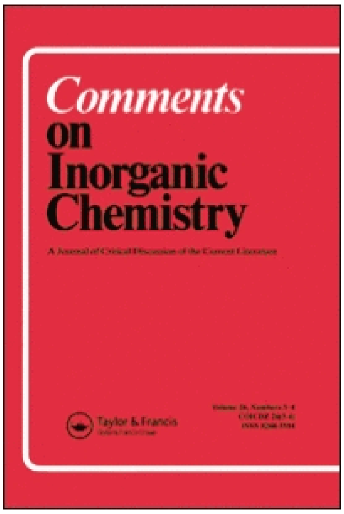


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

The 2,4,6-Tris(trifluoromethyl)phenyl Substituent: An Ideal Combination of Steric and Electronic Stabilization

Frank T. Edelmann[a]
[a] Institut für Anorganische Chemie der Universität Göttingen, Göttingen, Germany

To cite this Article Edelmann, Frank T.(1992) 'The 2,4,6-Tris(trifluoromethyl)phenyl Substituent: An Ideal Combination of Steric and Electronic Stabilization', Comments on Inorganic Chemistry, 12: 5, 259 — 284
To link to this Article: DOI: 10.1080/02603599208055166
URL: http://dx.doi.org/10.1080/02603599208055166

The 2,4,6-Tris(trifluoromethyl)phenyl Substituent: An Ideal Combination of Steric and Electronic Stabilization

FRANK T. EDELMANN
Institut für Anorganische Chemie
der Universität Göttingen,
Tammannstr. 4,
W-3400 Göttingen,
Germany

The chemistry of the 2,4,6-tris(trifluoromethyl)phenyl substituent (= R_F) is reviewed. This ligand combines steric bulk with the possibility of electronic stabilization. Despite the electron-withdrawing nature of the CF_3 groups, the electron-donating ability via the lone pairs at the fluorine atoms is the most important factor in the stabilization of low-coordinated main-group derivatives. This is demonstrated by a number of X-ray structure determinations which show significant intramolecular metal–fluorine interactions.

Key Words: *bulky ligands, 2,4,6-tris(trifluoromethyl)phenyl substituent, electronic stabilization, low coordination numbers*

1. INTRODUCTION

Kinetic stabilization is the method of choice when it comes to synthesizing multiple bonds between heavier main-group elements. In general, kinetic stabilization is achieved by the use of sterically demanding substituents.[1] A substantial number of bulky ligands has been successfully employed. Among these are substituents like

Comments Inorg. Chem.
1992, Vol. 12, No. 5, pp. 259–284
Reprints available directly from the publisher
Photocopying permitted by license only

t-butyl, mesityl, 2,4,6-tri(*i*-propyl)phenyl, 2,4,6-tri(*t*-butyl)phenyl (= "supermesityl"), pentamethylcyclopentadienyl, bis(trimethylsilyl)methyl and tris(trimethylsilyl)methyl. Especially useful for the stabilization of low coordination numbers around transition metal atoms are bulky amido ligands such as $-N(SiMe_3)_2$, $-N(SiMe_2Ph)_2$ and $-NMes(BMes_2)$.[2] In addition, bulky transition metal fragments like $Cp^*Fe(CO)_2$ have been shown to effectively stabilize diphosphenes, arsaphosphenes and phosphaalkenes.[3] Other classes of novel main-group compounds which have become available through the use of bulky ligands are disilenes,[4] germylenes[5] and stannylenes,[6] phospha- and arsa-alkines[7-10] as well as compounds containing Si=N,[11] Si=P,[12] P=Sb[13] and As=As[14] multiple bonds.

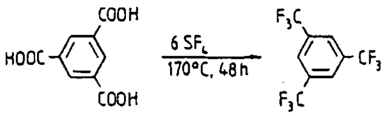
This article focuses on just another bulky substituent, 2,4,6-tris(trifluoromethyl)phenyl (= R_F). What is it that justifies a review article on a single substituent and what makes this bulky ligand so special? Clearly R_F should be regarded as a bulky ligand, although the steric requirements of R_F do not significantly exceed those of mesityl. For steric reasons only, one would not expect R_F to even stabilize a diphosphene derivative $R_FP{=}PR_F$ because dimesityldiphosphene is not a stable compound. Unlike all other substituents mentioned above the three CF_3 groups impose a strong electron-withdrawing effect on the R_F ligand. Less obvious but even more important is the possibility of forming short metal–fluorine contacts to the *ortho*-CF_3 groups of R_F. It will be shown that it is the combination of all three effects which make the 2,4,6-tris(trifluoromethyl)phenyl substituent a truly unique ligand and a highly versatile building block in main-group chemistry.

2. THE PARENT HYDROCARBON

1,3,5-tris(trifluoromethyl)benzene, the parent hydrocarbon, was discovered by McBee and Leech in 1947.[15] The original preparation involves chlorination of mesitylene and subsequent fluorination of the intermediate 1,3,5-tris(trichloromethyl)benzene to give 1,3,5-tris(trifluoromethyl)benzene in 49% yield. This preparation was part of a research program to evaluate aromatic polyfluorides as heat transfer fluids and hydraulic fluids. In another early report McBee and Sanford described the synthesis of 1-chloro-2,4,6-

tris(trifluoromethyl)benzene.[16] This compound was obtained by two successive treatments of 1-chloro-2,4,6-tris(trichloromethyl)-benzene with HF at 70 and 100°C (70–80% yield) and served as an intermediate in the preparation of 2,4,6-tris(trifluoromethyl)-styrene. Attempts to polymerize 2,4,6-tris(trifluoromethyl)styrene failed because of the steric effect of two *ortho*-trifluoromethyl groups.

In 1987 Chambers *et al.* reported a new synthesis of 1,3,5-$(CF_3)_3C_6H_3$.[17] It involves fluorination of benzene-1,3,5-tricarboxylic acid with SF_4 at elevated temperatures. The reported yield, however, was only 33%. By a slight modification of the reaction conditions it was possible to improve the preparation of 1,3,5-tris(trifluoromethyl)benzene in our lab quite significantly.[18] Heating of 130 g of benzene-1,3,5-tricarboxylic acid with 600 g of SF_4 in a 1l-Monel cyclinder at 170°C for 48 h routinely gives a 90–95% isolated yield of 1,3,5-$(CF_3)_3C_6H_3$:

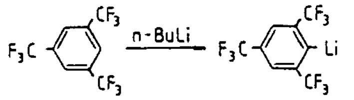


For synthetic purposes it was found necessary to wash the crude product thoroughly with dilute NaOH in order to completely remove SOF_2 and byproducts containing COF-groups. Pure 1,3,5-$(CF_3)_3C_6H_3$ has a faint, characteristic odor and boils at 118–120°C under atmospheric pressure.[15,17,18] The melting point is 9.0°C. The ^1H, ^{13}C and ^{19}F NMR spectra have been reported by Takahashi *et al.*[19] Although the physiological properties of 1,3,5-tris(trifluoromethyl)benzene have not been studied in detail, the compound should be considered as being rather toxic.

3. R_FLi: THE KEY INTERMEDIATE

Since all preparations of compounds containing the R_F substituent start with R_FLi this important intermediate shall be discussed in some detail. The first report concerning the generation of R_FLi dates back to 1950, when McBee and Sanford used the reaction of 1-chloro-2,4,6-tris(trifluoromethyl)benzene and n-butyllithium for an *in situ* preparation of the lithium reagent.[16] Subsequent treatment of R_FLi with acetaldehyde produced 2,4,6-tris(trifluoromethyl)-α-methylbenzyl alcohol in 55% yield. The acidity of 1,3,5-tris(trifluoromethyl)benzene has been determined by Streitwieser *et al.* but the generation of R_FLi was not mentioned in this study.[20]

An improved synthesis of R_FLi via direct metallation of 1,3,5-tris(trifluoromethyl)benzene with n-butyllithium was described by Chambers *et al.* in 1987[17]:



The reaction is carried out in diethyl ether at reflux temperature. Addition of CH_3OD to the reaction mixture after 1 h caused the formation of the mono-deuterated derivative in 90% yield. Although the original preparation of R_FLi was carried out on a 10 mmol scale it was found that the reaction works equally well with 0.1 mol or even 0.2 mol of 1,3,5-tris(trifluoromethyl) benzene. It should be pointed out, however, that the product yields of reactions involving R_FLi as an intermediate rarely exceed ca. 40–45%. The reasons for this phenomenon are presently not fully understood. Lithiation of 1,3,5-tris(trifluoromethyl)benzene can also be carried out in THF solution at −78°C though the resulting highly colored solutions of R_FLi are thermally quite unstable with respect to the formation of LiF.[21] Thus the method does not represent an improvement over the original preparation using diethyl ether.

Normally R_FLi is prepared *in situ* and the resulting solutions in diethyl ether/hexane are used without any further purification. A crystalline diethyl ether adduct, $[R_FLi{\cdot}Et_2O]_2$, can be isolated by complete removal of the solvent and recrystallization of the residue from hexane.[22] Although in our hands the isolated material proved to be quite stable, extreme caution should be exercised when handling solid $[R_FLi{\cdot}Et_2O]_2$. Other groups have reported occasional explosions of solid R_FLi. Crystalline $[R_FLi{\cdot}Et_2O]_2$ is quite air-sensitive and decomposes violently upon contact with protic solvents such as acetone.[23]

$[R_FLi{\cdot}Et_2O]_2$ was fully characterized by a low-temperature single-crystal X-ray analysis and NMR methods.[22] The X-ray analysis already reveals the most striking feature common to many R_F

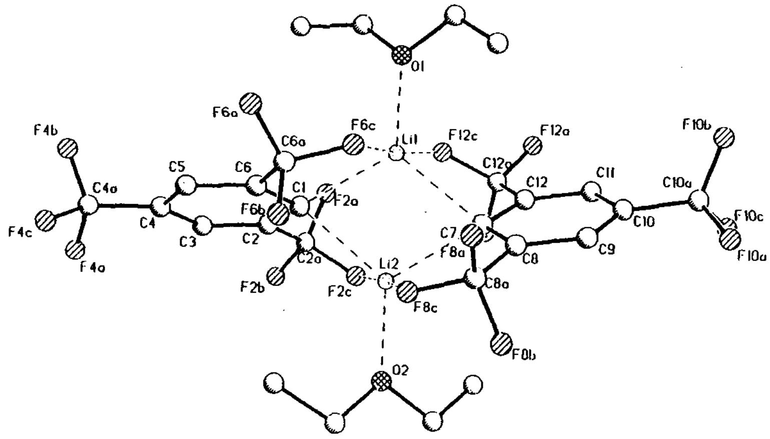


FIGURE 1 Molecular structure of $[R_FLi{\cdot}Et_2O]_2$.

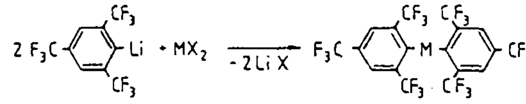
derivatives: the dimeric form of $[R_FLi{\cdot}Et_2O]_2$ is stabilized by lithium–fluorine interactions (Fig. 1).

The coordination geometry around lithium can be described as a distorted trigonal bipyramid. The equatorial positions are occupied by the *ipso* carbon atoms of the phenyl rings and an oxygen of a coordinated diethyl ether ligand. A planar Li_2C_2 unit forms the central part of the dimeric molecule. Two fluorine atoms from *ortho*-CF_3 groups, one from each phenyl ring, are coordinated in the axial positions. Although the Li···F distances are fairly long (av. 225.2 pm) these lithium–fluorine interactions have to be considered the main stabilizing factor in the dimeric $[R_FLi{\cdot}Et_2O]_2$ molecule. The ^{19}F NMR spectrum in toluene-d_8 shows between +20 and −60°C only two signals [δ −63.4 (*p*-CF_3) and −63.2 (*o*-CF_3) ppm], thus indicating that in solution all four *ortho*-CF_3 groups are equivalent on the NMR timescale. Accordingly the ^7Li NMR spectrum exhibits a singlet at −1.24 ppm.

4. TRANSITION METAL DERIVATIVES (GROUP 7, 11 AND 12)

The chemistry of transition metal compounds containing σ-bonded R_F ligands is an open field where a lot of interesting work remains to be done. Initial studies have indicated that R_F is not likely to be a good ligand for early transition metals in their high oxidation states. Treatment of either $NbCl_5$ or WCl_6 with various equivalents of R_FLi did not produce any isolable compounds.[24] On the other hand Herrmann *et al.* reported that $(R_F)_2Zn$ (*vide infra*) cleanly reacts with Re_2O_7 to give stable R_FReO_3.[25] A poorly characterized copper derivative was obtained by reacting R_FLi with copper(I) iodide. The structure of the copper(I) species is unknown and the presence of "R_FCu" was indicated only by its conversion to 2,4,6-tris(trifluoromethyl)biphenyl via reaction with iodobenzene.[17]

The most significant novel results have been obtained with R_F derivatives of the group 12 elements. R_FLi was found to react with anhydrous $ZnCl_2$ to give $(R_F)_2Zn$ in moderate yield (41%).[26]



M = Zn,Cd,Hg

The corresponding cadmium and mercury compounds were prepared analogously from cadmium diiodide or mercury dichloride, respectively.[17,27] The thermally stable zinc derivative can be purified either by vacuum distillation or by recrystallization from hexane, whereas $(R_F)_2Hg$ is easily obtained in a pure form by sublimation. In contrast, the cadmium derivative is thermally more labile. During an attempted distillation it decomposed completely, with formation of metallic cadmium. Single crystal X-ray structural analyses revealed that $(R_F)_2Zn$, $(R_F)_2Cd(MeCN)$ and $(R_F)_2Hg$ are monomeric in the solid state (Figs. 2–4).[27]

In all three compounds the central metal atom binds two R_F moieties. This results in two-coordinate zinc and mercury, but in the cadmium compound three-coordination is observed due to the additional binding of a solvent acetonitrile molecule. Both the zinc and the cadmium structures are unique. In the case of zinc, only three diaryl compounds have been previously structurally characterized. Two of these are the four-coordinate compounds $(C_6F_5)_2ZnX_2$ (X = THF or tetramethyltetrazene) and the third is $(Ph_2Zn)_2$ which was reported in 1990.[28] The two-coordinate monomeric structure of $(R_F)_2Zn$ therefore represents a new structural type for zinc diaryls. The formation of this novel monomer, in

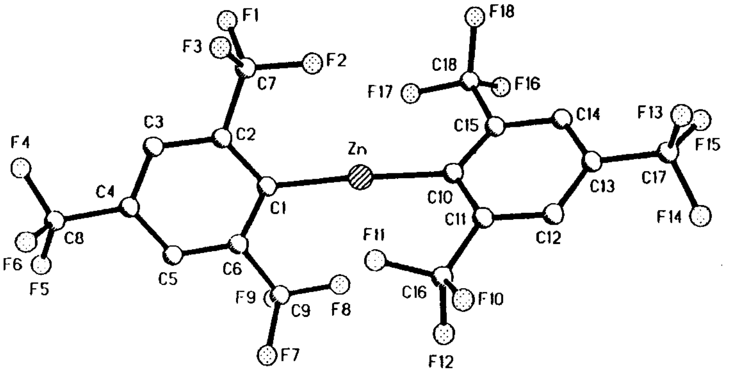


FIGURE 2 Molecular structure of $(R_F)_2Zn$.

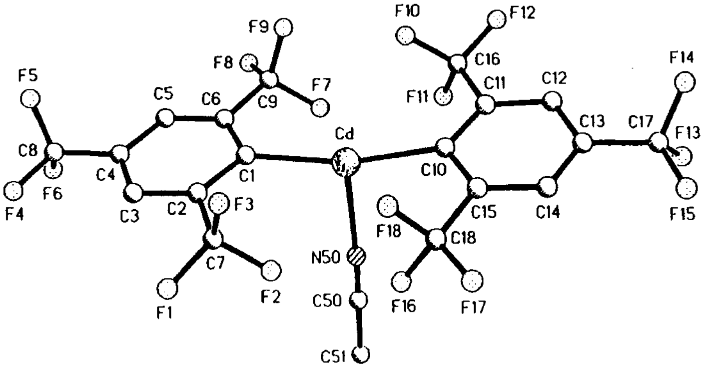


FIGURE 3 Molecular structure of $(R_F)_2Cd(MeCN)$.

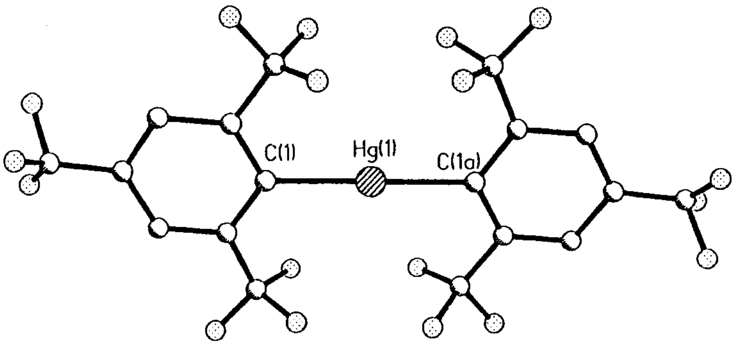


FIGURE 4 Molecular structure of $(R_F)_2Hg$.

contrast to the dimeric structure observed for $(Ph_2Zn)_2$, is due to the steric and electronic properties of the *ortho*-CF_3 substituents of R_F. $(R_F)_2Cd(MeCN)$ is the first structurally characterized three coordinate cadmium diaryl. The cadmium atom has a planar "T-shaped" coordination geometry. In $(R_F)_2Hg$ the two-coordinate mercury atom lies on an inversion center resulting in a linear C–Hg–C linkage. A zero degree twist angle between the planes of the two aromatic rings is observed.

5. GROUP 13 DERIVATIVES: AN OPEN FIELD

The chemistry of R_F derivatives containing group 13 elements remains largely undeveloped. R_FBCl_2 and $(R_F)_2BCl$ have been briefly mentioned.[29] Both compounds are formed upon treatment of boron trichloride with two equivalents of R_FLi. Crystalline R_FGaCl_2 has been obtained in 55% yield from R_FLi and $GaCl_3$.[24] Apparently no attempts have been made to synthesize aluminium and thallium derivatives containing the R_F ligand. An interesting but unexplored aspect could be the use the R_F substituent to stabilize inorganic ring systems such as boron–phosphorus or gallium–phosphorus rings.

6. GROUP 14 DERIVATIVES: A STABLE DIARYL STANNYLENE AND PLUMBYLENE

Some major achievements in the field of R_F chemistry have been obtained with the heavier group 14 elements. This section also includes a number of purely organic R_F compounds.[17,30] Especially notable among these is the carboxylic acid chloride, R_FCOCl.[26,30] This compound might serve as a key starting material for the synthesis of the hitherto unknown phosphaalkyne R_FCP. R_FCOCl is prepared in 32% yield from R_FCOOH and thionyl chloride. Due to steric hindrance R_FCOOH fails to undergo normal esterification with ethanol.[30] Only two silicon derivatives, R_FSiMe_3[17] and $(R_F)_2SiF_2$, have been described. $(R_F)_2SiF_2$ is the only isolable product when R_FLi is reacted with $SiCl_4$ in a 2:1 molar ratio.[23] Clearly the formation of the difluoride is a result of fluorine exchange reactions involving CF_3 groups of the R_F ligands.

The most significant results have been achieved with the synthesis of stable carbene homologues containing the heavy main-group elements tin and lead. The novel diarylstannylene $(R_F)_2Sn$ was synthesized from R_FLi and $SnCl_2$ (45%).[31] After recrystallization from hexane the compound forms air- and moisture-sensitive yellow crystals. The ^{119}Sn NMR spectrum of $(R_F)_2Sn$ shows nine lines of a thirteen-line multiplet (centered at δ 723 ppm) which results from coupling with the fluorine atoms of the *ortho*-CF_3

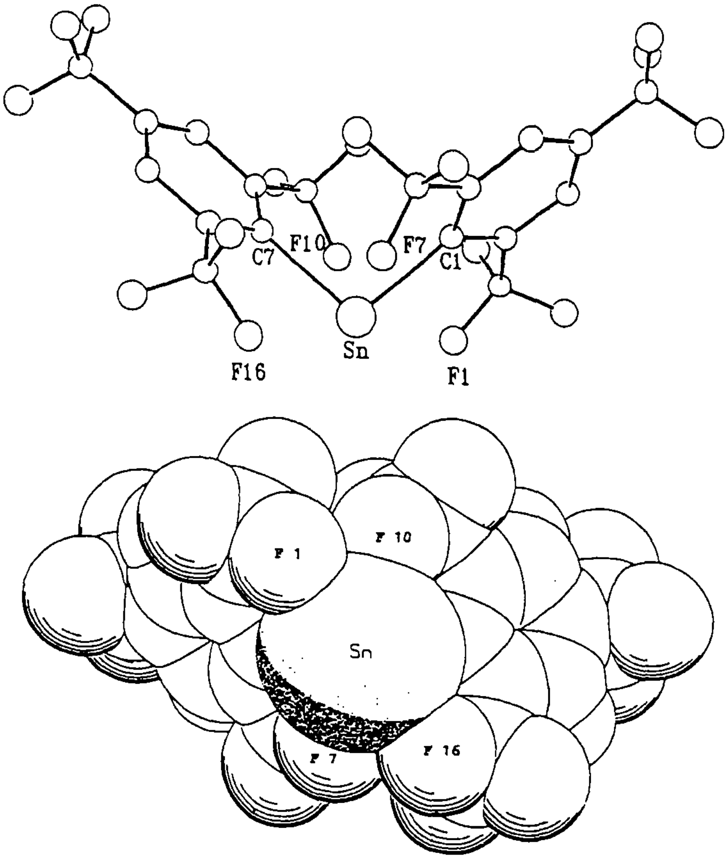


FIGURE 5 Molecular structure and space filling model of $(R_F)_2Sn$.

groups ($^4J(^{119}SnF)$ = 239.5 Hz). As shown by an X-ray structure determination the diarylstannylene $(R_F)_2Sn$ is a monomer in the solid state, and is stabilized by intramolecular fluorine–tin contacts (Fig. 5).

The shortest tin–tin distance is 6.31 Å. Although steric protection of the tin(II) center certainly plays an important role in its stability, a space filling model of $(R_F)_2Sn$ reveals that the *ortho*-CF_3 groups form intramolecular fluorine–tin contacts, leaving one side of the molecule sterically unprotected. These structural features make $(R_F)_2Sn$ a thermally stable (mp 73°C) though highly reactive species. Initial reactivity studies have shown that $(R_F)_2Sn$ represents a very useful starting material for the synthesis of novel tin(IV) derivatives containing the R_F ligand.[21] As a typical carbene homologue $(R_F)_2Sn$ cleanly inserts into the sulfur–sulfur bond of PhSSPh to give $(R_F)_2Sn(SPh)_2$. $(R_F)_2SnCl_2$ is obtained by chlorination of $(R_F)_2Sn$ with $SnCl_4$. $(R_F)_2SnCl_2$ reacts with two quivalents of $Ag(O_2CCF_3)$ to give $(R_F)_2Sn(O_2CCF_3)_2$ whose structure was determined by X-ray diffraction. $[(R_F)_2Sn]_2AgO_3SCF_3$, a silver complex containing the diarylstannylene as a donor ligand, was prepared by treatment of $(R_F)_2Sn$ with AgO_3SCF_3. Controlled oxidation of $(R_F)_2Sn$ with dry oxygen leads to trimeric $[(R_F)_2SnO]_3$ which contains a six-membered Sn_3O_3 ring. Treatment of $(R_F)_2Sn$ with mesityl azide (molar ratio 2.5:1) results in elimination of N_2 and formation of $[(R_F)_2Sn]_2NMes$ (75–80% yield), the first compound containing the three-membered azadistanniridine ring system. Dark red crystalline $[(R_F)_2Sn]_2NMes$ was fully characterized by a single crystal X-ray analysis (Fig. 6).[32]

When the molar ratio between $(R_F)_2Sn$ and mesityl azide was changed to 1:3.5 the five-membered stannatetrazole ring $(R_F)_2SnN_4Mes_2$ was the main reaction product. $[(R_F)_2Sn]_2NMes$ was found to be thermally unstable in solution. In toluene solution at ca. 60°C a [2 + 1]-cycloreversion is observed to give a mixture of $(R_F)_2Sn$ and the stannaimine $(R_F)_2Sn{=}NMes$, which finally dimerizes to yield the stable diazadistannetane derivative $[(R_F)_2SnNMes]_2$.[21,32] Double insertion of $(R_F)_2Sn$ into the oxygen–oxygen bond of $(Ph_3P)_2Pt(O_2)$ gave a product containaing a five-membered PtSnOSnO-ring.[21]

The steric and electronic properties of R_F also allowed the synthesis of the first stable diarylplumbylene.[33] Addition of R_FLi to

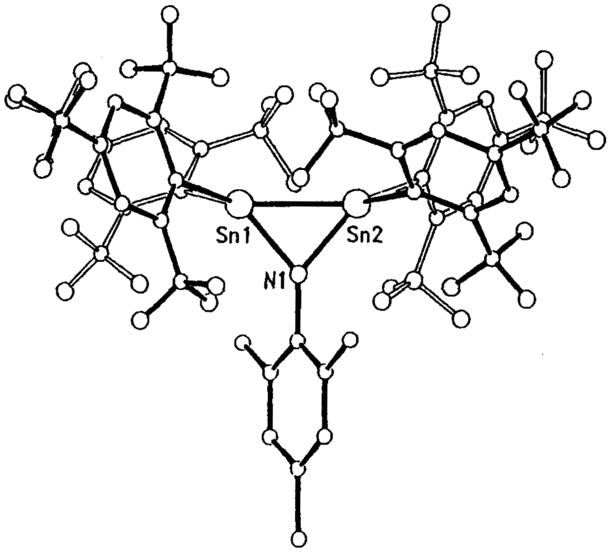
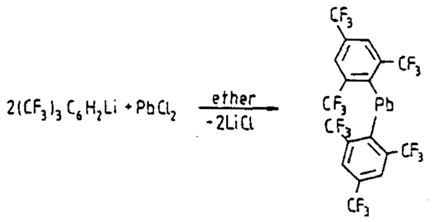


FIGURE 6 Molecular structure of $[(R_F)_2Sn]_2NMes$.

a suspension of $PbCl_2$ in ether results in a clear yellow solution from which bright yellow $(R_F)_2Pb$ can be isolated in 33% yield after recrystallization from hexane.



$(R_F)_2Pb$ is thermally stable to its melting point (58°C). In contrast to $[(Me_3Si)_2CH]_2Pb$ the diarylplumbylene is neither light sensitive nor thermochromic. The ^{207}Pb NMR spectrum of $(R_F)_2Pb$ displays a multiplet (11 lines of the 13 expected lines were observed) at δ 4878 ppm ($^4J(^{207}PbF)$ = 358 Hz). The single-crystal X-ray structural analysis reveals that $(R_F)_2Pb$, like the corresponding tin derivative, is monomeric in the solid state (Fig. 7).

Four intramolecular Pb–F contacts contribute to the unusual stability of the diarylplumbylene. The angle at lead is 94.5°. Com-

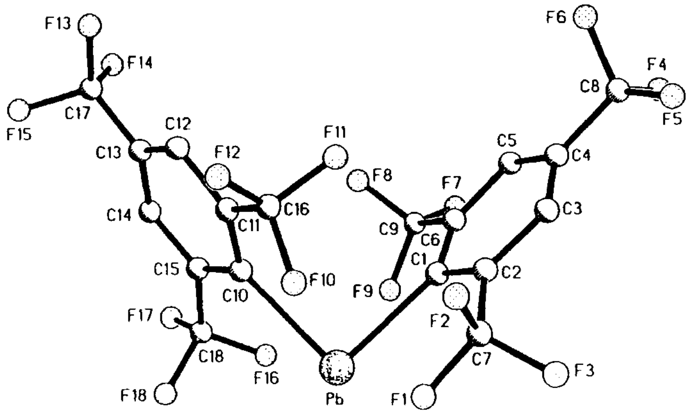
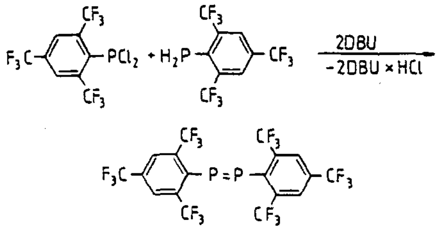


FIGURE 7 Molecular structure of $(R_F)_2Pb$.

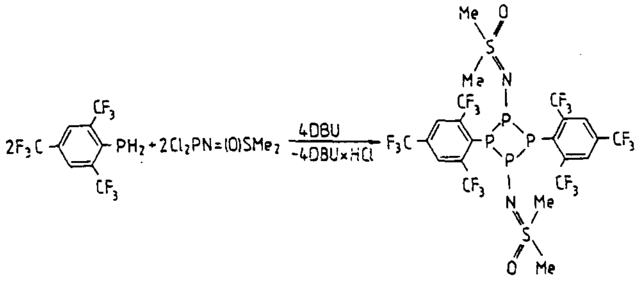
pared to its tin analogue the reactivity of $(R_F)_2Pb$ appears to be somewhat limited.[23] $(R_F)_2Pb$ fails to insert into the sulfur–sulfur bond of PhSSPh and chlorination results in the formation of $PbCl_2$. More interesting is the reaction of $(R_F)_2Pb$ with two equivalents of R_FSH (*vide infra*) which yields the solvent-free thiolate $(R_FS)_2Pb$ as a lemon yellow solid.[33] During an attempted recrystallization of this thiolate from toluene oxygen contamination lead to the formation of a bright yellow crystalline solid. An X-ray structure determination showed this material to be the unusual oxygen-centered lead thiolate cluster $Pb_5O(SR_F)_8$.[23] Mesityl azide reacts with $(R_F)_2Pb$ to give primarily azomesitylene, MesN=NMes, together with metallic lead. PbS was found to be the only lead-containing product when $(R_F)_2Pb$ was reacted with elemental sulfur.[23]

7. GROUP 15 DERIVATIVES: THE DIPHOSPHENE $R_FP{=}PR_F$

Phosphorus derivatives containing the R_F substituent constitute a fairly large and well investigated class of compounds. Simple derivatives include R_FPCl_2, R_FPClF, R_FPF_2 and $(R_F)_2PCl$ which are prepared by treatment of R_FLi with the appropriate amounts of phosphorus trihalide.[18,29,34] R_FPCl_2, a colorless moisture-sensitive liquid, is obtained in 63% yield. The dichlorophosphine is easily reduced by $LiAlH_4$ to give the primary phosphine R_FPH_2 (61% yield).[18] This result is in contrast to the observation that 2,6-$(CF_3)_2C_6H_3PH_2$ could not be prepared via $LiAlH_4$ reduction of 2,6-$(CF_3)_2C_6H_3PCl_2$.[35] Condensation of R_FPCl_2 with R_FPH_2 in the presence of a base (DBU) allows easy access to the unusually stable diphosphene $R_FP{=}PR_F$ (60% yield).[18]



The pale yellow crystals of $R_FP{=}PR_F$ are air-stable and melt without decomposition at 186°C. The diphosphene can be recrystallized without decomposition from boiling toluene or acetonitrile. The ^{31}P NMR signal (δ 474 ppm, 11 of 13 expected lines, $^4J(PH)$ = 23 Hz) falls in the range which is characteristic for diphosphene derivatives. Although the reactivity of $R_FP{=}PR_F$ is apparently low, a few stable carbonyl complexes, $(R_FP{=}PR_F)ML_n$ (ML_n = $Fe(CO)_4$, $Cr(CO)_5$, $Mo(CO)_5$) and $(R_FP{=}PR_F)[ML_n]_2$ (ML_n = $Fe(CO)_4$, $Cr(CO)_5$), have been isolated.[36] The combination of R_F with an electron-donating substituent, $(Me_2S(O){=}N-)$, did not allow the isolation of a stable diphosphene. When $Me_2S(O){=}N-PCl_2$ was reacted with R_FPH_2 in the presence of DBU the only isolable product was the cyclotetraphosphine derivative $[Me_2S(O){=}N]_2(R_F)_2P_4$, which formally results from a [2 + 2]-cycloaddition of the reactive diphosphene intermediate.[18]



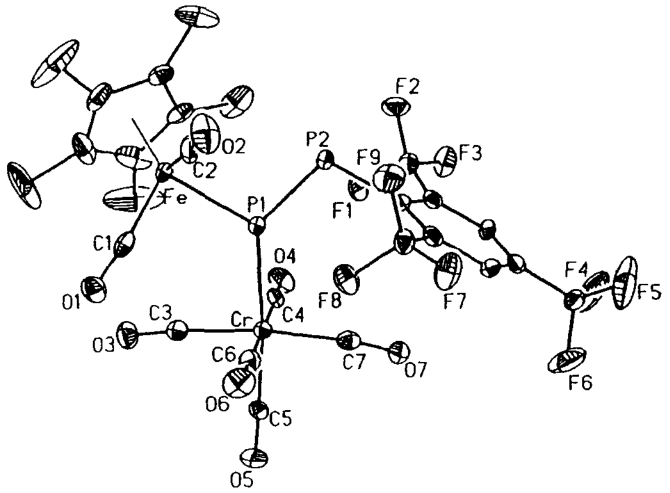


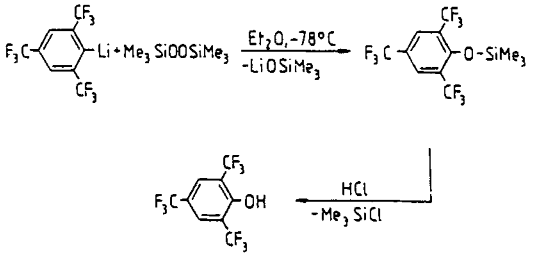
FIGURE 8 Molecular structure of $Cp^*(CO)_2Fe{-}P[Cr(CO)_5]{=}P{-}R_F$.

It was possible to trap the unstable diphosphene derivative $Me_2S(O){=}N{-}P{=}P{-}R_F$ by adding $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ to the reaction mixture at low temperature. The $(Ph_3P)_2Pt$ adduct of the diphosphene was isolated in 44% yield as an orange crystalline solid. R_FPCl_2 also served as the starting material for the synthesis of a number of interesting diphosphenyl metal complexes.[36-38] The reaction of $Cp^*(CO)_2FeP(SiMe_3)_2$ with R_FPCl_2 in THF at $-78°C$ produces a dark red solution which contains the novel diphosphenyl complex $Cp^*(CO)_2Fe{-}P{=}P{-}R_F$ (^{31}P NMR: δ 468.8 (d, $^1J(PP)$ = 585 Hz, $P{-}R_F$), 815.5 (d, $^1J(PP)$ = 585 Hz, P–Fe). The phosphine substitution product $Cp^*(PPh_3)(CO)Fe{-}P{=}P{-}R_F$ was prepared analogously. Both metal substituted diphosphenes are thermally labile and decompose above ca. 0°C in solution. A significant stabilization is achieved by complexation of one or both phosphorus atoms with metal carbonyl fragments. Thus treatment of *in situ* prepared $Cp^*(CO)_2Fe{-}P{=}P{-}R_F$ with $(CO)_5Cr$(cyclooctene) gives $Cp^*(CO)_2Fe{-}P[Cr(CO)_5]{=}P{-}R_F$ as an orange-red crystalline material. Dark red $Cp^*(PPh_3)(CO)Fe{-}P[Cr(CO)_5]{=}P{-}R_F$ was prepared analogously. The molecular structure of $Cp^*(CO)_2Fe{-}P[Cr(CO)_5]{=}P{-}R_F$ was determined by X-ray crystallography ($d_{P\text{-}P}$ = 2.047(2) Å) (Fig. 8).

Much less is known about R_F derivatives of the heavier group 15 elements and so far no attempts have been made to synthesize any homologues of the multiply bonded species $R_FP{=}PR_F$. R_FLi readily reacts with arsenic trifluoride to give the disubstituted product $(R_F)_2AsF$ (67%). Colorless cyrstalline $(R_F)_2AsF$ is easily sublimed at 65°C/1 torr. $LiAlH_4$ reduction of $(R_F)_2AsF$ produces the secondary arsine $(R_F)_2AsH$ in 70% yield.[24] The synthetic potential of these two arsenic derivatives has not been explored. Antimony trichloride reacts with R_FLi in a 1:1 or 1:2 molar ratio. Colorless R_FSbCl_2 and $(R_F)_2SbCl$ have been isolated in moderate yields.[23,29] Two well-characterized bismuth derivatives are known: $(R_F)_2BiCl$ and $(R_F)_3Bi$. The latter represents the only example of a metal atom accommodating three bulky R_F ligands. Bright yellow crystalline $(R_F)_3Bi$ has been structurally characterized by an X-ray analysis.[39] Three weak bismuth–fluorine contacts give the central bismuth atom a distorted octahedral coordination geometry. $(R_F)_3Bi$ is air-sensitive in the solid state. R_FOH (*vide infra*) was detected as one of the decomposition products.

8. GROUP 16 DERIVATIVES: THE CHEMISTRY OF R_FOH AND R_FSH

Group 16 derivatives currently represent the largest group of compounds in R_F chemistry. The phenol and the thiol, R_FOH and R_FSH, have been found to be highly valuable precursors for a number of unusual R_F derivatives. The preparation of R_FOH involves treatment of R_FLi with $Me_3SiOOSiMe_3$ to give R_FOSiMe_3 which is not isolated. Reaction of the silylether intermediate with dry HCl gas produces R_FOH in 63% yield.[40]



The phenol forms an oily liquid with a pungent smell. It served as a starting material for a variety of main-group and transition metal phenoxides. $LiOR_F \times 0.75\ Et_2O$ and $NaOR_F \times 1.5$ THF have been obtained from the phenol and n-BuLi or NaH, respectively.[41] A convenient, high-yield preparation of the alkali metal phenoxides involves the reaction of R_FOH with the corresponding bis(trimethylsilylamides), $MN(SiMe_3)_2$ (M = Li,Na,K). The molecular structures of $[NaOR_F(THF)_2]_2$ and $[KOR_F(THF)_3]_2$ have been determined by X-ray diffraction (Figs. 9 and 10).[42]

Both compounds are dimeric. In each case the R_FO group bridges the two metal atoms, thus forming a nearly planar M_2O_2 core. There are two weak Lewis acid–base interactions between the sodium and *ortho*-fluorine atoms in $[NaOR_F(THF)_2]_2$ and two strong potassium–fluorine contacts in $[KOR_F(THF)_3]_2$. The most striking feature is the bridging THF ligands found in the potassium phen-

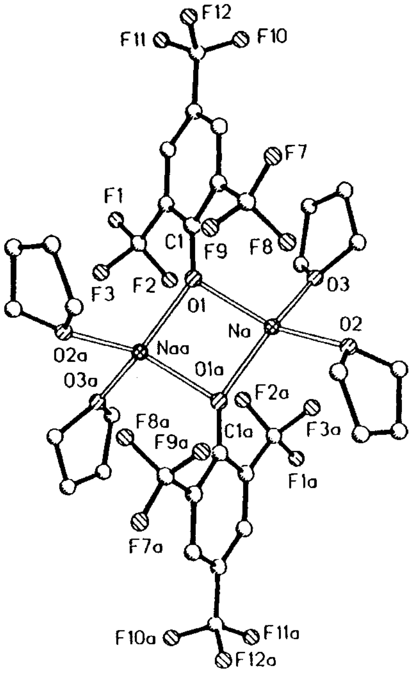


FIGURE 9 Molecular structure of $[NaOR_F(THF)_2]_2$.

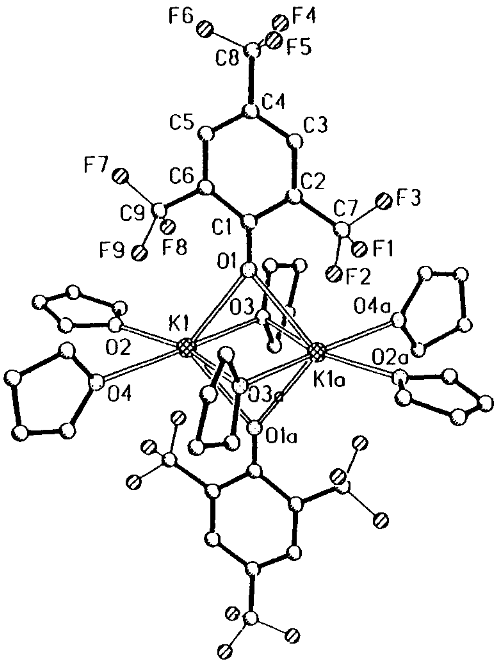
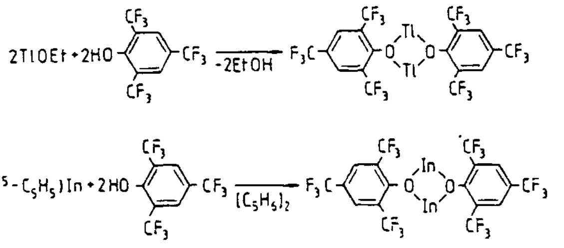


FIGURE 10 Molecular structure of $[\mathrm{KOR_F(THF)_3}]_2$.

oxide. Bridging THF has been found before only in two other structures.[42] Bis(phenoxides) have been isolated as their THF adducts $(\mathrm{R_FO})_2\mathrm{M(THF)}_x$ (x = 1, M = Ba,Ge,Sn; x = 2, M = Cd; x = 3, M = Mg,Ca,Mn) with various main-group and transition metals.[41] They are prepared either by treatment of $\mathrm{R_FOH}$ with reactive metal derivatives ($\mathrm{Mg(OEt)_2}$, $\mathrm{CaH_2}$, $\mathrm{BaH_2}$) or by reaction of $\mathrm{NaOR_F} \times 1.5$ THF with the corresponding metal halides ($\mathrm{GeCl_2} \times$ dioxane, $\mathrm{SnCl_2}$, $\mathrm{MnCl_2}$, $\mathrm{CdI_2}$). The compounds $(\mathrm{R_FO})_2\mathrm{Mg(THF)_3}$ and $(\mathrm{R_FO})_2\mathrm{Mn(THF)_3}$ are isostructural. The coordination geometry around the metal atoms can be described as a distorted tetragonal pyramid. Other transition metal complexes containing the $\mathrm{R_FO}$ ligand include $\mathrm{Cp^*TiCl_2(OR_F)}$ and $(\mathrm{R_FO})_2\mathrm{WCl_2F_2}$. The latter compound resulted from a reaction of $\mathrm{R_FOH}$ with $\mathrm{WCl_6}$ (dark red crystals, 42% yield). Obviously in this case $\mathrm{R_FOH}$ acts as a fluorinating agent towards an intermediate tetrachloro derivative. For steric reasons, only four amido groups in $\mathrm{W_2(NMe_2)_6}$

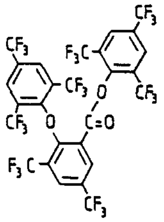
can be substituted by R_FO. The reaction of $W_2(NMe_2)_6$ with R_FOH (molar ratio 1:4) gives dark red, air- and moisture-sensitive $W_2(NMe_2)_2(OR_F)_4$ in 44% yield.[41] The length of the tungsten–tungsten triple bond in this complex is 2.334(1) Å. An unexpected result was obtained during an attempt to synthesize a xenon phenoxide, $Xe(OR_F)_2$.[41] XeF_2 and two equivalents of R_FOH were reacted in a Monel cylinder at room temperature in the absence of solvent. A colorless crystalline solid was isolated which was shown to be the hitherto unknown peroxide R_FOOR_F. The peroxo derivative is thermally quite stable and melts without decomposition at 94°C.

Like R_F itself the R_FO ligand has been found to effectively stabilize unusually low coordination numbers around metal atoms. The most striking examples are the thallium(I) and indium(I) derivatives of R_FOH. Dimeric $[R_FOTl]_2$ is prepared in 80% yield by a reaction of R_FOH with thalliumethoxide.[40] Similarly R_FOH reacts with CpIn to give dimeric $[R_FOIn]_2$ (67%).[43] Both phenoxides form colorless, air- and moisture-sensitive crystalline solids which have been fully characterized by spectroscopy as well as X-ray cyrstallography.



These compounds represent the first structurally characterized examples of two-coordination at thallium and indium. The two coplanar R_F rings are in a perpendicular position with respect to the central planar M_2O_2 core.

An attempted synthesis of $(R_FO)_3Bi$ was unsuccessful. Instead, reaction of anhydrous $BiCl_3$ with three equivalents of R_FONa in diethylether resulted in the unexpected formation of a highly crowded condensation product.[44] The X-ray structure determination revealed that this product arises from coupling of three R_FO units under elimination of three *ortho*-fluorine atoms.



Another highly versatile precursor in R_F chemistry is the thiol R_FSH which was first described by Chambers *et al.* in 1987.[17] It is usually prepared by treatment of R_FLi with elemental sulfur followed by acidic hydrolysis. Just like the phenol R_FSH forms an oily liquid with a pungent odor. Oxidation of the free thiol with I_2 yields the corresponding disulfide (90%, colorless crystals).[23,26,44] The disulfide is chemically inert and fails to undergo sulfur–sulfur bond cleavage with chlorine or $Cp^*_2Sm(THF)_2$.[23] Various main-group and transition metal derivatives of R_FSH have been prepared either by metathesis reactions between $NaSR_F$ and metal halides or via protolysis of metal bis(trimethylsilyl)amides with R_FSH. The latter route is also the method of choice for the preparation of $NaSR_F$ and KSR_F. Treatment of $NaN(SiMe_3)_2$ or $KN(SiMe_3)_2$ with R_FSH in toluene solution gave the unsolvated metal thiolates in ca. 90% yield. The remarkable polymeric structures of their THF adducts have been determined by X-ray methods (Figs. 11 and 12).[42]

In $[NaSR_F(THF)_2 \times 0.25\ THF]_n$ alternating six-coordinate sodium atoms and doubly bridging sulfur atoms form the backbone of a zigzag "chain" polymer. There are two strong Lewis acid–base interactions between sodium and *ortho*-CF_3 fluorine atoms. In $[KSR_F(THF)]_n$ each sulfur atom is triply bridging and this results in the formation of a "ladder" polymer. Each potassium atom is coordinated by three sulfur atoms and one oxygen of a THF ligand. Several potassium–fluorine contacts are also observed. A closely related ladder-shaped polymer structure was found in the thallium thiolate $[TlSR_F \times 0.5\ dioxane]_n$.[45] $TlSR_F$ was prepared initially from $NaSR_F$ and Tl_2CO_3 in acetonitrile (80%). A more convenient preparation, however, involves the reaction of R_FSH with TlOEt in hexane solution, which produces analytically pure $TlSR_F$ as a colorless precipitate (87% yield). Coordination of three R_FS li-

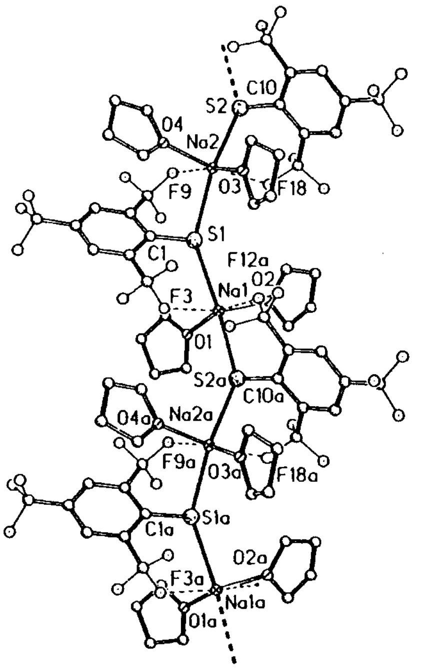


FIGURE 11 Molecular structure of $[NaSR_F(THF)_2 \times 0.25\ THF]_n$.

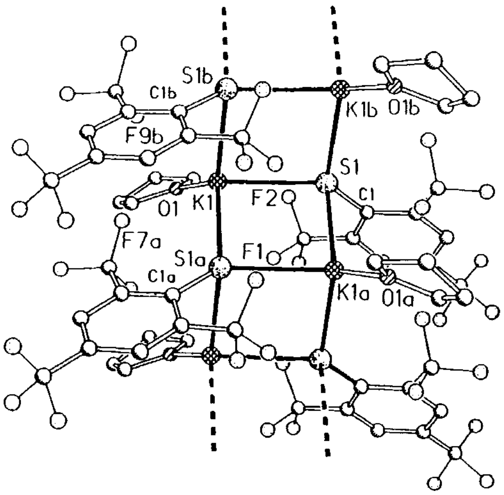
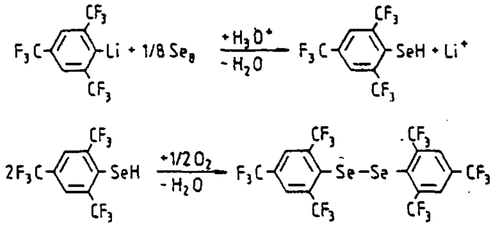


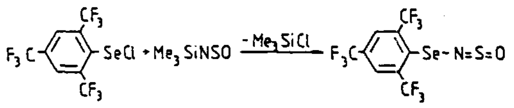
FIGURE 12 Molecular structure of $[KSR_F(THF)]_n$.

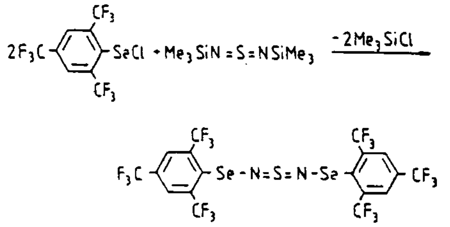
gands is observed in the indium derivative $(R_FS)_3In(Et_2O)$.[46] This colorless material is obtained in nearly quantitative yield when $InCl_3$ is reacted with three equivalents of $NaSR_F$ in diethylether. A thiolate analogue of $[TlOR_F]_2$ was not accessible. Instead, a disproportionation reaction occurred when CpIn was reacted with R_FSH and the only isolable product was again $(R_FS)_3In(Et_2O)$ together with indium metal.[26]

Another element which provides a particularly rich R_F chemistry is selenium. Red selenium readily inserts into R_FLi to give an intermediate lithium selenolate "R_FSeLi" which has not been isolated in a pure state. Solutions of the initial reaction product of R_FLi and Se_8 are highly air-sensitive. Complete air oxidation leads to the formation of R_FSeSeR_F which is isolated as an air-stable yellow solid (48% yield, mp 65°C, δ ^{77}Se = 512 ppm).[47]



The large torsion angle around the Se-Se bond (C-Se-Se-C 104.1°) is a result of repulsive interactions between opposing *ortho*-CF_3 groups. In contrast to the rather unreactive disulfide the Se-Se bond in R_FSeSeR_F is easily cleaved by Cl_2 or Br_2. The reaction products, R_FSeCl and R_FSeBr, respectively, form dark brown crystalline solids. These low-melting materials (R_FSeCl: mp 30°C, R_FSeBr: mp 42°C) are highly volatile and can be easily purified by vacuum sublimation. R_FSeCl also served as a starting material for novel selenium-nitrogen compounds. Orange $R_FSeN{=}S{=}O$ was prepared by reacting R_FSeCl with $Me_3SiN{=}S{=}O$ in diethylether (92% yield). An X-ray structure determination of $R_FSeN{=}S{=}O$ shows that the torsion angle Se-N-S-O is 0°.[47] Similarly $Me_3SiN{=}S{=}NSiMe_3$ reacts with two equivalents of R_FSeCl to give yellow $R_FSeN{=}S{=}NSeR_F$ (89%).





Insertion reactions of carbenes and carbene-like fragments into the Se–Se bond of R_FSeSeR_F have also been studied.[26,47] R_FSeSeR_F cleanly reacts with diazomethane to give $R_FSeCH_2SeR_F$ as colorless needles (73%). The isolobal carbene-fragment $(Ph_3P)_2Pt$ can be inserted via treatment of R_FSeSeR_F with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$. $(Ph_3P)_2Pt(SeR_F)_2$ is isolated as an orange air-stable solid (69% yield). Facile reduction of the Se–Se bond is achieved with divalent samarium. $Cp^*{}_2Sm(THF)_2$ reacts with R_FSeSeR_F to give the trivalent organosamarium selenolate $Cp^*{}_2Sm(SeR_F)(THF)$ as an orange-red cyrstalline solid (Fig. 13).[48]

Quite in contrast to the variety of compounds containing R_FS and R_FSe ligands, tellurium R_F chemistry has proved to be very limited. This is demonstrated by the difficulty in synthesizing the ditelluride R_FTeTeR_F. Unlike the easily accessible diselenide R_FTeTeR_F has not been isolated in an analytically pure state. Finely divided tellurium powder does not react with R_FLi in

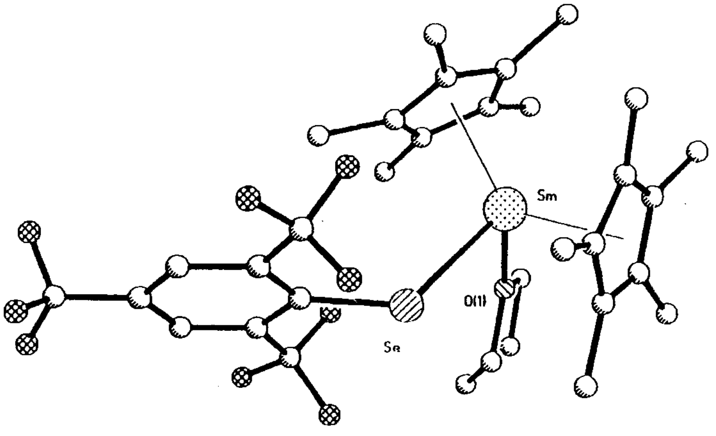


FIGURE 13 Molecular structure of $Cp^*{}_2Sm(SeR_F)(THF)$.

ether/hexane solution. Even ultrasonic activation does not induce the formation of "R_FTeLi."[23] In THF solution some reaction occurs but this is mainly due to the facile decomposition of R_FLi in this solvent (*vide supra*).[21] However, the lithium tellurolate forms when n-Bu_3PTe is used as a soluble source of tellurium. Removal of all volatile components followed by controlled oxidation with $K_3[Fe(CN)_6]$ yields reasonably pure R_FTeTeR_F as a dark red, very light-sensitive oil.[23] Decomposition in the presence of light results in the precipitation of elemental tellurium and formation of yellow R_FTeR_F. This thermally stable monotelluride was also obtained when R_FLi was reacted with $TeCl_4$ (25% yield).[26] So far no further reactions of R_FTeTeR_F have been investigated.

9. CONCLUSIONS AND FUTURE OUTLOOK

Since its "rediscovery" in 1987[17] the 2,4,6-tris(trifluoromethyl)phenyl substituent (= R_F) has turned out to be a highly versatile building block especially in main-group chemistry. This is mainly due to the special combination of stabilizing effects induced by the R_F ligand. Part of the stabilizing influence of R_F is due to steric shielding. The most important factor is the electron-donating ability via the lone pairs at the fluorine atoms. It is the possibility of forming intramolecular contacts to *ortho*-fluorine atoms that makes R_F unique compared to common bulky ligands used for kinetic stabilization. A small number of similar fluorinated aryl substituents has been used frequently, but none of them can compete with R_F. A stable diarylstannylene as well as a diphosphene derivative containing the 2,6-bis(trifluoromethyl)phenyl substitutent have been reported. However, the lithiation of the parent hydrocarbon 1,3-bis(trifluoromethyl)benzene requires the use of tetramethyl-ethylenediamine-n-butyllithium complex which complicates the workup of the products.[35,49] Further disadvantages have been observed for the related 2-dimethylamino-4,6-bis(trifluoromethyl) substituent. In this case the formation of isomeric products has been reported and the stabilizing influence of this ligand does not come close to that of R_F.[26,50]

Several open fields should stimulate further research in R_F chemistry. The derivative chemistry of the reactive carbene homologues

$(R_F)_2Sn$ and $(R_F)_2Pb$ is currently under active investigation and the synthetic potential of the phenolate and thiolate anions R_FO- and R_FS- is far from being exhausted. R_F derivatives of the heavier alkali metals are an interesting synthetic target and virtually nothing is known about transition metal complexes containing σ-bonded R_F ligands. The synthesis of inorganic ring systems bearing R_F substituents is yet another area where interesting results can be anticipated.

Acknowledgments

I thank especially Professor Herbert W. Roesky for his generous support of this work and for stimulating my interest in fluorine chemistry. Various and talented contributions have been made by a number of co-workers, whose names appear in the list of references. The studies were financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. I am also grateful to Dr. Hansjörg Grützmacher, Dr. Sally Brooker, Dr. Dietmar Stalke and Professor John W. Gilje (University of Hawaii) for helpful discussions and valuable contributions. Special thanks are due to Mr. Klaus Keller who prepared all the SF_4 and 1,3,5-tris(trifluoromethyl)benzene used for these studies. R_F chemistry at Göttingen would not have been possible without his help.

References

1. A. H. Cowley, Acc. Chem. Res. **17**, 386 (1984).
2. P. P. Power, Comments Inorg. Chem. **8**, 177 (1989).
3. L. Weber, K. Reizig, D. Bungardt and R. Boese, Organometallics **6**, 110 (1987).
4. R. West, Pure Appl. Chem. **56**, 163 (1984).
5. L. Lange, B. Meyer and W.-W. du Mont, J. Organomet. Chem. **329**, C17 (1987).
6. M. Veith and O. Recktenwald, Top. Curr. Chem. **104**, 57 (1982).
7. M. Regitz and P. Binger, Angew. Chem. **100**, 1541 (1988); Angew. Chem. Int. Ed. Engl. **27**, 1484 (1988).
8. J. F. Nixon, Chem. Rev. **88**, 1327 (1988).
9. M. Regitz, Chem. Rev. **90**, 191 (1990).
10. G. Märkl and H. Sejpka, Angew. Chem. **98**, 286 (1986); Angew. Chem. Int. Ed. Engl. **25**, 264 (1986).
11. C. N. Smit, F. M. Lock and F. Bickelhaupt, Tetrahedron Lett. **25**, 3011 (1984).
12. M. Hesse and U. Klingebiel, Angew. Chem. **98**, 638 (1986); Angew. Chem. Int. Ed. Engl. **25**, 649 (1986).
13. V. D. Romanenko, E. O. Klebanski and L. N. Markovskii, Zh. Obshch. Khim. **55**, 2141 (1985).
14. C. Couret, J. Escudie, Y. Madule, H. Ranaivonjatovo and J.-G. Wolf, Tetrahedron Lett. **24**, 2769 (1983).

15. E. T. McBee and R. E. Leech, Ind. Eng. Chem. **39**, 394 (1947).
16. E. T. McBee and R. A. Sanford, J. Am. Chem. Soc. **72**, 5574 (1950).
17. G. E. Carr, R. D. Chambers, T. F. Holmes and D. G. Parker, J. Organomet. Chem. **325**, 13 (1987).
18. M. Scholz, H. W. Roesky, D. Stalke, K. Keller and F. T. Edelmann, J. Organomet. Chem. **366**, 73 (1989).
19. K. Takahashi, A. Yoshino, K. Hosokawa and H. Muramatsu, Bull. Chem. Soc. Jpn. **58**, 755 (1985).
20. A. Streitwieser, personal communication recorded in M. Hudlicky, *Chemistry of Organic Fluorine Compounds* (Ellis-Horwood, New York), 2nd Edn., p. 548.
21. H. Grützmacher, unpublished results.
22. D. Stalke and K. H. Whitmire, J. Chem. Soc., Chem. Commun. 833 (1990).
23. F. T. Edelmann, unpublished results.
24. M. Scholz, Ph.D. Thesis, Universität Göttingen.
25. C. de Bellefon and W. A. Herrmann, unpublished results.
26. N. Bertel, Ph.D. Thesis, Universität Göttingen.
27. S. Brooker, N. Bertel, D. Stalke, M. Noltemeyer, H. W. Roesky, G. M. Sheldrick and F. T. Edelmann, Organometallics, in press.
28. P. R. Markies, G. Schat, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets and A. L. Spek, Organometallics **9**, 2243 (1990).
29. K. B. Dillon, H. P. Goodwin, T. A. Straw and R. D. Chambers, Poster P7, 1. Euchem Conference on "Phosphorus, Silicon, Boron and Related Elements in Low Coordination States," Paris-Palaiseau, Aug. 22–26, 1988.
30. R. Filler, W. K. Gnandt, W. Chen and S. Lin, J. Fluor. Chem. **52**, 99 (1991).
31. H. Grützmacher, H. Pritzkow and F. T. Edelmann, Organometallics **10**, 23 (1991).
32. H. Grützmacher and H. Pritzkow, Angew. Chem. **103**, 976 (1991); Angew. Chem. Int. Ed. Engl. **30**, 1017 (1991).
33. S. Brooker, J.-K. Buijink and F. T. Edelmann, Organometallics **10**, 25 (1991).
34. L. Heuer, P. G. Jones and R. Schmutzler, J. Fluor. Chem. **46**, 243 (1990).
35. J. Escudie, C. Couret, H. Ranaivonjatovo, M. Lazraq and J. Satgé, Phosphorus Sulfur **31**, 27 (1987).
36. H. Schumann, Ph.D. Thesis, Universität Bielefeld, 1990.
37. L. Weber, H. Schumann and R. Boese, Chem. Ber. **123**, 1779 (1990).
38. L. Weber and H. Schumann, Chem. Ber. **124**, 265 (1991).
39. K. H. Whitmire, D. Labahn, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, J. Organomet. Chem. **402**, 55 (1991).
40. H. W. Roesky, M. Scholz, M. Noltemeyer and F. T. Edelmann, Inorg. Chem. **28**, 3829 (1989).
41. H. W. Roesky, M. Scholz and M. Noltemeyer, Chem. Ber. **123**, 2303 (1990).
42. S. Brooker, F. T. Edelmann, T. Kottke, H. W. Roesky, G. M. Sheldrick, D. Stalke and K. H. Whitmire, J. Chem. Soc., Chem. Commun. 144 (1991).
43. M. Scholz, M. Noltemeyer and H. W. Roesky, Angew. Chem. **101**, 1419 (1989); Angew. Chem. Int. Ed. Engl. **28**, 1383 (1989).
44. K. H. Whitmire, H. W. Roesky, S. Brooker and G. M. Sheldrick, J. Organomet. Chem. **402**, C4 (1991).
45. D. Labahn, E. Pohl, R. Herbst-Irmer, D. Stalke, H. W. Roesky and G. M Sheldrick, Chem. Ber. **124**, 1127 (1991).
46. N. Bertel, M. Noltemeyer and H. W. Roesky, Z. Anorg. Allg. Chem. **588**, 102 (1990).
47. N. Bertel, H. W. Roesky, F. T. Edelmann, M. Noltemeyer and H.-G. Schmidt, Z. Anorg. Allg. Chem. **586**, 7 (1990).

48. A. Recknagel, M. Noltemeyer, D. Stalke, U. Pieper, H.-G. Schmidt and F T. Edelmann, J. Organomet. Chem. **411**, 347 (1991).
49. M. P. Bigwood, P. J. Corvan and J. J. Zuckerman, J. Am. Chem. Soc. **103** 7643 (1981).
50. D. E. Grocock, T. K. Jones, G. Hallas and J. D. Hepworth, J. Chem. Soc C 3305 (1971).