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Preparation of Highly Reactive Metal Powders. Direct Reaction of Nickel, Cobalt, and Iron Metal Powders with Arene Halides

Sir:

In a series of papers starting in 1972, we have described a general procedure for the preparation of highly reactive metal powders.[1-14] Earlier we reported the preparation of metal slurries prepared by reducing a metal salt in the presence of a phosphine.[9] The synthetic utility of those slurries was in many cases limited to the preparation of organometallic compounds containing that same phosphine. In this manuscript, we report the preparation of highly reactive metal powders of nickel, cobalt, and iron. Like palladium, whose related chemistry we reported,[12] these powders readily react with pentafluorophenyl halides to yield solvent-coordinated organometallic compounds whose coordinated solvents are readily displaced by other ligands and yield isolatable organometallic compounds.

Simple alkyls and aryls of transition metals have been of interest for quite some time.[15] That they are still of current interest and possess a rich chemistry is demonstrated by the recent preparation of pentafluorophenyl compounds of cobalt and nickel stabilized by π-bonded arenes.[16,17] With the metal atom vaporization technique, these interesting organometallic compounds were obtained in 10% and 55% yields.

Reduction in ethereal solvents such as 1,2-dimethoxyethane (glyme) or tetrahydrofuran (THF) of anhydrous nickel halides with 2 equiv or slightly more of lithium and in the presence of about 5% naphthalene based on lithium results in a thick black slurry in a colorless solution. The reaction is usually complete in 3–16 h. This black material is not pyrophoric when exposed to air, yet it shows exceptional reactivity. Such a nickel slurry reacts at room temperature or slightly above with only 1 equiv of iodopentafluorobenzene (eq 1), resulting in a deep orange-brown

$$2\mathrm{Ni} + 2\mathrm{C_6F_5I} \rightarrow \mathrm{Ni(C_6F_5)_2} + \mathrm{NiI_2} \qquad (1)$$

solution and disappearance of most of the black powder. The solution contains a mixture of the solvated species $\mathrm{Ni(C_6F_5)_2}$ and $\mathrm{NiI_2}$.

Addition of 2 equiv of triethylphosphine to such a solution results in a mildly exothermic reaction and an immediate change of color to yellow-green. Workup resulted in a 69% yield of *trans*-$\mathrm{Ni(C_6F_5)_2[P(C_2H_5)_3]_2}$.[18]

The reaction of a nickel slurry obtained from $\mathrm{NiX_2}$ (X = Cl, Br, I) with iodopentafluorobenzene undoubtedly proceeds via $\mathrm{Ni(C_6F_5)I}$, which disproportionates to $\mathrm{Ni(C_6F_5)_2}$ and $\mathrm{NiI_2}$. The intermediate $\mathrm{Ni(C_6F_5)I}$ is strongly implicated since the reaction of nickel powder obtained from $\mathrm{NiBr_2}$ with $\mathrm{C_6F_5Br}$ and the subsequent trapping of the organonickel compound with $\mathrm{P(C_2H_5)_3}$ result in *trans*-$\mathrm{Ni(C_6F_5)Br[P(C_2H_5)_3]_2}$. The product of this reaction suggests that the solvent glyme is acting as a stabilizing ligand for $\mathrm{Ni(C_6F_5)Br}$ since in the absence of any ligands $\mathrm{Ni(C_6F_5)Br}$ decomposes above −80 °C.[17]

$\mathrm{NiCl_2}$, $\mathrm{NiBr_2}$, and $\mathrm{NiI_2}$ yielded nickel slurries which showed similar reactivity with $\mathrm{C_6F_5I}$. However, $\mathrm{C_6F_5Br}$ and a nickel slurry obtained by reducing $\mathrm{NiI_2}$ followed by trapping the organonickel compound with triethylphosphine resulted in a 38% yield of *trans*-$\mathrm{Ni(C_6F_5)_2[P(C_2H_5)_3]_2}$ on the basis of $\mathrm{NiI_2}$ used. Essentially the identical reaction with a nickel slurry obtained from $\mathrm{NiBr_2}$ resulted in an 8% yield of *trans*-$\mathrm{Ni(C_6F_5)Br[P(C_2H_5)_3]_2}$. This enhancement of reactivity of a less-reactive aromatic halide such as bromide with a metal powder derived from the iodide salt of the metal has also been observed with palladium. It strongly suggests that these metal slurries facilitate halogen–halogen exchange of the haloarenes.[19]

Anhydrous cobalt halides have also been reduced with lithium in a similar manner,[20] and the resulting black powders show greater reactivity than nickel powders toward pentafluorophenyl halides. Cobalt powders derived from $\mathrm{CoCl_2}$ were found to be somewhat more reactive than those obtained from $\mathrm{CoBr_2}$ or $\mathrm{CoI_2}$.

The reaction at room temperature between a cobalt slurry and 1 equiv of $\mathrm{C_6F_5I}$ initially is mildly exothermic and results in a deep blue-green solution. After 5 h, most of the black powder has disappeared. Treating this mixture of solvated $\mathrm{Co(C_6F_5)_2}$ and $\mathrm{CoI_2}$ with 2 equiv of $\mathrm{P(C_2H_5)_3}$ per cobalt atom results in a 57% yield of $\mathrm{Co(C_6F_5)_2[P(C_2H_5)_3]_2}$.[21]

Because $\mathrm{C_6F_5Br}$ with the nickel slurry yielded $\mathrm{Ni(C_6F_5)Br}$, an attempt was made to obtain this elusive cobalt analogue.[22] The reaction between a cobalt slurry obtained from $\mathrm{CoBr_2}$ and 1 equiv of $\mathrm{C_6F_5Br}$ at room temperature yielded a deep green-blue solution. Trapping of the products with $\mathrm{P(C_2H_5)_3}$ resulted in a 29% yield of $\mathrm{Co(C_6F_5)_2[P(C_2H_5)_3]_2}$ as the only organocobalt compound.

Since the solvent ethers cannot be removed completely from the slurries even with prolonged pumping, we have not been able to prepare the $\mathrm{M(C_6F_5)_2}$(π-arene), M = Co, Ni, compounds whose very labile π-arene is displaced by ethers. Slurries of Ni and Co prepared by potassium reduction in refluxing toluene did not yield

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(18) *trans*-$\mathrm{Ni(C_6F_5)_2[P(C_2H_5)_3]_2}$ was obtained as golden-yellow crystals from $\mathrm{CH_2Cl_2}$, after *trans*-$\mathrm{NiI_2[P(C_2H_5)_3]_2}$ was removed by extracting the mixture with several small portions of 2-propanol.

(19) One of the referees notes that in an earlier paper[9] we reported the preparation of $\mathrm{Ni(C_6F_5)Br[(C_6H_5)_3P]_2}$ from a slurry obtained from $\mathrm{NiI_2}$, $\mathrm{(C_6H_5)_3P}$, and K which was then allowed to react with $\mathrm{C_6F_5Br}$. Halogen exchange occurs in that system, and the compound should have been reported as the *iodo* derivative.

(20) Examination by VPC of the solvent used in an active-metal preparation before and after reduction showed the formation of volatile organic materials which were not originally present in the solvent. This suggested that a portion of the lithium is involved in cleaving the solvent; hence, we carried out a reduction with excess lithium, noting the first appearance throughout the entire solution of the green color of lithium naphthalide. The unreacted lithium was removed and weighed. This experiment indicated that about 2.3 equiv of lithium per divalent metal salt are necessary to obtain a light green coloration in solution. The exact ratio is determined for each metal salt, and in subsequent reductions, the amount of Li used is just slightly below this value. The slurries prepared in this manner are slightly more reactive than the already very reactive ones obtained by using a 2:1 lithium–metal halide ratio, and also result in slightly higher yields of the organometallic compounds. The preparation of an iron, cobalt, or nickel slurry is identical; a typical preparation of an iron slurry is as follows: a 50 mL two-necked flask equipped with a magnetic stirrer and a condenser topped with an argon inlet was charged with 1.248 g (0.00985 mol) of anhydrous $\mathrm{FeCl_2}$ (Cerac, Inc.) quickly weighed in air, 0.158 g (0.0228 mol) of lithium (freshly cut and cleaned), and 0.151 g (0.00118 mol) of naphthalene. To this mixture under argon was added via syringe 15 mL of freshly distilled glyme, and the mixture was stirred. After 24 h, a black slurry existed in a light beige colored solution. The ratio of Li to $\mathrm{NiBr_2}$ and $\mathrm{CoCl_2}$ is also 2.3:1. The slurries of nickel and cobalt are obtained in colorless solutions. Upon preparation, these metal slurries are allowed to settle, and about half of the solvent is removed via syringe prior to the addition of the organic halide.

(21) $\mathrm{CoI_2[P(C_2H_5)_3]_2}$ was readily removed from the mixture with several small portions of methanol. The remainder was recrystallized from $\mathrm{CH_2Cl_2}$ by slow solvent evaporation to yield greenish-yellow crystals of $\mathrm{Co(C_6F_5)_2[P(C_2H_5)_3]_2}$. The pure compound, which was identified by its mass spectrum, is stable to air in the solid state and very slowly decomposes in solution. The solid decomposes above 140 °C to a deep blue liquid.

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any organometallic compounds with C_6F_5I.

The ethers coordinated to $M(C_6F_5)_2$ (M = Ni, Co, Fe) themselves are quite labile and can be readily displaced with a variety of other ligands. The solvated $Ni(C_6F_5)_2$ reacts instantly at room temperature with $(C_6H_5)_2PH$ to yield, upon workup and recrystallization from toluene, amber-yellow, diamagnetic crystals of $Ni(C_6F_5)_2[(C_6H_5)_2PH]_2 \cdot C_6H_5CH_3$[23] in 31% yield based on nickel.

The preparation of $Ni(C_6F_5)_2[(C_6H_5)_2PH]_2 \cdot C_6H_5CH_3$ via $Ni(C_6F_5)_2$ is noteworthy in that the reaction of a nickel halide with $(C_6H_5)_2PH$ results in $Ni[(C_6H_5)_2P][(C_6H_5)_2PH]_2$.[24] Thus, this organonickel compound would not be directly available via standard arylating reagents.

The displacement of the ether molecule from $Ni(C_6F_5)_2$ is not limited to phosphines. Addition of pyridine to the orange-brown mixture of solvated $Ni(C_6F_5)_2$ and NiI_2 immediately results in a greenish-yellow mixture and the formation of $Ni(C_6F_5)_2(C_5H_5N)_2$.[25] Preliminary evidence indicates that other amines as well as isocyanides also react to yield derivatives of $Ni(C_6F_5)_2$.

$FeCl_2$ reduced in the usual manner with Li in glyme results in a black slurry in a colorless or lightly brown solution. The black iron powder, though, differs from other transition metals reported by us in that it is pyrophoric. The reaction of this powder with C_6F_5I is very exothermic; hence, the slurry is cooled to about 0 °C for the slow addition of 1 equiv of C_6F_5I. The mixture is stirred at 50 °C for 20 h even though it appears most of the reaction is complete in about 2 h. The deep brown solution contains solvated $Fe(C_6F_5)_2$ and FeI_2. This mixture absorbs CO at room temperature and atmospheric pressure without any color change and results in the formation of $Fe(C_6F_5)_2(CO)_2(C_4H_{10}O_2)_2$[26] in 60% yield.

This compound undoubtedly is 6-coordinate with one of the glymes being a molecule of crystallization. On the NMR time scale ($CDCl_3$), both molecules of glyme are equivalent. The IR spectrum of this compound in the carbonyl region is more complex than would be expected for either a cis or a trans arrangement of the carbonyl groups and suggests a mixture of isomers. Such mixtures of isomers have been observed in related compounds of iron.[27] The analogous reaction employing C_6F_5Br as the organic halide yields the same compound.

The reactivity of these metal powders is not limited to activated halides. For example, a 2:1 mixture of a nickel slurry and iodobenzene reacted quantitatively (98% conversion) after 1 h at 85 °C and resulted in a 65% yield of biphenyl, with the remainder benzene. A Ni/THF slurry prepared by codeposition of nickel vapor and THF has been reported to react with iodobenzene and yield 8% biphenyl.[28] The reaction of a nickel slurry, obtained from $NiBr_2$, and bromobenzene resulted in 90% of the bromobenzene reacting after 24 h at 85 °C. The yield of biphenyl was 20% with the remainder benzene. As far as we known, this is the first report of an Ullman-type coupling of an unactivated aryl bromide with nickel under such mild conditions.

In reaction mixtures containing a haloarene and a halogen different than that of the haloarene, we observe halogen–halogen exchange of the haloarene. For example, in a reaction mixture of iodobenzene and a nickel slurry derived from $NiBr_2$, some bromobenzene forms before it reacts further. Similarly, bromobenzene and a nickel slurry containing iodide result in some iodobenzene forming prior to its subsequent reaction. The facile halogen–halogen exchange we observe may allow coupling of very nonreactive haloarenes by employing slurries obtained by reducing NiI_2.

The reactions of the nonactivated haloarenes, iodobenzene, and bromobenzene with the nickel slurry were carried out under relatively dilute and mild conditions. This nickel slurry appears so far to be an exceptional coupling reagent. We are presently conducting further studies of these systems, which we will report on in the near future, as well as on the chemistry of these and other metals.

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[23] Crystals were completely black before melting: mp 161–162 °C; IR (Nujol) ν (P–H) 2360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (aromatic m, 25 H), 2.32 (aliphatic s, 3 H). Anal. Calcd for $C_{43}H_{30}F_{10}NiP_2$: C, 60.24; H, 3.53; F, 22.16. Found: C, 59.74; H, 3.70; F, 21.71.

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[25] The small amount of light green crystals, presumably $NiI_2(C_5H_5N)_4$, which may also be obtained is washed out with water and the remaining material recrystallized from CH_2Cl_2 to yield small, straw-yellow diamagnetic crystals of $Ni(C_6F_5)_2(C_5H_5N)_2$ in 40% yield; mp >280 °C, discolors at about 250 °C. Anal. Calcd for $C_{22}H_{10}F_{10}N_2Ni$: C, 47.95; H, 1.83; F, 34.48; N, 5.08. Found: C, 47.81; H, 1.83; F, 34.26; N, 5.07.

[26] A slow stream of CO was bubbled through the stirred solution for about 2 h (tenfold excess), and then all volatiles were removed under vacuum. The crude material was dissolved in 15 mL of CH_2Cl_2 and anaerobically filtered. Slow solvent evaporation under an inert atmosphere resulted in diamagnetic, yellow, and moisture-sensitive crystals. The crystals often are covered with a brown oily residue which is readily removed by washing the crystals with a small amount of 2:1 hexane–CH_2Cl_2 mixture: mp (sealed tube) dec >90 °C; IR (Nujol) 2090 (s), 2076 (w), 2020 (vs), 1993 (m), 1976 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.58 (s, 4 H), 3.41 (s, 6 H). Both resonances are shifted downfield from those of free glyme in $CDCl_3$. Anal. Calcd for $C_{22}H_{20}F_{10}FeO_6$: C, 42.19; H, 3.22; F, 30.34. Found: C, 42.35; H, 3.30; F, 30.54.

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Role of Ferryl (FeO^{2+}) Complexes in Oxygen Atom Transfer Reactions. Mechanism of Iron(II) Porphyrin Catalyzed Oxygenation of Triphenylphosphine

Sir:

For some time, it has been suspected that under certain circumstances oxygen can react with PFe^{II} (P = a porphyrin dianion) to yield the ferryl complex $PFe^{IV}O$.[1-3] Ferryl complexes have been postulated to exist as stable intermediates in enzymatic reactions (peroxidase compound II),[4] as the active oxidants in mixed-function oxidases,[5] and as a reactive species in aliphatic hydroxylation by hydrogen peroxide–ferrous ion.[6] Recent work in this laboratory has indicated that transient ferrylporphyrin complexes are present during the decomposition of iron(III) peroxoporphyrin complexes via reaction 1[7,8] and has allowed

$$2P\mathrm{Fe^{III}OOFe^{III}}P \rightarrow 2P\mathrm{Fe^{III}OFe^{III}}P + \mathrm{O_2} \tag{1}$$

low-temperature spectroscopic observation of a moderately stable (at −80 to −30 °C) ferryl complex, $BPFe^{IV}O$ (B = *N*-methylimidazole, pyridine, piperidine), which is formed via reaction 2.[9] We now present evidence for the role of ferryl complexes in oxygen atom transfer reactions.

$$P\mathrm{Fe^{III}OOFe^{III}}P + 2\mathrm{B} \rightarrow 2\mathrm{B}P\mathrm{Fe^{IV}O} \tag{2}$$

B*P*FeO reacts with triphenylphosphine at −80 °C in toluene solution over a period of several hours to give triphenylphosphine

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