

Invited Contribution from Recipient of ACS Award for Creative Work in Fluorine Chemistry

Playing the Keyboard of Fluorine Chemistry^{†,‡}

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Organometallic fluorides of main group and transition elements are described starting with monocyclopentadienyl derivatives of the group 4 metals and their adducts with AlMe₃. Host–guest type compounds such as [(η^5 -C₅Me₄Et)TiF₃]₄CaF₂ and supramolecular assemblies such as Ag(S₄(CN)₂)₂AsF₆ are also observed. Finally some aluminum–fluorine compounds including derivatives of aluminum(I) are described.

La chimie crée son objet.

Marcelin Berthelot

Introduction

The discovery of fluorine by Henri Moissan in 1886 is a landmark in the history of chemistry. In the past five decades fluorine chemistry has developed from a curiosity to a ubiquitously found discipline. Many recent advances in solid-state chemistry, polymer chemistry, coordination chemistry, main group element chemistry, and organometallic chemistry have relied on the physical and chemical properties of the most electronegative element, fluorine. Many fluorine compounds are used in various areas of daily life and industry. This attests to the interdisciplinary nature of research in fluorine chemistry.

Clemens Winkler, who discovered germanium in 1886, reported on the characteristics of elements:

*The world of chemical events
resembles a stage on which an
unbroken succession of scenes is played out.
The cast consists of the elements.
Each is assigned its unique role,
be it that of walk-on or principal character.*

Without any doubt fluorine has become during the past decades a principal character in research and application. My experience in fluorine chemistry spans over a time of nearly 40 years of research, and therefore I can give only a flavor of the adventure and the beauty of this field.

Organometallic Fluorides of Main Group and Transition Elements

In recent years we have started to synthesize compounds containing both the metal–fluorine and the metal–carbon bond. The corresponding chlorides and bromides are well-known and have a broad application, e.g., as Grignard reagents and Ziegler–Natta type catalysts. The C–M–F compounds have a very polar metal–fluorine bond, resulting often in fluorine bridge formation, and a more covalent rather weak carbon–metal bond that is easily cleaved by HF or oxidative fluorinating agents. Thus the scarcity of organometallic fluorides has been due to the lack of convenient methods of introducing fluorine into these compounds.¹

*Chemistry provides not only the mental discipline,
but an adventure and an aesthetic experience.*

Cyril Hinshelwood

Following Cyril Hinshelwood, we had the adventure and the aesthetic experience of introducing a new fluorinating reagent for the preparation of a great series of exciting compounds. Me₃SnF has proven to be a versatile reagent for halide metathesis reactions of group 4–6 and main group chlorides. This compound is easily available starting from Me₃SnCl and sodium fluoride using a mixture of water and alcohol as a solvent. The preparation of Me₃SnF and its function as a

[†] Dedicated to Prof. Paul Hagenmüller.

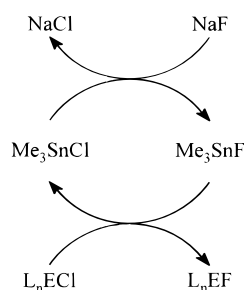
[‡] This paper is based on the address for the 1999 ACS Award for Creative Work in Fluorine Chemistry presented at the ACS Fourteenth Winter Fluorine Conference, St. Petersburg, Florida, January 21, 1999.

(1) (a) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425–3468. (b) Jagirdar, B. R.; Murphy, E. F.; Roesky, H. W. *Prog. Inorg. Chem.* **1999**, *48*, 351–455. (c) Dorn, H.; Murphy, E. F.; Shah, S. A. A.; Roesky, H. W. *J. Fluorine Chem.* **1997**, *86*, 121–125. (d) Witt, M.; Roesky, H. W. *Prog. Inorg. Chem.* **1992**, *40*, 353–444. (e) Roesky, H. W.; Haiduc, J. *J. Chem. Soc., Dalton Trans.* **1999**, 2249–2264.



Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the University of Göttingen, Germany, where he obtained his Diploma in 1961 and doctoral degree in 1963. After one year of postdoctoral work at DuPont in Wilmington, DE, he made his habilitation at the University of Göttingen. In 1971 he became full professor in Frankfurt/Main, and since 1980 he has been a full professor and director of the Institute of Inorganic Chemistry at the University of Göttingen. He has been a visiting professor at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, Tokyo Institute of Technology, and Kyoto University and also frontiers lecturer at Texas A&M University at College Station, University of Texas at Austin, and University of Iowa at Iowa City. He is a member of the Academy of Sciences at Göttingen, the New York Academy of Sciences, the Academy of Scientists "Leopoldina" in Halle, the Berlin-Brandenburgische Academy, and the Academia Europaea in London. He served as the vice president of the German Chemical Society during 1995, and in the period from 1996 to 1998 he was the speaker of Wöhler Vereinigung für Anorganische Chemie. He has received many awards, e.g., the Dr.rer.nat.h.c. of Bielefeld, Brünn, and Bucharest Universities, Alfred-Stock-Memorial Award, and French Alexander-von-Humboldt award. In 1998 he obtained the Grand Prix de la Maison de la Chimie and, very recently (1999), the ACS Award for Creative Work in Fluorine Chemistry. More than 750 publications, articles, patents, and books document his research activity in the areas of inorganic chemistry and materials science. He is well-known for his chemical demonstrations in public. (Photo: Fotoatelier Wilder, Göttingen.)

Scheme 1. Recycling of Me_3SnF as a Fluorinating Agent



recyclable fluorinating reagent are shown in Scheme 1. Trimethyltin chloride generated during the metathesis is readily removed in vacuo. While trimethyltin fluoride is only slightly soluble in common organic solvents, the progress of the reaction can be followed by its disappearance as a suspension. Consequently halide metathesis, using Me_3SnF in a stoichiometric amount, has proven to be one of the most reliable routes to the corresponding fluorides.²

Monocyclopentadienyl Derivatives of Group 4

Preferentially substituted cyclopentadienyl derivatives of group 4 were prepared due to the higher solubility of these fluorides in organic solvents. This is demonstrated with Cp^*ZrF_3

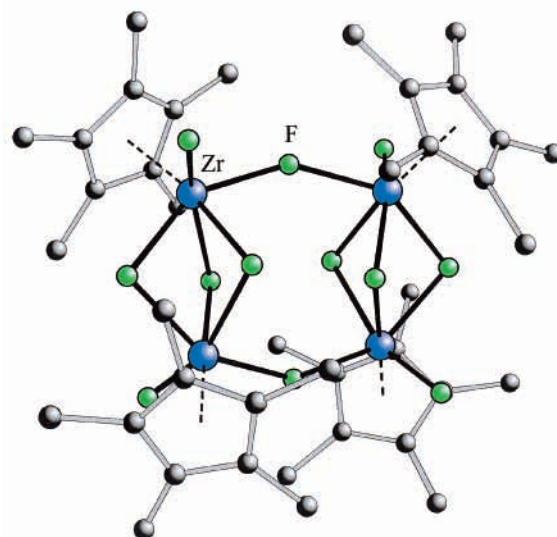


Figure 1. Molecular structure of $[\eta^5\text{-C}_5\text{Me}_5\text{ZrF}_3]_4$.

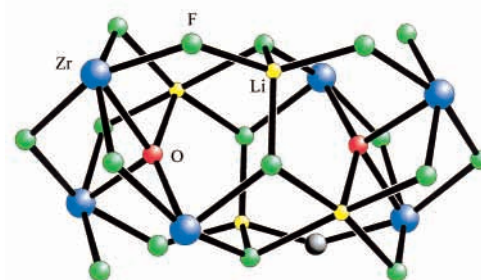


Figure 2. Core structure of $(\eta^5\text{-C}_5\text{Me}_5\text{Zr})_6\text{F}_{18}\text{Li}_4\text{O}_2$. The C_5Me_5 groups and one fluorine atom are omitted for clarity.

(Figure 1) ($\text{Cp}^* = \text{C}_5\text{Me}_5$). It is a tetramer in the solid state as well as in solution. The inorganic Zr_4F_{12} core is surrounded by the organic groups. Moreover, the replacement of Cp by Cp^* in monocyclopentadienyl complexes of transition metals results in significant changes in chemical reactivity, stability, and sensitivity to moisture.

Mixed fluoro-chloro zirconium and hafnium cyclopentadienyl derivatives cannot be prepared from the trichlorides using Me_3SnF . A reverse strategy was employed using fluoro-chloro exchange of Cp^*MF_3 ($\text{M} = \text{Zr}, \text{Hf}$) with Me_3SiCl at room temperature to yield the mixed complexes of composition $\text{Cp}^*\text{MF}_2\text{Cl}$ in almost quantitative yield. Under the conditions reported we observed selective replacement of the four terminal fluorines in Cp^*ZrF_3 by chlorines and the formation of Me_3SiF . The exchange proceeds with retention of the tetrameric core structure of Cp^*ZrF_3 . The bromide analogue $\text{Cp}^*\text{ZrF}_2\text{Br}$ was prepared using Me_3SiBr .³

Curiously, Li_2O elimination is favored over competing substitution when Cp^*ZrF_3 is treated with $\text{LiO}(2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)$. The resulting aggregate $(\text{Cp}^*\text{Zr})_6\text{F}_{18}\text{Li}_4\text{O}_2$ is described as a "waisted ellipsoid" (Figure 2).⁴ The zirconium atoms possess coordination number five in a distorted square pyramidal geometry.

- (2) (a) Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F. *Organometallics* **1994**, *13*, 1251. (b) Roesky, H. W.; Herzog, A.; Keller, K. Z. *Naturforsch. B* **1994**, *49*, 981.
- (3) Murphy, E. F.; Murugavel, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 579.
- (4) Künzel, A.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Chem. Soc., Chem. Commun.* **1995**, 2145.

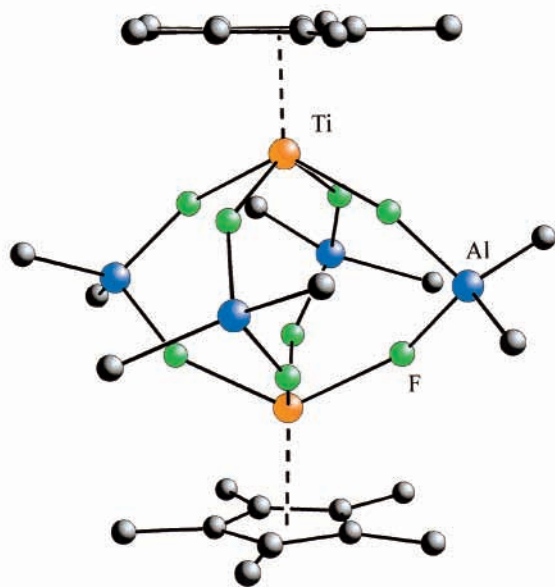


Figure 3. Molecular structure of the cluster $(\eta^5\text{-C}_5\text{Me}_5\text{Ti})_2\text{F}_8(\text{AlMe}_2)_4$.

It is said that fluorides of group 4 metals have no catalytic activity. In contrast to these findings we observed that cyclopentadienylzirconium and -titanium fluorides in the presence of methylalumoxane (MAO) as cocatalyst are highly active for the polymerization of ethylene and styrene, respectively. This reflects the proverb of Sigmund Freud:

*In that which we see, in that which we find,
there may be both error and truth combined.*

The cyclopentadienyltitanium fluoride catalyzed polymerization of styrene is noteworthy as syndiospecific polymer is obtained in the absence of any chiral discriminating reagent. The activity has been increased up to a factor of 50 compared to that of the chlorinated congeners.⁵ Moreover, we studied in detail the reaction of AlMe_3 with Cp^*TiF_3 , Cp^*ZrF_3 , and Cp^*HfF_3 , respectively. To our surprise the reaction of Cp^*TiF_3 and AlMe_3 leads to the cluster $(\text{Cp}^*\text{Ti})_2\text{F}_8(\text{AlMe}_2)_4$ (Figure 3) with titanium in the formal oxidation state III. We assume that a radical mechanism is involved in the product formation, rather than a hydride intermediate postulated for the corresponding AlEt_3 reaction, where a β -hydrogen abstraction is observed.⁶ Cp^*ZrF_3 and AlMe_3 in a 1:1 molar ratio yield the tricyclic system $[\text{Cp}^*(\text{Me})\text{Zr}(\mu\text{-F})\text{AlMe}_2(\mu\text{-F})_2]_2$ (Figure 4) with selective exchange of fluorine atoms for methyl groups. The resulting Me_2AlF will act as a ligand bridging two zirconium atoms. If the same reaction is carried out with an excess of AlMe_3 , in addition to methane evolution and Me_2AlF formation, a cluster $(\text{Cp}^*\text{Zr})_3\text{Al}_6\text{Me}_8(\text{CH})_5(\text{CH}_2)_2$ is obtained in good yield having no fluorine atoms (Figure 5). The structure exhibits four $\mu_4\text{-CH}$ and one $\mu_3\text{-CH}$ methylidene groups as well as two $\mu_3\text{-CH}_2$ methyldiene units between the metal centers.⁷ The missing

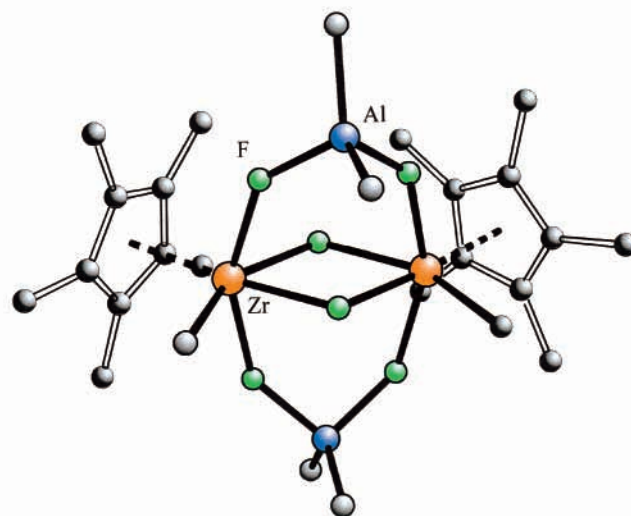


Figure 4. Representation of the molecular structure of $[\eta^5\text{-C}_5\text{Me}_5\text{Zr}(\mu\text{-F})\text{AlMe}_2(\mu\text{-F})_2\text{Me}]_2$.

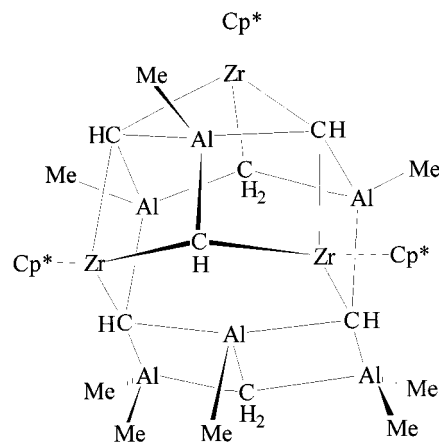


Figure 5. Representation of compound $(\text{Cp}^*\text{Zr})_3\text{Al}_6\text{Me}_8(\text{CH})_5(\text{CH}_2)_2$ in the molecular structure.

carbon species is the carbide in this cluster, and this reminds us of the saying of Woody Allen:

*List number 5—six undershirts, six undershorts, six handkerchiefs—
has always left the investigators wondering, especially because
of the complete absence of socks.*

To study the first step of the reaction of an organometallic fluoride with an aluminum alkyl we choose $[\text{Cp}^*\text{TiFO}]_4$ and AlMe_3 . The compound $[\text{Cp}^*\text{TiFO}]_4$ (Figure 6) contains an eight-membered ring with terminal bound fluorine atoms. The reaction with AlMe_3 at low temperatures proceeds from the mono to the tetra adduct. We were able to characterize by single-crystal X-ray structural analysis the tris- and tetra-substituted adducts (Figure 7). The figure indicates that the four terminal fluorine atoms are coordinated to AlMe_3 and the eight-membered Ti_4O_4 ring becomes nonplanar. Moreover, it was found that the tetra adduct dissociates at -10°C to yield the tris adduct. At room temperature, the adducts are unstable and a mixture of products is formed containing fluorine and methyl groups.⁸ In summary, these investigations have shown that due to the electron deficiency of alkylaluminum compounds they exhibit electrophilic reactions with organotitanoxane fluorides, indicated by an adduct formation in the first step and elongation of the Ti-F bond lengths.

(5) Kaminsky, W.; Lenk, S.; Scholz, V.; Roesky, H. W.; Herzog, A. *Macromolecules* **1997**, *30*, 7647.

(6) (a) Yu, P.; Montero, M. L.; Barnes, C. E.; Roesky, H. W.; Usón, I. *Inorg. Chem.* **1998**, *37*, 2595. (b) Yu, P.; Müller, P.; Said, M. A.; Roesky, H. W.; Usón, I.; Bai, G.; Noltemeyer, M. *Organometallics* **1999**, *18*, 1669.

(7) (a) Herzog, A.; Roesky, H. W.; Zak, Z.; Noltemeyer, M. *Angew. Chem.* **1994**, *106*, 1035; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 967. (b) Herzog, A.; Roesky, H. W.; Jäger, F.; Steiner, A.; Noltemeyer, M. *Organometallics* **1996**, *15*, 909.

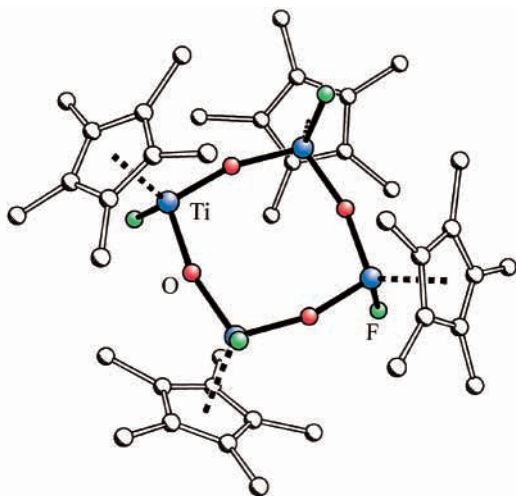


Figure 6. Molecular structure of $[\eta^5\text{-C}_5\text{Me}_5\text{TiFO}]_4$.

Ti - F 1.9593 Å
Al - F 1.8961 Å

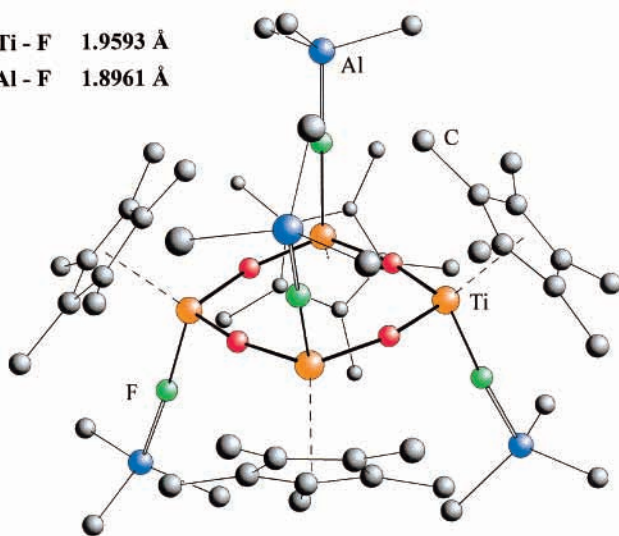


Figure 7. Adduct of four molecules of AlMe_3 with $[\eta^5\text{-C}_5\text{Me}_5\text{TiFO}]_4$.

Host–Guest-Type Compounds

It is a profound and necessary truth that the deep things in science are not found because they are useful; they are found because it was possible to find them.

Robert Oppenheimer

We were able to find host–guest-type compounds in organo-titanium fluoride chemistry, when Cp^*TiF_3 is treated with NaF or KF , respectively. The resulting $(\text{Cp}^*\text{TiF}_3)_4 \cdot 2\text{NaF}$ contains an internal and an external sodium cation. The $[(\text{Cp}^*\text{TiF}_3)_4\text{NaF}_2]^-$ anion (Figure 8) resembles the structure of the sodium cation coordinated to 12-crown-4. The external sodium can be selectively exchanged with the Ph_4P^+ cation. No reaction occurs with calcium difluoride, which is probably a consequence of

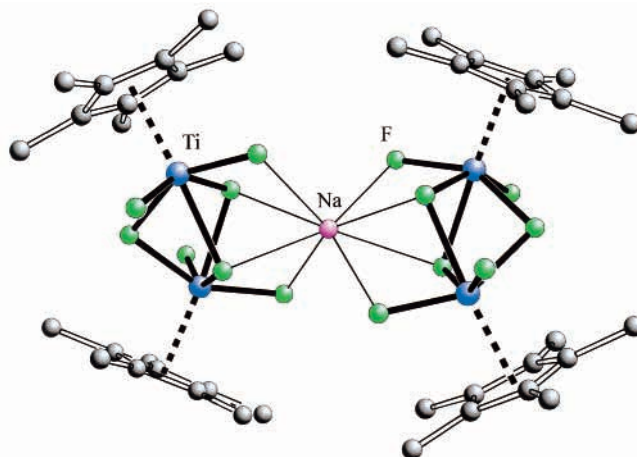


Figure 8. Representation of the anion $[(\eta^5\text{-C}_5\text{Me}_5\text{TiF}_3)_4\text{NaF}_2]^-$, a structural analogue of the sodium cation in 12-crown-4.

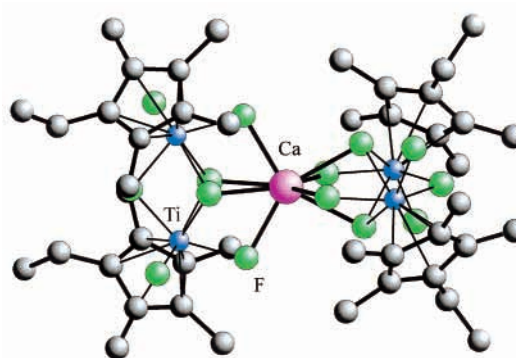


Figure 9. Plot of the molecular structure of $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TiF}_3]_4\text{CaF}_2$ in the crystal. Hydrogen atoms are omitted for clarity.

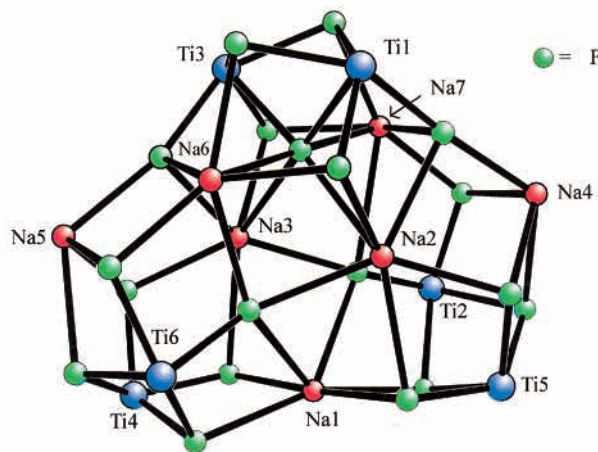
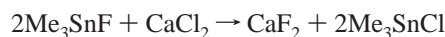


Figure 10. Core of the structure of $(\eta^5\text{-C}_5\text{Me}_5\text{TiF}_2)_6(\text{NaF})_7$.

the high lattice energy. Consequently, when calcium difluoride is generated in situ in the presence of $(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TiF}_3$, compound $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TiF}_3]_4 \cdot \text{CaF}_2$ is formed (Figure 9). The CaF_2 is obtained according to the following equation:



The structure of $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TiF}_3]_4\text{CaF}_2$ was determined by X-ray single-crystal analysis and shows the calcium atom to be coordinated to eight fluorine atoms. The $\text{Ca}-\text{F}$ bond lengths are comparable to those found in CaF_2 . In contrast the

(8) (a) Yu, P.; Pape, T.; Usón, I.; Said, M. A.; Roesky, H. W.; Montero, M. L.; Schmidt, H.-G.; Demsar, A. *Inorg. Chem.* **1998**, *37*, 5117. (b) Yu, P.; Roesky, H. W.; Demsar, A.; Albers, T.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem.* **1997**, *109*, 1846; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1766. (c) Roesky, H. W.; Sotoodeh, M.; Noltemeyer, M. *Angew. Chem.* **1992**, *104*, 869; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 864. (d) Roesky, H. W.; Leichtweis, I.; Noltemeyer, M. *Inorg. Chem.* **1993**, *32*, 5102. (e) Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F. *Organometallics* **1994**, *13*, 1251.

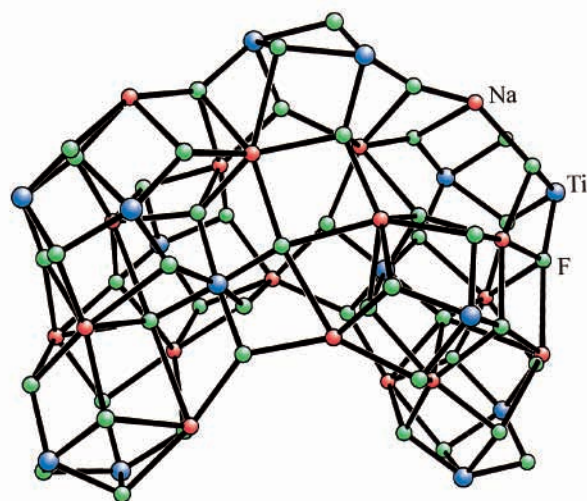


Figure 11. Core of the structure of $(\eta^5\text{-C}_5\text{Me}_5\text{TiF}_2)_{12}(\text{TiF}_3)_2(\text{NaF})_{18}$.

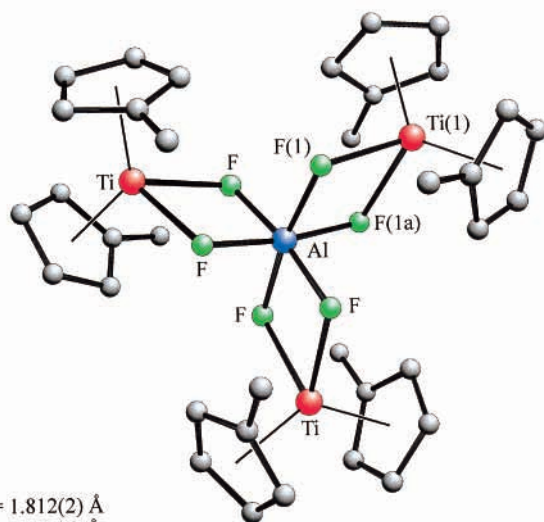


Figure 12. Soluble Werner-type coordination complex.

reaction of Cp^*TiF_3 with Ca leads to a titanium(III) derivative of composition $(\text{Cp}^*\text{TiF}_2)_6\text{CaF}_2 \cdot 2\text{THF}$. The calcium atom has a coordination number of eight with four long (mean, 2.53 Å) and four short (mean, 2.26 Å) Ca–F bond distances. It is noteworthy that the CaF_2 complexes are soluble in THF, toluene, benzene, and chloromethane.⁹

Nearly 250 years ago, Georg Christoph Lichtenberg wrote

We see in nature not words, but rather only the first letters of words and if we then wish to read, we discover that the now so-called words are again merely first letters of others.

Thus, the reduction of Cp^*TiF_3 with sodium amalgam demonstrates very clearly how changing a single reaction parameter can affect the nature of the product obtained. Reaction of Cp^*TiF_3 in the absence of dppe (bis(diphenylphosphino)ethane) yields $(\text{Cp}^*\text{TiF}_2)_6(\text{NaF})_7 \cdot 2.5\text{THF}$ (Figure 10) and in its

(9) (a) Sotoodeh, M.; Leichtweis, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Chem. Ber.* **1993**, *126*, 913. (b) Roesky, H. W.; Sotoodeh, M.; Noltemeyer, M. *Angew. Chem.* **1992**, *104*, 869; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 864. (c) Pevec, A.; Demsar, A.; Gramlich, V.; Petricek, S.; Roesky, H. W. *J. Chem. Soc., Dalton Trans.* **1997**, 2215.

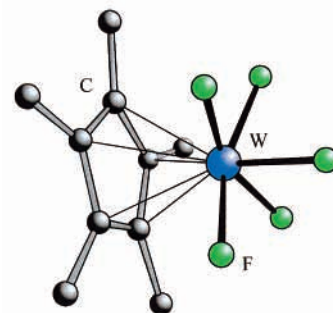


Figure 13. Molecular structure of $\eta^5\text{-C}_5\text{Me}_5\text{WF}_5$. Hydrogen atoms are not shown.

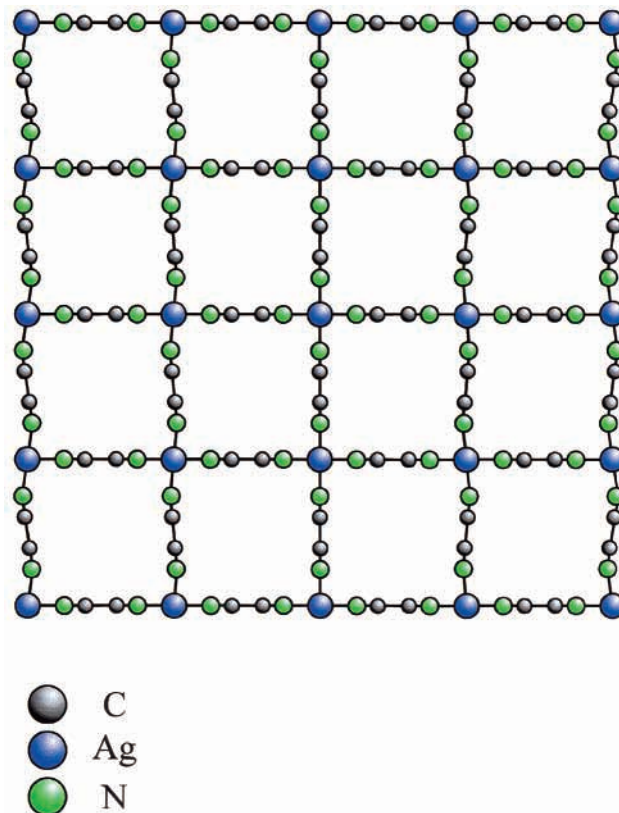


Figure 14. Plot of the reaction product of AgAsF_6 and cyanogen. The AsF_6^- anions are not shown.

presence gives $(\text{Cp}^*\text{TiF}_2)_{12}(\text{TiF}_3)_2(\text{NaF})_{18} \cdot 6\text{THF}$ (Figure 11). During the reaction the color of the solution changed from red to dark green without precipitation of any sodium fluoride.

Reduction of $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{TiF}_2$ with aluminum yields $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{TiF}_2]_3\text{Al}$. The three four-membered AlF_2Ti rings exhibit unsymmetrical Al–F bond lengths and surround the central aluminum atom in a “propeller-like” fashion (Figure 12). This example clearly demonstrates the symbiosis between Werner coordination compounds (AlF_6^{3-}) and the organic titanocene.¹⁰

Name the greatest of all investors: It is chance.

This proverb was written by Mark Twain. We had the chance, when we exposed Cp^*WF_4 to oxygen to generate a tungsten(VI)

(10) (a) Liu, F.-Q.; Kuhn, A.; Herbst-Irmer, R.; Stalke, D.; Roesky, H. W. *Angew. Chem.* **1994**, *106*, 577; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 555. (b) Liu, F.-Q.; Stalke, D.; Roesky, H. W. *Angew. Chem.* **1995**, *107*, 2004; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1872. (c) Liu, F.-Q.; Gornitzka, H.; Stalke, D.; Roesky, H. W. *Angew. Chem.* **1993**, *105*, 447; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 442.

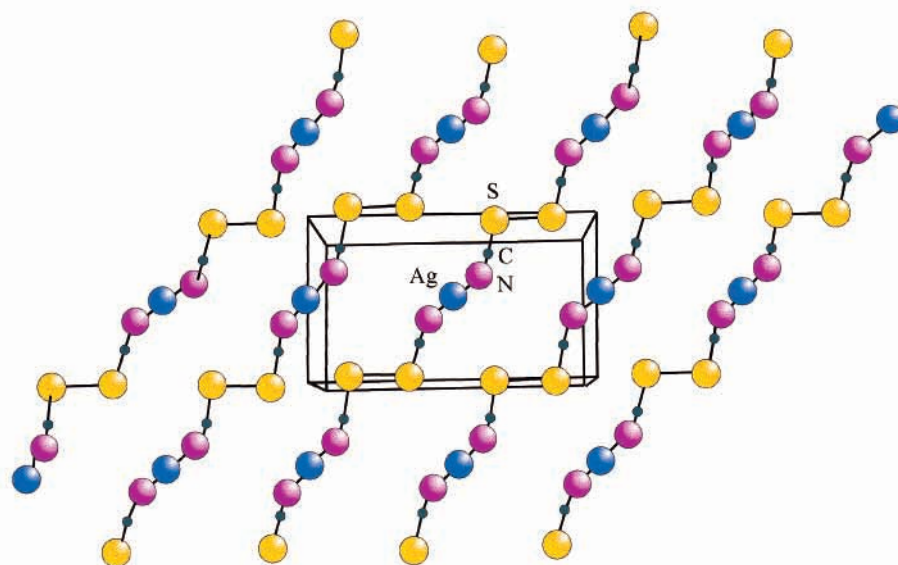


Figure 15. Chainlike structure of $\text{Ag}(\text{S}_2(\text{CN})_2)_2\text{AsF}_6$. The anions are omitted for clarity.

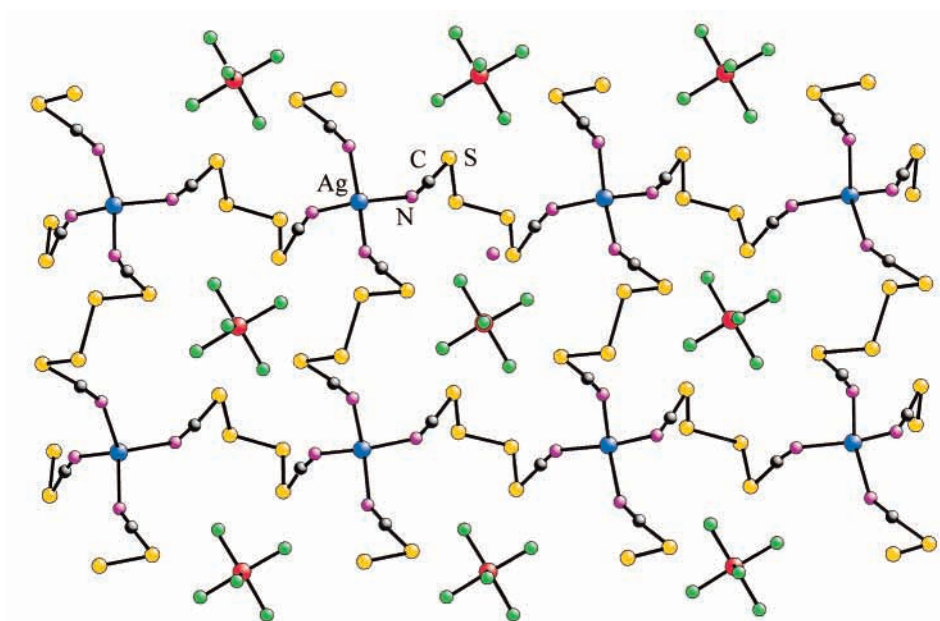


Figure 16. Sheetlike structure of $\text{Ag}(\text{S}_4(\text{CN})_2)_2\text{AsF}_6$.

complex containing fluorine and oxygen. However, we observed the formation of Cp^*WF_5 as well as $\text{Cp}^*\text{WO}_2\text{F}$. Compound Cp^*WF_5 (Figure 13) is surprisingly a monomer in the solid state and in solution. The X-ray structural analysis exhibits a square-bipyramidal geometry with the Cp^* occupying one apex and tungsten lying out of the plane of the square base (average $\text{F}-\text{W}-\text{F}$ 158°). Cp^*WF_5 is the only known monocyclopentadienylmetal(VI) halide¹¹ complex of group 6.

Supramolecular Assemblies

Ideas in fluorine chemistry are lovely, however to realize them is often the hell.

In the preceding section we have shown the ability of fluorine to act as a bridging ligand and thereby assist in the assembly

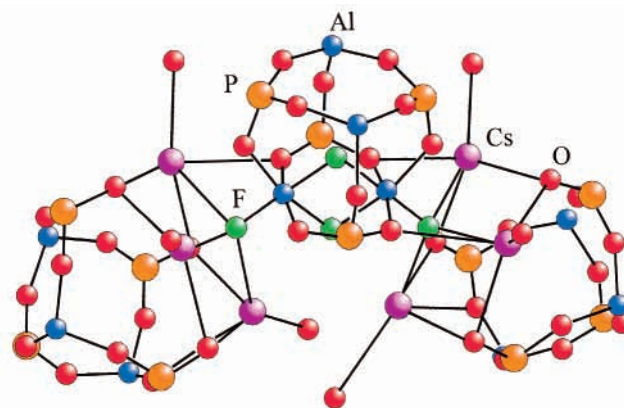


Figure 17. Molecular structure of an aggregate showing the mineralizing effect of fluorine.

of large aggregates. To test the dependence of fluoride-assisted cluster aggregation, we chose to use AgAsF_6 . This compound

(11) Köhler, K.; Herzog, A.; Steiner, A.; Roesky, H. W. *Angew. Chem.* **1996**, *108*, 331; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 295.

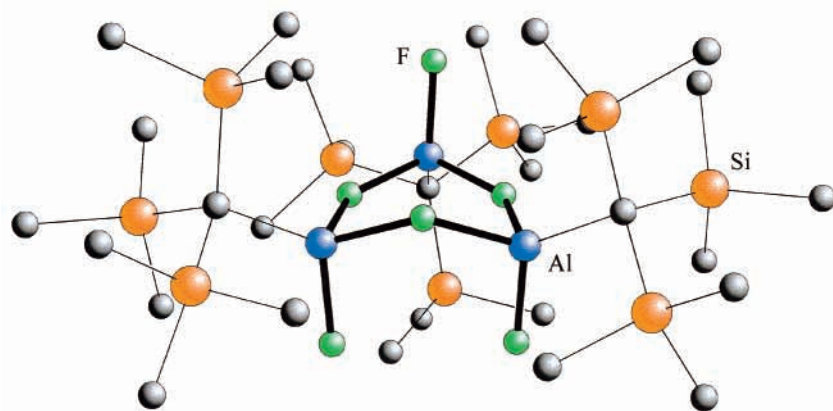


Figure 18. Molecular structure of $[(\text{Me}_3\text{Si})_3\text{CAIF}_2]_3$.

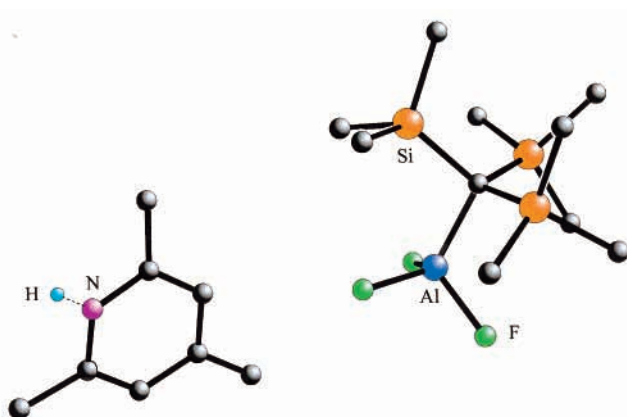


Figure 19. Plot of the molecular structure of $[\text{Me}_3\text{C}_5\text{H}_2\text{NH}][(\text{Me}_3\text{Si})_3\text{CAIF}_3]$.

is easily soluble in liquid SO_2 , a very weakly coordinating solvent. Moreover, according to Pearson's HSAB concept, Ag^+ is a soft acid and should preferentially coordinate with bases to generate a metal-assisted framework. Consequently we reacted elemental sulfur with AgAsF_6 to yield the first coordination compound of S_8 -sulfur, $\text{Ag}(\text{S}_8)_2\text{AsF}_6$. The X-ray structure shows that the silver atoms achieve four coordination by 1,3-linkages to two eight-membered sulfur rings.¹²

Under very similar conditions AgAsF_6 was reacted with cyanogen, dithiocyanogen, and tetrathiocyanogen, respectively, to yield polymeric structures (Figures 14–16). In Figure 14 the silver atoms have a square-planar coordination sphere, while in Figure 15 the cations form a threadlike zigzag polymer. For $\text{Ag}(\text{S}_4(\text{CN})_2)_2\text{AsF}_6$ (Figure 16) we observed for the cations a sheetlike structure.¹³

The structure-directing and mineralizing properties of fluorine are well-known in microporous materials. A molecular example was obtained by reacting $\text{Cs}(i\text{-Bu}_3\text{AlF})$ with *tert*-butylphosphonic acid (Figure 17). A characteristic feature of this aggregate is the $\text{FAl}(\mu\text{-F})_2\text{AlF}$ unit formed from two edge-sharing octahedra.¹⁴

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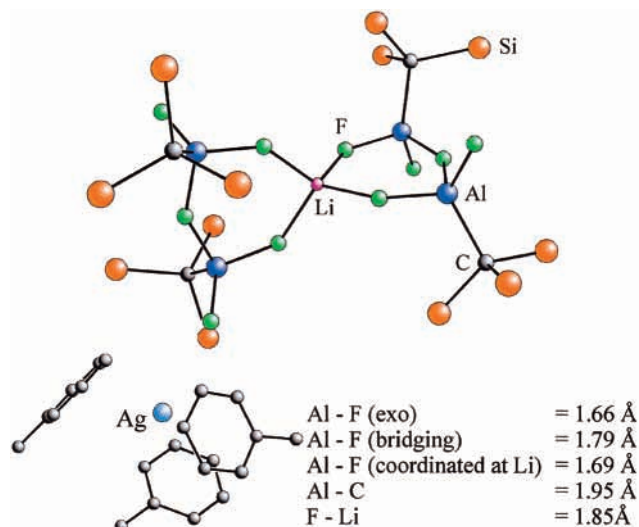


Figure 20. Molecular structure of the silver–lithium complex $[\text{Ag}(\text{toluene})_3]^+[\{((\text{Me}_3\text{Si})_3\text{C})_2\text{AlF}_3\}_2\text{Li}]^-$.

Aluminum–Fluorine Compounds

*Everything has its science, with the exception of catching fleas:
That is an art.*

Dutch proverb

Quite novel chemistry has emerged from studies of preparing compounds containing aluminum–fluorine bonds. While AlCl_3 is a convenient starting material for the preparation of aluminum compounds due to its good solubility in coordinating organic solvents and its low-lying melting point (192.6 °C, 1700 mbar), AlF_3 is an unreactive solid that melts approximately 1100 °C higher than AlCl_3 . Moreover, the Al–F bond is one of the strongest bonds in fluorine chemistry and, consequently, the easy formation of AlF_3 is due to a thermodynamic sink. Therefore, the preparation of soluble RAIF_2 compounds turned out to be an art.

The aluminum compound $(\text{Me}_3\text{Si})_3\text{CAICl}_2$ was first prepared in low yield by Eaborn et al.¹⁵ by the reaction of $(\text{Me}_3\text{Si})_3\text{CLi}$ and AlCl_3 . However, the reaction of Me_2AlCl and $(\text{Me}_3\text{Si})_3\text{CLi}$ in THF gave $(\text{Me}_3\text{Si})_3\text{CAI}(\text{Me}_2)\cdot\text{THF}$ in high yield. $(\text{Me}_3\text{Si})_3\text{CAI}(\text{Me}_2)\cdot\text{THF}$ is easily converted to $(\text{Me}_3\text{Si})_3\text{CAIF}_2\cdot\text{THF}$ and Me_4Sn using Me_3SnF . The solvent-free $[(\text{Me}_3\text{Si})_3\text{CAIF}_2]_3$ was obtained by heating the THF adduct in vacuo to 200 °C for

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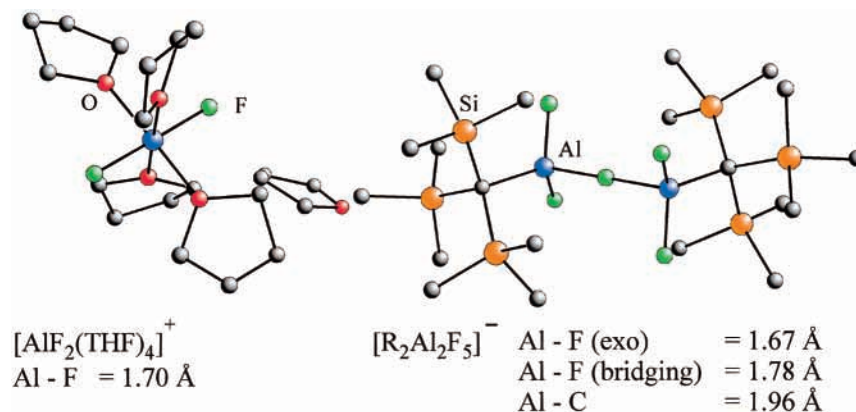


Figure 21. Plot of the cation $[\text{AlF}_2(\text{THF})_4]^+$ and the anion of $[\text{((Me}_3\text{Si)}_3\text{C)}_2\text{Al}_2\text{F}_5]^-$.

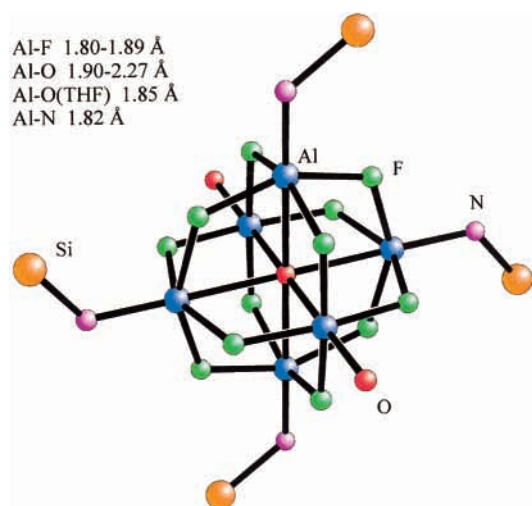


Figure 22. Perspective view of the core of the aluminum-fluorine-oxygen cluster.

several hours. The X-ray structural analysis (Figure 18) of $[(\text{Me}_3\text{Si})_3\text{CAIF}_2]_3$ exhibits a six-membered alternating aluminum-fluorine ring and three terminal fluorine atoms. The six-membered ring forms a boat conformation comparable to that observed in $[(\text{Me}_3\text{Si})_3\text{CGaMe}(\mu\text{-OH})]_3$ with two of the terminal fluorine atoms located above and below this ring. The bridging Al-F bond lengths range from 1.795 to 1.815 Å, while the terminal Al-F bonds range from 1.657 to 1.681 Å.

Treatment of $[(\text{Me}_3\text{Si})_3\text{CAIF}_2]_3$ with 2,4,6-trimethylpyridine hydrogen fluoride results in the ring opening and the formation of $[\text{Me}_3\text{C}_5\text{H}_2\text{NH}]^+[(\text{Me}_3\text{Si})_3\text{CAIF}_3]^-$ (Figure 19), while the reaction of *n*-Bu₄NHF₂ and AlMe₃ gives the stable difluoride $[n\text{-Bu}_4\text{N}][\text{AlMe}_2\text{F}_2]$ with elimination of methane. Presently we are investigating in general the reaction of an organometallic compound and a hydrogen difluoride salt to yield the corresponding organometallic difluoride anion.¹⁶

Men (and women) are not as different from molecules as they think....

Roald Hoffmann

In this sense we were interested in the preparation of fluorine complexes with weak and strong interactions.¹⁶ We thought to achieve this goal by assembling an organometallic fluoride cluster where the added metal ion is outside the core with no fluoride interactions. In the synthetic strategy a soft (Ag^+) and a hard (Li^+) cation were used according to the HSAB concept of Pearson.¹⁷ Consequently the reaction of $[(\text{Me}_3\text{Si})_3\text{CAIF}_2]_3$

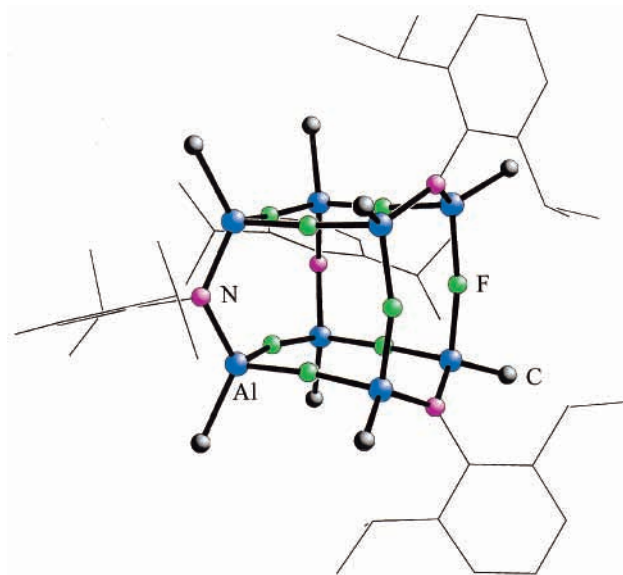


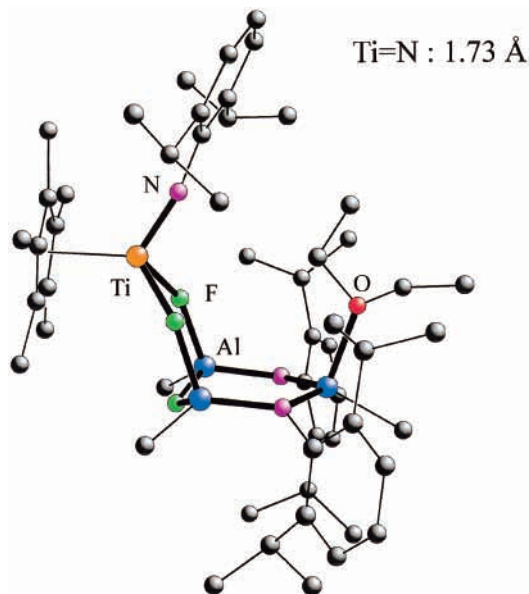
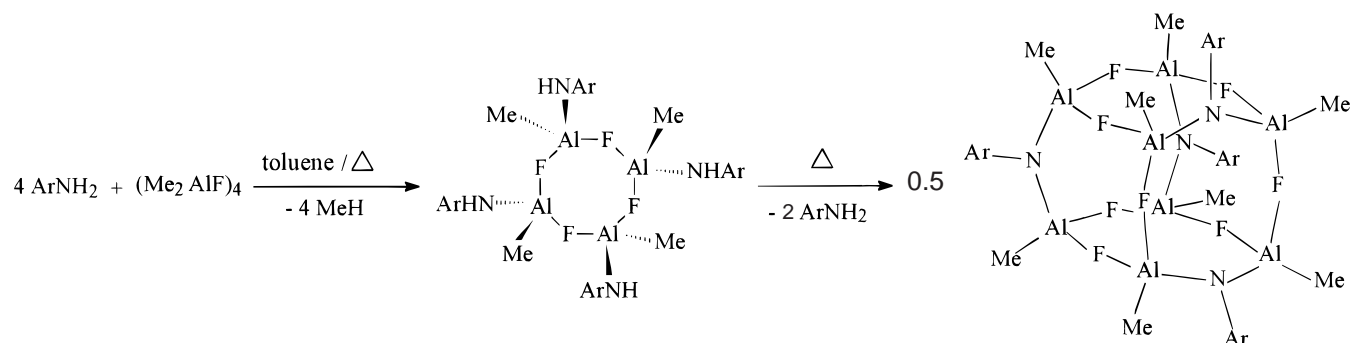
Figure 23. Perspective view of the aluminum-fluorine-nitrogen cage compound.

with AgF in the presence of LiCl resulted in the formation of $[\text{Ag}(\text{toluene})_3]^+[\text{((Me}_3\text{Si})_3\text{C)}_2\text{Al}_2\text{F}_5]_2\text{Li}^-$ (Figure 20). The Ag^+ cation does not show any interaction with the fluorine atoms and instead is surrounded by three toluene molecules. The structural analysis confirms that the hard Li^+ is incorporated into the cluster and is coordinated to hard fluorines and the soft Ag^+ is outside the cluster and shows no interactions with the anion.

The reaction of $[(\text{Me}_3\text{Si})_3\text{CAIF}_2]_3$ with AgF₂ in *n*-hexane instead resulted in an insoluble solid. The solid when treated with THF afforded $[\text{AlF}_2(\text{THF})_4]^+[\text{((Me}_3\text{Si})_3\text{C)}_2\text{Al}_2\text{F}_5]^-$ (Figure 21). Although Ag^{2+} is comparatively hard, it was not possible to incorporate the Ag^{2+} in the aluminum fluorine aggregate.^{16d}

Albert Einstein mentioned *fantasy is more important than knowledge*. This became true when we treated the aminoalane

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Scheme 2. Preparative Route to the Aluminum–Fluorine–Nitrogen Cage Compound**Figure 24.** Ring system containing a titanium–nitrogen double bond.

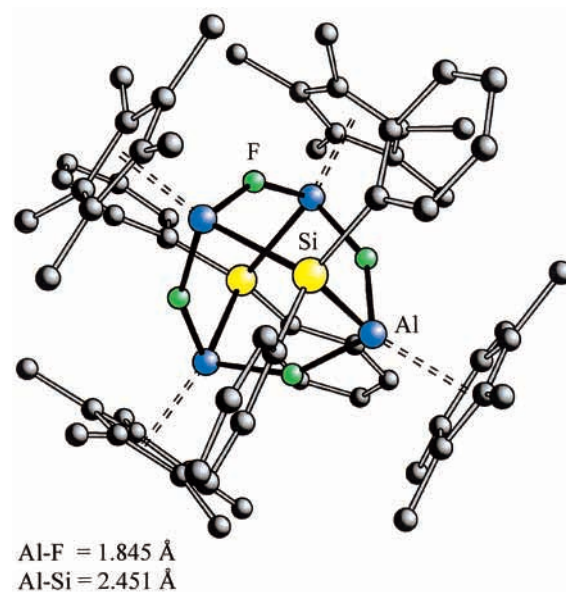
$(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{AlMe}_2$ with Me_3SnF in toluene and the trimeric $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{AlF}_2]_3$ was formed with a six-membered alternating aluminum–fluorine ring. However, in THF the monomeric THF adduct is obtained, which is converted to the aluminum–fluorine–oxygen cluster (Figure 22) with elimination of two molecules of $(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NHSiMe}_3$.^{16c} Each aluminum atom of the cluster is six-coordinate. The aluminum atoms are each bonded to four fluorine atoms and to the central oxygen atom. In addition, one THF molecule is coordinated to each of two aluminum atoms in trans position. The other four aluminum atoms are bearing the $(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)$ group. The fluorine atoms each bridge two aluminum atoms.

Immanuel Kant, the philosopher, wrote

...but although all our knowledge begins with experience, it does not follow that it arises from experience.

There is a lot of experience using AlN and AlF_3 as high-melting, temperature-stable solids that are insoluble in organic solvents. Consequently in the last years soluble precursors of both compounds have become available which lead to AlN and AlF_3 , respectively, upon elimination of organic groups under relatively mild conditions. Moreover, we have combined the two systems to synthesize soluble precursors containing aluminum, fluorine, and nitrogen.

Compound $[\{\text{MeAl}(\mu\text{-F})\}_2\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]_4$ was obtained as colorless crystals after a two-step elimination reaction from

**Figure 25.** Molecular structure of $[(\eta^5\text{-C}_5\text{Me}_5\text{AlF})_2\text{Si}(\text{C}_6\text{H}_5)_2]$. Hydrogen atoms are omitted for clarity.

$(\text{Me}_2\text{AlF})_4$ and $(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NH}_2$ (Scheme 2). In the first step of the reaction, one methyl group at each aluminum atom of the eight-membered starting material $(\text{Me}_2\text{AlF})_4$ is replaced by a $(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NH}$ substituent with methane elimination. In the second step at higher temperatures $(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NH}_2$ is eliminated with formation of the first Al–F–N cage compound (Figure 23). The aluminum atoms are all coordinated in a slightly distorted tetrahedral arrangement, while all fluorine atoms are in μ_2 -bridging positions.¹⁸ The trimeric iminoalane¹⁹ $(\text{ArNAlMe})_3$ (Ar = $2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) with coordination number three at aluminum and nitrogen reacts with Cp^*TiF_3 to an adamantane-like intermediate, which under treatment with diethyl ether yields the Al–F–Ti–N ring system with a titanium–nitrogen double bond (Figure 24). This is the first compound containing a Ti=N double bond obtained by a metathesis reaction.²⁰

Aluminum(I) Compounds

Aluminum(I) compounds have been prepared in my group by reduction of aluminum dichlorides and diiodides using a sodium–potassium alloy. An alternative high-temperature method

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was developed by Schnöckel and co-workers.²¹ Oxidative addition of Ph_2SiF_2 to the aluminum(I) complex $(\text{Cp}^*\text{Al})_4$ affords $[(\text{Cp}^*\text{AlF})_2\text{SiPh}_2]_2$ (Figure 25). The molecular core of this compound consists of a novel eight-membered Al_4F_4 ring capped by two silicon atoms.²² The complex $[(\text{Cp}^*\text{AlF})_2\text{SiPh}_2]_2$ represents a rare example of a structurally characterized compound containing an unprecedented example of two Al–Si–Al bridges. $(\text{Cp}^*\text{Al})_4$ and $[(\text{Me}_3\text{Si})_3\text{CAL}]_4$ are valuable precursors for a variety of new reactions.

In summary, organometallic fluorides of transition and main group metals have become an important group of compounds. Thus far, the main focus has been the synthesis and character-

ization of these systems, and this has been outlined. Although the utility of these new compounds as catalysts for polymerization reactions has been demonstrated, the ability of the fluoride to form both terminal and bridging ligand types may be taken as an advantage to prepare novel and new compounds that can be expected to exhibit new structures and potentially useful applications. However, in fluorine chemistry it is always wise to follow Yogi Berra: *I don't want to make the wrong mistake.*

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft. I am very thankful to my students and post-docs; their names have been mentioned in the references. Moreover, I am very grateful to the crystallographers Professor G. M. Sheldrick, Professor P. Jones, Professor D. Stalke, Professor Z. Zak, Dr. Noltemeyer, Dr. I. Usón, H.-G. Schmidt, and others quoted in the literature.

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