Preparation of Organometallic Compounds from Highly Reactive Metal Powders

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The formation of novel organometallic compounds by the reaction of organic substrates with finely divided metal powders represents a powerful tool for the synthetic chemist. The direct reaction with a zerovalent metal is the only viable method of synthesis for many of these compounds. Accordingly, chemists have been actively developing new methods for increasing the reactivity of metal powders toward organic substrates. Three principal approaches have been developed in recent years: the metal vaporization method, sonochemistry, and the preparation of finely divided metal powders by the reduction of metal salts. A number of new methods of synthesis have resulted from these studies.

A SIGNIFICANT FRACTION OF THE WORLD ECONOMY IS INvolved with metals. Although a substantial portion of this activity involves the use of metals as catalysts in the petrochemical industry, more and more metals are being used in the synthesis of specialty chemicals as well as bulk chemicals. A wide variety of chemical transformations are carried out with homogeneous organometallic reagents. In most cases, each organometallic reagent has its own characteristic chemo-, regio-, and stereoselectivity. In many cases, the desired organometallic reagent is prepared by a chemical transformation of one organometallic reagent into the desired reagent. The final organometallic reagent will, however, contain only those functional groups that can tolerate all of these manipulations. In many cases, the final organometallic reagent would be able to tolerate a number of functional groups. Hence, any approach that could be used to directly prepare this final reagent would be useful.

One such approach would be the direct reaction of an organic molecule with a metal. An example is the reaction of an organic halide with Mg to generate a Grignard reagent:

$$RX + Mg \rightarrow R\text{–}Mg\text{–}X \qquad (1)$$

This reaction is a classic example of an oxidative-addition reaction. However, the Grignard reagent will tolerate only a very limited number of functional groups (for example, ketones, esters, aldehydes, nitriles, and epoxides will react with Grignard reagents). Grignard reagents are extremely useful because of their ability to add to a variety of functional groups forming carbon-carbon bonds. One other primary use of Grignard reagents as well as organolithium reagents is the generation of other organometallic reagents by a metathesis reaction:

$$RMgX \text{ (or RLi)} + MX_2 \rightarrow RMX + MgX_2 \text{ (or LiX)} \qquad (2)$$

$$M = Cd, Zn, Ni, Pt, Pd, Fe, In, Tl, Co, Cr, Mo, W, Cu$$

For the majority of these metals, it would not be possible to prepare the corresponding organometallic species by the direct reaction of the metal with an organic halide because of the low reactivity of the metal. Accordingly, ever since Frankland first reported the oxidative addition of Zn to alkyl iodides in 1849, chemists have been searching for ways to enhance the direct reaction of zerovalent metals with organic substrates (*1*). Early approaches generally included (i) grinding or milling the metal to a finely divided state in an inert atmosphere; (ii) addition of a catalytic amount of I_2, which is highly successful with Mg; (iii) entrainment methods, which make use of the slow addition of highly reactive organic substrates such as CH_2BrCH_2Br throughout the reaction; (iv) use of polar solvents; (v) use of high-temperature, sealed tube reactions; or (vi) addition of inorganic salts (*2*). These approaches were developed in many cases simply by trial and error. A logical approach to increase the reactivity of organic molecules at a metal surface would appear to be found in an understanding of the detailed mechanism of the reaction such as the oxidative-addition reaction. Unfortunately, for the vast majority of metals mentioned above, few if any data are available.

The only reaction that has been studied in detail is that of organic halides at a Mg surface (the Grignard reaction). Whitesides and co-workers have carried out a series of elegant studies (*3*). Several significant factors were delineated from these studies. The rate of reaction with organic iodides and bromides is proportional to the organic halide concentration and to the Mg surface area, which suggests that the reaction occurs at the metal-solution interface. Also, the data suggested that the most plausible limiting, rate-determining step was electron transfer from the metal to the organic halide. As the lifetime of the resulting radical anion would be expected to be very short, this is also tantamount to carbon-halogen bond cleavage. Lack of steric effects on rates also suggested that preadsorption of the alkyl halide onto the Mg surface seems improbable.

Other studies with single crystals have been conducted in an attempt to answer the question of whether the electron transfer is innersphere or outersphere (*4*). However, no definitive conclusion was reached. Whitesides and co-workers also argued that the low susceptibility of Grignard formation to poisoning argues against competitive adsorption by other solution components. However, Burns and Rieke demonstrated that, when highly reactive Mg is used, Grignard formation can be totally inhibited at low temperatures (−78°C) by the presence of certain Lewis bases such as alkyl nitriles (*5*). This result would strongly support a mechanism in

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which adsorption of the organic halide occurs first, followed by the rate-limiting electron transfer.

Another controversial aspect of the mechanism of Grignard formation is the fate of the organic radicals formed after the rate-limiting, single-electron transfer from the Mg surface. There is general agreement that the formation of Grignard reagents involves the intermediacy of free radicals (*6–8*). Whether these radicals are adsorbed on the Mg surface, exist free in the solution close to the Mg surface, or are involved in an equilibrium between these two species is not entirely settled. An analytical model has been presented by Garst *et al.*, which assumes that the radicals "diffuse freely in solution at all times" (*9*). Ashby and Oswald presented data that indicate that approximately 25% of the Grignard reagent is formed from radicals that diffuse into the solvent phase and then return to the Mg surface to receive a second electron and form the Grignard reagent (*10*). Recently, however, Walborsky and Rachon presented data that demonstrate that several secondary and vinyl chiral halides lead to Grignard reagents with retention of configuration as high as 71% (*11*). As some of these model systems involve radicals with known inversion rates as high as 10^{11} s^{-1}, the results strongly support surface-adsorbed radicals at least for these species.

Two primary conclusions can be drawn from these studies. First, a reaction at a metal surface can be expected to be a function of surface area. Hence, any process that increases the effective surface area should have a rate-enhancing effect. In conjunction with this is the obvious desirability of removing all passivating surface-oxide coatings. Second, for oxidative-addition reactions the rate-limiting step for Mg is single-electron transfer, which is likely to be the rate-limiting step for most metals.

General Methods of Metal Activation

In recent years, three major approaches have developed for increasing the reactivity of metal powders: metal vaporization, use of ultrasound, and reduction of metal salts. An in-depth review of each approach is beyond the scope of this article and only the reductions of metal salts will be treated in detail.

The work initiated by Skell and co-workers in the early 1960s on carbene chemistry proved to have a profound influence on the chemistry of metals and metal powders (*12*). These were the first studies in which high temperatures were used to generate unstable gaseous species under vacuum inside a reaction vessel cooled to liquid-nitrogen temperatures. It was shown that highly reactive, vaporized carbon species could be generated from a carbon arc. Researchers carried out a number of novel reactions by condensing the highly reactive carbon species with organic compounds on the liquid nitrogen–cooled walls of the vessel.

It was only a matter of time before this technique was applied to main group metals as well as transition metals (*13–19*). These studies clearly demonstrated that all metal atoms can be considered to be highly reactive. The cocondensation of metal atoms with a wide variety of organic and inorganic substrates proved to be a powerful new approach to the formation of many heretofore unknown organometallic compounds. A variation on this method was the cocondensation of metal atoms with solvents such as benzene, tetrahydrofuran (THF), and hexane (*19*). Upon melting, a slurry of finely divided metal particles was obtained that exhibited high reactivity, particularly toward oxidative-addition reactions. Although the metal slurries prepared in this manner were highly reactive, they were not as reactive toward oxidative addition as the metal powders prepared by reduction of metal salts (discussed below). The basic metal-vaporization approach was remarkably successful in the synthesis of novel arene and π-complexes but was of limited value in organic synthesis. One of the principal reasons for this difference is that the organic substrate must be volatile; this would prove intractable for many large organic materials. However, the technique of reacting metal atoms with ligands in cold solutions has been reported. This suggests the possibility of performing such reactions with large, nonvolatile organic molecules (*20, 21*).

The use of ultrasound to accelerate heterogeneous reactions is increasing rapidly (*22–25*). This technique has generated a field of study that is commonly labeled sonochemistry. Much of the rapid rise in the popularity of sonochemistry stems from the fact that ultrasound can be delivered safely, conveniently, and with inexpensive equipment. Ultrasound can affect chemical reactions at a metal-solution interface when the sound waves induce "cavitation" or the rapid growth and sudden collapse of bubbles at the metal-solution interface. The rapid collapse leads to intense, localized pressure and temperature differentials as well as electric discharges. Principal uses have involved the generation of organolithium, organozinc, and organocopper reagents. The majority of examples reported involved organic halides, which can be considered to be "quite reactive" toward standard activated metals. The primary advantages include reduced reaction times and temperatures, increased yields, and in some cases superior regioselectivity. Luche and co-workers (*25*) demonstrated that less reactive alkyl and aryl bromides can be utilized if a metathesis step is included. Sonication of the organic halide, Li, and metal salt of the desired organometallic reagent ultimately yields the desired organometallic reagent. The process involves the initial formation of an organolithium reagent. Thus, this procedure precludes the presence of most functional groups in the organic halide.

Reduction of Metal Salts

In 1972, my co-workers and I reported a general approach for preparing highly reactive metal powders by reducing metal salts in ethereal or hydrocarbon solvents, using alkali metals as reducing agents (*2, 26, 27*). Several basic approaches are possible, and each has its own particular advantages. For some metals, all approaches lead to metal powders of identical reactivity. However, for some metals one method can lead to far superior reactivity. High reactivity, for the most part, refers to oxidative-addition reactions. Since our initial report, several other reduction methods have been reported including metal-graphite compounds and the Mg-anthracene complex (*28*).

Although our initial entry into this area of study involved the reduction of $MgCl_2$ with potassium biphenylide, our early work concentrated on reductions without the use of electron carriers. In this approach, reductions are conveniently carried out with an alkali metal and a solvent whose boiling point exceeds the melting point of the alkali metal:

$$MX_n + nK \rightarrow M^* + nKX \qquad (3)$$

The metal salt to be reduced must also be partially soluble in the solvent, and the reductions are carried out under an Ar atmosphere. The reductions are exothermic and generally are complete within a few hours. In addition to the metal powder, one or more moles of alkali salt are generated. Convenient systems of reducing agents and solvents include K and THF, Na and 1,2-dimethoxyethane, and Na or K with benzene or toluene.

A second general approach is to use an alkali metal in conjunction with an electron carrier such as naphthalene. The electron carrier is normally used in less than stoichiometric proportions, generally 5 to 10% by mole, based on the reduction of the metal salt. This procedure allows reductions to be carried out at ambient temperatures or at least at lower temperatures than in the previous approach, which requires refluxing. A convenient reducing metal is Li. Not only is the procedure much safer when Li is used rather than Na or K, but in many cases the reactivity of the metal powders is greater.

A third approach is to use a stoichiometric amount of preformed lithium naphthalide. This approach allows for very rapid generation of the metal powders in that the reductions are diffusion-controlled. Very low to ambient temperatures can be used for the reduction. In some cases the reductions are slower at low temperatures because of the low solubility of the metal salts. This approach frequently generates the most active metals, as the relatively short reduction times at low temperatures lead to reduced sintering (or growth) of the metal particles.

For many of the metals generated by one of the above three general methods, the finely divided black metals settle after standing for a few hours, leaving a clear, and in most cases colorless, solution. The solvent can be removed via cannula. Thus the metal powder can be washed to remove the electron carrier as well as the alkali salt, especially if it is a Li salt. Moreover, a different solvent may be added at this point, providing versatility in solvent choice for subsequent reactions. An important aspect of the highly reactive metal powders is their convenient preparation. Also, the apparatus required is very inexpensive and simple.

Physical Characteristics of Highly Reactive Metal Powders

The reductions generate a finely divided black powder. Particle size analyses indicate a range of sizes from 1 to 2 μm to the submicrometer range depending on the metal and, more importantly, on the method of preparation. In cases such as Ni and Cu, black colloidal suspensions are obtained that do not settle and cannot be filtered. In some cases, even centrifugation is not successful. It should be pointed out that the particle size analyses as well as surface area studies have been done on samples that have been collected, dried, and sent off for analysis and likely have experienced considerable sintering. Scanning electron microscopy (SEM) photographs reveal a range from sponge-like material to polycrystalline material (*2*). X-ray powder diffraction studies for metals such as Al and In show diffraction lines for both the metal and the alkali salt; x-ray powder diffraction studies for Mg and Co show lines only for the alkali salt. This result suggests either that the metal in this latter case is amorphous or that the particle size is less than 0.1 μm. In the case of Co, a sample heated to 300°C under Ar and then reexamined showed diffraction lines due to Co, suggesting the small crystallites had sintered upon heating (*26*).

Electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy have been carried out on several metals, and in all cases the metal has been shown to be in the zerovalent state. Bulk analysis also clearly shows that the metal powders are complex materials containing in many cases significant quantities of C, H, O, halogens, and alkali metal.

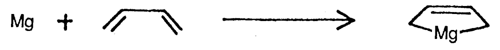
General Reaction Characteristics of Metal Powders

The finely divided black metal powders obtained by the reduction of metal salts exhibit very high chemical reactivities relative to their commercial counterparts or metal powders prepared by other methods. This high reactivity allows a number of metals to now undergo oxidative-addition reactions that were not previously possible. The net result has been the preparation of a number of novel organometallic species, in many cases with a wide variety of functional groups present. Several new synthetic transformations have been developed and dramatic enhancement of yields of known reactions have been obtained as a result of the much lower reaction temperatures or shorter reaction times or both. This approach has been used to prepare highly reactive Mg, Zn, Al, In, Th, U, Tl, Cr, Mn, Fe, Ni, Co, Cd, Cu, Pt, Pd, and Ca. It is anticipated that this approach will yield finely divided highly reactive metals for most of the metals in the periodic table.

A detailed understanding of the origins of the high reactivity is not in hand. It is clear that the metals are generated in a finely divided state, that they have high surface areas, and that they are relatively free of oxide coatings. This large increase in surface area may account for the high reactivity. However, as the reactivity toward oxidative-addition reactions substantially exceeds the reactivity of the metal slurries prepared by the metal vaporization–cocondensation technique and as these metal powders appear to have surface areas similar to those of our metals, it would appear that other factors are also involved. Absorbed anions generated from solvent cleavage during reduction or the alkali salts generated or both may facilitate electron transfer in the rate-limiting step. High densities of dislocations and imperfections may also accelerate reaction rates.

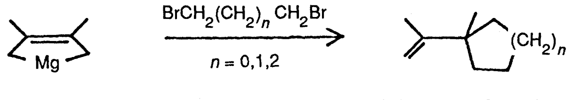
Magnesium. Perhaps the most widely known and used organometallic reagent is the Grignard reagent. Although commonly thought to be completely general, there are many organic halides that do not form Grignard reagents. Also, in some cases the Grignard reagents are not stable under the reaction conditions that commonly involve refluxing in THF. Use of highly reactive Mg prepared by the reduction method dramatically extends the Grignard reaction to many organic halides considered unreactive, including organic chlorides and even organic fluorides. Our early reports primarily involved reduction of $MgCl_2$ or $MgBr_2$ with K (*2, 26, 27*). However, recent studies have shown not only that reductions with Li and naphthalene as an electron carrier are safer and more convenient but also that the metal is more reactive (*5*). The high reactivity of the Mg is demonstrated by its ability to form a Grignard reagent with bromobenzene in a few minutes at −78°C. Chlorobenzene reacts even at 0°C. Most dramatic is the ability to generate a Grignard reagent from fluorobenzene. Most organic textbooks today still state that one cannot form Grignard reagents from aryl fluorides. High yields of Grignard reagents have been prepared from a wide variety of alkyl, vinyl, and aryl halides. In many of these cases, standard conditions with ordinary Mg turnings either do not work or give low yields. A simple example that demonstrates the advantage of generating Grignard reagents at low temperatures is the reaction of 3-halophenoxypropane (*26*). Although the Grignard reagent is easy to generate at room temperature or above, it eliminates the phenoxy group by an S_N2 reaction to generate cyclopropane. This reaction is, in fact, a standard way to prepare cyclopropanes, and the cyclization cannot be stopped. However, by using the highly reactive Mg, one can prepare the Grignard reagent at −78°C and it does not cyclize at these low temperatures. It then can be added to a variety of other substrates in standard Grignard reactions.

In 1967, Ramsden demonstrated that under forcing conditions Mg will react with 1,3-butadiene to generate a bis-Grignard reagent (shown as a metallocycle, but it is really a polymer) (*29*):



(4)

Inorganic chemists have made considerable use of this and other symmetrical 1,3-dienes in the synthesis of a wide variety of transition-metal complexes. Organic chemists, however, made little use of this chemistry, primarily because of the difficulty of preparation. This is particularly true for unsymmetrical 1,3-dienes and dienes with several alkyl groups about the double bonds. The use of highly reactive Mg allows the reaction to proceed readily at room temperature with a wide variety of 1,3-dienes (*30*). A number of novel transformations were reported, based on the use of these bis-Grignard reagents. Among the reactions reported was the ready formation of 4-, 5-, and 6-membered ring carbocycles containing a quaternary center.



(5)

This route promises to be a particularly rich area of study.

Zinc. The direct reaction of Zn metal with organic iodides dates back to Frankland's work of 1850. Several modes of activation of the metal have been reported (*26*). Even using these activating methods, one is essentially limited to alkyl iodides and alkyl bromides. However, Zn slurries prepared by the reduction of anhydrous Zn salts undergo ready oxidative addition to alkyl iodides, bromides, and chlorides. Moreover, they readily react with vinyl bromides as well as aryl iodides and bromides. Significantly, these substrates can contain a wide spectrum of functional groups including esters, nitriles, ketones, and other halides (*31*). It was not possible to prepare these functionalized organozinc compounds before these methods were discovered, as the only approach to these compounds was by metathesis reactions with Grignard or organolithium reagents. The organozinc reagents can be added to Cu(I) salts to prepare heterocuprates, which can be cross-coupled with acid chlorides to generate highly functionalized ketones (*32*). These heterocuprates will also undergo conjugate addition to α,β-unsaturated ketones. With the highly reactive Zn it is also possible to carry out the Reformatsky reaction (reaction of α-bromoester with Zn in the presence of aldehyde or ketone to yield β-hydroxyesters) at room temperature or below with near quantitative yields (*2, 26*). One of the most useful reactions involving Zn is the Simmons-Smith reaction, which is a general approach for the preparation of cyclopropanes. It commonly uses a Zn-Cu couple with the highly reactive diiodomethane. The highly reactive Zn prepared by metal salt reductions is so reactive toward diiodomethane that the reaction is difficult to control. Methylene bromide, which is much easier to work with, reacts readily to give near quantitative yields of the corresponding cyclopropanes. Even the much less reactive 1,1-dibromoethane reacts to yield methyl-substituted cyclopropanes (*2, 26*).

Cadmium. Organocadmium reagents have traditionally been used in a cross-coupling reaction with acid chlorides to yield ketones. However, the primary approaches to these reagents were metathesis reactions with Grignard or organolithium reagents, which precluded any functionality. Highly reactive Cd powders prepared by the reaction of Cd salts were found to undergo oxidative-addition reactions with alkyl and aryl iodides and bromides to directly yield organocadmium reagents (*26*). Significantly, these reactions tolerated a wide variety of functional groups. These organocadmium reagents were found to undergo a number of cross-coupling reactions.

Nickel. Nickel metal has been used for many years in a variety of catalysts. However, the direct reaction of Ni powders to generate organometallic complexes was limited to one or two highly reactive organic halides such as allylic or benzylic iodides or bromides. In marked contrast, the reduction of Ni(II) halides with Li yields a highly reactive Ni powder that undergoes oxidative addition to aryl, vinyl, and alkyl carbon-halogen bonds (*2, 26*). Moreover, these substrates can contain a variety of functional groups. These novel organonickel reagents perform a variety of cross-coupling reactions. Numerous substituted iodo- and bromobenzenes gave the corresponding biphenyls in good to high yields. The cross-coupling of benzyl halides with acid chlorides mediated by the active Ni gives high yields of the corresponding benzyl ketones. One can prepare 3-arylpropane-nitriles by refluxing a mixture of benzyl halides, bromoacetonitrile, and activated Ni in dimethoxyethane. Also, the activated Ni undergoes oxidative addition to α-halonitriles, which will add to aryl or alkyl aldehydes to give the corresponding β-hydroxynitriles in good yields. The organonickel reagents do not add to ketones; this chemoselectivity should prove to be quite useful. Several other transformations mediated by the active Ni have been reported (*2, 26*).

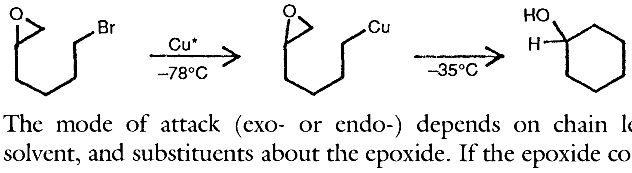
Copper. The use of organocopper reagents in synthesis has been growing dramatically over the past few years. The Ullmann biaryl synthesis involves the reaction of Cu powder with aryl iodides containing electron-withdrawing groups. Typically the reactions are run in sealed tubes at temperatures of 100° to 300°C for times ranging from hours to days. Of much more synthetic utility are the organocopper, lithium diorganocuprates, and various heterocuprate reagents developed over the past few years. These organocopper reagents are usually prepared by the metathesis of organolithium or Grignard reagents with Cu(I) salts. Accordingly, the presence of functionality is severely limited. Recently, we have reported that reduction of copper halide phosphine complexes yields an extremely reactive zerovalent Cu reagent (*33*). Although this Cu reagent is not characterized yet, its reactivity is highly dependent on the choice of phosphine:

$$\mathrm{CuI \cdot PR_3 + Li\ naphthalide \rightarrow Cu(0)_{\mathit{y}} \cdot (PR_3)_{\mathit{x}} + LiI} \qquad (6)$$

The more electron-donating the phosphine, the more reactive the zerovalent Cu reagent is. As the reagent appears to be homogeneous, we suggest that a novel Cu cluster is produced. The Cu solutions are very dark and do contain solid black material that is presumably Cu metal. Accordingly, it is possible that an equilibrium exists between some soluble highly reactive cluster and the finely divided Cu metal.

The zerovalent Cu reagent is highly reactive toward oxidative-addition reactions. Primary alkyl iodides and bromides react at temperatures as low as −78°C in a few minutes to generate an organocopper species $\mathrm{R'Cu \cdot PR_3}$. The reactivity of the organocopper is highly dependent on the particular phosphine used in the initial complex. A greater electron-donating tendency in the phosphine leads to a more nucleophilic organocopper reagent. Not only will primary halides react but also aryl and vinyl iodides and bromides will undergo oxidative addition at room temperatures or below (in some cases as low as −10° or −20°C).

Several significant features should be noted. Although much work remains to be done, these organocopper reagents appear to undergo most of the standard reactions of organocopper reagents as well as the lower and higher order cuprates. Moreover, these organocopper reagents can tolerate a wide spectrum of functionality, including esters, nitriles, ketones, other halides, and even remote epoxides (*33*). The organocopper reagents can be cross-coupled with acid chlorides to produce ketones. They can be conjugatively added to α,β-unsaturated ketones. They will ring open epoxides. The ability to prepare an organocopper reagent containing an epoxide has resulted in a new carbocyclization reaction shown below:



(7)

The mode of attack (exo- or endo-) depends on chain length, solvent, and substituents about the epoxide. If the epoxide contains a remote ester group, the alkoxide anion generated in the epoxide ring-opening can attack the ester group, yielding a lactone. This tandem carbocyclization-lactonization is one example of the multitude of intramolecular reactions that are likely to be developed with these highly functionalized organocopper reagents.

As the highly reactive Cu is soluble, it can directly metallate insoluble polymers. For example, the polymer of *p*-bromostyrene can readily be converted into the corresponding organocopper derivative with the highly reactive Cu. This organocopper species, in turn, can react with a variety of electrophiles to prepare highly derivatized insoluble polymers. Starting with a phosphine-containing polymer, highly reactive Cu can be prepared that is bound to the polymer. This reagent will, in turn, react with alkyl and aryl halides to generate organocopper reagents (*34*).

Other metals. The limited length of this article does not permit the discussion of the chemistry of active Al, In, Th, U, Cr, Mn, Fe, Co, Pt, Tl, and Ca metals prepared by the reduction of metal salts (*2, 26*). For most of these metals, little development has been carried out. However, it is anticipated that extensive chemistry will be developed for most of these metal powders.

Conclusions

The chemistry of organic substrates with metal powders is a powerful synthetic tool. Although many advances have been made, it is clear that this area of study can best be described as being in its infancy. A better understanding of the mechanistic details of the reactions of organic substrates at a metal surface will surely lead to still better ways to activate a metal, which will ultimately lead to the development of many new chemical transformations as well as new catalysts.

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