ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY, VOL. 27

TRIFLUOROMETHYL DERIVATIVES OF THE TRANSITION METAL ELEMENTS

JOHN A. MORRISON

Department of Chemistry, University of Illinois, Chicago, Chicago, Illinois

I. Introduction

The first preparation of an organometallic compound that contained a perfluoroalkyl group occurred in 1949 when bis(trifluoromethyl)mercury was formed during the interaction of CF_3I with elemental mercury. Although no trifluoromethyl cadmium derivatives were isolated, the synthesis of the mercurial was reported to proceed most readily if the mercury had been present in the form of a cadmium amalgam (*1*). In addition to being the first demonstration that perfluoroalkyl ligands could be chemically bonded to metallic or metalloid centers, the results of this study are of interest in that they well illustrate some of the fundamental differences between the chemistry of hydroalkyl and perfluoroalkyl organometallic compounds.

One of these differences is that if a methylated derivative of any particular metal-containing compound should be desired, there is a rich and diverse variety of potentially suitable alkyl-donating agents available from which the most effective can be chosen. Classic examples of methyl donors include Grignard reagents and species such as methyl lithium, dimethyl zinc, or trimethyl aluminum compounds.

ISBN 0-12-023627-3

Each of these alkylating agents is readily available and each has a characteristic and well-known reactivity. The successful preparation of hexamethyl tungsten is one fairly recent example of the necessity of having a number of alternative reagents for a given synthesis (*2*).

If the analogous perfluoromethyl organometallic compound should be required, however, no such arsenal of ligand-exchange reagents currently exists. The trifluoromethyl derivatives of lithium, magnesium, or aluminum might all be seemingly obvious candidates, but these compounds are either unknown, or have been shown to be unsuitable trifluoromethyl sources for organometallic compounds. Even bis(trifluoromethyl)mercury which, at least by analogy to dimethylmercury, might have been expected to be an excellent trifluoromethyl ligand-exchange reagent has been thought to be completely unreactive in this type of procedure until very recently (*3–6*).

Thus one of the reasons that a broadly based series of fluoroalkylating agents is not currently known is that many of the compounds which might have been expected to make up that series are thermally unstable. Others have appeared to be unreactive. Another important reason may be a result of the comparatively recent origins of fluorocarbon chemistry. The simplest fluorocarbon, CF_4, was apparently synthesized as early as the 1880s by Moissan, but even this compound was not obtained in a pure state until 1930 (*7*). Systematic studies of the higher homologs were not initiated until 1937 (*8*). Trifluoromethyl iodide, the reagent utilized in the preparation of bis(trifluoromethyl)mercury above, was itself unknown until 1948.

At the present time much less is known about fluorocarbon compounds than hydrocarbons in general, and, in particular, much less effort has been expended in the synthesis of fluorocarbon transition metal complexes than in the preparation of their hydrocarbon analogs. It is not entirely inconceivable that a complete series of reagents which is comparable in effectiveness to alkyl ligand-exchange reagents but which could be used to form perfluorocarbon derivatives might yet be developed. Such a series of reagents, however, is still to be uncovered.

One concrete measure of the amount of knowledge which is currently available about fluorocarbon–transition metal complexes is that until recently the entire field could be comprehensively surveyed in one very short chapter in a larger review (*9–12*). Within the past few years, however, the volume of work has grown to the extent that this type of treatment is no longer possible. Therefore the present discussion narrowly focuses upon only one aspect of fluorocarbon chemistry: the synthesis of compounds that contain trifluoromethyl groups bonded to transition metals.

While it is limiting to restrict the coverage to only one type of ligand, of course, there are several mitigating aspects. First, on balance, trifluoromethyl derivatives are arguably the most representative sigma-bonded fluorocarbon complexes. For example, the compounds to be discussed are neither the most, nor the least thermally stable fluorocarbon–metal species. Second, the synthetic approaches to be described are very representative of the types of reactions employed in the formation of all sigma-bonded perfluorocarbon–transition metal compounds. The only classes of preparative reactions that are commonly used for heavier fluoroalkyl complexes but are not utilized in the formation of trifluoromethyl derivatives employ either fluoroalkene or fluoroalkyne insertions (*9–13*). Third, much of the current work in this area has been designed to search for new synthetic approaches to the preparation of perfluoroalkyl-substituted metals and metalloids. As a matter of convenience, these studies have almost exclusively utilized the trifluoromethyl ligand.

The development of new types of reagents for the formation of perfluoroalkyl derivatives of metals is of interest since, as discussed below (Section II), the types of trifluoromethyl complexes which could be prepared until quite recently have been severely limited by the synthetic methods that have been historically available. Virtually all of the trifluoromethyl-containing transition metal species prepared prior to the 1980s arose from only two types of reactions: thermal decarbonylations of trifluoroacetyl complexes or oxidative additions of CF_3I.

Each of these synthetic methods is limited to low valent metal complexes; in each case at most two CF_3 groups have been substituted onto a metal ion. In Section III some of the contemporary approaches that have been designed to curtail the enforced reliance upon only two precursors are indicated and some of the early results from these preliminary studies into the chemistry of trifluoromethyl-containing transition metal compounds are presented.

II. Early Synthetic Approaches

A. THERMAL DECARBONYLATIONS OF TRIFLUOROACETYL DERIVATIVES

The initial synthesis of a trifluoromethyl-substituted transition metal compound occurred when trifluoroacetyl manganese pentacarbonyl was first formed, then thermally decarbonylated as shown in Eqs. (1) and (2) (*14–16*).

$$CF_3COCl + NaMn(CO)_5 \longrightarrow \underset{(75\%)}{CF_3COMn(CO)_5} + NaCl \tag{1}$$

$$CF_3COMn(CO)_5 \xrightarrow{110\text{–}160^\circ C} \underset{(92\%)}{CF_3Mn(CO)_5} + CO \tag{2}$$

This indirect, two-step procedure for the synthesis of trifluoromethyl derivatives of transition metals was developed after it had become evident that the reaction of CF_3I with metallate ions such as $Mn(CO)_5^-$ resulted in the formation of the iodide rather than the expected trifluoromethyl derivative, as indicated in Eq. (3) (*16*).

$$2CF_3I + NaMn(CO)_5 \longrightarrow IMn(CO)_5 + NaI + C_2F_6 \tag{3}$$

The formation of the iodo derivative is a result of the relative electronegativities of the two potential ligands, CF_3 and I. Since the electronegativity of the CF_3 group is higher than iodine, the reaction of CF_3I with metal anions results in the formation of the iodide rather than the trifluoromethyl derivative. For methyl iodide, however, iodine is more electronegative than the alkyl, thus the reactions of CH_3I with metallates typically result in the formation of the methyl derivatives.

In the years since the original study, it has been determined that a variety of trifluoroacetyl sources including trifluoroacetyl fluoride, CF_3COF, and trifluoroacetic anhydride, $(CF_3CO)_2O$, can also be effectively employed in reactions designed to generate trifluoroacyl species analogous to that shown in Eq. (1). Although the coupling reaction to form the acyl derivatives occurs at ambient or subambient temperatures in each case and the isolated yields of the trifluoroacetyl derivatives appear to be very similar with any of these sources of the perfluoroacyl ligand, trifluoroacetic anhydride has been most commonly used in recent studies, possibly because of the availability and the ease of handling of the material. Sodium and lithium have been employed as the counterions for the metallic substrate.

Since 1959, a number of other trifluoromethyl transition metal derivatives have been formed from thermal decarbonylations of trifluoroacetyl complexes. Examples of compounds which have been formed by trifluoromethyl migration are listed in Table I.

Evidence for CO insertions into CF_3–metal bonds, a reaction which is presumably the reverse of the methyl migration step, has been sought in several instances (*25*), but, as yet, no CF_3–metal derivative generated in this manner has been isolated. However, upon UV irradiation of $CF_3Mn(CO)_5$ held at 17 K, vibrational spectra were obtained that were consistent with the formation of a trifluoroacetyl manganese species. The product was not separated (*26*).

TABLE I

TRIFLUOROMETHYL MIGRATIONS OF TRIFLUOROACETYL DERIVATIVES[a]

Product	Reagent	Temperature (°C)	Yield (%)	References
	[Cr/Mo/W]			
$CF_3Mo(Cp)(CO)_3$	$CF_3COMo(Cp)(CO)_3$	120	60	*17*
	[Mn/Tc/Re]			
$CF_3Mn(CO)_5$	$CF_3COMn(CO)_5$	130	92	*14–16*
$CF_3Mn(CO)_3(P(O\phi)_3)_2$	$CF_3COMn(CO)_3(P(O\phi)_3)_2$	60	—	*18*
	[Fe/Ru/Os]			
$(CF_3)_2Fe(CO)_4$	$(CF_3CO)_2Fe(CO)_4$	98	55	*19*
$CF_3Fe(Cp)(CO)_2$	$CF_3COFe(Cp)(CO)_2$	—	33^b	*17*
	[Co/Rh/Ir]			
$CF_3Co(CO)_4$	$CF_3COCo(CO)_4$	55	—	*15, 20, 21*
$CF_3Co(CO)_3P(O\phi)_3$	$CF_3COCo(CO)_3P(O\phi)_3$	65	80	*22*
$CF_3Co(CO)_3P\phi_3$	$CF_3COCo(CO)_3P\phi_3$	130	—	*21*
$CF_3Ir(CO)(CF_3CO_2)(Cl)(P\phi_3)_2$	$CF_3COIr(CF_3CO_2)(Cl)(P\phi_3)_2$	75	30	*23*
$CF_3Ir(CO)(Cl)_2(P\phi_3)_2$	$CF_3COIr(Cl)_2(P\phi_3)_2$	75	60	*23*
	[Ni/Pd/Pt]			
$CF_3Pt(Cl)(PCH_3\phi_2)_2$	$CF_3COPt(Cl)(PCH_3\phi_2)_2$	210	78	*24*

[a] $Cp = \eta^5\text{-}C_5H_5$; $\phi = C_6H_5$.

[b] Complex decarbonylated photochemically.

In a few instances, rather than coupling of the trifluoroacetyl ligand to a metal anion, the perfluoroacyl compound has been oxidatively added to neutral Pt(0) or Ir(I) complexes. Thus the compounds $Pt(P\phi_3)_2L$, where $L = P\phi_3$ or $\phi C{\equiv}C\phi$, react with $(CF_3CO)_2O$ to form $(CF_3CO)Pt(CF_3CO_2)(P\phi_3)_2$ which can be recovered unchanged after 24 h at 110°C. Similarly, Vaska's complex or closely related species such as $Ir(Br)(CO)(P\phi_3)_2$ or $Ir(Cl)(CO)(PCH_3\phi_2)_2$ also oxidatively add $(CF_3CO)_2O$ or CF_3COCl which results in six coordinate trivalent iridium complexes (*23*).

The reaction of the dinitrogen complex $Ir(Cl)(N_2)(P\phi_3)_2$ with $(CF_3CO)_2O$ or CF_3COCl, yields $(CF_3CO)Ir(CF_3CO_2)(Cl)(P\phi_3)_2$ or $(CF_3CO)Ir(Cl)_2(P\phi_3)_2$, respectively, along with elemental nitrogen. As indicated in Table I, at 75°C trifluoromethyl migrations yield the (trifluoromethyl)(carbonyl) complexes readily in the last two compounds (*23*). Trifluoroacetyl chloride has also been found to add to the platinum complex $Pt(PCH_3\phi_2)_4$ to afford $(CF_3CO)Pt(Cl)(PCH_3\phi_2)_2$ which releases CO only at 210°C (*24*).

Immediately upon their isolation, trifluoromethyl-containing derivatives of (low valent) transition metals were universally found to be much more robust, both thermally and oxidatively, than their methylated counterparts. Many perfluoromethyl complexes, for example, have been found to be unreactive in air whereas the corresponding methyl derivatives are air sensitive. Under anaerobic conditions a number of trifluoromethylated species decompose at temperatures approximately 100°C higher than the analogous methylated compounds.

The enhanced stability of the fluorine-containing derivatives has commonly been rationalized by either of two arguments. The first of these is based upon the apparent decrease in the C–F force constants that were derived from the vibrational spectra of compounds such as $CF_3Mn(CO)_5$ when compared to the C–F force constants that were obtained from compounds such as CF_3I. Pi backbonding from the filled metal orbitals to the unoccupied carbon–fluorine antibonding orbitals in the CF_3 group was invoked to explain a strong metal–carbon bond while simultaneously accounting for a weakened carbon–fluorine bond (*17, 27, 28*).

Alternative explanations of the phenomena (*24, 29*) are buttressed by photoelectron spectra and computational results (*30, 31*). These studies indicate that the strengthened metal–carbon bonds in trifluoromethyl-containing complexes are a result of sigma-bonding effects. The latter interpretations are, in essence, an application of Bent's rule. In trifluoromethyl derivatives, fluorine is bonded to carbon by means of carbon hybrid orbitals that have more *p* character than the orbitals used by carbon to form carbon–hydrogen bonds in the corresponding methyl compound. Thus the bond from carbon to the metal has more carbon 2*s* character in trifluoromethylated species than in the analogous methylated species. In this analysis the increased stability of the CF_3 derivatives is ultimately traceable to a lower energy, more electronegative orbital of the carbon atom which has been used to form the carbon–metal bond. The predicted result of this "rehybridization" is not only a shorter, stronger bond from the metal to carbon, but also stronger bonds from the metal to all of the other ligands (*30*).

While it will undoubtedly require an appreciable amount of effort to precisely and definitively resolve the exact differences between analogous CF_3– and CH_3–metal bonds, there is no doubt that, in general, perfluoroalkyl–metal bonds are shorter by some 0.05 Å than the corresponding alkyl–metal bonds (*32–35*). In one case, the platinum complexes $R_2Pt(SP)$, where R = CF_3 or CH_3 while SP = $o\text{-}C_2H_3C_6H_4P\phi_2$, directly comparable X-ray structural data have been obtained. The crystallographic results indicate that the carbon platinum bond lengths are 2.082 and 2.032 Å in the bis(trifluoromethyl) compound while the corresponding distances are found to be 2.166 and 2.052 Å, respectively, in the isostructural dimethyl derivative (*36*).

Over the years the preparative sequence outlined above has yielded a number of perfluoromethyl transition metal derivatives, including the first examples of this type of compound. Even a cursory perusal of Table I suggests a number of other metallic anions that most likely could be employed to generate trifluoromethylated species that are currently unknown. There are, however, a number of severe limitations upon this method which preclude its utility as a general synthetic technique.

The first of these inherent difficulties is that even a moderately reactive metallate such as $CpFe(CO)_2^-$ can displace fluoride ion by means of a nucleophilic attack on the ligated trifluoroacetyl group. This reaction presumably results in an unstable bimetallic species which decomposes under the reaction conditions (*17*). Thus, in some instances, the yield of the desired trifluoroacyl substrate is inevitably low, often less than 10%.

A second limitation of the procedure is related to the ease with which the fluoroacyl complex can be decarbonylated. Examination of the entries in Table I indicates that for the carbonyl compounds that have been studied, trifluoromethyl migrations accompanied by the loss of CO occur readily: 130°C for $CF_3COMn(CO)_5$, 98°C for $(CF_3CO)_2Fe(CO)_4$, and 55°C for $CF_3COCo(CO)_4$. However, substitution of CO by other ligands (except phosphites) typically strengthens the remaining metal–carbon bonds in the molecule. Dramatically increased temperatures are then required for the preparation of the substituted trifluoromethyl derivative. The monophosphine $(CF_3CO)Co(CO)_3P\phi_3$, for example, yields the trifluoromethyl compound only at 130°C.

In many instances the decomposition of substituted trifluoroacyl organometallic compounds by alternative routes occurs at temperatures that are lower than those that would apparently be required for thermal decarbonylation. For example, $CF_3COMn(CO)_4P\phi_3$ does not yield the trifluoromethyl derivative upon heating (*22*). Neither $(CF_3CO)Mn(CO)_3(P\phi_3)_2$ nor $(CF_3CO)Co(CO)_2(P\phi_3)_2$ gave the expected perfluoroalkyl product upon thermal decomposition (*18, 37*). Similarly, the substituted iron carbonyl $CF_3COFe(Cp)(CO)_2$ could not be decarbonylated thermally, although CO evolution was observed upon UV photolysis (*17*).

A third limitation arises because metal–ligand bond strengths in compounds formed by the transition metal elements located toward the bottom of the periodic table are generally greater than the bond strengths of the corresponding species that contain elements found higher in the table. As a result, trifluoroacetyl derivatives of the former are typically more difficult to decarbonylate than in the latter. For example, $CF_3COMo(Cp)(CO)_3$ forms the expected trifluoromethyl derivative at 120°C, but the analogous tungsten compound could not be decarbonylated either thermally or upon photolysis (*17*).

To date, the only trifluoromethyl migrations that have been observed in compounds of the elements that are located in the third row of the transition metals occur in the two Ir(I) complexes which, as noted in Table I, retain the CO linkage after alkyl migration, in $CF_3CORe(CO)_5$ (*38*), and in the platinum(II) species for which a temperature of 210°C was required to initiate the decarbonylation. While the conditions of the last reaction clearly indicate that CF_3–Pt bonds are very stable, many if not most organometallic species cannot survive this type of treatment, and the application of the technique to the heavier transition metals is therefore expected to be quite limited.

Some of the inherent limitations in this method of forming trifluoromethyl compounds can presumably be overcome. One approach would be to examine catalytic decarbonylations, a type of reaction that has been observed for hydrocarbon acyl derivatives but not, as yet, for fluorocarbon acyl compounds (*39*). In one reaction that is at least formally related, the preparation of $(CF_3)_2Hg$ by the decarboxylation of $(CF_3CO_2)_2Hg$, the loss of CO_2 occurs readily only in the presence of added K_2CO_3 (*40*).

However, in the final analysis, the fundamental limitation of the technique described above is that it is yet to be demonstrated that more than two CF_3 groups can be affixed to any transition metal center by means of thermal decarbonylation–methyl migration reactions. Thus this procedure is extremely useful for the synthesis of certain categories of trifluoromethyl transition metal compounds, provided that only one or at most two CF_3 groups are desired, but it cannot be regarded as a generally applicable synthetic method.

B. TRIFLUOROMETHYL IODIDE OXIDATIVE ADDITIONS AND OXIDATIONS

The reactions of trifluoromethyl iodide with the main group elements and elemental mercury were extensively investigated by Emeléus and his students almost as soon as the reagent became available in quantity. Trifluoromethyl iodide was shown to readily oxidize a number of elements, most notably those below nitrogen in Group VA, and the trifluoromethyl ligand was observed to possess a considerable amount of pseudohalogen character (*5*).

The first successful syntheses utilizing trifluoromethyl iodide in transition metal chemistry were reported by Stone and his students. Stone reasoned that if CF_3I would not react with transition metal anions to form trifluoromethyl derivatives [see Eq. (3)] then perhaps compounds containing perfluoroalkyl substituents could be generated by the oxidative addition of perfluoroalkyl halides to low valent transition metal substrates (*9, 10*). The first reported trifluoromethyl-substituted transition metal complex prepared by this route is shown in Eq. (4) (*41*).

$$CF_3I + (\eta^5\text{-}C_5H_5)Co(CO)_2 \xrightarrow[17\ h]{45°C} CF_3Co(C_5H_5)(CO)I \qquad (4)$$

The reaction of CF_3I with low valent metals is remarkable for the very mild conditions that are required. Typically, trifluoromethyl iodide and the transition metal species are maintained at ambient temperatures for periods of time which range from a few minutes to a few days. When employed at all, solvents are noninteractive and, at most, only gentle heating is required. The utility of oxidative addition reactions with trifluoromethyl iodide has been demonstrated in numerous systems and representative examples are presented in Table II.

As indicated in Table II, the complexes examined thus far have all contained coordinatively unsaturated d^8 or d^{10} metal ions, as has most commonly been the case in oxidative addition reactions of alkyl halides with transition metal substrates. Almost all of the products of these reactions are immediately recognizable as having arisen from an oxidative addition reaction, but in some instances the species isolated, e.g., $CF_3Au(P\phi_3)$ (*59*), $(CF_3)_2Pt(COD)$ (*54*), and $CF_3Pt(PEt_3)_2I$ (*55*), were found to be in the same oxidation state as the reagents that had been originally employed.

Several lines of evidence indicate that these reactions also proceed through oxidative addition steps. For example, in the reaction of $(CH_3)_2Pt(PEt_3)_2$ with CF_3I, while 90% of the platinum was later found as the divalent platinum compound $CF_3Pt(PEt_3)_2I$ (Table II) the remaining 10% was isolated as the Pt(IV) complex, $CF_3Pt(CH_3)_2(PEt_3)_2I$ (*55*). Similarly, in the reaction of the gold complexes CH_3AuL with CF_3I, only monovalent gold products were found when $L = P\phi_3$, but for $L = PCH_3\phi_2$, both monovalent and trivalent gold products were formed. When $L = P(CH_3)_2\phi$ or $P(CH_3)_3$, only trivalent gold species were obtained (*59*). In the reaction where L = trimethylphosphine, the oxidative addition step [which yields $CF_3Au(CH_3)(PMe_3)I$] and a subsequent ligand-exchange reaction of this intermediate with the reagent $CH_3Au(PMe_3)$ [which gives the products actually isolated, CF_3Au-

$(CH_3)_2(PMe_3)$ and $Au(PMe_3)I$] were both monitored by NMR (*59*). Additionally, the tetravalent platinum compounds, $CF_3Pt(CH_3)_2(PMe_2\phi)_2I$ and $CF_3Pt(CH_3)(PMe_2\phi)_2I_2$ thermally extrude C_2H_6 and CH_3I, respectively, at temperatures of 180 and 225°C (*56*). Aside from being another indication that CF_3–metal bonds are stronger (or at least less reactive) than CH_3–metal bonds, the last reactions also demonstrate that reductive eliminations of alkanes or alkyl iodides do proceed in the trifluoromethyl–platinum system.

Presumably, the formation of $(CF_3)_2Pd(P(OMe)_3)_2$ from $Pd(P(OMe)_3)_4$ (*52*) and the synthesis of $(CF_3)_2Pt(COD)$ from $(CH_3)_2Pt(COD)$ (*54*) are the results of a series of successive oxidative addition and reductive elimination steps. In these instances the triphenylphosphite and the cyclooctadiene ligands appear to be insufficiently basic to allow the postulated tetravalent metal species to exist as much more than reactive intermediates.

Complete mechanistic investigations of the oxidative addition reactions of CF_3I to metal substrates have not been carried out; thus, whether the reactions in Table II occur by concerted additions or radical pathways is, in general, not yet known. The oxidation of $CH_3Au(PMe_3)$, however, has been found to be substantially slowed (but not entirely stopped) by the addition of galvinoxyl (*59*), indicating that a radical mechanism is important in the oxidative addition of CF_3I to gold substrates. Alternatively, the product distribution of $R_fCo(III)$-(base)L species, where base = tetradentate Schiff base while L = H_2O or pyridine, obtained from the oxidative addition of CF_3I to Co(I) complexes has been interpreted in terms of a more polar addition mechanism in the cobalt system (*60*).

As was the case with Table I, reference to Table II immediately indicates several other types of reactions that might be profitably examined. One of the more notable omissions in Table II is the lack of oxidative additions to d^7 and d^9 metal complexes. Although it is known that CF_3Br does react with $Pt(P\phi_3)_4$ to generate $CF_3Pt(P\phi_3)_2Br$ (*61*), sources of the trifluoromethyl ligand other than CF_3I have been little examined. Additionally, while $(CF_3)_2NOIr(CO)(P\phi_3)_2$ has been reported to oxidatively add CF_3I, thus forming $CF_3Ir[(CF_3)_2NO]$-$(CO)(P\phi_3)_2I$ in 55% yield (*62*), reactions involving metal substrates which already contain perfluoroalkyl groups have received very little attention.

The limitations of the oxidative addition method in the preparation of trifluoromethyl derivatives appear to be those inherent in this general type of reaction. The most productive substrates have been low valent, electron-rich, coordinatively unsaturated species, preferably

TABLE II

Oxidative Additions of CF_3I to Transition Metal Compounds[a]

Product	Reagent	Yield (%)	References
	[Fe/Ru/Os]		
$CF_3Fe(CO)_4I$	$Fe(CO)_5$	6	*42*
	[Co/Rh/Ir]		
$CF_3Co(Cp)(CO)I$	$(Cp)Co(CO)_2$	8 (51)	*41* (*43*)
$CF_3Rh(Cp)(CO)I$	$(Cp)Rh(CO)_2$	60	*44*
$CF_3Rh(Cp^*)(PF_3)I$	$(Cp^*)Rh(PF_3)_2$	72	*45*
$\{CF_3Rh(Cp)I\}_2$	$(Cp)Rh(C_2H_4)_2$	80	*46*
$CF_3RhCl(CO)(PMe_2\phi)_2I$	$RhCl(CO)(PMe_2\phi)_2$	73	*47*
$CF_3RhBr(CO)(PMe_2\phi)_2I$	$RhBr(CO)(PMe_2\phi)_2$	70	*47*
$CF_3Ir(Cp)(CO)I$	$(Cp)Ir(CO)_2$	40	*43*
$CF_3Ir(Cp^*)(CO)I$	$(Cp^*)Ir(CO)_2$	78	*48*
$CF_3IrCl(CO)(P\phi_3)_2I$	$IrCl(CO)(P\phi_3)_2$	57	*23*
$CF_3IrCl(CO)(PMe\phi_2)_2I$	$IrCl(CO)(PMe\phi_2)_2$	49	*49*
	[Ni/Pd/Pt]		
$CF_3Ni(P\text{-}n Bu_3)_2I$	$Ni(COD)(P\text{-}n Bu_3)_2$	50	*50*
$CF_3Pd(P\phi_3)_2I$	$Pd(P\phi_3)_4$	78	*51*
$CF_3Pd(dppe)I$	$Pd(dppe)_2$	47	*51*
$(CF_3)_2Pd[P(OMe)_3]_2$	$Pd[P(OMe)_3]_4$	12	*52*
$CF_3Pt(P\phi_3)_2I$	$Pt(P\phi_3)_4$	80	*51*
$CF_3Pt(dppe)I$	$Pt(dppe)_2$	12	*51*
$CF_3Pt(PMe\phi_2)_2I$	$Pt(PMe\phi_2)_4$	40	*53*
$(CF_3)_2Pt(COD)$	$(CH_3)_2Pt(COD)$	61	*54*
$CF_3Pt(PEt_3)_2I$	$(CH_3)_2Pt(PEt_3)_2$	90	*55*
$CF_3Pt(CH_3)_2(PMe_2\phi)_2I$	$(CH_3)_2Pt(PMe_2\phi)_2$	80	*56*
$CF_3Pt(CH_3)_2(AsMe_2\phi)_2I$	$(CH_3)_2Pt(AsMe_2\phi)_2$	97	*56*
$CF_3Pt(CH_3)(PMe_2\phi)_2I_2$	$(CH_3)Pt(I)(PMe_2\phi)_2$	62	*56*
$CF_3Pt(C{\equiv}CCH_3)_2(AsMe_3)_2I$	$Pt(C{\equiv}CCH_3)_2(AsMe_3)_2$	49	*57*
$CF_3Pt(C_6H_5)_2(PMe_2\phi)_2I$	$Pt(C_6H_5)_2(PMe_2\phi)_2$	74	*58*
	[Cu/Ag/Au]		
$CF_3Au(P\phi_3)$	$CH_3Au(P\phi_3)$	100	*59*
$CF_3Au(CH_3)(PMe_3)I$	$CH_3Au(PMe_3)$	—	*59*

[a] Me = CH_3; ϕ = C_6H_5; Cp = η^5-C_5H_5; Cp* = η^5-$(CH_3)_5C_5$; COD = η^4-1,5-cyclooctadiene; dppe = η^2-$\phi_2PCH_2CH_2P\phi_2$.

those containing metals from the lower rows of the periodic table. The addition of CF_3I to relatively electron-poor metals, or the addition of more than two CF_3 groups to any metal center is yet to be demonstrated.

Other reactions of CF_3I with transition metal substrates that have

TABLE III

TRIFLUOROMETHYL IODIDE OXIDATIONS OF METAL SPECIES

Product	Reagent	Reference
	[Cr/Mo/W]	
$CF_3Cr(H_2O)_5^{2+}$	$Cr(aq)^{2+}$	*63*
$CF_3Cr(Cl)_2(CH_3CN)_3$[a]	$Cr(Cl)_2(CH_3CN)_2$	*64*
	[Fe/Ru/Os]	
$CF_3Fe(Cp)(CO)_2$	$Me_3GeFe(Cp)(CO)_2$	*65*
$CF_3Fe(Cp)(CO)_2$	$Me_3SnFe(Cp)(CO)_2$	*65*
	[Co/Rh/Ir]	
$CF_3Co(CO)_4$	$Co_2(CO)_8$	*66*[b]
$CF_3Co(CO)_4$	$Me_3SnCo(CO)_4$	*66*[b]
$CF_3Co(dmg)_2py$	$\{Co(dmg)_2py\}_2$	*67*[c]
	[Ni/Pd/Pt]	
$CF_3Ni(Cp)(CO)$	$\{Ni(Cp)(CO)\}_2$	*68, 69*
$CF_3Ni(P\phi_3)_2(I)_2$	$Ni(P\phi_3)_2(C_2H_4)$	*70*
	[Cu/Ag/Au]	
CF_3Cu[a]	Cu	*71*

[a] Probable product.

[b] UV irradiation employed.

[c] dmg = dimethyl glyoximate (1−).

resulted in the formation of trifluoromethyl–metal bonds are listed in Table III. Oxidations, oxidative cleavages, and other reactions that do not appear to have resulted from simple two electron oxidative additions to a metallic species are represented. The ultimate limitation upon reagents such as CF_3I in reactions of the type indicated in Table III is that whereas the trifluoromethyl ligand is quite electron withdrawing once bonded to a metal, compounds that contain the CF_3 group are usually not especially powerful oxidizing agents. Trifluoromethyl iodide, for example, is typically somewhat less reactive than diiodine.

Once the trifluoromethyl-containing organometallic compounds have been formed, ligand-exchange reactions usually proceed readily. The first example was reported by Hieber, who observed that NO reacted cleanly with $CF_3Co(CO)_3P(O\phi)_3$ to afford $CF_3Co(NO)_2P(O\phi)_3$ quantitatively (*22*).

Displacement of CO by triphenylphosphine, either photochemically, as in $CF_3Mo(Cp)(CO)_3$ and $CF_3Fe(Cp)(CO)_2$ (*25*), or thermally, as in $CF_3M(Cp)(CO)I$, M = Co, Rh, or Ir, (*43, 72*) and $CF_3Ni(Cp)(CO)$ (*69*), results in the formation of the monosubstituted triphenylphosphine complexes in 49–96% yield. Similarly, pyridine has been used to displace bridging iodine (*46*) or H_2O (*60*) in trifluoromethyl–metal complexes. The interaction of PF_3 with $CF_3Co(CO)_4$ results in the stepwise replacement of CO by PF_3, resulting in the formation of the fluctional species, $CF_3Co(PF_3)_n(CO)_{4-n}$ ($n = 1–4$). Trifluorophosphine has also been shown to displace CO in the trifluoromethyl manganese carbonyl system (*73*).

The chelating ligand 1,2-bis(diphenylphosphino)ethane (dppe) has been found to react with $CF_3Mo(Cp)(CO)_3$ (*25*) or $(CF_3)_2Pt(COD)$ (*74*) to generate the dppe complexes in 80 and 83% yields, respectively. The cyclooctadiene ligand in $(CF_3)_2Pt(COD)$ has also been replaced with (2-vinylphenyl)diphenylphosphine in 91% yield (*36*), and by a number of other bases, including isocyanide, 4-methylpyridine, $PMe_2\phi$, $AsMe_3$, Bipy, $Sb\phi_3$, $As\phi_3$, and $\phi_2PC{\equiv}CP\phi_2$ (*54*). Additionally, the reaction of $CF_3Co(Cp)(CO)I$ with potassium polypyrazolylborates, $K(C_3H_3N_2)_nBH_{4-n}$, has resulted in the formation of the bidentate complexes $CF_3Co(Cp)\{(C_3H_3N_2)_2BH_2\}$ and $CF_3Co(Cp)\{(C_3H_3N_2)_3BH\}$ in 60–70% yield (*75*).

Interchanges of one electron-donating ligands by metathetical reactions have been reported for $CF_3Pt(PMe\phi_2)_2Cl$ with LiBr (*24*), for $CF_3Pt(PEt_3)_2I$ with $AgSCF_3$ (*55*), and for $CF_3Pt(PMe_2\phi)_2I$ with $AgNO_3$ (*76*), the reactions resulting in the halo or pseudohalo, or nitro platinum complexes in good yield in each case. A valuable alternative synthetic route involves the preparation of the cationic metal complex by means of the reaction of $AgBF_4$ or $AgPF_6$ with, for example, $CF_3Pt(PMe_2\phi)_2I$. This reaction forms the solvated cation, e.g., $CF_3Pt(PMe_2\phi)_2(solvent)^+$, where the solvent is typically acetone or methanol. Subsequent addition of the sodium salts of Br^-, Cl^-, NCO^-, NCS^-, N_3^-, NO_2^-, or CN^- then generates the desired neutral platinum complex (*76*). Platinum hydrides are formed from the reaction of $CF_3Pt(P\phi_3)_2(solvent)^+$ with BH_4^- (*61, 77*) while the addition of LiCl to the rhodium cation $CF_3Rh(CO)(PMe_2\phi)_2Cl^+PF_6^-$ forms $CF_3Rh(CO)(PMe_2\phi)_2Cl_2$ in 85% yield (*47*).

The solvent associated with the cationic platinum complex $CF_3Pt(PMe_2\phi)_2(CH_3OH)^+$ is also easily displaced by a variety of Lewis bases (L) including L = $PMe_2\phi$, $P\phi_3$, $As\phi_3$, $Sb\phi_3$, CO, isocyanide, and a number of nitrogenous bases like pyridine. These reactions result in cationic products of the type $CF_3Pt(PMe_2\phi)_2L^+PF_6^-$ (*76*).

C. SUMMARY

Reference to Tables I–III indicates a fairly large number of trifluoromethyl transition metal derivatives that have been synthesized by means of the types of reactions that were developed during the early stages of the study of trifluoromethyl transition metal compounds. On balance, trifluoromethyl-substituted compounds of electron-rich, low valent transition metal species are relatively easily synthesized and usually much more stable than the analogous methylated moieties.

Many of the recent efforts in this area of chemistry have been designed to explore the chemistry of the trifluoromethyl species prepared by these reactions. Among the more interesting results have been the construction of carbene and tetramethylcyclobutadiene ligands affixed to trifluoromethyl platinum cations (*78*), the synthesis of difluorocarbene complexes like $(Cp)Mo(CO)_3CF_2^+$ (*79*), the formation of $(CF_3)_2CS$ from $CF_3Re(CO)_5$ (*38*), and the insertion reaction of SO_2 into CF_3–metal bonds (*80*).

Another area of current interest is related to the biological activity that is observed in a number of fluorinated and partially fluorinated organic compounds. The synthesis of trifluoromethyl aliphatic compounds (*81*) and trifluoromethyl pyrimidine nucleosides (*82*) from trifluoromethyl copper, as well as the preparation of CF_3Cu itself from the reaction of elemental copper with $(CF_3)_2Hg$ (*83*) have all been recently examined. The formation of trifluoromethylcobalamin (*84*) and the preparation of trifluoromethyl Co(III) (salen) complexes (*85*) have been reported, along with the results of the defluorination on detrifluoromethylation reactions that are observed under reductive conditions. As the realization that fluorinated organic compounds are effective for such disparate uses as chemotherapeutic agents, ulcer remedies, treatments for myocardial infarctions, and blood substitutes, the amount of effort expended in this particular area of fluorine chemistry will doubtlessly increase.

What reference to Tables I–III does not indicate, however, is any indication of a compound containing more than two trifluoromethyl groups attached to a metal atom, or many examples of early transition metal trifluoromethyl derivatives. The early results of a number of synthetic techniques designed to ultimately result in more general routes to the preparation of trifluoromethylated transition metal compounds are presented below.

III. More Recent Developments

A. SYNTHESES WITH ACTIVATED METALS AND TRIFLUOROMETHYL RADICALS

Clearly, the synthesis of a broad spectrum of trifluoromethyl transition metal compounds, including multiply substituted derivatives of metals in their higher oxidation states, requires a much different approach than the thermal decarbonylations or oxidative additions described above. During the last decade a number of studies have been directed toward the preparation of trifluoromethyl–metal compounds in which the metals were in their usual oxidation states and the products were uncomplicated by the presence of ligands other than CF_3 or halide. In a number of instances relatively sophisticated experimental techniques have been employed in what might be generically termed a "second generation" of studies devoted to the preparation of trifluoromethyl-containing compounds. In each of these experiments at least one of the reagents has been activated through the addition of energy from an external source.

A number of the first of the second generation experiments were carried out by Klabunde, who observed that metal atom reactions of Zn, Ni, Pd, and Ag with CF_3I resulted in the formation of the ligand-free monosubstituted compounds CF_3ZnI, CF_3NiI, CF_3PdI, and CF_3Ag, respectively (*86–90*). Palladium atoms were also found to react with CF_3COCl yielding $CF_3COPdCl$, which extrudes CO at low temperature (*87*). Although the ligand-free species are generally very reactive, and often decompose at low temperatures, the palladium compounds, CF_3PdX, were found to be surprisingly stable at ambient temperature in the presence of air (*87, 88*).

During approximately the same period of time, Lagow investigated the synthetic applications of the reactions between metal halides and CF_3 radicals which had been generated from radio frequency discharges in C_2F_6. These studies resulted in the initial syntheses of the fully substituted compounds $(CF_3)_4Sn$, $(CF_3)_4Ge$, $(CF_3)_2Te$, and $(CF_3)_3Bi$ (*91, 92*) as well as the first evidence for a species containing a xenon–carbon bond (*93*). The Group IVA organometallic compounds were the first examples of metallic or metalloid centers which had been substituted by as many as four trifluoromethyl groups.

More recently, this group has explored the reactions of metal atoms with a variety of radicals that have also been formed by discharge methods. In the later studies, compounds such as CF_3HgSCF_3 (*94*), $(CF_3)_2Ni$, and $(CF_3)_2Pd$ were prepared, the last two being isolated as the trimethylphosphine adducts (*95*).

A number of other recent experiments using activated reagents have also been directed toward the preparation, or more efficient preparation of trifluoromethyl Group IIB compounds. Among the more novel methods described has been the reaction of CF_3I with Zn in the presence of ultrasonic excitation. The CF_3ZnI that was presumably formed subsequently reacted with organic halides to yield trifluoromethylated organic species (*96*). Additionally, the electrochemical oxidation of Zn or Cd in the presence of CF_3I reportedly forms $CF_3ZnI_2^-$ or $CF_3CdI_2^-$, if tetraalkyl ammonium iodide salts have been added, or $CF_3ZnI \cdot$ bipy, if 2,2′-bipyridine had been added to the solution in which the oxidation took place (*97, 98*).

One of the important direct results of the studies by Lagow and Klabunde is that for the first time it was demonstrated that a number of trifluoromethylated organometallic compounds such as $(CF_3)_4Sn$, $(CF_3)_4Ge$, and CF_3PdI which contain a high proportion of CF_3 ligands are much more stable thermally than had been previously anticipated. Thus, inherently, there appears to be no reason that a number of other metallic species in their normal (high) oxidation states might not also form derivatives in which the majority or even all of the ligands are trifluoromethyl groups.

A second, more indirect result of these studies is that for the first time large amounts, ~10 g, of each of the bis(trifluoromethyl)Group IIB compounds became readily available. Bis(trifluoromethyl)mercury, for example, in addition to the syntheses indicated previously (*1, 40*), can also be conveniently prepared by any of a number of alternative methods, ranging from the direct fluorination of $(CH_3)_2Hg$ to the reaction of mercury halides with CF_3 radicals (*99*). The other disubstituted compounds of Group IIB, $(CF_3)_2Cd \cdot L_2$ and $(CF_3)_2Zn \cdot L_2$, can be easily prepared from $(CF_3)_2Hg$ as described below (*100, 101*).

While this second generation of experiments has resulted in the preparation of a number of interesting and unusual compounds, specialized and often relatively expensive equipment has generally been required to successfully carry out the desired synthesis. In order for preparations of trifluoromethylated organometallic compounds to become practical in many laboratories, a less exotic approach appeared to be desirable. One seemingly obvious synthetic technique that had never been thoroughly examined was ligand-exchange reactions between the trifluoromethyl derivatives of electropositive elements and, for example, metal halides.

B. Trifluoromethyl Group IIB Ligand Exchange Reactions

As mentioned in Section I, one of the first aspects of the chemistry of trifluoromethylated organometallic compounds to be examined was the possibility of CF_3 ligand-exchange reactions utilizing CF_3Li, CF_3MgI, or $(CF_3)_2Hg$ as reagents. These early experiments, which occurred very shortly after the initial preparation of CF_3I, indicated that the lithium and magnesium trifluoromethyl species decompose at very low temperatures and CF_3 transfer to other metallic centers could not be reliably demonstrated. The mercurial, reportedly, did not serve as a source of trifluoromethyl ligands (*3–6*).

However, during the separation of Group IVA trifluoromethyl compounds such as $(CF_3)_2GeBr_2$ from the other products of the reaction between CF_3 radicals and $GeBr_4$ (*91*), ligand-exchange reactions that resulted in CF_3GeBr_3 and $(CF_3)_3GeBr$ were observed to proceed with little or no difluorocarbene elimination (*99*). These observations eventually led to a reinvestigation of the reactions of $(CF_3)_2Hg$ with the halides of germanium and tin.

Bis(trifluoromethyl)mercury was found to react at elevated temperatures with both tin and germanium tetrahalides, resulting in a number of CF_3-containing compounds including the fully substituted derivative of germanium, $(CF_3)_4Ge$ [Eq. (5)]. The reaction of tin tetrabromide with $(CF_3)_2Hg$, on the other hand, yielded only CF_3SnBr_3 and $(CF_3)_2SnBr_2$, as shown in Eq. (6) (*102*).

$$\underset{}{GeI_4 + (CF_3)_2Hg} \xrightarrow{150°C} \underset{(15\%)}{(CF_3)_4Ge} + \underset{(72\%)}{(CF_3)_3GeBr} \tag{5}$$

$$SnBr_4 + (CF_3)_2Hg \xrightarrow{125°C} \underset{(10\%)}{(CF_3)_2SnBr_2} + \underset{(54\%)}{CF_3SnBr_3} \tag{6}$$

The reactions of $Sn(CH_3)_4$ and $Pb(CH_3)_4$ with $(CF_3)_2Hg$ were also examined. They result solely in the monosubstituted compounds $CF_3Sn(CH_3)_3$ and $CF_3Pb(CH_3)_3$ which were obtained in 20 and 94% yields, respectively. The reaction of $CF_3Sn(CH_3)_3$ with $(CF_3)_2Hg$ was found to result in only trace amounts of the disubstituted species, $(CF_3)_2Sn(CH_3)_2$ (*103*).

In order to determine why more complete substitution was not observed with the tin-containing halides, the reaction between $SnBr_4$ and $(CF_3)_2Hg$ was examined in further detail (*104*). The results of the study indicated that the trisubstituted tin derivative, $(CF_3)_3SnBr$, did appear to be formed during the reaction, but at the temperatures required for the ligand-exchange process to proceed, ~110°C, decomposition of the product occurred immediately. Thus in contrast to previous reports, the mercurial, $(CF_3)_2Hg$, does readily undergo ligand exchanges at elevated temperatures. For some elements, such as tin and lead, however, the activation energy for the ligand interchange with the mercurial is sufficiently high that the more fully substituted products are thermally unstable under the conditions required for their formation. Obviously, a stronger trifluoromethyl donor was desirable.

Although no trifluoromethyl derivatives of cadmium had ever been isolated, their attempted synthesis was particularly appealing from several viewpoints. First, alkyl cadmium reagents are typically more reactive than their mercury analogs; presumably the same might be true of the perfluoroalkyl derivatives. Second, the early observation that $(CF_3)_2Hg$ was not formed directly from CF_3I and Hg, but was efficiently prepared in the presence of elemental cadmium (*1*), implied that trifluoromethyl cadmium species were capable of at least a transient existance. Third, NMR spectra obtained from pyridine solutions of $(CF_3)_2Hg$ and $Cd(CH_3)_2$ had been interpreted in terms of CF_3 ligand interchanges between cadmium and mercury (*105*), again implying that CF_3–cadmium compounds might well be sufficiently stable to isolate.

Bis(trifluoromethyl(mercury and dimethyl cadmium were found to readily exchange ligands at ambient temperature in a number of basic solvents, including THF, glyme, diglyme, and pyridine (*100, 106*). In each of these solvents the formation of an equilibrium mixture containing all possible methyl and trifluoromethyl derivatives of mercury and cadmium occurs within a few hours. The bis(trifluoromethyl)cadmium · solvent adducts can be easily purified since the disubstituted cadmium trifluoromethyl species is strongly dicoordinated to the basic solvent in which it was prepared. Thus excess solvent, as well as any other organometallic compounds present, can be removed by prolonged pumping under vacuum which leaves only the nonvolatile $(CF_3)_2Cd$ adduct remaining as a free flowing white powder (*106*).

The reactivity of the base adducts of $(CF_3)_2Cd$ with several classes of compounds has been examined. The first type of reaction explored was Lewis base substitutions such as the formation of $(CF_3)_2Cd \cdot 2$ pyridine from $(CF_3)_2Cd \cdot$ glyme. These exchanges proceed readily in quantitative yield and the nature of the base attached to the cadmium center markedly affects the reactivity of the compound. The adducts of strongly coordinating bases, such as pyridine, are generally much more stable thermally, but less reactive in ligand exchanges than the adducts of less strongly basic donors such as THF. As yet $(CF_3)_2Cd$, which is not complexed by base, has not been isolated.

Of the bis(trifluoromethyl)cadmium derivatives obtained to date, the glyme adduct, $(CF_3)_2Cd \cdot$ glyme, is the best compromise between chemical reactivity and thermal stability; this compound appears to be almost a classic example of a "lightly stabilized" species, one which is stabilized enough to be isolatable but which is still quite reactive (*107*). That this material is a much more effective reagent than, for example, $(CF_3)_2Cd \cdot 2$ pyridine, can be most easily seen from the results of the reactions of these compounds with a second class of substrates, the halides of germanium and tin. Within 15 min at ambient temperature

$(CF_3)_2Cd \cdot$ glyme reacts with $GeBr_4$ to form $(CF_3)_4Ge$ in 43% yield whereas $(CF_3)_4Sn$ is generated from $SnBr_4$ in 66% yield, again at ambient temperature. Neither $(CF_3)_4Ge$ nor $(CF_3)_4Sn$ resulted from the interaction of $(CF_3)_2Cd \cdot$ 2pyridine with the metal tetrahalides (*106*).

One of the best known reactions of dialkyl cadmium compounds is that with acyl halides which results in the formation of ketones. The reactions of $(CF_3)_2Cd \cdot$ glyme with CH_3COBr and C_6H_5COCl were the third class of reactions of the trifluoromethylating reagent examined. However, the mixed trifluoromethylalkyl or -aryl ketones were not observed. The organic products obtained were the acyl fluorides (95% yield) along with difluorocarbene. The latter could be stereospecifically trapped at temperatures as low as −78°C. The addition of either lithium or magnesium halides to the reaction mixture did not affect the outcome (*106*).

Finally, to determine if $(CF_3)_2Cd \cdot$ glyme would transfer CF_3 groups to transition metal species, the reactions of a fourth type of substrate, low valent late transition metal complexes, have been examined. At ambient temperature the dihalo bis(trialkylphosphine) adducts of each of the elements of the nickel triad have been found to react with equimolar amounts of the cadmium reagent to form the air stable monosubstituted derivatives, $(CF_3)BrNiL_2$, $(CF_3)BrPdL_2$, and $(CF_3)IPtL_2$ where L = PEt_3 or P-$n$$Bu_3$. The yields range from 60 to 70% (*108*). In the presence of an excess of $(CF_3)_2Cd \cdot$ glyme, the disubstituted palladium and platinum derivatives, $(CF_3)_2PdL_2$ and $(CF_3)_2PtL_2$, can be isolated in ~40% yield. The reaction of the nickel compound, $Br_2Ni(PEt_3)_2$ with an excess of the trifluoromethylating reagent does result in $(CF_3)_2Ni(PEt_3)_2$ (*108*). However, in the absence of a trapping agent the reaction proceeds further. The species eventually obtained from the reaction include $(CF_3)ClNi(PEt_3)_2$, where the chloride arises from the solvent employed, CH_2Cl_2, and series of fluoroalkenes which are bonded to the nickel atom. Both of these types of products appear to be derived from the decomposition of $(CF_3)_2Ni(PEt_3)_2$ via a carbene mechanism (*109*).

At the present time the preparation of the trifluoromethylated derivatives of low valent transition metals by ligand-exchange reactions appears to be quite general. However, as exemplified by the nickel reaction above, the utility of the method is obviously subject to the inherent stability of the desired product. In many cases, such as the preparation of the trifluoromethyl derivatives of the cyclopentadienyl cobalt system, $(CF_3)Co(Cp)(CO)I$ and $(CF_3)_2Co(Cp)(CO)$, the reaction of the dihalide with $(CF_3)_2Cd \cdot$ glyme represents the simplest reaction sequence currently known (*110*). The types of reactions that are currently under investigation in attempts to extend the effectiveness of trifluoromethyl ligand exchanges are discussed below.

C. PROSPECTS

As was originally noted in Section I, a complete series of trifluoromethyl ligand exchange reagents is currently unknown. The results obtained within the past few years, however, do indicate that the development of such a series is probable. The mercurial, $(CF_3)_2Hg$, has been recently shown to serve as a trifluoromethyl donor and this compound is the reagent of choice for transformations in which the products desired are sufficiently stable to withstand the prolonged exposure to the temperatures of ~100°C that are required (*104, 110*). The mercurial has also been recently shown to be active in another type of reaction, oxidative additions to low valent transition metal complexes that result in products such as $CF_3Pt(HgCF_3)(P\phi_3)_2$ (*111*) and $CF_3Ru(HgCF_3)(CO)_2(P\phi_3)_2$ (*112*).

One of the very important traditional uses for alkyl mercury compounds has been their use as reagents in preparations of more reactive organometallic compounds. The trifluoromethyl mercurial is also beginning to demonstrate a similar utility as a precursor, for example, in the synthesis of the more reactive reagent $(CF_3)_2Cd \cdot$ glyme. The latter material is clearly a superior agent for the formation of products of only limited thermal stability, since it is active at ambient temperatures and the reactions generally require only a few minutes, or at most a few hours.

Two aspects of ligand-exchange reactions are under active study at present. The first of these areas is the development of the chemistry of the bis(trifluoromethyl)zinc adducts. Like the cadmium compound, $(CF_3)_2Zn$ is isolatable only if complexed by 2 mol of base. The $(CF_3)_2Zn \cdot 2$ pyridine species (*101*), however, exchanges ligands only at a sluggish rate (*113*). The adducts of the less basic solvents examined to date yield complexes that are exceedingly reactive but very difficult to purify.

The second area of contemporary interest is the attempted formation of fully substituted trifluoromethyl derivatives of high valent transition metal species. At −30°C in ether, the reaction between hexabromotungsten and $(CF_3)_2Cd \cdot$ glyme proceeds smoothly, but the product decomposes at temperatures near 0°C with the formation of C_2F_4, WF_6, and WOF_4. The decomposition of the presumed $W(CF_3)_6$ appears to be autocatalytic in nature, but seems to be much less violent than the decomposition of $(CH_3)_6W$ (*2*). While experiments continue, the difficulty is clearly related to the instability of the desired product, and not the lack of an effective ligand transfer reagent.

REFERENCES

1. Emeleus, H. J., and Haszeldine, R. N., *J. Chem. Soc.* 2948, 2953 (1949).
2. Galyer, L., Mertis, K., and Wilkinson, G., *J. Organomet. Chem.* **85,** C37 (1975).
3. Poulet, R. J., MTP *Int. Rev. Sci. Inorg. Chem. Ser. One* **3,** 127 (1972).
4. Chambers, R. D., "Fluorine in Organic Chemistry." Wiley, New York, 1973.
5. Emeléus, H. J., "The Chemistry of Fluorine and Its Compounds." Academic Press, New York, 1969.
6. Clark, H. C., *Adv. Fluorine Chem.* **3,** 19 (1963).
7. Lebeau, P., and Damiens, A., *C. R. Acad. Sci. (Paris)* **191,** 939 (1930); Ruff, O., and Keim, R., *Z. Anorg. Allgem. Chem.* **192,** 249 (1930).
8. Simons, J. H., and Block, L. P., *J. Am. Chem. Soc.* **59,** 1407 (1937).
9. Treichel, P. M., and Stone, F. G. A., *Adv. Organomet. Chem.* **1,** 143 (1964).
10. Bruce, M. I., and Stone, F. G. A., *Prep. Inorg. React.* **4,** 177 (1968).
11. Banks, R. E., "Fluorocarbons and their Derivatives." MacDonald, London, 1970.
12. Banks, R. E., and Barlow, M. G., "Fluorocarbon and Related Chemistry, Vol. 1–3." Chemical Society, London, 1971–1976.
13. Current developments in the area of fluorine containing organometallic compounds are surveyed annually *in* Abel, E. W., and Stone, F. G. A., "Organometallic Chemistry." Chemical Society, London.
14. Coffield, T. H., Kozikowski, J., and Closson, R. D., *Abstr. Int. Conf. Coord. Chem., 5th, London 1959* p. 126.
15. Mc Clellan, W. R., *J. Am. Chem. Soc.* **83,** 1598 (1961).
16. Beck, W., Hieber, W., and Tengler, H., *Chem. Ber.* **94,** 862 (1961).
17. King, R. B., and Bisnette, M. B., *J. Organomet. Chem.* **2,** 15 (1964).
18. Hieber, W., Hofler, M., and Muschi, J., *Chem. Ber.* **98,** 311 (1965).
19. Hensley, D. W., Wurster, W. L., and Stewart, R. P., *Inorg. Chem.* **20,** 645 (1981).
20. Heck, R. F., and Breslow, D. S., *J. Am. Chem. Soc.* **84,** 2499 (1962).
21. Hieber, W., Beck, W., and Lindner, E., *Naturforschung* **16b,** 229 (1961).
22. Hieber, W., Muschi, J., and Duchatsch, H., *Chem. Ber.* **98,** 3924 (1965).
23. Blake, D. M., Shields, S., and Wyman, L., *Inorg. Chem.* **13,** 1595 (1974).
24. Bennett, M. A., Chee, H., and Robertson, G. B., *Inorg. Chem.* **18,** 1061 (1979).
25. See, for example, King, R. B., Kapoor, R. N., Pannell, K. H., *J. Organomet. Chem.* **20,** 187 (1969); King, R. B., King, A. D., Iqbal, M. Z., and Frazier, C. C., *J. Am. Chem. Soc.* **100,** 1687 (1978).
26. Ogilvie, J. F., *J. Chem. Soc. Chem. Commun.* 323 (1970).
27. Clark, H. C., and Tsai, J. H., *J. Organomet. Chem.* **7,** 515 (1967).
28. Cotton, F. A., and Wing, R. M., *J. Organomet. Chem.* **9,** 511 (1967).
29. Graham, W. A. G., *Inorg. Chem.* **7,** 315 (1968).
30. Hall, M. B., and Fenske, R. F., *Inorg. Chem.* **11,** 768 (1972).
31. Lichtenberger, D. L., and Fenske, R. F., *Inorg. Chem.* **13,** 486 (1974).
32. Churchill, M. R., *Perspect. Struct. Chem.* **3,** 91 (1970).
33. Churchill, M. R., and O'Brien, T. A., *J. Chem. Soc. A* **161** (1970).

34. Crump, D. B., and Payne, N. C., *Inorg. Chem.* **12,** 1663 (1973).

35. Manojlovic-Muir, L., Muir, K. W., Solomun, T., Meek, D. W., and Peterson, J. L., *J. Organomet. Chem.* **146,** C26 (1978).

36. Bennett, M. A., Chee, H., Jeffery, J. C., and Robertson, G. B., *Inorg. Chem.* **18,** 1071 (1979).

37. Hieber, W., and Duchatsch, H., *Chem. Ber.* **98,** 2933 (1965).

38. Thiele, G., Liehr, G., and Lindner, E., *J. Organomet. Chem.* **70,** 427 (1974); Lindner, E., personal communication, 1983.

39. Alexander, J. J., and Wojcicki, A., *Inorg. Chem.* **12,** 74 (1973); Kuhlmann, E. J., and Alexander, J. J., *J. Organomet. Chem.* **174,** 81 (1979).

40. Knunyants, I. L., Komissarov, Ya. F., Dyatkin, B. L., and Lantseva, L. T., *Izv. Akad. Nauk SSSR Ser. Khim.* **22,** 943 (1973).

41. King, R. B., Treichel, P. M., and Stone, F. G. A., *J. Am. Chem. Soc.* **83,** 3593 (1961).

42. King, R. B., Stafford, S. L., Treichel, P. M., and Stone, F. G. A., *J. Am. Chem. Soc.* **83,** 3604 (1961).

43. Gardner, S. A., and Rausch, M. D., *Inorg. Chem.* **13,** 997 (1974).

44. McCleverty, J. A., and Wilkinson, G., *J. Chem. Soc.* p. 4200 (1964).

45. King, R. B., and Efraty, A., *J. Organomet. Chem.* **36,** 371 (1972).

46. Mukhedkar, A. J., Mukhedkar, V. A., Green, M., and Stone, F. G. A., *J. Chem. Soc. A* 3158 (1970).

47. Clark, H. C., and Reimer, K. J., *Can. J. Chem.* **54,** 2077 (1976).

48. King, R. B., and Efraty, A., *J. Organomet. Chem.* **27,** 409 (1971).

49. Collman, J. P., and Sears, C. T., *Inorg. Chem.* **7,** 27 (1968).

50. Cundy, C. S., *J. Organomet. Chem.* **69,** 305 (1974).

51. Rosevear, D. T., and Stone, F. G. A., *J. Chem. Soc. A* 164 (1968).

52. Empsall, H. D., Green, M., and Stone, F. G. A., *J. Chem. Soc. Dalton Trans.* 96 (1972).

53. Mukhedkar, A. J., Green, M., and Stone, F. G. A., *J. Chem. Soc. A* 947 (1970).

54. Clark, H. C., and Manzer, L. E., *J. Organomet. Chem.* **59,** 411 (1973).

55. Dixon, K. R., Moss, K. C., and Smith, M. A. R., *J. Chem. Soc. Dalton Trans.* 990 (1975).

56. Clark, H. C., and Ruddick, J. D., *Inorg. Chem.* **9,** 2556 (1970).

57. Chisholm, M. H., and Rankel, L. A., *Inorg. Chem.* **16,** 2177 (1977).

58. Appleton, T. G., Clark, H. C., and Manzer, L. E., *J. Organomet. Chem.* **65,** 275 (1974).

59. Johnson, A., and Puddephatt, R. J., *J. Chem. Soc. Dalton Trans.* 1360 (1976).

60. Van Den Bergen, A., Murray, K. S., and West, B. O., *J. Organomet. Chem.* **33,** 89 (1971).

61. Michelin, R. A., Belluco, U., and Ros, R., *Inorg. Chem. Acta* **24,** L33 (1976).

62. Booth, B. L., Haszeldine, R. N., and Holmes, R. G. G., *J. Chem. Soc. Chem. Commun.* 489 (1976).

63. Malik, S. K., Schmidt, W., and Spreer, L. O., *Inorg. Chem.* **13,** 2986 (1974).

64. Van Den Bergen, A. M., Murray, K. S., Sheahan, R. M., and West, B. O., *J. Organomet. Chem.* **90,** 299 (1975).

65. Bichler, R. E. J., Clark, H. C., Hunter, B. K., and Rake, A. T., *J. Organomet. Chem.* **69,** 367 (1974).

66. Beveridge, A. D., and Clark, H. C., *J. Organomet. Chem.* **11,** 601 (1968).

67. Schrauzer, G. N., and Windgassen, R. J., *J. Am. Chem. Soc.* **88,** 3738 (1966).

68. McBride, D. W., Dudek, E., and Stone, F. G. A., *J. Chem. Soc.* 1752 (1964).

69. Rausch, M. D., Chang, Y. F., and Gordon, H. B., *Inorg. Chem.* **8,** 1355 (1969).

70. Ashley-Smith, J., Green, M., and Stone, F. G. A., *J. Chem. Soc. A* 3019 (1969).

71. Kobayashi, Y., and Kumadaki, I., *Tetrahedron Lett.* 4095 (1969); McLoughlin, V. C. R., and Thrower, J., *Tetrahedron* **25,** 5921 (1969).

72. Burns, R. J., Bulkowski, P. B., Stevens, S. C. V., and Baird, M. C., *J. Chem. Soc. Dalton Trans.* 415 (1974).

73. Udovich, C. A., Krevalis, M. A., and Clark, R. J., *Inorg. Chem.* **15,** 900 (1976); Miles, W. J., and Clark, R. J., *Inorg. Chem.* **7,** 1801 (1968).

74. Appleton, T. G., and Bennett, M. A., *Inorg. Chem.* **17,** 738 (1978).

75. King, R. B., and Bond, A., *J. Am. Chem. Soc.* **96,** 1334 (1974).

76. Appleton, T. G., Chisholm, M. H., Clark, H. C., and Manzer, L. E., *Inorg. Chem.* **11,** 1786 (1972).

77. Del Pra, A., Zanotti, G., Bardi, R., Belluco, U., and Michelin, R. A., *Cryst. Struct. Commun.* **8,** 729 (1979).

78. Chisholm, M. H., and Clark, H. C., *J. Am. Chem. Soc.* **94,** 1532 (1972).

79. Reger, D. L., and Dukes, M. D., *J. Organomet. Chem.* **153,** 67 (1978).

80. von Werner, K., and Blank, H., *J. Organomet. Chem.* **195,** C25 (1980).

81. Kobayashi, Y., Yamamoto, K., and Kumadaki, I., *Tetrahedron Lett.* 4071 (1979).

82. Kobayashi, Y., Kumadaki, I., and Yamamoto, K., *J. Chem. Soc. Chem. Commun.* 536 (1977).

83. Kondratenko, N. V., Vechirko, E. P., and Yagupolskii, L. M., *Synthesis* **11,** 932 (1980).

84. Tachkova, E. M., Gurevich, V. M., Rudakova, I. P., and Yurkevich, A. M., *Sov. J. Bioorg. Chem.* **4,** 1180 (1978).

85. Brockway, D. J., West, B. O., and Bond, A. M., *J. Chem. Soc. Dalton Trans.* 1891 (1979).

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

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

88. Klabunde, K. J., Anderson, B. B., and Neuenschwander, K., *Inorg. Chem.* **19,** 3719 (1980).

89. Klabunde, K. J., *J. Fluorine Chem.* **7,** 95 (1976).

90. Klabunde, K. J., *Angew. Chem. Int. Ed. Engl.* **14,** 287 (1975).

91. Lagow, R. J., Gerchman, L. L., Jacob, R. A., and Morrison, J. A., *J. Am. Chem. Soc.* **97,** 518 (1975).

92. Morrison, J. A., and Lagow, R. J., *Inorg. Chem.* **16,** 1823 (1977).

93. Turbini, L. J., Aikman, R. E., and Lagow, R. J., *J. Am. Chem. Soc.* **101,** 5833 (1979).

94. Bierschenk, T. R., and Lagow, R. J., *Inorg. Chem.* **22,** 359 (1983).

95. Firsich, D. W., and Lagow, R. J., *J. Chem. Soc. Chem. Commun.* 1283 (1981).

96. Ishikawa, N., and Kitazume, T., *Abstr. Winter Fluorine Conf., 6th, Daytona Beach, 1983.*

97. Osman, A., and Tuck, D. G., *J. Organomet. Chem.* **169,** 255 (1979).

98. Habeeb, J. J., Osman, A., and Tuck, D. G., *J. Organomet. Chem.* **185,** 117 (1980).

99. Lagow, R. J., and Morrison, J. A., *Adv. Inorg. Chem. Radiochem.* **23,** 177 (1980) and references therein.

100. Krause, L. J., and Morrison, J. A., *J. Chem. Soc. Chem. Commun.* 671 (1980).

101. Liu, E. K. S., *Inorg. Chem.* **19,** 266 (1980).

102. Lagow, R. J., Eujen, R., Gerchman, L. L., and Morrison, J. A., *J. Am. Chem. Soc.* **100,** 1722 (1978).

103. Eujen, R., and Lagow, R. J., *J. Chem. Soc. Dalton Trans.* 541 (1978).

104. Krause, L. J., and Morrison, J. A., *Inorg. Chem.* **19**, 604 (1980).

105. Dyatkin, B. L., Martynov, B. I., Knunyants, I. L., Sterlin, S. R., Fedorov, L. A., and Stumbrevichute, Z. A., *Tetrahedron Lett.* 1345 (1971).

106. Krause, L. J., and Morrison, J. A., *J. Am. Chem. Soc.* **103**, 2995 (1981).

107. Hosokawa, T., and Maitlis, P. M., *J. Am. Chem. Soc.* **95**, 4924 (1973).

108. Krause, L. J., and Morrison, J. A., *J. Chem. Soc. Chem. Commun.* 1282 (1981).

109. Krause, L. J., Ph.D. thesis, University of Illinois, Chicago, 1981.

110. Ontiveros, C., and Morrison, J. A., in preparation.

111. Sokolov, V. I., Bashilov, V. V., and Reutov, O. A., *J. Organomet. Chem.* **97**, 299 (1975).

112. Clark, G. R., Hoskins, S. V., and Roper, W. R., *J. Organomet. Chem.* **234**, C9 (1982).

113. Ontiveros, C., Liu, E. K. S., and Morrison, J. A., in preparation.