INORGANIC COMPOUNDS CONTAINING THE TRIFLUOROACETATE GROUP

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I. Introduction

Inorganic trifluoroacetates have been known for some 50 years, the first studies being completed by Swarts (*247*) in 1922. Trifluoroacetate derivatives have now been prepared for nearly all of the elements, the majority of them involving normal oxidation states; for example, there are a large number of trifluoroacetato complexes of chromium(III), nickel(II), copper(II), and tin(IV). Although simple electronegativity arguments would lead one to expect that this group could maintain its identity when bonded to atoms in high oxidation states, this does not appear to be the case. Thus no trifluoroacetato complexes of platinum(IV) or gold(III) have been reported, and lead(IV) trifluoroacetate readily decomposes to the lead(II) compound (*192*). Complexes involving the trifluoroacetate group coordinated to metal atoms in low oxidation states are, however, well known. For instance, $(\pi\text{-Cp})W(CO)_3(O_2CCF_3)$ (*57*), $Re(CO)_5(O_2CCF_3)$ (*57*, *137*), and $Ir(CO)(PPh_3)_2(O_2CCF_3)$ (*237*) have been characterized, but clearly the carbonyl and the other ligands play the major role in stabilizing these low oxidation states.

Although a considerable amount of data has now been reported concerning the physical and chemical properties of inorganic compounds containing the trifluoroacetate group, little attempt has been made previously to report and examine these properties in a systematic manner. This review will attempt to do this and to show that, although trifluoroacetate is a member of the carboxylate family, it has individual characteristics which lead to some unique and interesting chemistry.

II. Trifluoroacetic Acid

Before describing the preparation and properties of trifluoroacetate compounds in general, particular consideration will be given to the parent acid. The normal commercial preparation of trifluoroacetic acid is the electrolytic fluorination of acetyl fluoride or chloride (*210*). Other preparative methods include the oxidation of trifluorotoluidine or other trifluoromethyl aryl derivatives (*247*) and the hydrolysis of trifluoroacetylchloride (*6*).

The physical properties of liquid trifluoroacetic acid are given in Table I. At normal temperatures it is a colorless liquid which fumes readily in moist air and has a powerful odor.

Trifluoroacetic acid is known to form cyclic dimers in the vapor phase which appear to be analogous to those formed by acetic acid. An electron diffraction study of gaseous trifluoroacetic acid identified monomeric and dimeric species, the $O—H\cdots O$ bond in the latter being estimated as 2.76(6) Å, which is essentially the same value as found for the acetic acid dimer (*133*). The heats of dissociation of $(CH_3CO_2H)_2$ and $(CF_3CO_2H)_2$ in the gas phase have been determined as 15.3 (*205*) and 14.1 kcal $mole^{-1}$ (*250*) respectively. In a mixture of the two acid vapors, a heterodimer is formed which is more stable than either of the homodimers, with a heat of dissociation of 17 kcal $mole^{-1}$ (*159*). An elegant vibrational study of isolated trifluoroacetic acid monomers and dimers trapped in argon and neon matrices has been accomplished by Redington and Lin (*202*). This study not only allowed the vibrational spectra of both species to be unequivocally identified but also resolved some difficulties concerning the vibrational spectra of the trifluoroacetate group. Furthermore, the results indicate that a very low barrier hinders internal rotation of the CF_3 group in the acid.

TABLE I

PHYSICAL CONSTANTS OF LIQUID TRIFLUOROACETIC ACID

Property	Value	Reference
Melting point	−15.2°C	(*115*)
Boiling point	72.4°C (760 Torr)	(*247*)
Liquid range	87.6°C	
Density	1.535 gm/ml (25°C)	(*247*)
Viscosity	8.76×10^{-3} poise (25°C)	(*201*)
Dielectric constant	8.2 (30°C)	(*56*)
Specific conductance	3.5×10^{-7} mho (25°C)	(*251*)
K_{as}	4×10^{-14} $mole^2$ $liter^{-2}$	(*109*)
pK_a	±0.25 (25°C)	(*115*)
Enthalpy of formation	253 kcal $mole^{-1}$	(*146*)
Heat of vaporization	8.3 kcal $mole^{-1}$ (72.4°C)	(*199*)
Trouton constant	24 cal deg^{-1} $mole^{-1}$	
Dipole moment	2.3 D	(*199*)

The nature of the association of trifluoroacetic acid in inert and slightly basic solvents is still disputed. Murty and Pitzer (*178*) have suggested that infrared spectra indicate that a linear association of trifluoroacetic acid molecules occurs in such media; however, further such measurements obtained by Kirszenbaum *et al.* (*141*) appear to conflict with this interpretation.

The ^1H and ^{19}F NMR line parameters obtained for a powdered sample of trifluoroacetic acid have been interpreted (*72*) on the basis of dimeric molecules in this phase. However, the arrangement of these dimers in the crystal lattice appears to differ from that in trichloroacetic acid.

Trifluoroacetic acid is a nonoxidizing acid whose aqueous solutions are comparable in strength with those of the mineral acids (*115*), but as a bulk solvent it is weakly acidic and does not even protonate water (*236*). Trifluoroacetic acid is also weakly basic and is a nonelectrolyte in 100% sulfuric acid (*21*). One of the major difficulties of using pure trifluoroacetic acid is its remarkable affinity for water and, to maintain an anhydrous medium, a small quantity of trifluoroacetic anhydride is usually added. This affinity for water is so pronounced that trifluoroacetic acid will dehydrate oxyacids and, for example, converts sulfuric acid into polysulfuric acid.

Trifluoroacetic acid is quite a good solvent for organic and inorganic materials, and its ability to function as a nonaqueous solvent has been reviewed (*199*). A large range of organic solvents are completely miscible with the acid, which is also capable of dissolving proteins (*135*) and certain polymers (*248*). The ^1H NMR spectra of many organic substances may be conveniently recorded in trifluoroacetic acid since, not only do they have a reasonable solubility, but also the solvent has only one resonance absorption at low fields (-1.71 ppm) (*128*). Trifluoroacetic acid is a useful reaction medium for many organic reactions (*37*, *79*); it allows selective substitution to proceed very readily (*35*), and it is perhaps the best solvent for the platinum-catalyzed hydrogenation of ketones (*195*). Trifluoroacetic acid and, indeed, many of its salts have been used to initiate stereospecific polymerization of unsaturated hydrocarbons such as butadiene (*98*, *269*).

Trifluoroacetic acid is also a good solvent for most organometallic compounds, and the preparation of hydrido complexes by oxidative addition of the solvent to these solutes is a useful route to such compounds. These reactions will be considered in more detail in Section III since they clearly lead to the formation of metal trifluoroacetates. Trifluoroacetic acid is also a good solvent for the halogens, although it does react with them to a limited extent (*38*). The ionic behavior of several simple electrolytes in 100% trifluoroacetic acid has been studied by Simons and Lorentzen (*236*) and Harriss and Milne (*107*). The rather low conductivities of these solutions indicate that it is not a very good ionizing solvent, as would be expected in view of its relatively low dielectric constant. Furthermore, the dependence of ionic mobility on cation radius is different from that for aqueous media, suggesting that ion solvation is much less important in trifluoroacetic acid than in water. The large spread in the values of the limiting equivalent conductivities for the alkali metal trifluoroacetates in trifluoroacetic acid (*107*) indicates that the cation makes a large contribution to the total conductivity and, thus, the anion probably conducts by diffusion rather than by the self-dissociation, proton-transfer mechanism operating (*207*) for the solvent anions in water or sulfuric acid.

III. Synthesis of Metal Trifluoroacetates

This section will describe the range of preparative methods that have been used to obtain metal trifluoroacetates, each being illustrated by selected examples. However, no attempt will be made to give a comprehensive list of the compounds synthesized by any particular route.

In the first detailed investigations of metal trifluoroacetates, Swarts (*247*) described the preparations of the simple trifluoroacetate salts of Na(I), ammonium, Ba(II), Al(III), Tl(I), Pb(II), Fe(II), Cu(II), Ag(I), Hg(I), and Hg(II) by reacting the corresponding metal oxide, hydroxide, carbonate, or sulfate with an excess of an aqueous solution of trifluoroacetic acid. All of these preparations produced an aqueous solution of the trifluoroacetate salt and, by carefully heating these solutions under reduced pressure, the anhydrous metal trifluoroacetate was obtained in each case. Purification of the compounds by sublimation proved to be unsuccessful, the compounds having very low volatilities; even at 180° to 200°C and 1 Torr, very little sublimate was obtained and this was usually contaminated with decomposition products. Swarts observed that the anhydrous salts were very hygroscopic and frequently had to be handled in a dry atmosphere. This involatility and moisture sensitivity are general features of anhydrous inorganic trifluoroacetate compounds.

Hara and Cady (*105*) obtained many simple trifluoroacetate salts, using methods similar to those of Swarts, in a study that extended the range of known trifluoroacetates to include those of the lanthanide [La(III), Ce(III), Pr(III), and Nd(III)] and actinide [Th(IV) and U(VI)] metals. These workers prepared anhydrous aluminum(III) trifluoroacetate by treating freshly amalgamated aluminum in aqueous trifluoroacetic acid and decanting the solution off the amalgam before evaporating to dryness. Magnesium(II) and zinc(II) trifluoroacetates were similarly prepared from the corresponding metal. Compound $UO_2(O_2CCF_3)_2$ was obtained by the addition of U_3O_8 to aqueous trifluoroacetic acid and by the direct conversion from the corresponding acetate by treatment with trifluoroacetic acid. This was the first use of carboxylate exchange for the synthesis of a metal trifluoroacetate, a route which has also been employed for the synthesis of $Mo_2(O_2CCF_3)_4$ (*52*) and $Rh_2(O_2CCF_3)_4$ (*127*, *267*). The mechanism of this latter carboxylate exchange reaction has been followed by ^1H NMR and mass spectrometry. The reaction involves a stepwise exchange of trifluoroacetate for the acetate cage: the first substitution has a labilizing effect and the second substitution occurs twice as fast as the first. After the formation of $Rh_2(O_2CCH_3)_2(O_2CCF_3)_2$ the reaction proceeds at a much slower rate until the completely exchanged $Rh_2(O_2CCF_3)_4$ is formed (*23*).

Sartori and Weidenbruch developed several synthetic methods in preparing Group IV metal trifluoroacetates (*213–215*) which have been widely employed in other studies. Halide exchange with trifluoroacetic acid at ambient temperatures was used to prepare $Si(O_2CCF_3)_4$, $3TiO(O_2CCF_3)_2 \cdot 2CF_3CO_2H$, $Zr(O_2CCF_3)_4$, $Hf(O_2CCF_3)_4$, and $Th(O_2CCF_3)_4$ from the corresponding tetrachlorides. Metathesis with $Hg(O_2CCF_3)_2$ in trifluoroacetic acid afforded $Ge(O_2CCF_3)_4$ and $Sn(O_2CCF_3)_4$ from $GeCl_4$ and $SnCl_4$, respectively. These latter two trifluoroacetates were also obtained by the action of trifluoroacetic acid on the appropriate tetraphenyl derivative dissolved in benzene. Some extensions of the synthetic procedures developed by Sartori and Weidenbruch include the following. Halide exchange may be effected by the action of trifluoroacetic acid or anhydride on covalent fluorides [Eqs. (1) (*184*) and (2) (*74*, *179*).] Compound $Hg(OSeF_5)_2$ has been shown to react metathetically with CF_3COCl to afford trifluoroacetylpentafluoroselenate, $SeF_5(O_2CCF_3)$ (*221*). Sharp *et al.* (*224–228*) have prepared a large number of anhydrous transition metal trifluoroacetates by salt elimination reactions using stoichiometric quantities of the anhydrous metal chloride and a solution of silver trifluoroacetate in dried nitromethane or ether. Similarly, King and Kapoor (*137*) have obtained several organometallic trifluoroacetates by reacting the corresponding organometallic metal halide with a 5% excess of silver trifluoroacetate in methylene chloride solution at room temperature. Among the compounds prepared by these latter authors were $Mn(CO)_5(O_2CCF_3)$, $(\pi\text{-Cp})_2Ti(O_2CCF_3)_2$, and $(\pi\text{-allyl})Fe(CO)_3(O_2CCF_3)$, and several similar compounds involving other perfluorocarboxylato groups were also characterized in this study. Cleavage of metal–carbon σ-bonds by trifluoroacetic acid has allowed the preparation of $Me_2In(O_2CCF_3)$ (*42*), $(CH_2{=}CH)_2Sn(O_2CCF_3)_2$ (*89*), and $Re(CO)_5(O_2CCF_3)$ (*57*) from Me_3In, $(CH_2{=}CH)_4Sn$, and $MeRe(CO)_5$, respectively.

$$Cs[IF_4] + 4(CF_3CO)_2O \longrightarrow Cs[I(O_2CCF_3)_4] + 4CF_3COF \qquad (1)$$

$$XeF_2 + CF_3CO_2H \xrightarrow[1\frac{1}{2}\text{ hr}]{-24^\circ C} FXe(O_2CCF_3) + HF \qquad (2)$$

Trifluoroacetato complexes have also been obtained by the displacement of ligands, other than those described in the foregoing, using trifluoroacetic acid or its salts. Thus hydrido displacement has been achieved to prepare $(\pi\text{-Cp})_2Zr(O_2CCF_3)_2$ from $(\pi\text{-Cp})_2ZrH_2$ (*262*), and $(Ph_3P)_3Os(H)(O_2CCF_3)$ from $(Ph_3P)_4OsH_4$ (*208*), by the action of trifluoroacetic acid. Carbonyl groups may also be substituted by trifluoroacetate groups; thus, for example, the reaction of $W(CO)_6$ with $Et_4N(O_2CCF_3)$ in diglyme at 120°C affords $[W(CO)_5O_2CCF_3]^-$ (*218*). The dimeric complex $[(\pi\text{-Cp})V(O_2CCF_3)_2]_2$, which has interesting magnetic properties (see Section V, B), has also been obtained by carbonyl displacement, in this instance by refluxing $(\pi\text{-Cp})V(CO)_4$ in trifluoroacetic acid (*150*).

Compound $[Cr(CO)_5(O_2CCF_3)]^-$ may be prepared by oxidative substitution of $Ag(O_2CCF_3)$ or $Hg(O_2CCF_3)_2$ on $[Cr_2(CO)_{10}]^{2-}$ (*218*). Transition metal hydrido complexes have been obtained by oxidative addition reactions of trifluoroacetic acid which often lead to the formation of trifluoroacetato complexes. Equation (3) is an example of such a

$$(Ph_3P)_2Pt\{C(CF_3)_2NMe\} + CF_3CO_2H \longrightarrow (Ph_3P)_2Pt(H)\{C(CF_3)_2NMe\}(O_2CCF_3) \quad (3)$$

complex formed by the simple addition of the acid to the metal center (*13*). Oxidative addition may also occur for certain complexes containing acetylenic or olefinic ligands, the hydrogen adding to the unsaturated ligand which then undergoes a π- to σ-bonded rearrangement, and the trifluoroacetate groups coordinating to the metal, for example, Eqs. (4) and (5) (*19*).

$$(F_3C\cdot C{\equiv}CF_3)Pt(PPh_3)_2 + CF_3CO_2H \longrightarrow (F_3C\cdot CH{=}C\cdot CF_3)Pt(PPh_3)_2(O_2CCF_3) \quad (4)$$

$$(F_2C{=}CF_2)Pt(PPh_3)_2 + CF_3CO_2H \longrightarrow (HF_2C\cdot CF_2)Pt(PPh_3)_2(O_2CCF_3) \quad (5)$$

Trifluoroacetato complexes of transition metals have also been obtained from oxidative elimination reactions in which neutral π-acceptor ligands have been displaced in reactions with trifluoroacetic acid. These reactions may lead to hydrido complexes [Eqs. (6) (*253*) and (7) (*26*)] or they may not [Eqs. (8) (*39*) and (9) (*19*)].

$$(Ph_3P)_2Pt(C_2H_4) + CF_3CO_2H \longrightarrow (Ph_3P)_2Pt(H)(O_2CCF_3) \quad (6)$$

$$(Ph_3P)_2Ir(N_2)Cl + CF_3CO_2H \longrightarrow (Ph_3P)_2Ir(H)Cl(O_2CCF_3) \quad (7)$$

$$\{(MeO)_3P\}_2Ru(CO)_3 + 2CF_3CO_2H \longrightarrow \{(MeO)_3P\}_2Ru(CO)_2(O_2CCF_3)_2 \quad (8)$$

$$(Ph_3P)_2Pt(PhC{\equiv}CPh) + 2CF_3CO_2H \longrightarrow (Ph_3P)_2Pt(O_2CCF_3)_2 + \textit{trans}\text{-stilbene} \quad (9)$$

Reaction (9) presumably proceeds via an intermediate analogous to that produced in Eq. (4). Allyltrifluoroacetate effects oxidative displacement with biscyclooctatetraenenickel(O) to form bis(π-allylnickeltrifluoroacetate) whose ESR spectrum is consistent with its formulation as a nickel(II) complex (*59*, *60*). This latter complex is a versatile polymerization catalyst for conjugated dienes (see Section VIII, C) (*166*).

IV. Trifluoroacetate Compounds of the s- and p- Block Elements

A. Group I

The simple salts $M(O_2CCF_3)$ (where $M = Li, Na, K, Rb, Cs, NH_4$, or NEt_4) have been isolated and characterized in a variety of studies (*4*, *28*, *54*, *84*, *105*, *109*, *243*, *247*), and their infrared spectra have been described in some detail. The crystal structure of $NH_4(O_2CCF_3)$ has been determined (*54*) and each oxygen atom shown to be involved in two N—H···O hydrogen bonds.

Hydrogen bonding between two trifluoroacetate ions has constituted an important aspect of the study of this bonding since very short bonds may be obtained (*143*, *144*, *173*, *242*). The ^1H NMR spectra of solutions of the alkali metal and some quaternary ammonium trifluoroacetates in trifluoroacetic acid over a range of concentrations have been interpreted in terms of the formation of the hydrogen ditrifluoroacetate anion $[H(O_2CCF_3)_2]^-$ (*128*). The salts $M[H(O_2CCF_3)_2]$ (where $M = Na, K, Rb$, or Cs) and some of their deuterium analogs have been isolated and characterized (*99*, *143*, *144*, *163*). A recent neutron diffraction study (*163*) on these potassium salts has provided the most accurate structural data presently available for the trifluoroacetate group. The structure of the centrosymmetric hydrogen ditrifluoroacetate anion identified in $K[H(O_2CCF_3)_2]$ is illustrated in Fig. 1. The dimensions of these trifluoroacetate groups, most of which agree within experimental error with those reported for $NH_4(O_2CCF_3)$ (*54*), are presented in Table XI (see Section VII, B).

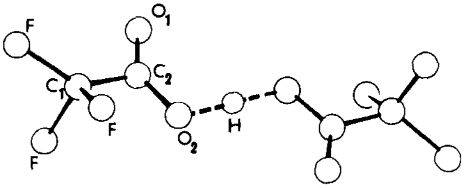


FIG. 1. The structure of the hydrogen ditrifluoroacetate anion in $K[H(O_2CCF_3)_2]$. From Macdonald *et al.* (*163*) with permission.

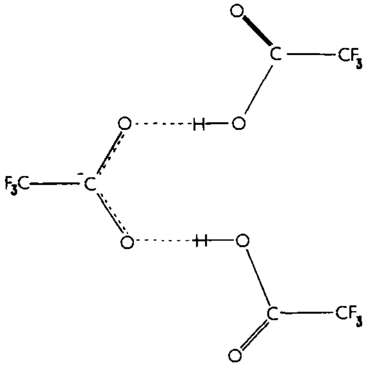


FIG. 2. Suggested structure for the anions in $Na(O_2CCF_3)\cdot 2CF_3CO_2H$ (*143*).

The salt $Na(O_2CCF_3)\cdot 2CF_3CO_2H$ and its deutero analog have been characterized, and the structure shown in Fig. 2 has been suggested for their anions (*143*).

B. GROUP II

The simple trifluoroacetates of all the alkaline earth elements have been reported (*36*, *105*, *247*, *268*). Compound $Be(O_2CCF_3)_2$ was obtained in a study of several beryllium haloacetates and, although a deliberate attempt was made to prepare basic beryllium trifluoroacetate, $Be_4O(O_2CCF_3)_6$, by the thermal decomposition of the simple salt, none could be obtained (*268*). Also $Be_4O(O_2CCF_3)_6$ does not appear to be produced when beryllium carbonate is treated with trifluoroacetic acid and the solution extracted with chloroform (*122*, *174*).

C. GROUP III

The known trifluoroacetates of boron, aluminum, indium, and thallium are summarized in Table II.

The preparation of $H[B(O_2CCF_3)_4]$ [Eq. (10)] (*25*), is directly analogous to the preparation of the superacid $H[B(HSO_4)_4]$ in oleum (*83*). Attempts to isolate $B(O_2CCF_3)_3$ from these trifluoroacetic acid

$$H_3BO_3 + 3(CF_3CO)_2O \longrightarrow H[B(O_2CCF_3)_4] + 2CF_3CO_2H \qquad (10)$$

solutions afforded only $B_2O(O_2CCF_3)_4$. However, this simple tris-trifluoroacetate may be obtained by the reaction between BCl_3, and CF_3CO_2H in *n*-pentane; the compound is unstable at its melting point (88°C) and decomposes to $B_2O(O_2CCF_3)_4$ (*92*).

TABLE II

TRIFLUOROACETATO COMPLEXES OF GROUP III ELEMENTS

Compound	Reference
$B(O_2CCF_3)_3$	(*92*)
$B_2(O_2CCF_3)_4$	(*92*)
$B_2O(O_2CCF_3)_4$	(*109*)
$\{(CF_3CO_2)_2B\}_2O$	(*92*)
$M[B(O_2CCF_3)_4]$	M = H or Cs (*109*)
$PhB(O_2CCF_3)_2$	(*92*)
$R_2B(O_2CCF_3)$	R = Et (*256*), Bu^n, or Ph (*92*)
$Al(O_2CCF_3)_3$	(*12, 105, 247*)
$Al(X)(O_2CCF_3)_2$	X = Cl (*12*) or OH (*3, 12*)
$AlCl_2(O_2CCF_3)$	(*247*)
$In(OH)(O_2CCF_3)_2$	(*125*)
$Me_2In(O_2CCF_3)$	(*42*)
$Tl(O_2CCF_3)$	(*203, 247*)
$Tl(O_2CCF_3)_3$	(*168, 249*)
$PhTl(O_2CCF_3)_2$[a]	(*154*)
$PhTl(O_2CCF_3)_2 \cdot L$	L = bipy or *o*-phen (*154*)
$(C_6F_5)_2Tl(O_2CCF_3)$	(*63*)
$(C_6F_5)_2Tl(O_2CCF_3) \cdot L$	L = Ph_3PO, Ph_3AsO (*64*), bipy, or *o*-phen (*63*)

[a] A very large number of other arylthallium bistrifluoroacetates have been obtained by the direct thallation of aromatic compounds (*40, 168, 169, 170, 203*) (see Section VIII, B).

Compound $Me_2In(O_2CCF_3)$ sublimes rapidly at 100°C under reduced pressure and is notable as one of the few metal trifluoroacetato complexes that has a reasonable volatility. Consistent with this volatility, $Me_2In(O_2CCF_3)$ dissolves in nitromethane as the covalent monomer (*42*). Also $(C_6F_5)_2Tl(O_2CCF_3)$ dissolves as discrete molecules in this solvent; however, in methanol it behaves as a 1:1 electrolyte (*63*).

The colorless, photosensitive, hygroscopic solid, $Tl(O_2CCF_3)_3$ is conveniently prepared by heating under reflux a suspension of Tl_2O_3 in trifluoroacetic acid. A solution of this salt in the acid constitutes a powerful reagent for the direct thallation of aromatic compounds [Eq. (11)] (*168*). Such products are usually soluble in most organic solvents

$$ArH + Tl(O_2CCF_3)_3 \xrightarrow{CF_3CO_2H} ArTl(O_2CCF_3)_2 + CF_3CO_2H \qquad (11)$$

and are powerful and versatile synthetic intermediates in organic chemistry (see Section VIII, B) (*40, 169, 170, 203*). TheseArTl$(O_2CCF_3)_2$ derivatives show a tendency to decompose to the more stable $Ar_2Tl(O_2CCF_3)$ derivatives if their solutions are stored for long periods (*169*).

D. GROUP IV

Table III lists the trifluoroacetato complexes of silicon, germanium, tin, and lead that have been characterized. Although a large number of organotin(IV) trifluoroacetates have been reported, the only complete series $R_nSn(O_2CCF_3)_{4-n}$ (where $n = 0$–4) is the R = vinyl series. Peruzzo *et al.* (*194*) obtained $(CH_2{=}CH)_3Sn(O_2CCF_3)$ by the exchange reaction of $(CH_2{=}CH)_4Sn$ and $Na(O_2CCF_3)$. The dropwise addition of $(CH_2{=}CH)_4Sn$ to anhydrous CF_3CO_2H at room temperature results

TABLE III

TRIFLUOROACETATO COMPLEXES OF THE GROUP IV ELEMENTS

Compound	Reference
$Si(O_2CCF_3)_4$	(*213, 214, 215*)
$SiO(O_2CCF_3)_2$	(*213, 214*)
$MeSi(O_2CCF_3)_3$	(*9*)
$Et_2Si(O_2CCF_3)_2$	(*8*)
$X_3Si(O_2CCF_3)$	X = Cl (*214*) or Me (*9*)
$Ge(O_2CCF_3)_4$	(*120, 215*)
$RGe(O_2CCF_3)_3$	R = Me or CF_3 (*120*)
$Me_2Ge(O_2CCF_3)_2$	(*120*)
$R_3Ge(O_2CCF_3)$	R = Et (*10*) or Ph (*215*)
$Ag_2[Ge(O_2CCF_3)_6]$	(*120*)
$Ag_2[RGe(O_2CCF_3)_5]$	R = Me or CF_3 (*120*)
$Sn(O_2CCF_3)_2$	(*68*)
$Sn(O_2CCF_3)_4$	(*215*)
$(CH_2{=}CH)Sn(O_2CCF_3)_3$	(*114, 130*)
$R_2Sn(O_2CCF_3)_2$	R = Me (*211*), Et (*8, 11*) or $CH_2{=}CH$ (*123*)
$Me(n\text{-}C_5H_{11})Sn(O_2CCF_3)_2$	(*11*)
$R_3Sn(O_2CCF_3)$	R = Me (*197, 259*), Et (*171, 217*), Pr^n (*216*), Bu^n (*211, 216*), $CH_2{=}CH$ (*94*), Ph (*85, 164*), or trineophenyl, Me_2PhCCH_2 (*164*)
$Me_2RSn(O_2CCF_3)$	R = Bu^n or $n\text{-}C_5H_{11}$ (*11*)
$R_2ClSn(O_2CCF_3)$	R = Me, Bu^n, or Ph (*232*)
$(CH_2{=}CH)_2Sn(O_2CCF_3)_2 \cdot 2L$	L = Ph_3PO or hexamethylphosphoramide, or 2L = bipy, *o*-phen, en, or *N,N′*-ethylenebis(salicylideneimine) (*123*)
$PhSnO(O_2CCF_3)$	(*198*)
$Ph_4Sn_2(O_2CCF_3)_2$	(*196*)
$(CH_2{=}CH)_2Sn\{Mn(CO)_5\}(O_2CCF_3)$	(*123*)
$[SnF_n(O_2CCF_3)_{6-n}]^{2-}$	n = 2, 3, or 4 (*66*)
$Pb(O_2CCF_3)_2$	(*247*)
$Pb(O_2CCF_3)_4$	(*49, 118, 162, 192*)

in an immediate and exothermic reaction that yields $(CH_2{=}CH)_2$-$Sn(O_2CCF_3)_2$ (*123*). This latter compound has remarkably stable vinyl–tin bonds. It can be recovered unchanged from CF_3CO_2H solution after refluxing at atmospheric pressure for several days, and, only under forcing conditions, does this reaction lead to loss of a further vinyl group (*114*, *130*). This contrasts with the ready replacement of all the vinyl groups of $(CH_2{=}CH)_4Sn$ by alkanoic acids (*114*).

Infrared, Mössbauer, and ^1H NMR spectra suggest that solid $Me_3Sn(O_2CCF_3)$ (*197*, *259*) and $Ph_3Sn(O_2CCF_3)$ (*85*) are polymeric, with pentacoordinated tin(IV) atoms; the structure is shown in Fig. 3. These

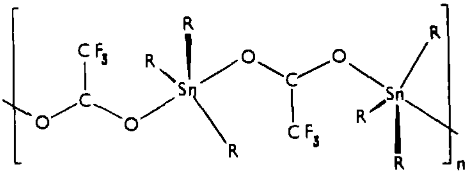


FIG. 3. Suggested structure for solid $R_3Sn(O_2CCF_3)$ where R = Me or Ph (*197*).

compounds are soluble in carbon tetrachloride and the shifts in the carboxylato stretching frequencies, for the former compound, have been interpreted in terms of a breakdown of the polymeric chain to give monomeric complexes containing unidentate trifluoroacetato groups (*197*).

Compound $Pb(O_2CCF_3)_4$ is only stable in the solid state or in fluorinated solvents such as CF_3CO_2H or C_6F_6, and it appears to have unique powers as an oxidant toward hydrocarbons (see Section VIII, A) (*192*).

E. GROUP V

Table IV summarizes the trifluoroacetato complexes of the Group V elements that have been characterized. The simple trifluoroacetates of arsenic, antimony, and bismuth(III) have been isolated only recently, following the reaction of the corresponding trichloride with $Ag(O_2CCF_3)$ in CH_2Cl_2 (*123*) and, for the bismuth derivative, by the reaction of Bi_2O_3 with $(CF_3CO)_2O$ (*200*). These are reasonably volatile compounds which are extremely moisture-sensitive.

Compound $Me_2As(O_2CCF_3)$ is unusual in that it may be thermally decarboxylated to the corresponding perfluoromethyl derivative (*55*); normally such reactions are unsuccessful (*61*, *123*).

The compounds $R_3Sb(O_2CCF_3)_2$ appear to be covalent monomers and the positions of their infrared carboxylato stretching frequencies have been used as evidence that the molecules involve five-coordinate antimony(V) with two unidentate trifluoroacetato groups (*97*).

The ^{19}F NMR spectra have shown that SbF_5 acts as an acceptor acid in CF_3CO_2H to form $H[SbF_5(O_2CCF_3)]$ (*108*); the reaction is analogous to the behavior of SbF_5 in liquid HF (*94*).

TABLE IV

TRIFLUOROACETATO COMPLEXES OF THE GROUP V ELEMENTS

Compound	Reference
$PF_2(O_2CCF_3)$	(*82*)
$As(O_2CCF_3)_3$	(*123*)
$As(O_2CCF_3)_3 \cdot bipy$	(*123*)
$Me_2As(O_2CCF_3)$	(*55*)
$Na[AsO(O_2CCF_3)_2]$	(*200*)
$Sb(O_2CCF_3)_3$	(*123*)
$R_3Sb(O_2CCF_3)_2$	R = Me or Ph (*97*)
$Ph_4Sb(O_2CCF_3)$	(*96*)
$H[SbF_5(O_2CCF_3)]$	(*108, 109*)
$Bi(O_2CCF_3)_3$	(*123, 200*)
$Na[Bi(O_2CCF_3)_4]$	(*200*)

F. GROUP VI

Trifluoroacetate derivatives of the Group VI elements are confined to the monosubstituted selenium(VI) fluoride, $SeF_5(O_2CCF_3)$ (*221*), and the hexatrifluoroacetatotellurate(IV) anion, $[Te(O_2CCF_3)_6]^{2-}$, which has been isolated as the sodium salt (*200*).

G. GROUP VII

Iodine is the only halogen that has been shown to form trifluoroacetato complexes. These have been identified for iodine(I), $I(O_2CCF_3)$ (*32, 112, 119*); iodine(III), $I(O_2CCF_3)_3$ (*212*), $Cs[I(O_2CCF_3)_4]$, and $Cs_3[IF_n(O_2CCF_3)_{6-n}]$ (where $n = 2$, 4, or 6) (*183, 184*); and iodine(V), $IO_2(O_2CCF_3)$ (*200*) and $K[IO_2(O_2CCF_3)_2]$ (*183*). These complexes may be prepared by the action of trifluoroacetic anhydride on an appropriate iodine oxide or fluoride derivative. For example, KIO_3 reacts with $(CF_3CO)_2O$ in MeCN at ca. $-40^{a}C$ to afford $K[IO_2(O_2CCF_3)_2]$; in the analogous reaction with $KBrO_3$ an explosion occurs with evolution of Br_2, CO_2, and C_2F_6 (*183*).

H. GROUP VIII

As would be anticipated, the noble gas trifluoroacetates are confined to xenon.

Compounds $Xe(O_2CCF_3)_2$ and $XeF(O_2CCF_3)$ have been obtained in several studies (*74, 179, 239*) by the reactions of XeF_2 with CF_3CO_2H. These compounds are thermally unstable with respect to Xe, XeF_2, CO_2, and C_2F_6 and are, thus, potentially explosive (*76*). Iskraut *et al.* (*124*) have claimed the preparation of $Xe(O_2CCF_3)_4$ and $Xe(O_2CCH_3)_4$; however, these results await confirmation (*179*).

V. Trifluoroacetato Complexes of the d-Transition Metals

A. TITANIUM, ZIRCONIUM, HAFNIUM (AND THORIUM)

The titanium(II) derivatives $Ti(O_2CCF_3)X$ (where X = Cl or Br) have been prepared by the reaction between $Ti(O_2CCF_3)_2$ and the corresponding thionyl halide in ether. All of these titanium(II) trifluoroacetates are effective as catalysts for the stereospecific polymerization of butadienes (*44*).

The other trifluoroacetates of these elements that have been characterized are $Ti(O_2CCF_3)_3$ (*225*), $TiO(O_2CCF_3)_2$, $Zr(O_2CCF_3)_4$, $Hf(O_2CCF_3)_4$, $Th(O_2CCF_3)_4$ (*122, 213, 215*), and the bis-π-cyclopentadienyl complexes $(\pi\text{-Cp})_2Ti(O_2CCF_3)_2$ and $(\pi\text{-Cp})_2Zr(O_2CCF_3)_2$ which have been prepared in several studies (*22, 31, 71, 73, 137, 262*). The absence of $Ti(O_2CCF_3)_4$ is interesting since, not only are the corresponding compounds known for the other Group IV elements, Zr, Hf, Th (*122, 213, 215*), Si, Ge, Sn (*214, 215*), and Pb (*49, 118, 162, 192*) but also titanium(IV) tetraalkanoates, $Ti(O_2CR)_4$, have been reported (*126*). The tetrakistrifluoroacetato complexes of Zr(IV), Hf(IV), and Th(IV) are hygroscopic solids that are nonvolatile at temperatures up to 180°C (*122*) and, if maintained at higher temperatures, they decompose to yield $(CF_3CO)_2O$, CF_3COF, COF_2, CO_2, and CO as the volatile products (*215*). The mass spectra of these $M(O_2CCF_3)_4$ (where M = Zr, Hf, or Th) compounds contain peaks up to 800 mass units, and in each spectrum no peak corresponding to the $M(O_2CCF_3)_4^+$ parent ion is observed. These data show that the compounds are polymeric in the solid state and are, thus, presumed to involve bridging trifluoroacetato groups. However, $Zr(O_2CCF_3)_4$, $Hf(O_2CCF_3)_4$, and $Th(O_2CCF_3)_4$ all dissolve in polar organic solvents as discrete molecules. Since, in each case, there are only very slight shifts ($\pm 2\ cm^{-1}$) in the carboxylato stretching frequencies between the solid and the solution phases, it seems reasonable to propose (see Section VII, D) that the monomeric solution species contain only bidentate trifluoroacetato groups (*122*). In this context it is interesting to note that several other compounds of formula ML_4 (where M = Zr, Hf, or Th, and L is a bidentate ligand) are eight coordinate (*160*, *191*) with the arrangement of the ligand donor atoms about the metal being either square antiprismatic, for example, $Zr(acac)_4$ (*233*) and $Th(acac)_4$ (*100*), or trigonal dodecahedral, for example $Na_4[Zr(C_2O_4)_4]\cdot 3H_2O$ (*95*) and $Th(S_2CNEt_2)_4$ (*34*). Considerations of ligand–ligand repulsions for these two stereochemistries have led to the suggestion that for these ML_4 complexes, which involve bidentate ligands of a short "bite" such as nitrate, oxalate, or trifluoroacetate, the trigonal dodecahedral structure is favored over the square antiprismatic one (*3*, *27*). Therefore, it would seem reasonable to suggest that the tetrakistrifluoroacetates of zirconium, hafnium, and thorium(IV) contain eight-coordinated metal atoms, with the monomeric solution species containing four bidentate ligands arranged to give a dodecahedral MO_8 unit.

B. VANADIUM

Four trifluoroacetato complexes of vanadium have been characterized: $[(\pi\text{-}Cp)V(O_2CCF_3)_2]_2$ (*150*), $[Me_2(stearyl)_2N][VCl_4(O_2CCF_3)]$ (*20*), $NH_4[VO(O_2CCF_3)_3]$, and $VO_2(O_2CCF_3)$ (*200*). The first of these is of the most interest. This compound has a dimeric structure (Fig. 4) with four bridging trifluoroacetato groups but no metal–metal bond

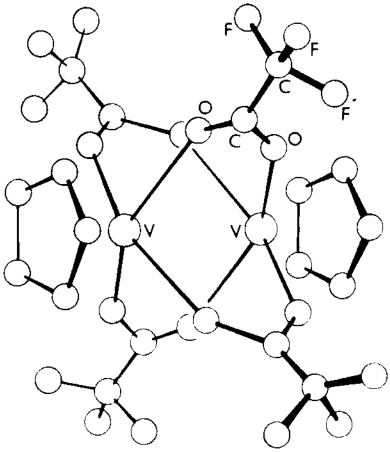


FIG. 4. The molecular structure of the (π-cyclopentadienyl)ditrifluoroacetatovanadium(III) dimer, $[(\pi\text{-}Cp)V(O_2CCF_3)_2]_2$. From Larin *et al.* (*150*) with permission.

(V···V = 3.7 Å). Compound $[(\pi\text{-Cp})V(O_2CCF_3)_2]_2$ and its acetate analog have abnormally low room-temperature magnetic moments (μ_{eff} = 1.55 and 1.71 μ_B per vanadium, respectively) which decrease with decreasing temperature. These magnetic properties thus arise because of the interaction of the d^2 configurations of each vanadium(III) center via the π orbitals of the carboxylato groups.

C. CHROMIUM, MOLYBDENUM, AND TUNGSTEN

The known trifluoroacetato complexes of chromium, molybdenum, and tungsten are given in Table V. An X-ray structure determination (*52*) has shown that $Mo_2(O_2CCF_3)_4$ possesses the centrosymmetric structure illustrated in Fig. 5. The Mo—Mo distance of 2.090(4) Å is not significantly different from that of 2.11(1) Å found in the analogous dimeric acetate (*152*), and the Mo—Mo stretching frequencies in the Raman spectra occur at 393 and 406 cm^{-1}, respectively. A quantitative assessment of the effect of coordination in the vacant axial positions of such a structure has been achieved for $Mo_2(O_2CCF_3)_4$, where the pyridine adduct, $Mo_2(O_2CCF_3)_4 \cdot 2py$, has been prepared and its crystal structure determined (*51*). The Mo—Mo separation of 2.129(2) Å is slightly longer than in the parent compound, with weak coordination of pyridine [Mo—N = 2.548(8) Å] compared to that of trifluoroacetate [Mo—O = 2.116(4) Å], and the Mo—Mo—N interbond angles = 171.0(2)°. Consistent with the slightly greater metal–metal separation, the Mo—Mo stretching frequency in the Raman spectrum of

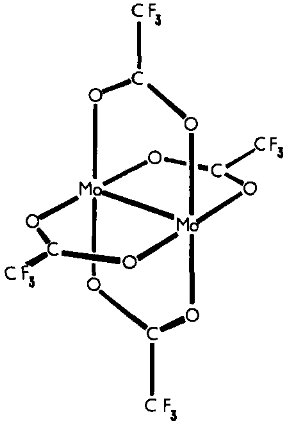


FIG. 5. Structure molybdenum(II) trifluoroacetate, $Mo_2(O_2CCF_3)_4$. From Cotton and Norman (*52*) with permission.

TABLE V

TRIFLUOROACETATO COMPLEXES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

Compound	Reference
$Et_4N[Cr(CO)_5(O_2CCF_3)]$	(*218*)
$Cr(O_2CCF_3)_2 \cdot nEt_2O$	$n = 0$ or 1 (*116, 117*)
$Cr(O_2CCF_3)_3$	(*28, 91, 123, 156, 228, 255*)
$[Cr(NH_3)_5(O_2CCF_3)](ClO_4)_2$	(*58, 272*)
$CrO_2(O_2CCF_3)_2$	(*91*)
$Et_4N[Mo(CO)_5(O_2CCF_3)]$	(*218*)
$Mo(CO)_2H(O_2CCF_3) \cdot 2THF$	(*98*)
$(\pi\text{-}Cp)Mo(CO)_2(L)(O_2CCF_3)$	L = CO (*57*) or $(PhO)_3P$ (*139*)
$[(\pi\text{-}Cp)Mo(NO)(O_2CCF_3)_2]_2$	(*137*)
$Mo_2(O_2CCF_3)_4$	(*52*)
$Mo_2(O_2CCF_3)_4 \cdot 2L$	L = py (*51*), Ph_3P, MeOH (*190*), bipy, or phen (*123*)
$(\pi\text{-}Cp)_2Mo(O_2CCF_3)_2$	(*102, 106*)
$Et_4N[W(CO)_5(O_2CCF_3)]$	(*218*)
$(\pi\text{-}Cp)W(CO)_3(O_2CCF_3)$	(*57*)
$(\pi\text{-}Cp)_2W(O_2CCF_3)_2$	(*102, 106*)

$Mo_2(O_2CCF_3)_4 \cdot 2py$ is lowered to 367 cm^{-1}. A weakening of the Mo—Mo bond by coordination of the axial donor ligands might be expected since these ligands share the same metal orbitals as those used to form the metal–metal σ bond. Further evidence for this effect is provided by the Mo—Mo stretching frequencies for $Mo_2(O_2CCF_3)_4$ in several solvents, which decrease from the solid state value in a manner that roughly correlates with increasing donor strength of the solvent (*51, 190*).

Compound $Cr_2(O_2CCF_3)_4$ and its 1:1 ether adduct (*116, 117*) appear to be structurally similar to $Mo_2(O_2CCF_3)_4$ and $Mo_2(O_2CCF_3)_4 \cdot 2py$, respectively, but with a significantly weaker metal–metal interaction. This interaction is probably also less than that in $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ [where the Cr—Cr separation is 2.362(1) Å (*50*)] since the chromium(II) trifluoroacetates are paramagnetic, whereas the acetate is diamagnetic. The extent of the paramagnetism (μ_{eff} of $Cr_2(O_2CCF_3)_4 \cdot 2Et_2O$ = 0.85 μ_B at room temperature) is, however, consistent with significant spin exchange between the two d^4 centers, presumably via a direct Cr—Cr interaction and, as in $[(\pi\text{-}Cp)V(O_2CCF_3)_2]_2$ (*150*), the bridging trifluoroacetato groups.

D. MANGANESE AND RHENIUM

The only trifluoroacetato complex of rhenium that has been prepared is $Re(CO)_5(O_2CCF_3)$ (*57, 137*). The corresponding manganese compound has been reported by King and Kapoor (*137*) who prepared it by the metathetical reaction between $Mn(CO)_5Br$ and $Ag(O_2CCF_3)$ in CH_2Cl_2. Green *et al.* (*102*) also claimed to have prepared this compound by reacting (σ-allyl)$Mn(CO)_5$ with CF_3CO_2H; however, the properties reported differ significantly from those of King and Kapoor whose results have been confirmed by a further study (*89*). The ESCA spectrum of $Mn(CO)_5(O_2CCF_3)$ has been recorded and compared with those of other $Mn(CO)_5X$ (where X = Br, I, Me, or CF_3) molecules (*16*). The values of the carbonyl carbon and oxygen 1s-electron-binding energies increase as $X = Me < I < Br < CF_3 < O_2CCF_3$, consistent with the trifluoroacetate group being the strongest electrophilic substituent in this series (*89*).

Substitution of the carbonyl ligands of $Mn(CO)_5(O_2CCF_3)$ has been achieved with several nitrogen-, oxygen-, phosphorus-, and sulfur-donor ligands (*89*, *138*). Compounds $Mn(CO)_3L_2(O_2CCF_3)$ [where $L = P(OR)_3$ or $L_2 = R_2PCH_2CH_2PR_2$ and R = Me or Ph, or L_2 = *cis*-$Ph_2PCH{=}CHPPh_2$] have been obtained by photochemical substitution using ultraviolet irradiation of a mixture of $Mn(CO)_5(O_2CCF_3)$ and the ligand in benzene–hexane solution at room temperature. Under these conditions, PPh_3 and $Mn(CO)_5(O_2CCF_3)$ afford a mixture of $Mn(CO)_3(PPh_3)_2(O_2CCF_3)$ and $Mn(CO)_2(PPh_3)_3(O_2CCF_3)$, and attempts to separate these complexes by chromatography on alumina resulted in decomposition with liberation of PPh_3 (*138*). However, when the corresponding reaction is carried out in refluxing chloroform the complex $Mn(CO)_3(PPh_3)_2(O_2CCF_3)$ is obtained exclusively. These latter conditions have also led to the isolation of other $Mn(CO)_3L_2(O_2CCF_3)$ complexes [where L = py, Ph_3PO, or $(Me_2N)_3PO$ and L_2 = bipy, phen, dithiohexane, or $C_6H_5SCH_2CH_2SC_6H_5$] (*89*). The stable isomer for the majority of these $Mn(CO)_3L_2(O_2CCF_3)$ complexes is the expected *facial* one in which the three carbonyl groups are mutually cis and, thus, no carbonyl group competes with any other such group trans to it, for the electron density of any d_π orbital. However, for the disubstituted triphenylphosphine complex, the steric requirements of these ligands favors that they adopt a trans arrangement; thus $Mn(CO)_3(PPh_3)_2(O_2CCF_3)$ is isolated from chloroform as the *meridional* isomer.

Manganese(II) trifluoroacetate (*225*, *228*) and its adducts $Mn(O_2CCF_3)_2 \cdot nL$ (where L = py and n = 2 or 4; L = pyridine-*N*-oxide and n = 1; or L = γ-picoline and n = 1, 2, or 4) (*7*) have been characterized. Compound $Mn(acac)_2(O_2CCF_3)$ aids the polymerization of methylmethacrylate and vinyl acetate and is reduced to $Mn(acac)(O_2CCF_3)$ in these processes (*187*, *188*).

E. IRON, RUTHENIUM, AND OSMIUM

Table VI lists the known trifluoroacetato complexes of iron, ruthenium, and osmium. Photochemical substitution reactions of various tricovalent phosphorus-donor ligands with (π-allyl)Fe(CO)$_2$(O$_2$CCF$_3$) and (π-Cp)Fe(CO)$_3$(O$_2$CCF$_3$), analogous to those described in the preceding for Mn(CO)$_5$(O$_2$CCF$_3$), have afforded (π-allyl)Fe(CO)(*cis*-Ph$_2$PCH=CHPPh$_2$)(O$_2$CCF$_3$), (π-Cp)Fe(CO)(PR$_3$)(O$_2$CCF$_3$) (where R = Ph, OMe, or OPh), and (π-Cp)FeL$_2$(O$_2$CCF$_3$) (where L$_2$ = Me$_2$PCH$_2$CH$_2$PMe$_2$, Ph$_2$PCH$_2$CH$_2$PPh$_2$, or *cis*-Ph$_2$PCH=CHPPh$_2$), the ^{1}H and ^{19}F NMR spectra of which were reported (*138*).

TABLE VI

TRIFLUOROACETATO COMPLEXES OF IRON, RUTHENIUM, AND OSMIUM

Compound	Reference
(π-allyl)Fe(CO)L$_2$(O$_2$CCF$_3$)	L$_2$ = (CO)$_2$ (*137*) or *cis*-Ph$_2$PCH=CHPPh$_2$ (*138*)
(π-Cp)Fe(CO)L(O$_2$CCF$_3$)	L = CO (*137*) or PR$_3$ (where R = Ph, OMe, or OPh) (*138*)
(π-Cp)FeL$_2$(O$_2$CCF$_3$)	L$_2$ = R$_2$PCH$_2$CH$_2$PR$_2$ (where R = Me or Ph) or *cis*-Ph$_2$PCH=CHPPh$_2$ (*138*)
Fe(O$_2$CCF$_3$)$_2\cdot n$H$_2$O	n = 0 (*105*, *225*, *228*, *247*, *255*) or 2 (*247*)
Fe(O$_2$CCF$_3$)$_3$	(*227*)
FeL(O$_2$CCF$_3$)	L = *N*,*N*′-ethylenebis(salicylideneiminato), *N*,*N*′-ethylenebis-(5,6-benzosalicylideneiminato), or *N*,*N*′-phenylenebis(salicylideneiminato) (*158*)
Fe$_3$O$_4$(O$_2$CCF$_3$)	(*247*)
[Fe$_3$O(O$_2$CCF$_3$)$_6$]O$_2$CCF$_3$	(*247*)
Ru(H)(PPh$_3$)$_3$(O$_2$CCF$_3$)	(*209*)
Ru(H)(PPh$_3$)$_2$L(O$_2$CCF$_3$)$_n$	n = 1, L = PPh$_3$, CO, or n = 3, L = NO (*208*)
Ru(Cl)(PPh$_3$)$_2$(CO)(O$_2$CCF$_3$)	(*208*)
Ru(PPh$_3$)$_2$(CO)(O$_2$CCF$_3$)$_2$	(*208*)
Ru(CO)$_2$(PR$_3$)$_2$(O$_2$CCF$_3$)$_2$	R = Ph (*45*) or OMe (*39*)
[Ru(NH$_3$)$_5$(O$_2$CCF$_3$)](ClO$_4$)$_2$	(*246*)
Os(H)(PPh$_3$)$_3$(O$_2$CCF$_3$)	(*208*)
Os(Cl)(PPh$_3$)$_3$(CO)(O$_2$CCF$_3$)	(*208*)
Os(PPh$_3$)$_2$(CO)$_n$(O$_2$CCF$_3$)$_2$	n = 1 or 2 (*208*)

Compound [Fe$_3$O(O$_2$CCF$_3$)$_6$](CF$_3$CO$_2$) (*247*), in common with the other basic carboxylates of iron(III) (*189*), probably has a structure closely related to that of the basic chromium(III) carboxylato complexes (*80*).

F. COBALT, RHODIUM, AND IRIDIUM

The trifluoroacetato complexes of cobalt, rhodium, and iridium that have been isolated and characterized are listed in Table VII. An X-ray diffraction study of crystalline $(Ph_4As)_2[Co(O_2CCF_3)_4]$ has shown that the trifluoroacetato groups are essentially unidentate and give approximately tetrahedral coordination about the cobalt(II), as shown in Fig. 6 (*25*). Although the bulk magnetic and electronic spectral properties are similar to those of tetrahedral cobalt(II) complexes, the interpretation of the polarized single crystal d-d spectra and the temperature variation of the principal magnetic moments require that the elongation of the

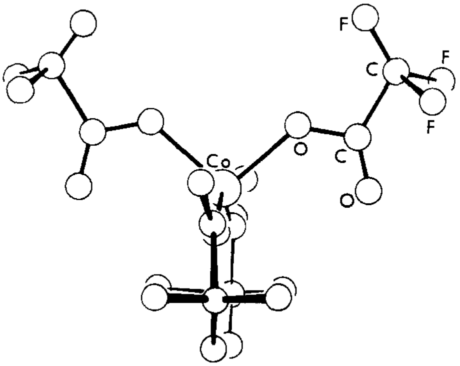


FIG. 6. Structure of the tetratrifluoroacetatocobalt(II) anion in $(Ph_4As)_2$-$[Co(O_2CCF_3)_4]$. Reprinted with permission from *Inorganic Chemistry* **5**, 1422 (1966). Copyright by the American Chemical Society.

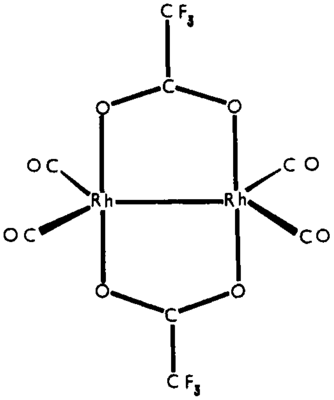


FIG. 7. Suggested structure for dicarbonyl trifluoroacetatorhodium(I) $[Rh(CO)_2(O_2CCF_3)]_2$. From Lawson and Wilkinson (*151*) with permission.

TABLE VII

TRIFLUOROACETATO COMPLEXES OF COBALT, RHODIUM, AND IRIDIUM

Compound	Reference
$(\pi\text{-Cp})Co(CO)(C_3F_7)(O_2CCF_3)$	(*137*)
$Co(O_2CCF_3)_2 \cdot nL$	$n = 0$ (*225, 228*), or $n = 1$ and L = pyridine *N*-oxide or γ-picoline-*N*-oxide (*7*); or $n = 2$ or 4 and L = pyridine or γ-picoline (*7, 155*)
$CoX(O_2CCF_3)$	X = Cl or Br (*44*)
$(Ph_4As)_2[Co(O_2CCF_3)_4]$	(*24, 25*)
$Co_3(Cl)SO_4(dme)_3(O_2CCF_3)_3$	dme = dimethoxyethane (*76*)
$[Co(NH_3)_5(O_2CCF_3)](ClO_4)_2$	(*148, 175*)
cis-$[CoL_4(O_2CCF_3)_2](ClO_4)$	$L_2 = 2NH_3$ or en (*148, 149*)
trans-$[CoL_4(O_2CCF_3)_2]Cl$	$L_2 = 2NH_3$ or en (*148, 149*)
$[Co(trien)(O_2CCF_3)_2](ClO_4)$	(*147, 149, 155*)
$Rh(PPh_3)_2L(O_2CCF_3)$	L = CO or PPh_3 (*208*)
$[Rh(CO)_2(O_2CCF_3)]_2$	(*151*)
$Rh(PPh_3)_2(O_2CCF_3)$	(*47*)
$Rh(PPh_3)_2(NO)(O_2CCF_3)$	(*208*)
$Rh_2(O_2CCF_3)_4$	(*23, 127, 267*)
$Rh_2(O_2CCF_3)_4 \cdot 2L$	L = EtOH (*267*), Me_2CO, Me_2SO (*142*), or py (*244*)
$[Rh(NH_3)_5(O_2CCF_3)](ClO_4)$	(*78, 175*)
$Ir(Ph_3P)_2(H)L(O_2CCF_3)$	L = Cl or CO (*26, 46, 237*)
$Ir(Ph_3P)_2(H)Cl(CO)(O_2CCF_3)$	(*26, 237*)
$Ir(Ph_3P)_2CO(H)_n(O_2CCF_3)_{3-n}$	$n = 1$ or 2 (*208*)
$[Ir(NH_3)_5(O_2CCF_3)](ClO_4)_2$	(*78, 175*)

tetrahedron of the four nearer oxygen atoms *and* the effect of the other four oxygen atoms be taken into account (*90*).

Addition of thionyl chloride to a tenfold excess of cobalt(II) trifluoroacetate in purified dimethoxyethane (dme) under nitrogen affords red crystals of $Co_3(Cl)SO_4(dme)_3(O_2CCF_3)_3$. These crystals contain discrete molecules that comprise trinuclear units of cobalt(II) atoms arranged in an equilateral triangle of side 3.786(2) Å. These atoms are held together by three bridging systems, a central chlorine atom, a triply bridging sulfato group, and three bridging trifluoroacetato groups each spanning one side of the triangle. Each metal achieves a distorted octahedral coordination, the dme molecules acting as bidentate ligands (*76*).

The structure of $Rh_2(O_2CCF_3)_4$ (*23, 127, 267*) and the adducts $Rh_2(O_2CCF_3)_4 \cdot 2L$ [where L = EtOH (*267*), Me_2CO, Me_2SO (*142*), or py (*244*)] appear to be analogous to those described for the corresponding molybdenum(II) compounds (Section V, C). Thus, $Rh_2(O_2CCH_3)_4 \cdot 2H_2O$ has been shown by X-ray diffraction to have this type of structure

(*50*) and, as described earlier (Section III), $Rh_2(O_2CCF_3)_4$ may be prepared by carboxylate exchange from this acetate (*127*, *267*). It has been suggested that $[Rh(CO)_2(O_2CCF_3)]_2$ has the bridged carboxylato structure illustrated in Fig. 7, which probably also involves a direct metal–metal interaction (*151*).

G. Nickel, Palladium, and Platinum

The known trifluoroacetato complexes of nickel, palladium, and platinum are given in Table VIII. Cryoscopic measurements on benzene or cyclohexane solutions of $[(\pi\text{-allyl})Ni(O_2CCF_3)]_2$ support its dimeric formulation. The structure illustrated in Fig. 8 has been proposed for this compound, which is an effective catalyst for the stereospecific polymerization of butadienes (see Section VIII, C) (*59*, *60*, *166*, *270*).

TABLE VIII

Trifluoroacetato Complexes of Nickel, Palladium, and platinum

Compound	Reference
$[(\pi\text{-R})Ni(O_2CCF_3)]_2$	R = allyl (*59*, *270*) or crotyl (*153*, *234*)
$[Ni(H)AR_3](O_2CCF_3)$	A = P, As, or Bi (*70*)
$Ni(O_2CCF_3)_2$	(*225*, *228*)
$Ni(O_2CCF_3)_2 \cdot nL$	n = 1 and L = pyridine-*N*-oxide, quinoline (*7*), phen, or bipy (*123*); n = 2 or 4 and L = pyridine or γ-picoline (*7*, *155*)
$NiX(O_2CCF_3)$	X = Cl or Br (*44*)
$Ni(O_2CCF_3)_2(\text{phenylethylene})_2 \cdot 2H_2O$	(*140*)
$Pd(O_2CCF_3)_2$	(*176*, *244*)
$Pd(O_2CCF_3)_2 \cdot L$	L = Me_2CO (*244*, *245*)
$Pd(O_2CCF_3)_2 \cdot 2L$	L = Ph_3P, Ph_3As, py, or Me_2SO (*244*, *245*, *257*)
$Pt(RC{=}CHPh)(PPh_3)_2(O_2CCF_3)$	R = H or Me (*165*)
$Pt(PhC{=}CHMe)(PPh_3)_2(O_2CCF_3)$	(*165*)
$Pt(RC{=}CHR)(PPh_3)_2(O_2CCF_3)$	R = CF_3 (*19*) or Ph (*165*)
$Pt(F_2CCF_2H)(PPh_3)_2(O_2CCF_3)$	(*19*)
$Pt\{(CF_3)_2CNR\}(PPh_3)_2(O_2CCF_3)$	n = 1, R = Me or n = 0, R = H (*13*)
$Pt(H)(PR_3)_2(O_2CCF_3)_{2-n}(H)_n$	R = Et (*14*) or Ph (*253*), n = 0 or 1
$Pt(PPh_3)_2(O_2CR)(O_2CCF_3)$	R = Me, Et or CF_3 (*19*)

Compound $Pd(O_2CCF_3)_2$ dissolves in warm acetone to yield the air-stable $Pd(O_2CCF_3)_2 \cdot Me_2CO$, which is dimeric in ethyl acetate solution and is presumed to have a di-μ-trifluoroacetato structure analogous to that suggested for $[Rh(CO)_2(O_2CCF_3)]_2$ (Fig. 7). However, $Pd(O_2CCF_3)_2 \cdot 2AsPh_3$ appears to be monomeric in benzene (*244*).

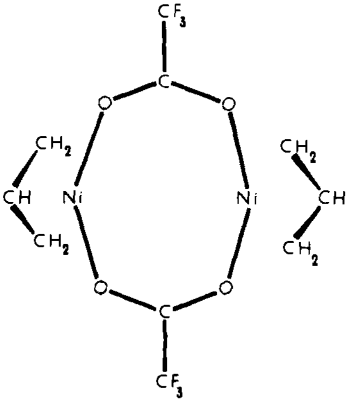


FIG. 8. Suggested structure for the dimer of π-allyl trifluoroacetatonickel(II), $[(\pi\text{-allyl})Ni(O_2CCF_3)]_2$ (*60*).

H. COPPER, SILVER, AND GOLD

A large number of trifluoroacetato complexes of copper have been prepared (Table IX), the majority of these being N-donor ligand adducts of $Cu(O_2CCF_3)_2$. The dimeric configuration adopted by copper(II) acetate and its adducts (*104*, *260*) does not appear to be adopted as a general rule by the analogous trifluoroacetato complexes. Thus, anhydrous copper(II) trifluoroacetate has a room-temperature magnetic moment of 1.81 μ_B and its magnetic susceptibility conforms to the Curie–Weiss law between 94° and 297°K; the small negative θ value thus obtained suggests a weak antiferromagnetic exchange interaction between the metal centers, perhaps indicative of a polymeric structure (*255*). The majority of copper(II) trifluoroacetate adducts possess two or four other ligands per copper atom and are thus presumed not to have a dimeric structure (*1*, *2*, *4*). Also, those adducts that involve only one addended ligand per copper atom may not be dimeric. Thus, of all the 1:1 α-picoline adducts of the copper(II) salts of halogen-substituted acetates, only the trifluoroacetate is monomeric, all of the other haloacetate derivatives being dimeric (*136*). Evidence for antiferromagnetic exchange between copper(II) centers has been obtained for $Cu(O_2CCF_3)_2\cdot$quinoline (*1*) and $Cu(O_2CCF_3)_2\cdot$dioxan (*258*); however, in the latter instance the ESR spectrum also shows the presence of a mononuclear copper(II) species. The compound $Cu_2(O_2CCF_3)_4\cdot$1,4-di-(2′-pyridyl)aminophthalizine may have a dimeric structure with two bridging and two terminal trifluoroacetato groups (*254*).

Attempts have been made to correlate the occurrence or nonoccurrence of a binuclear structure for copper(II) carboxylates with the

pK_a of the parent acid (*134, 157, 167*). For parent acids with a pK_a of less than ca. 4, the binuclear structure would appear to be unstable because the residual positive charge on the copper atoms is too great to allow their close proximity favored in this structure. The apparent nonappearance of a dimeric structure for the majority of copper(II) derivatives of trifluoroacetic acid ($pK_a = \pm 0.25$) is thus consistent with this view.

TABLE IX

TRIFLUOROACETATO COMPLEXES OF COPPER

Compound	Reference
$Cu(O_2CCF_3)$	(*29, 30, 67, 219, 225*)
$Cu(CO)(O_2CCF_3) \cdot nCF_3CO_2H$	$n = 0$ or 1 (*219*)
$Cu(PPh_3)_2(O_2CCF_3)$	(*67*)
$Cu(Ph_2PR)_3(O_2CCF_3)$	R = Me (*67*), Ph (*67, 103*), or *p*-MeC_6H_4 (*177*)
$Cu(Ph_2PCH_2CH_2PPh_2)(O_2CCF_3)$	(*67*)
$Cu(PPh_3)(2,9\text{-}Me_2phen)(O_2CCF_3)$	(*103*)
$Cu(O_2CCF_3)_2$	(*134, 225, 227, 228, 247, 255*)
$Cu(Cl)(O_2CCF_3)$	(*226*)
$Cu(O_2CCF_3)_2 \cdot L$	L = H_2O (*258*), isoquinoline, pyridine-*N*-oxide, 3-Brpy, 2,6- or 3,5-lutidine (*4*), 2-Clpy (*2, 4*), α-picoline (*136*), quinoline (*1*), 1,2- or 1,3-propanediamine (*172*), or dioxan(*258*)
$Cu(O_2CCF_3)_2 \cdot 2L$	L = py, α-, β-, or γ-picoline (*2, 4, 136, 155, 224*), 2-Etpy, 2-Clpy (*4*), quinoline (*1*), 2,6-lutidine (*4*), pyridine-*N*-oxide, or γ-picoline-*N*-oxide (*224*), amines (*172*),
$Cu(O_2CCF_3)_2 \cdot 4L$	L = py (*14, 155, 224*), 3-Brpy, β-picoline, quinoline (*4*), or γ-picoline (*224*)
$Cu_2(O_2CCF_3)_4 \cdot L$	L = 1,4-di-(2′-pyridyl)aminophthalizine (*254*)
$[Cu_2OH(quinoline)_2(O_2CCF_3)_3]_2$	(*161*)

The only copper(II) trifluoroacetate shown by diffraction studies to involve trifluoroacetato groups bridging two metal atoms in relatively close proximity is $[Cu_2OH(quinoline)_2(O_2CCF_3)_3]_2$ (*161*). X-Ray analysis has shown that the compound has a novel tetranuclear structure, each copper atom having a distorted square pyramidal environment. Four of the trifluoroacetato groups in the unit form bridges from the apical position of one copper atom to a basal site of another such atom; the other two are each coordinated as a unidentate ligand in the basal plane of a copper atom. The magnetic susceptibility data show that a substantial copper–copper interaction is present in this compound. The relatively large metal–metal separations of 2.996(4) and 3.347(5) Å, together with the relative orientations of the copper coordination polyhedra, do not favor a direct metal–metal interaction. Thus, as in the case of $[(\pi\text{-Cp})V(O_2CCF_3)_2]_2$ (*150*), magnetic exchange via the π-orbitals of the bridging trifluoroacetato groups seems to be indicated.

Compound $Cu(CO)(O_2CCF_3){\cdot}CF_3CO_2H$ is obtained by reacting copper(I) oxide with a trifluoroacetic acid–anhydride mixture under an atmosphere of carbon monoxide; the acid solvate molecule may be removed by pumping at room temperature and further such treatment then affords $Cu(O_2CCF_3)$ (*219*).

In a large number of studies (e.g., *110*, *119*, *228*, *247*), $Ag(O_2CCF_3)$ has been prepared, and its reactions with metal and nonmetal halides have been used widely for the preparation of the corresponding trifluoroacetato complexes (see Section III). Swarts (*247*) has also reported the preparation of $AgL(O_2CCF_3)$ (where L = I or C_6H_6). Compound $Ag(O_2CCF_3)$ has been shown to react with halogens in fluorinated solvents according to Eq. (12) and $AgI(O_2CCF_3)$ has been isolated and

$$2Ag(O_2CCF_3) + X_2 \longrightarrow AgX(O_2CCF_3) + AgX \qquad (12)$$

characterized (*53*). A mixture of I_2 and $Ag(O_2CCF_3)$ is a powerful iodinating reagent (*79*) and iodinates aromatic compounds in positions expected for attack by an electrophilic reagent. Similarly, Br_2 and $Ag(O_2CCF_3)$ form a powerful brominating mixture, which, at low temperatures, reacts by an electrophilic mechanism (*112*). Furthermore, the reactions of Cl_2, Br_2, and I_2 with $Ag(O_2CCF_3)$ at elevated temperatures afford a convenient synthesis of the corresponding trifluoromethylhalides (*53*, *110*).

Compound $Au(PPh_3)(O_2CCF_3)$ has been prepared by the reaction of $Ag(O_2CCF_3)$ with Ph_3PAuCl, the complex being monomeric in chloroform solution (*185*). Also $Ag(PPh_3)(O_2CCF_3)$ has been reported (*93*). The complex $\{(p\text{-MeC}_6H_4)_3P\}_3Ag(O_2CCF_3)$ has been shown by ^{31}P NMR studies to disproportionate into $(p\text{-MeC}_6H_4)_2Ag(O_2CCF_3)$ and $[(p\text{-MeC}_6H_4)_4Ag]CF_3CO_2$ in dichloromethane solution (*177*).

I. ZINC, CADMIUM, AND MERCURY

Table X lists the trifluoroacetato complexes of zinc, cadmium, and mercury that have been prepared. Mercury(II) trifluoroacetates in trifluoroacetic acid have been used widely in organic syntheses since they effect fast mercuration reactions of aromatic rings (*35*, *241*),

TABLE X

TRIFLUOROACETATO COMPLEXES OF ZINC, CADMIUM, AND MERCURY

Compound	Reference
$Zn(O_2CCF_3)_2$	(*225*, *227*)
$Zn(O_2CCF_3)_2 \cdot L$	L = pyridine-*N*-oxide or γ-picoline-*N*-oxide (*224*)
$Zn(O_2CCF_3)_2 \cdot 2L$	L = H_2O (*180*), py, or γ-picoline (*224*)
$Zn(py)_4(O_2CCF_3)_2$	(*224*)
$Cd(O_2CCF_3)_2$	(*105*)
$Hg_2(O_2CCF_3)_2$	(*238*, *247*)
$Hg(O_2CCF_3)_2$	(*65*, *229*, *230*)
$Hg(O_2CCF_3)_2 \cdot nL$	n = 1 and L = PPh_3 (*172*), bipy, or phen (*61*, *186*); or n = 2 and L = H_2O (*247*) or PPh_3 (*62*)
$HgX(O_2CCF_3)$	X = OH (*247*), Me (*77*), CF_3 (*178*, *229*), Ph (*223*), C_6F_5 (*65*), or CF_3S (*69*)

analogous to the reactions described for thallium(III) trifluoroacetate; these complexes also undergo specific addition across non-conjugated double bonds (see Section VIII, B) (*223*, *229*, *230*). The thermal decarboxylation of $Hg(O_2CCF_3)_2$ (*5*) and $Hg(O_2CCF_3)_2 \cdot L$ (where L = bipy or phen) (*48*) are described in Section VIII, A.

VI. Trifluoroacetato Complexes of the f-Block Elements

The tris-trifluoroacetates, $M(O_2CCF_3)_3$, have been reported for the lanthanides La, Ce, Pr, Nd, and Sm (*105*, *206*, *263*). However, the most extended range of lanthanide trifluoroacetate complexes are the hexafluoroacetylacetonato derivatives $Ln(hfac)_2(O_2CCF_3) \cdot 2H_2O$ (where Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, or Y) (*204*). Compound $Sm(NH_3)_2(O_2CCF_3)_3$ has been isolated (*263*) and $Nd(phen)(O_2CCF_3)_3$, just as analogous carboxylato complexes of neodymium, is used as a liquid laser, the medium being a deuterated solvent (*113*). Other laser systems of this type employ $Nd(O_2CCF_3)_3$–$AlCl_3$ or $Nd(O_2CCF_3)_3$–$ZrCl_4$ in $POCl_3$ or $PSCl_3$ (*81*, *264*).

The properties of $Th(O_2CCF_3)_4$ (*122*, *213*, *215*) have already been described (Section V, A). Also $U(O_2CCF_3)_4$ has been reported (*220*), but since few data were given concerning its properties, further characterization would be desirable. Compound $Pu(O_2CCF_3)_4 \cdot xH_2O$ has been prepared by allowing aerial oxidation of a solution of Pu(III) in CF_3CO_2H (*43*).

Hara and Cady (*105*) prepared $UO_2(O_2CCF_3)_2$ by carboxylate exchange from the corresponding acetate and showed that the compound is very moisture-sensitive and virtually insoluble in trifluoroacetic acid.

VII. Physical Properties of Trifluoroacetates

A. STRUCTURES

The possible modes of bonding of carboxylate groups to metal atoms have been described by Oldham (*189*) and thus far, for the trifluoroacetate group, three of these modes have been identified by diffraction studies. The $NH_4(O_2CCF_3)$ is composed of ions linked by hydrogen bonds (*54*); $(Ph_4As)_2[Co(O_2CCF_3)_4]$ (Fig. 6) (*25*) and $[CuOH(quinoline)_2(O_2CCF_3)_3]_2$ (*161*) contain unidentate trifluoroacetato groups. The last-mentioned compound also possesses syn-syn-bridging trifluoroacetato groups, which have also been identified in $[(\pi\text{-Cp})V(O_2CCF_3)_2]_2$ (see Fig. 4) (*150*), $Mo_2(O_2CCF_3)_4$ (see Fig. 5) (*52*), $Mo_2(O_2CCF_3)_4{\cdot}2py$ (*51*), and $Co_3(Cl)SO_4(dimethoxyethane)_3(O_2CCF_3)_3$ (*76*). The anions of $K[H(O_2CCF_3)_2]$ and $K[D(O_2CCF_3)_2]$ (see Fig. 1) (*163*) are perhaps best considered as examples of unidentate trifluoroacetato groups since the hydrogen bonding is strong and specific to one oxygen atom of each carboxylate group.

Although the definitive characterization of trifluoroacetate structures is limited to the foregoing data, the modes of coordination of this group in other compounds may be inferred with some confidence. Thus, bonding considerations would appear to restrict the trifluoroacetato group to unidentate coordination in $PF_2(O_2CCF_3)$ (*82*), $AuPPh_3(O_2CCF_3)$ (*185*), $[M(NH_3)_5(O_2CCF_3)]^{2+}$ [where M = Cr (*58, 272*), Co (*147, 148*), Rh (*78, 175*), or Ir (*78*)], and $[M(CO)_5(O_2CCF_3)]^{n-}$ [where $n = 0$ and M = Mn (*89, 102, 137*) or Re (*57, 137*); or $n = 1$ and M = Cr, Mo, or W (*218*)]. No compounds have yet been shown by diffraction studies to contain symmetrically bidentate trifluoroacetato groups. However, since they are known to occur for the related ligands acetate (e.g., *265, 271*), carbonate (e.g., *18, 231*), and nitrate (*3*), it is likely that this mode of coordination will be characterized for the trifluoroacetate group. Such coordination was favored earlier (Section V, A) for monomeric $M(O_2CCF_3)_4$ [where M = Zr, Hf, or Th (*122, 213, 215*)] and, since $Cr(O_2CCF_3)_3$ also dissolves as a molecular unit in acetone (*122*) where its d-d spectrum is typical of an octahedral chromium(III) complex (*122, 228*), it too would seem to involve bidentate trifluoroacetato groups.

The non-volatility of most metal trifluoroacetates clearly implies the presence of bridging trifluoroacetato groups in the solid state, presumably with the anti–anti or syn–anti configurations. Such arrangements have already been favored for the structures of solid $M(O_2CCF_3)_4$ (where M = Zr, Hf, or Th) (Section V, A) and $Me_3Sn(O_2CCF_3)$ (Section IV, D) (see Fig. 3). The tendency for acetato groups to bridge metal centers has also been noted (*32*). A particular structural feature of the transition metal trifluoroacetates is the formation of dimeric units with two or four trifluoroacetato ligands bridging the two metal centers which may be as close as 2.1 Å, e.g., in $Mo_2(O_2CCF_3)_4$ (*52*), or as far apart as 3.7 Å, e.g., in $[(\pi\text{-}Cp)V(O_2CCF_3)_2]_2$ (*150*). However, it seems probable that trifluoroacetate is less able than acetate to support such a structure, presumably because of the higher residual charge on the two metal atoms in close proximity. Thus the Mo—Mo stretching frequencies are 393 and 406 cm^{-1} in $Mo_2(O_2CCF_3)_4$ and $Mo_2(O_2CCH_3)_4$, respectively; $Cr_2(O_2CCF_3)_4 \cdot 2Et_2O$ is paramagnetic to the extent of 0.87 μ_B at room temperature, whereas $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ is diamagnetic, and $Cu(O_2CCF_3)_2$ and its adducts generally appear not to possess the dimeric structures characteristic of the corresponding acetato complexes.

B. DIMENSIONS

The most accurate structural data for trifluoroacetate groups are those obtained from neutron diffraction studies of $K[H(O_2CCF_3)_2]$ and $K[D(O_2CCF_3)_2]$ (see Fig. 1) (*163*), and their average dimensions are given in Table XI. The dimensions obtained in the other diffraction studies of trifluoroacetato compounds agree within experimental error with those quoted in Table XI in all respects except the length of the C—O bonds and the magnitude of the C—C—O interbond angles. In $NH_4(O_2CCF_3)$ (*54*), no distinction between the two C—O bonds of length 1.269(5) Å, or between the two C—C—O interbond angles of 115.8(3)°, was observed. The different geometries of the carboxylate

TABLE XI

DIMENSIONS AND THEIR ESTIMATED STANDARD DEVIATIONS OF THE TRIFLUOROACETATE GROUPS IN $K[H(O_2CCF_3)_2]$ AND $K[D(O_2CCF_3)_2]$[a,b]

Bond	Length (Å)	Interbond Angle	Value (degrees)
C—F	1.325(6)	F—C—F	107.7(6)
C—C	1.541(2)	F—C—C	111.3(7)
C—O(1)	1.215(2)	C—C—O(1)	119.6(1)
C—O(2)	1.268(3)	C—C—O(2)	111.3(1)
O(2)····O(2′)	2.437(4)	O—C—O	129.2(2)

[a] Data from Ref. *163*.

[b] The dimensions quoted are averaged over the two salts.

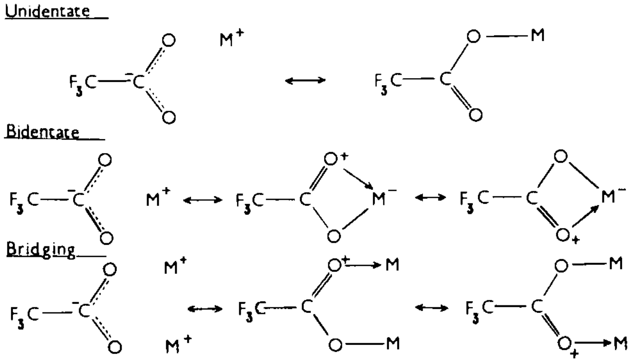


FIG. 9. Principal valence bond structures of unidentate, bidentate, and bridging trifluoroacetato groups.

groups in these potassium and ammonium salts are expected since, in the $[H(O_2CCF_3)_2]^-$ and $[D(O_2CCF_3)_2]^-$ ions, there is strong hydrogen bonding which only involves the O(2) atom of each trifluoroacetate ion, whereas in $NH_4(O_2CCF_3)$ both oxygen atoms of the anions participate in two N—H···O bonds of length ca. 2.9 Å. By applying these results to trifluoroacetato complexes, it is anticipated that, for unidentate coordination, the C—O bond involving the noncoordinated oxygen atom will be significantly shorter than that involving the coordinated one and that the C—C—O interbond angles may be different, whereas, for bidentate and bridging trifluoroacetato groups, no real difference in C—O bond lengths or C—C—O interbond angles is expected. These views are also consistent with simple valence bond arguments (Fig. 9). The relatively large estimated standard deviations of dimensions reported for $(Ph_4As)_2$ $[Co(O_2CCF_3)_4]$ (*25*) do not allow for any distinction between the C—O bond lengths and C—C—O interbond angles within the trifluoroacetato groups. The oxygen atoms of each of the bridging trifluoroacetato groups of $[(\pi\text{-}Cp)V(O_2CCF_3)_2]_2$ (*150*), $Mo_2(O_2CCF_3)_4$ (*52*), $Mo_2(O_2CCF_3)_4 \cdot 2py$ (*51*), and $Co_3(Cl)SO_4(\text{dimethoxyethane})_3(O_2CCF_3)_3$ (*76*) appear to be equivalent within the accuracy of these structure determinations. However, considerably more structural data are required before the dimensions of the carboxylate portion of coordinated trifluoroacetate groups can be regarded as established.

C. ^{19}F NUCLEAR MAGNETIC RESONANCE SPECTRA

The ^{19}F NMR spectra have been recorded for only a small percentage of the compounds described in Sections IV, V, and VI. However, the compounds studied in this respect have ranged from high oxidation states, e.g., $CrO_2(O_2CCF_3)_2$ (*91*) and $Pb(O_2CCF_3)_4$ (*122*), through intermediate, e.g., $Zn(O_2CCF_3)_2$ and $Hg(O_2CCF_3)_2$ (*122*), to low oxidation states, e.g., $Au(PPh_3)(O_2CCF_3)$ (*185*) and $Re(CO)_5(O_2CCF_3)$ (*137*), and have involved some twenty different metal atoms. In each case the room-temperature ^{19}F NMR spectrum consists of a single resonance clearly indicating essentially free rotation of the CF_3 moiety about the C—C bond at normal temperatures, as expected in view of the spectral results of Redington and Lin (*202*). The position of this resonance is in the range 74–79 ppm upfield of $CFCl_3$ for all the compounds studied with the exception of $Au(PPh_3)(O_2CCF_3)$ where it was observed (*185*) at 69.1 ppm upfield of $CFCl_3$. The spread of ^{19}F chemical shifts for trifluoroacetates is, therefore, very small when compared to the known range (*266*) for such nuclei, which extends from CH_3F at 278 to UF_6 at -746 ppm relative to $CFCl_3$. This, together with the difficult interpretation of ^{19}F chemical shifts, clearly limits the utility of ^{19}F NMR data for the interpretation of effects such as the nature and/or strength of the coordination of the trifluoroacetate group. However, it should be noted that recent studies have claimed that the nature of hydroxyl groups in natural products may be ascertained by converting them into trifluoroacetyl ones with trifluoroacetic anhydride; then the ^{19}F chemical shifts of such groups are capable of differentiating between primary, secondary, tertiary, and aromatic environments (*261*).

D. VIBRATIONAL SPECTRA

The highest symmetry that a trifluoroacetate group can possess, if free rotation about its C—C bond is not possible, is C_s. The ^{19}F NMR studies described earlier indicated that essentially free rotation about the C—C bond of trifluoroacetate groups occurs in solution at room temperature; in this situation the symmetry may be approximated to C_{2v} if both oxygen atoms are equivalent or to C_s if they are not. Although C_{2v} symmetry might be appropriate for an isolated trifluoroacetate group, in a crystal lattice and/or an individual molecule, vibrational coupling will occur between a trifluoroacetate group and other similar and/or different groups. This coupling will result in a splitting of the degenerate modes and a relaxation of selection rules. Therefore, the infrared and Raman spectra of compounds containing a trifluoroacetate group would be expected to contain peaks corresponding to virtually all of the fifteen normal vibrational modes of this group. Thus the number of infrared and Raman bands observed for a trifluoroacetate group is expected to be independent of its environment, and distinctions

TABLE XII

VIBRATIONAL FREQUENCIES OF TRIFLUOROACETATE GROUPS IN $K[H(O_2CCF_3)_2]$[a]

Mode	Frequency (cm^{-1}) Infrared	Frequency (cm^{-1}) Raman[b]
CO_2 asym. stretch	1792	1725
CO_2 sym. stretch	1420	1441
CF_3 stretch	1226	1190
CF_3 stretch	1160	1164
CF_3 stretch	1128	1150
C—C stretch	828	846
OCO def.	791	734
CF_3 bend	706	710 sh
CF_3 bend	590	630 vb
CF_3 bend	520	518
CCO γ bend	440	428
CCO δ bend	385	324
ω CF_3 wag	270	272
ρ CF_3 wag	265	269

[a] Data from Ref. *173*.

[b] sh = shoulder; vb = very broad.

between the various modes of bonding must be made on the basis of band positions and/or their relative intensities.

The vibrational spectra exhibited by trifluoroacetate groups have been the subject of much discussion (*17*, *41*, *87*, *88*, *132*, *178*) and their assignment has only recently been clarified by the elegant matrix isolation studies of trifluoroacetic acid monomers and dimers by Redington and Lin (*202*) and the detailed study of the infrared and Raman spectra of $K[H(O_2CCF_3)_2]$ and $Cs[H(O_2CCF_3)_2]$ (and their deuterated analogs) by Miller *et al.* (*173*). Table XII lists the trifluoroacetate vibrational frequencies of the latter salts. The vibrational spectra of the trifluoroacetate groups of other compounds are usually very similar to those presented in this table except that, as would be anticipated from the earlier discussion of the dimensions of this group, some variation in the carboxylate stretching frequencies is observed. Several attempts have been made to correlate the stretching frequencies of oxyanions with the extent and nature of their coordination (*3*, *75*, *86*, *131*, *155*, *181*, *252*). In the case of carboxylates, attention has focused on the positions and separations of the antisymmetric and symmetric carboxylate stretching frequencies. The data collected in Table XIII (although lacking the necessary diffraction studies for confirmation of

TABLE XIII

INFRARED CARBOXYLATE STRETCHING FREQUENCIES OF VARIOUS TYPES OF TRIFLUOROACETATE GROUPS

		$\nu(CO_2)$ (cm^{-1})			
Compound	Nature of trifluoroacetate group	Antisymmetric	Symmetric	Δ	References
$NH_4(O_2CCF_3)$	Ionic	1667	1465	202	(*122*)
$K(O_2CCF_3)$	Ionic^a	1678	1437	241	(*122*)
$Cs(O_2CCF_3)$	Ionic^a	1678	1427	251	(*122*)
$Cr(O_2CCF_3)_3$	Bidentate^a	1710	1490	220	(*122*)
$Zr(O_2CCF_3)_4$(solution)	Bidentate^a	1662	1483	179	(*122*)
$Mo_2(O_2CCF_3)_4$	Bridging	1592 1572	1459	~133	(*52*)
$Rh_2(O_2CCF_3)_4 \cdot 2EtOH$	Bridging^a	1664	1467	197	(*267*)
$Zr(O_2CCF_3)_4$(solid)	Bridging^a	1660	1481	179	(*122*)
$Me_3Sn(O_2CCF_3)$(solid)	Bridging^a	1652	1340	312	(*197*)
$(Ph_4As)_2[Co(O_2CCF_3)_4]$	Unidentate	1692	1421	271	(*122*)
$Mn(CO)_5(O_2CCF_3)$	Unidentate^a	1694	1416	278	(*89*)
$Au(PPh_3)(O_2CCF_3)$	Unidentate^a	1695	1406	289	(*185*)
$Me_3Sn(O_2CCF_3)$(solution)	Unidentate^a	1720	1290	430	(*197*)
CF_3CO_2H	Unidentate^a	1819	1415	404	(*202*)

^{a} Unconfirmed by diffraction studies.

many of the structures) indicate that the positions of the infrared carboxylate stretching frequencies do not afford a general distinction between the various types of trifluoroacetate groups. This is not surprising since, not only do simple valence bond arguments (see Fig. 9) anticipate that little distinction between ionic, bridging, and bidentate trifluoroacetate groups should be achieved in this manner, but also that the vibrational frequencies of coordinated trifluoroacetate groups will depend on the nature (*182*) and oxidation state of the central atom and the other groups bonded to this atom. However, in situations where the latter parameters are unchanged, the C—O stretching frequencies of a trifluoroacetato group may differentiate between unidentate coordination, on the one hand, and ionic, bidentate, or bridging, on the other. This view has been used to support the inference that $Me_3Sn(O_2CCF_3)$ is polymeric in the solid state with bridging trifluoroacetato groups and monomeric in CCl_4 solution with unidentate trifluoroacetato groups (*197*). The shift in the asymmetric (CO_2) stretching frequency from 1652 to 1720 cm^{-1} would appear to be genuine evidence of this effect, however, the values of the symmetric (CO_2) stretching frequency of 1340 and 1290 cm^{-1} appear to be unusually low in comparison with the other values in Table XIII.

It remains to be seen whether further work will establish other means of identifying the nature of trifluoroacetate groups from their vibrational spectra. A possibility that does not appear to have been explored fully in this respect is the relative intensity of the antisymmetric and symmetric CO_2 stretching frequencies, for both infrared and Raman spectra.

VIII. Reactions of Metal Trifluoroacetates

A. DECARBOXYLATION

The reactions of Na(I), K(I), Ba(II), Ag(I), Hg(II), and Pb(II) trifluoroacetates with iodine at elevated temperatures has been shown to be a convenient synthesis of trifluoroiodomethane, CF_3I, by Haszeldine (*110*). Similar reactions of $Ag(O_2CCF_3)$ with chlorine or bromine give the corresponding trifluoromethylhalide.

Compound $Me_2As(O_2CCF_3)$ may be thermally decarboxylated to give Me_2AsCF_3 (*55*). Thermal decarboxylation of $Hg(O_2CCF_3)_2$ proceeds readily at 300°C to give $CF_3Hg(O_2CCF_3)$ (*5*) which may be converted into CF_3HgI by treatment with $NaI{\cdot}2H_2O$. This latter mercury(II) derivative is a convenient source of difluorocarbene (*222*). Also $Hg(O_2CCF_3)_2{\cdot}L$ (where L = bipy or phen) may be decarboxylated at their melting points (ca. 200°C) to afford the corresponding trifluoromethyl derivatives (*48*).

The preceding reactions represent rare conversions of trifluoroacetates into trifluoromethyl derivatives; such thermal decarboxylation reactions are usually unsuccessful (*61*, *123*, *193*). Thus, attempts to prepare $M(CF_3)_n$ (where $n = 2$ and M = Hg; or $n = 3$ and M = P or As) by heating the appropriate element with $Ag(O_2CCF_3)$ failed in their objective (*111*). Studies by Sharp *et al.* (*228*) and by Sartori and Weidenbruch (*215*) on trifluoroacetato complexes have shown that, although decarboxylation frequently does occur, the products obtained are M, MO_x, CO_2, $(CF_3CO)_2O$, C_2F_6, COF_2, and CF_3COF. Swarts (*247*) and Simons *et al.* (*235*) also produced $(CF_3CO)_2O$ and CF_3COF by thermal decomposition of $Na(O_2CCF_3)$ and $Ba(O_2CCF_3)_2$, respectively.

The failure of trifluoroacetate decarboxylation as a general synthetic procedure is perhaps not surprising since such reactions are usually of limited utility. Furthermore, trifluoroacetate groups are quite resistant to decarboxylation which is more difficult to achieve for Na(O_2CCF_3) than for Na(O_2CCCl_3) or Na(O_2CCBr_3) (*33*). Auerbach *et al.* (*15*) have shown that the activation energies for the decarboxylation of Na(O_2CCF_3) and Na(O_2CCCl_3) are 42 and 32 kcal mole^{-1}, respectively. The former reaction proceeds by a first-order mechanism in ethylene glycol and a convenient rate is only achieved at ca. 180°C.

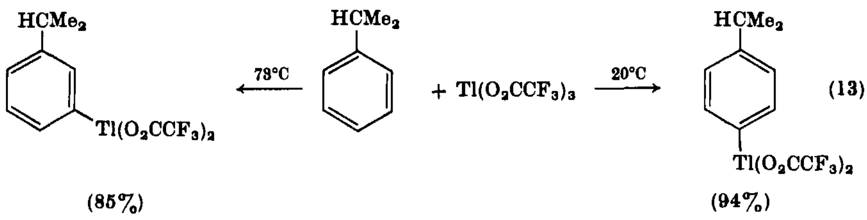
Lead(IV) trifluoroacetate trapped in a benzene matrix at liquid nitrogen temperatures has been shown to afford $CF_3\cdot$ radicals when irradiated by ultraviolet light (*162*). Thus photolytic decarboxylation of trifluoroacetates would appear to merit further investigation.

B. METAL–TRIFLUOROACETATE BOND CLEAVAGE

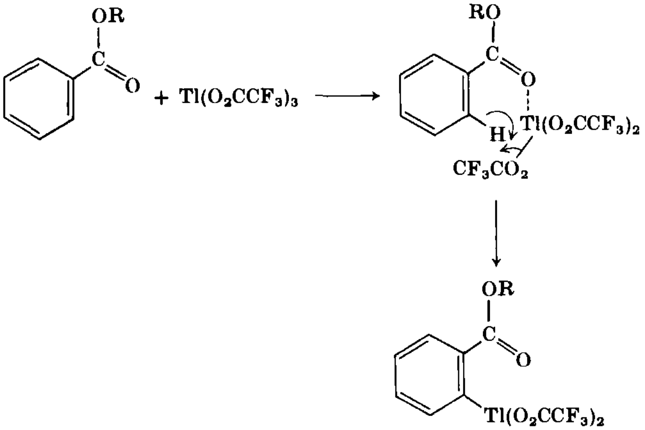
Since trifluoroacetic acid is a relatively strong acid, its conjugate base $CF_3CO_2^-$ is relatively weak and M—O_2CCF_3 bonds are usually quite labile. This lability is indicated by the moisture sensitivity of most trifluoroacetato complexes. Therefore, these complexes have potential value as synthetic intermediates as illustrated by the following examples.

1. Elimination of Trifluoroacetic Acid

Although thallium(III) acetate fails to react with aromatic compounds under mild conditions, thallium(III) trifluoroacetate will effect rapid electrophilic thallation of a wide range of aromatic substances (*40*, *168*, *169*, *170*, *203*) according to the general reaction [Eq. (11)]. These reactions are very rapid and are usually completed in a few minutes at room temperature for activated aromatic nuclei, to give stable colorless solids that generally crystallize from solution. The orientation of thallation in such reactions may be influenced by temperature [Eq. (13)], or by the substituents on the aromatic nucleus.



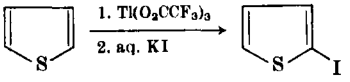
Thus bulky groups usually prevent ortho substitution [e.g., Eq. (13)]. However, substituents such as benzoic acid and its esters, which are able to complex the incoming thallium atom, result in almost exclusive ortho substitution [Eq. (14)],



(14)

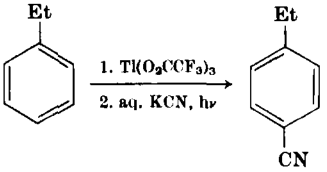
At present such metallation reactions have only been developed for the trifluoroacetates of thallium(III) and mercury(II) (*35*, *241*), and they clearly offer considerable scope for the extension of the organometallic chemistry of these elements.

Displacement of the metal from the aromatic nucleus may be effected by a variety of reactants, as illustrated for thallium(III) by Eqs. (15,) (16), and (17).



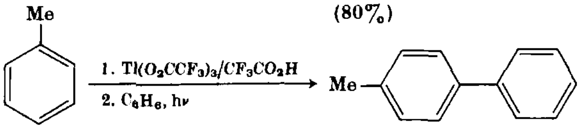
(82%)

(15)



(80%)

(16)



(91%)

(17)

This sequential process of thallation followed by displacement represents a new and versatile method for aromatic substitution.

Thallium(III) trifluoroacetate will also eliminate trifluoroacetic acid in reactions with compounds containing N—H bonds (*40*, *240*). Thus, brief treatment of octaethylporphyrin in CH_2Cl_2 and tetrahydrofuran with an excess of $Tl(O_2CCF_3)_3$ followed by chromatography on deactivated alumina affords the complex shown in Fig. 10. This was the first unambiguous characterization of a thallium(III) porphyrin (*240*).

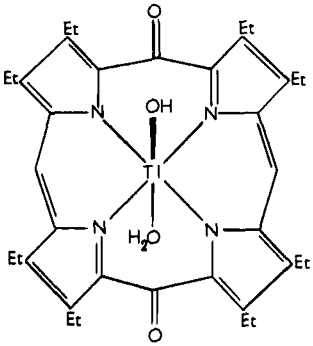


FIG. 10. Thallium(III) octaethylporphyrin complex. From Smith (*240*) with permission.

Lead(IV) trifluoroacetate undergoes reductive elimination of trifluoroacetic acid in the presence of both alkyl and aryl C—H bonds [Eq. (18)].

$$RH + Pb(O_2CCF_3)_4 \longrightarrow R(O_2CCF_3) + Pb(O_2CCF_3)_2 + CF_3CO_2H \qquad (18)$$

In this respect $Pb(O_2CCF_3)_4$ appears to have unique powers as an oxidant toward hydrocarbons, and, thus, nonactivated molecules, such as heptane or benzene, are converted to their trifluoroacetoxy-substitution products, $C_7H_{15}O_2CCF_3$ and $C_6H_5O_2CCF_3$, respectively. Subsequent mild hydrolysis completes a convenient route to the corresponding alcohol or phenol (*192*).

2. *Other Trifluoroacetate Elimination Reactions*

Salt elimination reactions have been used to obtain the divinyl tin(IV) derivatives, $(CH_2{=}CH)_2Sn(O_2CCF_3)(Mn(CO)_5)$, $(CH_2{=}CH)_2Sn(Mn(CO)_5)_2$, $[(CH_2{=}CH)_2SnFe(CO)_4]_2$, and $(CH_2{=}CH)_2Sn(Co(CO)_4)_2$, by reacting $(CH_2{=}CH)_2Sn(O_2CCF_3)_2$ with the sodium salt of the appropriate carbonyl anion, as exemplified in Eq. (19) (*123*). Such

$$(CH_2{=}CH)_2Sn(O_2CCF_3)_2 + 2Na[Mn(CO)_5] \longrightarrow$$
$$(CH_2{=}CH)_2Sn(Mn(CO)_5)_2 + 2Na(O_2CCF_3) \qquad (19)$$

divinyltin derivatives are usually difficult to obtain since in reactions of $(CH_2{=}CH)_2SnR_2$ (where R = alkyl or aryl) compounds, it is usually the tin–vinyl bonds that are cleaved. These salt elimination reactions are, of course, directly analogous to those commonly used to form metal–metal bonds from halogeno complexes (e.g., Refs. *121*, *145*). However in the foregoing system, the trifluoroacetato complex is easier to prepare and handle than the corresponding halogeno derivatives.

The elimination of the trifluoroacetate ion has been used synthetically in ligand substitution reactions of the $[M(CO)_5(O_2CCF_3)]^-$ (where M = Cr, Mo, or W) anions; Eq. (20) is typical of these reactions.

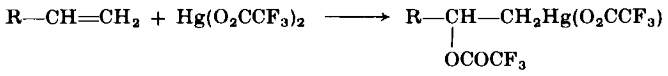
$$Et_4N[Cr(CO)_5(O_2CCF_3)] + py \xrightarrow[CH_2Cl_2]{Et_3O^+BF_4^-} Cr(CO)_5py + Et(O_2CCF_3) + Et_2O + Et_4NBF_4 \qquad (20)$$

Such substitutions are completed within a few seconds at room temperature and afford the neutral product $M(CO)_5L$ in high yield for a wide variety of neutral Lewis bases (L) (*89*).

The base hydrolysis of $[Co(NH_3)_5(O_2CCF_3)]^{2+}$ and the analogous complexes of rhodium, iridium, and chromium(III) appears to involve the concerted attack of two hydroxide ions—one bonding to the acyl carbon atom of the trifluoroacetato group, and the other deprotonating the first (*58*, *129*).

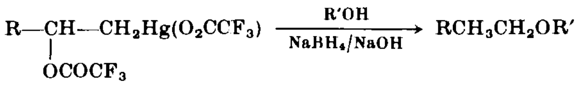
3. *Addition across Olefinic Bonds*

Mercury(II) trifluoroacetate finds frequent employment in organic synthesis (*223*, *229*, *230*) since it adds rapidly, stereospecifically, and quantitatively across nonconjugated olefinic bonds, for example, Eq. (21). The mercurated products thus prepared may be readily converted



$$R{-}CH{=}CH_2 + Hg(O_2CCF_3)_2 \longrightarrow R{-}\underset{\displaystyle OCOCF_3}{\underset{|}{CH}}{-}CH_2Hg(O_2CCF_3) \qquad (21)$$

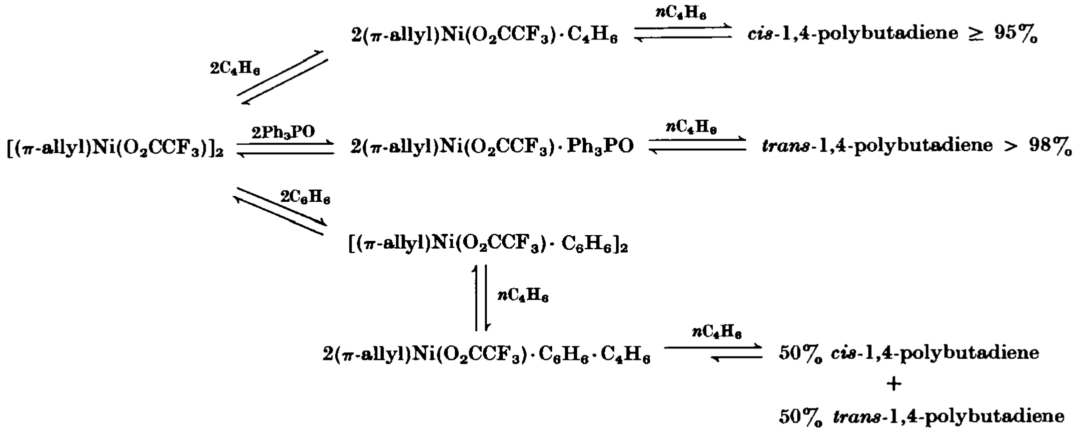
to a variety of compounds that retain this stereospecificity, for example, Eq. (22)



$$R{-}\underset{\displaystyle OCOCF_3}{\underset{|}{CH}}{-}CH_2Hg(O_2CCF_3) \xrightarrow[NaBH_4/NaOH]{R'OH} RCH_3CH_2OR' \qquad (22)$$

C. Catalysis

Metal trifluoroacetates are used as catalysts in several industrial processes. The use of $[(\pi\text{-allyl})Ni(O_2CCF_3)_2]_2$ in the stereospecific polymerization of butadiene has been studied in some detail (*59*, *60*, *166*,



SCHEME 1.

The effect of ligands on the type of polymer obtained from 1,3-butadiene for [(π-allyl)Ni(O_2CCF_3)] catalysis (*166*).

270). In saturated hydrocarbons, this compound induces the polymerization of 1,3-butadiene to yield polymers with cis-1,4 contents as high as 95% of the total saturation. By adding appropriate amounts of other ligands, it is possible to affect the nature of the solution species and, hence, to change the type of polymer obtained (Scheme 1).

Also $Mo(CO)_2H(O_2CCF_3)\cdot 2THF$ (*98*), $M(O_2CCF_3)_2$, and $MX(O_2CCF_3)_2$ (where M = Ti, Co, or Ni and X = Cl or Br) (*44*) have been employed to catalyze stereospecific butadiene polymerization. Compounds $Mn(acac)_2(O_2CCF_3)$ (*187*) and $Mn(acac)(O_2CCF_3)$ (*187*, *188*), have been shown to be efficient catalysts in the preparation of polymers and copolymers of vinyl compounds from the corresponding monomers; $Cr(O_2CCF_3)_3$ is used in vulcanization, such as the production of carboxynitroso rubbers (*156*).

In so far as metal trifluoroacetates have been used as catalysts, the features of trifluoroacetate groups that would appear to be valuable in this respect include their ability to support a structure in which two or more metal centers are in close proximity, the ease with which they may be displaced from the coordination of an atom to generate sites for catalysis, together with their thermal stability and chemical inertness that minimize unwanted side reactions.

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