions, preparation of zero-valent derivatives, and catalytic reactions. Several new organo-metallic complexes with potential catalytic activity were proposed.

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B. SUMMARY OF RESULTS

1. Cobalt

Cobalt powders prepared by the lithium reduction of cobalt chloride in glyme in the presence of a catalytic quantity of naphthalene as an electron carrier were found to have a reactivity towards certain organic halides comparable to that of metal powders prepared by the metal atom vapor technique. For example, cobalt powders reacted with C_6F_5I to give solvated $Co(C_6F_5)_2$ and CoI_2 . The former was isolated in 57% yield as $Co(C_6F_5)_2(PEt_3)_2$ after the addition of PEt_3 . Similarly C_6F_5Br reacted with cobalt and PEt_3 to give the same product in 29% yield.

Reaction of dichlorodiphenylmethane with cobalt powders at room temperature proceeded to give the coupling product, tetraphenylethylene, in yields up to 70%. Some attempts were made to trap the diphenylcarbene moiety or its cobalt complex by addition of cyclohexene or phosphine ligands respectively. These attempts were not successful however.

The cobalt employed in these reactions was generated over a period of 6-18 hours or more at room temperature using a catalytic amount of naphthalene. Although the kinetics of particle growth under these conditions (in the presence of alkali metal salts and strong donor solvents) are unknown to us, it seemed reasonable that the smallest and presumably most reactive cobalt particles were being lost due to sintering with the formation of larger less reactive particles or lost through reaction with the solvent.

Preparation of the metal at lower temperatures was therefore expected to afford a more highly reactive metal by decreasing the rate of particle growth and reaction with the solvent. It was soon discovered that at low temperature ($-20 - -78^{\circ}\text{C}$) reductions went to completion much more slowly than those done at room temperature. We attributed this to a kinetic effect in the initial electron transfer from the alkali metal to the naphthalene. In addition, the solubilities of cobalt halides and lithium naphthalide were much lower at low temperature.

In order to avoid the slow electron transfer problem, we have begun to use preformed lithium naphthalide solutions. These were prepared at temperatures above 0°C by treating the required amount of lithium in glyme with a greater than stoichiometric quantity of naphthalene. Such solutions constitute a very powerful reducing medium which will eventually start to reduce the solvent especially at or above room temperature. Thus an excess amount of naphthalene was used to assure rapid and complete dissolution of the lithium. The solution of lithium naphthalide was cooled to $-20 - -78^{\circ}\text{C}$ and the cobalt halide added as a dry powder or as a slurry in cold glyme. These reactions took place within an hour or two as evidenced by the disappearance of the dark green naphthalide color. These reductions were probably not homogeneous owing to the low solubility of the cobalt halide and because a large portion of the lithium naphthalide had frozen out of solution. The metal powders prepared using this modified procedure were undoubtedly more finely divided than those obtained by previous methods. This fact was

obvious in the much slower sedimentation rates observed for the powders prepared by the new method. Some metal remained suspended in the solvent even after prolonged centrifugation. We estimated that no more than a few percent of the cobalt remained suspended however.

In a related experiment, cobalt powder from a potassium naphthalide reduced cobalt chloride was examined using ESCA. These studies revealed the presence of elemental cobalt and cobalt oxide and/or hydroxide on the surface of the powder particles as well as carbon, cationic potassium and anionic chlorine. Sputtering profiles showed that the atomic percent composition of cobalt, potassium and chlorine increased to a depth of ca. 30 Å and that the oxygen content decreased to a depth of ca. 90 Å. Beyond these depths the atomic percent composition was essentially invariant to at least 210 Å. Scanning Auger micrographs indicated a fairly uniform surface distribution for any particular element. Elemental analysis of the powder gave the following percent compositions: C, 5.06; H, 0.60; Cl, 31.07; K, 35.17; Co, 23.53. Powder diffraction photographs of this cobalt sample showed only lines attributable to potassium chloride. From these data we concluded that elemental cobalt was present in a potassium chloride matrix and that the cobalt was either amorphous or was less than 0.1 microns in size such that it produced an undetectably diffuse X-ray diffraction pattern.

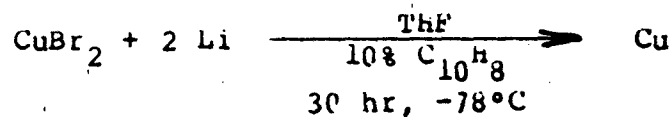
Using cobalt prepared according to the lithium naphthalide procedure we have succeeded in preparing dicobalt octacarbonyl under relatively mild conditions. The freshly prepared metal was

washed with fresh glyme and hexane and then treated in hexane with carbon monoxide at 95 atm for several days at 110°C. From this reaction a 79% yield of $\text{Co}_2(\text{CO})_8$ was isolated. A separate experiment showed that most of the reaction had occurred in the first 48 hours when conversion to the carbonyl was found to be 73% complete. In other experiments, a 47% yield was obtained in 16 hours under similar conditions and a 17% yield after two hours at room temperature. Cobalt powders that have been washed and dried reacted exothermically with carbon monoxide, however very little $\text{Co}_2(\text{CO})_8$ was isolated. Elemental analysis of the recovered metal showed an enormous increase in the amount of carbon present by contrast to the metal before treatment with carbon monoxide. The fate of the oxygen from the carbon monoxide is presently unknown. The analytical data have effectively ruled out the formation of cobalt oxide in any appreciable quantity.

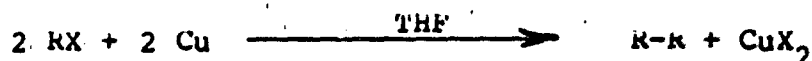
We have not as yet looked at the organic chemistry of the lithium naphthalide derived cobalt powders in any detail. One reaction we did try was the reaction of cobalt with 1,4-iodonitrobenzene. Not all of the products of this reaction were characterized. It was found that at least 12% of the starting material suffered attack at the nitro group and not at the expected site, the phenyl-iodine bond. The starting material had reductively coupled via the nitrogen atoms of the nitro group to give 4,4'-diiodoazobenzene and 4,4'-diiodoazoxybenzene in roughly equal amounts (6%). In a related experiment, cobalt was reacted with nitrobenzene resulting in a 38% yield of azobenzene.

2. Copper

Activated copper was prepared by the reduction of cupric bromide with lithium in THF at -78°C in the presence of a catalytic amount of naphthalene according to the following equation.



A well behaved reaction was used to study the reactivity of the copper powders and to determine the combination of starting materials and reaction conditions which would produce the most highly reactive form of metal. The probe reaction used to assess the reactivity of the copper was the Ullman coupling of organic halides.



When allyl bromide and ortho-iodonitrobenzene were used for the organic halides, the following results were obtained.

RX	Temperature	% yield of R-R	
		1 hour	2 hours
allyl bromide	25°C	57%	60%
ortho- $\text{IC}_6\text{H}_4\text{NO}_2$	65°C	--	25%

At room temperature copper powders rapidly sintered to form larger unreactive aggregates, therefore the metal halide reductions had to be done at lower temperature. Under such conditions, approximately two days were required for complete reduction. To shorten the reduction time, we began to use preformed solutions of lithium naphthalide in THF. To these solutions, the copper halide was quickly added at room temperature. Under these conditions, the reductions were usually complete after 0.5 hour and gave a much more reactive form of copper as shown by the following results.

RX	Temperature	% yield of R-R	
		1 hour	2 hours
allyl bromide	25°C	87%	99%
C ₆ F ₅ I	65°C	49%	56%

Changing the solvent for the coupling reaction to a higher boiling ether, such as dioxane, and increasing the Cu/RX ratio from 1/1 to 2/1 optimized the coupling reaction.

RX	Solvent	Temperature	% R-R
C ₆ H ₄ CH ₂ Br	dioxane	101°C	92
allyl bromide	THF	65°C	99
C ₆ F ₅ I	dioxane	101°C	91
ortho-C ₆ H ₄ INO ₂	dioxane	101°C	81

reduction of the more soluble organosulfide or phosphine complexes of Cu(I) at 0°C in THF gave a copper powder of even greater reactivity which coupled organic halides in good yields under mild conditions.

RX	Copper Salt	% yield of R-R	
		2 hr at 25°C	24 hr at 65°C
$C_6H_5CH_2Br$	$CuI(PEt_3)$	92	95
ortho- $C_6H_4INO_2$	$CuI(PEt_3)$	76	87
ortho- $C_6H_4BrNO_2$	$CuCl[S(CH_3)_2]$	--	87

When C_6F_5I was reacted with copper prepared from $CuI(PEt_3)$ and the mixture quenched in water, an 80-90% yield of the reduced product, pentafluorobenzene, was obtained to the complete exclusion of the coupling product, decafluorobiphenyl. Quenching the reaction mixture with D_2O gave deuteropentafluorobenzene in 92% isotopic purity. It, after adding the C_6F_5I , the THF was replaced with a higher boiling solvent such as mesitylene, and then benzoyl chloride added at reflux, pentafluorobenzophenone was formed in 25% yield. These data suggested that we were forming the organocuprate complex, $C_6F_5Cu(PEt_3)$ directly from the aryl halide and copper metal. The phosphine ligand imparts exceptional stability to the complex and elevated temperatures were required to force this complex to undergo typical organocuprate chemistry with benzoyl chloride.

3. Magnesium

A new preparation of active magnesium was first reported by us in 1972 and expanded upon in the following years. The early method of activation used elemental potassium to reduce magnesium salts partially dissolved in refluxing ethereal solvents. Certain metal salts present during reduction, particularly potassium iodide, dramatically increased the reactivity of the magnesium powders produced. A variety of substrates were reacted with the magnesium from this Mg/K/KI recipe to show its versatility.

Under the auspices of the Army Grant, much additional work has been accomplished. A new reduction method has been developed, using Li as the reducing agent. Because of lithium's high melting point an electron carrier must be employed. Naphthalene is the carrier of choice, being commonly available and giving more active Mg than biphenyl. The amount of electron carrier employed was not critical, but 5-10 mol% naphthalene, based on lithium, gave reduction times of 8-16 hours.

The reactivity of this new form of magnesium was compared to that obtained using the previous method and commercial magnesium by preparing the Grignard Reagent of para-chlorotoluene and quantifying the toluene formed after hydrolysis. The results are summarized here.

Magnesium source	Temp.	% Grignard Formation			
		5 min	10 min	30 min	60 min
Commercial	22°C	0	9	0	0
MgCl/K/KI	0°C	26	46	73	85
MgCl ₂ /Li/naphthalene	0°C	30	60	85	96

In addition to the obvious safety benefits, the lithium reduced magnesium was slightly more reactive, and reductions could be performed at room temperature. Also the need to dry and anhydrously weigh KI was removed. The lithium chloride and naphthalene could be removed by simply allowing the slurry to settle, decanting the supernatant, washing with fresh solvent, and then repeating the process. By this method, 98% of the naphthalene and 78% of the lithium chloride could be removed. Further washings removed additional amounts, however in most cases no washings were necessary.

Typically, Grignard chemistry has been limited to organic halides. It is not always convenient to convert the intended reaction site to a halogen. We have therefore investigated the use of other nonhalogen leaving groups. Tosylates were prime candidates since they are formed under base catalyzed conditions and would compliment the acid conditions used to generate organic halides. The tosylates have, to date, given only coupling products when reacted with activated magnesium. This was expected, since Grignard Reagents were known to readily couple with tosylates. It

is probable that by using proper conditions, any Grignard chemistry in addition to coupling may be accomplished. The following are some representative reactions.

Mg/ROT	Tosylate	Result
2.5	PhCH ₂ OTs	84% PhCH ₂ CH ₂ Ph
2.0	PhOTs	no reaction
1.0	TsO(CH ₂) ₆ OTs	TsO(CH ₂) _n OTs, n = 36

At reflux, dibenzyl ether underwent formal insertion of magnesium into its C-O bond. The Grignard formed was carbonated and hydrolyzed to give phenylacetic acid in 30% yield. This seems to be the only example of a Grignard Reagent formed from an ether. There are examples of ether cleavage, however these do not include any Grignard type reactions. We are currently investigating other pseudo-halides such as nitriles, triflates and carbonates.

Another significant development was the formation of Grignard Reagents from 3-haloethers. Upon formation of the reagent at room temperature, cyclization to cyclopropane with concurrent elimination of alkoxide immediately occurred. Using activated magnesium, the Grignard Reagent may be formed at -78°C and reacted in the expected fashion. This reaction has opened new areas of Grignard chemistry which were previously closed due to the thermal instability of the Grignard Reagent.

4. Palladium

Highly reactive palladium powders have been generated by several routes. Two early methods involved the reduction of palladium halides or their triorganophosphine complexes with potassium in refluxing THF or glyme. These powders were found to be much more reactive than those prepared under similar conditions in diethyl ether, aromatic or aliphatic hydrocarbons. We have also discovered that palladium powders prepared from preformed phosphine complexes or phosphine complexes prepared in situ were more reactive than those powders prepared from the uncomplexed palladium halides.

With the exception of metal prepared by metal atom vaporization techniques there had been no reports prior to our work of palladium undergoing oxidative addition across a carbon halogen bond. Palladium powders prepared from the palladium halide triethylphosphine complexes were found to be reactive towards oxidative addition across carbon halogen bonds and carbon pseudo-halogen bonds with the following results.

Organic Halide	Complex	% Yield
C_6F_5Br	$Pd(Br)(C_6F_5) \cdot 2PEt_3$	76
C_6H_5Cl	$Pd(Cl)(C_6H_5) \cdot 2PEt_3$	54
C_6H_5Br	$Pd(Br)(C_6H_5) \cdot 2PEt_3$	63
C_6H_5I	$Pd(I)(C_6H_5) \cdot 2PEt_3$	52
C_6H_5CN	$Pd(CN)(C_6H_5) \cdot 2PEt_3$	26

The last reaction in the table was particularly interesting since it suggested that insertion of the transition metal into a carbon cyanide bond had occurred.

There existed some questions about the nature of the palladium formed in these reactions. Certain low oxidation state palladium complexes, $\text{Pd}(\text{PR}_3)_n$, $n = 3, 4$, are known to attack carbon halogen bonds and such species could have formed under the conditions used in our early experiments. In order to remove these ambiguities we began to use lithium and a catalytic quantity of naphthalene to reduce uncomplexed palladium halides. Using a catalytic quantity of naphthalene and excess lithium, we found that approximately 2.6 equivalents of lithium were consumed in the reduction of PdCl_2 . Elemental analysis showed that the black powders obtained contained more lithium than could be accounted for as lithium chloride. At least one alloy of palladium and lithium was known, however, our X-ray powder diffraction work failed to reveal any such material. The X-ray data were interpreted as showing crystalline palladium metal (corroborated with ESCA data) lithium and lithium chloride to be present.

Palladium powders prepared in this way were found to react with the powerful electrophile $\text{C}_6\text{F}_5\text{I}$ at reflux in glyme to give $\text{Pd}(\text{C}_6\text{F}_5)(\text{I})^*$ glyme in 16% isolated yield. This complex contained a weakly bound molecule of glyme which was easily displaced by a variety of ligands with the results shown.

Ligand	Product	% Yield
PEt ₃	Pd(C ₆ F ₅) (1) * 2PEt ₃	77
BIPY	Pd(C ₆ F ₅) (1) * BIPY	59
SEt ₂	[Pd(C ₆ F ₅) (1) * SEt ₂] ₂	38
1,5-COD	Pd(C ₆ F ₅) (1) * (1,5-COD)	19

In these reactions the glyme adduct was not isolated but was instead treated with the desired ligand.

Palladium powders prepared by this new route were found to react with aryl and benzyl chlorides and bromides at room temperature. No organometallic complexes were isolated, however the organic products obtained upon hydrolysis were identified with the following results.

RX	RX/Pd	Solvent	% Yield at 1 hr		
			R-H	R-R	R-X
p-chlorotoluene	0.827	THF	35	6	56
p-bromotoluene	0.326	THF	88	0	10
benzyl chloride	0.323	glyme	54	38	0
p-chlorotoluene	0.328	glyme	25	3	66

The relatively high ratio of reduced products to coupled products suggested that, as in the case of the copper experiments, a fairly stable organometallic intermediate had formed.

C. LIST OF PUBLICATIONS AND TECHNICAL REPORTS

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The Direct Formation of Organocopper Compounds by Oxidative Addition of Zero-valent Copper to Organic halides, Greg W. Ebert and Reuben D. Rieke, submitted to J. Am. Chem. Soc.

Preparation, Characterization, and Chemistry of Highly Reactive Cobalt, Gary L. Rochfort, Ashley Taylor, and Reuben D. Rieke, submitted to Organometallics.

D. LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

Postdoctoral Students

- (a) Dr. A.V. Kavaliunas, Ph.D. University of Iowa, now with Eastman Kodak, Rochester, New York.
- (b) Dr. G.L. Kochfort, Ph.D., University of Minnesota, now with Monsanto Co., St. Louis, Missouri.

Graduate Students

- (a) David Delguidice, M.S., September 1984, now with American Starch, New Jersey.
- (b) Greg Ebert, still working towards Ph.D.
- (c) Timothy Burns, still working towards Ph.D.
- (d) Peracy Li, Ph.D., August, 1981, now with IBM, Research Triangle Park, North Carolina

Undergraduate Students

Elizabeth Burkhardt, now a graduate student at University of California-Berkeley.

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20. ABSTRACT CONTINUED:

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 recently have shown that this approach will work with transition metals including nickel, palladium, platinum, cobalt, iron, and uranium. We proposed to study the chemistry of these highly reactive metals. We wished to examine these metals in a variety of oxidative-insertion reactions, preparation of zero-valent derivatives, and catalytic reactions. Several new organo-metallic complexes with potential catalytic activity were proposed.

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