

Organic Chemistry of Metal Vapors

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An intense interest in the synthetic uses of high-temperature species at low temperature has developed in recent years. Metal atoms (vapors)¹ are among the most easily produced high-temperature species, and their synthetic chemistry is interesting and useful. This Account deals with the organic chemistry of these metal vapors, especially transition-metal vapors.

The chemistry of high-temperature species is an old and fruitful field. Most studies of high-temperature species have been carried out at low temperature (e.g., 77 K). Reasons for low temperature are twofold: (1) reaction rates are slowed down so that intermediate reactive species can be observed spectroscopically (i.e., matrix isolation spectroscopy); (2) usually the high-temperature species must be generated in a vacuum system, and in order to maintain low vapor pressures in the system all incoming reactants must be immediately condensed.

Many reactive particles can be considered to come under the heading of high-temperature species. Hydrogen atoms,² organic radicals,³ alkali metal atoms,^{2,4} divalent carbon,⁵ boron,⁶ silicon,⁷ free atoms of the transition elements,⁸ and others have been produced. However, even though there have been many excellent flow system and matrix isolation studies of such species,^{2,8} only in very recent years have chemists really started using these materials on a synthetic basis, that is, as reagents to make new, interesting, and usually isolable compounds. In this regard, Timms⁹ has written an excellent review in an attempt to orientate the whole field of synthesis employing high-temperature species at low temperature. Many species are discussed in that review of 1972, which mainly covered inorganic reactions. Since that time, however, much work has been done, most of it concerned with organic reactions of metal atoms.

Metal Vaporizations

Using metal vapors as chemical reagents sounds exotic. However, for many years industrial concerns

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have vaporized metals for deposition as thin films on materials ranging from plastics to clean metal films, and the technology needed even for carrying out industrial scale continuous vaporizations is available. Only in very recent years have chemists begun to apply these vaporization methods in chemical reactions.

Most metals vaporize as mainly monatomic species.¹ Thus, the metallic elements may now be studied in their atomic state, and we can begin to fill a void concerning their chemistry. That is, much is known about the chemistry of metals through their compounds, but very little is known about the chemistry of the elements themselves. *The vaporization method yields these elements in reactive high chemical potential states, a condition which allows each element to have a rich and varied chemistry of its own at low temperature.*

Pioneering Work

Skell and Wescott¹⁰ must be given much of the credit for bringing things to the point where synthesis can be carried out using high-temperature species. They devised a carbon vapor reactor for study of the reactions of carbon species, C₁, C₂, and C₃, with organic compounds at 77 K (−196°C).¹¹ Carbon was vaporized by arcing carbon electrodes in a vacuum chamber. The resulting carbon vapor was codeposited with organic substrates on the liquid-nitrogen-cooled walls of the reactor. Today, the same basic reactor design is used for most metal-vapor chemistry.

At the same time that the Skell and Wescott work

- (1) B. Siegel, *Q. Rev. Chem. Soc.*, **19**, 77 (1965).
- (2) E. W. R. Steacie, "Atomic and Free Radical Reactions", 2nd ed, Reinhold, New York, N.Y., 1954; R. J. Cvetanovic, *Adv. Photochem.*, **1**, 115 (1963).
- (3) A. M. Brass and H. P. Broida, "Formation and Trapping of Free Radicals", Academic Press, New York, N.Y., 1960.
- (4) Von B. Mile, *Angew. Chem.*, **80**, (13), 519 (1968).
- (5) W. Kirmse, "Carbene Chemistry", Academic Press, New York, N.Y., 1971; M. Jones, Jr., and R. A. Moss, Ed., "Carbenes", Vol. 1, Wiley, New York, N.Y., 1973.
- (6) P. L. Timms, *Chem. Commun.*, 258 (1968).
- (7) P. S. Skell and P. W. Owen, *J. Am. Chem. Soc.*, **94**, 5434 (1972); also cf. *ibid.*, **89**, 3933 (1967).
- (8) D. M. Mann and H. P. Broida, *J. Chem. Phys.*, **55**, 84 (1971); M. Poliakoff and J. J. Turner, *J. Chem. Soc., Perkin Trans. 2*, 70, 93 (1974); D. W. Green and D. M. Gruen, *J. Chem. Phys.*, **60**, 1797 (1974); G. A. Ozin and A. V. Voet, *Acc. Chem. Res.*, **6**, 313 (1973).
- (9) P. L. Timms, *Adv. Inorg. Radiochem.*, **14**, 121 (1972).
- (10) P. S. Skell, L. D. Wescott, J. P. Golstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965).
- (11) P. S. Skell, J. J. Havel, and M. J. McGlinchey, *Acc. Chem. Res.*, **6**, 97 (1973).

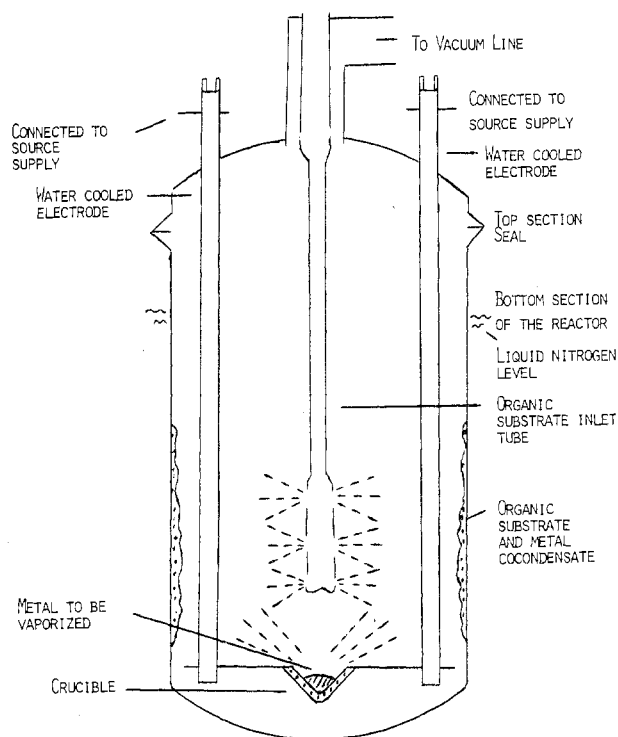


Figure 1.

appeared, Timms, Kents, Ehlert, and Margrave published their first detailed work on the low-temperature chemistry of high-temperature-generated SiF_2 . They used techniques similar to those of Skell and Wescott.¹²

Timms was the first to apply these techniques to metals.¹³ He has been concerned with inorganic as well as organic substrates, and has modified and improved the method to the point where it is now a viable synthetic technique.⁹

The amounts of metals that can be vaporized in current reactors are substantial, usually 0.5–2 g, sometimes up to 50 g, and reactors capable of handling kilograms of metals may be feasible.¹⁴

Apparatus, Reaction Conditions, and Limitations

We have designed an apparatus that is simple to assemble and operate. A description of it was published previously,^{15,16} and the theory and operation of it are explained in Timms' article⁹ and by Figure 1. A simple metal atom reactor of this type, suitable for undergraduate laboratory work as well as for research, will soon be marketed by Kontes–Martin Glass Co.

In this apparatus metals are vaporized using resistive heating. The metal vapor deposits on the inside walls of the reactor while vapors of organic substrate are directed through a shower head and codeposited in the same area. Low-temperature walls are required from a practical viewpoint since, in order to maintain good vacuum and not allow the substrate to come

into the zone of the high-temperature source, the reactants must immediately be condensed. This must be a temperature where the vapor pressure of the reactants is $\leq 10^{-5}$ Torr. Experimentally, this is not difficult to achieve since liquid nitrogen cooling is satisfactory. However, higher temperatures are sometimes desirable in terms of increased reaction rates between the substrate and high-temperature species. A competing low activation energy process is always repolymerization of the vaporized species, which is often a serious problem, one that will be discussed in more detail later.

Similar codeposition setups can be used employing metal vaporizations with electron guns,^{7,9,17} arcs,¹⁸ and lasers.¹⁹ Metals Mg, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Pd, Pt, Cu, Ag, Zn, and Cd have all been vaporized using resistive heating and our simple apparatus. Also, by resistive heating others have vaporized Mo, W, Au, Ge, and Sn as well. Thus, we are not limited in vaporization techniques. Instead, the main disadvantage in using a vapor deposition reactor such as the one described is the substrate vaporization. It must enter the reactor as a vapor, which limits its boiling range to about -80 to $+200^\circ\text{C}$ at atmospheric pressure. Substrates boiling below that (N_2 , CO , $\text{CH}_2=\text{CH}_2$) cause high vapor pressures in the reactor, and substances boiling above that cause difficulty in just passing them into the reactor even under good vacuum. Refinements of the apparatus utilizing heated inlet passages or liquid inlets with "flash pans" extend the range somewhat. However, in order to study solid or liquid substrates dissolved in solutions, Timms^{20,21} and Green¹⁷ have cleverly devised rotating solution reactors where the metal vapors proceed upward into a cold film of solution on the upper inside of the reactor, or are sprayed onto the walls as a solution by a rapidly rotating disk. The vaporization source is stationary, but the reactor revolves in a cold bath exactly like a rotary evaporator apparatus. The low-temperature bath is cold enough to keep the vapor pressure of the solvent and substrate low enough so that the metal can be vaporized.^{20,21} Alkane solvents are best since they appear not to interact with metal atoms.

We have carried out solution-phase metal atom reactions using the reactor shown in Figure 1.^{15,16} However, special vaporization sources were employed so that the metal vapor was directed downward into a cold, stirred solution of the desired reagents. This method does appear to have wide applicability, and will certainly find more and more use in our laboratories.

Organic Reactions

The reactivity of each metal–substrate pair depends on a number of complicated factors. Among these are acid–base properties, electronic spin state of the metal atom, availability of orbitals for π com-

(12) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **87**, 2824 (1965).

(13) P. L. Timms, *Chem. Commun.*, 1525 (1968).

(14) W. Reichelt, Symposium "Metal Atoms in Chemical Synthesis," Mercksche Gesellschaft für Kunst und Wissenschaft e.v., Darmstadt, West Germany, May 1974, *Angew. Chem.*, **87**, 239 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 218 (1975).

(15) K. J. Klabunde, *Angew. Chem.*, **87**, 309 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 287 (1975).

(16) K. J. Klabunde and H. F. Efnér, *Inorg. Chem.*, **14**, 789 (1975).

(17) F. W. S. Benfield, M. L. H. Green, J. S. Ogden, and D. Young, *J. Chem. Soc., Chem. Commun.*, 866 (1973).

(18) P. S. Skell and J. E. Girard, *J. Am. Chem. Soc.*, **94**, 5518 (1972); also private communications with P. S. Skell and J. E. Girard.

(19) E. Koerner von Gustorf, O. Jaenicke, and O. E. Polansky, *Angew. Chem., Int. Ed. Engl.*, **11**, 532 (1972).

(20) P. L. Timms, *Chem. Eng. News*, **52**, 23 (April 29, 1974); R. MacKenzie and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 650 (1974).

(21) P. L. Timms, *Angew. Chem.*, **87**, 295 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 273 (1975).

plexation, and, very crudely, the energy input (heat of vaporization) to the metal. Probably most important are the acid-base properties and the π complexation (very low activation energy processes, which is needed for very low temperature reactions). Indeed, one of the most efficient reactions we have found is Ca atoms (strong base) with perfluoro olefins (capable of accepting bases and possessing π systems).²² Furthermore, it would be expected that metals with low ionization potentials would interact efficiently with electron-acceptor systems. Also, weak bonds (e.g., C-I) should be susceptible to radical-type processes with metal atoms, and metals with readily available d orbitals, such as the transition metals, should complex well with organic compounds possessing nonbonding electrons or π electrons.

Intuitively, it would be expected that electron-transfer processes (charge transfer), radical abstraction processes, and σ -donor and π -donor complexations should take place when organic molecules are allowed to cocondense with metal atoms. However, always in competition with these processes is the repolymerization of the metal atoms. Since this repolymerization is of obvious importance (with regard to metal film formations and to efficiency of metal atom-substrate reactions), a great deal of research regarding this process is warranted. As yet, little definitive work has been done.

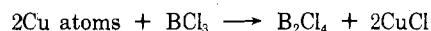
Regarding the dimerization of metal atoms in a low-temperature matrix Hanlan and Ozin have found the dimers to be readily formed and reactive with CO to form unusual metal carbonyl dimers (by matrix isolation spectroscopy).²³ From qualitative observations in our laboratory we can say that, unless nonbonding or π electrons are available in the chemical substrate being deposited with the metal atoms (so that low-temperature complex formation can occur), the metal atoms will rapidly repolymerize at 77 K. Thus, alkanes have little effectiveness at preventing metal atom recombination at 77 K. Perfluoroalkanes behave similarly to alkanes in this respect, which would indicate that nonbonding electrons that are tightly held (nonbasic) are not effective in complexation with metal atoms.

Organohalides with Metal Atoms. The formation of Grignard reagents is a famous reaction of a metal with organohalides. Skell and Girard¹⁸ were able to produce the long-sought-after nonsolvated Grignard reagents simply by cocondensing Mg atoms with R-X. The formation of these RMgX reagents did not take place immediately upon -196°C cocondensation. Apparently first a black RX-Mg complex was formed that rearranged to RMgX on matrix warm-up. Although not yet investigated in much detail, Skell and Girard's nonsolvated Grignard reagents exhibited unusual properties. Thus, acetone was not added by the nonsolvated reagents—only proton abstraction took place. Also, crotonaldehyde added the Grignard 1,2 rather than 1,4 as normally.¹⁸

Skell and Girard have made the only comparisons of thermally vaporized metal vs. arc vaporized metal. Thermally (resistively heated) vaporized Mg yields atoms in a ground singlet state which readily form

charge-transfer complexes at low temperature with alkyl halides and ammonia. However, arc vaporized Mg (brilliant purple arc) yields high concentrations of excited triplet state Mg atoms which react in radical-type processes.¹⁸

Timms reported very early on the reactions of Cu, Ag, and Au atoms with alkyl halides.^{9,13} These metals, especially Cu, acted as halogen atom abstraction reagents. Alkyl radicals were formed which coupled and disproportionated. In some situations these types of reactions can be synthetically useful, i.e., B_2Cl_4 can be produced in 10-g batches.²⁴



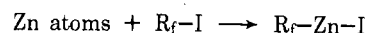
The radical-abstraction work is somewhat reminiscent of Skell's early work on the vapor-phase reactions of Na-K vapor with organohalides.²⁵ Here, however, high temperatures were employed, and some Wurtz-type syntheses were quite successful.

Allyl halides react with metal atoms. Piper and Timms²⁶ cocondensed Ni atoms with allyl chloride and allyl bromide to yield the π -allyl dimers. The re-



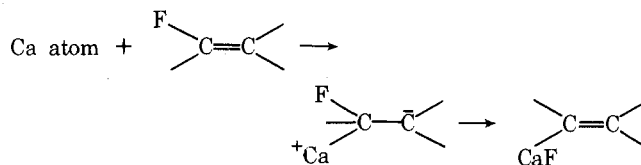
actions were efficient, and this serves as a good method for producing the complexes. Platinum atoms²⁷ reacted with allyl halides in the same fashion, as did palladium atoms²⁸ (under some conditions even palladium metal itself reacts with allyl halides).

Most of our metal atom research has been concerned with organohalide reactions. First, we reported on the production of nonsolvated perfluoroorganozinc halides.²⁹ Only iodides reacted with the



readily formed zinc vapor. It was interesting to find that these nonsolvated R_fZnI compounds were reactive and unstable even at relatively low temperatures, which is not true for the solvated analogs.³⁰ In the case of CF_3ZnI , decomposition to yield CF_2 readily took place.

Calcium atoms reacted very efficiently with perfluoro olefins and hexafluorobenzene to yield C-F insertion.²² This is the only C-F metal atom insertion reported. Perfluoro alkanes did not react, but perfluoro unsaturated systems were quite capable of accepting the strong-base calcium atom.



Our interest in these metal atom oxidative insertion reactions (alternative terminology, oxidative addition to metal atoms) continued. In the transition-metal series many fascinating species can be envisioned by carrying out these insertions. For example,

(24) P. L. Timms, *J. Chem. Soc. A*, 830 (1972).

(25) P. S. Skell and R. G. Deorr, *J. Am. Chem. Soc.*, **89**, 4688 (1967).

(26) M. J. Piper and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 50 (1972).

(27) P. S. Skell and J. J. Havel, *J. Am. Chem. Soc.*, **93**, 6687 (1971).

(28) H. F. Efner, unpublished results from this laboratory.

(29) K. J. Klabunde, M. S. Key, and J. Y. F. Low, *J. Am. Chem. Soc.*, **94**, 999 (1972).

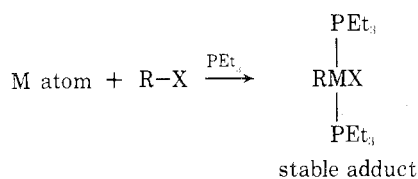
(30) R. D. Chambers, W. K. R. Musgrave, and J. Savory, *J. Chem. Soc.*, 1993 (1962).

(22) K. J. Klabunde, J. Y. F. Low, and M. S. Key, *J. Fluorine Chem.*, **2**, 207 (1972).

(23) L. A. Hanlan and G. A. Ozin, *J. Am. Chem. Soc.*, **96**, 6324 (1974).

the formation of $RNiX$, $RPdX$, and $RPtX$ seemed interesting since $RPdX$ species (no other ligands) have been proposed as reaction intermediates in a number of important reactions,³¹ such as palladium-promoted arylations, alkylations, etc. Similarly, $RCOPdCl$ has been discussed as a likely short-lived species in palladium-catalyzed CO insertion reactions, olefin carbonylations, and reaction mechanisms relating to the Rosenmund reduction.^{31,32}

Using the metal atom technique we succeeded in synthesizing some RMX and $RCOMX$ ($M = Ni, Pd, Pt$) species.^{15,33-35} Although we expected high reactivity and thermal instabilities for many of these, the low temperature and inert conditions afforded by this technique served to stabilize the species. So after completion of the codeposition of M atoms and $R-X$, the reaction matrix could be warmed to some desired temperature (e.g., -78°) and then a secondary substrate added to react with or trap the RMX species.



For nickel, we found that *alkyl* halide reactions only yielded NiX_2 and products resulting from R -coupling and disproportionation reactions. No direct evidence for $RNiX$ was obtained, although it is possibly an intermediate en route to products. Similar results were obtained for C_6H_5NiX . However, in the case of R_fNiX and C_6F_5NiX , low-temperature trapping studies were successful, and trapping experiments at different temperatures showed that C_6F_5NiCl was formed at very low temperature ($< -130^\circ C$), and decomposed about $-80^\circ C$.¹⁵

For palladium, no direct evidence for $RPdX$ was obtainable when $R = CH_3, C_2H_5$. Products attributable to R formation were found, although these products could also be explained in terms of $RPdX$ reactions.³⁴ Palladium atoms with C_6H_5Br yielded C_6H_5PdBr . This species was found to be unstable on warming above ca. $-100^\circ C$.³⁴ However, palladium atoms with C_6F_5X yielded C_6F_5PdX , found to be stable at room temperature and only slightly sensitive to air or water. We expected the C_6F_5 moiety to lend stability to the RMX species, but were surprised to find such good stability for this formally coordinatively unsaturated compound. This material can be isolated as a red-brown powder, is soluble in organic solvents (dimeric and trimeric), and adds ligands instantaneously to form the bis adducts (*trans*).³⁶ Perfluoroalkylpalladium halides are also stable compounds according to our results. Thus, $CF_3Br, CF_3I,$

(31) (a) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518, 5526, 5531, 5535, 5546 (1968); P. M. Henry, *Tetrahedron Lett.*, 2285 (1968); T. Hosokawa, C. Calvo, H. B. Lee, and P. M. Maitlis, *J. Am. Chem. Soc.*, **95**, 4914, 4924 (1973); (b) R. F. Heck and J. P. Nolley, Jr., *J. Org. Chem.*, **37**, 2320 (1972); H. A. Dieck and R. F. Heck, *J. Am. Chem. Soc.*, **96**, 1133 (1974).

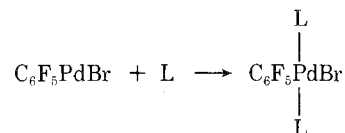
(32) J. Tsuji, M. Morikawa, and J. Kiji, *J. Am. Chem. Soc.*, **86**, 4851 (1964); *Tetrahedron Lett.*, 1437 (1963); J. Tsuji, K. Ohno, and T. Kajimoto, *ibid.*, 4565 (1965).

(33) K. J. Klabunde and J. Y. F. Low, *J. Organomet. Chem.*, **51**, C33 (1973).

(34) K. J. Klabunde and J. Y. F. Low, *J. Am. Chem. Soc.*, **96**, 7674 (1974).

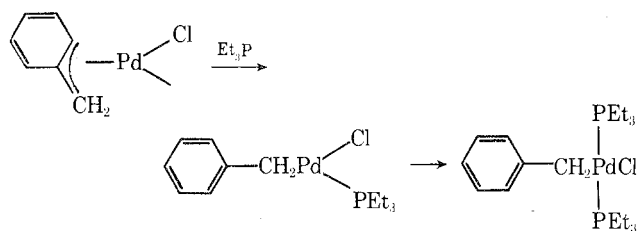
(35) K. J. Klabunde, J. Y. F. Low, and H. F. Efner, *J. Am. Chem. Soc.*, **96**, 1984 (1974).

(36) B. B. Anderson, unpublished results from this laboratory.



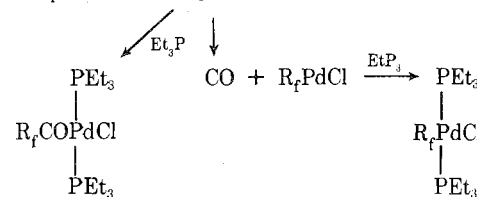
C_2F_5I , and $n-C_3F_7I$ yield R_fPdX compounds that are soluble in organic solvents and only moderately air and temperature sensitive.

One nonfluorinated $RPdX$ compound has been found to be stable at room temperature; that is $C_6H_5CH_2PdCl$ formed efficiently from Pd atoms and $C_6H_5CH_2Cl$. This material is a rust-colored solid soluble in some organic solvents and air sensitive. It decomposes in solution at about $40^\circ C$, and at $100^\circ C$ in the solid state. Spectral evidence (NMR, uv) tends to indicate allyl-type bonding with the arene system.^{37,38} On incremental addition of Et_3P to this compound (I), a π - to σ -rearrangement is observed first (loss of allyl type bonding), and then a second mole of Et_3P is taken up to form the stable bisphosphine adduct.³⁷ The chemistry of $C_6H_5CH_2PdCl$ is



quite interesting, and corresponds to that which would be predicted on the basis of Heck's proposal of $C_6H_5CH_2PdCl$ as a catalysis intermediate.^{31b} Other similar compounds that have good stability are $C_6H_5CH(CF_3)PdCl$ and various Me-substituted systems. In some of the substituted systems, low-temperature NMR studies indicate that preferred conformers can be frozen out.

Acyl halides also oxidatively add to palladium atoms. In all examples studied the resultant product readily liberated CO. In carrying out low-temperature Et_3P trapping studies and product analyses, we were able to learn a lot about what R groups stabilized the intermediates, their thermal stabilities, and modes of decomposition. In the case of $R = n-C_3F_7$ the $R_fCOPdCl$ could be trapped at $-78^\circ C$, but when $R = CF_3$ some $R_fCOPdCl$ and R_fPdCl were trapped, and when $R_f = C_6F_5$ only R_fPdCl was trapped.



Platinum atoms reacted with C_6F_5Br and $C_6H_5CH_2Cl$ to yield stable $RPdX$ compounds. In the case of C_6F_5PtBr , addition of Et_3P yielded both the *cis* and *trans* bisphosphine adducts (in the Pd case

(37) J. S. Roberts, unpublished results from this laboratory; J. S. Roberts and K. J. Klabunde, *J. Organomet. Chem.*, **85**, C13 (1974).

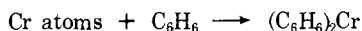
(38) R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966); F. A. Cotton and M. D. LaPrade, *ibid.*, **90**, 5418 (1968).

only trans complexes have been found).

Thus, using the metal atom technique we have been able to produce some interesting RMX species that have not as yet been available by other techniques. Information on stabilities and modes of decomposition has been obtained. The most interesting facet of this work is that some of these RMX species are much more stable than any one would have anticipated. More structural and chemical properties need determination, and other metals are being investigated (such as Co, Fe, Mn, and Ti).

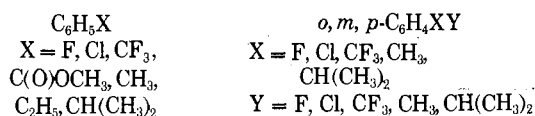
Some general observations we have made in these studies have been useful: (1) efficiency of oxidative addition to metal atoms follows the order C-I > C-Br > C-Cl; (2) aryl and benzyl halides react much more efficiently than alkyl halides. Product yields, matrix color changes, and previous knowledge of arene-metal complexes tend to indicate that π -arene-metal complexes first form before oxidative insertion occurs. This tends to "cage or preserve" the metal atoms and to prevent them from polymerization with themselves in the matrix. The π complexation would be a very low activation energy process, and then on matrix warm-up, probably during color change, the higher activation energy C-X insertion must occur.

Arene (π Complexes with Metal Atoms). One of the most important developments in the metal atom field has been synthesis of bis(arene) sandwich compounds.³⁹ This was a needed breakthrough in



terms of speed and convenience in synthesis, and in expanding the scope of arene sandwich compounds available (conventional reducing Friedel-Crafts methods are quite limited as to what substituents can be tolerated on the arene ring). Now a host of variously substituted bis(arene)chromium(0) compounds have been made simply by condensing Cr atoms with the appropriate arene ligand.^{16,39-43}

Bis(arene) Cr(0) complexes



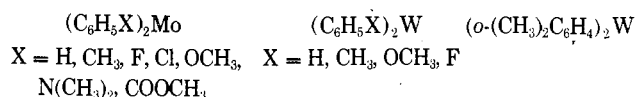
It is most interesting that these normally air-sensitive complexes are stabilized to air oxidation by electronegative substituents.^{16,41,42} We have been most concerned with the F- and CF_3 -substituted systems^{15,16,44} and found, for the *m*- and *p*- $(\text{CF}_3)_2\text{C}_6\text{H}_4$ ligands, that the sandwich chromium complexes were formed in good yield and were indefinitely stable to air at room temperature, and even for short periods of time at 200°C. Probably the first step in the oxidative decomposition of these compounds is the one-electron oxidation of chromium(0) to chromium(1+), which would be disfavored by the presence of electronegative substituents, and this is dramatically dem-

onstrated by studying polarographic one-electron oxidations (collaborative work with P. Treichel and G. Essenmacher). Furthermore, recent X-ray crystallographic evidence indicates that F and CF_3 have very significant effects on the structures of these sandwich compounds of V as well as of Cr (collaborative work with L. Radonovich and C. Zuerner).

In related spectroscopic investigations, McGlinchey and Tan⁴³ have recently made some careful ^{19}F NMR studies on a series of substituted bis(arene)-chromium(0) complexes and conclude that the overall electron-withdrawing effect of a π -bonded Cr on each ring is similar to the effect of four ring fluorine substituents (on a noncomplexed benzene ring). They point out the interesting possibility of carrying out nucleophilic substitution of fluoride on $(\text{C}_6\text{H}_4\text{F}_2)_2\text{Cr}$ as readily as can be done with hexafluorobenzene, and find methoxide effective in this respect.

Although halogen substitution directly on the aromatic ring (F, Cl), lends some added air stability, it also imparts explosive character to some of these sandwich compounds. In the case of hexafluorobenzene as a ligand, the complexes were so sensitive and explosive that a pure compound has not been isolable from the C_6F_6 -Cr system (similar results have been obtained with the C_6F_6 -V⁴⁴ and C_6F_6 -Ni⁴⁴ systems). With fluorinated benzenes only two fluorine substituents can be tolerated. Higher fluorine content (three-six fluorines) results in unstable, very explosive complexes.⁴⁵ Endothermic compounds can be obtained utilizing the metal atom technique, and we should be wary of all halogenated π complexes because of the potentially highly exothermic M-X bond formation that can occur on decomposition. So far no problems have been encountered with CF_3 -substituted systems, however.

Silvon, Van Dam, and Skell have been able to prepare bis(arene) complexes of Mo and W.⁴⁶ These



metals have very high heats of vaporization, but amounts up to about 0.5 g can be sublimed by careful resistive heating of wires of Mo or W.

Benfield, Green, Ogden, and Young have employed an electron gun in a rotating reactor for vaporizing Mo and Ti.¹⁷ These workers were also able to synthesize $(\text{C}_6\text{H}_6)_2\text{Mo}(0)$, as well as a very intriguing sandwich compound of Ti: $(\text{C}_6\text{H}_6)_2\text{Ti}$. This material must be isolated with great care because of its sensitivity and possible autocatalytic decomposition (probably induced by the presence of Ti metal film). It is the first true example of a Ti(0) sandwich complex and is red-orange and diamagnetic.

We have synthesized a series of bis(arene)vanadium(0) complexes by vaporizing V from resistively



heated tungsten boats.^{15,16,44} These compounds are much more sensitive to air than the analogous Cr compounds. However, again electron-withdrawing

(39) P. L. Timms, *Chem. Commun.*, 1033 (1969).

(40) P. L. Timms, *J. Chem. Educ.*, 49, 782 (1972).

(41) R. Middleton, J. R. Hull, S. R. Simpson, C. H. Tomlinson, and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 120 (1973).

(42) P. S. Skell, D. L. Williams-Smith, and M. J. McGlinchey, *J. Am. Chem. Soc.*, 95, 3337 (1973).

(43) M. J. McGlinchey and T. S. Tan, *Can. J. Chem.*, 52, 2439 (1974).

(44) K. J. Klabunde and H. F. Efner, *J. Fluorine Chem.*, 4, 115 (1974).

(45) Private communications with P. L. Timms.

(46) M. P. Silvon, E. M. Van Dam, and P. S. Skell, *J. Am. Chem. Soc.*, 96, 1945 (1974).

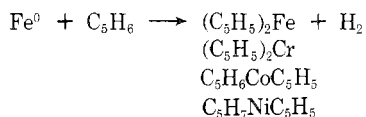
groups have a stabilizing effect, CF_3 being the best substituent to use.

Mixed cyclic complexes are also available utilizing metal atoms. As evidence of this, Van Dam and Skell reported that W atoms cocondensed with arene-cyclopentadiene mixtures yielded mixed sandwich complexes with W-H bonding:⁴⁷ $[(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)\text{WH}]$.

Evidence for unstable arene π complexes has also been found. The first such observation was from an iron atom-benzene cocondensation yielding a very explosive unstable material.³⁹ Iron atoms with toluene formed a complex that could be warmed to -94° and then allowed to react with PF_3 to yield bis(trifluorophosphine)tolueneiron(0).⁴⁸ A number of unstable arene complexes were found when a series of transition metals (V, Cr, Mn, Fe, Co, Ni, and Pd) were cocondensed with hexafluorobenzene and benzene.^{15,44}

By condensing substrate mixtures with metal vapors, Timms and coworkers⁴¹ have prepared $\text{Cr}(\text{arene})(\text{PF}_3)_3$ complexes (arenes = benzene, hexafluorobenzene, cumene, and mesitylene). Similarly, iron vapor condensed with a mixture of benzene and PF_3 yielded $\text{C}_6\text{H}_6\text{Fe}(\text{PF}_3)_2$. The $\text{C}_6\text{F}_6(\text{PF}_3)_3$ was formed in low yield, but is very stable, which is interesting in light of the fact that $(\text{C}_6\text{F}_6)_2\text{Cr}$ is not stable and is very explosive.

Diene-Metal Atom Reactions. Timms demonstrated that cyclopentadiene was reactive with metal atoms.^{9,39} Ferrocene could be produced with hydrogen gas as a by-product. Similarly, chromocene^{9,42}



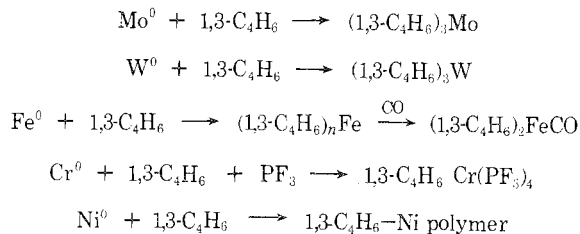
could be synthesized, but in the cases of Co and Ni hydrogen transfers took place, yielding the compounds shown.⁹ No hydrogen was evolved in the Ni reaction, and trihapto as well pentahapto bonding to nickel resulted.

Recently Mo and W atoms have been condensed with cyclopentadiene. In these cases hydrogen was not evolved, and $(\text{C}_5\text{H}_5)_2\text{MH}_2$ derivatives were formed.^{47,49} By extrapolation, then, it is possible that Cr atoms plus cyclopentadiene initially yield the dihydride derivative $(\text{C}_5\text{H}_5)_2\text{CrH}_2$ which decomposes to yield chromocene and hydrogen. Iron may go through a similar pathway. However, studies on mechanisms are needed and would be of great interest since labile M-H bonds may be involved.

1,5-Cyclooctadiene also interacts well with transition-metal atoms. The known bis(1,5-cyclooctadiene)platinum(0) complex was synthesized employing Pt atoms.²⁷ Also, MacKenzie and Timms recently disclosed the preparation of the very unusual compound bis(1,5-cyclooctadiene)iron(0) by reaction of Fe atoms with a solution of the diene in methylcyclohexane solvent.^{20,21} This compound is formally coordinatively unsaturated, similar in that sense to the

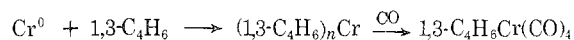
RPdX compounds previously discussed.

Skell and coworkers^{42,50-52} synthesized some extremely interesting 1,3-butadiene complexes of transition metals. Some reactions and products are shown.



The most interesting are tris(1,3-butadiene)molybdenum and -tungsten.⁵¹ These are air and thermally stable materials. Recent X-ray studies showed that the diene molecules are wrapped around the metal atoms so that all 12 carbons are equidistant from the metal.⁵³ These materials represent rare examples of compounds where Mo and W are zerovalent without CO ligand stabilization.

Koerner von Gustorf and coworkers have also interacted butadiene with iron atoms as well as with Cr atoms.¹⁹ Subsequent reaction of the diene-Cr complex with CO yielded a butadienechromium carbonyl complex of limited stability. This complex had been



proposed earlier as a catalysis intermediate, and this work elucidated some of the properties of this labile species. In these metal atom studies, laser heating was employed for the metal vaporizations, and large-scale reactions could readily be carried out.¹⁹ This method would appear to have considerable promise for doing large-scale vaporizations of refractory metals, and perhaps for the generation and study of electronically excited metal atoms.

Olefins with Metal Atoms. Propene has been cocondensed with metals Al, Co, Dy, Er, Ni, Pd, Pt, and Zr in initial orientating experiments in an attempt to demonstrate differences and similarities between the metals.⁵⁴ Organometallic products were not isolated and characterized, but rather were decomposed with D_2O to mark C-M bonds. Aluminum atoms with propene yielded mainly 1,2-dialuminoalkanes (σ bonding),⁵⁵ whereas Ni and Pt yielded mainly π complexes (unlabeled propene released on D_2O addition).^{27,42,54} In the aluminum work some 1,4-dialumino- C_6 products were also formed.⁵⁵ Matrix isolation spectroscopy work in conjunction with product analysis indicated that the dialuminoalkanes were indeed formed from aluminum atoms at -196°C (not on warming of the matrix or from active aluminum surfaces or clusters).⁵⁵

Indirect evidence has been obtained for the formation of π -allylnickel hydride from the reaction of Ni

(50) P. S. Skell, J. J. Havel, D. L. Williams-Smith, and J. J. McGlinchey, *J. Chem. Soc., Chem. Commun.*, 1098 (1972).

(51) P. S. Skell, E. M. Van Dam, and M. P. Silvon, *J. Am. Chem. Soc.*, **96**, 626 (1974).

(52) D. L. Williams-Smith, L. R. Wolf, and P. S. Skell, *J. Am. Chem. Soc.*, **94**, 4042 (1972).

(53) M. Yevitz and P. S. Skell, International Union of Crystallography Intercongress Symposium on Intra- and Intermolecular Forces, August 14-16, 1974, The Pennsylvania State University, Series 2, Vol. 2, paper E9.

(54) P. S. Skell, *Proc. Int. Congr. Pure Appl. Chem.*, **23** (4), 215 (1971).

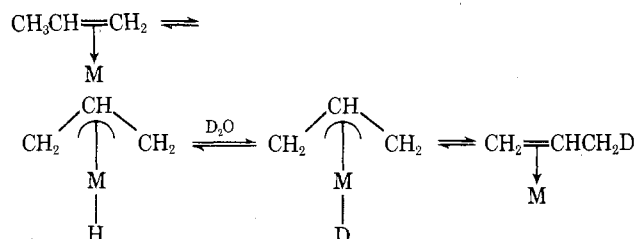
(55) P. S. Skell and L. R. Wolf, *J. Am. Chem. Soc.*, **94**, 7919 (1972).

(47) E. M. Van Dam, W. N. Brent, M. P. Silvon, and P. S. Skell, *J. Am. Chem. Soc.*, **97**, 465 (1975).

(48) D. L. Williams-Smith, L. R. Wolf, and P. S. Skell, *J. Am. Chem. Soc.*, **96**, 4042 (1974).

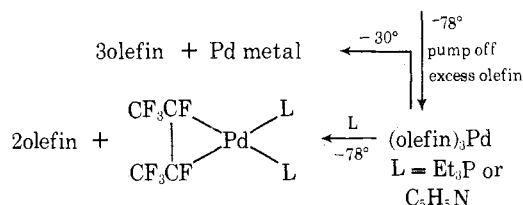
(49) M. J. D'Amiello and E. K. Barefield, *J. Organomet. Chem.*, **76**, C50 (1974).

atoms with propene.⁴² Thus, the condensate from propene and Ni atoms yields both nondeuterated propene and monodeuteriopropene upon D₂O hydrolysis. In further support of the π -allyl Ni-H interme-

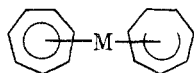


diate, cocondensation of C₃H₆ plus C₃D₆ with Ni atoms leads to H-D scrambled products.⁵⁰

We have found that perfluoro olefins form complexes with Ni, Pd, and Pt atoms at low temperature.³⁵ On warm-up the complexed olefin is released unchanged. The (olefin)₃Pd complex shown below reacted with triethylphosphine³⁵ or with pyridine²⁸ to form the corresponding (olefin)PdL₂ species in high yields. Since the olefin becomes σ bonded in the complexes, this reaction sequence is an example of oxidative addition of a C-C bond to a palladium atom.³⁵



Acetylenes, Trienes, and Tetraenes with Metal Atoms. Bis(cycloheptatriene)chromium(0) has been synthesized using Cr atoms plus cycloheptatriene.⁴² With Mo and W atoms, however, hydrogen transfers took place, and the interesting η^7, η^5 systems were obtained.⁴⁷



Some acetylenes were trimerized to benzenes by chromium vapor, but no bis(arene)chromium(0) complexes could be isolated from the reaction mixtures.⁴² The absence of the bis(arene) sandwich complexes indicates that probably only one arene ring was generated and bonded to chromium at any time.

Acid Anhydrides with Metal Atoms. Hexafluoroacetic anhydride codeposited with palladium atoms yielded a complex that slowly deposited palladium metal while in solution at room temperature.³⁵ The structure of this material has not been determined as yet, but on addition of Et₃P to the complex, *cis*-bis-(triethylphosphine)perfluoroacetatopalladium(II)((Et₃P)₂Pd(OCOCF₃)₂) was formed. Formally, this is an example of the C-O oxidative insertion by palladium. However, it is likely that the initial complex is zerovalent in palladium.

Active Metal Slurries Formed from Metal Atom-Solvent Cocondensations. Currently, there is great interest in the production and chemistry of high-surface-area clean-metal slurries.⁵⁶ We have found metal vapors to be useful in this regard. Thus,

Mg vapor cocondensed with tetrahydrofuran (THF) followed by warming yielded a black Mg-THF slurry that was extremely reactive for Grignard reagent preparations.⁵⁷

An active Ni-THF slurry can be produced similarly. This slurry, as is the case with Mg, has very finely divided metal present and can actually be manipulated by syringe. This Ni slurry is quite reactive with organohalides, and, in cases such as benzyl chloride and iodobenzene, can be used as coupling reagent under very mild conditions.⁵⁸ In attempts to learn more about the physical and structural aspects of the metal powder resulting from Ni-THF codeposition followed by pump-off of excess THF, we have utilized electron-scanning microscopy and X-ray powder techniques as well as chemical reactions. These studies have shown the material is actually a nickel(0) etherate (Ni:THF \approx 5:1), has essentially no crystalline character, and is in the form of small globules in the 0.5- μm range.^{28,58} On pyrolysis this material decomposes with the formation of Ni-Ni bonds, leading to large Ni crystals.

Currently we are studying other metal atom-solvent systems. One aspect of the work is to produce "solvated metal atoms", and polyethers and arenes appear to be promising substrates from preliminary data. We find that Ni atoms can be solvated by toluene at low temperature and have used this Ni-toluene solution for the low-temperature deposition of small nickel crystallites on alumina. These materials, as well as the metal slurries that can be made, should have many uses in chemical synthesis and catalysis. It is encouraging that the metal-ether slurries show good storage properties (if kept under a rigorous argon atmosphere).

General Observations

The metal atom method gives us a wide scope in the synthesis of new organometallic compounds, some of them very "high-energy materials". Uses of these new materials will very likely be closely related to homogeneous catalysis because they often are "coordinatively unsaturated". Active-metal slurries formed this way also have promise, particularly for use in low-temperature organometallic synthesis schemes.

Useful aspects of the technique are: (1) reactors are becoming quite simplified and larger scale, (2) bulk metals are cheap chemical reagents, and (3) the method can serve as a quick indicator of what organometallic compounds have good stability, and then more conventional methods can be devised for synthesizing these materials.

Financial support from the National Science Foundation (GP-42376) and also the outstanding work of Dr. James Y. F. Low, Howard F. Efner, John S. Roberts, Bruce B. Anderson, and Thomas O. Murdock are appreciated.

(56) R. D. Rieke and L. C. Chao, *Synth. React. Inorg. Met.-Org. Chem.*, **4**, 101 (1974); R. D. Rieke and P. M. Hudnall, *J. Am. Chem. Soc.*, **94**, 7178 (1972); R. D. Rieke, S. J. Uhm, and P. M. Hudnall, *J. Chem. Soc., Chem. Commun.*, 269 (1973); R. D. Rieke and S. E. Bales, *ibid.*, 879 (1973); R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.*, **96**, 1775 (1974); C. A. Brown and V. K. Ahuja, *J. Org. Chem.*, **38**, 2226 (1973).

(57) K. J. Klabunde, H. F. Efner, L. Satek, and W. Donley, *J. Organomet. Chem.*, **71**, 309 (1974).

(58) T. O. Murdock, unpublished observations from this laboratory.