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- (30) Solubilization of **10** in neutral deuterium oxide (25 °C) leads instantaneously (on the NMR time scale) to exchange of the terminal, acetylenic proton.
- (31) The overwhelming preference for removal of propargyl vs. allylic protons is in accord with the much greater electron-withdrawing power of the ethynyl group than the vinyl group.<sup>32-34</sup>
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- (40) Private communication from Dr. R. P. Halliday, Norwich Pharmacol Co., Norwich, N.Y.

A. Krantz,\* G. S. Lipkowitz

Department of Chemistry, State University of New York  
Stony Brook, New York 11794

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## Highly Reactive Transition Metal Powders. Oxidative Insertion of Nickel, Palladium, and Platinum Metal Powders into Aryl-Halide Bonds

Sir:

We have reported a new procedure for producing highly reactive metal powders.<sup>1,2</sup> This procedure consists of reduction of a metal salt from an ethereal or hydrocarbon solvent with an alkali metal. The primary consideration is that the metal salt in question be partially soluble in the solvent used. In most cases, the alkali metal used had a melting point lower than the boiling point of the solvent;<sup>2</sup> however, this is not necessary in all cases. In this paper we wish to report that, using a modification of this approach, highly reactive transition metal slurries can be prepared. Nickel, palladium, and platinum produced by this method are found to undergo oxidative insertion into C-X bonds and in some cases at relatively low temperatures.

Oxidative addition of RX to transition metals has been observed using the metal atom or metal vaporization approach of Skell.<sup>3,4</sup> Klubunde has reported that nickel and palladium, when cocondensed with aryl halides, readily undergo oxidative insertion into the carbon-halogen bond.<sup>5-8</sup> Cocondensation of nickel or palladium with pentafluorobromobenzene and triethylphosphine gave good yields of the bromopentafluorobis(triethylphosphine)metal complex. The corresponding solution reaction of common commercial nickel powders or

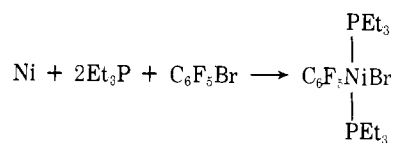
palladium powders with aryl halides has not been observed due to the poor reactivity of these and most other transition metals toward oxidative addition.

Initially we tried the standard approach of reduction of NiI<sub>2</sub>, NiBr<sub>2</sub>, or NiCl<sub>2</sub> with potassium in refluxing THF. Finely divided black nickel powders were obtained; however, they showed rather limited reactivity toward oxidative insertion into carbon-halogen bonds. Similar results were found with palladium.

We have demonstrated with several of the main group elements that the reactivity of the resulting metal is highly dependent on such factors as the solvent, reducing agent, anion, or in the case of some metals the presence of additional alkali salts.<sup>2,9,10</sup> In the case of the transition metals to be discussed in this paper, the presence of a triaryl- or trialkylphosphine during the reduction yields a highly reactive metal slurry. When triethylphosphine is added to NiI<sub>2</sub> in THF, the well known and highly soluble diiodobis(triethylphosphine)nickel(II) complex is formed. Addition of 2 mol of potassium to this mixture, and then heating at reflux, yields a very fine black metal slurry of nickel. The reduction time is very dependent upon the type of phosphine used. For example, when triethylphosphine or triphenylphosphine were used the reduction times were approximately 20 and 2 h, respectively.

The particle size of the black powder is much smaller than that resulting from the standard procedure without the presence of the triethylphosphine. Elemental imaging of the black nickel powder using energy dispersive analysis at a magnification of 5000 indicated that the distribution of nickel, potassium, and iodide is essentially random. When the reduction is completed, the precipitated KI is obtained in almost quantitative yields. These facts, coupled with the fact that the black metal slurry does not flash when added to water, strongly indicates that no potassium remains after the reduction and that the black slurry contains considerable nickel (0).

Not only is the particle size smaller when the reduction is carried out in the presence of the triethylphosphine but the reactivity of the metal toward oxidative additions is greatly enhanced. Upon the addition of pentafluorobromobenzene to the black nickel slurry produced<sup>11</sup> in the presence of triethylphosphine, a rapid reaction occurred yielding bromopentafluorophenylbis(triethylphosphine)nickel(II) in 60% yield.



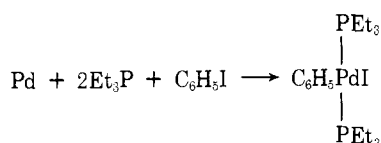
Triphenylphosphine seems to have a similar effect. In fact, nickel slurries produced by reducing NiI<sub>2</sub> in the presence of triphenylphosphine are more reactive than those generated with the triethylphosphine procedure. Addition of pentafluorobromobenzene to the black nickel slurry at -78 °C resulted in an almost immediate reaction. Workup of the reaction yielded 46% of the bromopentafluorophenylbis(triphenylphosphine)nickel(II). Thus, the nickel generated by this method appears to be more reactive but the yield of the oxidative addition product was slightly less. These two sets of experiments suggest that the reaction was not occurring via oxidative addition of the tetrakis(triethylphosphine)nickel(0) or the tetrakis(triphenylphosphine)nickel(0) complexes. Parshall<sup>12</sup> and others<sup>13</sup> have shown that the tetrakis(triphenylphosphine)nickel(0) complex is less reactive than the tetrakis(triethylphosphine)nickel(0) complex in oxidative additions into aryl-halogen bonds. In several cases, reaction of the tetrakis(triphenylphosphine)nickel(0) complex with aryl halides often requires several hours of refluxing. Thus, it would

appear that with these highly reactive black slurries reaction is occurring mainly at the metal surface.<sup>19</sup>

One additional reaction that we carried out which further demonstrates the high reactivity of the nickel slurry is with triethyl phosphite. The highly reactive nickel powder was generated in the presence of triphenylphosphine; to this mixture, triethyl phosphite was added at  $-78^{\circ}\text{C}$ . After 10 min, the mixture was warmed to room temperature and stirred for 1 h. Workup of the reaction mixture yielded over 40% of the tetrakis(triethylphosphite)nickel(0) complex.<sup>18</sup>

The procedure is readily applied to other transition metals.

The reduction of  $\text{PdCl}_2$  with potassium in the presence of triethylphosphine in THF yields a highly reactive black palladium slurry. Addition of pentafluorobromobenzene to the metal slurry produces a rapid reaction.<sup>14</sup> After 1 h the reaction was worked up, yielding 76% of the bromopentafluorophenylbis(triethylphosphine)palladium(II).<sup>15,20</sup> Addition of iodobenzene to the palladium slurry at room temperature for 1 h produced the new complex iodophenylbis(triethylphosphine)palladium(II) in 52% yield.<sup>16</sup>



The reaction has been extended to unreactive halides. The exceptionally high reactivity of the slurries produced by this procedure is exemplified by the reaction of the palladium slurry with chlorobenzene to give the chlorophenylbis(triethylphosphine)palladium(II) in 54% yield based on the palladium halide used.

In a similar manner, highly reactive platinum slurries can be prepared by reduction of platinum halides in the presence of phosphines. The addition of pentafluorobromobenzene to the platinum slurry yielded the known *trans*-bromopentafluorophenylbis(triethylphosphine)platinum(II) in 40% yield, based on the platinum halide used. The reaction has been extended to other aryl halides.

In addition to Ni, Pd, and Pt, we have obtained preliminary evidence that reactive metal powders of Co, Fe, and Cr can be generated by this procedure.

The ability to generate highly reactive transition metal slurries with very simple apparatus will be of extensive value to synthetic inorganic, organic, and organometallic chemistry. We will report in the near future on additional chemistry of the nickel, palladium, and platinum slurries as well as the other transition metals mentioned.

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- $\text{C}_6\text{F}_5\text{Br}$  (4.0 g) was slowly added. Stirring was maintained for 1 h and then the reaction was worked up. Yields are based upon  $\text{NiCl}_2$ .
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- All known complexes had identical melting point, IR, and NMR data with published results.
- The new complex had the correct IR, NMR, and analysis data.
- Alfred P. Sloan Fellow, author to whom correspondence should be sent, at North Dakota State University.
- In preliminary studies, the nickel powders have proven to be a good hydrogenation catalyst. Other catalytic studies with these metals are underway.
- Attempts to find any tetrakis(triethylphosphine)nickel(0) or tris(triethylphosphine)nickel(0) complexes in the reaction mixture have failed. However, it is clear that part of the nickel is in the form of Ni(II) or Ni(I) compounds.
- Up to 30% of the oxidative insertion products may be resulting from soluble Pd complexes. These complexes may include the tetrakis(triethylphosphine)Pd(0) and tris(triethylphosphine)Pd(0) complexes.

Reuben D. Rieke,<sup>\*17</sup> Walter J. Wolf  
Nikola Kujundzić, Arunas V. Kavaliunas

Department of Chemistry, North Dakota State University  
Fargo, North Dakota 58102

Department of Chemistry, University of North Carolina  
Chapel Hill, North Carolina 27514

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## Stereochemistry in Trivalent Nitrogen Compounds. 32. Torsional Barriers in Trinitrobenzenesulfenamides<sup>1</sup>

Sir:

Sulfenamides<sup>2</sup> exhibit substantial barriers to torsion about the sulfur-nitrogen formal single bond.<sup>3</sup> The barriers are greatly increased when the substituent at the sulfonyl sulfur atom is electron withdrawing. The linear free energy correlation for a series of para-substituted benzenesulfenamides<sup>3d</sup> afforded a Hammett reaction constant of  $-2$  and a comparison of the effect of meta and para substituents in the same system indicated that the effect was due to "throughresonance" of the aromatic  $\pi$ -system with an orbital on sulfur. As a result of this polar effect, the barriers in 2,4-dinitrobenzenesulfenamides were the highest which had yet been observed for torsion about N-S formal single bonds. It was of interest to examine the previously unknown 2,4,6-trinitrobenzenesulfenamides. If the barrier to stereomutation were raised by the third nitro group by an amount comparable to the effect of the first two, the sulfenamide configurational unit would have sufficient stereostability in some instances to permit isolation at room temperature of configuratively stable stereoisomers.

We now report the synthesis of a number of representative 2,4,6-trinitrobenzenesulfenamides whose barriers are in sharp variance with the high barriers expected. Instead, the barriers are considerably lower than those in the corresponding dinitrobenzenesulfonyl derivatives and are not much greater than the benzenesulfonyl analogues. Two examples serve to illustrate this point. The barrier in *N,N*-diisopropyl-2,4,6-trinitrobenzenesulfenamide, **2b**, 17.6 kcal/mol, is significantly lower than that in **1b**, 20.6 kcal/mol, and only somewhat higher than that in *N,N*-diisopropylbenzenesulfenamide, 14.3 kcal/mol. The sulfonylsulfonamide **2a** provides a more dramatic example. Figure 1 illustrates the change in barriers in this compound and four related compounds as a function of the number of nitro groups in the benzenesulfonyl residue. As in-