Coordinated Trifluoromethanesulfonate and Fluorosulfate

GEOFFREY A. LAWRANCE

Department of Chemistry, The University of Newcastle, Newcastle, New South Wales 2308, Australia

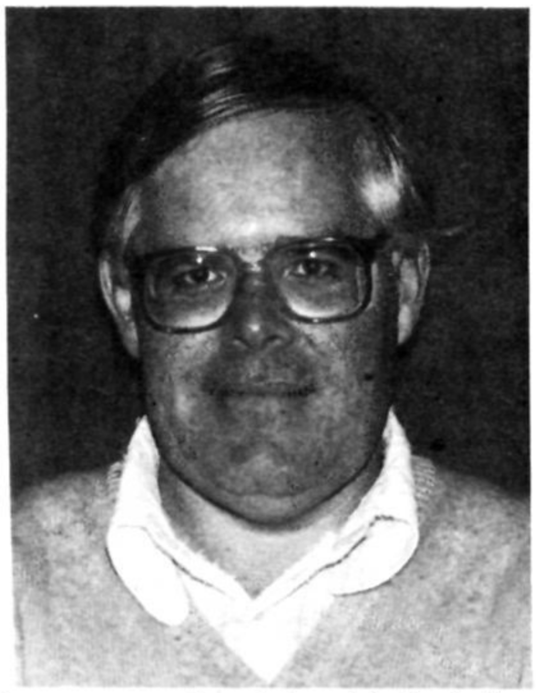
Received May 30, 1985 (Revised Manuscript Received September 5, 1985)

Contents

I. Introduction

The diversity of compounds, particularly transition-metal compounds, incorporating as ligands what have been regarded in the past as poorly coordinated anions has increased rapidly in recent years. One of the reasons for this interest has been a recognition of the value of these compounds as inorganic synthons, that is, as precursors to a range of derivatives formed by substitution of the relatively labile ligand by ligands of greater nucleophilicity. Likely candidates as leaving groups include the anions perchlorate (ClO_4^-), fluorosulfate (FSO_3^-), tetrafluoroborate (BF_4^-), and trifluoromethanesulfonate ($CF_3SO_3^-$). Of these ions, $CF_3SO_3^-$ and FSO_3^- are arguably the most accessible, safe, and stable. Compounds with covalently bound trifluoromethanesulfonate and fluorosulfate are now quite extensive and continue to grow in number. Their literature dominates other contenders, and consequently they have been selected for detailed review. The similarities of the RSO_3^- ions (R = F, CF_3) are sufficiently compelling to allow consideration of their chemistry in concert.

Of the two anhydrous acids, fluorosulfuric acid has the longer history; it was first synthesized in 1889,[1] with patents for its synthesis appearing some decades later.[2,3] Trifluoromethanesulfonic acid was first prepared in the 1950s,[4,5] with a patent for its synthesis appearing in that decade.[6] The anhydrous acids are both high-boiling dense liquids (CF_3SO_3H, bp 162 °C, density 1.696 g/mL; FSO_3H, bp 162.7 °C, density 1.726 g/mL). For CF_3SO_3H, the monohydrate and several polyhydrates are known and form as crystalline solids which have been characterized by X-ray crystal structure analyses.[7,8] The analogous hydrates of FSO_3H are less well-known, but apparently form under certain controlled conditions.[9] Both are strong acids; measurement of the Hammett constants in acetic acid indicate that trifluoromethanesulfonic acid is a stronger acid than perchloric acid and slightly stronger than fluorosulfuric acid.[10] Arguably, CF_3SO_3H is the strongest monobasic acid known, although FSO_3H is clearly of similar strength.[10-12]



Geoffrey A. Lawrance was born in Ipswich, Australia, and obtained B.Sc. and Ph.D. degrees from the University of Queensland and a Dip.Ed. from the University of Melbourne. He has held academic posts at the University of Melbourne and the Australian National University and is currently Senior Lecturer in inorganic chemistry at the University of Newcastle, Australia. His research covers aspects of the synthesis, reactivity, and reaction mechanisms of coordination complexes, and he was awarded the Rennie Memorial Medal of the Royal Australian Chemical Institute for research in 1982. He is married with two young sons. A particular research interest in inorganic reaction mechanisms has been reviewed previously in *Accounts of Chemical Research*. One other current research interest is the reactivity and synthetic utility of complexes of coordinated trifluoromethanesulfonate, the subject of this review.

The alkali metal ion and tetraalkylammonium ion salts of both trifluoromethanesulfonic acid and fluorosulfuric acid are soluble in a wide range of protic and aprotic solvents; the use of tetraalkylammonium trifluoromethanesulfonates as supporting electrolytes in nonaqueous electrochemistry has been recognized.[13] Both simple cation and metal complex cation salts of $CF_3SO_3^-$ and FSO_3^- show good solubility in polar solvents; for complexes, this is a property of some value. Unlike perchlorate, these ions are not oxidizing anions and therefore are inherently safer to handle. No oxidation of various divalent metal ions by trifluoromethanesulfonic acid was detected after 24 h in 1.0 M acid at 570 K.[14]

The electron-withdrawing properties of the CF_3–, F–, and $-SO_2-$ groups suggest that the $CF_3SO_3^-$ and FSO_3^- anions may act as good leaving groups; the trifluoromethanesulfonate ion has found favor in this role in organic chemistry.[15-19] The properties and some reactions of the acids CF_3SO_3H[20,21] and FSO_3H[22] have been reviewed. The inertness and low nucleophilicity of the

0009-2665/86/0786-0017$06.50/0

anions suggest that they can have a useful role as both indifferent anions and relatively labile leaving groups in inorganic chemistry, paralleling their role in organic chemistry. Particularly with metal complexes, this has been recognized and exploited in recent years. The formation and reactions of bound RSO_3^- (R = F, CF_3) are reviewed in this article. Clearly the title belies a personal bias toward coordination complexes; however, examples of covalently bound FSO_3^- and $CF_3SO_3^-$ throughout the periodic table will be addressed, although emphasis may lie on transition-metal chemistry, where striking advances have been made in the past decade.

Of the two anions, there is developing a preference for $CF_3SO_3^-$ as an inert and indifferent anion and as a labile ligand. In water, CF_3SO_3H ionizes completely and simply via

$$CF_3SO_3H + H_2O \rightarrow H_3O^+ + CF_3SO_3^- \quad (1)$$

However, FSO_3H can undergo several reactions,[22-24] namely

ionization: $$FSO_3H + H_2O \rightleftharpoons H_3O^+ + FSO_3^- \quad (2)$$

fast hydrolysis: $$FSO_3H + H_2O \rightleftharpoons H_2SO_4 + HF \quad (3)$$

slow hydrolysis: $$FSO_3^- + H_2O \rightleftharpoons HSO_4^- + HF \quad (4)$$

and the latter two reactions clearly impair its virtue as an inert and indifferent anion, at least in aqueous solution. Importantly, it has been shown recently that coordinated $CF_3SO_3^-$ in $Co(NH_3)_5(OSO_2CF_3)^{2+}$ hydrolyzes cleanly and completely in dilute aqueous acidic or basic solution with simple Co–O cleavage.[25] The analogue $Co(NH_3)_5(OSO_2F)^{2+}$ in dilute aqueous acid undergoes cleavage during aquation to produce F^- and SO_4^{2-}; this scission also occurs in dimethyl sulfoxide.[26] This propensity for degradation of bound FSO_3^- implies that $CF_3SO_3^-$ is the preferred anion, at least where reactions in protic or polar solvents are envisaged. Nevertheless, examples of bound FSO_3^- are almost as numerous as those of bound $CF_3SO_3^-$, and since it is apparent that in many cases the above reactivity of FSO_3^- is not relevant, it remains appropriate to address the chemistry of both bound fluorosulfate and bound trifluoromethanesulfonate. The majority of the literature in this area has appeared in the last two decades; reports continue to appear apace, and review of bound trifluoromethanesulfonate and fluorosulfate seems timely.

II. Synthesis and Characterization

A. Ionic vs. Covalent RSO_3^-

1. Simple Salts

The ions $CF_3SO_3^-$ and FSO_3^- are relatively large ($\bar{V}$ in water for FSO_3^- is 47.8 $cm^3\ mol^{-1}$[27] and for $CF_3SO_3^-$ is 80.4 $cm^3\ mol^{-1}$[28]) and are species of low nucleophilicity. There is a tendency with metal ions to form simple salts that are usually ionic in the solid state and certainly ionized in solution. Salts of practically all metal ions have been prepared.[20-22,29-33] While it does not bear directly on the topic of this review, it may be appropriate to summarize particularly the more common routes used for synthesis of simple salts:[20,22,23]

(a) Salts from chloride salts by dissolution of the metal chloride in anhydrous acid is the most common method,[31-34]

$$MCl_n + nRSO_3H \rightarrow M(SO_3R)_n + nHCl\uparrow \quad (5)$$

which can be employed also with a variety of other halide and oxyanion salts.

(b) Salts from sulfate salts via barium sulfate in an appropriate solvent is a particularly useful method when dealing with acid-sensitive compounds.[35]

$$M(SO_4)_n + nBa(RSO_3)_2 \rightarrow M(SO_3R)_{2n} + nBaSO_4\downarrow \quad (6)$$

(c) Salts may be obtained from halide salts by using $Ag^IRSO_3^-$ in an appropriate solvent.[36]

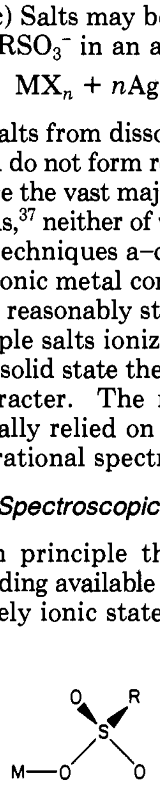
$$MX_n + nAg(RSO_3) \rightarrow M(RSO_3)_n + nAgX\downarrow \quad (7)$$

Salts from dissolution of the metal in the anhydrous acid do not form readily under even vigorous conditions, since the vast majority of metals are inert to the boiling acids,[37] neither of which is regarded as an oxidizing acid.

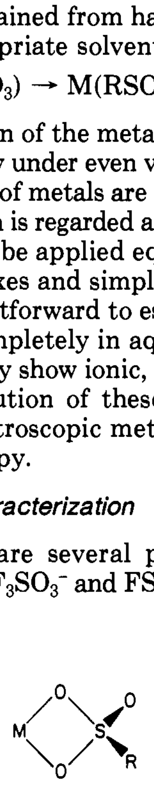
Techniques a–c can be applied equally well to both cationic metal complexes and simple cations.[33] While it is reasonably straightforward to establish that these simple salts ionize completely in aqueous solution, in the solid state they may show ionic, covalent, or mixed character. The resolution of these possibilities has usually relied on spectroscopic methods, particularly vibrational spectroscopy.

2. Spectroscopic Characterization

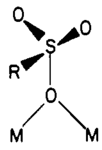
In principle there are several possible modes of bonding available to $CF_3SO_3^-$ and FSO_3^- apart from the purely ionic state:



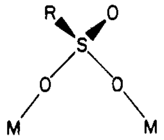
1



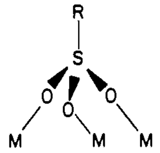
2



3



4



5

$M^{n+}\cdot(RSO_3^-)$

6

Evidence for most of **1**–**5** has been forthcoming in the solid state and will be discussed in the course of the review. In solution, however, the coordinated ligands so far defined are almost exclusively of structure **1**. The bidentate structure **2** is unlikely to exist in solution, given the strain in four-membered chelate rings generally and the low nucleophilicity of RSO_3^-, although a bridging situation like **4** is a little more likely. The alternative in solution of a tightly bound ion pair (**6**) rather than a definite M–O bond is unlikely, although it cannot be dismissed in solvents of low dielectric constant. The measured ion-pairing constant for ClO_4^- with $Cr(DMF)_6^{3+}$ in dimethylformamide (DMF) is over 30-fold smaller than with the small Cl^-, while no K_{IP} could be measured for $B(C_6H_5)_4^-$;[38] apparently, relatively large ions of low nucleophilicity are not good candidates for forming strong ion pairs. Both FSO_3^-

TABLE I. Vibrational Modes for Ionic and Covalent FSO_3^-

	ionic FSO_3^- (C_{3v})		covalent FSO_3^- (C_s)	
assignment	normal mode	example,[a] cm^{-1}	normal mode	example,[b] cm^{-1}
$\nu_s(SO_3)$	$\nu_1(A_1)$	1082	$\nu_1(A')$	1098
$\nu(SF)$	$\nu_2(A_1)$	786	$\nu_2(A')$	842
$\delta_s(SO_3)$	$\nu_3(A_1)$	566	$\nu_3(A')$	562
$\nu_a(SO_3)$	$\nu_4(E)$	1287	$\nu_6(A')$, $\nu_8(A'')$	1207, 1308
$\delta_a(SO_3)$	$\nu_5(E)$	592	$\nu_7(A')$, $\nu_9(A'')$	607, 633
δ_{rock}	$\nu_6(E)$	409	$\nu_4(A')$, $\nu_5(A'')$	422, 431

[a] $K(FSO_3)$. [b] $Cu(FSO_3)_2$.

and $CF_3SO_3^-$ are no smaller than ClO_4^- and are similarly of low nucleophilicity; hence **6** is not a likely structure in solution. Unbound RSO_3^- in solution will be essentially dissociated.

Overwhelmingly, characterization of binding for RSO_3^- has relied on vibrational spectroscopy. The tetrahedral ion FSO_3^- is of C_{3v} symmetry as a free ion and should exhibit six fundamental vibrations, all IR and Raman active. Upon coordination, the symmetry is lowered to C_s; only with structure **5** would the C_{3v} symmetry be preserved. For C_s, the three degenerate E modes of C_{3v} would split, yielding in principle nine normal modes.[39-43] Expected modes with different symmetries, assignments, and examples are collected in Table I. Apart from the increase in the number of normal modes upon covalent bond formation, some shifts in the positions of vibrations associated with the sulfuryl group occur. The simplicity of the vibrational spectroscopic technique has led to its popularity for elucidating structure in the solid state where covalently bound FSO_3^- is suspected. The success of the technique has been validated on several occasions when an X-ray crystal structure of the compound under study has also been determined, thus clearly defining the coordination geometry.

The closely related $CF_3SO_3^-$ anion likewise lends itself to characterization by vibrational spectroscopy. However, here the situation is not so clear-cut. Unambiguous assignments of vibrational modes is not possible due to the mixing of CF_3 and SO_3 vibrational modes and accidental coincidences of these modes arising particularly in the stretching region.[44] An assignment of the IR spectrum of ionic $CF_3SO_3^-$ as the Ag^+ salt has been made;[45] in the stretching region, $\nu[SO_3(E)]$ and $\nu[SO_3(A_1)]$ were assigned at 1270 and 1043 cm^{-1}, respectively, with $\nu[CF_3(A_1)]$ and $\nu[CF_3(E)]$ at 1237 and 1167 cm^{-1}, respectively. This differs from an earlier assignment of the SO_3 stretching modes in the Na^+ salt at 1280 and 1240 cm^{-1} and the CF_3 stretching modes at 1175 and 1035 cm^{-1}.[44] Despite the inherent problems, IR spectroscopy has been used on many occasions to identify bound or ionic $CF_3SO_3^-$.[46-49] The stretching region offers the most significant shifts and multiplicities upon coordination. Characteristically, the band near 1280 cm^{-1} for ionic $CF_3SO_3^-$ is shifted to higher wavenumber, appearing near 1380 cm^{-1} for monodentate-bound trifluoromethanesulfonate.[47,49] Bidentate and bridging $CF_3SO_3^-$ modes have been assigned on the basis of shifts and multiplicities of bands in the stretching region,[44,47] although such assignments are arguably more tenuous. While the analysis of IR spectra of $CF_3SO_3^-$ is less secure than in the case of FSO_3^- the technique offers a facile method of characterization and finds favor as one of the few accessible methods for characterizing samples that may be too reactive to study in solution.

For diamagnetic compounds in solution, ^{19}F NMR spectroscopy is clearly a technique of potential value, providing a suitable inert solvent can be found. To date, relatively few studies of RSO_3^- metal complexes are extant, and most reports relate to nonmetallic compounds. Various xenon(II) compounds with FSO_3^- have been studied by NMR. In these cases both ^{19}F and ^{129}Xe spectra can be recorded and ^{19}F–^{129}Xe spin coupling evaluated.[50-54] Spectra of these species have usually been measured at temperatures well below 0 °C in solvents such as BrF_5 or FSO_3H. NMR of SbF_5–RSO_3H superacid mixtures has detected the presence of species such as $H[RSO_3–SbF_5]$.[55,56] Adducts with PF_5, AsF_5,[57] germanium polyfluorides,[58,59] and boron, tin, tantalum, niobium, vanadium, and sulfur polyfluorides[59] have been detected only from solution NMR studies at low temperatures. With transition-metal complexes, ^{19}F NMR has been involved in assigning a polymeric structure with bridging FSO_3^- in $WO(SO_3F)_4$,[60] while the spectrum of the *mer*-$Rh(OSO_2F)Cl_2[P(CH_3)_2(C_6H_5)]_3$ intermediate has been reported.[61] Clearly, much more use of NMR spectroscopy could be made with diamagnetic metal complexes.

Mössbauer spectroscopy has been employed as an aid in characterization of tin compounds with bound RSO_3^-.[46,62-65] The Mössbauer spectrum of a xenon complex of FSO_3^- has also appeared.[66] The technique provides information on the ligand environment of the central atom, which in concert with other physical methods may indicate covalently bound RSO_3^-. The use of this method is strictly limited by the choice of central atom, however, and its applicability can be by no means considered general. Other techniques such as diffuse reflectance electronic spectroscopy,[67,68] electron spin resonance spectroscopy,[69,70] conductivity,[71] magnetic susceptibility,[67,70,72-74] and molecular weight determination[75-77] have been used for characterization, but none offer the universality and simplicity of vibrational spectroscopy or the finiteness of X-ray crystallography.

3. *X-ray Crystallography*

The single-crystal X-ray structures of a range of compounds with covalently bound FSO_3^- and $CF_3SO_3^-$ have been published, and several of the proposed structures **1**–**5** have been observed. Crystallography indicates exclusively O-bonding; there is no structural evidence for participation of the fluorine atom on FSO_3^- in bonding, although this possibility has been raised on at least one occasion.[78] In all cases where covalency occurs in the structure, the situation is clear-cut; for example, the (μ-fluorosulfato)bis(fluoroxenon(II)) cation has a Xe–O bond of 2.21 Å, far too short to support only ionic interactions since the purely ionic (van der Waals contact) distance would be 3.7 Å in that case.[79] Nevertheless, particularly with transition-metal compounds, M–O distances for coordinated RSO_3^- are longer than usual M–O distances, indicative of the low degree of nucleophilicity of these ions. For example, the Fe(II)–OSO_2CF_3 bond in (η^5-pentamethylcyclopentadienyl)(trifluoromethanesulfonato)iron(II) dicarbonyl is 2.007 (3) Å compared with 1.957 Å for Fe(II)–OOCH in an analogue.[80,81] Further, a Pd(II)–OSO_2CF_3 bond at 2.271 Å has been observed, whereas a

TABLE II. Compounds with Covalent RSO_3^- Characterized by X-ray Crystal Structure Analysis

compound	RSO_3^- coord mode[a]	M–O, Å	molecular shape	ref
$I(OSO_2F)_2I$	1	2.09, 2.26	T-shaped, trans-O	83
$[(XeF)_2FSO_3]AsF_6$	4	2.21	linear $FXe^{II}O$	79
$(CH_3)_2Sn(OSO_2F)_2$	4	2.24	O_h Sn(IV); polymer	84
$(Me_5cp)Fe(CO)_2(OSO_2CF_3)$	1	2.007	tetrahedral Fe(II)	80
$[Cu_4(OH)_4(OSO_2CF_3)_2(N'_4)_4]^{2+}$	4	2.50–2.68	cubane-like tetramer[b]	85
$Me_2Au(OH_2)(OSO_2CF_3)$	1	2.201	square-planar Au(III)[c]	76
$Pd(NHEt_2)(OSO_2CF_3)(L)$	1	2.271	square-planar Pd(II)[d]	82
$(cp)_2Ti(OSO_2CF_3)_2$	1	2.003	tetrahedral Ti(IV)[e]	86
$[Cu(OSO_2CF_3)]_2 \cdot C_6H_6$	5	2.00–2.22	square-planar Cu(I)[f]	87
$[Cu(OSO_2CF_3)] \cdot$cyclohexene	5	2.04–2.22	distorted tetrahedral Cu(I)[g]	88

[a] Given in terms of structures 1–5 drawn in the text. [b] $N'_4 = N(C_5H_5N)_3$; Cu–OH 2.38–2.40 Å; RSO_3^- spanning vertices of cluster. [c] Au(III)–OH_2 2.157 Å. [d] L = (3-diethylamino)propionyl. [e] cp = cyclopentadienyl anion. [f] Infinite chains of Cu units cross-linked in sheets by C_6H_6 molecules. [g] Tetrameric units interconnected by Cu–O–Cu bridges to give infinite chains.

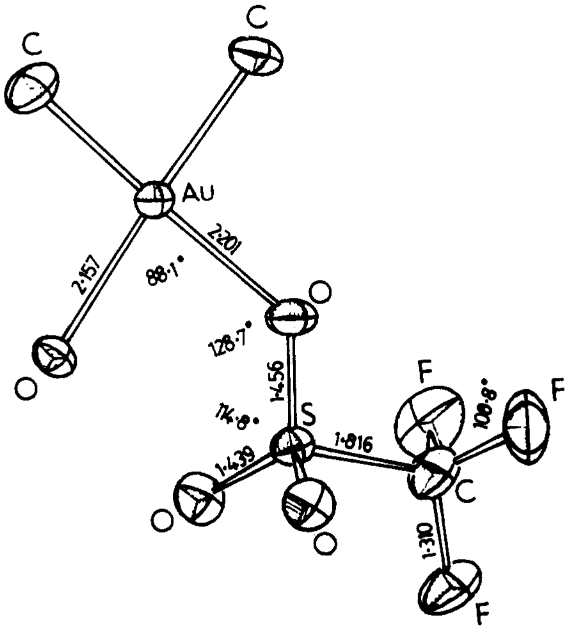


Figure 1. ORTEP drawing of the molecule $Au(CH_3)(OSO_2CF_3)(OH_2)$ showing the coordinated trifluoromethanesulfonate and selected bond lengths and bond angles.[76] [Adapted from *Inorganic Chemistry* with the permission of the copyright holder.]

typical Pd(II)–O bond is ~2.0 Å, although the trans-acyl group does influence the bonding in that case.[82] Structural studies reported to date are collected in Table II[76,79,80,82-88] along with bond lengths and modes of coordination. Typical unidentate bonding of $CF_3SO_3^-$ is illustrated for the $(CH_3)_2Au(OH_2)(OSO_2CF_3)$ complex in Figure 1.

B. Main-Group Compounds

There are many examples of covalently bound FSO_3^- and $CF_3SO_3^-$ with main-group elements. The compounds formed usually have strictly limited stability in solution and may even undergo thermal decomposition at relatively low temperatures. Further, most of the syntheses require stringent anhydrous conditions, and some involve the use of vacuum-line techniques. Some compounds have not been isolated, but have been detected by NMR spectroscopy at low temperatures in solvents such as liquid SO_2 and BrF_5. While many do not exhibit the relative robustness of transition-metal complexes of coordinated RSO_3^-, and hence have a more limited synthetic usefulness, they represent an important group of compounds, and it would be improper in a review of this type to bypass them.

1. Tin(IV)

Compounds of mainly tin(IV) represent one well-known group. Simple displacement reactions with anhydrous acids at or above room temperature exemplify the synthetic technique commonly employed, e.g.

$$R_2SnCl_2 + 2HX \rightarrow R_2SnX_2 + 2HCl\uparrow \qquad (8)$$

where X = FSO_3^-, $CF_3SO_3^-$, and also $PO_2F_2^-$.[62] Similarly, reactions of $SnCl_2$, $Sn(OAc)_4$, and $Sn(CH_3)_4$ with CF_3SO_3H yield a variety of $Sn-OSO_2CF_3$ species.[46] Alternative routes can be applied, such as reaction with the anhydride of trifluoromethanesulfonic acid,[89] e.g., eq 9, reaction with peroxodisulfuryl difluoride at and

$$(CH_3)_3Sn-O-Sn(CH_3)_3 + (CF_3SO_2)_2O \rightarrow 2(CH_3)_3Sn(OSO_2CF_3) \qquad (9)$$

above room temperature,[63] e.g., eq 10, or reaction with

$$2SnCl_4 + 3S_2O_6F_2 \rightarrow 2SnCl(OSO_2F)_3 + 3Cl_2 \qquad (10)$$

ClO_2SO_3F to extend the coordination number,[65] as in eq 11. These reactions, described specifically for

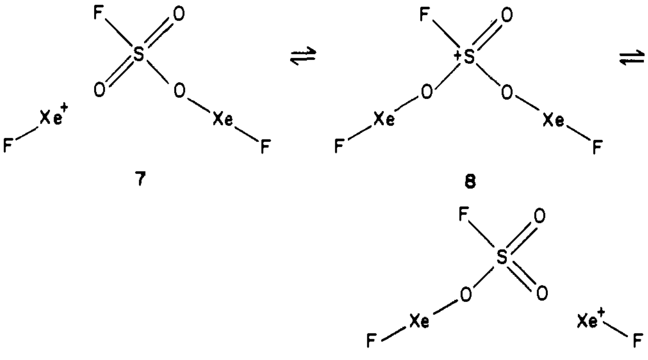
$$2ClO_2SO_3F + Sn(OSO_2F)_4 \rightarrow (ClO_2)_2[Sn(OSO_2F)_6] \qquad (11)$$

Sn(IV), are the conventional routes to covalently bound RSO_3^- compounds of the main-group elements in general.

A variety of spectroscopic techniques (IR, Raman, Mössbauer) have been applied, and covalency has been confirmed by a crystal-structure analysis of $(CH_3)_2Sn(OSO_2F)_2$.[84] Vibrational spectroscopy has been routinely applied. Raman and IR spectra of $Sn(OSO_2F)_2$ indicate appreciable covalent character,[41] since more than six fundamental vibrations of FSO_3^- are seen. The analogue $Sn(OSO_2CF_3)_2$, however, shows $\nu[SO_3(E)]$ near 1260, 1280 cm^{-1}, typical of ionic $CF_3SO_3^-$. For $Sn(OSO_2CF_3)_4$ these bands occur at 1350, 1375 cm^{-1}, and $Sn-OSO_2CF_3$ bonding is implied in that case.[46] The compound of formula $Sn(OSO_2CF_3)_3$ is best regarded as $Sn^{II}[Sn^{IV}(OSO_2CF_3)_6]$, since Mössbauer spectroscopy clearly defined both Sn(II) and Sn(IV), while IR bands at 1360, 1390 cm^{-1} imply coordination of $CF_3SO_3^-$ about octahedral Sn(IV).

2. Xenon(II)

Compounds of the noble gas xenon are now well-known. The first reported reaction of excess anhydrous FSO_3H with XeF_2 at room temperature produced a green-yellow solution which eventually decomposed to Xe and $S_2O_6F_2$.[90] A similar intermediate obtains from reaction of XeF_6 and FSO_3H, and it was proposed that Xe–OSO_2F bonding occurred. Soon after, the species $XeF(OSO_2F)$ and $Xe(OSO_2F)_2$ were reported from like reactions with XeF_4, in addition to $XeF_5(OSO_2F)$, a volatile yet quite stable white solid at room temperature which melted with decomposition only above 70 °C.[53,54] Reaction of XeF with several strong protic acids yielded solid $Xe(OSO_2CF_3)F$, $Xe(OSO_2F)F$, and $Xe(OClO_3)_2$, all of which were thermodynamically unstable and underwent decomposition to xenon and other products such as XeF_2 and $S_2O_6F_2$ obtained from $Xe(OSO_2F)F$ on melting.[91] The synthesis and characterization of $[(FXe)_2(SO_3F)](AsF_6)$ from reaction of XeF_3^+ with HSO_3F[52] culminated in an X-ray structural characterization of this species, where FSO_3^- bridges two XeF units.[79] The bonding in that case was described in terms of structure **8** together with contributions from structures **7** and **9**.


7

8

9

The high-resolution ^{129}Xe NMR spectra of $FXe(OSO_2F)$, $[(FXe)_2SO_3F]^+$, and $FXe(OSO_2F)MOF_4$ (M = Mo, W), where ^{19}F–^{129}Xe spin–spin coupling is observed,[50] confirmed the existence of these species in solution in solvents such as BrF_5 and FSO_3H at temperatures below −40 °C. Further, the $Xe(OSO_2F)^+$ ion and $Xe(OSO_2F)_2$ have been characterized in FSO_3H solution at low temperature by ^{129}Xe and ^{19}F NMR spectroscopy.[51]

3. *Halide Compounds*

Halogens in oxidation states I and III may incorporate bound RSO_3^-. Various halide(I) complexes $X(OSO_2R)$ (X = Cl, Br, I) and $Br(OSO_2F)_2^-$ are known,[92–96] as are the I(III) compound $I(OSO_2F)_3$[64,95] and the ions $I(OSO_2F)_4^-$[92] and $I(OSO_2F)_2^+$.[64] The related compounds $I_2(OSO_2F)$ and $I_7(OSO_2F)$ have been reported, the latter being a polymer in the liquid state.[95] An X-ray crystal structure of $I(OSO_2F)_2I$ has confirmed the existence of covalent bonds.[83]

Oxidative addition of halogen or interhalogen to $I(OSO_2F)$ produces $IX_2(SO_3F)$ and $I_2X(SO_3F)$, which are apparently ionic solids, forming solvated IX_2^+ and I_2X^+ solvated cations in FSO_3H.[97] The $I(OSO_2F)_2^+$ cation can be generated by reaction of $I(OSO_2F)_3$ via

$$Sn(OSO_2F)_4 + 2I(OSO_2F)_3 \rightarrow [I(OSO_2F)_2][Sn(OSO_2F)_6] \quad (12)$$

performed in $S_2O_6F_2$ solvent for several days at room temperature.[64] A reaction of $BrSO_3F$ in excess $Sn(OSO_2F)_4$ yields eventually the Br(III) analogue,[64] where oxidation of Br(I) by $S_2O_6F_2$ must be involved. Reactions involving peroxydisulfuryl difluoride most likely involve the $FSO_2O\cdot$ radical,[98] which can act as an efficient oxidant. The $I(OSO_2F)_4^-$ anion may be generated by reaction of (perfluoroalkyl)iodine fluorosulfate with $(CF_3)_2CFI$.[92]

4. *Other Main-Group Elements*

A wide range of polyfluorides also incorporating RSO_3^- have been studied, almost exclusively by ^{19}F NMR spectroscopy in solution. The octahedral compounds of P(VI), As(VI), Ge(VI), S(VI), Se(VI), Sb(V), and Sn(IV) with RSO_3^- bound are known, with usually unidentate coordination. Species apparently observed include $PF_5(OSO_2R)$,[57,59] $AsF_5(OSO_2R)$,[57,59] $SeF_5(OSO_2R)$,[99] *cis*- and *trans*-$SnF_4(OSO_2R)_2^{2-}$,[59] *cis*- and *trans*-$GeF_4(OSO_2R)_2$,[58] *cis*-$SF_4(OSO_2R)_2$,[59,100] *mer*-$GeF_3(OSO_2R)_3$,[58] $SbF_5(OSO_2F)^-$,[56,101,102] and $SbF_2(OSO_2R)_4^-$.[101] Apparently dimeric species of octahedral Sb(V) form with bridging bidentate RSO_3^-, namely $SbCl_4(OSO_2R)$[77,103] $SbF_3(OSO_2R)_2$,[104] $SbF_4(OSO_2R)$,[104] and $Sb_2F_9(OSO_2R)$,[104] with structures assigned largely on the basis of IR and Raman spectroscopy.

Reaction of CF_3SO_3X (X = Cl, Br) with covalent inorganic chlorides such as $COCl_2$ and $SiCl_4$ give excellent yields of $(CF_3SO_3)_2CO$ and $(CF_3SO_3)_2SiCl_2$.[96] CF_3SO_3Cl also oxidatively adds to unsaturated inorganic compounds such as CO and SO_2 to yield CF_3SO_3COCl and $CF_3SO_2OSO_2Cl$, respectively; the reactivity of FSO_2OBr is similar.[96] Synthesis, properties, and reactions of the imide $(CF_3SO_3)_2NH$ have recently appeared.[105] The compounds $Tl(OSO_2CF_3)_3$ and $M(OSO_2F)_3$ (M = Bi, Ga, In, Tl) are known,[106–109] where bidentate bridging RSO_3^- is suggested. Adducts of these with ligands such as pyridine, dimethyl sulfoxide, and pyridine oxide form readily.[107,109] Some organo–main-group compounds coordinating RSO_3^- are also known, namely $(CH_3)_3Si(OSO_2CF_3)$,[96,110] $(CH_3)_3Ge(OSO_2CF_3)$,[111] and arylthallium trifluoromethanesulfonates.[108] All the above species rely largely on vibrational spectroscopy for evidence of RSO_3^- coordination. The distinction between ionic and covalent nature cannot be clearly drawn, since many compounds have no lengthy existence outside the solid state and dissociate or react readily in solution. Nevertheless, covalent bonding of $CF_3SO_3^-$ and FSO_3^- to a range of main-group elements under favorable circumstances has been firmly established, and presages like coordination with metal complexes.

C. Organometallic Compounds

In a little over a decade, a large number of reports of metal–carbon bonded species also incorporating an M–OSO_2R bond have appeared. Several of these compounds have been characterized by X-ray crystal-structure analysis, while others have been identified by spectroscopic methods or else their existence as intermediates has been implied by reactivity trends of the compound in comparison with other coordinated monoanions. The two most common methods of synthesis are either direct replacement of other ligands by RSO_3^- or else oxidative addition of the ester RSO_3CH_3 or acid RSO_3H to a low-valent metal complex. Also included in this section must be the Cu(I) and Ag(I) trifluoromethanesulfonates which form complexes with organic molecules like benzene where M–OSO_2R bonds exist; these species are efficient catalysts of several organic reactions.

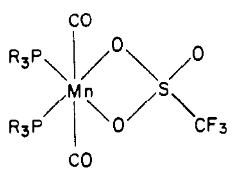
1. Displacement Reactions

Reaction of the gold(III) complex $(H_3C)_3Au(PR'_3)$, where $R' = C_6H_5$, in benzene with anhydrous acids at room temperature yields particularly $(H_3C)_2Au(PR'_3)(OSO_2CF_3)$ and CH_4;[112] selective displacement of the alkyl group cis to the $P(C_6H_5)_3$ ligand occurs, presumably due to activation of that site from the trans effect of the CH_3^- ligand. This gold(III) complex, detected by NMR spectroscopy at low temperature, undergoes spontaneous reductive elimination of C_2H_6 with formation of the gold(I) compound $(CF_3SO_3)Au(PR'_3)$; reactivity with coordinated trifluoromethanesulfonate is substantially greater than with other coordinated anions. In a similar system,[76] reaction of $[(H_3C)_2AuI]_2$ occurs via eq 13. The intermediate here is isolable, and

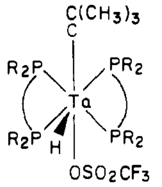
$$\begin{array}{l} [(H_3C)_2AuI]_2 + 2Ag(OSO_2CF_3)\cdot\tfrac{1}{2}C_6H_6 \longrightarrow \\ \qquad\qquad [(H_3C)_2Au(OSO_2CF_3)]_2 + 2AgI \\ \qquad\qquad\qquad \downarrow \\ \qquad\qquad 2C_2H_6 + 2Au(OSO_2CF_3) \end{array} \quad (13)$$

the dimeric structure was assigned on the basis of molecular weight measurements; presumably bidentate bridging trifluoromethanesulfonate exists to complete a square-planar geometry about each Au(III) center. Recrystallization from pentane/toluene yields the monomer $(H_3C)_2Au(OH_2)(OSO_2CF_3)$ rather than the dimer, indicating the sensitivity of bridging $CF_3SO_3^-$ to even traces of water. In toluene/benzene with *trans*-cyclooctene, reaction generates C_2H_6 and $(trans\text{-}C_8H_{14})_3Au(CF_3SO_3)$, where the triflate is apparently ionic. The $(H_3C)_2Au(OH_2)(OSO_2CF_3)$ compound does contain unidentate O-bound $CF_3SO_3^-$, however, determined from an X-ray crystal structure analysis;[76] the Au(III)–OSO_2CF_3 bond (2.201 Å) is somewhat longer than the Au–OH_2 bond (2.157 Å). A relatively long M–OSO_2CF_3 bond (2.271 Å) was also reported in the crystal structure of the Pd(II) complex (diethylamine)[3-(diethylamino)propionyl trifluoromethanesulfonato]palladium(II),[82] and these observations are consistent with the expected low degree of nucleophilicity of $CF_3SO_3^-$.

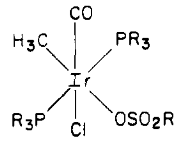
Rapid displacement of the η^3-allyl ligand occurs when $Mn[P(OCH(CH_3)_2)_3]_2(\eta^3\text{-}C_3H_5)(CO)_2$ is reacted with excess CF_3SO_3H in ether.[113] The product $Mn[P(OCH(CH_3)_2)_3]_2(CO)_2(OSO_2CF_3)$ is presumed to involve pseudooctahedral Mn(I), so a bidentate $CF_3SO_3^-$ in various stereoisomers such as 10 has been proposed.



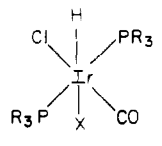
10



11



12



13

Such a coordination geometry for $CF_3SO_3^-$ would be quite strained, and a dimer with bidentate but bridging $CF_3SO_3^-$ may be an option. With CF_3SO_3H, $HMn(CO)_5$ yields $Mn(CO)_5(OSO_2CF_3)$ and H_2, with the trifluoromethanesulfonate ion probably occupying the sixth coordination site as a unidentate,[114] although it is readily displaced by CO.

Reaction of $Ta(CC(CH_3)_3)(DMPE)_2Cl$ (DMPE = $(H_3C)_2PCH_2CH_2P(CH_3)_2$) with CF_3SO_3H yields $[Ta(CHC(CH_3)_3)(DMPE)_2(OSO_2CF_3)]$;[75] differential vapor pressure molecular weight determination in tetrahydrofuran is consistent with the complex being neutral and the trifluoromethanesulfonate coordinated. At low temperature, the intermediate 11 is presumed to form prior to insertion of H^- into the carbon-bonded ligand. In CF_3SO_3H at 0 °C, $Pt(PR_3)_2(C_2H_4)$ reacts to release C_2H_6 and C_2H_4. The intermediate Pt(II) complex reacts with LiCl in acetone to form $Pt(PR_3)_2Cl_2$, and coordinated $CF_3SO_3^-$ is presumed to be involved in the intermediate;[115] the proposed intermediate is $Pt(PR_3)_2(H)(OSO_2CF_3)$ or a bis(trifluoromethanesulfonato) analogue, since the former is known to form separately by reaction of $Pt(PR_3)_2(H)Cl$ with $Ag(CF_3SO_3)$. The Ru(II) compounds $Ru(CO)_2Cl_2(LL)$ and $Ru(CO)_2(OAc)_2(LL)$ (LL = phen, bpy) both react smoothly with neat CF_3SO_3H upon heating to generate *cis,cis*-$Ru(CO)_2(LL)(OSO_2CF_3)_2$ complexes,[116,117] with further displacement of coordinated $CF_3SO_3^-$ possible. Likewise, reaction of $Fe(cp)(CO)[P(CH_3)_3][C(Si(CH_3)_3){=}C{=}O]$, where cp = cyclopentadienyl anion, with trifluoromethanesulfonic acid yields $Fe(cp)(CO)[P(CH_3)_3](OSO_2CF_3)$.[118] A related iron(II) compound, (η^5-pentamethylcyclopentadienyl)(trifluoromethanesulfonato)iron(II) dicarbonyl, has been characterized structurally, and the Fe–OSO_2CF_3 bond (2.007 Å) is clearly indicative of covalent bonding.[80] Field-desorption mass spectrometry of this compound showed that the coordinated $CF_3SO_3^-$ was present in the molecular ion.[119] Chiral $Re(cp)(NO)(PR'_3)(CH_3)$ with CF_3SO_3H forms CH_4 and $Re(cp)(NO)(PR'_3)(OSO_2CF_3)$ with optical retention, and the molecular ion with bound $CF_3SO_3^-$ appears in the mass spectrum.[120] Also, FSO_3^- can increase the coordination number of several carbonyls by binding reversibly, as indicated from low-temperature NMR spectroscopy.[121]

Reaction of Cu_2O, carbon monoxide, and sulfonic acids including CF_3SO_3H yields reasonably stable species of formula $Cu(CO)(SO_3R)$.[122] The X-ray structure of the ethanesulfonic acid complex shows the copper(I) is four-coordinate tetrahedral, with infinite chains and the RSO_3^- bound by all three oxygen atoms to copper(I) ions. The ability of copper(I) to bind sulfonates will be addressed again later with respect to $M(CF_3SO_3)\cdot$organics.

Reaction of coordinated halides with silver trifluoromethanesulfonate in an appropriate inert solvent has been successfully applied on several occasions. With a cyclopentadienyl Ti(IV) complex, the reaction[86]

$$(\pi\text{-}C_5H_5)_2TiCl_2 + 2Ag(CF_3SO_3) \rightarrow (\pi\text{-}C_5H_5)_2Ti(OSO_2CF_3)_2 + 2AgCl \quad (14)$$

occurs where the tetrahedral Ti(IV) has two covalently bound $CF_3SO_3^-$, characterized by crystal structure analysis. Reaction of thienylchloromercury(II) with $Ag(CF_3SO_3)$ produces a thienyl(trifluoromethanesulfonato)mercury(II) intermediate,[123] which readily decomposes at room temperature to (2,2′-dithienyl)mercury(II). Coordinated trifluoromethanesulfonate may also occur in a mercury phosphine oxide.[124] Certainly coordination of $CF_3SO_3^-$ to mercury(II) has been observed following reaction of $[Hg(Me_2SO)_6](CF_3SO_3)_2$ with benzene, to form the $(C_6H_5)Hg(Me_2SO)_2(OSO_2CF_3)$ compound, since the cation $[(C_6H_5)Hg(OSO_2CF_3)]^+$ was detected in the mass spectrum.[125] Reaction of the same starting material in methanol with C_2H_4 yields the (2-methoxyethyl)(trifluoromethanesulfonato)mercury(II) compound.

2. Oxidative Addition Reactions

Square-planar d^8 iridium(I) compounds react with H_3COSO_2R to give oxidative addition products. The compound *trans*-$Ir(CO)Cl(PR'_3)_2$ oxidatively adds both $CF_3SO_3CH_3$ and FSO_3CH_3 to form highly labile iridium(III) products $IrCl(CO)(PR'_3)(CH_3)(OSO_2R)$, where the configuration **12** is apparently adopted.[126,127] Oxidative addition to the *trans*-$Ir(CO)Br[P(C_6H_5)_3]_2$ analogue has also been studied.[128] With *trans*-$IrCl(N_2)(PR'_3)_2$, trans addition of RSO_3CH_3 yields the apparently octahedral intermediate $IrCl(OSO_2R)(CH_3)(N_2)(PR'_3)_2$.[48,129] The conditions of reaction, where the reactants are mixed in benzene at 77 K and allowed to warm to room temperature, does not lead to displacement of dinitrogen, although further reaction with other coordinating anions in methanol appears to generate a five-coordinate species that readily forms an adduct with carbon monoxide. Oxidative addition of RSO_3CH_3 to other low-valent metals is possible; for example, $(cp)Co(CO)_2$ with FSO_3CH_3 yields $(cp)(CO)Co(CH_3)(OSO_2F)$.[130]

Certain reactions involve both oxidative addition of RSO_3CH_3 and concomitant displacement of other ligands and are best described as oxidative elimination reactions:

$$M^{n+}L_xX_z + RSO_3CH_3 \rightarrow M^{(n+2)+}L_x(CH_3)(OSO_2R)X_{z-2} + 2X \quad (15)$$

For example, $(cp)_2Zr[P(CH_3)(C_6H_5)_2]_2$ mixed with FSO_3CH_3 in deuteriobenzene loses two $P(CH_3)(C_6H_5)_2$ ligands, and the Zr(II) is oxidized to Zr(IV) during addition.[131] Some $(cp)_2Zr(OSO_2F)_2$ is also detected in this reaction. Likewise, $Pt(PR'_3)_3$ with FSO_3CH_3 forms $Pt(PR'_3)_2(CH_3)(OSO_2F)$.[132]

Apart from oxidative addition, it is apparent that other reactions may occur when using the acid esters. Halogen abstraction reactions may occur; for example, *mer*-$Rh(P(CH_3)_2C_6H_5)_3Cl_3$ with FSO_3CH_3 produces simply *mer*-$Rh(P(CH_3)_2C_6H_5)_3Cl_2(OSO_2F)$, characterized by NMR and IR spectroscopy.[61,132] This is essentially the reaction operating also when *trans*-$PtCl(H)(PR_3)_2$ reacts with FSO_3CH_3 in benzene in the presence of $H_5C_6C{\equiv}CC_6H_5$, since the major product is $Pt(H_5C_6C{=}CHC_6H_5)(PR'_3)_2(OSO_2CF_3)$.[133] Oxidation of the metal atom has been observed for $MoCl_2(DPE)_2$ with FSO_3CH_3, since $[MoCl_2(DPE)_2](SO_3F)$ is the product.[132] Alkylation of a coordinated ligand is also a possibility, as observed when ferricyanide reacts with FSO_3CH_3, forming $[Fe(CN)(CNCH_3)_5](SO_3F)_2$.[132] The attempted oxidative addition of FSO_3CH_3 to $(cp)Fe(CO)_2^-$ did not generate $(cp)Fe(CO)_2(CH_3)(OSO_2F)$; rather, the *S*-methoxysulfenate complex $(cp)Fe(CO)_2(SO_2CH_3)$ was identified by NMR and IR spectroscopy,[134] so S–F cleavage must be involved.

Apart from the methyl esters, the free acids $HOSO_2R$ can oxidatively add to iridium(I) complexes. Treatment of $IrCl(CO)(PR'_3)_2$ with $HOSO_2F$ generated the Ir(III) compound $IrCl(CO)(PR'_3)_2(H)(OSO_2F)$.[135] Likewise, $Ir(PR'_3)_2LCl$ (L = CO, N_2) oxidatively adds various acids to form $Ir(PR'_3)_2LCl(H)(X)$.[136-138] The compounds formed are apparently of structure **13**, since the X-ray crystal structure of the X = BF_4^- compound is of this geometry.[138]

It is notable that, apart from iridium(I), few reports of oxidative addition of RSO_3H or RSO_3CH_3 to square-planar d^8 compounds have appeared. Given the facility of this type of compound for oxidative addition, it is reasonable to expect that like reactions should occur with other d^8 metal ions.

3. Copper(I) and Silver(I) Compounds

The benzene solvate of copper(I) trifluoromethanesulfonate has received particular attention due to its value as a catalyst. $[Cu(trif)]_2{\cdot}C_6H_6$ has been used for promoting relatively mild acylations of arenes and heterocycles by selenol esters[139] and for selectively forming biaryls;[140] it is a highly active catalyst for the cyclopropanation of olefins with diazo compounds[141] and is often superior to $BF_3{\cdot}OEt_2$ for transformations of diazo compounds.[142] In the penultimate example, the unique selectivity was attributed to coordination of olefins by the electrophilic copper(I) compound; likewise, the silver(I) analogue activates sp C–H bonds in terminal alkynes by π-coordination.[143] The $[Cu(OSO_2CF_3)]_2{\cdot}C_6H_6$ compound was shown by vapor pressure osmometry to be undissociated in solution,[71] and a crystal structure analysis showed it consists of infinite chains of $Cu(OSO_2CF_3)$ units cross-linked in sheets by benzene molecules, with each trifluoromethanesulfonate oxygen bound to a copper(I) ion.[87] The X-ray crystal structure of the related copper(I) trifluoromethanesulfonate cyclohexene complex has also appeared recently.[88]

The silver(I) analogue of the copper(I) system has been studied,[144] while various other synthetic[145-147] and photochemical[148] reports involving copper(I) trifluoromethanesulfonate have appeared. Mixed copper(I)–silver(I) hexanuclear clusters with $CF_3SO_3^-$ as bidentate or monodentate bridging ligands have also been prepared.[149] While detailed review of this specialized area is beyond the scope of this review, it is notable that the enhanced solubility of both coordinated and ionic trifluoromethanesulfonate compounds and the resistance of $CF_3SO_3^-$ to redox reactions are likely to be important factors in the success of these catalysts.

D. Coordination Complexes

1. Simple Displacement Reactions

By far, the majority of examples of coordinated RSO_3^- arise from the simple substitution of a RSO_3^- for some other coordinating anion or molecule. This displacement can be generally represented as

$$[ML_mX_y]^{n+} + yHOSO_2R \rightarrow [ML_m(OSO_2R)_y]^{n+} + yHX \quad (16)$$

With displaced ions such as Cl^- or Br^-, the product HX may be readily removed from the RSO_3H solution in a stream of inert gas[33] and the product precipitated by addition of ether at or below room temperature. However, the reaction need not be restricted to halides; most oxyanions can be displaced, although consideration must be given to hazards arising from release of certain anhydrous acids such as $HClO_4$. With an excess of anhydrous acid, reaction usually proceeds to completion at or above room temperature. Neutral ligands may also be displaced; coordinated water may be replaced simply by heating RSO_3^- salts of aqua complexes,[35] as in

$$[Co(NH_3)_5(OH_2)](CF_3SO_3)_3 \xrightarrow{\Delta} [Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2 + OH_2\uparrow \quad (17)$$

Although the methods have not been applied, in principle reaction of halo complexes or sulfato complexes with silver and barium salts of RSO_3^-, respectively, in poorly coordinating solvent may lead to bound RSO_3^- following removal of the halide as insoluble AgX and removal of the sulfate as insoluble $Ba(SO_4)$. The latter techniques may be appropriate where the precursor or product are acid or heat sensitive and hence not approachable by normal routes.

Displacement reactions reported can be subdivided into two groups: those with largely amine donors in the nonparticipating coordination sites and those with other donors in those sites.

(a) **Complexes with Bound RSO_3^- Not Incorporating Amine Donors**. Fluorosulfato and trifluoromethanesulfonato complexes of the early members of the d-block are quite well represented. Reaction of $TiCl_3(OCH_3)$ with $HOSO_2F$ produces $TiCl_2(OCH_3)(OSO_2F)$;[150] the 1:1 adducts with pyridine, 1,2-ethanediamine, and dimethyl sulfoxide show evidence for bound FSO_3^- from IR data, although the precursor appears to involve FSO_3^- of C_{3v} symmetry, suggesting tridentate coordination or ionic character. Titanium tetrachloride reacts with excess FSO_3H to form $TiCl_2(OSO_2F)_2$;[78] $TiCl_3(OSO_2CF_3)$, $TiCl_2(OSO_2CF_3)_2$, and $TiCl(OSO_2CF_3)$ are also known.[110,151] With titanium in excess, $TiCl_4$ with FSO_3H produces a compound of stoichiometry $TiCl_{3.33}(OSO_2F)_{0.66}$.[78] The unprecedented coordination of FSO_3^- by all oxygens and fluorine was claimed,[78] but seems highly unlikely. Structural assignments for these compounds in general are not well established.

Both $Zr(OSO_2CF_3)_4$ and $Th(OSO_2CF_3)_4$ have been reported.[110] Reaction of Zr(IV) acetate with FSO_3H produced $Zr(OAc)_n(OSO_2F)_{4-n}$, $n = 1$–4,[152] where both bidentate and tridentate FSO_3^- are implied in various cases. With VCl_3, FSO_3H produces hexacoordinate $V(OSO_2F)_3$ with bidentate FSO_3^-,[153] which readily forms adducts with neutral coordinating molecules; vanadium(III), oxovanadium(IV), and oxovanadium(V) $CF_3SO_3^-$ analogues are also known.[153] $CF_3SO_3^-$ displaces CF_3COO^- from $CrO_2(OOCCF_3)_2$ to form involatile and sparingly soluble $CrO(OSO_2CF_3)_2$, a polymer with bridging $CF_3SO_3^-$ assigned from IR and electronic spectroscopy.[47] Reaction of hexaquochromium(III) with 9 M CF_3SO_3H and chromatography on cation-exchange resin detected the $Cr(OH_2)_5(OSO_2CF_3)^{2+}$ ion and small amounts of higher complexes at higher concentrations of acid;[154] $CF_3SO_3^-$ is displaced faster than NO_3^- but slower than ClO_4^- in the pentaaquachromium(III) system.

The heavier elements also coordinate RSO_3^-. $Pt(PR'_3)_2Cl_2$ with CF_3SO_3H forms $Pt(PR'_3)_2Cl(OSO_2CF_3)$.[115] Uranyl acetate and thorium(IV) acetate yield species such as $UO_2(SO_3F)_2$ and $Th(SO_3F)_4$; uranium compounds in other oxidation states, $UO(SO_3F)_2$, $U(SO_3F)_4$, and $U(SO_3F)_6^{2-}$, also are apparently present.[156,157] Structural characterization of the f-block compounds, based principally on IR spectroscopy, does not permit concrete assignment of coordination geometry.

(b) **Amine Complexes with Coordinated RSO_3^-.** Inert and usually octahedral metal complexes with principally N-donor amine (or in some cases imine) ligands can coordinate RSO_3^- as a unidentate ligand. Commonly, reaction of the chloro analogue with anhydrous acid generates the required complex. Characterization of such compounds has usually been by a combination of infrared, electronic and NMR spectroscopy, elemental microanalysis, and reactivity trends. The RSO_3^- ions are relatively labile, and up to three have been coordinated to inert metal ions with N-donors in the other sites. Almost all reported examples involve d^3, d^5, or d^6 metal ions, overwhelmingly with $CF_3SO_3^-$ bound.

Iron(III) *meso*-tetraphenylporphyrinate trifluoromethanesulfonate has been reported in an uncommon d^5 intermediate spin state;[158,159] structural characterization of the weakly coordination ClO_4^- analogue[158] strongly indicates $CF_3SO_3^-$ bonding occurs also. To date, no X-ray crystal structure of an amine complex with coordinated $CF_3SO_3^-$ has appeared. However, such structures for organometallic compounds are known, and other physical evidence has made the case for RSO_3^- coordination indisputable in this area.

With d^6 cobalt(III) amines, quite a number of examples have appeared in recent years. The simple complexes $[Co(NH_3)_5(OSO_2CF_3)]^{2+}$ and $[Co(NH_3)_5(OSO_2F)]^{2+}$ have both been prepared and characterized,[26,49,160,161] and the $OClO_3^-$ analogue is known.[162] In the absence of moisture, these compounds exist as stable solids. The d^6 analogues of Rh(III), Ir(III), and Pt(IV) have been reported,[161] as well as the Ru(II)[163] and Os(II)[164] analogues. The d^3 Cr(III) pentaammine[161] and the d^5 Ru(III)[161,163] and Os(III)[164] pentaammines are also known. Pentakis(methylamine) analogues of the pentaammines of Co(III), Rh(III), and Cr(III) were prepared by reaction of the chloro precursors with CF_3SO_3H at or above room temperature for several days.[161] Reaction of the Cr(III) and Co(III) complexes at elevated temperature, which is normally employed for the ammine complexes, causes some alkylamine ligand dissociation in these cases.

Bis(trifluoromethanesulfonato) bis(ethane-1,2-diamine) complexes of Co(III), Rh(III), and Ir(III) form from reaction of the chloro precursors at elevated temperature in the anhydrous acid for extended periods.[161] The cis stereochemistry occurs, and may be confirmed from ^1H and ^{13}C NMR in CF_3SO_3H as solvent. The similar electronic spectra of *cis*-$Co(en)_2(OSO_2CF_3)_2^+$ and *cis*-$Co(tren)(OSO_2CF_3)_2^+$ [165] (tren = *N,N*-bis(2-aminoethyl)-1,2-diaminoethane) further confirm the stereochemistry in the former, since only the cis stereochemistry may exist in the latter complex. While the cis geometry is preferred because cis complexes are more stable in polar solvents than trans isomers,[166] *trans*-

TABLE III. Electronic Spectra of Inert Transition-Metal Amine Complexes Containing Coordinated Trifluoromethanesulfonate in Anhydrous CF_3SO_3H

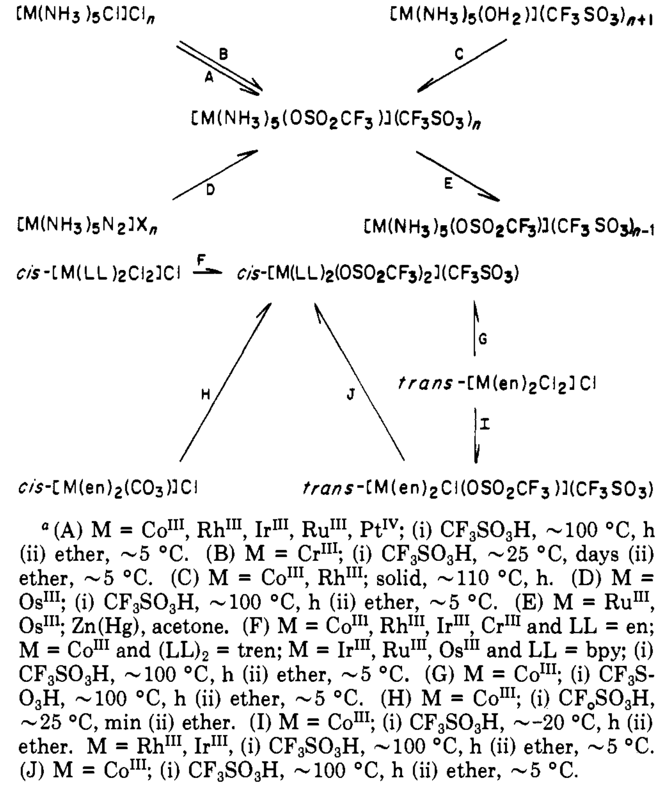
complex	λ, nm (ε, M^{-1} cm^{-1})	ref
$Co(NH_3)_5(OSO_2CF_3)^{2+}$	524 (45.8), 465 sh (33), 345 (40.6)	49
$Rh(NH_3)_5(OSO_2CF_3)^{2+}$	333 (103), 267 (84)	161
$Ir(NH_3)_5(OSO_2CF_3)^{2+}$	315 sh (150), 270 (22)	161
$Cr(NH_3)_5(OSO_2CF_3)^{2+}$	499 (36.8), 364 (31.7)	161
$Ru(NH_3)_5(OSO_2CF_3)^{2+}$	284 (790)	161
$Os(NH_3)_5(OSO_2CF_3)^{2+}$	447 (50), 290 sh (108), 235 (843)	202
$Pt(NH_3)_5(OSO_2CF_3)^{3+}$	299 (186)	161
$Co(NH_2CH_3)_5(OSO_2CF_3)^{2+}$	542 (58.9), 490 sh (51), 362 (67.3)	161
$Rh(NH_2CH_3)_5(OSO_2CF_3)^{2+}$	335 (142), 275 (144)	161
$Cr(NH_2CH_3)_5(OSO_2CF_3)^{2+}$	506 (49.1), 374 (45.8)	161
cis-$Co(en)_2(OSO_2CF_3)_2^+$	590 sh (33), 508 (80.1), 374 (105.3)	49
cis-$Rh(en)_2(OSO_2CF_3)_2^+$	321 (193), 271 (142)	161
cis-$Ir(en)_2(OSO_2CF_3)_2^+$	464 sh (10), 368 sh (34), 296 sh (142), 272 (184), 243 (156)	161
cis-$Cr(en)_2(OSO_2CF_3)_2^+$	497 (69.8), 380 (42.7)	161
cis-$Co(tren)(OSO_2CF_3)_2^+$	516 (122), 371 (93)	165
trans-$Rh(en)_2Cl(OSO_2CF_3)^+$	407 (43), 270 sh (127)	161
trans-$Ir(en)_2Cl(OSO_2CF_3)^+$	502 sh (16), 428 sh (25), 334 (51), 275 sh (60), 241 (110)	161
fac-$Co(dien)(OSO_2CF_3)_3$	553 (108.5), 385 (57.3)	49
fac-$Co(tacn)(OSO_2CF_3)_3$	556 (115), 383 (60)	209

$Ir(en)_2(OSO_2CF_3)Cl^+$ is known,[161] and reaction of *trans*-$Co(en)_2Cl_2^+$ with CF_3SO_3H at or below 0 °C can generate *trans*-$Co(en)_2(OSO_2CF_3)Cl^+$,[167] although when the temperature is raised, isomerization to the cis complex and further halide substitution occur. With $Co(dien)Cl_3$ (dien = 1,5-diamino-3-azapentane) and CF_3SO_3H, a neutral compound, $Co(dien)(OSO_2CF_3)_3$, with three-coordinated $CF_3SO_3^-$ was isolated.[49] Assignment of a *fac* geometry to this complex was later supported by synthesis of $Co(tacn)(OSO_2CF_3)_3$[168] (tacn = 1,4,7-triazacyclononane), the ligand of which must coordinate with *fac* geometry since the electronic spectra of the two complexes are very similar.

The d^6 *cis*-$[Ir(bpy)_2Cl_2]Cl$ with CF_3SO_3H yields the *cis*-$[Ir(bpy)_2(OSO_2CF_3)_2](CF_3SO_3)$ complex,[169] and similar chemistry with ruthenium and osmium diimines $M(bpy)_2(OSO_2CF_3)_2^{0/1+}$ has been explored.[170,171] Reports of complexes of ruthenium and osmium amines or imines with coordinated $CF_3SO_3^-$ are expanding;[28,116,117,161,170–174] these complexes have already been used for further syntheses and will be described in detail in a later section. Apart from d^3, d^5, and d^6 metal complexes, one example of a d^8 metal ammine is known: $Pt(en)(Cl)(OSO_2CF_3)$ was made from the dichloro precursor reacting with CF_3SO_3H at elevated temperatures.[175]

The collected electronic spectra of inert amine complexes with coordinated trifluoromethanesulfonate (Table III) have permitted an accurate placement of $CF_3SO_3^-$ in spectrochemical series. By comparison with other pentaammine complexes,[176] trifluoromethanesulfonate can be placed between Cl^- and N_3^-.[161] Further, ligand field parameters Δ and *B* were estimated from the energies of the first two symmetric ligand field bands of $Rh(NH_3)_5(OSO_2CF_3)^{2+}$, assuming octahedral character for the ($^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$) transitions. This yielded $\Delta = 31\,300$ cm^{-1} and $B = 506$ cm^{-1}, with a nephelauxetic ratio $\beta_{35} = 0.70$.[161] The high value of β_{35}, compared with other rhodium complexes, is indicative of a very low nephelauxetic effect for $CF_3SO_3^-$. This high β_{35} is evidence for a relatively very low covalent contribution to bonding, and together with the low energy of the purely electrostatic component of bonding defined from the observed Δ, allows for ready removal of $CF_3SO_3^-$. Lower values of β_{35} for weak field and comparatively soft ligands like SCN^- and N_3^- indicate a greater covalent contribution, which enhances stability of the M–L bond in those cases.

SCHEME I[a]



[a] (A) M = Co^{III}, Rh^{III}, Ir^{III}, Ru^{III}, Pt^{IV}; (i) CF_3SO_3H, ~100 °C, h (ii) ether, ~5 °C. (B) M = Cr^{III}; (i) CF_3SO_3H, ~25 °C, days (ii) ether, ~5 °C. (C) M = Co^{III}, Rh^{III}; solid, ~110 °C, h. (D) M = Os^{III}; (i) CF_3SO_3H, ~100 °C, h (ii) ether, ~5 °C. (E) M = Ru^{III}, Os^{III}; Zn(Hg), acetone. (F) M = Co^{III}, Rh^{III}, Ir^{III}, Cr^{III} and LL = en; M = Co^{III} and $(LL)_2$ = tren; M = Ir^{III}, Ru^{III}, Os^{III} and LL = bpy; (i) CF_3SO_3H, ~100 °C, h (ii) ether, ~5 °C. (G) M = Co^{III}; (i) CF_3SO_3H, ~100 °C, h (ii) ether, ~5 °C. (H) M = Co^{III}; (i) CF_oSO_3H, ~25 °C, min (ii) ether. (I) M = Co^{III}; (i) CF_3SO_3H, ~−20 °C, h (ii) ether. M = Rh^{III}, Ir^{III}, (i) CF_3SO_3H, ~100 °C, h (ii) ether, ~5 °C. (J) M = Co^{III}; (i) CF_3SO_3H, ~100 °C, h (ii) ether, ~5 °C.

The common methods of synthesis developed for producing inert metal amine complexes with coordinated trifluoromethanesulfonate are collected in Scheme I for pentamine and bis(diamine) compounds. At present, only one example with coordinated fluorosulfate has appeared,[26] and the decomposition of the coordinated ligand in dilute aqueous acid in that case clearly indicates that $CF_3SO_3^-$ is a better choice when one wishes to use the complexes for further reactions.

2. Reactions with Anhydrides and Esters

The anhydride of trifluoromethanesulfonic acid, $(CF_3SO_2)_2O$, and the ester $CF_3SO_3CH_3$ have been employed in synthesis. Reaction of salts of high oxidation state oxo compounds of Cr, W, Mo, and Ti with (CF_3-

$SO_2)O$ yields $MO_2(OSO_2CF_3)_4^{2-}$ (M = Cr, Mo, W), $CrO_2(OSO_2CF_3)_3$, and $Ti(OSO_2CF_3)_6^{2-}$,[177] while $Cr(CF_3SO_3)_3$ can be made by refluxing $CrO_2(OSO_2CF_3)_3$ in the anhydride.[47] Unidentate or bidentate coordination in various species is implied in these octahedral complexes from IR spectroscopy. Reaction of HgO and $(CF_3SO_2)_2O$ with $(C_6H_5)N(CH_3)_2$ at -20 °C yields $Hg(OSO_2CF_3)_2 \cdot (C_6H_5)N(CH_3)_2$,[178] a new olefin cyclization agent, where coordination of trifluoromethanesulfonate is implied. Room temperature reaction of $Mo_2(OOCH)_4$ with acid and anhydride for several days produces the dimer $[Mo_2(OH_2)_4(OSO_2CF_3)_2]^{2+}$, where bidentate bridging $CF_3SO_3^-$ is implied from IR spectroscopy.[179] The reactivity of trifluoromethanesulfonic anhydride allowed reaction of 1 equiv with $\{Fe_4S_4[S(C_6H_5)]_4\}^{2-}$ in an aprotic solvent to proceed with displacement of one $C_6H_5S^-$ ligand to give the cluster $\{Fe_4S_4[S(C_6H_5)]_3(OSO_2CF_3)\}^{2-}$, whose redox couple differs by ~0.1 V from the parent,[180] thus defining the substitution process.

3. Oxidation-Coordination Reactions

Peroxydisulfuryl difluoride, employed successfully with main-group compounds for introducing coordinated fluorosulfate, has also been applied successfully on a limited scale with metal compounds. Even gold metal is oxidized in excess $S_2O_6F_2$ to yield $Au(SO_3F)_3$.[181] The metal(0) carbonyls of V, Cr, Fe, Mn, and Co are oxidized by $S_2O_6F_2$ also, with $VO(SO_3F)_3$, $Cr(SO_3F)_3$, $Mn(SO_3F)_4$, $Co(SO_3F)_2$, $FeO(SO_3F)$, and $Fe(CO)_4(SO_3F)_2$ isolated.[182] The last compound, when heated to 100 °C, dissociates CO to form $Fe(SO_3F)_2$. From IR spectroscopy, evidence for more than one type of bound FSO_3^- is forthcoming; for example, $VO(FSO_3)_3$ appears to contain both monodentate and bidentate ions. Interpretations are colored somewhat by expectations based on the conventional coordination numbers for these metal ions. All of $W(CO)_6$, $WOCl_4$, and WCl_6 react with $S_2O_6F_2$ to produce polymeric $WO(FSO_3)_4$,[60] assigned as six-coordinate W(VI) with bridging FSO_3^- from ^{19}F NMR and Raman spectroscopy. Various Ir(III) and Ir(IV) complexes derive from extended reactions in $S_2O_6F_2/FSO_3H$, namely $Ir(SO_3F)_3$, $Ir(SO_3F)_4$, and $Ir(SO_3F)_6^{2-}$.[74] Metal carbonates react according to

$$2MCO_3 + S_2O_6F_2 \rightarrow 2MO(FSO_3) + 2CO_2 \quad (18)$$

for M = Mn, Co, and Ni, while $Ag_2O(FSO_3)$ forms from Ag_2CO_3 in a like manner.[183] Similarly, cerium(III) carbonate yields $CeO(FSO_3)$ with covalent FSO_3^-.[184] Peroxydisulfuryl difluoride is related to peroxydisulfate, since both contain $Y-O_2-Y$ units; both are good oxygenating agents, and there are obviously some similarities in their reactivities.

Oxidation of gold with excess liquid $BrSO_3F$ forms $Au(FSO_3)_3$, while addition of Br_2 extends the synthesis to generate $Au(FSO_3)_4^-$.[185] Likewise, Pd metal with $BrSO_3F$ or $S_2O_6F_2$ generates $Pd(FSO_3)_2$ and $Pd(FSO_3)_3$, the former polymeric with tridentate FSO_3^-, the latter best regarded as $Pd^{II}[Pd^{IV}(FSO_3)_6]$ with unidentate FSO_3^-.[73] Reduction of $Pd(OSO_2F)_6^{2-}$ by Br_2 in liquid SO_2 yields $BrSO_3F$ and square-planar, diamagnetic $Pd(OSO_2F)_4^{2-}$.[186]

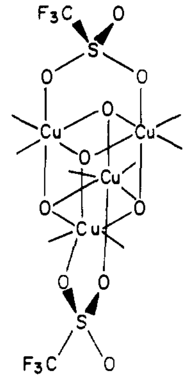
Although they do not bear directly on the title of this subsection, it is noted that some cases of insertion of the Lewis acid SO_3 into M-F bonds to form $M-OSO_2F$ complexes have appeared. CrO_2F_2 with SO_3 gives $CrO_2(SO_3F)_2$,[187] while the like reaction with UF_6 in the gas phase or in $CFCl_3$ solution yields $UF_2(SO_3F)_3$;[188] like reactions with XeF_6 and CrF_5 are known.[189,190]

4. Ligation of Metal Salts

Adducts of usually labile metal salts of RSO_3^- formed by reaction with potentially coordinating molecules have produced complexes that in the solid state appear to have RSO_3^- coordinated. While these compounds usually have no significant existence in aqueous solution, evidence for covalency of RSO_3^- in the solid state or aprotic solvents is in some cases compelling. $M(pyridine)_4(FSO_3)_2$ (M = Ni, Cu, Zn) has been prepared, where FSO_3^- may act as a unidentate ligand.[70] Various similar $ML_4(CF_3SO_3)_2$ complexes (L = pyridine or substituted pyridines; M = Ni, Co) are known,[72] with high-spin six-coordination indicated. From electronic spectroscopy of such compounds, $CF_3SO_3^-$ and FSO_3^- appear to be better coordinators than ClO_4^- and BF_4^-, but worse than ReO_4^-, Cl^-, and Br^-.

$VO(FSO_3)_2^{2-}$ forms adducts with pyridine and quinoline that are polymeric, while $TiCl_2(FSO_3)_2$ forms 1:1 adducts with pyridine, quinoline, and dimethyl sulfoxide, with FSO_3^- retained as a monodentate ligand.[192] Reaction of $TiCl_2(FSO_3)_2$ with acetylacetone produces apparently $Ti(acac)_2(FSO_3)_2$,[192] although retention of FSO_3^- rather than Cl^- is a little surprising.

Axial trifluoromethanesulfonate coordination is implied by optical and ESR studies of $CuL_2(CF_3SO_3)_2$ (L = 2,2′,2″-tripyridylamine), prepared by reaction of $Cu(CF_3SO_2)_2$ and L in methanol or by recrystallization of $[CuL(NCCH_3)_2]$ $(CF_3SO_3)_2$ from acetone ether mixture.[69] The reaction of $[Cu(OSO_2CF_3)]_2 \cdot C_6H_6$ with L in benzene has been studied in some detail, and in the presence of molecular oxygen a cubane-like tetramer with $CF_3SO_3^-$ spanning two vertices of the cluster forms (14); $Cu-OSO_2CF_3$ distances are somewhat longer than Cu-OH but are fully consistent with covalent bonding.[85]



14

Fluorosulfate ion adds readily to $Au(FSO_3)_3$ to form the readily isolable $Au(OSO_2F)_4^-$ ion.[193] A square-planar Au(III) environment with unidentate $CF_3SO_3^-$ is consistent with the observed diamagnetism, and indeed the X-ray crystal structure of the analogue $K[Au(NO_3)_4]$[194] supports this assignment.

Metal(I) compounds $Cu(CF_3SO_3)$ and $Ag(CF_3SO_3)$ add phosphine ligands in aprotic solvent. Both $Ag(PR'_3)_n(CF_3SO_3)$, n = 1-3, and $Ag(PR'_3)_4(CF_3SO_3)$ are known,[195] as are $Cu(PR'_3)_n(CF_3SO_3)$, n = 1-4.[196,197] The n = 1 compounds are dimeric with bridging $CF_3SO_3^-$, while the $n = 4$ compounds are ionic. The intermediate species ionize in solution, but may contain bound $CF_3SO_3^-$ in the solid state. An acetonitrile complex of copper(I) trifluoromethanesulfonate has also been reported.[198] Adducts of $Fe(FSO_3)_2$ with various N-donor molecules appear to contain covalent FSO_3^- in the solid state in several examples.[68] Mercury(II) trifluoromethanesulfonate forms a phosphido-bridged pentamer $[Hg_5(\mu\text{-}Cy_2P)_5(CF_3SO_3)_2]$ with dicyclohexylphosphine,[199] while the $Hg(CN)(OSO_2CF_3)$ complex exists in equilibrium with $Hg(CN)_2$ and $Hg(CF_3SO_3)_2$ in dimethyl sulfoxide.[200] While many of the compounds described in this section do not have the robustness of RSO_3^- complexes of inert metal ions, evidently RSO_3^- can coordinate effectively to labile transition-metal ions.

III. Kinetics of Substitution of Coordinated RSO_3^-

As a consequence of the inductive effects of CF_3–, F–, and $-SO_2-$ groups, (trifluoromethyl)sulfonyl and fluorosulfonyl groups are among the strongest electron-withdrawing groups known.[15] The trifluoromethanesulfonate anion in particular has found favor as an excellent leaving group in nucleophilic substitution reactions in organic chemistry.[15-19] It has been established that RSO_3^- is a better leaving group than I^- from CH_3X.[201] Further, CH_3OSO_2F reacts more rapidly than CH_3I in oxidative addition to an iridium(I) complex to generate a complex with coordinated FSO_3^-.[128] The leaving group capacity of RSO_3^- in organic chemistry has been observed to extend to metal-bound RSO_3^-, where ready substitution of RSO_3^- by a range of better nucleophiles has been observed qualitatively. With organometallic compounds, this has been established by several independent studies[61,112,127,129,133,135] and is now well established in coordination chemistry.[33,161] It is the relative lability of RSO_3^- over other anions that promises a synthetic role for complexes with bound RSO_3^-, and recently there have been reported several studies where this lability has been quantified, particularly with $CF_3SO_3^-$.

The first measurement of a substitution rate for coordination RSO_3^- was reported by Taube and Scott in 1971,[154] who found that trifluoromethanesulfonate bound to chromium(III) in $Cr(OH_2)_5(OSO_2CF_3)^{2+}$ aquated tenfold slower than $OClO_3^-$ but tenfold faster than ONO_2^- on the same metal ion. More recently, the rate of acid aquation of both $CF_3SO_3^-$ and FSO_3^- from their respective pentaamminecobalt(III) complexes have been reported.[25,26,49] The relative labilities of these ligands can be directly compared with a wide range of other leaving groups (Table IV), where it can be readily seen that the two anions are of similar lability and only tenfold less labile than coordinated perchlorate. This obvious lability of RSO_3^- compared with other common anions is maintained when coordination is to other metal ions such as Cr(III), Rh(III), Ru(III), and even Ir(III)[161] and Os(III)[202] (Table IV). In fact, the relative lability of $CF_3SO_3^-$ increases down the cobalt triad for the pentammines when compared with Cl^- analogues, at least for aquation reactions: the k_{obsd} ratio for Co:Rh:Ir with trifluoromethanesulfonato is 103:72:1, but is 17 000:600:1 for chloro complexes.[161] The trifluoromethanesulfonate ion aquates some 10^4 to 10^6 times faster than the chloride ion from these metals. Lability is maintained in base-catalyzed hydrolysis of the pentaammines[203] and on the pentakis(methylamine) analogues,[161,203] as can be seen readily from the data collected in Table V. For organometallics, explicit rate constants have not been reported, but half-lives for reactions with nucleophiles are known to be short.[61,112,127,129,133,135]

TABLE IV. Aquation Rates for Pentaamminecobalt(III) Complexes with Various Ligands and for (Trifluoromethanesulfonato)pentaamminemetal Complexes in Acid at 25 °C

$Co(NH_3)_5L^{n+}$ complexes			$M(NH_3)_5(OSO_2CF_3)^{n+}$ complexes		
L	k_{obsd}, s^{-1}	ref	M	k_{obsd}, s^{-1}	ref
$CF_3SO_3^-$	2.68×10^{-2}	49	Co(III)	2.68×10^{-2}	49
FSO_3^-	2.2×10^{-2}	26	Rh(III)	1.87×10^{-2}	161
ClO_4^-	1.0×10^{-1}	162	Ir(III)	2.61×10^{-4}	161
$CH_3SO_3^-$	2.0×10^{-4}	25	Cr(III)	1.24×10^{-2}	161
NO_3^-	2.7×10^{-5}	*a*	Ru(III)	9.3×10^{-2}	161
Cl^-	1.7×10^{-6}	*b*	Os(III)	1.8×10^{-3}	202
$^-OOCCH_3$	2.7×10^{-8}	*c*	Pt(IV)	$>10^{-5}$	161
$OC(CH_3)_2$	4.1×10^{-2}	49			
$OP(OCH_3)_3$	2.5×10^{-4}	*d*			
$OS(CH_3)_2$	2.2×10^{-5}	*e*			
$OHCH_3$	5.9×10^{-5}	49			
OH_2	5.9×10^{-6}	*f*			
NH_3	5.8×10^{-12}	*g*			

[a] Brønsted, J. N. *Z. Phys. Chem.* **1926**, *122*, 383. [b] Adamson, A. W.; Basolo, F. *Acta Chem. Scand.* **1955**, *9*, 1261. [c] Monacelli, F.; Basolo, F.; Pearson, R. G. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1241. [d] Schmidt, W.; Taube, H. *Inorg. Chem.* **1963**, *2*, 698. [e] Reynolds, W. F.; Birus, M.; Asperger, S. *J. Chem. Soc., Dalton Trans.* **1974**, 716. [f] Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642. [g] Newton, A. M.; Swaddle, T. W. *Can. J. Chem.* **1974**, *52*, 2751.

TABLE V. Comparison of Aquation and Base Hydrolysis Rate Constants of $M(NH_2R)_5X^{2+}$ (X = Cl^-, $CF_3SO_3^-$) Compounds at 25 °C[161,203]

M	R	X	k_{aq}, s^{-1}	k_{OH}, M^{-1} s^{-1}
Co	H	$CF_3SO_3^-$	2.4×10^{-2}	1.0×10^4
		Cl^-	1.7×10^{-6}	0.8
		$(k_{tr}/k_{Cl})^a$	(1.4×10^4)	(1.25×10^4)
Co	CH_3	$CF_3SO_3^-$	8.7×10^{-2}	2.1×10^7
		Cl^-	3.7×10^{-5}	3.8×10^4
		(k_{tr}/k_{Cl})	(2.4×10^3)	(5.5×10^2)
Rh	H	$CF_3SO_3^-$	1.91×10^{-2}	46
		Cl^-	3.8×10^{-8}	1.1×10^{-4}
		(k_{tr}/k_{Cl})	(5.0×10^5)	(4.2×10^5)
Rh	CH_3	$CF_3SO_3^-$	3.47×10^{-2}	7.0×10^3
		Cl^-	2.6×10^{-8}	4.4×10^{-3}
		(k_{tr}/k_{Cl})	(1.3×10^6)	(1.6×10^6)
Cr	H	$CF_3SO_3^-$	1.09×10^{-2}	2.5
		Cl^-	8.7×10^{-6}	1.9×10^{-3}
		(k_{tr}/k_{Cl})	(1.25×10^3)	(1.3×10^3)
Cr	CH_3	$CF_3SO_3^-$	6.43×10^{-4}	2.0×10^3
		Cl^-	2.6×10^{-7}	4.3×10^{-1}
		(k_{tr}/k_{Cl})	(2.5×10^3)	(4.6×10^3)
Ir	H	$CF_3SO_3^-$	2.30×10^{-4}	1.36×10^{-2}
		Cl^-	1.1×10^{-9}	4.8×10^{-8}
		(k_{tr}/k_{Cl})	(2.1×10^5)	(2.8×10^5)

[a] Value in parentheses represents the rate enhancement for $CF_3SO_3^-$ over Cl^- as leaving group.

Bond cleavage in $Co(NH_3)_5(OSO_2CF_3)^{2+}$ has been shown to occur exclusively (>99%) by Co–O rather than O–S cleavage by ^{18}O tracer studies of acid aquation.[25] However, solvolysis of $Co(NH_3)_5(OSO_2F)^{2+}$ occurs with concurrent S–F cleavage, since $Co(NH_3)_5F^{2+}$ can be detected as a significant product.[26] The amount of fluoropentammine formed is acid-dependent in water, with 26% detected in 0.01 M $HClO_4$ but <0.4% detected in 0.01 M NaOH. This S–F cleavage is not re-

TABLE VI. Rate Constants for Solvolysis of $M(NH_3)_5(OSO_2CF_3)^{2+}$ Complexes at 25 °C in Various Polar Solvents[206]

solvent	k(Co), s^{-1}	k(Rh), s^{-1}	k(Ir), s^{-1}	Co:Rh:Ir
water	2.68×10^{-2}	1.89×10^{-2}	2.61×10^{-4}	103:72:1
methanol	9.5×10^{-4}	5.91×10^{-4}	1.41×10^{-5}	67:42:1
dimethyl sulfoxide	1.35×10^{-2}	3.11×10^{-3}	1.14×10^{-4}	118:27:1
dimethylformamide	1.56×10^{-2}	6.78×10^{-3}	1.83×10^{-4}	85:37:1
acetonitrile	4.63×10^{-4}	1.65×10^{-4}	7.5×10^{-6}	62:22:1
pyridine	1.16×10^{-2}	2.06×10^{-3}	9.95×10^{-5}	116:21:1

stricted to aqueous solution, since 44% $Co(NH_3)_5F^{2+}$ was found upon reaction in dimethyl sulfoxide. It was suggested that O → F isomerization of the ligand occurs, with the F-bonded metal complex acting as a leaving group in subsequent F–S bond cleavage.[26] The possible complication of F–S bond cleavage in reactions of bound fluorosulfate, observed for at least cobalt(III)-bound complexes, indicates that the robust coordinated trifluoromethanesulfonate will have greater general applicability in synthesis and probably accounts for recent emphasis being placed on $CF_3SO_3^-$ as a labile and replaceable ligand.

Apart from the several studies of hydrolysis reactions of trifluoromethanesulfonato pentaammine complexes in aqueous acid or base,[25,49,161,203–205] where the properties of $CF_3SO_3^-$ as a labile leaving group have been carefully investigated, it is notable that other solvolysis reactions have been studied. Rate constants for solvolysis of $M(NH_3)_5(OSO_2CF_3)^{2+}$ (M = Co, Rh, Ir) in a range of polar and potentially coordinating solvents have been determined.[206] For all solvents studied with each metal (Table VI) a rate ratio for Co:Rh:Ir of approximately 90:40:1 is preserved, with the progressively slower rate constant from cobalt to iridium arising in the activation entropy term for all solvents except water, suggesting a mechanistic uniqueness for this solvent probably tied to its unique hydrogen-bonding capacity. While the relationships between rate constant and solvent properties have been probed,[206] it is the demonstrated ability of alcohols, sulfoxides, amides, nitriles, phosphate esters, and amines to replace $CF_3SO_3^-$ readily under mild conditions that is of importance from a synthetic viewpoint.

Complexes containing two bound $CF_3SO_3^-$ lose both rapidly and sequentially in acid hydrolysis. Hydrolysis of *cis*-$Co(en)_2(OSO_2CF_3)_2^+$, for example, proceeds via

$$cis\text{-}Co(en)_2(OSO_2CF_3)_2^+ \xrightarrow{k_1} cis\text{-}Co(en)_2(OSO_2CF_3)(OH_2)^{2+} \xrightarrow{k_2} cis\text{-}Co(en)_2(OH_2)_2^{3+} \quad (19)$$

with $k_1 = 2.2 \times 10^{-2}$ s^{-1} and $k_2 = 8.6 \times 10^{-3}$ s^{-1}.[161] This behavior differs from that generally observed for $Co(en)_2X_2^{n+}$ complexes, since $k_2 \ll k_1$ usually; for example, for X = Cl$^-$, $k_1/k_2 = 150$,[207] compared with $k_1/k_2 = 2.6$ for X = $CF_3SO_3^-$. The rate constants for *cis*-$Co(en)_2(OSO_2CF_3)_2^+$ correspond closely to the purely statistical expectation of $k_1 = 2k_2$; this relationship may also hold for $Co(tren)(OSO_2CF_3)_2^+$ [165,208] and is observed for other *cis*-$M(en)_2(OSO_2CF_3)_2^+$ complexes (M = Rh, Ir, Cr). This behavior is consistent with bound trifluoromethanesulfonate displaying relatively weak covalent bonding, with the strength of the second bound $CF_3SO_3^-$ little affected by loss of the first from the coordination sphere. The sequential loss of trifluoromethanesulfonate implied strongly on cobalt(III) has been followed for iridium(III), where hydrolysis is substantially slower, by NMR spectroscopy.[161,209] Aquation reactions of the *trans*-$M(en)_2Cl(OSO_2CF_3)^+$ complexes (M = Rh, Ir) show only one fast aquation step, which from NMR evidence occurs with stereoretention; both rhodium and iridium complexes generally aquate with stereoretention, contrasting with cobalt. Loss of the three $CF_3SO_3^-$ ligands from $Co(dien)(OSO_2CF_3)_3$ and $Co(tacn)(OSO_2CF_3)_3$ is also rapid,[49,209] so lability is a general phenomenon.

IV. Synthetic Applications of Bound RSO_3^-

Apart from simple adduct-formation reactions mentioned earlier, reactions of fluorosulfate and trifluoromethanesulfonate compounds of main-group elements (except carbon) employing the lability of these ions are few. Even in those adduct reactions, such as addition of pyridine to $Bi(OSO_2F)_3$,[107] displacement of RSO_3^- is not necessarily a consequence of the reaction. Nevertheless, the synthetic usefulness of certain compounds, such as reactions involving *cis*-$SF_4(OSO_2F)_2$,[100] has gained recognition. Perhaps the thermodynamic instability or absence of any finite existence in many common solvents vitiates synthetic utility of main-group compounds in many cases. Comparatively, organometallic and coordination compounds containing coordinated trifluoromethanesulfonate or fluorosulfate are robust and often readily isolable as pure solids. Since the relative lability of RSO_3^- compared to other common anions is maintained throughout the d-block metal ions, metal compounds with coordinated RSO_3^- have a general utility, providing a site (or sites) for facile substitution processes. Already these inorganic synthons have had considerable application, and new routes to compounds previously inaccessible or available only via complex and low-yielding paths have been reported and will be discussed subsequently. Of the two anions, trifluoromethanesulfonate is attracting the lion's share of attention, since it lacks the potential reactivity of fluorosulfate discussed earlier and represents a genuinely indifferent anion.

A. Organometallic Compounds

Reactivity of coordinated trifluoromethanesulfonate with first-row d-block compounds has been demonstrated on only a few occasions, yet these examples, appropriately enough, serve to illustrate some of the potential for bound $CF_3SO_3^-$ in synthesis. $(\pi\text{-}C_5H_5)_2Ti(OSO_2CF_3)_2$ is sufficiently reactive to allow substitution of trifluoromethanesulfonate by nitrate upon reaction with $(H_5C_2)_3NH^+NO_3^-$ in an aprotic solvent, forming $(\pi\text{-}C_5H_5)_2Ti(NO_3)_2$.[210] The manganese(I) compound $Mn(CO)_5(OSO_2CF_3)$ contains a particularly labile trifluoromethanesulfonate, since reaction with carbon monoxide to form a hexacarbonyl is very fast;[114] in fact, it appears that Mn(I)–OSO_2CF_3 association is weaker than that of Mn(I)–$OClO_3$ in this case, with acetonitrile also being preferred as a ligand. Formal displacement of η^3-allyl on manganese(I) by CF_3SO_3H in ether forms **10**; this intermediate is readily substituted, since in the presence of diene the new complex $[Mn(diene)(CO)_2(PR'_3)_2](CF_3SO_3)$ can be prepared,[113] thus permitting facile exchange of unsaturated π-bonded organic molecules.

The reactivity of $CF_3SO_3^-$ on first-row organometallics extends to the second- and third-row metals. In view of the large number of examples of iridium(III) compounds with bound $CF_3SO_3^-$ and FSO_3^-, it is not surprising that subsequent reactions of these complexes dominate this section. The intermediates $IrCl(CO)(PR'_3)_2(CH_3)(OSO_2R)$ ($R = F, CH_3$) are readily substituted by other ions or nucleophiles, offering a convenient route to a series of iridium(III) complexes.[127] All of the ligands F^-, Cl^-, Br^-, I^-, NCS^-, NCO^-, N_3^-, NO_2^-, NO_3^-, CH_3COO^-, p-$CH_3C_6H_4SO_3^-$, and $(NC)C(CN)_2$ have been introduced; further, reaction with $Pt(CN)_4^{2-}$ produces a dimer with a bridging cyanide. Both the low nucleophilicity of $CF_3SO_3^-$ and FSO_3^- and the versatility of the technique are illustrated in this example. The similar compound $IrCl(OSO_2R)(CH_3)(N_2)(PR'_3)_2$ ($R = F, CF_3$) reacts with the anions Cl^-, Br^-, I^-, NCO^-, CH_3COO^-, NO_3^-, and NO_2^- in methanol at room temperature to form the five-coordinate iridium(III) compounds $IrCl(X)(CH_3)(PR'_3)_2$, where both RSO_3^- and N_2 have been displaced.[129] These coordinatively unsaturated products readily form 1:1 adducts with carbon monoxide. The $IrCl(CO)(PR'_3)(H)(OSO_2R)$ compounds ($R = F, CF_3$) show ready displacement of RSO_3^- by ions like Cl^-, Br^-, SCN^-, and $SeCN^-$.[135,137] A more extensive study of $IrCl(H)(OSO_2CF_3)(CO)(PR'_3)_2$ showed that reaction with weak neutral σ- and π-donor ligands like $NCCH_3$, $P(C_6H_5)_3$, OH_2, $(CH_3)_2CO$, tetrahydrofuran, and C_2H_4 occurs with replacement of $CF_3SO_3^-$ in each case.[136,138]

On second-row rhodium, the one study by NMR spectroscopy in CH_2Cl_2 at low temperature showed that the intermediate *mer*-$RhCl_2[P(CH_3)_2C_6H_5]_3(OSO_2F)$ reacts readily at −60 °C with nitromethane, displacing FSO_3^-, while with extra $P(CH_3)_2C_6H_5$, the ionic complex $\{RhCl_2[P(CH_3)_2C_6H_5]_4\}(FSO_3)$ forms.[61] The facility of these substitutions at low temperature is notable. With third-row metals, reactions are also facile. Reaction of $Pt(OSO_2F)(H_5C_6C{=}CHC_6H_5)(PR'_3)_2$ with tetraethylammonium chloride in chloroform proceeds quantitatively to the chloro analogue.[133] Similarly, $Pt(PR'_3)_2Cl_2$ can be isolated from the reaction of lithium chloride in acetone with the trifluoromethanesulfonato precursor.[115] While it is not a simple substitution reaction, it is notable that spontaneous reductive elimination from $(CH_3)_2Au(PR'_3)(OSO_2CF_3)$ to form C_2H_6 and $Au(PR'_3)(OSO_2CF_3)$ is about 10^5-fold more facile than with the nitrato analogue and more reactive again than for CF_3COO^-, Cl^-, and CH_3COO^- analogues.[112] In the same paper, substitution of the gold(III) complex $(CH_3)_2Au(PR'_3)(OSO_2CF_3)$ by triphenylphosphine to form $[Au(CH_3)_2(PR'_3)_2](CF_3SO_3)$ is reported.

With d^6 ruthenium(II) carbonyl diimines, $Ru(CO)_2(LL)(OSO_2CF_3)_2$ (LL = phen, bpy), substitution by acetonitrile to form $Ru(CO)_2(LL)(NCCH_3)_2$[116,117] or by further phen or bpy to form $[Ru(CO)_2(LL)_2](CF_3SO_3)_2$[116,117] where mixed bidentate LL ligands may be coordinated have been reported. These types of substitutions have close parallels in reactions of coordination compounds, discussed in the next section. While quite a range of organometallic compounds have been synthesized from bound RSO_3^- intermediates, there is clearly opportunity for expansion now that the general lability of RSO_3^- in these systems has been established.

B. Coordination Complexes

It is in the area of coordination chemistry that extensive applications of coordinated trifluoromethanesulfonato precursors in synthesis have been made in only the last 5 years. Clearly, it is here that the versatility of these synthons has been best illustrated, so it is fitting that the last descriptive section of this review be reserved for their discussion. Their versatility is based on several now well-established bases:

(a) The trifluoromethanesulfonato precursors can be readily prepared as stable and pure solids.

(b) Relative lability of bound trifluoromethanesulfonate is maintained throughout the d-block metal ions.

(c) The precursor complexes and trifluoromethanesulfonate salts of the products exhibit excellent solubility in a wide range of polar solvents, particularly in the poorly coordinating solvents sulfolane and acetone which are commonly employed when reaction with a solid potential ligand is envisaged.

1. Coordination of Nucleophilic Solvents

Direct dissolution of trifluoromethanesulfonato complexes in a wide range of solvents has been applied successfully to synthesis of a wide range of solvent-bound complexes. Essentially all complexes dissolve with complete aquation in water, but the range of applicable solvents is far more extensive. The trifluoromethanesulfonato pentaammine complexes of cobalt(III), rhodium(III), iridium(III), and chromium(III) are solvated by alcohols, sulfoxides, amides, nitriles, phosphate esters, and acids;[49,161,206,211,212] the products are isolable as solids simply by solvent evaporation or precipitation with diethyl ether. A strong case has even been made for coordination of acetone, from freeze-drying of an acetone solution of (trifluoromethanesulfonato)pentaamminecobalt(III), although the acetone ligand is labile, having a half-life of ~15 s in aqueous acid at 25 °C.[49] Sulfolane is an even weaker ligand, on cobalt(III) at least, and no strong case can be made for its coordination,[49] although coordination may occur with heavier d-block ions. The pentakis(methylamine)cobalt(III) complexed solvent analogues can be prepared simply in a like manner.[204] Further, solvent complexes from $Co(en)_2(OSO_2CF_3)_2^+$[149,161] and $Co(tren)(OSO_2CF_3)_2^+$[165,208] have been prepared and characterized. Even with $[Mo_2(OH_2)_4(OSO_2CF_3)_2]^{2+}$, reaction in acetonitrile eventually leads to $[Mo_2(NCCH_3)_8]^{4+}$.[179] Isotopically labeled solvents, such as $^{17}OH_2$, may be introduced into the coordination sphere without isotopic dilution[213] by $CF_3SO_3^-$ substitution.

Steric influences can play a part in solvolysis reactions of trifluoromethanesulfonato complexes. For example, $Co(NH_2R)_5(OSO_2CF_3)^{2+}$ ions form alcohol complexes with methanol, ethanol, and 2-propanol more readily with $R = CH_3$ than occurs with $R = H$; the only evidence for coordination of 2-methyl-2-propanol is for the R = H compound and comes from NMR experiments.[49,209] The subsequent loss of OHR ligands by aquation occurs with rate constant ratios of 1:10:13:60 for OH_2:$OHCH_3$:$OHCH_2CH_3$:$OHCH(CH_3)_2$, perhaps reflecting increasing steric influences.[49] Solubility of the precursor trifluoromethanesulfonato complex is also relevant, although potentially coordinating nucleophilic solvents are generally sufficiently polar to dissolve the reactant.

2. *Coordination of Neutral Solids*

Not all potential ligands are liquids at or near room temperature. For example, urea and cyanamide are potentially good ligands, but are solids. Coordination of these ligands previously required vigorous conditions and involved tedious fractional recrystallizations to obtain products in relatively low yield.[214] In situ generation of a labile leaving group, such as occurs from nitrosation of azidopentaammine complex in the presence of the potential ligand in a poorly coordinating solvent,[215] is not feasible since the potential ligands are themselves susceptible to nitrosation. However, simple and high-yielding syntheses of complexes of urea and cyanamide arise merely from reaction of the ligands in sulfolane or acetone with a trifluoromethanesulfonato complex.[33] This type of reaction has been applied to pentaamminecobalt(III),[49] pentaamminerhodium(III),[216] pentakis(methylamine)cobalt(III),[204] and pentaamminechromium(III)[211,212] to coordinate urea and like molecules. In the Cr(III) case, where vigorous reaction conditions can lead to ammine loss, this synthetic method has allowed coordination of urea to pentaamminechromium(III) for the first time. An advantage of the synthetic technique is that it permits complexation and even recrystallization in the absence of water, should the product prove sensitive to water attack.

Reactions in other solvents have also been successfully applied. With *cis*-$[Ir(bpy)_2(OSO_2CF_3)_2]^+$ coordination of a third bipyridyl ligand occurs in high yield when reaction is performed in ethylene glycol.[169] With triphenylphosphine in the same solvent *cis*-$[Ir(bpy)_2(PR'_3)H]^{2+}$ is formed, while two hydride ligands are coordinated in ethanol–water upon addition of borohydride.[169] The neutral complex $Ag(PR'_3)_3(OSO_2CF_3)$ in methanol with additional triphenylphosphine forms $Ag(PR'_3)_4{}^+CF_3SO_3{}^-$.[195] In a potentially coordinating solvent such as methanol, of course, final coordination may proceed via the solvent complex; this is most likely the case in acetone also, but that solvent is readily displaced. Reactions of trifluoromethanesulfonates of low solubility in water, as for $Co(tacn)(OSO_2CF_3)_3$ with triphosphate forming $Co(tacn)(P_3O_{10}H_2)$,[168] proceed via aqua complexes. In certain cases, essentially heterogeneous reactions may occur, as is reportedly the case in the formation of $Pt(PR'_3)_2(NH_2CH_2COO)$ from reaction of $Pt(PR'_3)_2Cl(OSO_2CF_3)$ with glycine,[155] although even strictly limited solubility in a chosen solvent may be sufficient to permit the actual reaction to occur in the solution phase.

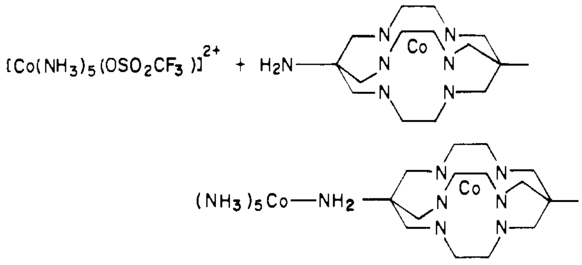
3. *Dimer Formation*

The lability of coordinated $CF_3SO_3{}^-$ has been put to good use in developing facile routes to ligand-bridged transition-metal dimers. A wide range of simple bridging ligands with the capacity to coordinate to two metal ions simultaneously are known, and routes to a substantial number of complexes of these already exist in the inorganic chemical literature. However, it is only recently that high-yielding and mild routes have been developed based on substitution of trifluoromethanesulfonate.

One of the first reports involved synthesis of binuclear complexes with a bridging imidazole anion, where a (trifluoromethanesulfonato)(tetraphenylporphinato)iron(III) monomer was linked to copper and zinc amines.[217] This type of linkage has recently been explored for the simple complexes $[M(NH_3)_5(imidH)]^{3+}$ with $[M'(NH_3)_5(OSO_2CF_3)]^{2+}$ (M = Co, Rh, Ir) reacting in sulfolane in the presence of a noncoordinating base, whence $[(NH_3)_5M\text{-imid-}M'(NH_3)_5]^{5+}$ can be formed.[218] This last example illustrates a quite general reaction in sulfolane or acetone

$$[M(NH_3)_5(LL)]^{n+} + [M'(NH_3)_5(OSO_2CF_3)]^{2+} \xrightarrow[\text{solvent}]{} [(NH_3)_5M\text{-}LL\text{-}M'(NH_3)_5]^{(n+3)+} \quad (20)$$

which may require addition of some noncoordinating base (e.g., triethylamine) depending on the form of the pendant arm of the potentially bridging ligand LL. Of course, variations on this theme are immediately obvious. One successfully applied involves reaction with the macrobicycle (1-amino-8-methyl-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane)cobalt(III):[219]

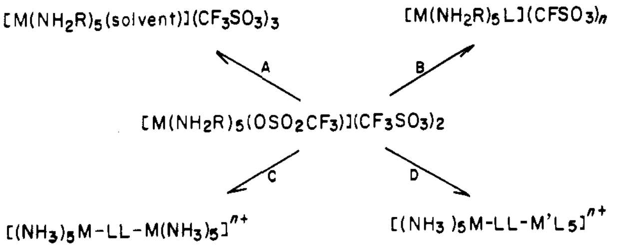


(21)

An area where this type of reaction is receiving particular attention is that of ruthenium and osmium chemistry. Reaction of 2 mol of $[Ru(NH_3)_5(OSO_2CF_3)]^+$, generated by the in situ zinc reduction of the ruthenium(III) complex in acetone, with 1 mol of 4,4′-bipyridyl followed by air oxidation and precipitation with iodide yields the Ru(III)/Ru(II) dimer with bridging 4,4′-bipyridyl.[163] This high-yielding reaction can be applied to a range of other potentially bridging ligands; even the dication $[(4,4'\text{-bpy})^+CH_2]_2CH_2$ binds to ruthenium.[220] Bis(pentaammineruthenium) bridged by 1,4-dicyanobicyclo[2.2.2]octane and a mixed Ru(III)/Co(III) dimer with the same bridging ligand have also been reported recently, prepared from the $Ru(NH_3)_5(OSO_2CF_3)^{2+}$ precursor.[172] With osmium, the reactions investigated to form bridged dimers from trifluoromethanesulfonato precursors generally parallel those of ruthenium.[173] Apart from simple amine complexes, study of trifluoromethanesulfonato complexes of ruthenium diimines is proceeding, with a view to forming dimers.[221] These types of complexes may be of photochemical and photophysical interest relevant to aspects of solar energy conversion research. More generally, constraining two metal ions to close proximity by linking them coordinatively is of interest for studying electron-transfer processes and for mimicing certain active sites of metalloproteins with more than one metal ion present. In principle, trimers of more extended polymers may be accessible, for example

$$2M(NH_3)_5(LL)^{n+} + M'(en)_2(OSO_2CF_3)_2{}^+ \rightarrow ((NH_3)_5M\text{-}LL)_2M'(en)_2{}^{(2n+3)+} \quad (22)$$

SCHEME II[a]



[a] (A) Coordinating solvent; M = Co^{III}, Rh^{III}, Ir^{III}, Cr^{III} and R = H or CH$_3$. (B) Acetone or sulfolane, coordinating ligand L, neutral or ionic; M = Co^{III}, Rh^{III}, Ir^{III}, Cr^{III}, Ru^{III}, Os^{III} and R = H or CH$_3$. (C) M = Ru^{III}, Os^{III} and LL = pyrazine, 4,4-'bpy; (i) acetone, Zn-(Hg),LL (ii) oxidation. (D) M = Co^{III}, Rh^{III}, Ir^{III}, Ru^{III}; various LL-M'L$_5$ added in sulfolane or acetone.

although no serious investigations of these seem to have been addressed.

The types of reactions in which trifluoromethanesulfonato pentaamine complexes have been employed to date have been collected in Scheme II. This scheme applies to inert octahedral complexes; like reactions occur with other amine complexes, and together these represented the vast majority of examples. Clearly, there are opportunities for extension beyond these boundaries.

V. Conclusion

There now exists extensive and irrefutable evidence for covalent bonding of both trifluoromethanesulfonate and fluorosulfate anions to elements throughout the periodic table, particularly to main-group and transition-metal elements. Of the possible modes of binding available to RSO$_3^-$, the majority have been defined or inferred in the solid state. In solution, it is as a unidentate that RSO$_3^-$ is commonly found, and this is not inconsistent with its behavior as a ligand of relatively low nucleophilicity. The lability of RSO$_3^-$, particularly CF$_3$SO$_3^-$, has been clearly defined from reactivity and kinetic behavior; relative lability even extends to coordination to metal ions regarded as very inert. Despite the ease of replacement of RSO$_3^-$, facile syntheses of compounds with coordinated RSO$_3^-$ have been developed, based largely but not entirely on reactions in the readily available anhydrous acids.

At least for coordination complexes, the ability to prepare, in high yield, labile trifluoromethanesulfonato complexes that are commonly air-stable analytically pure solids identifies these complexes as potentially valuable inorganic synthons. A preference for M-OSO$_2$CF$_3$ rather than M-OSO$_2$F has developed, principally as a consequence of uncertainties regarding the inertness of the FSO$_3^-$ ion discussed above. It is as synthetic intermediates that metal complexes of coordinated CF$_3$SO$_3^-$ have shown exceptional potential, and one presumes that the activity in this area which has developed in only the last five years will continue to expand. In organometallic chemistry, oxidative addition of RSO$_3$H or RSO$_3$CH$_3$ to d^8 metal compounds demonstrably offers a simple route to d^6 octahedral compounds with a labile substitution site, and this is one readily identifiable area where further research could be contemplated. The extensive literature that has developed in the field of covalent fluorosulfate and trifluoromethanesulfonate in largely the last two decades augurs well for expansion in the future. It is hoped that this first review devoted specifically to coordinated trifluoromethanesulfonate and fluorosulfate can serve as both a reference source and a prompt for future synthesis and application of such compounds.

Acknowledgments. The collaboration with other researchers in producing my own contribution in this field deserves a special mention. Their names appear in various citations in the references. Without this combined scientific assault our results would have been much diminished. In particular, recognition should go to Professor A. M. Sargeson, Australian National University, for his participation and leadership in aspects of this research.

References

(1) Thorpe, T. E.; Kirman, W. *J. Chem. Soc.* **1892**, 921.
(2) Farbendindustrie, A.-G. Fr. Patent 808991, 937; *Chem. Abstr.* **1937**, *31*, 6833^2.
(3) Stephenson, R.; Watson, W. E. U.S. Patent 2430963, 1947; *Chem. Abstr.* **1947**, *42*, 2734d.
(4) Haszeldine, R. N.; Kidd, J. M. *J. Chem. Soc.* **1954**, 4228.
(5) Haszeldine, R. N.; Kidd, J. M. *J. Chem. Soc.* **1956**, 173.
(6) Brice, T. J.; Trott, P. W. U.S. Patent 2732398, 1956; *Chem. Abstr.* **1956**, *50*, 13982h.
(7) Delaphane, R. G.; Lundgren, J. O. *Acta Crystallogr.*, Sect B: *Struct. Crystallogr. Cryst. Chem.* **1975**, *31*, 2208.
(8) Lundgren, J. O. *Acta Crystallogr.*, Sect B: *Struct. Crystallogr. Cryst. Chem.* **1978**, *34*, 2428, 2432.
(9) Paul, R. C.; Paul, K. K.; Malhotra, K. C. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 689.
(10) Gramstad, T. *Tidsskr. Kjemi, Bergves. Metall.* **1959**, *19*, 62.
(11) Engelbrecht, A.; Rode, B. M. *Monatsh. Chem.* **1972**, *103*, 1315.
(12) Atkins, P. J.; Palling, D. J.; Poon, N. L.; Hall, C. D. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1107.
(13) Fujinaga, T.; Sakamoto, I. *Pure Appl. Chem.* **1982**, *52*, 1387.
(14) Fabes, L.; Swaddle, T. W. *Can. J. Chem.* **1975**, *53*, 3053.
(15) Hendrickson, J. B.; Sternbach, D. D.; Bair, K. W. *Acc. Chem. Res.* **1977**, *10*, 306.
(16) Hansen, R. L. *J. Org. Chem.* **1965**, *30*, 4322.
(17) Streitwieser, A., Jr.; Wilkins, C. L.; Keilman, E. *J. Am. Chem. Soc.* **1968**, *90*, 1598.
(18) MunSu, T.; Sliwinski, W. F.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1969**, *91*, 5386.
(19) Dueber, T. E.; Stang, P. J.; Pfeifer, W. D.; Summerville, R. H.; Imhoff, M. A.; Schleyer, P. von R.; Hummel, K.; Bocher, S.; Harding, C. E.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 521.
(20) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.
(21) Stang, P. J. *Aldrichimica Acta* **1983**, *16*, 15.
(22) Eibeck, R. E. "Kirk-Othmer Encyclopedia of Chemical Technology," 3rd ed.; Grayson, M.; Eckroth, D., Eds.; Wiley: New York, 1980; Vol. 10, p 812.
(23) Woolf, A. A. *J. Chem. Soc.* **1954**, 2840.
(24) Traube, W.; Reubke, E. *Ber. Dtsch. Chem. Ges.* **1921**, *54B*, 1618.
(25) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M.; Jackson, W. G. *Inorg. Chem.* **1981**, *20*, 1647.
(26) Jackson, W. G.; Begbie, C. M. *Inorg. Chem.* **1981**, *20*, 1654.
(27) Maurey, J. R.; Wolff, J. *J. Inorg. Nucl. Chem.* **1963**, *25*, 312.
(28) Lawrance, G. A. *Inorg. Chem.* **1982**, *21*, 3687.
(29) Massaux, J.; Duyckaerts, G. *Anal. Chim. Acta* **1974**, *73*, 416.
(30) Jansky, M. T.; Yoke, J. T. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1707.
(31) Edwards, D. A.; Stiff, M. J.; Woolf, A. A. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 427.
(32) Woolf, A. A. *J. Chem. Soc. A* **1967**, 355.
(33) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. *Inorg. Synth.* **1985**, *24*, Chapter 5.
(34) Haynes, J. S.; Sams, J. R.; Thompson, R. C. *Can. J. Chem.* **1981**, *59*, 669.
(35) Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1982**, *21*, 2089.
(36) Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Aust. J. Chem.* **1982**, *35*, 1561.
(37) Brazier, J. N.; Woolf, A. A. *J. Chem. Soc. A* **1967**, 99.
(38) Lo, S. T. D.; Swaddle, T. W. *Inorg. Chem.* **1976**, *15*, 1881.
(39) Goubeau, J.; Milne, J. B. *Can. J. Chem.* **1967**, *45*, 2321.
(40) Qureshi, A. M.; Carter, H. A.; Aubke, F. *Can. J. Chem.* **1971**, *49*, 35.
(41) Birchall, T.; Dean, P. A. W.; Gillespie, R. J. *J. Chem. Soc. A* **1971**, 1777.

(42) Ruoff, A.; Milne, J. B.; Kaufmann, G.; Leroy, M. J. F. *Z. Anorg. Allg. Chem.* **1970**, *372*, 199.
(43) Robinson, E. A. *Can. J. Chem.* **1961**, *39*, 247.
(44) Miles, M. B.; Doyle, G.; Cooney, R. P.; Tobias, R. S. *Spectrochim. Acta, Part A* **1969**, *25*, 1515.
(45) Bürger, H.; Burczyk, K.; Blaschette, A. *Monatsh. Chem.* **1970**, *101*, 102.
(46) Batchelor, R. J.; Ruddick, J. N. R.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1977**, *16*, 1414 and references therein.
(47) Brown, S. D.; Gard, G. L. *Inorg. Chem.* **1975**, *14*, 2273.
(48) Blake, D. M. *J. Chem. Soc., Chem. Commun.* **1974**, 815.
(49) Dixon, N. E.; Jackson, W. G.; Lawrance, G. A.; Lancaster, M. J.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470.
(50) Schrobilgen, G. J.; Holloway, J. H.; Granger, P.; Brevard, C. *Inorg. Chem.* **1978**, *17*, 980.
(51) Keller, N.; Schrobilgen, G. J. *Inorg. Chem.* **1981**, *20*, 2118.
(52) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 1694.
(53) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 765.
(54) Desmarteau, D. D.; Eisenberg, M. *Inorg. Chem.* **1972**, *11*, 2641.
(55) Brunel, D.; Germain, A.; Commeyras, A. *Nouv. J. Chim.* **1978**, *2*, 275.
(56) Commeyras, A.; Olah, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 2929.
(57) Chevrier, P. J.; Brownstein, S. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1397. Yeats, P. A.; Aubke, F. *J. Fluorine Chem.* **1974**, *4*, 243.
(58) Brownstein, S. *Can. J. Chem.* **1980**, *58*, 1407.
(59) Brownstein, S.; Bornais, J.; Latremouille, G. *Can. J. Chem.* **1978**, *56*, 1419.
(60) Dev, R.; Cady, G. H. *Inorg. Chem.* **1972**, *11*, 1134.
(61) Eaborn, C.; Farrell, N.; Murphy, J. L.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1976**, 58.
(62) Tan, T. H.; Dalziel, J. R.; Yeats, P. A.; Sams, J. R.; Thompson, R. C.; Aubke, F. *Can. J. Chem.* **1972**, *50*, 1843.
(63) Yeats, P. A.; Poh, B. L.; Ford, B. F. E.; Sams, J. R.; Aubke, F. *J. Chem. Soc., Dalton Trans.* **1970**, 2188.
(64) Yeats, P. A.; Landa, B.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1976**, *15*, 1452.
(65) Yeats, P. A.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1973**, *12*, 328.
(66) De Waard, H.; Buhshpan, S.; Schrobilgen, G. J.; Holloway, J. J.; Martin, D. *J. Chem. Phys.* **1979**, *70*, 3247.
(67) Lee, K. C.; Aubke, F. *Can. J. Chem.* **1977**, *55*, 2473.
(68) Paul, R. C.; Kumar, R. C.; Verma, R. D. *J. Indian Chem. Soc.* **1979**, *56*, 251.
(69) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969.
(70) Alleyne, C. S.; Thompson, R. C. *Can. J. Chem.* **1974**, *52*, 3218.
(71) Solomon, R. G.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1972**, 559.
(72) Byington, A. R.; Bull, W. E. *Inorg. Chim. Acta* **1977**, *21*, 239.
(73) Lee, K. C.; Aubke, F. *Can. J. Chem.* **1979**, *57*, 2058.
(74) Lee, K. C.; Aubke, F. *J. Fluorine Chem.* **1982**, *19*, 501.
(75) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710.
(76) Komiya, S.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1977**, *16*, 2138.
(77) Paul, R. C.; Kumar, R. C.; Verma, R. D. *Indian J. Chem., Sect. A* **1978**, *16*, 695.
(78) Dalziel, J. R.; Klett, R. D.; Yeats, P. A.; Aubke, F. *Can. J. Chem.* **1974**, *52*, 231.
(79) Gillespie, R. J.; Schrobilgen, G. J.; Slim, D. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1003.
(80) Humphrey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355.
(81) Darensbourg, D. J.; Day, C. S.; Fischer, M. B. *Inorg. Chem.* **1981**, *20*, 3577.
(82) Anderson, O. P.; Packard, A. B. *Inorg. Chem.* **1979**, *18*, 1129.
(83) Collins, M. J.; Denes, G.; Gillespie, R. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1296.
(84) Allen, F. A.; Lerbscher, J.; Trotter, J. *J. Chem. Soc. A* **1971**, 2507.
(85) Dedert, P. L.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 3509.
(86) Thewalt, U.; Klein, H. P. *Z. Kristallogr.* **1980**, *153*, 307.
(87) Dines, M. B.; Bird, P. H. *J. Chem. Soc., Chem. Commun.* **1973**, 12.
(88) Timmermans, P. J. J. A.; Mackor, A.; Spek, A. L.; Kojić-Prodić, B. *J. Organomet. Chem.* **1984**, *276*, 287.
(89) Roesky, H.; Wiezer, H. *Chem. Ber.* **1971**, *104*, 2258.
(90) Eisenberg, M.; Desmarteau, D. D. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 29.
(91) Wechsberg, M.; Bulliner, P. A.; Sladky, F. O.; Mews, R.; Bartlett, N. *Inorg. Chem.* **1972**, *11*, 3063.
(92) Shack, C. J.; Christe, K. O. *J. Fluorine Chem.* **1980**, *16*, 63.
(93) Fokin, A. V.; Studnev, Yu. N.; Rapkin, A. I.; Potarina, T. M.; Kuznetsova, L. D. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1980**, 2641. Johnson, W. M.; Macklin, J. W. *Inorg. Chem.* **1978**, *17*, 2283.
(94) Johnson, W. M.; Cady, G. H. *Inorg. Chem.* **1973**, *12*, 2481.
(95) Chung, C.; Cady, G. H. *Inorg. Chem.* **1972**, *11*, 2528. Roberts, J. E.; Cady, G. H. *J. Am. Chem. Soc.* **1959**, *81*, 4166. *Ibid.* **1960**, *82*, 352.
(96) Johri, K. M.; Katsuhara, Y.; Desmarteau, D. D. *J. Fluorine Chem.* **1982**, *19*, 227.
(97) Wilson, W. W.; Aubke, F. *Inorg. Chem.* **1974**, *13*, 326.
(98) Dudley, F. B.; Cady, G. H. *J. Am. Chem. Soc.* **1963**, *85*, 3375.
(99) Reichert, W. L.; Cady, G. H. *Inorg. Chem.* **1973**, *12*, 769.
(100) Kitazume, T.; Shreeve, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 492.
(101) Gillespie, R. J. *Acc. Chem. Res.* **1968**, *1*, 202.
(102) Fokin, A. V.; Studnev, Yu. N.; Krotovich, I.; Furin, G. G. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1981**, 927.
(103) Binder, G. E.; Schmidt, A. *Z. Anorg. Allg. Chem.* **1980**, *467*, 197.
(104) Wilson, W. W.; Aubke, F. *J. Fluorine Chem.* **1979**, *13*, 431.
(105) Foropoulos, J., Jr.; Desmarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720.
(106) Storr, A.; Yeats, P. A.; Aubke, F. *Can. J. Chem.* **1972**, *50*, 452.
(107) Paul, R. C.; Singh, S.; Kumar, R. C.; Sharma, R. D.; Verma, R. D. *Indian J. Chem., Sect. A* **1979**, *17*, 273.
(108) Deacon, G. B.; Smith, R. N. M. *J. Fluorine Chem.* **1980**, *15*, 85.
(109) Paul, R. C.; Sharma, R. D.; Singh, S.; Verma, R. D. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1919.
(110) Schmeisser, M.; Sartori, P.; Lippsmeier, B. *Chem. Ber.* **1970**, *103*, 868.
(111) Steipien, C.; Carter, H. A.; Aubke, F., unpublished results cited in: Dalziel, J. R.; Aubke, F. *Inorg. Chem.* **1973**, *12*, 2707.
(112) Komiya, S.; Koshi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7599.
(113) Stuhl, L. S.; Muetterties, E. L. *Inorg. Chem.* **1978**, *17*, 2148.
(114) Trogler, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 6459.
(115) Foley, P.; Whitesides, G. M. *Inorg. Chem.* **1980**, *19*, 1402.
(116) Black, D. St. C.; Deacon, G. B.; Thomas, N. C. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 317.
(117) Black, D. St. C.; Deacon, G. B.; Thomas, N. C. *Aust. J. Chem.* **1982**, *35*, 2445. *Polyhedron* **1983**, *2*, 409.
(118) Voran, S.; Malisch, W. *Angew. Chem.* **1983**, *95*, 151.
(119) Henis, N. B. H.; Lamanna, W.; Humphrey, M. B.; Bursey, M. M.; Brookhart, M. S. *Inorg. Chim. Acta* **1981**, *54*, L11.
(120) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.
(121) Bonazza, B. R.; Lillya, C. P.; Magyar, E. S.; Scholes, G. *J. Am. Chem. Soc.* **1979**, *101*, 4100.
(122) Doyle, G.; Eriksen, K. A.; Van Engen, D. *Inorg. Chem.* **1983**, *22*, 2892.
(123) Obafemi, C. A. *J. Organomet. Chem.* **1981**, *219*, 1.
(124) Eichbichler, J.; Peringer, P. *Inorg. Chim. Acta* **1980**, *43*, 121.
(125) Peringer, P. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1501.
(126) Strope, D.; Shriver, D. F. *J. Am. Chem. Soc.* **1973**, *95*, 8197.
(127) Strope, D.; Shriver, D. F. *Inorg. Chem.* **1974**, *13*, 2652.
(128) Burgess, J.; Hacker, M. J.; Kemmitt, R. D. W. *J. Organomet. Chem.* **1974**, *72*, 121.
(129) Smith, L. R.; Blake, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 3302.
(130) Garzon, G. G. *Acta Sud Am. Quim.* **1981**, *1*, 119.
(131) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.
(132) Eaborn, C.; Farrell, N.; Murphy, J. L.; Pidcock, A. *J. Organomet. Chem.* **1973**, *55*, C68.
(133) Eaborn, C.; Farrell, N.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1973**, 766.
(134) Jablonski, C. R. *J. Organomet. Chem.* **1977**, *142*, C25.
(135) Garzon, G. *Ecletica Quim.* **1979**, *4*, 29.
(136) Olgemoeller, B.; Bauer, H.; Beck, W. *J. Organomet. Chem.* **1981**, *213*, C57.
(137) Olgemoeller, B.; Beck, W. *Chem. Ber.* **1981**, *114*, 2360.
(138) Olgemoeller, B.; Bauer, H.; Loebermann, H.; Nagel, U.; Beck, W. *Chem. Ber.* **1982**, *115*, 2271.
(139) Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1980**, *102*, 860.
(140) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *J. Org. Chem.* **1977**, *42*, 2047.
(141) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300.
(142) Doyle, M. P.; Trudell, M. L. *J. Org. Chem.* **1984**, *49*, 1196.
(143) Lewandos, G. S.; Maki, J. W.; Ginnebaugh, J. P. *Organometallics* **1982**, *1*, 1700.
(144) Dines, M. B. *J. Organomet. Chem.* **1974**, *67*, C55.
(145) Ten Hoedt, R. W. M.; van Koten, G.; Noltes, J. G. *J. Organometal. Chem.* **1979**, *179*, 227.
(146) Ten Hoedt, R. W. M.; van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1980**, *201*, 327.
(147) Hurtado, R. J.; Casillas, R. V.; Ogura, T. *Transition Met. Chem. (Weinheim, Ger.)* **1977**, *2*, 91.
(148) Evers, J. M.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 423.
(149) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *Inorg. Chem.* **1977**, *16*, 1782.

(150) Paul, R. C.; Bajaj, S.; Kumar, R. C.; Verma, R. D. *Indian J. Chem., Sect. A* **1978**, *16*, 174.

(151) Noftle, R. E.; Cady, G. H. *Inorg. Chem.* **1966**, *5*, 2182.

(152) Singh, S.; Bedi, M.; Verma, R. D. *J. Fluorine Chem.* **1982**, *20*, 107.

(153) Paul, R. C.; Kumar, R. C.; Verma, R. D. *J. Fluorine Chem.* **1978**, *11*, 203. Singh, S.; Gill, M. S.; Verma, R. D. *J. Fluorine Chem.* **1985**, *27*, 133.

(154) Taube, H.; Scott, A. *Inorg. Chem.* **1971**, *10*, 62.

(155) Olgemoeller, B.; Olgemoeller, L.; Beck, W. *Chem. Ber.* **1981**, *114*, 2971.

(156) Paul, R. C.; Singh, S.; Verma, R. D. *J. Fluorine Chem.* **1980**, *16*, 153.

(157) Paul, R. C.; Singh, S.; Verma, R. D. *J. Indian Chem. Soc.* **1981**, *58*, 24.

(158) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.

(159) Boersma, A. D.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 581.

(160) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 841.

(161) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2940.

(162) Harrowfield, J. MacB.; Sargeson, A. M.; Singh, B.; Sullivan, J. C. *Inorg. Chem.* **1975**, *14*, 2864.

(163) Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. *Inorg. Synth.* **1985**, *24*, in press.

(164) Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.

(165) Curtis, N. J.; Lawrance, G. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1923.

(166) Jackson, W. G.; Fee, W. W. *Inorg. Chem.* **1975**, *14*, 1161 and references therein.

(167) Comba, P.; Curtis, N. J.; Sargeson, A. M., unpublished results.

(168) Haight, G. P., Jr.; Hambley, T. W.; Hendry, P.; Lawrance, G. A.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 488.

(169) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 403.

(170) Lay, P. A.; Sargeson, A. M.; Taube, H. *Inorg. Synth.* **1985**, *24*, in press.

(171) Lay, P. A.; Sargeson, A. M.; Ware, D. C.; Taube, H., unpublished data.

(172) Anderes, B.; Collins, C. T.; Lavallee, D. K. *Inorg. Chem.* **1984**, *23*, 2201.

(173) Magnuson, R. H.; Lay, P. A.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 2507.

(174) Hambley, T. W.; Lawrance, G. A. *Aust. J. Chem.* **1984**, *37*, 435.

(175) Lawrance, G. A., unpublished results.

(176) Shimura, Y.; Tsuchida, R. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 311.

(177) Thurston, V.; Ludvig, M.; Gard, G. L. *J. Fluorine Chem.* **1982**, *20*, 609.

(178) Nishizawa, M.; Yakenaka, H.; Nishide, H.; Hayashi, Y. *Tetrahedron Lett.* **1983**, *24*, 2581.

(179) Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2774.

(180) Johnson, R. W.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5338.

(181) Johnson, W. M.; Dev, R.; Cady, G. H. *Inorg. Chem.* **1972**, *11*, 2260.

(182) Brown, S. D.; Gard, G. L. *Inorg. Chem.* **1978**, *17*, 1363.

(183) Dev, R.; Cady, G. H. *Inorg. Chem.* **1971**, *10*, 2354.

(184) Dev, R.; Johnson, W. M.; Cady, G. H. *Inorg. Chem.* **1972**, *11*, 2259.

(185) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1980**, *19*, 119.

(186) Lee, K. C.; Aubke, F. *Can. J. Chem.* **1981**, *59*, 2835.

(187) Brown, S. D.; Green, P. J.; Gard, G. L. *J. Fluorine Chem.* **1975**, *5*, 203.

(188) Wilson, W. W.; Naulin, C.; Bougon, R. *Inorg. Chem.* **1977**, *16*, 2252.

(189) Desmarteau, D. D. *Inorg. Chem.* **1972**, *11*, 2641.

(190) Brown, S. D.; Gard, G. L. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 19.

(191) Paul, R. C.; Sharma, N. C.; Verma, R. D.; Sharma, D. K. *Indian J. Chem., Sect. A* **1976**, *14*, 705.

(192) Paul, R. C.; Kumar, R. C.; Verma, R. D. *J. Less-Common Met.* **1978**, *58*, 1.

(193) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1979**, *18*, 389.

(194) Garner, C. D.; Wallwork, S. C. *J. Chem. Soc. A* **1970**, 3092.

(195) Kuhn, N.; Schmidt, R.; Sartori, P. *Chem.-Ztg.* **1982**, *106*, 267.

(196) Dines, M. B. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1380.

(197) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *Inorg. Chim. Acta* **1977**, *21*, L9.

(198) Ogura, T. *Transition Met. Chem. (Weinheim, Ger.)* **1976**, *1*, 179.

(199) Peringer, P.; Eichbichler, J. *J. Organomet. Chem.* **1983**, *241*, 281.

(200) Peringer, P. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 205.

(201) Schleyer, P. V. R.; Sliwinski, W. F.; van Dine, G. W.; Schöllkopf, U.; Paust, J.; Fellenberger, K. *J. Am. Chem. Soc.* **1972**, *94*, 125 and references therein.

(202) Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.

(203) Curtis, N. J.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1986**, in press.

(204) Curtis, N. J.; Lawrance, G. A. *Inorg. Chem.* **1986**, in press.

(205) Jackson, W. G.; Randall, M. L.; Sargeson, A. M.; Marty, W. *Inorg. Chem.* **1983**, *22*, 1013. Jackson, W. G.; Begbie, C.; Randall, M. L. *Inorg. Chim. Acta* **1983**, *70*, 7. Jackson, W. G.; Fairlie, D. P.; Randall, M. L. *Inorg. Chim. Acta* **1983**, *70*, 197.

(206) Lawrance, G. A. *Inorg. Chem.* **1985**, *24*, 323.

(207) Chan, S. C. *J. Chem. Soc.* **1963**, 5137. *Ibid.* **1965**, 418.

(208) Curtis, N. J.; Lawrance, G. A., unpublished data.

(209) Lawrance, G. A.; Sargeson, A. M., unpublished data.

(210) Klein, H. P.; Thewalt, U. *J. Organomet. Chem.* **1981**, *206*, 69.

(211) Curtis, N. J.; Lawrance, G. A.; Sargeson, A. M. *Aust. J. Chem.* **1983**, *36*, 1495.

(212) Curtis, N. J.; Lawrance, G. A. *Inorg. Chim. Acta* **1985**, *100*, 275.

(213) Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1982**, 70.

(214) Balahura, R. J.; Jordan, R. B. *Inorg. Chem.* **1970**, *9*, 1567.

(215) Jordan, R. B.; Sargeson, A. M.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1091.

(216) Curtis, N. J.; Dixon, N. E.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 5347.

(217) Dessens, S. E.; Merrill, C. L.; Saxton, R. J.; Ilaria, R. L., Jr.; Lindsey, J. W.; Wilson, L. J. *J. Am. Chem. Soc.* **1982**, *104*, 4357.

(218) Lawrance, G. A.; Curtis, N. J., unpublished results.

(219) Lydon, J. D.; Sargeson, A. M., unpublished results.

(220) Attala, M.; Lawrance, G. A.; Summers, L. A. *Transition Met. Chem. (Weinheim, Ger.)* **1985**, *10*, 354.

(221) Lay, P. A., unpublished results.