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Review

Chemistry with weakly-coordinating fluorinated alkoxyaluminate anions: Gas phase cations in condensed phases?

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Dedicated to I.K.'s academic teacher Prof. Hansgeorg Schnöckel in Karlsruhe for all the support, advice and time he has provided and continues to provide.

Contents

Abstract

Many very simple and fundamentally important cations were initially observed in the gas phase, e.g. inside a mass spectrometer or even in space. The question arises, how to stabilize and study these gas phase cations in condensed phases. In this review, our work on the use of weakly-coordinating anions (WCAs) of type $[Al(OR^F)_4]^-$ and $[(R^FO)_3Al–F–Al(OR^F)_3]^-$ to investigate structural and chemical properties of such gas phase cations is highlighted. Ag^+ complexes with various weakly basic ligands such S_8, P_4S_3, P_4, C_2H_4 or $P_3N_3Cl_6$ as well as reactive binary P–X cations

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and carbocations are reviewed. This section is followed by a theoretical investigation that substantiates our claim that gas phase conditions may be approximated in condensed phases by the use of large WCAs. Hence, we carefully analyze the conditions necessary to stabilize salts of such delicate cations in solution as well as the solid state. To account for this ability of WCAs, we coined the expression *pseudo gas phase conditions* in condensed phases. Using a combination of quantum chemically calculated gas phase enthalpies and estimated lattice potential enthalpies in suitable Born–Fajans–Haber cycles, the explanation as well as the prediction of whether or not a certain compound may be formed is now possible. Some examples for such an approach are given.

Keywords: WCAs; Aluminate; Silver; Carbonium; Phosphorus

1. Introduction

Many of the cations a preparative chemist sketches on paper when elucidating a novel reaction mechanism have already been observed on experimental grounds, however, not in the condensed phases that synthetic chemists usually work in, but rather in the gas phase inside a mass spectrometer. If not accessible on experimental grounds, these cations (and other species) have been modeled in silico by one of the advanced quantum chemical methods, again formally in the gas phase at 0 K. One example for such a species was the ^{t}Bu cation $C(CH_3)_3^+$, which for every student is a key to understanding S_N1-type reactions. Due to the fundamental importance of this cation and through using very weakly basic conditions throughout it was possible to study the isolated ^{t}Bu cation. Initially this was only possible in solution [1], but later the first crystal structure appeared [2] and finally in 2004 a report on "Putting ^{t}Bu cation into a bottle" was published [3]. To put a gas phase cation into a bottle in condensed phases the cation must be partnered with a suitable anion. Clearly one needs very special anions of low nucleophilicity and basicity to allow the formation of stable salts of such interesting but very reactive cations. The class of anions that allows the stabilization of such cations is called weakly-coordinating anions (WCAs), as it is evident from earlier work that *non-coordination* can never be achieved in condensed phases. Rather one can exchange a few strongly coordinating interactions for many but very weakly-coordinating interactions. Thus, WCAs allow one to stabilize strongly acidic gas phase species, highly electrophilic metal and non-metal cations or weakly-bound Lewis acid–base complexes of metal cations [4–8]. Examples of this kind of unusual and fundamentally important cations include $Au(Xe)_4^{2+}$ [9], Xe_2^+ [10], HC_{60}^+ [11], Mes_3Si^+ [12], $Ag(CO)_2^+$ [13], N_5^+ [14], $Si(Cp^*)^+$ ($Cp^* = C_5(CH_3)_5$) [15], $P(Cp^*)_2^+$ [16] or $Ir(CO)_6^{3+}$ [17]. In this respect we clearly view WCA chemistry as an "enabling chemistry". Thus cations otherwise incompatible with condensed phases may be stabilized in the environment of such WCAs. This may be seen in analogy to chemistry done with large and bulky organic substituents such as Wiberg's $Si(^{t}Bu)_3$ ligand [18] or Power's bulky terphenyl ligands [19] that allow one to prepare otherwise unstable moieties. Similarly, a close relation to chemistry with large and weakly-coordinating cations such as NMe_4^+, $C_5H_6NMe_6^+$ (1,3,5-hexamethylpiperidinium), $S(NMe_2)_3^+$, $Ph_3PNPPh_3^+$ and $P(NMe_2)_4^+$ exists [20].

Apart from being very useful in fundamental chemistry, WCAs have a very strong standing in applied chemistry. Thus, WCAs are important for homogenous catalysis [21,22], polymerizations [8,23], electrochemistry [24], ionic liquids [25,26], photolithography [27], lithium ion batteries, super capacitors and many more [28]. Accordingly, a large number of WCAs have been introduced that were recently reviewed by one of us [6]. A collection of state of the art WCAs is shown in Fig. 1.

Neglecting the classical $[BF_4]^-$ and $[MF_6]^-$ anions, WCAs tend to be relatively bulky anions in which the negative charge is dispersed over a large surface area. Among the anions usually viewed as WCAs are fluorometallates of the type $[M_nF_{5n+1}]^-$ (M = As, n = 2; Sb, n = 2–4). Other types of WCAs are halogenated and (trifluoro)methylated carboranes $[CB_{11}X_nH_{12-n}]^-$ (n = 0–12, X = F, Cl, Br, I, CH_3, CF_3) [4,29], polyfluorinated tetraaryl- or tetraalkylborates $[B(R^F)_4]^-$ ($R^F = CF_3, C_6F_5, C_6H_3(CF_3)_2$ and others) [30], dimeric borates $[X(B(C_6F_5)_3)_2]^-$ (X = CN, NH_2 and others) [7,31], tetra- or hexateflatometallates $[M(OTeF_5)_n]^-$ (n = 4, M = B [32]; n = 6, M = As [33], Sb [34,35], Bi [33], Nb [34,36]) and bistriflimides $[(R^FSO_2)_2N]^-$ [37] (Fig. 1).

A frequently used approach to synthesize new WCAs is to attach large sterically demanding fluorinated alkyl or aryl groups to a Lewis acidic central atom (see above). A recent development in WCA chemistry that combines the latter approach with the oxygen linked but sterically shielded teflate ($OTeF_5$) based anions, is the use of poly and perfluorinated alkoxy ligands OR^F that produce a smooth and non-adhesive "teflon-coated" surface on the anion [38]. However, in contrast to the teflate anions, these do not liberate anhydrous HF upon hydrolysis and are therefore easier to handle in conventional laboratories. Using aluminium as a central atom, this leads to alkoxyaluminate anions of type $[Al(OR^F)_4]^-$ ($R^F = C(H)(CF_3)_2$, $C(CH_3)(CF_3)_2$ and $C(CF_3)_3$) [38,39], the chemistry of which is highlighted in the present article.

2. Fluorinated alkoxyaluminates

2.1. Synthetic aspects

The fluorinated alkoxyaluminates of the formula $[Al(OR^F)_4]^-$ are representatives of the $[M(OR^F)_n]^-$ and $[M(OAr^F)_n]^-$ series of WCAs [22,38–44]. They have been used in our group since 1999, but were first reported by Strauss and coworkers [42]. With the large number of peripheral C–F bonds (36 in total), $[Al(OC(CF_3)_3)_4]^-$ is, together with $[CB_{11}(CF_3)_{12}]^-$, presumably the least coordinating anion known. However, the carborane anion is explosive. In contrast to the normally easily hydrolyzed alkoxyaluminates, the $[Al(OC(CF_3)_3)_4]^-$ anion is stable in 6N nitric acid [38]. This stability towards hydrolysis was attributed to steric shielding

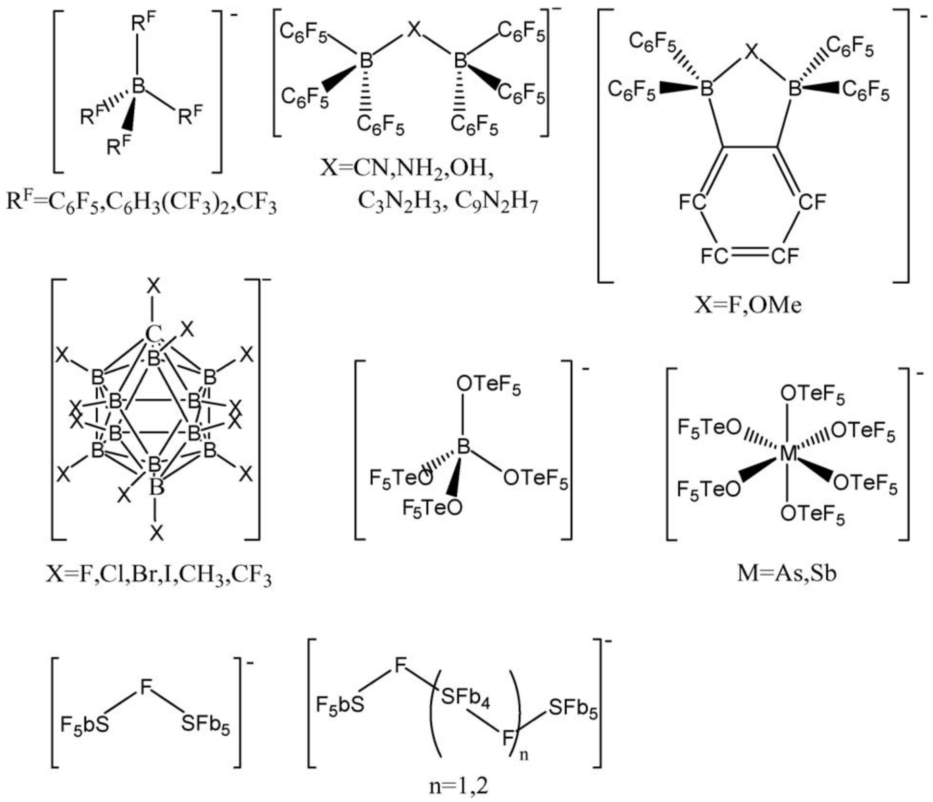


Fig. 1. Overview on some of the larger WCAs mentioned above.

of the oxygen atoms, provided by the bulky $C(CF_3)_3$ groups, as well as to electronic stabilization due to perfluorination. The electron withdrawing effect of the fluorinated ligand can be demonstrated by the increased acidity of the fluorinated $HOC(H)(CF_3)_2$ ($pK_a = 9.5$) and $HOC(CF_3)_3$ ($pK_a = 5.5$) alcohols in comparison to the non-fluorinated $HOC(CH_3)_3$ ($pK_a = 19.3$) [39]. Thus, perfluoro^{t}butanol is 14 orders of magnitude more acidic than non-fluorinated ^{t}butanol. Therefore, the $[Al(OC(CF_3)_3)_4]^-$ anion may be viewed as the complex anion of the (non-existent) $H^+[Al(OC(CF_3)_3)_4]^-$ super acid.

One of the major advantages of these aluminates is that they are easily accessible on a preparative scale: they can be prepared with little synthetic effort on a 200 g scale with well over 95% yield within 2 days in common inorganic/organometallic laboratories; $Li[Al(OC(CF_3)_3)_4]$ is also commercially available (Strem Chemicals, USA). However, since the original publications on the syntheses of the Li^+ and Ag^+ salts of different alkoxyaluminates appeared [38,39], the preparations have been modified and improved. Therefore, we would like to describe alterations to the preparation of several of the basic starting materials, including some hidden details that might not be obvious. Unless otherwise stated, the recommendations are valid for the preparation of all Li^+ and Ag^+ salts presented in this article.

The syntheses of all $[Al(OR^F)_4]^-$ starting materials begin with the preparation of the Li^+-salts using $LiAlH_4$ and the appropriate commercially available alcohols (Eq. (1)) [38,39].

$$LiAlH_4 + 4HOR^F \rightarrow Li + [Al(OR^F)_4]^- + 4H_2 \qquad (1)$$

Note, that commercially available $LiAlH_4$ is best purified by extraction with diethyl ether in an extraction frit. The purified $LiAlH_4$ is a white powder. Care has to be taken that all traces of Et_2O are removed by weighing the sample to a constant weight and drying in vacuo (10^{-3} mbar approx.) with heating to 80 °C (not higher! Use a water bath, since $LiAlH_4$ explodes at about 120 °C). The alcohols ($HOC(H)(CF_3)_2$, $HOC(CH_3)(CF_3)_2$ and $HOC(CF_3)_3$) were purchased from P&M Invest, Russia (www.fluorine.ru; 1–3 US$ per g) and were first degassed, then distilled prior to use. The alcohols have very low boiling points, especially the perfluorinated $HOC(CF_3)_3$ (b.p. = 45 °C), and are very volatile. Thus, they tend to evaporate from the reaction through a standard reflux condenser. Instead we use a double reflux condenser connected to a cryostat and set to a temperature of −20 °C. With this procedure it is not necessary to use a large excess of the alcohol (4.1 equivalents).

The solvent toluene, which was used as a solvent in the original publication, always caused a discoloration of the product with some grayish precipitate (Al^0?) and made an additional purification by sublimation necessary. Therefore it was replaced by hexane or heptane. While the occurrence of side reactions is significantly diminished in aliphatic solvents, it may happen that the $LiAlH_4$ does not completely react, especially in large scale reactions above 50 g. If residual Al–H bonds are in the mixture, the white powder reacts noisily with water (add approx. 100 mg to water. If a clear solution without hissing noise results the product is O.K.). Alternatively you may use Raman spectroscopy to detect Al–H bonds. To avoid this problem, which is

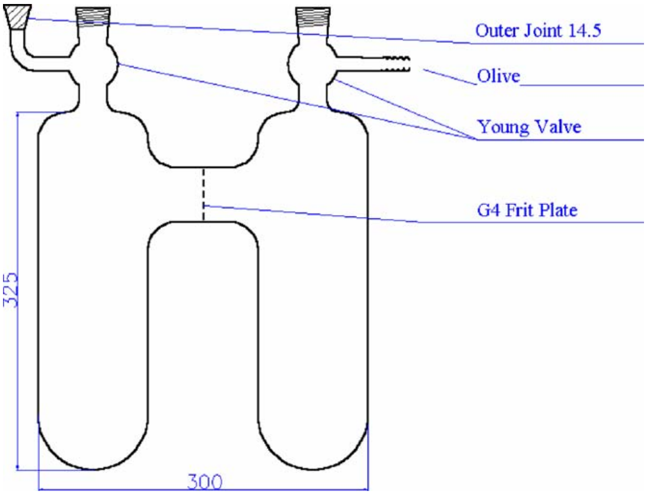


Fig. 2. Two bulbed Schlenk vessel with Young valves and G4 frit plate. Measures are given in mm.

caused by the poor solubility of the product even during reflux, it is absolutely necessary to finely grind the $LiAlH_4$ prior to use.

With these precautions, purified and finely ground $LiAlH_4$, reflux over night in aliphatic solvent, double reflux condenser set to −20 °C, the synthesis of the $LiAl(OR^F)_4$ salts is done in our group in >95% yield within two days in scales of up to 200 g.

Most other salts can then be prepared in high yield via metathesis reactions with precipitation of LiX (X = F, Cl, Br, BF_4). Currently a variety of different starting materials such as Cs^+ [40], Ag^+ [38], Tl^+ [41], CPh_3^+ [40], $H(OEt_2)_2^+$ [45], NR_4^+ [46], NO^+ [47] and NO_2^+ [48] salts of the WCA $[Al(OR^F)_4]^-$ are available. The Li aluminates themselves have been used in catalysis [42], and as electrolytes [39,43]. $[Al(OC(Ph)(CF_3)_2)_4]^-$ based ionic liquids have been investigated in transition metal catalysis [26].

Among these starting materials, Ag^+ salts are currently most frequently used in our group and therefore the synthesis has also improved over the years. Once again, an important input factor is the use of pure reagents: If the $LiAl(OR)_4$ salts were obtained by the procedure described above and are free of residual Al–H bonds, the Li^+ salts do not have to be sublimed, but the purity should be checked by NMR and IR or Raman spectroscopy. AgF has been purchased from Apollo Scientific, UK, exclusively; it should have a light orange/beige color and be stored with the exclusion of light. If AgF has a quite dark brownish or even greenish–blackish color, it should not be used for this reaction. It should be noted that the conversion of the Li into the Ag salts failed with newly bought AgF of another supplier (that had a quite dark color). In a glove box, the Li salt and 1.3 eq. AgF are weighed into one side of a special two bulbed Schlenk vessel with Young valves and frit plate (Fig. 2).

The reagents are suspended in CH_2Cl_2 (50 ml/10 g Li^+ salt approx.); the vessel is evacuated until the solvent starts to boil and left under the vapor pressure of the solvent. Therefore it is crucial to test, if the apparatus is leak tight prior to use! The mixture is left in an ultrasonic bath over night. The solution should have turned slightly brownish with only little of a dark brown (almost black) precipitate left. The darker the color of the solution, the more residual Al–H was presumably present. It appears that the dark color is due to colloidal Ag^0. Prior to filtration the solution is stored in a −20 to −30 °C freezer for at least 3 h to check whether unreacted Li^+ salt is still present (formation of a white microcrystalline precipitate). If not, the reaction is finished and the solution can be filtered. Afterwards the Ag^+ salt is dried in vacuo, finely ground in a glove box, placed in a new flask and left directly hooked to a vacuum line (10^{-3} mbar) until a constant weight is achieved. With this procedure one gets rid of the last traces of coordinated solvent and obtains solvent free naked $Ag^+[Al(OR^F)_4]^-$.

For the preparation of $H(Et_2O)_2^+[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) [49], the last of the frequently used starting material presented herein, $LiAl(OR^F)_4$ is suspended with CH_2Cl_2 (20 g per 500 ml) and Et_2O (2.5 eq.) in a normal round bottom flask with a glass valve. The suspension is frozen to 77 K and 1.05 eq. of HX gas (X = Cl or Br) are condensed directly onto the mixture. Afterwards the reaction is allowed to reach room temperature and stirred overnight with precipitation of LiX. Note that the flask is left under the vapor pressure of the solvent and therefore has to be tested if it is leak tight prior to use. The LiX precipitate is filtered off (if it is too fine and goes through the G4 frit, one should remove all the volatiles and dissolve the residue once again before filtering) and the resulting product is dried in a similar way to the Ag^+ salt. With this procedure one may prepare 20 g batches of $H(OEt_2)_2^+[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$).

Even though the $[Al(OR^F)_4]^-$ anion is remarkably stable, we repeatedly observed that $[Al(OR^F)_4]^-$ decomposed in the presence of very electrophilic cations such as $P_2X_5^+$ (X = Br, I) at temperatures above −20 °C with formation of the fluoride bridged $[(R^FO)_3Al–F–Al(OR^F)_3]^-$ anion [50,51]. According to an analysis of the structural parameters, this anion is more stable than $[Al(OR^F)_4]^-$ [51,52]; its negative charge is dispersed over a surface built from 54 peripheral C–F bonds versus 36 C–F bonds in $[Al(OR^F)_4]^-$ (Fig. 3). Therefore the $[(R^FO)_3Al–F–Al(OR^F)_3]^-$ anion is supposed to be the least coordinating anion currently known. The silver salt of the $[(R^FO)_3Al–F–Al(OR^F)_3]^-$ anion can be prepared by the reaction of $Ag[Al(OR^F)_4]$ with freshly distilled PCl_3 in CH_2Cl_2 solution (Eq. (2)) within 5 days and 85% yield (10 g scale) [53].

$$\begin{aligned}&2Ag[Al(OR^F)_4] + 2PCl_3\\&\quad\rightarrow Ag[R^FO)_3Al–F–Al(OR^F)_3] + Cl_2POR^F + OPCl_3\\&\qquad + AgCl + C_4F_8\end{aligned} \tag{2}$$

All of the side products except the insoluble AgCl are volatile. So pure $Ag^+[(R^FO)_3Al–F–Al(OR^F)_3]^-$ remains as the sole soluble compound in the filtrate.

2.2. Crystallographic aspects

Since X-ray crystallography is one of the crucial techniques to characterize the compounds presented in this article, one has to mention difficulties in obtaining good X-ray structures with these anions and some tricks to overcome them.

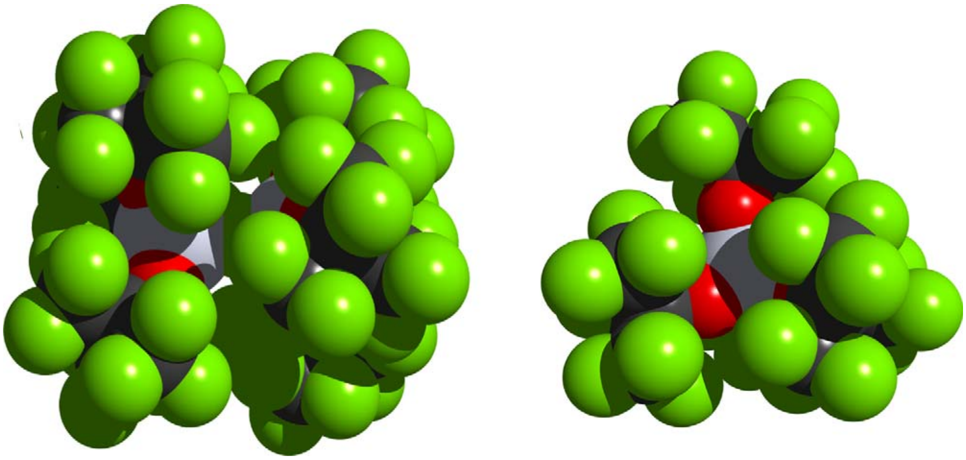


Fig. 3. Comparison of the space filling models of $[(R^FO)_3Al–F–Al(OR^F)_3]^-$ and $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$). One should note the better steric shielding of the most basic oxygen atoms in the fluoride bridged anion.

2.2.1. Crystal growth

First of all, several compounds tend to crystallize poorly. Usually the $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) anion is worst in this respect, especially if the cation is inorganic with no strong solid state anion cation contacts (e.g. $Ag(P_4)_x^+$ [54], $Ag(P_4S_3)_x^+$ [55], $Ag(S_8)_x^+$ [56]). For such highly soluble salts, a technique is used where almost all of the solvent is removed and a very concentrated oily residue is obtained. Only very small amounts of solvent should be left to enable diffusion and crystallization. From these "oils" crystals grow slowly within several days (this is best done at RT, eventually by slight cooling). Usually cations with C–H bonds crystallize better, likely through the formation of many assisting H–F contacts (e.g. $Ag(C_2H_4)_3^+$ [57], ammonium [46] and $H(OEt_2)_2^+$ [45] salts). A technique which is more suitable for these less soluble compounds comprises in the use of the already mentioned and described two bulb Schlenk vessels (Fig. 2): These vessels allow one to change the concentrations of the solutions without opening the system and being in danger of O_2/H_2O intrusion, simply by applying a temperature gradient to both sides of the vessel (e.g. one side at RT the other at 0 °C). Once the right concentration is reached, crystallization can be achieved by cooling the solution very slowly and gently (i.e. in a freezer at 5 °C with the vessel packed in insulating rubber foam/styro foam).

2.2.2. Crystal mounting and data collection

Crystal selection and mounting has been performed exclusively in perfluoropolyalkyl ether oil of various viscosities (purchased from ABCR, Germany). When the crystals were grown at very low temperature or were very sensitive to temperature, they were mounted with a simple cooling device. With this cooling technique, based on evaporating liquid nitrogen, crystals can be mounted between −40 and −20 °C. Transfer to the goniometer was done as quickly as possible, eventually supported by a cold Dewar vessel for the goniometer head.

Since all alkoxyaluminates and especially $[Al(OC(CF_3)_3)_4]^-$ tend to vigorous thermal movement as well as disordering of the CF_3 and $C(CF_3)_3$ groups, measurements are carried out at very low temperatures, typically between 100 and 150 K. At these temperatures, the structures of the anions are usually fine. At higher measurement temperatures the distances and angles of the anions normally have to be fixed by appropriate restraints such as SADI as well as a strong dampening during refinement (e.g. DAMP 500 to DAMP 1000 in the SHELX suite of programms). An example for such a restraint file is deposited (SADI restraints that fix one $C(CF_3)_3$ group).

2.2.3. Twinning

One of the main goals of both techniques described in the previous section is to grow the crystals as slowly as possible to avoid twinning, one of the main causes of problems at solving the crystal structures. Generally these techniques work very well to avoid normal twinning, where crystals are macroscopically grown together. However, we regularly observe merohedral twinning, which is caused by the $\bar{4}$ point symmetry of the $[Al(OR^F)_4]^-$ anions ($R^F = C(CF_3)_3$). If the cation has the same or higher point symmetry (e.g. PX_4^+, X = Br, I), the compounds can crystallize with a truly tetragonal cell, where Al and P atoms reside on special positions with $\bar{4}$ site symmetry and $Z = 2$. However, when a cation with lower symmetry but similar size (e.g. $P_2X_5^+$, X = Br, I; $H(EtO_2)_2^+$) crystallizes with the highly symmetric $[Al(OR^F)_4]^-$ anion the lattice parameters are almost the same; this necessarily leads to merohedral twinning (Table 1) [45,50].

The cations of all structures presented in Table 1 reside on similar positions; however, since $H(Et_2O)_2^+$ and $P_2X_5^+$ have low

Table 1
Lattice constants and cell volumes of truly or pseudo tetragonal structures of different $[Al(OR^F)_4]^-$ salts ($R^F = C(CF_3)_3$)

Parameter	PI_4^+	$P_2I_5^+$	PBr_4^+	$P_2Br_5^+$	$H(Et_2O)_2^+$
T (K)	150	200	200	200	150
$a = b$ (Å)	13.978(2)	14.510(3)	13.640(2)	14.016(3)	14.060[a]
c (Å)	9.4045(19)	9.778(2)	9.449(2)	9.694(2)	9.876
V (Å^3)	1837.4(5)	2058.6(7)	1758.0(5)	1904.3(7)	1952.2
Twinned	No	Yes	No	Yes	Yes

[a] Average value of 14.054 and 14.065 Å, since the structure could only be solved in the monoclinic space group $P2_1$ due to twinning.

point symmetries (2 and *m*, respectively), it is clear that for these cations it is impossible to reside on a special position with local $\bar{4}$ symmetry without twinning. In the case of the $P_2Br_5^+$ salt, it was also possible to obtain a triclinic structure without twinning when crystals were grown at −80 °C and measured at 150 K. Cell parameters ($a = 9.829(2)$ Å, $b = 13.702(3)$ Å, $c = 13.906(3)$ Å, $\alpha = 90.79(3)°$, $\beta = 94.08(3)°$, $\gamma = 90.31(3)°$, $V = 1867.9(6)$ Å^3) were similar to the 200 K phase, but no disorder was evident in this structure [50].

In summary, disorder of the $C(CF_3)_3$ groups can be reduced as well as merohedral twinning problems suppressed by measuring the X-ray data of the crystals at the lowest possible temperature (i.e. 100 K for standard X-ray diffractometers). Altogether, twinning and disordering lead to problems with solving/refining the structures that can not be overcome for approximately one in every fourth data set, i.e. to put it positive: 75% of the data collections are successful.

3. Weakly-bound Lewis acid–base complexes of the Ag$^+$-cation

Many complexes of the late transition metal Ag$^+$ and weak Lewis bases such as S_8, P_4 or C_2H_4 were previously unknown in condensed phases, but had already been characterized in the gas phase by one of the advanced mass spectrometric methods. Recent examples include complexes of Li$^+$ or Ag$^+$ with S_n ($n = 2$–8), P_4 and C_2H_4. Unfortunately, all MS methods are hampered by the lack of structural information provided by this technique. Thus, although it has been established that the $[Ag(P_4)_n]^+$, $[Ag(S_8)_n]^+$ and $[Ag(C_2H_4)_n]^+$ ($n = 1, 2$) cations exist in the gas phase, their geometries remained unknown, with the exception of quantum chemical calculations and a distorted $[Ag(S_8)_2]^+$ salt with the $[AsF_6]^-$ anion [58,59]. Lewis acid–base complexes of weak (polydentate) Lewis bases reside within shallow potential energy wells on extended potential energy surfaces (PES). Thus, it proved very difficult to verify conclusions drawn from the delicate quantum chemical calculations on experimental grounds. However, such complexes are now accessible in the solid state, if provided with a suitable WCA such as the alkoxyaluminates. Some of these gas phase cations in condensed phases will be detailed in the following section.

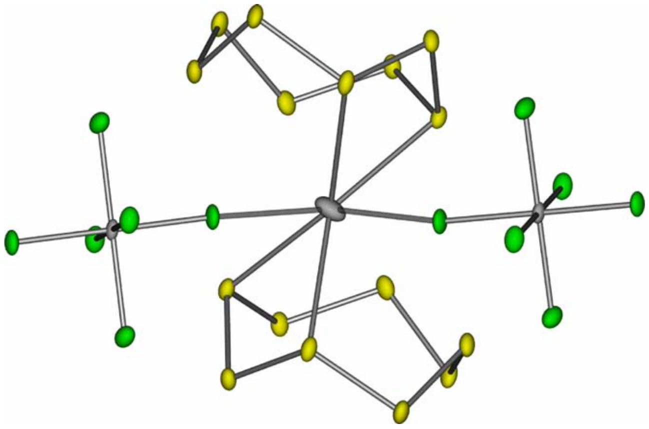


Fig. 4. Section of the solid-state structure of $(S_8)_2AgSbF_6$: coordinated MF_6^- anions that lead to a distortion of the $Ag(S_8)_2^+$ structure.

3.1. *Ag(S$_8$)-complexes*

It has been shown by mass spectrometry that Ag$^+$ and S_8 give complexes of type $Ag(S_8)_x^+$ ($x = 1, 2$). The only available structural model for such complexes was $(S_8)_2AgMF_6$ (M = As, Sb) [58,59], however, due to anion coordination it is unlikely that the gaseous $Ag(S_8)_2^+$ cation will adopt the same geometry (Fig. 4).

Therefore, the larger $[Al(OR^F)_4]^-$ anions were used to approximate the still unknown geometries of gaseous $Ag(S_8)_x^+$. The compounds $(S_8)AgAl(OC(H)(CF_3)_2)_4$ and $[Ag(S_8)_2][Al(OC(CF_3)_3)_4]$ were obtained [56] and include the first examples of undistorted homoleptic metal S_8-complexes, i.e. the almost C_{4v}-symmetric $[Ag(\eta^4\text{-}S_8)]^+$ and the approximately centrosymmetric $[Ag(\eta^4\text{-}S_8)_2]^+$ cations in Fig. 5. As also shown by

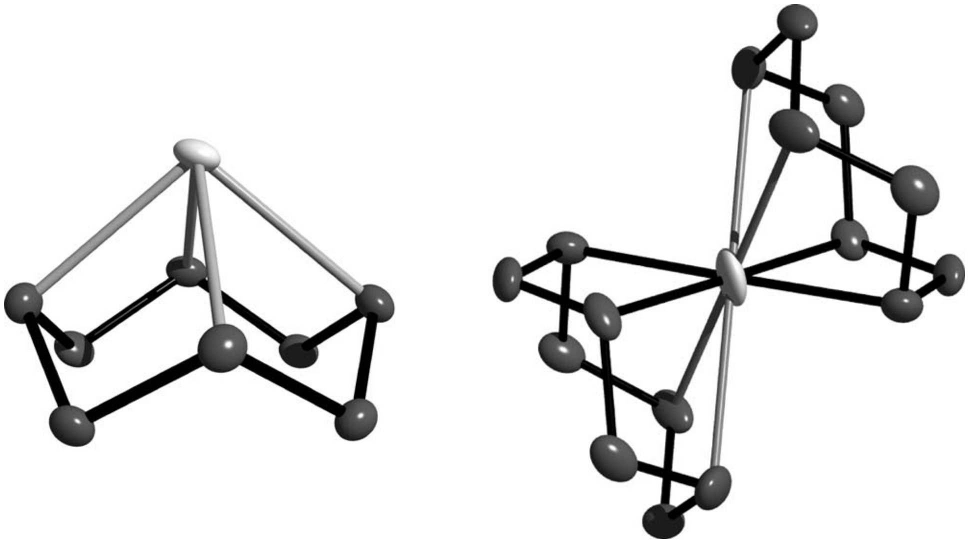
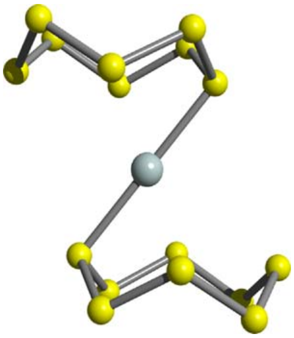
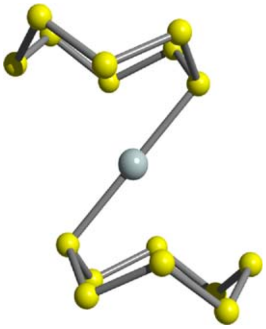
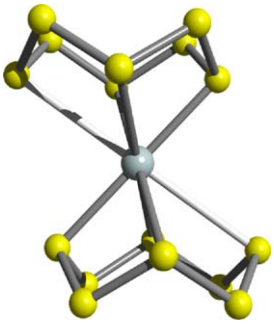
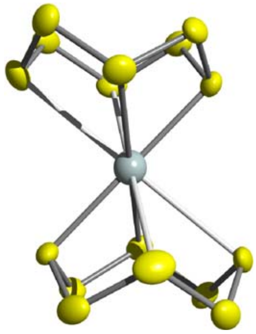


Fig. 5. The cations of the solid-state structures of $[(S_8)Ag][Al(OC(H)(CF_3)_2)_4]$ (left) and $[Ag(S_8)_2][Al(OC(CF_3)_3)_4]$ (right).

Table 2
Geometries and the four sets of shortest Ag–S distances of the experimental and several calculated $Ag(S_8)_2^+$ cation structures (in Å units)

BP/TZVPP	B3LYP/TZVPP	(RI-)MP2/TZVPP	Solid-state structure
			
2.539	2.593	2.609	2.700
3.225	3.316	2.989	2.929
3.281	3.321	2.994	3.179
3.842	3.906	3.408	3.342

quantum chemical calculations, they provide the best structural models for the gaseous AgS_8^+ and AgS_{16}^+ cations.

It should be noted that quantum chemical calculations of these cations are rather difficult and without the experimental structures, it would have been hard to establish the quality of the computation (Table 2).

Weak dispersive Ag–S interactions are structure determining and, therefore, DFT and HF-DFT theory failed to describe the $Ag(S_8)_x^+$ cations. Only MP2 calculations with a large basis set (TZVPP) gave minimum geometries close to the experiment.

Recently also computational studies on various $M(S_x)_y^+$ (M = Li, Ca, V, Cu; x = 4, 8; y = 1, 2) complexes were published that should be acknowledged in this context [60].

3.2. Complexes with P_4S_3

Similar to the Ag–S_8 complexes, the coordination chemistry of small inorganic cage or ring molecules such as P_4S_3 is of fundamental interest, as the structural knowledge on intact, coordinated P_4S_3 cages is rather limited [61]. Normally, the P_4S_3 molecule degrades upon coordination to transition metal fragments and phosphide or sulfide groups are incorporated into the complex [62,63]. Since it was possible to obtain undistorted homoleptic S_8 complexes with the weak Lewis acid Ag^+ in the presence of the WCAs $[Al(OR^F)_4]^-$, we extended our investigations to the coordination behavior of undistorted P_4S_3, with the goal to learn more about the most reactive coordination sites of this molecule. Prior to our work only few examples of intact P_4S_3 cages coordinated to transition metal atoms were known [61]. All of them were exclusively bound through the apical P-atom. No coordination of an S-atom or a P-atom of the P_3 basis was reported, however, S-coordination was postulated as a possible pathway for the sulfidic degradation [62,64]. The Ag–P_4S_3 complexes revealed the first polymeric Lewis acid–base adducts of $Ag[Al(OR^F)_4]$ (one-dimensional chains), which prior to this had always led to isolated molecular or salt structures [55]. With the more basic $[Al(OR^F)_4]^-$ anion ($R^F = C(CH_3)(CF_3)_2$), one anion remained coordinated to the silver atom in addition to one bridging P_4S_3 cage (Fig. 6), however, with the least basic perfluorinated aluminate with $R^F = C(CF_3)_3$ a cationic polymer of the general formula $[Ag(P_4S_3)_2{}^+]_\infty$ with no anion contacts formed (Fig. 7).

From this study it was evident that – in contrast to P_4 below – P_4S_3 has sterically active lone pair orbitals on all atoms. Although incorporating a cyclo P_3 unit similar to P_4, molecular P_4S_3 prefers η^1 coordination. Moreover, the structures of $(P_4S_3)AgAl(OC(H)(CF_3)_2)_4$ and $[Ag(P_4S_3)_2][Al(OC(CF_3)_3)_4]$ revealed the first examples of a sulfur coordination within P_4S_3. All cage atoms are similar with respect to their coordination behavior. Thus, P_3S_3 can act in a 1,3-, 2,4 or 3,4-fashion as a bridging ligand. This flexible S or P coordination is the starting point for the frequently observed further degradation of the P_4S_3 molecule. After our report that all atoms of the P_4S_3 cage may be coordinated, several reports on such coordination modes appeared [65].

3.3. Complexes with P_4

In a pioneering MS study, two binary silver-phosphorus cations were observed: AgP_4^+ and AgP_8^+. On the basis of this mass spectrometric experiments and initial DFT-calculations a structure with two η^1-bound molecules was predicted. Similarly to the situation in the $[Ag(\eta^4\text{-}S_8)_n]^+$ cations unusual and weak bonding interactions in Ag^+–P_4 complexes can be stabilized by WCAs. In agreement with this, Ag^+–P_4 complexes containing one or two almost undistorted tetrahedral P_4 units can be formed, i.e. $(P_4)AgAl(OC(CH_3)(CF_3)_2)_4$ and $[Ag(P_4)_2][Al(OC(CF_3)_3)_4]$, which contain the first homoleptic metal P_4 cations (Fig. 8) [54]. In contrast to the initial computational prediction, the crystal structure determination revealed a $[Ag(P_4)_2]^+$-cation with D_{2h}-symmetry and two coplanar η^2-bound P_4-molecules.

To understand why η^2-coordination – if compared to η^1 or η^3 coordination – is favored by 27–76 kJ mol^{-1} [54], an

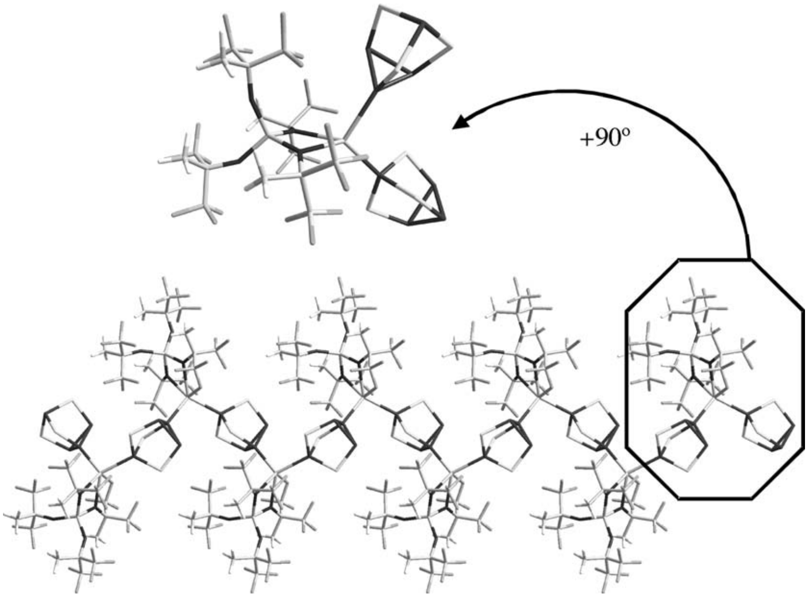


Fig. 6. Extended solid-state structure of $[Ag(P_4S_3)^+]_\infty$ with the more basic $[Al(OR^F)_4]^-$ anion ($R^F = C(CH_3)(CF_3)_2$).

analysis of the MO diagram of tetrahedral P_4 is helpful (Fig. 9):

s- and p-type orbitals are well separated and the lone pair orbitals have $3s^2$ character and are not available for coordination. Thus, coordination has to proceed through an interaction with the frontier orbitals (*HOMO*). The largest coefficient of the *HOMO* of P_4 (E symmetry) is found along the edge of the tetrahedron. The major contribution to the Ag–P bonding is made by donation of electron density from the edge centered *HOMOs* of P_4 to the empty 5s acceptor orbital of Ag^+ (*LUMO*). Due to this *HOMO–LUMO* interaction, the P_4 molecules prefer the side on over the end on coordination. For the same reason P_4 is protonated on the edge and not at the corner [66].

The synthesis of the $Ag(\eta^2\text{-}P_4)_2^+$ complex was also carried out using the fluoride bridged $[(R^FO)_3Al\text{–}F\text{–}Al(OR^F)_3]^-$ anion, where the least coordinating character of this anion was employed to clarify the question of the ground state geometry of the $Ag(\eta^2\text{-}P_4)_2^+$ cation (D_{2h}, D_2 or D_{2d}?) [53]. Calculations showed a very small energy difference of 5.2 kJ mol^{-1} between the planar (D_{2h}) and tetrahedral (D_{2d}) conformation

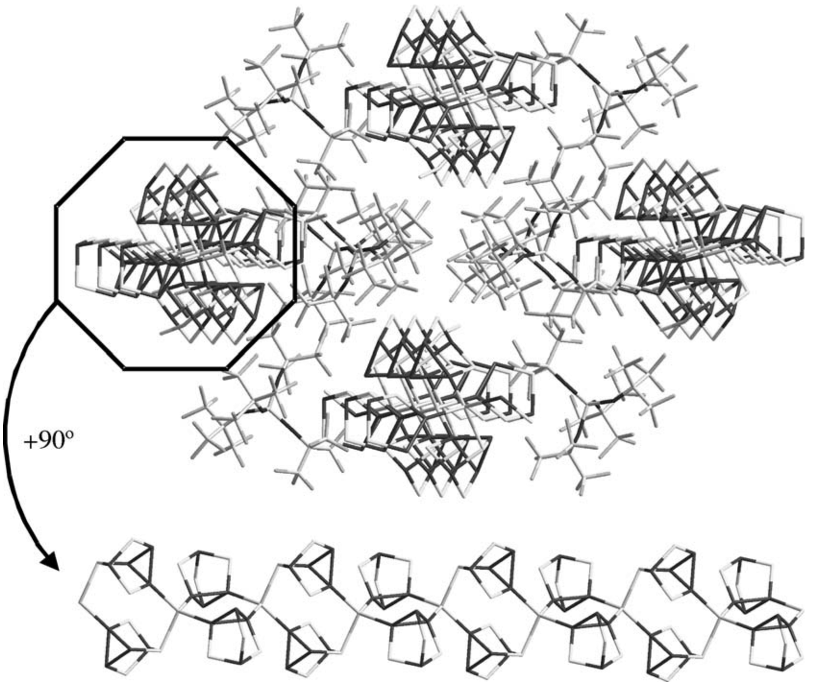


Fig. 7. Extended solid-state structure of $[Ag(P_4S_3)_2{}^+]_\infty\{[Al(OC(CF_3)_3)_4]^-\}_\infty$. At the bottom the infinite $[Ag(P_4S_3)_2{}^+]_\infty$ chain is shown and all anions were omitted for clarity.

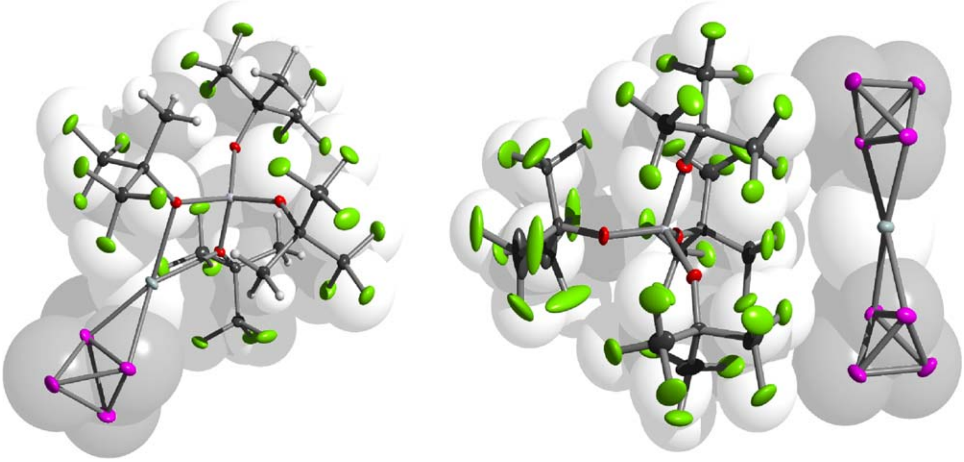


Fig. 8. Sections of the solid-state structures of $(P_4)AgAl(OC(CH_3)(CF_3)_2)_4$ and $[Ag(P_4)_2][Al(OC(CF_3)_3)_4]$.

[54]. According to other calculations, the most favorable structure is of D_2 symmetry [67,68]. In agreement with this computational data and NMR spectra it could be shown on experimental grounds that several orientations of the $Ag(\eta^2\text{-}P_4)_2^+$ cation are very close in energy, that the rotation around the Ag–(P–P–centroid) axis has no barrier and that the finally realized geometry in the solid state clearly depends on packing effects. These effects lead to an almost D_{2h} symmetric $Ag(\eta^2\text{-}P_4)_2^+$ cation (0°–10.6° torsion) for the more symmetrical $[Al(OR^F)_4]^-$ anion, but to a D_2 symmetric $Ag(\eta^2\text{-}P_4)_2^+$ cation with a 44° twist angle of the two AgP_2 planes for the less symmetrical $[(R^FO)_3Al\text{–}F\text{–}Al(OR^F)_3]^-$ anion (Fig. 10) [53,54].

This conclusion provides evidence that back bonding from the occupied $4d^{10}$ silver orbitals, suggested by DFT calculations to be in the order of 40–60 kJ mol^{-1} [67,68], is not structure determining, since in this case a structural preference for a 0° or 90° torsion angle would have been expected regardless of which anion was used.

3.4. *Complexes with cyclic hexachlorophosphazene $P_3N_3Cl_6$*

While cyclic phosphazenes of the general formula $(PNY_2)_n$ ($n = 3\text{–}7$) are prominent examples of inorganic ring systems [69–72], the trimers are of particular interest due to the planarity of the ring as well as their applications in polymer syntheses [69,73]. Accordingly, much research has been dedicated to this group of compounds [70,71]. $P_3N_3Y_6$ molecules (Y = alkoxy group, alkyl, NH_2, NHR, NR_2, etc.) are known to be versatile ligands for transition metals [70,74]. However, for the halogen substituted $P_3N_3X_6$ cyclophosphazenes the coordinating ability, i.e. the basicity of the ring nitrogen atoms, decreases rapidly. Therefore, the complex chemistry of halophosphazenes is far less developed and only a few complexes are known, e.g. $P_3N_3X_6$ (X = Cl, Br) with $AlBr_3$ [75], $P_3N_3F_6$ with MF_5 (M = P, Sb) [76], and $P_3N_3Cl_6$ with $Cr(CO)_3$ [77], $NiCl_2$ [78] and recently $VOCl_3$ [79]. Although they are poorly characterized and no solid-state

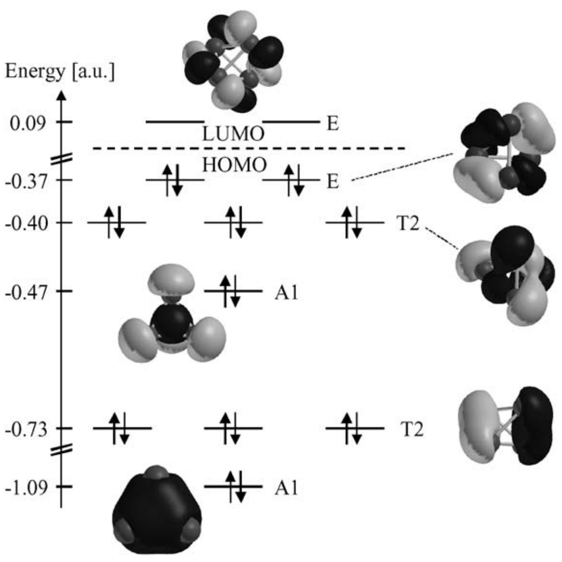


Fig. 9. Section of the MO diagram of tetrahedral P_4.

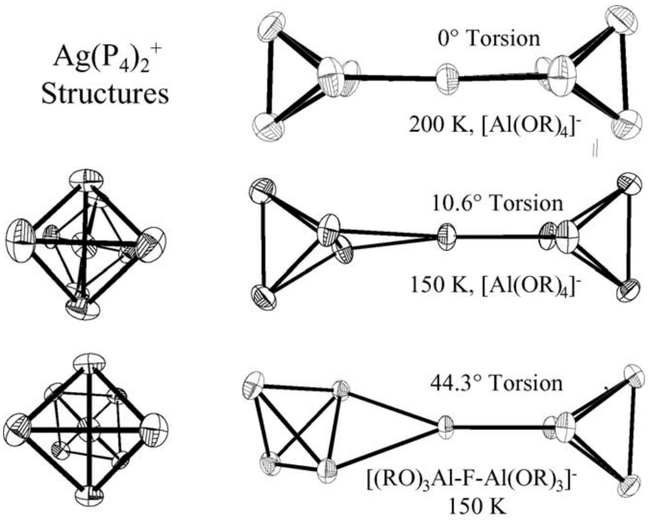
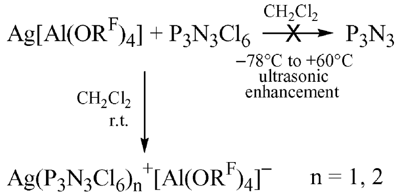


Fig. 10. Temperature and anion dependence of the orientations of the $Ag(\eta^2\text{-}P_4)_2^+$ cations ($[Al(OR^F)_4]^-$ and $[(R^FO)_3Al\text{–}F\text{–}Al(OR^F)_3]^-$ salts).



Scheme 1. Preference for formation of the $Ag(P_3N_3Cl_6)_n{}^+$ complex over the formation of the $P_3N_3Cl_5{}^+$ cation.

structure for such a complex has been reported, the last examples of these Lewis acid–base complexes are thought to play a key role in the polymerization to poly(dichlorophosphazene) [69,73,80].

Therefore, we were interested to react $P_3N_3Cl_6$ with $Ag^+[Al(OR)_4]^-$. The particular question was, whether $P_3N_3Cl_6$ would form a complex with the silver cation or would ionize and form the $P_3N_3Cl_5{}^+$ cation and AgCl. The experiments revealed a preference for coordination over ionization (Scheme 1).

Therefore the formation of the $P_3N_3Cl_5{}^+$ cation was assessed by ab initio calculations, including the formation of solid AgCl, with the result that it should be exergonic by 102 kJ mol^{-1}. However, the formation of the complex is also exergonic by 96 kJ mol^{-1} and the resulting driving force for a successful metathesis reaction (Scheme 1) is only 6 kJ mol^{-1}. Therefore, the stability of the $Ag(P_3N_3Cl_6)_2{}^+$ complexes is kinetic.

During this work, the first structurally characterized, homoleptic complexes of any metal and a halogen substituted cyclic triphosphazene, $(N\text{-}P_3N_3Cl_6)AgAl(OC(CH_3)(CF_3)_2)_4$ and $[Ag(N\text{-}P_3N_3Cl_6)_2][Al(OC(CF_3)_3)_4]$ were synthesized (Fig. 11) [81]. The complexes, which are very soluble even at low temperatures, are formed instantaneously at −78 °C and are stable in CH_2Cl_2 solution at least up to 60 °C, even with ultrasonic enhancement.

The approximately C_{2v} symmetric cationic complex in $(N\text{-}P_3N_3Cl_6)AgAl(OC(CH_3)(CF_3)_2)_4$ consists of a $P_3N_3Cl_6$ ring coordinated through the N atom to the Ag^+ cation but there are also significant interactions with the oxygen atoms of the anion. In contrast, $[Ag(N\text{-}P_3N_3Cl_6)_2][Al(OC(CF_3)_3)_4]$ forms a truly ionic structure due to the inferior coordinating ability of $[Al(OC(CF_3)_3)_4]^-$ compared to $[Al(OC(CH_3)(CF_3)_2)_4]^-$. This anion dependent coordination is in agreement with earlier observations and detailed below. The almost ideally D_{2h}-symmetric $[Ag(P_3N_3Cl_6)_2]^+$ complex consists of the Ag^+ cation centered between two coplanar $P_3N_3Cl_6$ rings. Interestingly the cation takes a sterically more demanding conformation where four chlorine atoms of the two ligands point directly at each other. According to BP86/SVP frequency calculations, the D_{2h}-symmetric structure found in the solid state is not the minimum energy structure. Instead a D_2-symmetric structure in which the two phosphazene rings are twisted by about 54.4° is found to be the global minimum. However, $\Delta_{(g)}$ for such a transformation amounts to only 1 kJ mol^{-1}. Therefore, the observed solid-state structure is caused by packing effects (cf. $Ag(P_4)_2{}^+$ isomers above, Fig. 12).

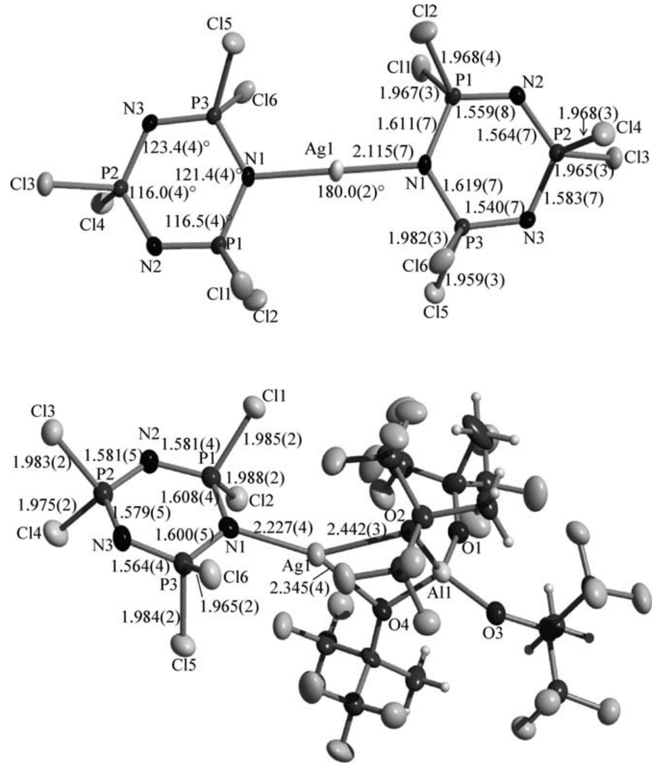


Fig. 11. Sections of the solid-state structures of $(N\text{-}P_3N_3Cl_6)AgAl(OC(CH_3)(CF_3)_2)_4$ (left) and $[Ag(N\text{-}P_3N_3Cl_6)_2]^+[Al(OC(CF_3)_3)_4]^-$ (right, the anion has been omitted for clarity).

3.5. Complexes with C_2H_4

After investigation of the coordination chemistry of groups 15 and 16 elemental rings and cages with the Ag^+-cation, it was obvious to extend this kind of chemistry. D. Deubel, a theoretician, became interested in the $Ag(P_4)_x{}^+$ cations and compared their bonding to that in $Ag(C_2H_4)_2{}^+$ [67] and, therefore, we decided to study these $Ag(C_2H_4)_x{}^+$ complexes on experimental grounds. Since the discovery of Zeise's salt $K[PtCl_3(C_2H_4)]$ in 1827 [82] the investigation of simple ethane–metal complexes is an area of continuing interest in all fields of chemistry, fueled by the interest in transformations of the coordinated C_2H_4 molecule. Several ethane–metal coordination modes including μ, η^2:η^2 are known. Ethene–silver complexes with very little back bonding served to formulate the Dewar–Chatt–Duncanson model for the binding of olefins to transition metal atoms [83]. However there is still much controversy about the nature of the bonding in $[Ag(C_2H_4)_n]^+$ ions ($n = 1$–3) with proposals ranging from mainly electrostatic to mainly covalent and mixtures thereof [84]. Although Ag–C_2H_4 complexes are textbook compounds, experimental information on this system is very limited [85] and only one disordered solid-state structure of a $[Ag(C_2H_4)_n]^+$ unit has been determined [86]. In the gas phase, $Ag(C_2H_4)_n{}^+$ cations have already been characterized by MS for $n = 1$ and 2 [87]. Using $[Al(OC(CF_3)_3)_4]^-$ as the WCA, a cationic $[Ag(C_2H_4)_3]^+$ complex with an ionic lattice in the solid state and an almost planar D_{3h} symmetric cation in a spoke wheel arrangement was synthesized (Fig. 13) [57].

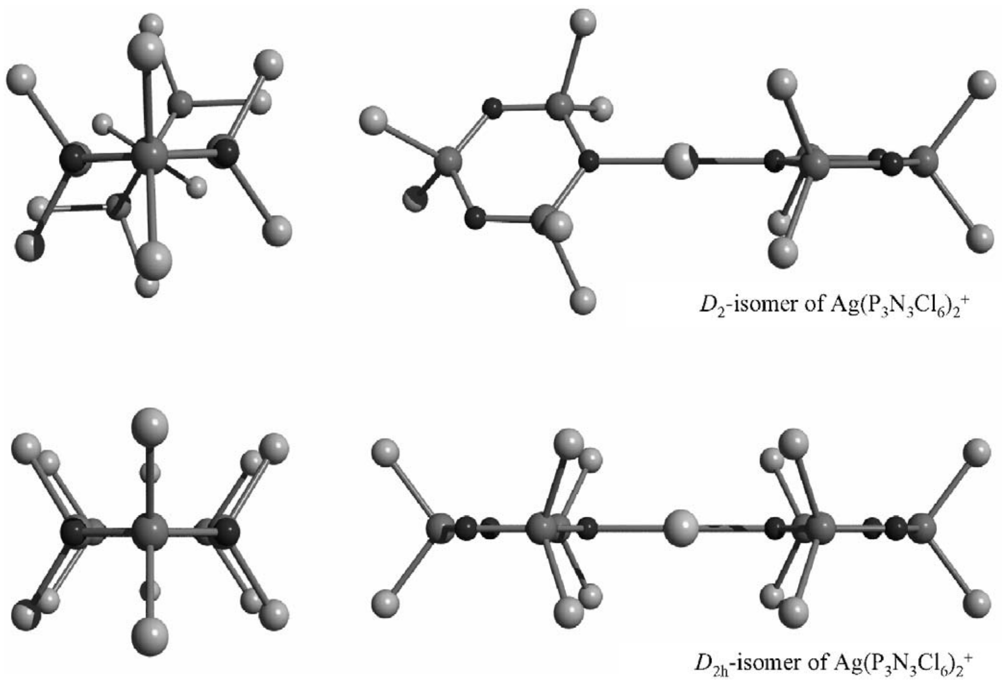


Fig. 12. MP2/TZVPP calculated upper D_2- and lower D_{2h}-structures of the $Ag(P_3N_3Cl_6)_2^+$ complex.

The synthesis and full characterization of $[Ag(C_2H_4)_3]^+$ $[Al(OC(CF_3)_3)_4]^-$ in condensed phases is rather remarkable, especially since only $Ag(C_2H_4)_n^+$ complexes with $n = 1, 2$ were observed in the gas phase. This is probably due to the low (calculated) binding energy of the third C_2H_4 molecule of $\Delta G^\circ = -55\,kJ\,mol^{-1}$ in the gas phase (MP2/TZVPP; see also Section 5).

3.6. Anion effects

To stabilize weakly-bound Lewis acid–base adducts of the presented type, anion–cation as well as solvent–cation interactions have to be minimized and must be smaller in magnitude than the interaction with the weakly basic ligand. The influence of the counterion may be illustrated by the series of silver complexes highlighted in the present article:

(i) Role of the counterion: From the solid-state structures it is evident that $[Al(OR^F)_4]^-$ anions with $R^F = C(H)(CF_3)_2$ and $C(CH_3)(CF_3)_2$ coordinate to the Ag^+ cation and give molecular compounds $(L)AgAl(OC(H)(CF_3)_2)_4$ (Scheme 2a). With the least basic anion, $[Al(OC(CF_3)_3)_4]^-$, P_4, P_4S_3, $P_3N_3Cl_6$ and S_8 are stronger Lewis bases towards the cation than the anion. Consequently, in the analogous

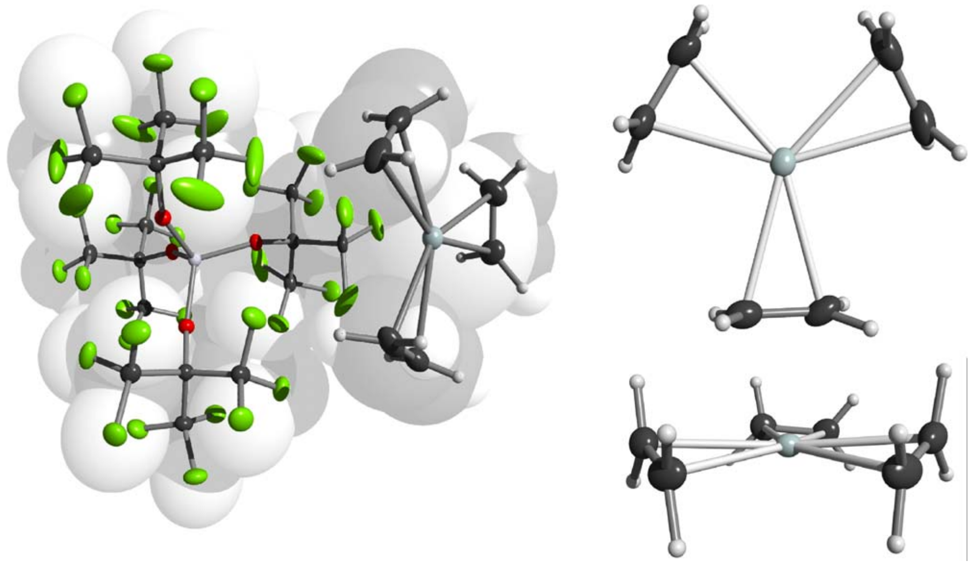
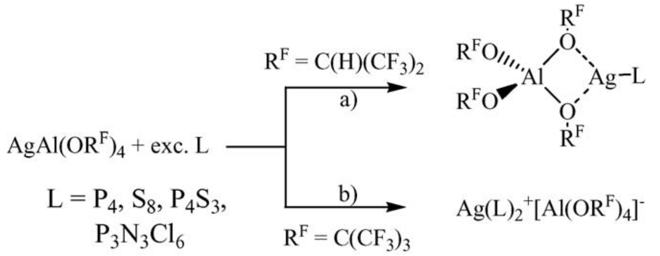
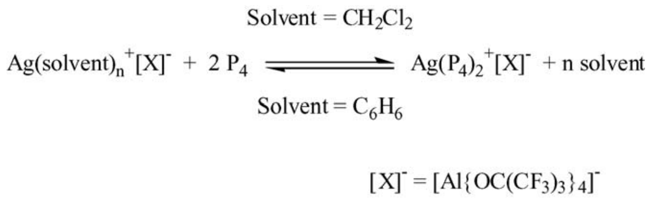


Fig. 13. Section of the solid-state structure of $[Ag(C_2H_4)_3]^+[Al(OC(CF_3)_3)_4]^-$.



Scheme 2. Counterion dependence of the structures of weakly-bound Lewis acid–base adducts of the silver cation.



Scheme 3. Solvent dependence of the stability of the structures of weakly-bound Lewis acid–base adducts of the silver cation.

reactions the Ag^+ cation coordinates two ligands L and forms $[Ag(L)_2]^+[Al(OC(CF_3)_3)_4]^-$ complexes with truly ionic structures (Scheme 2b).

(ii) Role of the solvent: When $Ag^+[Al(OC(CF_3)_3)_4]^-$ and 2 P_4 are mixed in CH_2Cl_2 the equilibrium of the reaction shown in Scheme 3 lies completely on the right hand side. However, replacing the weakly basic solvent CH_2Cl_2 for the towards Ag^+ more strongly coordinating solvent benzene C_6H_6 led to decomposition of the $Ag(P_4)_2^+$ cation, replacement of P_4 by C_6H_6 and formation of $Ag(C_6H_6)_2^+$. Thus in benzene the equilibrium lies completely on the left side [54].

To quantify these qualitative anion effects and especially the anion coordination (Scheme 3), we established the silver ion affinity scale (SIA) of several ligands towards the silver ion. Based on the solid-state structures, we formulated a comparative scale of the donor strength of the ligands $C_6H_5CH_3$ (Tol), 1,2-dichloroethane, CH_2Cl_2, P_4S_3, S_8, P_4 [55]. The structural basis for this assessment is shown in Fig. 14.

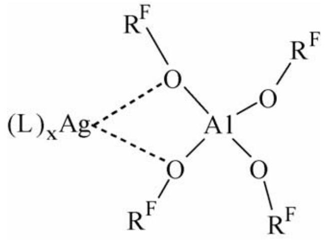


Fig. 14. Silver coordination in the Lewis acid–base complexes $(L)_xAgAl(OR^F)_4$ ($x = 1, 2$; $R^F = C(H)(CF_3)_2$, $C(CH_3)(CF_3)_2$).

Table 3
Ag—O bond valences s [v.u.] and SIA of several Lewis acid–base complexes[a]

Complex[a]	s		$\sum(s)$ = SIA
$(Tol)_2Ag\ [Al(OR')_4]$	0.119	0.118	0.236
$(C_2H_4Cl_2)_2Ag\ [Al(OR')_4]$	0.160	0.126	0.286
$(S_8)Ag\ [Al(OR')_4]$	0.252	0.080	0.332
$(P_4S_3)Ag\ [Al(OR')_4]$	0.190	0.179	0.379
$(P_3N_3Cl_6)Ag\ [Al(OR')_4]$	0.186	0.252	0.438
$(CH_2Cl_2)Ag\ [Al(OR'')_4]$	0.228	0.221	0.449
$(P_4)Ag\ [Al(OR'')_4]$	0.236	0.220	0.456

[a] $R' = C(H)(CF_3)_2$; $R'' = C(CH_3)(CF_3)_2$.

The stronger the interaction between the silver ion and the oxygen atoms of the anion, the weaker is the interaction of the ligand L with the silver ion and vice versa [55]. Thus, the strength of the Ag–L interaction is inversely proportional to the Ag–O distance. However, an ordering according to the average Ag–O bond lengths would imply a linear relation between bond energies and lengths, but it is known that this relation is better described by an exponential decrease of the bond energy with increasing bond lengths as included in I.D. Brown's bond valence method [88,89]. The higher the SIA value, the stronger the interaction between the silver ion and the oxygen atoms of the anion but the weaker the interaction of the ligand L with the silver ion. Table 3 shows the SIA and bond valences of several Lewis acid–base complexes.

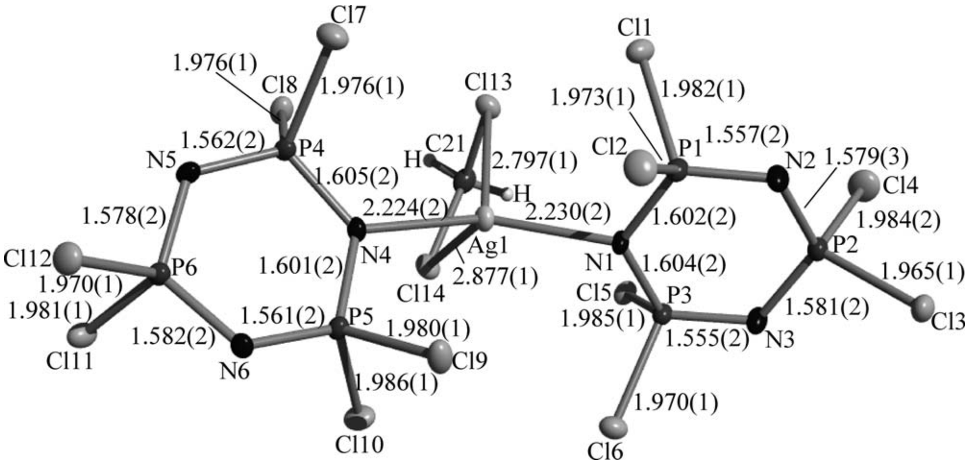


Fig. 15. Solid-state structure of the cation in $Ag(CH_2Cl_2)(N\text{-}P_3N_3Cl_6)_2[Al(OC(CF_3)_3)_4]$. Thermal ellipsoids were drawn at the 25% probability level [81].

Based on the SIA values of Table 3 the ligands can be ordered according to their donor strength: $C_6H_5CH_3 > 1,2$-dichloroethane $> S_8 > P_4S_3 > P_3N_3Cl_6 \approx CH_2Cl_2 \approx P_4$. The knowledge of the different SIA values allows one to predict whether certain complexes, especially with mixed ligands, can be formed or not: Only ligands with comparable SIA are able to form these kinds of mixed complexes. To give an example, the reaction of $Ag[Al(OR^F)_4]$ with $P_3N_3Cl_6$ in CH_2Cl_2 solution can lead to $Ag(P_3N_3Cl_6)_2^+$ (Fig. 11), as well as $Ag(CH_2Cl_2)(P_3N_3Cl_6)_2^+$, depending on the conditions during the crystallization (Fig. 15) [81]. This behavior is in agreement with the two similar SIA values of 0.449 and 0.438 (Table 3). However, all attempts to synthesize mixed complexes with P_4S_3 and S_8 (SIA = 0.370 versus 0.332, Table 3) failed and only the more stable $Ag(S_8)_2^+$ was formed [90].

4. Highly electrophilic cations

The present section attends to another major field of WCA-chemistry: highly electrophilic non-metal cations and reactive intermediates, which are otherwise at least very difficult or even impossible to synthesize and stabilize in condensed phases. Again, some additional information may be gained from mass spectrometric experiments as well as Q.M. calculations. Due to the coordinating ability (see also Section 3.6) of $[Al(OR^F)_4]^-$ with $R^F = C(H)(CF_3)_2$, $C(CH_3)(CF_3)_2$), reactions with P–X cations such as $P_2X_5^+$ (X = Br, I), led to an immediate decomposition of the anion. Thus, for the preparation of highly electrophilic cations the least coordinating and chemically most robust $[Al(OC(CF_3)_3)_4]^-$ and $[((F_3C)_3CO)_3Al–F–Al(OC(CF_3)_3)_3]^-$ anions were exclusively used.

Silver salt metathesis reactions as presented in this section provide an alternative approach to polyatomic non-metal cations. The latter cations are conventionally prepared by direct oxidation with strong Lewis acids or one/two electron oxidizers such as PtF_6, WCl_6, MF_5 (M = As, Sb, Nb, Au) [91,92] or AlX_3 (X = Cl, Br, I) [92] and transition metal halides/oxohalides.

4.1. Binary phosphorus-halogen cations

In the course of our investigations directed to the preparation of the still unknown homopolyatomic phosphorus cations we – fortuitously – found a simple approach to generate new binary phosphorus halogen cations. The knowledge on cationic or neutral binary P–X-species where X may be F, Cl, Br, I is still very sparse and limited to P^VX_5 (X = F, Cl), $P^VX_4^+$ (X = F–I) [93], $P^{III}X_3$ (X = F–I), $P^{III}{}_2I_5^+$ [94–96], $P^{II}{}_2X_4$ (X = F, Cl, I) and P_3X_5 (X = F, I [97]) (Fig. 16).

Solution studies showed the additional existence of small amounts of the phosphorus rich cage molecules P_4Br_2 and P_7I_3 in CS_2 solutions of P_4 and X_2 mixtures (X = Br, I). Structural data are only available for a few of these types, i.e. for the binary P–X cations only for PX_4^+ (X = Cl–I) [93] and $P_2I_5^+$ [94–96]. Binary phosphorus-iodine cations are very electrophilic and $P_2I_5^+$ immediately decomposed the EF_6^- counterions when prepared from P_2I_4 and $I_3^+EF_6^-$ (E = As, Sb) at −78 °C [95,96]. This kind of decomposition can be avoided by the use of the weakly basic $[Al(OC(CF_3)_3)_4]^-$ anion. Thus, a silver-salt metathesis of $Ag[Al(OC(CF_3)_3)_4]$ with PX_3 resulted in the formation of the highly reactive "$X_2P–X–Ag^+$" perhaps the closest possible approximation to the unknown free "PX_2^+" intermediates, which were previously only investigated in the gas phase [98]. Likely the active ingredient of such reactions is the $(CH_2Cl_2)Ag-X-PX_2^+$ cation shown in Fig. 17.

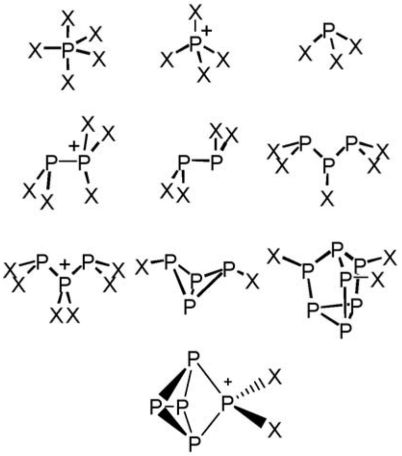


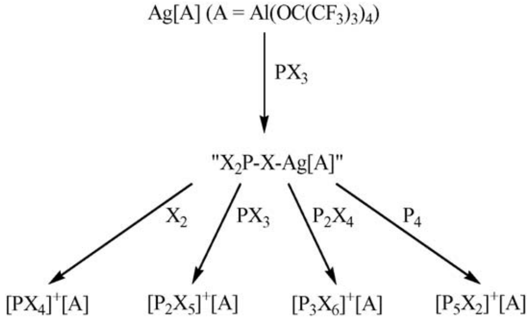
Fig. 16. Known neutral or cationic binary P–X-species (X = F, Cl, Br, I); note that some compounds only exist with one type of X.

This formal "PX_2^+" equivalent is a good PX_2^+ source and reacted with X_2, PX_3 and P_4 to quantitatively give stable but highly electrophilic and soluble PX_4^+, $P_2X_5^+$ [50], phosphorus rich $P_5X_2^+$ [50,52,53], as well as subvalent $P_3I_6^+$ [51] salts of the weakly basic $[Al(OC(CF_3)_3)_4]^-$ anion (Scheme 4).

Thus, the preparation of $[PX_4]^+$-salts (X = Br, I) with the $[Al(OC(CF_3)_3)_4]^-$ counterion is possible (Fig. 18). Recent results show that this reaction can be extended to the $[AsBr_4]^+$-salt [99,100]. These solid EX_4^+-salts are stable at room temperature for days. This stability may be contrasted by the absence of experimental evidence for PI_5 and $AsBr_5$ while $AsCl_5$ decomposes already at about −50 °C [101]. Similarly solid $PI_4^+[MF_6]^-$ (M = As, Sb) decomposes already at 0 °C [102].

Similarly, using two equivalents of PX_3 for the reaction, $P_2X_5^+$-salts (X = Br, I) were prepared (Fig. 19).

Dissolved $P_2X_5^+$ is fluxional on the time scale of ^{31}P NMR spectroscopy and disproportionates for X = I into reduced $P_3I_6^+$



Scheme 4. Reactions of the "PX_2^+" intermediate. For $P_3X_6^+$, X may be I for the other cations Br and I.

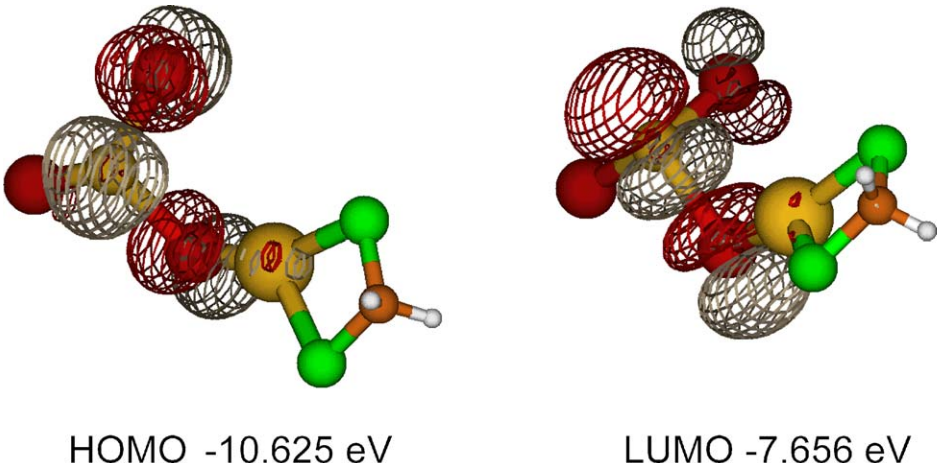


Fig. 17. Frontier orbitals of $(CH_2Cl_2)Ag\text{-}Br\text{-}PBr_2^+$ – the hypothetic source of the "PX_2^{+}" intermediate.

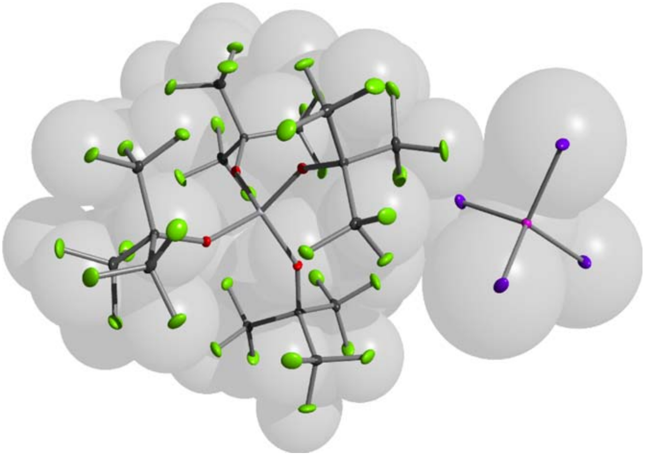


Fig. 18. Section of the solid-state structure of $[PI_4]^+[Al(OC(CF_3)_3)_4]^-$. Superposition of a space filling and a 25% probability ellipsoid model.

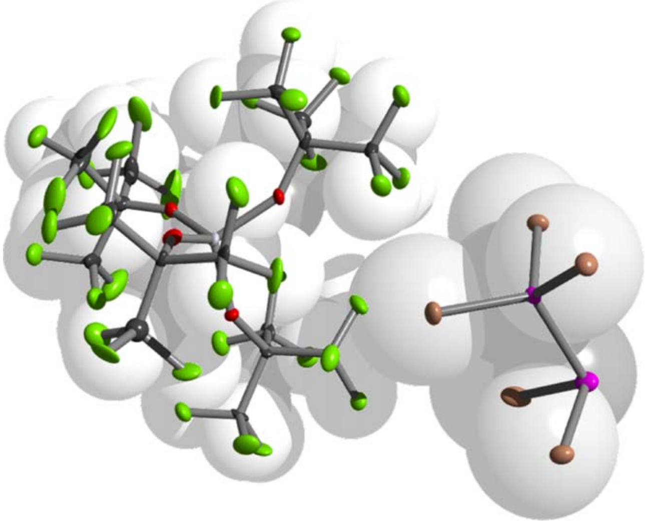


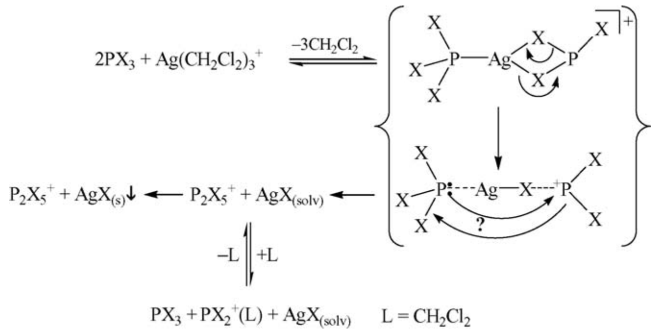
Fig. 19. Section of the solid-state structure of $[P_2Br_5]^+[Al(OC(CF_3)_3)_4]^-$. Superposition of a space filling and a 25% probability ellipsoid model.

and an oxidized species that was assigned as PI_4^+ [50]. $P_2Br_5^+$ is even more fluxional than $P_2I_5^+$ and is probably in equilibrium with $PBr_2^+(CH_2Cl_2)$ and PBr_3 (Scheme 5).

Due to this equilibrium, $P_2Br_5^+$ serves as a "PBr_2^{+}" source and reacts with insertion into the P_4 cage to give $P_5Br_2^+$ and PBr_3 [52]. However, the amount of free EX_2^+ available in the equilibrium in Scheme 5 is highest for the (hypothetical) $As_2Br_5^+$. Therefore, we did not succeed to prepare an $As_2Br_5^+$ salt but rather observed the immediate decomposition of the counterion due to the $AsBr_2^+(CH_2Cl_2)$ available in the equilibrium [100].

Unlike other oxidative methods, the silver salt metathesis approach also allows one to stabilize reduced subvalent cations. Thus, the interaction of the "PI_2^{+}" intermediate with P_2I_4 results in formation of the subvalent $P_3I_6^+$ cation (av. valency: 2.33), a derivative of the poorly characterized P_3I_5 [97]. Fig. 20 shows a section of the solid-state structure of $[P_3I_6]^+[(R^FO)_3Al\text{–}F\text{–}Al(OR^F)_3]^-$ ($R^F = C(CF_3)_3$), $[P_3I_6]^+[Al(OC(CF_3)_3)_4]^-$ is only marginally stable in the solid state.

The synthesis of $P_5X_2^+$ (X = Cl, Br, I) [50,52,53] salts with $[Al(OC(CF_3)_3)_4]^-$ revealed that the "PX_2^{+}" intermediate likely reacts with insertion into the P–P bond of P_4. The $P_5X_2^+$ cations are the first phosphorus rich binary P–X cations known and include a hitherto unknown phosphorus cage. Probably they are the closest approximation to the as yet unknown (on a preparative scale) homopolyatomic phosphorus cations, i. e.



Scheme 5. Proposed mechanism for the formation of the $P_2X_5^+$ cations.

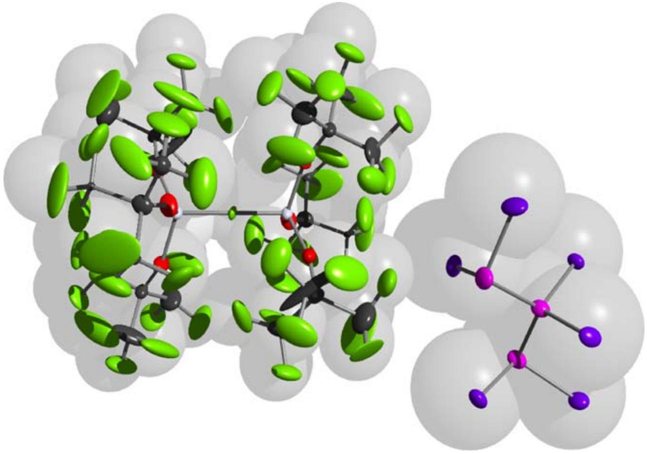


Fig. 20. Section of the solid-state structure of $[P_3I_6]^+[(CF_3)_3CO)_3Al–F–Al(OC(CF_3)_3)_3]^-$. Superposition of a space filling and a 25% probability ellipsoid model.

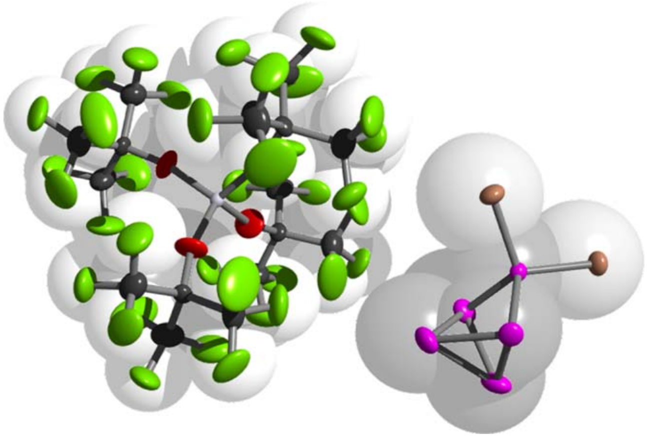
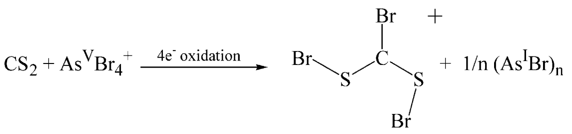


Fig. 21. Section of the solid-state structure of $[P_5Br_2]^+[Al(OC(CF_3)_3)_4]^-$. Superposition of a space filling and a 25% probability ellipsoid model.

"P_5^+". Fig. 21 shows a section of the solid-state structure of $[P_5Br_2]^+[Al(OC(CF_3)_3)_4]^-$.

4.2. Simple carbenium ions

In the course of our investigations into new arsenic-halogen-cations we fortuitously prepared a very simple but yet electronically very interesting carbenium ion: the $CS_2Br_3^+$ cation [99] (Fig. 22), which may be obtained by the quantitative reaction of $AsBr_4^+$ with CS_2 yielding $CS_2Br_3^+$ and a polymeric As^IBr (Eq. (3)).



$$CS_2 + As^VBr_4^+ \xrightarrow{4e^- \text{ oxidation}} [BrS\text{–}C(Br)\text{–}SBr]^+ + 1/n\,(As^IBr)_n \quad (3)$$

In this compound, $CS_2Br_3^+$ forms a planar 10 π-system. The six relevant π-orbitals (five occupied and one unoccupied, HF/TZVPP level) are shown in Fig. 23 as a projection along its C_s mirror plane.

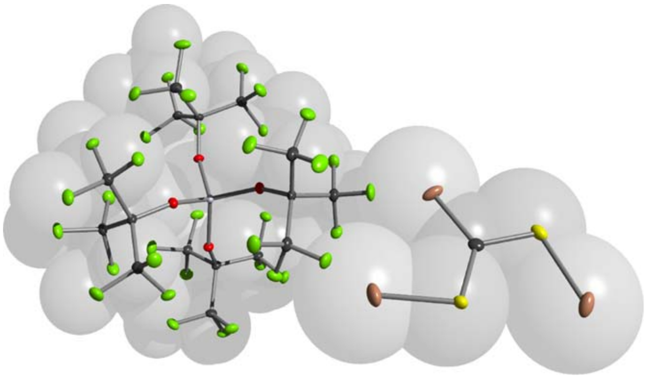


Fig. 22. Section of the solid-state structure of $[CS_2Br_3]^+[Al(OC(CF_3)_3)_4]^-$.

The C–Br bond length in $CS_2Br_3^+$ is very close to that expected for the simple CBr_3^+ cation (1.817 versus 1.813 Å (MP2/TZVPP)) and thus it appeared likely that simple binary carbon-halogen cations such as CX_3^+ may also be accessible by metathesis of CX_4 with Ag[A].

Small, highly-reactive carbon-based cations such as CX_3^+ (X = F–I) and others are frequently observed in fragmentation reactions of gaseous ions in the mass spectrometer and are thought to be reactive intermediates in organic synthesis. The closest structurally characterized approximations of this kind are Me_2CF^+ [103], $C(OH)_3^+$ and $(H_3CO)C(H)X^+$ salts (X = F, Cl) [104]. However, the heavier CX_3^+ cations with X = Cl–I were only prepared as long lived intermediates at −78 °C in SO_2ClF solution [105,106]. From recent computational work [107] it became clear that, contrasting earlier conclusions [105], cations bearing the heavier halogens should be thermodynamically more stable and less electrophilic than those with X = F, Cl [105,106]. Therefore we decided to examine the reaction of CI_4

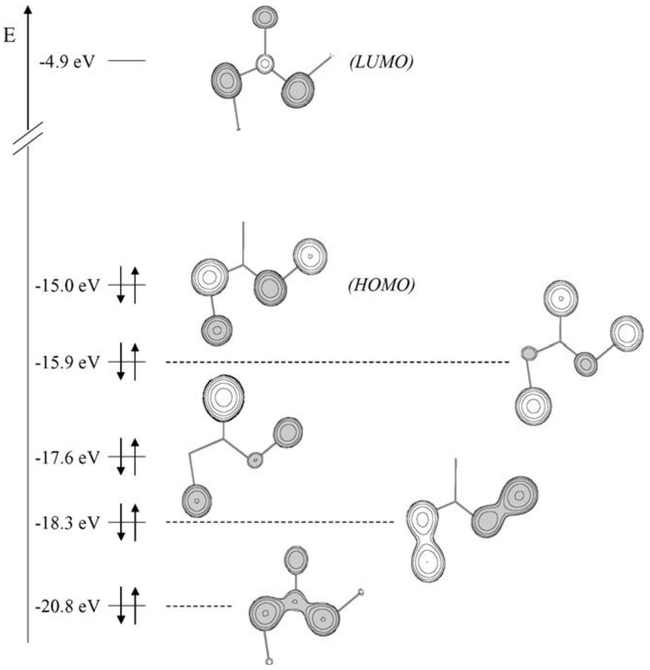


Fig. 23. The six π-MOs of $CS_2Br_3^+$ cation with their energies in (eV) shown as a projection along the mirror plane of the cation (HF/TZVPP level).

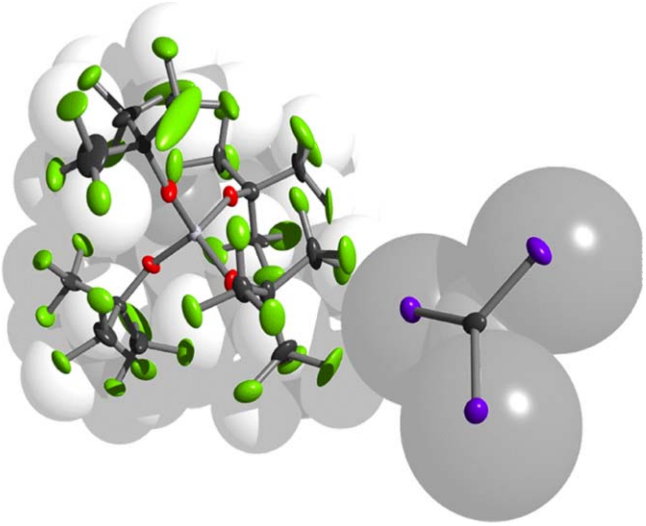


Fig. 24. Section of the solid-state structure of $[CI_3]^+[Al(OC(CF_3)_3)_4]^-$. Superposition of a space filling and a 25% probability ellipsoid model.

and $Ag[Al(OR^F)_4]$ with the goal to prepare $CI_3^+[Al(OR^F)_4]^-$ (and AgI). For the successful preparation of $CI_3^+[Al(OR^F)_4]^-$, the complete exclusion of light and the use of carefully purified diiodine free CI_4 is absolutely necessary; given this, the reaction is quantitative and the structure of $CI_3^+[Al(OR^F)_4]^-$ is shown in (Fig. 24) [108].

CI_3^+ was the first structurally characterized binary C–X-carbenium ion (X = H, F, Cl, Br, I). Approximately at the same time of our successful preparation of CI_3^+, Schrobilgen and coworkers presented CCl_3^+ and CBr_3^+ salts of the $[Sb(OTeF_5)_6]^-$ anion at the 2003 ACS Meeting in New Orleans that are published now [109]. Experimental and computational work finally showed that the Lewis acidity of the CX_3^+ cations decreases from F to I while it increases in the same direction for the isoelectronic BX_3 Lewis acids. To compare the Lewis acidities of BX_3 and CX_3^+ the fluoride ion affinity (FIA) is a well established measure (Table 4). The higher the FIA, the stronger is the Lewis acid.

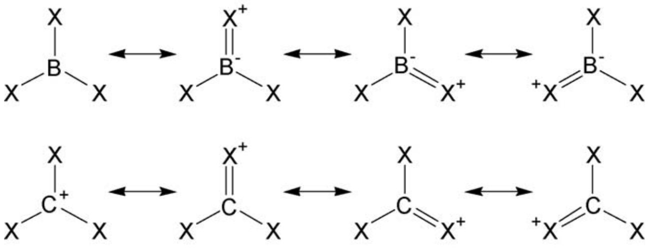
The data in the table includes solvation energies (COSMO model) and thus one may directly compare the Lewis acidities of the isoelectronic BX_3 and CX_3^+ particles in CH_2Cl_2 solution. CI_3^+ has about the same (very high) acidity as BBr_3 and BI_3, however, CF_3^+ is an exceedingly aggressive Lewis acid with little hope to be stabilized in condensed phases while BF_3 is a long known and only mild Lewis acid. Reasons for this discrepancy may be found in the more favorable charge delocalization of the heavier CX_3^+ cations while a similar stabilization for the boron halides involves charge separation and formation of a formal B^- center as shown in Scheme 6 [110].

Table 4
Fluoride ion affinities (FIAs) for CX_3^+ and BX_3 (X = H, F, Cl, Br, I)

X	$FIA(CX_3^+)$[a] in CH_2Cl_2[b]	$FIA(BX_3)$[a] in CH_2Cl_2[b]
H	501	164
F	497	225
Cl	359	279
Br	343	307
I	302	322

[a] MP2/TZVPP (kJ mol^{-1}).

[b] COSMO solvation model.



Scheme 6. Possible mesomeric structures of CX_3^+ and BX_3 (X = F–I).

The driving force for such an interaction is smaller in BX_3 and thus trends in the Lewis acidities of the isoelectronic CX_3^+ and BX_3 particles are opposite and follow, for CX_3^+, the trend expected by simple electronegativity arguments, with the less electronegative heavier halogens Cl to I providing a much greater stabilization than F [110].

4.3. Decomposition pathways of the $[Al(OC(CF_3)_3)_4]^-$ anion

As already mentioned at the end of Section 2, we repeatedly observed that $[Al(OR^F)_4]^-$ decomposed in the presence of very electrophilic cations such as $P_2X_5^+$ (X = Br, I) or Ag^+/PCl_3 or $SiCl_4$ mixtures with formation of the fluoride bridged $[(R^FO)_3Al–F–Al(OR^F)_3]^-$ anion [50,51]. Therefore we were interested to understand the pathway of that decomposition. Generally two different possibilities exist: the electrophilic cation attacks either the oxygen atom, the most basic site of the anion, or one of the 36 peripheral fluorine atoms (Scheme 7).

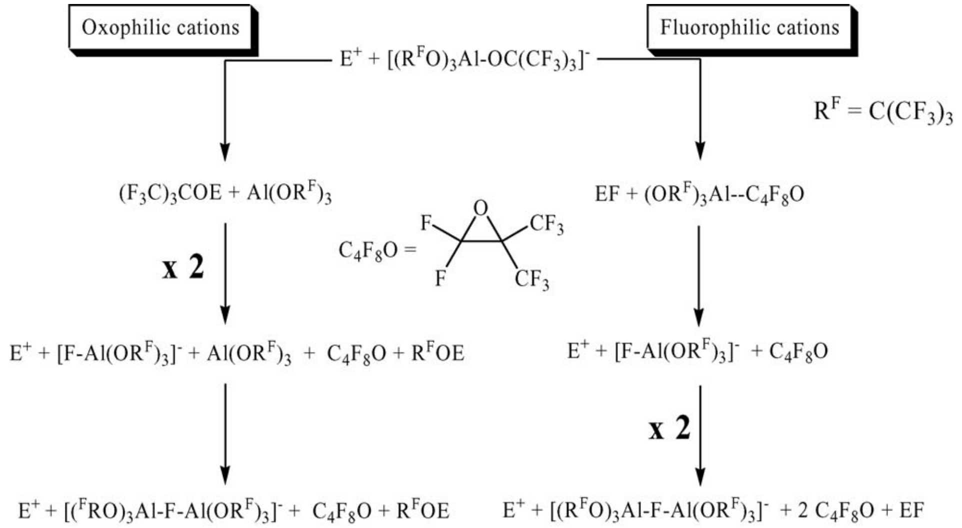
Oxophilic cations such as $P_2Cl_5^+$ initially attack one of the four O atoms and abstract an alkoxide group. The resulting R^FO-PCl_2 has been detected in low temperature ^{31}P NMR studies as a decett [111]. The generated $Al(OR^F)_3$ Lewis acid then abstracts an F^- ion from the R^FO-PCl_2 that is in close proximity and the formed $[F–Al(OR^F)_3]^-$ and $Al(OR^F)_3$ then give the fluoride bridged anion.

More fluorophilic cations such as $SiMe_3^+$, BI_2^+ or PBr_4^+ abstract one of the peripheral fluorine atoms. This attack is followed by a rearrangement of the alkoxy group and formation of a Lewis acid–base adduct of $Al(OR^F)_3$ and the epoxide $CF_2(O)C(CF_3)_2$. In the following step the epoxide is replaced by another abstracted fluoride ion from another $[Al(OR^F)_4]^-$ anion thereby forms the $[FAl(OR^F)_3]^-$ anion. This anion may now react with a second $Al(OR^F)_3$ by formation of the stable fluoride bridged $[(OR^F)_3Al–F–Al(OR^F)_3]^-$ anion.

Thus the decomposition may proceed by

(i) Ligand (R^FO^-) abstraction or
(ii) Fluoride ion abstraction.

The thermodynamic stability of the $[Al(OR^F)_4]^-$ and $[(R^FO)_3Al–F–Al(OR^F)_3]^-$ anion and that of another only CF_3



Scheme 7. Different decomposition pathways of the $[Al(OC(CF_3)_3)_4]^-$ anion depending on the nature of the electrophilic cation E^+.

Table 5
Calculated reaction enthalpies and free energies for selected decomposition reactions

Decomposition reaction	$\Delta H_{(g)}^\circ$	$\Delta G_{(g)}^\circ$	ΔG° (CH_2Cl_2)
$Al(OR^F)_4^- \rightarrow F^- + C_4F_8O \rightarrow Al(OR^F)_3$ [112]	603	561	316
$(R^FO)_3Al–F–Al(OR^F)_3^- \rightarrow F^- + C_4F_8O \rightarrow Al(OR^F)_2–F–Al(OR^F)_3$ [112]	674	645	379
$B(CF_3)_4^- \rightarrow F^- + F_2C \rightarrow B(CF_3)_3$ [112]	503 (509[a])	448 (458[a])	242
$Al(OR^F)_4^- + AsF_5 \rightarrow AsF_6^- + C_4F_8O \rightarrow Al(OR^F)_3$	179	180	91
$(R^FO)_3Al–F–Al(OR^F)_3^- + AsF_5 \rightarrow AsF_6^- + C_4F_8O \rightarrow Al(OR^F)_2–F–Al(OR^F)_3$	250	264	154
$B(CF_3)_4^- + AsF_5 \rightarrow AsF_6^- + F_2C \rightarrow B(CF_3)_3$	79 (74[a])	67	18
$Al(OR^F)_4^- \rightarrow Al(OR^F)_3 + OR^{F-}$	342		
$(R^FO)_3Al–F–Al(OR^F)_3^- \rightarrow Al_2(OR^F)_5F + OR^{F-}$	441 (363)[b]		
$B(CF_3)_4^- \rightarrow B(CF_3)_3 + CF_3^-$	490		

All values are given in $kJ\,mol^{-1}$.
[a] Value in parentheses taken from [113].
[b] kinetic (thermodynamic) value. See original publications [53,111].

based anion, i.e. $[B(CF_3)_4]^-$, with respect to (i) and (ii) are compared in Table 5.

Note that the decomposition reactions have been assessed through isodesmic reactions and should therefore be reliable (table and reactions deposited). Comparison to Table 5 shows that fluoride ion abstraction is easier for the $[B(CF_3)_4]^-$ borate, while ligand abstraction is the preferred process for the $[Al(OR^F)_4]^-$ anion. Which of the two mechanisms proceeds, depends on the bond enthalpies of the formed E–F or E–OR compounds and the strengths of the Al–O or C–F bonds in the $[Al(OR^F)_4]^-$ anion.

5. Stabilization of weakly-bound complexes – thermodynamic considerations on the special properties of WCA salts

The aim of the following section is to explain why cations like those described in Sections 3 and 4 can be stabilized in condensed phases and to provide a tool to predict whether there is any chance of forming a certain target cation or not. To keep the models in this section easy to understand, some rather rough approximations were made. Therefore the presented values should not be taken as absolute, but the general trend definitely holds (often through error cancellation in the models).

5.1. Gas phase cations in condensed phases?

WCAs may be used to crystallize salts of gas phase cations and help to verify the delicate quantum chemical calculations of these cations that often reside in shallow minima on an extended potential energy surface. An illustrative example of this approach is the geometry of the AgP_8^+ cation, which in 1995 was produced in the gas phase and analyzed by MS. Initial calculations suggested a $Ag(\eta^1\text{-}P_4)_2^+$ to be the global minimum [114]. However, recently it was shown by a X-ray crystal structure that the global minimum is best described as $Ag(\eta^2\text{-}P_4)_2^+$ (Section 3.3) [54]. This example clearly shows that conclusions drawn from gas phase studies are delicate and, if possible, should be validated in the condensed phase.

5.1.1. *"Pseudo gas phase conditions" in condensed phases*

To stabilize a given gas phase cation in condensed phases a counterion and usually also a solvent have to be introduced. However, the introduction of an anion is connected with the lattice energy (LE), which strongly influences the properties of any salt. Since the elements differentiating the gas phase and solid-state conditions are the anion–cation interactions (by definition these are zero in the gas phase), the major interaction in the solid state is the strong electrostatic field that results from the close contact of the charged species (=>lattice energy). According to the simple Kapustinskii equation (Eq. (4)) [115] lattice energies are inversely proportional to the sum of the ionic radii (or volumes in the modified Jenkins equation) [116] of the constituting ions [116]. Thus, the larger the ions, the lower the lattice energies of the salts, and the lower is the electrostatic interaction between them [117].

$$U = -\frac{120200\nu z^+ z^-}{r^+ + r^-}\left(1 - \frac{34.5}{r^+ + r^-}\right)\ \text{kJ mol}^{-1} \qquad (4)$$

where U is the lattice energy, r^+, r^- the ionic radii of the ions, ν the number of ions in the unit formula, and z^+, z^- are the charge of the ions.

For salts with large anions, the lattice energies are very low in comparison to classical salts like Li^+F^- or Cs^+F^-. In fact, they are so low that the lattice energy of the WCA salt $Ag(S_8)_2{}^+[Al(OR^F)_4]^-$, **I**, ($R^F = C(CF_3)_3$) of 326 kJ mol^{-1} in Table 6 approaches the values of the sublimation enthalpies of molecular solids of comparable atomic weight, i.e. that of C_{60} or C_{70} of 175 and 200 kJ mol^{-1} (cf. M_r(**I**) = 1588 versus 721 (C_{60}) and 841 (C_{70}) g mol^{-1}) [56,118–120]. Other interactions like dispersive van der Waals, dipole–dipole interactions, etc. are of at least one order of magnitude smaller than the lattice energies and, therefore, can be neglected in this 0th order approach [121].

Comparing the lattice energy of $Ag(S_8)_2{}^+[Al(OR^F)_4]^-$ (326 kJ mol^{-1}) to the lattice energies of typical salts such as Li^+F^- (1036 kJ mol^{-1}) and Cs^+F^- (740 kJ mol^{-1}) clearly shows that the environment of the ions in $Ag(S_8)_2{}^+[Al(OR^F)_4]^-$ more closely resembles to the situation in the gas phase (or a molecular solid) than the strong electrostatic field within a classical salt, e.g. Li^+F^- or Cs^+F^-. Large WCAs have diameters in the nanometer scale, i.e. 1.25 nm for $[Al(OR^F)_4]^-$ [38] or 1.20 nm for $[Sb(OTeF_5)_6]^-$ [34], and thus considerably separate anions and cations, which effectively diminishes coulombic interactions. Due to the highly fluorinated surface of most WCAs and the very low polarizability of elemental-fluorine bonds, dispersive interactions are weak and not structure determining. Therefore, the environment of the cations within the framework of an ensemble of large and very weakly-coordinating anions such as $Al(OR^F)_4{}^-$, $Sb(OTeF_5)_6{}^-$ or other suitable WCAs may be called "*pseudo gas phase conditions*" in the solid state [56].

Table 6
Thermochemical volume and lattice potential energies of several M^+X^- salts

Salt	$V_{\text{therm.}}$ (Å^3)	$U_{\text{pot.}}$ (kJ mol^{-1})
Li^+F^-	27	1036[a]
Cs^+F^-	43	740[a]
$Cs^+[AsF_6]^-$	128	568[b]
$Cs^+[Al(OR^F)_4]^-$[c]	776	362[b]
$Ag(S_8)_2{}^+[Al(OR^F)_4]^-$[c]	1169	326[b]

[a] Experimental value [118].
[b] Calculated from the thermochemical volumes [116].
[c] $R^F = C(CF_3)_3$.

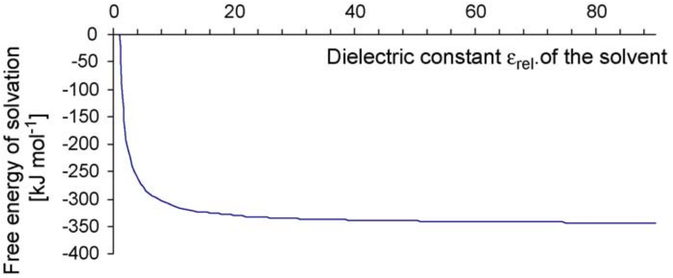


Fig. 25. Plot of the free solvation energy calculated with the Born equation for an univalent ion of radius 200 pm versus the dielectric constant of the solvent [122].

In solution "*pseudo gas phase conditions*" are also present: While salts with smaller anions are usually only soluble in polar media with high dielectric constants such as ethanol ($\varepsilon_{\text{rel.}} = 24$), CH_3CN ($\varepsilon_{\text{rel.}} = 35$), water ($\varepsilon_{\text{rel.}} = 81$), or even strong acids such as anhydrous HF ($\varepsilon_{\text{rel.}} = 83$), WCA salts are generally very soluble and allow the use of very non-polar solvents with low dielectric constants $\varepsilon_{\text{rel.}} = 2$–9 (toluene to CH_2Cl_2) [118]. In these low dielectric media solutions, the solvation energies that stabilize the dissolved ions with respect to the gas phase are greatly reduced (see Fig. 25 for a plot of the free solvation energy versus the dielectric constant of the solvent).

From Fig. 25 it may be noted that the effect of decreasing the DC of the solvent from HF ($\varepsilon_{\text{rel.}} = 83$) to ethanol ($\varepsilon_{\text{rel.}} = 24$) is much smaller than for changing ethanol for CH_2Cl_2 ($\varepsilon_{\text{rel.}} = 9$) or toluene ($\varepsilon_{\text{rel.}} = 2$); in low dielectric media only a minimal stabilization by solvation energies is provided for the ions. Thus, by using WCAs in combination with low dielectric media, gas phase conditions (with no stabilization by solvation) are also approximated in solution.

In summary one may therefore note: By the combination of WCAs and low dielectric media gas phase conditions are approximated in solution and in the solid state. To account for this property the expression "*pseudo gas phase conditions*" was coined [56].

5.2. *The effect of the anion size on lattice and solvation enthalpies*

The above mentioned high solubility of WCA salts obviously results from the decreased lattice potential enthalpies of these salts incorporating large counterions with diameters exceeding the one nanometer scale. Generally a salt is soluble if the sum of the free energies of solvation of the cation A^+ and the anion X^- is larger than the lattice potential enthalpy of the salt A^+X^- (Fig. 26):

If the anion X^- is very large and thus the lattice energy low, solvation Gibbs energies are larger than the lattice energies and hence the salt of a WCA is highly soluble.

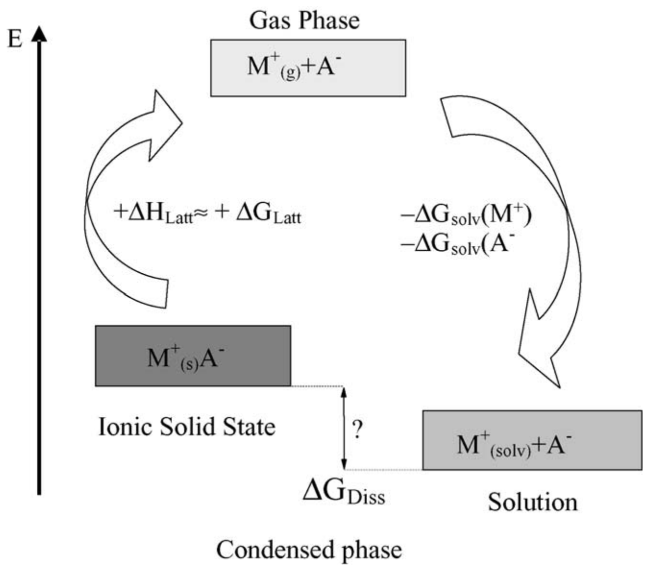


Fig. 26. Born–Fajans–Haber cycle for the dissolution of a soluble M^+A^- salt.

An example: Consider the effect of the anion size upon dissolution of an $A^+[X]^-$ salt in a non-polar solvent. A^+ shall be kept constant and roughly approximates K^+ (potassium/silver cation). $[X]^-$ is now changed from very small (halide anion) to very large (large WCA). Three non-polar solvents with dielectric constants of 2.2, 4.8 or 8.9 shall be approximated (i.e. similar to toluene, $CHCl_3$ or CH_2Cl_2). Now the lattice potential enthalpy is plotted against the sum of the free solvation energies of A^+ and $[X]^-$, all of which are dependent on the thermochemical volume of the salt $A^+[X]^-$ [123].

From Fig. 27 one notes that the solvation and lattice energies decrease rapidly with increasing size of the ions. The shapes of solvation and lattice energy curves differ: With increasing size of the anion the solvation energies relatively soon reach a plateau region and remain almost constant while the lattice energy decreases more steadily with increasing anion size. The less polar the solvent the later the intersection of the solvation energy with the lattice energy curve, which indicates the change from insoluble to soluble, is observed. This indicates that only very large anions X^- with a volume of larger than approximately 890 Å^3 induce a sufficiently low lattice energy to dissolve salts A^+X^- in toluene (dashed vertical line in Fig. 27). In more polar solvents such as $CHCl_3$ or CH_2Cl_2 the rough minimum size of the anion has to be less, that is 120 or 60 Å^3 (dashed vertical lines in Fig. 27). In agreement with this $M[Al(OR^F)_4]$ ($V_{therm.}$ = 762 Å^3) has some solubility in toluene but $M[BF_4]$ ($V_{therm.}$ = 77 Å^3) only in CH_2Cl_2. Of course these values should not be taken absolute and suffer from an exact evaluation of solvation effects, dispersion energies, temperature effects, etc.; however, the general trend holds: large WCAs lead to salts that are soluble in low dielectric solvents and that often are also soluble at very low temperatures.

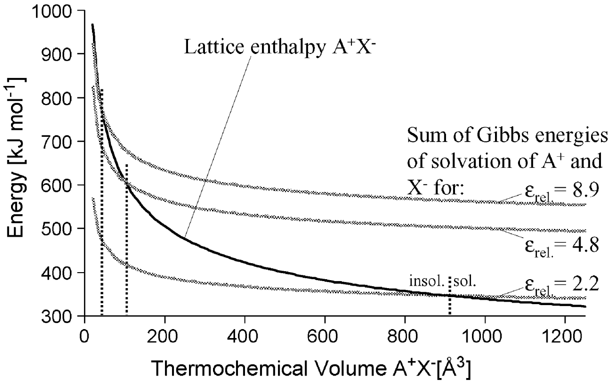
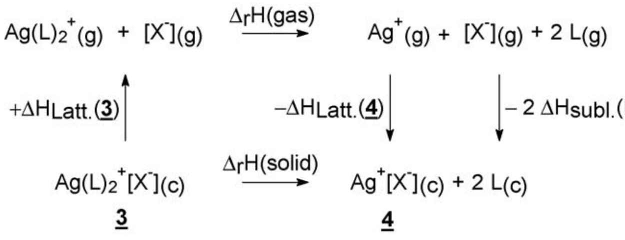


Fig. 27. Plot of the lattice enthalpy vs. the solvation Gibbs free energies for an A^+X^- salt. For the calculation the ionic radius of A^+ was kept constant at roughly that of a K^+/Ag^+ ion, and the ionic radius of X^- was changed from very small (halide) to very large (large WCA). The solvation enthalpies for A^+X^- in three non-polar solvents, with dielectric constants of 2.2, 4.8 or 8.9 (similar to toluene, $CHCl_3$ and CH_2Cl_2), were approximated.

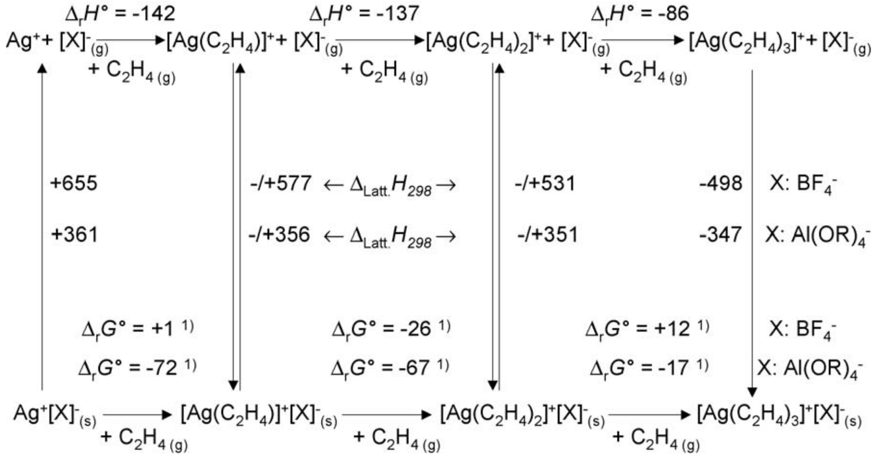
5.3. Stabilization of weakly-bound complexes

Apart from being weakly basic and stable to oxidation, another stabilizing term arises for weak Lewis acid–base adducts $M(L)_n{}^+[X]^-$ by using large counterions (M^+ = univalent cation, L = non charged weakly-bound ligand, X^- = suitable anion): The reduced gain in $M^+[X]^-$ lattice energy upon dissociation of $M(L)_n{}^+[X]^-$ into $M^+[X]^-$ and n L (see Scheme 8 for an example of a Born–Fajans–Haber cycle for the dissociation of an $Ag(L)_2{}^+[X]^-$ salt).

Let us explicitly consider two cases: $L = S_8$ and $[X]^- = [AsF_6]^-$ or $[X]^- = [Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) [56,58]. The calculated lattice potential enthalpies for $Ag(S_8)_2{}^+[X]^-$ are 393 and 327 kJ mol^{-1}, those of $Ag^+[X]^-$ are 586 and 361 kJ mol^{-1} (thermochemical volumes) [56,116]. The gas phase enthalpy $\Delta_r H$(gas) and the sublimation enthalpy of S_8 is the same in both cases, and therefore the only differences are due to the lattice energies. For $X = [AsF_6]^-$ the resulting gain in lattice energy upon dissociation is 193 kJ mol^{-1} while that for $X = [Al(OR^F)_4]^-$ is only 34 kJ mol^{-1}. Therefore, $Ag(S_8)_2{}^+[Al(OR^F)_4]^-$ is by 159 kJ mol^{-1} more stable against dissociation than the $[AsF_6]^-$ salt (as shown in Scheme 8). In other words, with the $[Al(OR^F)_4]^-$ anion one can stabilize $Ag(L)_2{}^+$ Lewis acid–base adducts of very weak bases L, for which the gas phase term $Ag(L)_{2(g)}{}^+ \rightarrow Ag_{(g)}{}^+ + 2L_{(g)}$ is up to 159 kJ mol^{-1} less endothermic than that with the $[AsF_6]^-$ anion.



Scheme 8. Born–Fajans–Haber cycle for the dissociation of a solid Lewis acid–base adduct $Ag(L)_2{}^+[X]^-$ into $Ag^+[X]^-$ and 2 L.



Scheme 9. Born–Fajans–Haber cycle for the formation of $[Ag(\eta^2\text{-}C_2H_4)_n]^+$ complexes; all energies given in kJ mol^{-1}; $^{(1)}$ contains 65 kJ mol^{-1} contribution to the Gibbs energy upon removal of free gaseous C_2H_4.

If the standard state of the ligand L in Scheme 8 is a gas, the contribution of the sublimation enthalpy $\Delta H_{\text{subl.}}(L)$, which enhances decomposition, is eliminated. For the above example $\Delta H_{\text{subl.}}(S_8) = 101$ kJ mol^{-1}, hence for two molecules of S_8 this is 202 kJ mol^{-1} in total. If the gas CO is used as a ligand, this destabilizing contribution is eliminated. Therefore one can prepare and characterize $Ag(CO)_2^+$ salts, although the gas phase dissociation enthalpy $\Delta H_{\text{diss.}}$ of $Ag(L)_{2(g)}^+$ giving $Ag_{(g)}^+$ and 2 $L_{(g)}$ is only 197 kJ mol^{-1} for L = CO (exp. value) [124], but 363 kJ mol^{-1} for L = S_8 (MP2/TZVPP) [56]. $\Delta(\Delta H_{\text{diss.}})$. This amounts to 363–197 = 166 kJ mol^{-1}, which is less than twice the sublimation enthalpy of L = S_8 (202 kJ mol^{-1}). This leads to the odd conclusion that (neglecting entropy) solid $Ag(S_8)_2^+[Al(OR^F)_4]^-$ is approximately 36 kJ mol^{-1} less stable towards dissociation into solid $Ag[Al(OR^F)_4]$ and solid S_8 than the (hypothetical) $Ag(CO)_2^+[Al(OC(CF_3)_3)_4]^-$ is towards decomposition into solid $Ag[Al(OR^F)_4]$ and gaseous CO. In agreement with this notion a $Ag(CO)_2^+$ salt with the $[B(OTeF_5)_4]^-$ anion, comparatively smaller than $[Al(OR^F)_4]^-$, was prepared in 1994 [13,125].

Another example underlines this conclusion: Ag^+ complexes of C_2H_4 (Section 3.5, Fig. 13) are of fundamental interest and, since they are difficult to stabilize in condensed phases, were intensively investigated by theory and mass spectrometry (MS) [87]. Again, considering two different counter anions $[X]^- = [BF_4]^-$ or $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) for the $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ cation, the calculated lattice potential enthalpies (thermochemical volumes) [116] for $[Ag(C_2H_4)_3]^+[X]^-$ are 498 and 347 kJ mol^{-1}, those of $Ag^+[X]^-$ are 655 and 361 kJ mol^{-1}.

The gas phase enthalpy $\Delta_r H$(gas) of C_2H_4 is the same in both cases, and, therefore, the only differences are due to the lattice energies. For $[X]^- = [BF_4]^-$ the resulting gain in lattice energy upon dissociation is 157 kJ mol^{-1} while that for $[X]^- = [Al(OR^F)_4]^-$ is only 14 kJ mol^{-1}. Therefore $[Ag(C_2H_4)_3]^+[Al(OR^F)_4]^-$ is 143 kJ mol^{-1} more stable against dissociation than the $[BF_4]^-$ salt. From Scheme 9 it is not surprising that $[Ag(C_2H_4)_3][BF_4]$ with a comparatively small $[BF_4]^-$ anion is only stable up to 0 °C in an atmosphere of C_2H_4 [85]. By contrast, $Ag(C_2H_4)_3^+[Al(OR^F)_4]^-$ may safely be handled in a glove box at ambient temperature with no signs of decomposition for several days.

Despite many earlier MS experiments, only $Ag(\eta^2\text{-}C_2H_4)_x^+$ complexes with $x = 1$, 2 are known on experimental grounds in the gas phase [87]. The formation and structural characterization of an $Ag(\eta^2\text{-}C_2H_4)_3^+[Al(OR^F)_4]^-$ salt with $x = 3$ was therefore surprising. However, the analysis of the Born–Haber cycle in Scheme 9 shows that the environment provided by the solid-state arrangement of the $[Al(OR^F)_4]^-$ anions is very close to the gas phase in thermal equilibrium at low temperature. The gas phase addition of a third molecule of gaseous C_2H_4 to gaseous $Ag(\eta^2\text{-}C_2H_4)_2^+$ was impossible in the MS presumably due to the low binding Gibbs energy of the third ligand ($\Delta G_{298} = -55$ kJ mol^{-1}). This points to the failure to remove the energy stored in translational, vibrational and rotational levels which in sum can be larger than the binding energy of the third ligand thus preventing coordination. In WCA salts, this internal energy can be removed through intermolecular vibrational coupling, thus allowing one to reach equilibrium conditions at a given temperature. In this respect, the *pseudo gas phase conditions* provided by the best WCAs in the solid state are even better than the gas phase inside a mass spectrometer where thermal equilibrium conditions are difficult to reach. Hence good WCAs such as the $[Al(OR^F)_4]^-$ or the fluoride bridged $[(R^FO)_3Al\text{–}F\text{–}Al(OR^F)_3]^-$ ($R^F = C(CF_3)_3$) anion shown above are the closest approximation to the ideal but hypothetical *non-coordinating anion*.

6. Conclusion and outlook

This article presents a cross section through the work with WCAs of type $[Al(OR^F)_4]^-$ ($R^F = C(H)(CF_3)_3$, $C(CH_3)(CF_3)_2$, $C(CF_3)_3$) or the fluoride bridged $[(R^FO)_3Al\text{–}F\text{–}Al(OR^F)_3]^-$ ($R^F = C(CF_3)_3$) and highlights their possibilities as well as their limits. It could be demonstrated that starting with the facile preparation of $Li[Al(OR^F)_4]$ several metal or non-metal cations can be introduced into the system in high yields. This allowed the subsequent syntheses of various starting materials for different challenges in WCA chemistry. Using weakly-coordinating fluorinated alkoxyaluminate anions, it is possible to prepare and characterize several very weak Lewis acid–base complexes of the silver cation in the condensed phase, e.g. silver adducts of molecular S_8, P_4S_3, P_4 or C_2H_4. Several of these cations were initially observed in the gas phase by mass spectrometry. Now stable salts of such species are known and therefore may be seen as a bridge between gas phase and condensed phase chemistry. Furthermore, it was also possible to stabilize cations hitherto not described in the gas phase, e.g. $Ag(C_2H_4)_3^+$. Only a $Ag(C_2H_4)_2^+$ is known by MS experiments. This points to the failure to release translational energy in the mass spectrometric gas phase experiment by rotational or vibrational relaxation processes as is possible in condensed phases. Thus, with a suitable WCA counterion even species too delicate to be prepared in the gas phase may be synthesized in condensed phases. One such compound is $Ag(C_2H_2)_4^+$, which we recently crystallized with the $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$) counterion [126].

Moreover, it was possible to stabilize a variety of highly electrophilic cations, such as PX_4^+, $P_2X_5^+$, $P_5X_2^+$, $P_3I_6^+$ or $CS_2Br_3^+$ and CX_3^+. All of the phosphorus based cations were likely derived from a Ag^+/PX_3 = "PX_2^+" intermediate (X = Br, I), which similarly to CX_3^+ [108] are gas phase cations [98]. Thus, we may conclude by stating that gas phase cations may be stabilized in the condensed phase, if suitable weakly-coordinating and chemically robust counterions are introduced.

Nevertheless, one should be aware of the limits of these anions: As soon as the donor strengths of ligands reside far below the donor strength of the chosen solvent or the anion respectively, one will observe solvates or anion coordination instead of the targeted complex as detailed in Section 3.6. This means that the solvent has to be replaced by another, less coordinating one. The choice of a suitable solvent very often turns out to be the crucial problem.

Amongst the reactive cations the main problem is decomposition of the anion or the solvent. Hence, $SiCl_3^+$ and PCl_2^+ are not stable with the $[Al(OR)_4]^-$ anion ($R = C(CF_3)_3$) in solution. By contrast the interaction of such cations often led, as described in Section 2, to salts of the $[((F_3C)_3CO)_3Al–F–Al(OC(CF_3)_3)_3]^-$ anion. Stability, however, is not an absolute but a relative term depending clearly on the environment: Many compounds are stable in the solid state at ambient temperature over weeks but start to decompose at −20 °C in solution. $P_2X_5^+$ and EX_4^+ salts of $[Al(OC(CF_3)_3)_4]^-$ are illustrative examples (E = P, As; X = Br, I) [50]. However, with conventional counterions like MF_6^- (M = As, Sb) salts of the latter cations decompose in the solid state at low temperatures (between 0 and −78 °C) [95,127].

Therefore, it is absolutely necessary to develop new, easily accessible, chemically robust but very weakly-coordinating anions. The small but relatively stable $[FAl(OR^F)_3]^-$ anion [128] provides an example for a compound that could extend the solid state stability of some reactive cation salts unstable with the homoleptic $[Al(OR^F)_4]^-$ WCA. Our long term goal in this direction is the preparation of the least coordinating and chemically most robust WCAs at the cheapest price. The future will show which applications of simple but fundamental cations may prosper from the availability of such very special anions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ccr.2005.10.023.

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[120] The sublimation enthalpies of C_{60} and C_{70} are rather high due to π-stacking. However, we did not find sublimation enthalpies for similarly heavy molecules like $Ag(S_8)_2^+[Al(OR^F)_4]^-$ and therefore decided to use the sublimation enthalpies of the heaviest molecules that we could find, i.e. C_{60} and C_{70}.

[121] Thus the coulombic part of the lattice energy of Na^+Cl^- is approximately +867 kJ mol^{-1}, the repulsion part −92 kJ mol^{-1}, the dispersion part +18 kJ mol^{-1} and the zero point energy −6 kJ mol^{-1} (see: U. Müller, Anorganische Strukturchemie, Teubner Studienbücher, 2nd ed., 1992, p. 38). The neglect of other than coulombic interactions holds especially

when the lattice energies shall be used in a suitable Born Haber cycle where salts are employed on both sides of the equation. Due to the similar nature of the additional dispersive van der Waals, dipole–dipole interactions they cancel on both sides, e.g. cf. with Scheme 7.

[122] The simple Born equation was used to approximate the free solvation enthalpy: $\Delta G_{\text{solv.}} = 0.5\{z^2eN_a/4\pi\varepsilon_0 r\}\{1 - 1/\varepsilon_{\text{rel.}}\}$. z = charge of the ion, e = charge of the electron, N_a = Avogadro's constant, ε_0 = dielectric constant of the vacuum, r = ionic radius of the ion in question, $\varepsilon_{\text{rel.}}$ = relative dielectric constant of the medium. For the plot, r was arbitrarily set to 2.0 Å.

[123] For the estimation of lattice versus solvation free energy effects the size of the cation A^+ was arbitrarily set to a thermochemical volume of 10 Å^3 equivalent to an ionic radius of about 1.3 Å and thus similar to that of K^+. Then the volume (radius) of the anion X^- was changed from 10 Å^3 (1.3 Å) to 1250 Å^3 (6.7 Å) and solvation as well as lattice energies were calculated for A^+X^-. Free energies of solvation were approximated by the Born equation, lattice potential enthalpies by the Jenkins' and Passmore's volume based equation.

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