The Facile Preparation of Weakly Coordinating Anions: Structure and Characterisation of Silverpolyfluoroalkoxyaluminates $AgAl(OR_F)_4$, Calculation of the Alkoxide Ion Affinity

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Abstract: Purified $LiAlH_4$ reacts with fluorinated alcohols HOR_F to give $LiAl(OR_F)_4$ ($R_F = -CH(CF_3)_2$, **2a**; $-C(CH_3)(CF_3)_2$, **2b**; $-C(CF_3)_3$, **2c**) in 77 to 90% yield. The crude lithium aluminates $LiAl(OR_F)_4$ react metathetically with AgF to give the silver aluminates $AgAl(OR_F)_4$ ($R_F = -CH(CF_3)_2$, **3a**; $-C(CH_3)(CF_3)_2$, **3b**; $-C(CF_3)_3$, **3c**) in almost quantitative yield. The solid-state structures of solvated **3a–c** showed that the silver cation is only weakly coordinated (CN(Ag) = 6–10; CN = coordination number) by the solvent and/or weak cation–anion contacts Ag–X (X = O, F, Cl, C). The strength of the Ag–X contacts of **3a–c** was analysed by Brown's bond-valence method and then compared with other silver salts of weakly coordinating anions (WCAs), for example $[CB_{11}H_6Cl_6]^-$ and $[M(OTeF_5)_n]^-$ (M = B, Sb, $n = 4$, 6). Based on this quantitative picture we showed that the $Al\{OC(CF_3)_3\}_4^-$ anion is one of the most weakly coordinating anions known. Moreover, the $AgAl(OR_F)_4$ species are certainly the easiest WCAs to access preparatively (20 g in two days), additionally at low cost. The Al–O bond length of $Al(OR_F)_4^-$ is shortest in the sterically congested $Al\{OC(CF_3)_3\}_4^-$ anion—which is stable in H_2O and aqueous HNO_3 (35 weight%)—and indicates a strong and highly polar Al–O bond that is resistant towards heterolytic alkoxide ion abstraction. This observation was supported by a series of HF-DFT calculations of OR^-, $Al(OR)_3$ and $Al(OR)_4^-$ at the MPW1PW91 and B3LYP levels (R = CH_3, CF_3, $C(CF_3)_3$). The alkoxide ion affinity (AIA) is highest for R = CF_3 (AIA = 384 ± 9 kJ mol^{-1}) and R = $C(CF_3)_3$ (AIA = 390 ± 3 kJ mol^{-1}), but lowest for R = CH_3 (AIA = 363 ± 7 kJ mol^{-1}). The gaseous $Al(OR_F)_4^-$ anions are stable against the action of the strong Lewis acid AlF_3 (g) by 88.5 ± 2.5 ($R_F = CF_3$) and 63 ± 12 kJ mol^{-1} ($R_F = C(CF_3)_3$), while $Al(OCH_3)_4^-$ decomposes with −91 ± 2 kJ mol^{-1}. Therefore the presented fluorinated aluminates $Al(OR_F)_4^-$ appear to be ideal candidates when large and resistant WCAs are needed, for example, in cationic homogenous catalysis, for highly electrophilic cations or for weak cationic Lewis acid/base complexes.

Keywords: ab initio calulations · alkoxides · aluminum · lithium · silver · weakly coordinating anions

Introduction

The stabilisation of highly electrophilic metal- and nonmetal cations as well as weak Lewis acid base complexes of metal cations is commonly achieved by replacing the normal counterion by a large and weakly coordinating anion (WCA).[1, 2] Consequently much work has been dedicated to the syntheses of new WCAs with a focus on the tailoring of cationic transition metal polymerisation catalysts.[1c, 3] Other recent uses of WCAs include attempts to prepare a free R_3Si^+ silylium ion,[4] the generation of stable fullerene cations,[5] the protonation of very weak bases (e.g., benzene),[1a] the formation of stable $[Ag(CO)]^+$ complexes,[6] the synthesis of a tricoodinated $[R_2Al(Do)]^+$ cation (Do = donor)[7] and the crystallisation of a binary silver-selenium complex of the weakly basic metastable Se_6 allotrope.[8] Several types of WCAs have now been established: halogenated and trifluoromethylated carboranes $[CB_{11}X_nH_{12-n}]^-$ ($n = 1-12$, X = F, Cl, Br, I, CH_3, CF_3),[9] polyfluorinated tetraarylborates $B(Ar_F)_4^-$ ($Ar_F = C_6F_5$, $C_6H_3(CF_3)_2$)[3b, 10] and tetra-[11, 12] and hexateflatometallates $M(OTeF_5)_n^-$ ($n = 4$, M = B; $n = 6$, M = As, Sb, Bi, Nb).[13, 14] A recent development is the use of poly- (and per-) fluorinated alkoxy ligands OR_F that prevent C–H bond activation and produce a smooth nonadhesive surface of the anion, that is, in $Al\{OC(Ph)(CF_3)_2\}_4^-$,[15] $Al(OC_6F_5)_4^-$,[16] $Nb(OC_6F_5)_6^-$[16] and $Nb\{OC(H)(CF_3)_2\}_6^-$.[15] Only scarce structural information about $M^IAl(OR_F)_4$ is available; however, additional very recent work on the coordinating abilities of these aluminates as well as two solid-state structures are given in Strauss's succeeding paper in this issue.[22] Some of the most promising compounds, for example, $LiAl\{OC(CF_3)_3\}_4$, are

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nearly insoluble in weakly basic solvents such as CH_2Cl_2, toluene or hexane (as observed by the author) at room temperature. It is known that silver salts are more soluble than their lithium counterparts. Moreover, silver salts of WCAs are commonly used in metathesis reactions and, therefore, we decided to investigate the chemistry of the silver polyfluoroalkoxyaluminates $AgAl(OR_F)_4$ [$OR_F = OCH(CF_3)_2$ (HFIP), $OC(Me)(CF_3)_2$ (HFTB), $OC(CF_3)_3$ (PFTB)]. Herein we present the facile high-yield synthesis and characterisation of several $AgAl(OR_F)_4$ species and discuss the coordination chemistry of their silver cation towards weakly basic solvents, that is, toluene, CH_2Cl_2, 1,2-$Cl_2C_2H_4$ and 1,3-$(CF_3)_2C_6H_4$.

Results

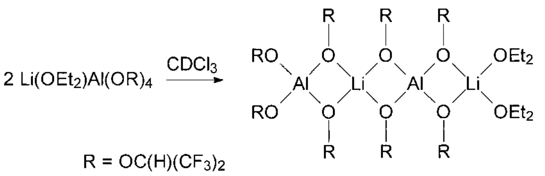
Syntheses: Two possible routes to $AgAl(OR_F)_4$ species were checked. The pathway as shown in Equations (1a)–(1c) involves the synthesis of a donor free trisalkoxyalane $Al(OR_F)_3$ (which are usually dimeric $Al_2(OR)_6$ species, e.g., R = *t*Bu).[17c] However, when "AlH_3"—generated in situ from $AlCl_3$ and $LiAlH_4$ in Et_2O at −78 °C—was treated with HO–C(H)$(CF_3)_2$ [Eq. (1a)] the rapid formation of the monomeric ether adduct Al(hfip)$_3$(OEt$_2$) (**1**-OEt$_2$; HFIP = OCH$(CF_3)_2$), as a distillable liquid, was observed. The compound **1**-OEt$_2$ was briefly noted in an earlier publication; however, no characterisation was given.[18] All attempts to remove the coordinated solvent by heat and exposure to a dynamic vacuum only led to a distillation at 65–70 °C and 1.5×10^{-2} mbar. A 70 eV EI-MS of **1**-OEt$_2$ did not show the molecular ion nor the $[Al(hfip)_3]^+$ peak, but the preferential loss of F, CF_3 or OC(H)$(CF_3)_2$ that appeared in 1.9, 16.7 and 75.8 % relative intensity and implies that **1** is a strong Lewis acid and that **1**-OEt$_2$ prefers other decomposition pathways rather than the loss of OEt$_2$. In earlier work[18] it was shown by NMR spectroscopy that Al(hfip)$_3$ coordinates two additional ethylenediamine molecules to give a pentacoordinate Al center. This parallels recent observations made for the homologous compound In(hftb)$_3$ (HFTB = OC$(CH_3)(CF_3)_2$), which is only isolable as a donor adduct and can coordinate up to three additional pyridine ligands.[19] To avoid the use of the coordinating solvent (OEt$_2$), one equivalent of $AlMe_3$ in heptane was added to HO–C(H)$(CF_3)_2$ (3 equiv) in toluene at 60 °C [Eq. (1a)], but this only gave an intensely red-violet solution. Removal of all volatiles gave a dark oil, the NMR spectra of which indicated the partial decomposition of the HFIP ligand (Al–F bond formation?). Efforts to separate the obtained mixture failed. Another difficulty arose from the attempted preparation of [{Ag(hfip)}$_n$] by reacting Me_3Si–HFIP with AgF [Eq. (1b)].

$$AlR_3 + 3\,HOR_F \rightarrow Al(OR_F)_3 + 3\,R\text{–}H \ (R = H,Me) \tag{1a}$$

$$R_FO\text{–}SiMe_3 + AgF \rightarrow 1/n[\{AgOR_F\}_n] + Me_3SiF \tag{1b}$$

$$Al(OR_F)_3(OEt_2) + 1/n[\{MOR_F\}_n] \rightarrow M\,Al(OR_F)_4(OEt_2) \ (M = Li, Ag) \tag{1c}$$

All reactions led to a dark brown inseparable mixture of products, which is likely to be due to the known instability of the silver-oxygen bond. However, reaction of Al(hfip)$_3$(OEt$_2$) (**1**-OEt$_2$) with donor free Li–OC(H)$(CF_3)_2$—prepared from HO–OC(H)$(CF_3)_2$ and *n*BuLi in hexane—according to Equation (1c) led to the formation of LiAl(hfip)$_4$(OEt$_2$) (**2a**-OEt$_2$). Compound **2a**-OEt$_2$ gave simple NMR spectra in the presence of diethyl ether that suggest the occurrence as an ion pair $[Li(OEt_2)_4]^+[Al(hfip)_4]^-$ in solution. However, recording the NMR spectra in pure $CDCl_3$ showed an aggregation, an interpretation of which is given in Equation (2).



(2)

Upon heating to 60 °C the two separate lines at δ^7Li (25 °C) = −0.6 and −0.9 coalesced and collapsed to a broad single line at δ^7Li (60 °C) = −0.8. Similarly the two separate OC(H)$(CF_3)_2$ lines at δ^1H (25 °C) = 4.57 and 4.68 coalesce at 60 °C giving one signal at δ^1H (60 °C) = 4.59. Comparison with the dimeric solid-state structure of **2a**[22] and with the solid-state structure of an isolated [Li{Al(hfip)$_4$}$_2$] complex presented in the succeeding publication[22] supports the interpretation given in Equation (2). All attempts to remove the coordinated molecule of OEt$_2$ by heat and exposure to a dynamic vacuum failed (150 °C, 1×10^{-3} mbar). Therefore the synthesis of $AgAl(OR_F)_4$ species according to Equations (3a) and (3b) was investigated.

$$LiAlH_4 + 4\,HOR_F \rightarrow LiAl(OR_F)_4 + 4\,H_2 \tag{3a}$$

$$LiAl(OR_F)_4 + AgF \rightarrow AgAl(OR_F)_4 + LiF \tag{3b}$$

Previous studies showed that the reaction in Equation (3 a) is capable of yielding all the desired $LiAl(OR_F)_4$ species,[15a, 20, 22] and initially best results were reported by using two equivalents of HOR_F and one equivalent of $LiAlH_4$ in F-113 (Cl_2FC–CF_2Cl) as a solvent.[21] However, this stoichiometry appeared unusual and might be due to the use of an inactive commercially available $LiAlH_4$ starting material. To avoid these problems the $LiAlH_4$ was purified by dissolution in OEt$_2$, filtration and removal of all volatiles at 80 °C and 5×10^{-3} mbar (constant weight). Utilising this $LiAlH_4$, four equivalents of HOR_F and heating the suspension under reflux in toluene led to the lithium aluminates LiAl(hfip)$_4$ (**2a**), LiAl(hftb)$_4$ (**2b**) and LiAl(pftb)$_4$ (**2c**) (HFIP = OCH$(CF_3)_2$; HFTB = OC$(CH_3)(CF_3)_2$; PFTB = OC$(CF_3)_3$), which are scarecely soluble at room temperature, in 77 to 90 % yield. The advantage of using purified $LiAlH_4$ was very recently confirmed by S. Strauss et al.;[22] however, for **2a** a higher yield of 94 % is reported by using F-113 as a solvent.[22] Compounds **2a**–**c** can be purified by sublimation at about 150 °C and 1×10^{-3} mbar, but already the crude product was sufficient for the following metathesis reaction with an excess of AgF (about 1.3–2.0 mol) to give the respective silver aluminates [Eq. (3b)]. Mixtures of AgF and **2c** in toluene or CH_2Br_2 alone did not lead to a reaction, while the combination of both (various compositions) led to a species which was NMR spectroscopically assigned as $[Ag(CH_2Br_2)(C_7H_8)][Al(pftb)_4]$. The synthesis of $AgAl(OR_F)_4$ species was more easily achieved with ultrasonic enhancement and utilising either of CH_2Cl_2, $1,2\text{-}Cl_2C_2H_4$ or $1,3\text{-}(CF_3)_2C_6H_4$ as a solvent. CH_2Cl_2 is especially convenient as a solvent, since the starting materials $LiAl(OR_F)_4$ and AgF are almost insoluble in CH_2Cl_2 at ambient temperature, while the silver compounds are highly soluble. Reaction (3b) led to the silver aluminates $[Ag(C_7H_8)_2Al(hfip)_4]$ (**3a**-$(C_7H_8)_2$), $[Ag(C_2H_4Cl_2)_2Al(hfip)_4]$ (**3a**-$(C_2H_4Cl_2)_2$), $[Ag(CH_2Cl_2)Al(hftb)_4]$ (**3b**-CH_2Cl_2), $[Ag(CH_2Cl_2)Al(pftb)_4]$ (**3c**-CH_2Cl_2), $[Ag(C_2H_4Cl_2)_3][Al(pftb)_4]$ (**3c**-$(C_2H_4Cl_2)_3$) and $[Ag\{C_6H_4(CF_3)\}_2Al(pftb)_4]$ (**3c**-$C_6H_4(CF_3)_2$), in about 95 % yield. Recrystallisation of **3a** from toluene gave crystals at low temperatures and mounting these crystals on a diffractometer while keeping the temperature below $-10\,^{\circ}C$ showed them to be **3a**-$(C_7H_8)_2$. Reaction of **3b**-CH_2Cl_2 with trace amounts of water gave the Al-O-Al bridged $[Ag(CH_2Cl_2)]_2[O\{Al(hftb)_3\}_2]$ (**4**), only characterised by its X-ray crystal structure [Eq. (4)].

$$2\,[Ag(CH_2Cl_2)Al(hftb)_4] + H_2O \rightarrow [\{Ag(CH_2Cl_2)\}_2][O\{Al(hftb)_3\}_2] + 2\,HO(HFTB) \quad (4)$$

However, in contrast to $Al(hfip)_4^-$ and $Al(hftb)_4^-$, the $Al(pftb)_4^-$ anion (silver and lithium salts)—incorporating the most acidic parent fluorinated alcohol $HOC(CF_3)_3$ employed [$pK_a = 5.4$, vs 9.3 (HFIP) and 9.6 (hftb)][22]—is stable in water as shown by a ^{27}Al NMR spectrum of this anion in water recorded seven days after dissolution; only one line at $\delta^{27}Al = 33.9$ (six coordinate aluminium, i.e., $Al(OH_2)_6^{3+}$, appears at about $\delta = 0$) was observed. Moreover it was impossible to determine the aluminium contents of spectroscopically pure salts of the $Al(pftb)_4^-$ anion hydrolised with aqueous HNO_3 (35 weight %) by back titration with $ZnSO_4$ and EDTA (six attempts); this strongly suggests the stability of this anion in half concentrated aqueous HNO_3.

Crystal structures: Details of the crystallographic studies are listed in Table 6 in the Experimental Section. The structural parameters of all silver aluminates are only described in this section and will be analysed in the succeeding paragraph.

*$[Ag(C_7H_8)_2Al(hfip)_4]$ (**3a**-$(C_7H_8)_2$)*: Two independent molecules of **3a**-$(C_7H_8)_2$ are found within the triclinic unit cell of this compound (space group $P\bar{1}$) which only differ with respect to the position of the methyl groups of the two bidentate coordinated toluene molecules per silver atom (see Figure 1). The silver cation has a 6+2 coordination formed by four Ag–C contacts at 2.363(5) to 2.647(6) Å, two Ag–O contacts at 2.541(3) to 2.715(3) Å and two weak Ag–F contacts at 3.377(6) to 3.505(7) Å. The orientation of the $Ag(C_7H_8)_2$ moieties is reminiscent to a sandwich complex. Two sets of Al–O bond lengths are found in the anion: $d(Al\text{–}O_{di}) = 1.718(3)$ Å (average, dicoordinate) and $d(Al\text{–}O_{tri}) = 1.751(3)$ Å (average, tricoordinate). The coordination of the aluminium atom is distorted tetrahedral as can be seen from the range of the O-Al–O bond angles of 96.9(1) to 115.7(1)°.

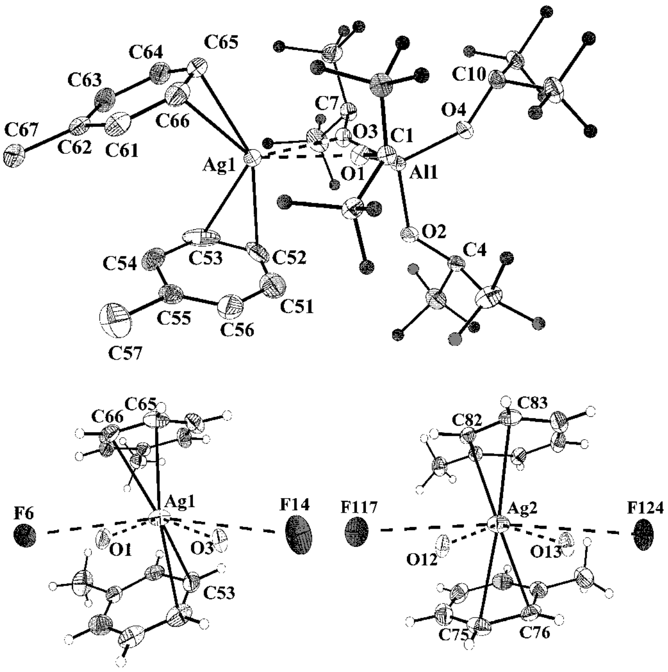


Figure 1. Solid-state structure of the $[Ag(C_7H_8)_2Al(hfip)_4]$ (**3a**-$(C_7H_8)_2$). Only one of the two independent molecules is shown. Since the main difference between the two molecules is found in the primary coordination environment of the silver atoms, drawings of both cations are shown. Thermal ellipsoids were drawn at the 25 % probability level, fluorine atoms (in dark grey) were drawn as circles with an arbitrary size. Selected bond lengths [Å] and bond angles [°]: Ag1–O1 2.596(2), Ag1–O3 2.599(2), Ag2–O12 2.541(2), Ag2–O13 2.715(2), Ag1–C65 2.363(5), Ag1–C52 2.435(6), Ag1–C53 2.593(6), Ag1–C66 2.647(6), Ag2–C83 2.416(4), Ag2–C76 2.469(5), Ag2–C75 2.484(5), Ag2–C82 2.496(4), Ag1–F6 3.374(6), Ag1–F14 3.482(6), Ag2–F117 3.397(6), Ag2–F124 3.505(6), Al1–O1 1.757(3), Al1–O2 1.715(3), Al1–O3 1.753(3), Al1–O4 1.725(2), Al2–O11 1.713(3), Al2–O12 1.746(3), Al2–O13 1.746(3), Al2–O14 1.718(3), *d*(C–O) 1.379 (average); Al1-O1-C1 127.1(2), Al1-O2-C4 133.0(2), Al1-O3-C7 129.0(2), Al1-O4-C10 143.8(2), Al2-O11-C101 153.8(2), Al2-O12-C104 128.5(2), Al2-O13-C107 127.5(2), Al2-O14-C110 126.7(2).

*$[Ag(C_2H_4Cl_2)_2Al(hfip)_4]$ (**3a**-$(C_2H_4Cl_2)_2$)*: The molecular compound **3a**-$(C_2H_4Cl_2)_2$ crystallises in the monoclinic space group $P2_1/c$ ($Z = 4$, see Figure 2). The silver ion is coordinated by two oxygen atoms of the anion at 2.492(2) and 2.576(2) Å and four chlorine atoms of two chelating $C_2H_4Cl_2$ solvent molecules at 2.7408(13) to 2.8260(12) Å. The local coordination environment of the Ag^+ ion is distorted octahedral. There are no Ag–F contacts below 3.353(2) Å; however, the Ag^+ ion resides in a "hole" formed by two oxygen atoms and four CF_3 groups, while the hydrogen atoms of the HFIP ligands point away from the Ag^+ ion. Two sets of Al–O bond lengths are observed: for the dicoordinate oxygen atoms $d(Al\text{–}O_{di}) = 1.726(2)$ Å (average) and for the tricoordinate oxygen atoms $d(Al\text{–}O_{tri}) = 1.751(2)$ Å (average). In the coordinated dichloroethane molecules, the C–Cl bond lengths range from 1.750(5) to 1.828(5) Å, which is close to the value found in gaseous $1,2\text{-}C_2H_4Cl_2$ (1.790 Å).[28] Four interionic hydrogen bonds between the hydrogen atoms of the dichloroethane ligands and the aluminate ion are found at $d(H\text{–}F) = 2.333(5)$, 2.661(5), 2.762(5) and 2.851(5) Å (sum of F and H van der Waals radii: 2.90 Å).

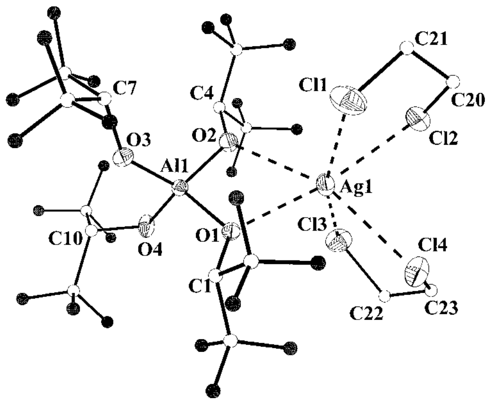


Figure 2. Solid-state structure of the $[Ag(C_2H_4Cl_2)_2Al(hfip)_4]$ (**3a**-$(C_2H_4Cl_2)_2$). Thermal ellipsoids were drawn at the 25% probability level, all hydrogen atoms were omitted for clarity, fluorine atoms (in grey) and carbon atoms (in white) were drawn as circles with an arbitrary size. Selected bond lengths [Å] and bond angles [°]: Ag1–O1 2.492(2), Ag1–O2 2.576(2), Ag1–Cl1 2.7408(13), Ag1–Cl3 2.7505(12), Ag1–Cl4 2.8203(12), Ag1–Cl2 2.8260(12), Al1–O4 1.724(2), Al1–O3 1.727(2), Al1–O2 1.744(2), Al1–O1 1.758(2), d(C–O) 1.384 (average); Al1-O1-C1 124.3(2), Al1-O2-C4 129.4(2), Al1-O3-C7 137.7(2), Al1-O4-C10 128.6(2), O1-Al1-O2 97.46(10), Al1-O1-Ag1 101.31(8), Al1-O2-Ag1 98.59(9).

*$[Ag(CH_2Cl_2)Al(hftb)_4]$ (**3b**-CH_2Cl_2)*: Figure 3 shows a representation of the solid-state structure of the $[Ag(CH_2Cl_2)$-$Al(hftb)_4]$ molecule. Compound **3b**-CH_2Cl_2 crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The silver atom in **3b**-CH_2Cl_2 is eight coordinate and has a distorted dodecahedral ligation sphere. Ag1 has two Ag–O contacts at 2.377(5) and 2.386(4) Å, four Ag–F contacts at 2.849(11) to 2.931(10) Å from the aluminate anion and two chlorine atoms at d(Ag–Cl) = 2.613(2) and 2.874(3) Å from the unsymmetrically chelating CH_2Cl_2 molecule. The CF_3 groups of the two HFTB ligands coordinating to the silver atom (e.g., those incorporating O1 and O2) point towards Ag1, while the methyl groups reside at the back side with no contact to Ag1. Two distinct Al–O bond lengths and Al-O-C bond angles are found around the di- and tricoordinate oxygen atoms of the aluminate ion in **3b**-CH_2Cl_2: $d(Al{-}O_{di}) = 1.715(5)$ Å $< d(Al{-}O_{tri}) = 1.766(5)$ Å (average) and $(Al\text{-}O_{di}\text{-}C) = 142.9(4) > (Al\text{-}O_{tri}\text{-}C) = 137.8(4)$ (average). The coordination of the aluminium atom is distorted tetrahedral as can be seen from the range of the O-Al-O bond angles of 93.2(2) to 116.6(2)°.

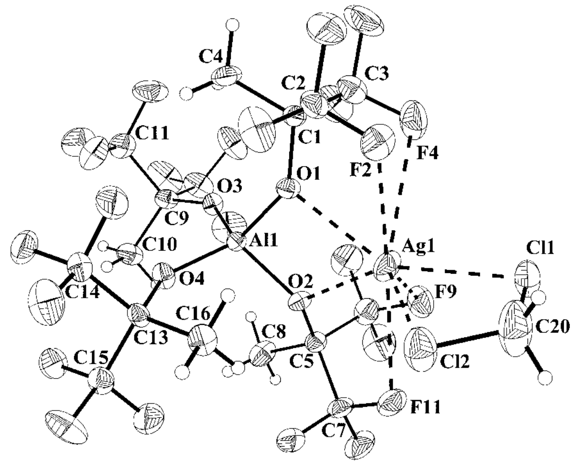


Figure 3. Molecular structure of $[Ag(CH_2Cl_2)Al(hftb)_4]$ (**3b**-CH_2Cl_2) in the solid state. Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths [Å] and bond angles [°]: Ag1–O2 2.377(5), Ag1–O1 2.386(4), Ag1–Cl1 2.613(2), Ag1–Cl2 2.874(4), Ag1–F2 2.857(10), Ag1–F4 2.931(11), Ag1–F9 2.924(10), Ag1–F11 2.849(11), Al1–O1 1.763(5), Al1–O2 1.768(5), Al1–O3 1.712(4), Al1–O4 1.717(5), Cl1–C 1.738(1), Cl2–C 1.663(11), d(C–O) 1.387(6) ± 0.010 (average), O1-Ag1-O2 65.2(2), Al1-O1-Ag1 100.0(1), Al1-O2-Ag1 100.1(1), O1-Al1-O2 93.2(2), Al1-O1-C1 138.0(4), Al1-O2-C5 137.6(4), Al1-O3-C9 143.8(4), Al1-O4-C13 141.9(4).

*$[Ag(C_2H_4Cl_2)_3][Al(pftb)_4]$ (**3c**-$(C_2H_4Cl_2)_3$)*: Compound **3c**-$(C_2H_4Cl_2)_3$ crystallises in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell; a view of the asymmetric unit is shown in Figure 4. In contrast to the molecular solid-state structures of **2a**, **3b**-(CH_2Cl_2), **3b**-$[C_6H_4(CF_3)_2]$ and **4**, compound **3c**-$(C_2H_4Cl_2)_3$ is a salt and consists of discrete $[Ag(C_2H_4Cl_2)_3]^+$ cations and $[Al(pftb)_4]^-$ anions that adopt a distorted CsCl structure. The Ag atom of the $[Ag(C_2H_4Cl_2)_3]^+$ cation is hexacoordinate with six Ag–Cl contacts to the bidentate $1,2\text{-}Cl_2C_2H_4$ ligands, in which the chlorine atoms form an irregular coordination polyhedron. The bond lengths d(Ag–Cl) range from 2.694(2) to 2.788(2) Å and with an average value of 2.742 Å. The shortest interionic contact to Ag1 is found at 4.319 Å (to Cl2′) and is purely nonbonding, while in the comparable $[Ag(CH_2Cl_2)_3]_2$-$[Ti(OTeF_5)_6]_2$ and $[Ag(CH_2Br_2)_3][Sb(OTeF_5)_6]$ complexes additional weak Ag–F contacts are present at 3.029(8) and 3.033(6) Å (Ti) or 3.196(7) Å (Sb).[14] Cl1 has one Cl–F contact at 3.249 Å, which is below the sum of the fluorine and chlorine van der Waals radii of 3.30 Å, and Cl3 and Cl5 have three weak Cl–F contacts at 3.34 (to Cl3), 3.41 (to Cl3) and 3.43 Å (to Cl5). The $[Ag(C_2H_4Cl_2)_3]^+$ cations are connected by five weak Cl–Cl′ contacts at 3.504–3.796 Å, which is about the sum of the isotropic Cl van der Waals radii of 3.60 Å, and form a chain (see Figure 4, right). The C–Cl bond lenghts in the cation range from 1.703(10) to 1.815(7) Å and are longest for Cl1 (1.815(7) Å) and Cl2 (1.780(6) Å), which both exhibit three Cl–Cl′ contacts. Shorter C–Cl bond lengths of 1.738 Å (average) are found for Cl3, Cl4, Cl5 and Cl6, which only have one weak Cl-Cl′ contact. The Al–O bond lengths and Al-O-C bond angles in the aluminate ion are equal and average to 1.725 ± 0.011 Å and 149.5 ± 1.4°. The coordination around the aluminium atom is almost tetrahedral and the O-Al-O bond angles range from 106.5(2) to 114.8(2)°.

*$[Ag\{C_6H_4(CF_3)_2\}Al(pftb)_4]$ (**3c**-$C_6H_4(CF_3)_2$)*: A representation of the solid-state structure of **3c**-$C_6H_4(CF_3)_2$ (monoclinic, space group $P2_1/c$, $Z = 4$) is shown in Figure 5. The silver atom in the molecule **3c**-$C_6H_4(CF_3)_2$ is η^3-coordinated by the carbon atoms of the electron poor $1,3\text{-}(CF_3)_2C_6H_4$ molecule (d(Ag–C) = 2.496(8) to 3.005(8) Å) and also has several weak Ag–O and Ag–F contacts; the coordination number of silver is ten. The two Ag–O contacts are 2.558(5) and 2.581(7) Å and the five Ag–F contacts range from 2.436(9) to 3.026(8) Å. The silver atom resides in position just off centre of the triangular face of the $Al(pftb)_4^-$ tetrahedron (i.e., the face spanned by the ligands incorporating O2, O3 and O4). The Al–O bond lengths and Al-O-C bond angles in the aluminate range from 1.684(5) to 1.769(4) Å and 147.0(4) to 166.9(5)°. The shorter Al–O bond lengths are associated with wide

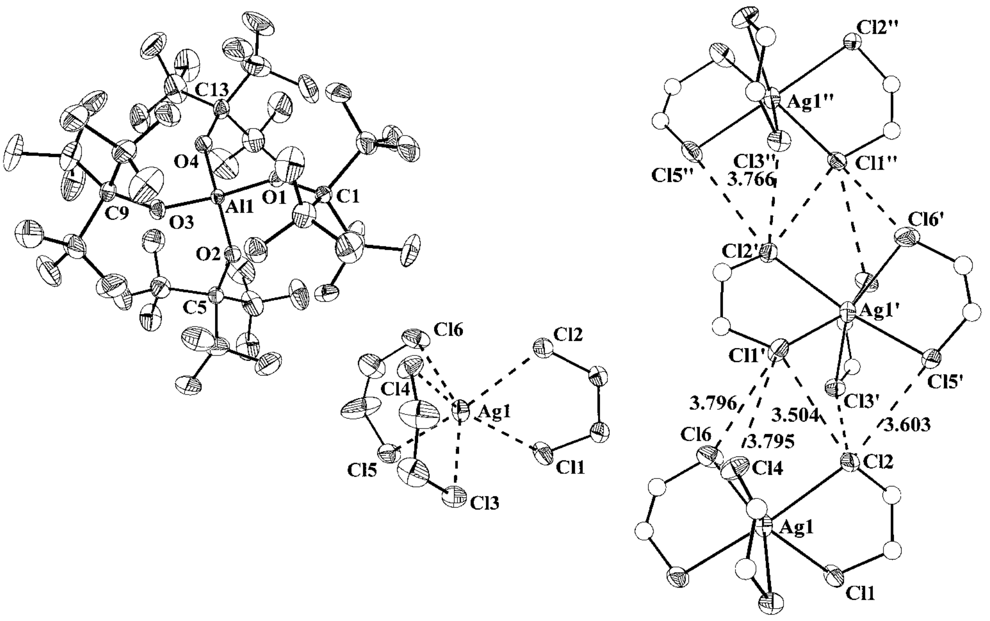


Figure 4. Solid-state structure of $[Ag(C_2H_4Cl_2)_3][Al(pftb)_4]$ (**3c**-$(C_2H_4Cl_2)_3$). All hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at the 25 % probability level. In the structure on the right the carbon atoms are drawn as circles with an arbitrary scale. Selected bond lengths [Å] and bond angles [°]: Ag1−Cl1 2.694(2), Ag1−Cl2 2.788(2), Ag1−Cl3 2.774(2), Ag1−Cl4 2.717(2), Ag1−Cl5 2.720(2), Ag1−Cl6 2.756(2), Al1−O1 1.736(3), Al1−O2 1.722(3), Al1−O3 1.714(3), Al1−O4 1.727(3), Cl1−C 1.815(7), Cl2−C 1.780(6), Cl3−C 1.756(7), Cl4−C 1.762(9), Cl5−C 1.703(10), Cl6−C 1.732(10), d(C−O) 1.343(3) ± 0.012 (average), Al1-O1-C1 148.1(3), Al1-O2-C5 149.1(3), Al1-O3-C9 151.7(3), Al1-O4-C13 149.1(3).

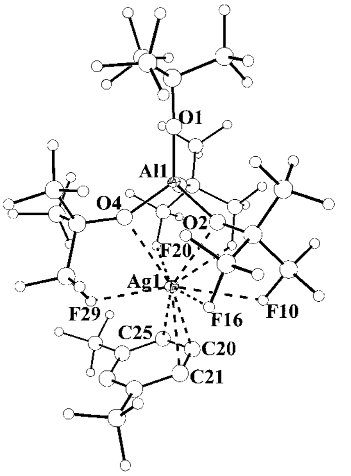


Figure 5. Solid-state structure of $[Ag\{C_6H_4(CF_3)_2\}Al(pftb)_4]$ (**3c**-$C_6H_4(CF_3)_2$)). Thermal ellipsoids are drawn at the 25 % probability level, all hydrogen atoms are omitted for clarity, all fluorine and carbon atoms are shown as small isotropic circles of an arbitrary scale. Selected bond lengths [Å] and bond angles [°]: Ag1−C20 2.496(8), Ag1−C21 2.596(7), Ag1−C25 3.005(8), Ag1−O2 2.558(5), Ag1−O4 2.581(7), Ag1−F29 2.436(9), Ag1−F10 2.722(8), Ag1−F16 2.928(9), Ag1−F20 2.943(9), Ag1−F25 3.026(8), Al1−O1 1.684(5), Al1−O2 1.769(4), Al1−O3 1.702(5), Al1−O4 1.759(5), Al1-O1-C1 166.9(5), Al1-O2-C5 147.0(4), Al1-O3-C9 166.7(6), Al1-O4-C13 152.5(5).

Al-O-C bond angles and vice versa, that is, d(Al1−O1) = 1.684(5) Å and Al1-O1-C1 = 166.9(5)°, d(Al1−O3) = 1.702(5) and Al1-O3-C9 = 166.7(6)°. The geometry around the Al atom is distorted tetrahedral as shown by the range of the O-Al-O bond angles of 97.6(3) to 117.7(3)°.

*$[Ag(CH_2Cl_2)]_2[O\{Al(pftb)_3\}_2]$ (**4**)*: Compound **4** crystallises in the monoclinic space group *C2/c* ($Z = 4$) and was only characterised by its X-ray crystal structure (shown in Figure 6). The molecule of **4** formally consists of an Al-O-Al bridged aluminate dianion $[O\{Al(pftb)_3\}_2]^{2-}$ and two formally single-positive cations $[Ag(\eta^1\text{-}CH_2Cl_2)]^+$, which enforce an almost ecliptic conformation of the two $Al(OR)_3$ units (torsion angle O1-Al1-Al1A-O3A 25.7(3)°) with weak contact of the two silver atoms at d(Ag1−Ag1A) = 3.504(2) Å (Ag1-O4-Ag1A 83.8(3)°).[23] The silver atoms are eight coordinate with three Ag−O contacts at 2.417(3) to 2.629(3) Å, one bond to a Cl atom of the monodentate CH_2Cl_2 ligand at 2.654(3) Å and four weak Ag−F contacts at 2.876(6) to 3.104(7) Å (see Figure 6, bottom). The two $Al(OR)_3$ units in **4** are linked by an almost linear Al-O-Al bridge (Al1-O4-Al1A = 174.5(3)°), for which the deviation from linearity points towards the centre of the Ag1−Ag1A vector and, therefore, may be caused by electrostatic Coulomb attraction between the (formally) Ag^+ cations and the O^{2-} dianion. The Al−O bond length (Al-O-C bond angle) of the dicoordinate oxygen atom O2 is shorter (wider) than that of the tricoordinate O1 and O3 atoms, that is, d(Al1−O2) = 1.727(3) Å, Al1-O2-C5 = 147.8(3), while d(Al−O) (Al-O-C) around O1 and O3 average to 1.787 ± 0.012 Å (136.9 ± 1.9°). The C−Cl bond lengths of the coordinated Cl1 atom is 0.009 Å longer than that of the noncoordinate Cl2 atom (1.756(7) vs. 1.747(8) Å).

Ab initio computations: To obtain thermochemical data, in order to calculate the alkoxide ion affinity and to assess the stability of gaseous $Al(OR)_4^-$ versus the strong Lewis acid AlF_3(g), we optimised the geometries of fluorinated and nonfluorinated species OR^-, $Al(OR)_3$, $Al(OR)_4^-$, $F_3Al{-}OR^-$ and AlF_3 at the B3LYP/TZV and MPW1PW91/TZV levels ($OR = OCH_3$, OCF_3). The larger species with the PTFB ($OC(CF_3)_3$) ligand were only optimised at the more affordable

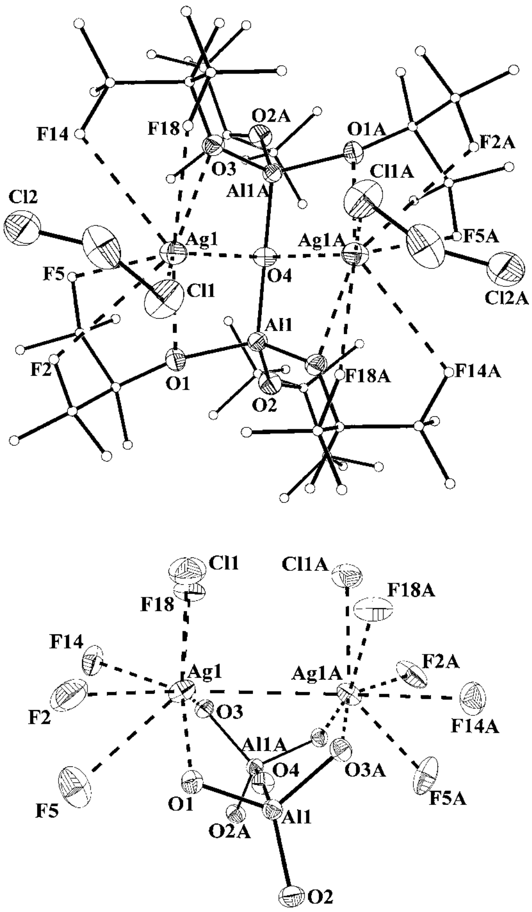


Figure 6. Molecular structure of $[Ag(CH_2Cl_2)]_2[O\{Al\{OC(Me)(CF_3)_2\}_3\}_2]$ (**4**) in the solid state. Thermal ellipsoids are drawn at the 25% probability level. All hydrogen atoms are omitted for clarity, all fluorine and carbon atoms in the structure on the left are shown as isotropic small circles of an arbitrary scale. Selected bond lengths [Å] and bond angles [°]: Ag1–O1 2.522(3), Ag1–O3 2.417(3), Ag1–O4 2.629(3), Ag1–Cl1 2.654(2), Ag1–F2 3.104(7), Ag1–F5 2.876(6), Ag1–F14 2.930(7), Ag1–F18 3.078(7), Al1–O1 1.775(3), Al1–O2 1.727(3), Al1–O3 1.798(3), Al1–O4 1.730(1), Cl1–C 1.756(7), Cl2–C 1.747(8), Ag1–Ag1A 3.504(2), Ag1-O4-Ag1A 83.8(3), Cl1-C-Cl2 112.5(4), Al1-O4-Al1A 174.5(3), Al1-O1-C1 138.3(3), Al1-O2-C5 147.8(3), Al1-O3-C9 135.0(2).

MPWPW91/SVP level. The structural parameters of all the calculated minimum geometries are collected in Table 1, Figure 7 and in ref. [24, 25].

The geometries calculated at the B3LYP and MPW1PW91 levels and with the TZV basis set are very similar and agree within 0.014 Å and 3.9°; the largest differences were found for the $Al(OCH_3)_3$ alane. The quality of the calculated aluminate structures is established by comparison with the experimental $Al(OR)_4^-$ geometries given in Table 2 (vide infra) and both are in good agreement. Experimental and computed aluminate structures show that the Al–O and C–O bond lengths are shorter and the Al-O-C bond angles are larger for species with fluorinated OR ligands and vice versa. The geometry of the alane $Al(pftb)_3$ was initially optimised in C_{3h} symmetry; however, the computation did not converge. Lowering the symmetry to C_1 led to the minimum geometry shown in Figure 7.

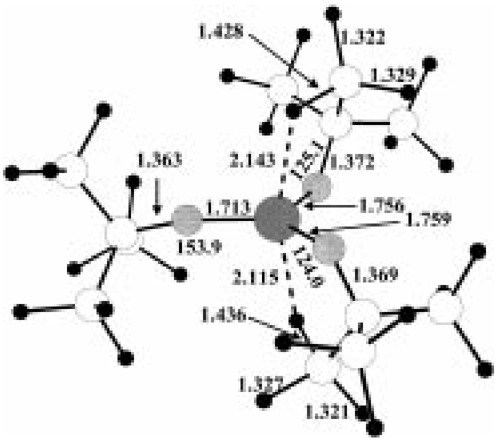


Figure 7. Calculated geometry of $Al(pftb)_3$ at the MPWPW91/SVP level. Fluorine atoms are shown as black, carbon atoms as white, oxygen atoms as light grey and the aluminium atom as dark grey shaded circle(s). Selected bond lengths are given in Å and bond angles in degrees.

The electron-deficient aluminium atom in $Al(pftb)_3$ is stabilised by two contacts at 2.115 and 2.143 Å to fluorine atoms of the PFTB ligands and the respective C–F bonds are elongated by about 0.1 Å. This stabilisation is geometrically only feasible for the larger and more flexible PFTB ligand and was, therefore, not observed for the smaller $Al(OR)_3$ (OR = OCH_3, OCF_3) molecules. The $Al(OR)_3$ alane geometries may be compared with $d(Al-O) = 1.647$ Å found on average in $Al(OAr)_3$ ($Ar = 2,6\text{-}t\text{Bu}_2\text{-}4\text{-MeC}_6H_2$)[33] or to $d(Al-O) = 1.696(2)$ Å and $Al\text{-}O\text{-}C = 158.4(2)°$ observed in the electronically comparable $Al(Odipp)(tmp)_2$ molecule (tmp = 2,2,6,6-tetramethylpiperidino, dipp = 2,6-diisopropylphenyl).[37] Experimental geometries of tricoordinate alanes $Al(OR)_3$ only substituted by aliphatic alkoxide ligands are, to the best of our knowledge, unknown. Due to the short C–O bond lengths and relatively long C–F bond lengths, the OCF_3^- anion has been the focus of several experimental and computational investigations[26] and shall not be discussed in here. However, the C–O and C–F bond lengths in $[\{(CH_3)_2N\}_3S]^+[OCF_3]^-$,[26c] the only well-ordered crystal structure of an OCF_3^- salt known to date, are 1.227 and 1.397 Å, respectively, and may be compared with our calculated values of 1.229 (1.228) Å and 1.487 (1.468) Å at the B3LYP (MPW1PW91) levels. As noticed earlier,[27] MPW1PW91 gives geometries closer to experimental data than B3LYP; however, here the differences are small.

Discussion

Molecular or salt structures of $Ag(L)Al(OR_F)_4$—energetic considerations: A question that presents itself is as to why **3a**-$(C_2H_4Cl_2)_2$, **3b**-CH_2Cl_2 and **3c**-$C_6H_4(CF_3)_2$ form a molecular lattice but **3c**-$(C_2H_4Cl_2)_3$ is a salt. $Al(OR_F)_4^-$ is an anion and thus may be expected to always form a saltlike structure. A part of the answer is given by the polarity of the solvents employed for crystallisation which follows: $1,3\text{-}(CF_3)_2C_6H_4$ ($\varepsilon = 5.98$) < CH_2Cl_2 ($\varepsilon = 8.93$) < $1,2\text{-}Cl_2C_2H_4$ ($\varepsilon = 10.42$) (ε = dielectric constant).[28] Crystals of the salt **3c**-$(C_2H_4Cl_2)_3$ were grown in the solvent with the highest polarity which provides the highest degree of stabilisation to the ion pair. In the less polar solvents CH_2Cl_2 and $1,3\text{-}(CF_3)_2C_6H_4$ the crystallisation

Table 1. Structural parameters and total atomic energies of all computed species OR^-, $Al(OR)_3$, $Al(OR)_4^-$ and $F_3Al{-}OR^-$.

	Symmetry	Level	d(Al–O) [Å]	d(C–O) [Å]	Al-O-C [°]	Total energy[a] [au]
$Al(OCH_3)_4^-$	S_4	B3LYP	1.783	1.418	131.4	– 703.41016
		MPW1PW91	1.776	1.408	131.2	– 703.24698
$Al(OCH_3)_3$	C_{3h}	B3LYP	1.692	1.422	151.7	– 588.12406
		MPW1PW91	1.681	1.408	155.6	– 587.99639
OCH_3^-	C_{3v}	B3LYP	–	1.379	–	– 115.15057
		MPW1PW91	–	1.372	–	– 115.10980
$F_3Al{-}OCH_3^-$	C_s	B3LYP	1.746	1.411	139.1	– 657.64487
		MPW1PW91	1.739	1.401	139.3	– 657.50585
$Al(OCF_3)_4^-$	S_4	B3LYP	1.738	1.283	180.0	– 1894.92390
		MPW1PW91	1.732	1.281	180.0	– 1894.49466
$Al(OCF_3)_3$	C_{3h}	B3LYP	1.676	1.319	179.0	– 1481.68497
		MPW1PW91	1.671	1.314	179.1	– 1481.35797
OCF_3^-	C_{3v}	B3LYP	–	1.229	–	– 413.09629
		MPW1PW91	–	1.228	–	– 412.98696
$F_3Al{-}OCF_3^-$	C_s	B3LYP	1.771	1.270	178.0	– 955.52969
		MPW1PW91	1.761	1.268	180.0	– 955.32338
$Al(pftb)_4^-$	S_4	B3LYP	1.765[b]	1.348[b]	149.4[b]	– 4748.43466
		MPW1PW91	1.765[b]	1.348[b]	149.4[b]	– 4747.31331
$Al(pftb)_3$	C_1	B3LYP	[c]	[c]	[c]	– 3621.80125
		MPW1PW91	[c]	[c]	[c]	– 3620.96025
$PFTB^-$	C_{3v}	B3LYP	–	1.292[b]	–	– 1126.48591
		MPW1PW91	–	1.292[b]	–	– 1126.20355
$F_3Al{-}PFTB^-$	C_1	B3LYP	1.810[b]	1.340[b]	141.1[b]	– 1668.85282
		MPW1PW91	1.810[b]	1.340[b]	141.1[b]	– 1668.47984

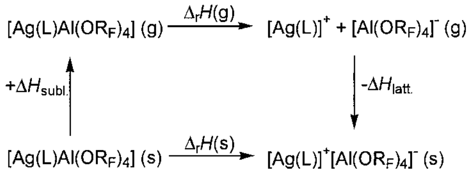
[a] Energies are only given at the highest level of theory employed, that is, those obtained with the 6–311 + G (2df,2p) basis set for OR = OCH_3, OCF_3 and the TZV basis set for PFTB. [b] MPWPW91/SVP geometry. [c] See Figure 7.

Table 2. Average E–O (E = Al, C) bond lengths and average Al-O-C bond angles in various aluminates $Al(OR)_4^-$.

	d(Al–O) [Å]	(Al–O-C) [°]	d(C–O)	Ref.
2a	1.746 ± 0.056	134.6	1.406 ± 0.020	[22]
$Al(O\textit{i}Pr)_4^-$	1.743 ± 0.020	126.5	1.455 ± 0.006	[34]
$ROAl(O\textit{i}dipp)_3^-$[a]	1.742 ± 0.008	138.5	1.402 ± 0.005	[35]
3b-CH_2Cl_2	1.740 ± 0.028	140.3	1.387 ± 0.010	this work
$Al\{O(2,6\textit{t}Bu_2Ph)\}_2(OBu)_2^-$	1.740 ± 0.026	145.1	1.388 ± 0.036	[36]
3a-$(C_2H_4Cl_2)_2$	1.738 ± 0.020	130.0	1.384 ± 0.010	this work
3a-$(C_7H_8)_2$	1.734 ± 0.023	133.7	1.379 ± 0.021	this work
$Al\{OC(Ph)(CF_3)_2\}_4^-$	1.730 ± 0.043	158.2	1.379 ± 0.013	[15a)]
3b-$C_6H_4(CF_3)_2$	1.728 ± 0.042	158.3	1.355 ± 0.011	this work
3c-$(C_2H_4Cl_2)_3$	1.725 ± 0.011	149.5	1.343 ± 0.012	this work

[a] RO = $O(CH_2)_4N(Me_2)Et^+$.

of molecular species is preferred. However, **3a**-$(C_2H_4Cl_2)_2$ also is a molecular species, but here the $Al(hfip)_4$ anion is more basic than the $Al(pftb)_4$ anion (vide infra) and, therefore, coordination is preferred. To gain insight in the energetics of this process, we constructed the following Born–Fajans–Haber cycle (see Scheme 1), which enabled us to derive limits for the gas-phase enthalpies of the reaction $Ag(L)Al(OR_F)_4 \rightarrow Ag(L)^+ + Al;(OR_F)_4^-$. The lattice potential enthalpies of the salts[29, 30] and the sublimation enthalpies of the molecular solids[31] were estimated.



Scheme 1. Born–Fajans–Haber cycle for the estimation of Δ_rH of the reaction $Ag(L)Al(OR_F)_4 \rightarrow [Ag(L)]^+[Al(OR_F)_4]^-$.

Δ_rH(s) in Scheme 1 is positive for the molecular species **3b**-CH_2Cl_2 and **3c**-$(C_6H_4(CF_3)_2)$, but negative for the salt **3c**-$(C_2H_4Cl_2)_3$. With the estimated sublimation enthalpies[31] and lattice potential enthalpies[29] we derive the following limits for the gaseous heats of reactions in Scheme 1: $\Delta_rH(g) \geq 123\,kJ\,mol^{-1}$ (**3a**-$(C_2H_4Cl_2)_2$), $\Delta_rH(g) \geq 144\,kJ\,mol^{-1}$ (**3b**-CH_2Cl_2), $\Delta_rH(g) \geq 39\,kJ\,mol^{-1}$ (**3c**-$(C_6H_4(CF_3)_2)$) and $\Delta_rH(g) \leq 8\,kJ\,mol^{-1}$ (**3c**-$(C_2H_4Cl_2)_3$). This shows that the silver ion in **3c**-$(C_2H_4Cl_2)_3$ is saturated by the six Ag–Cl contacts, but that the additional Ag^+–anion interactions stabilise the molecular species **3a**-$(C_2H_4Cl_2)_2$, **3b**-CH_2Cl_2 and **3c**-$[C_6H_4(CF_3)_2]$ by at least 123, 144 and 39 $kJ\,mol^{-1}$, respectively.

Al–O bond lengths in the $Al(OR_F)_4$ anions: does the increasing steric demand of the OR_F ligand lead to weaker Al–O bonds?: The fluorination of the parent alcohol's ROH of the OR_F ligands should have to two opposing effects: a) the OR_F ligand is more electronegative than the non fluorinated precursor OR and this leads to highly polar Al–O bonds. b) The steric requirement of the fluorinated alkoxy ligands is higher than that of the non substituted parent alcohol and the strain associated with the Al–O bond formation should, therefore, lead to a weakening of the Al–O bonds. Typical terminal Al–O bonds range from 1.57 Å in O = Al–X (X = F, Cl),[32] to 1.647 Å (av.) in monomeric $Al(OAr)_3$ (Ar = 2,6-$\textit{t}Bu_2$-4-MeC_6H_2),[33] 1.690 Å (av.) in $[Al(OtBu)_3]_2$[17] and 1.742 Å (av.) in $Al(OR)_4^-$ (R = iPr[34] or 2,6-$iPr_2C_6H_3$[35]). Aluminates $R'_xAl(OR)_{4-x}^-$ (x = 0–2) with O–E (E = Li, Na, H) contacts exhibit shorter Al–O bond lengths to the dicoordinate oxygen atoms (1.713 ± 0.026 Å) and longer distances to the tricoordinate oxygen atoms (1.778 ± 0.017 Å) (average of twelve crystal structures in refs. [15, 36, 37]). The average Al–O distances and average Al-O-C bond angles of several aluminates $Al(OR)_4^-$ are collected in Table 2.

Although the steric requirement of the $OC(CF_3)_3$ ligand introduces strain on the Al–O bond, the average Al–O bond lengths of the $Al[OC(CF_3)_3]_4^-$ anion with the bulkiest alkoxide ligand are the shortest of all the distances shown in Table 2. A general relationship between the average Al-O-C bond angle and the average Al–O and C–O distance is observed such that wide average Al-O-C bond angles correspond to shorter average Al–O and C–O bond distances and vice versa. This is attributed to a highly ionic Al–O bond that allows to adopt a bonding position that is independent of preferential orbital orientations as expected for a predominantly covalent Al–O bond. The higher the polarity of the Al–O bond the larger is the Coulomb contribution to the bond energy and the more easily follows the Al-O-C bond angle the steric requirements of the ligand.

The stability of the $Al(OR_F)_4^-$ anion—experimental considerations and computation of the alkoxide ion affinity: An important property of a weakly coordinating anion (WCA) is its stability versus ligand abstraction, which determines its usefulness to act as a counterion for a highly reactive cation. Ligand abstraction reactions were reported for several WCAs and include those of the $B\{C_6H_3(CF_3)_2\}_4^-$,[38a] $B(C_6F_5)_4^-$,[38b,c] $B(OTeF_5)_4^-$,[12] and $CB_{11}H_6Cl_6^-$.[39] As a rule, the stronger the corresponding Lewis acid of a given WCA, the more stable this anion will be against ligand abstraction. For the $Al(OR_F)_4^-$ anions, we showed $Al(hfip)_3$ in **1a** to be a strong Lewis acid so that the base OEt_2 was not released from **1a** even with heat and vacuum or in the mass spectrometer (see above). Moreover, the $Al(OR_F)_4^-$ ions exhibit short Al–O bond lengths and wide Al-O-C bond angles, which are indicative of a highly polar Al–O bond that is resistant against heterolytic cleavage, for example, against alkoxide ion abstraction.

For the fluoride-based anions MF_n^- (M = B, As, Sb, Pt,…; $n = 4, 6$) the fluoride ion affinity (FIA) of many species was determined experimentally and computationally as a quantitative measure of the stability of a given anion[30, 40] and, therefore, the computation of a similar property, the alkoxide ion affinity (AIA) of the $Al(OR)_4^-$ ion, was performed according to Equation (5).

$$Al(OR)_3(g) + OR^-(g) \rightarrow Al(OR)_4^-(g) \quad OR = OCH_3,\ OCF_3,\ OC(CF_3)_3 \quad (5)$$

The OCF_3 ligand served as a model for the larger $OC(CF_3)_3$ ligand (replace CF_3 by F) and could be examined with higher accuracy than the rather large $OC(CF_3)_3$ species. To test the influence of the fluorination of the alkoxide ligands on the AIA we also calculated the AIA of the nonfluorinated methoxy derivative. The calculated AIA*s*, are given in Table 3. [As for the FIA:[40] By definition the AIA always has a positive value, although the constituting reaction is highly exothermic (and thus a negative value would be expected)].

The computed AIA*s* of the $Al(OR)_4^-$ ions in Table 3 range from 356 to 393 kJ mol^{-1} and the values calculated by B3LYP and MPW1PW91 agree within 18 kJ mol^{-1}. As anticipated, the fluorination increases the AIA by 21 to 23 kJ mol^{-1}. The AIA of 390 ± 3 and 384 ± 9 kJ mol^{-1} of $Al\{OC(CF_3)_3\}_3$ and $Al(OCF_3)_3$ may then be compared with the FIA of AsF_5 which is in a similar range (430 kJ mol^{-1} [2, 40]). A more chemical answer to the stability of the $Al(OR)_4^-$ anions is given by the following isodesmic reaction [Eq. (6)]:[41, 42]

Table 3. Calculated AIAs [according to Eq. (5)].

Species	Level[a]	AIA [kJ mol^{-1}]
$Al(OCH_3)_3$	B3LYP	356
	MPW1PW91	370
$Al(OCF_3)_3$	B3LYP	375
	MPW1PW91	393
$Al(pftb)_3$	B3LYP	387
	MPW1PW91	393

[a] The calculated AIAs are only given at the highest level of theory employed, that is, those obtained with the 6–311 + G(2df,2p) basis set for $OR = OCH_3$, OCF_3 and the TZV basis set for PFTB.

$$Al(OR)_4^-(g) + AlF_3(g) \rightarrow Al(OR)_3(g) + F_3AlOR^-(g)$$
$$OR = OCH_3,\ OCF_3,\ OC(CF_3)_3 \quad (6)$$

Gaseous AlF_3 is one of the strongest Lewis acids known [FIA $AlF_3(g)$ = 481 kJ mol^{-1}, cf. FIA $AsF_5(g)$ = 430 kJ mol^{-1}[40]) and, therefore, the calculated reaction energies Δ_rU [Eq. (6)] provide information as to whether the $Al(OR)_4^-$ anion would decompose in the presence of this very strong acid or not (given in Table 4).

Table 4. Calculated reaction energies Δ_rU [Eq. (6)].

OR	Level[a]	Δ_rU [kJ mol^{-1}]
OCH_3	B3LYP	−93
	MPW1PW91	−89
OCF_3	B3LYP	+86
	MPW1PW91	+91
PFTB	B3LYP	+75
	MPW1PW91	+51

[a] The calculated Δ_rU are only given at the highest level of theory employed, that is, those obtained with the 6–311 + G (2df,2p) basis set for $OR = OCH_3$, OCF_3 and the TZV basis set for PFTB.

Both levels of theory agree within 4 to 24 kJ mol^{-1} on Δ_rU [Eq. (6)]. In reaction (6), the effect of fluorination showed strongly and $Al(OCF_3)_4^-$ and $Al\{OC(CF_3)_3\}_4^-$ were calculated to be stable against the action of gaseous AlF_3 by 88.5 ± 2.5 and 63 ± 12 kJ mol^{-1}, while the non-fluorinated $Al(OCH_3)_4^-$ was calculated to decompose ($\Delta_rU = -91 \pm$ kJ mol^{-1}). This implies that $Al(OCF_3)_3$ and $Al\{OC(CF_3)_3\}_3$ are are two of the strongest neutral Lewis acids known and shows that fluorination stabilises the $Al(OR_F)_4^-$ anions greatly versus heterolytic alkoxide ion abstraction making them suitable candidates to act as counterions of highly electrophilic cations.

$Al(OR_F)_4^-$ as a WCA—a comparison with known WCAs: Several solid-state structures of silver salts of WCAs are known. This allows the analysis of the strengths of the coordinating abilities of the $Al(OR_F)_4^-$ anions [$OR_F = OC(Me)(CF_3)_2$ (HFTB), $OC(CF_3)_3$ (PFTB)] towards the Ag^+ cation in comparison to other WCAs, especially to the

$CB_{11}H_6Cl_6^-$ anion which currently claims the title "least coordinating anion".[1a] Univalent Ag^+ compounds have coordination numbers (CNs) that range from two in $Ag(CN)_2^-$ to nine in $Ag\{B(OTeF_5)\}_4$. Higher CNs are generally attributed to a more ionic bonding situation in which fewer strong bonds are exchanged for a series of weak secondary bonds.[43] In this respect the bonding situation of the silver atom in all the newly prepared compounds $Ag(L)Al(OR_F)_4$ is highly ionic as seen from the range of the silver CNs of six to ten, which are comparable to those found for Ag(p-xylene)$CB_{11}H_6Cl_6$ (**5**; CN = 6),[9a] $Ag(C_6H_6)_2$-$CB_9H_7F_2$ (**8**; CN = 7),[9d] $[Ag(CH_2Cl_2)_3]_2Ti(OTeF_5)_6$ (**6**; CN = 8)[14] and $AgB(OTeF_5)_4$ (**7**; CN = 9)[12] (see Table 5). Another qualitative observation is the ability of WCAs to stabilise complexes with weakly basic solvents, for example, CH_2Cl_2 or arenes. Only if the interaction of the anion with the Ag^+ cation is weaker than complex formation with the solvent are compounds containing $Ag(L)_x^+$ cations (L = weakly basic solvent, $x = 1-3$) stable in the solid state. All of the newly prepared silver aluminates coordinate at least one solvent molecule; this shows that the $Al(OR_F)_4^-$ anion is weakly coordinating. To put this qualitative picture on a more quantitative basis we calculated the strengths (s) of each contact Ag–X (X = O, F, Cl, C) of all compounds $Ag(L)$-$Al(OR_F)_4$ as well as those found in **5**–**8** by Brown's bond-valence method.[44] The atomic valence of the Ag^+ cation is one and, therefore, the addition of all the bond valences s of the contacts to the Ag^+ cation which are below the sum of the respective van der Waals radii is expected to give a value close to unity (usually within ±5%).[44] Truly weakly coordinating anions should only give low values of s as an indication that no stronger coordination site remains in the anion. The lengths d(Ag–X) [in Å] and strengths s [in valence units (vu)] of the Ag–X contacts (X = O, F, Cl, C) of all newly prepared compounds $Ag(L)Al(OR_F)_4$ as well as those calculated for **5**–**8** are presented in Table 5.

The strengths of the Ag–X contacts in Table 5 range from $s = 0.03$ to 0.25 vu and all silver compounds have contacts of similar magnitude. The addition of all bond valences of each individual compound in Table 5 gives values from 0.93 to 1.06, which is close to the expected value and is a proof of the validity of the approach chosen. The strongest contacts of all compounds $Ag(L)Al(OR_F)_4$, except **3c**-$(C_6H_4(CF_3)_2)$, are formed towards the solvent molecule and not towards the anion, for example towards carbon in **3a**-$(C_7H_8)_2$ (0.23 vu), towards chlorine in **3a**-$(C_2H_4Cl_2)_2$ (0.17 vu), **3b**-CH_2Cl_2 (0.25 vu), **3c**-$(C_2H_4Cl_2)_3$ (0.19 vu) and **4** (0.22 vu). In **3c**-$(C_6H_4(CF_3)_2)$ the strongest contact is to a fluorine atom (0.21 vu) and the two Ag–O contacts are comparatively weak (0.12 and 0.13 vu). Compounds **6** and **8** also exhibit the strongest contacts towards the coordinated solvent molecule, but the $CB_{11}H_6Cl_6^-$ anion in **5** forms the strongest contact from a chlorine atom of the anion towards the silver cation (0.23 vu). However, the two Ag–C contacts of **5** to the coordinated molecule of *p*-xylene are only slightly weaker (0.19 and 0.17 vu) than the Ag–Cl contact. This shows that the coordination ability of the newly prepared $Al(OR_F)_4^-$ anions towards the Ag^+ cation is as low as in other established WCAs in **5**–**8**; this encourages us to further investigate the chemistry of these aluminates towards various highly electrophilic cations.

Table 5 shows that the basicity of the $Al(OR_F)_4^-$ anions has following order: $Al(hftb)_4^- > Al(hfip)_4^- > Al(pftb)_4^-$. The line width of the quadrupolar nucleus ^{27}Al ($I = 5/2$) is very sensitive to a distortion of the local symmetry and, therefore, the same conclusion as from Table 5 can be drawn from the line widths of the ^{27}Al NMR spectra of **3a**–**c**: increased coordination of the cation by the more basic anion leads to

Table 5. Bond lengths [in Å] and strengths (s) [in valency units vu] of Ag–X contacts (X = O, F, Cl, C) in several silver compounds containing WCAs. tol = toluene 1,3-Bis = 1,3-$(CF_3)_2C_6H_4$, 1,2-Di = 1,2-$Cl_2C_2H_4$.

	3a-$(C_7H_8)_2$ (s)	**3a**-$(C_2H_4Cl_2)_2$ (s)	**3b**-CH_2Cl_2 (s)	**4** (s)	**3c**-$C_6H_4(CF_3)_2$ (s)	**3c**-$(C_2H_4Cl_2)_3$ (s)	**5**[9a] (s)	**6**[14] (s)	**7**[12] (s)	**8**[9d] (s)
CN	8	6	8	8	10	6	6	8	9	7
Ag–O	2.569(0.13)	2.492(0.16)	2.377(0.23)	2.417(0.20)	2.558(0.13)				2.501(0.16)	Ag–H
	2.657(0.10)	2.576(0.13)	2.386(0.22)	2.522(0.15)	2.581(0.12)				2.601(0.12)	2.09(0.19)
				2.629(0.11)					2.756(0.08)	2.10(0.18)
Ag–F	3.385(0.03)		2.849(0.09)	2.876(0.08)	2.436(0.21)		3.029(0.06)	2.644(0.14)	3.19(0.04)	
	3.493(0.02)	2.857(0.08)	2.930(0.07)	2.722(0.11)		3.033(0.06)	2.717(0.12)			
			2.924(0.07)	3.078(0.05)	2.928(0.07)			2.730(0.11)		
			2.931(0.07)	3.104(0.05)	2.943(0.07)			2.773(0.10)		
					3.026(0.06)				2.824(0.09)	
									3.017(0.06)	
Ag–Cl		2.741(0.17)	2.613(0.25)	2.654(0.22)		2.694 0.19	2.640(0.23)	2.656(0.22)		
		2.751(0.16)	2.874(0.11)			2.717 0.18	2.679(0.20)	2.702(0.19)		
		2.820(0.13)				2.720 0.18	2.873(0.11)	2.719(0.18)		
		2.826(0.13)				2.756 0.16	2.926(0.10)	2.856(0.12)		
						2.774 0.15		3.030(0.07)		
						2.778 0.15		3.049(0.17)		
Ag–C	2.390(0.23)			2.496(0.16)		2.481(0.17)			2.47(0.18)	
	2.452(0.19)			2.596(0.12)		2.506(0.16)			2.49(0.17)	
	2.538(0.14)			3.005(0.03)					2.52(0.15)	
	2.572(0.13)									2.65(0.10)
Sum of s	0.97	[a]	1.01	0.93	1.06	1.01	0.97	0.95	0.97	1.00

[a] Four comparatively strong H–F hydrogen bonds of the $C_2H_4Cl_2$ molecules to the anion complete the contacts (v.s.) and, therefore, the sum of the Ag–X valency units s only add up to 0.71 vu.

broader lines. The line widths follow the same ordering as above and are 270 > 255 > 41 Hz (average values) for the silver species and 620 > 230 > 130 Hz for the lithium compounds. In the succeeding paper in this issue S. H. Strauss et al. conclude to the same order of basicity, based on several physical measurements.[22]

Conclusion

The facile, high-yield syntheses of several silver salts of weakly coordinating anions $AgAl(OR_F)_4$ [$OR_F = OC(H)(CF_3)_2$ (HFIP), $OC(CH_3)(CF_3)_2$ (HFTB), $OC(CF_3)_3$ (PFTB)] was achieved. The fluorination of the alkoxy ligands lead to a considerable strengthening of the Al–O bond as shown by an analysis of experimental and computational data. Strain introduced by the sterically more demanding PFTB ligand did not affect the Al–O bond length; on the contrary, the $Al(pftb)_4^-$ anion has the shortest average Al–O bond lengths. Moreover the $Al(pftb)_4^-$ anion is stable in water and aqueous HNO_3 (35 weight %). By HF-DFT calculations, we showed that the gaseous $Al(OCF_3)_4^-$ and $Al(pftb)_4^-$ anions are stable in the presence of the very strong Lewis acid $AlF_3(g)$ by 88.5 ± 2.5 and $63 \pm 12\ kJ\,mol^{-1}$. This indicates that the parent Lewis acids, $Al(OCF_3)_3(g)$ and $Al(pftb)_3$, are two of the strongest neutral Lewis acids known to date; the latter may also be accessible on a preparative scale. The $Al(OR_F)_4^-$ anions coordinate very weakly to the silver cation and the basicity decreases according to: $Al(hftb)_4^- > Al(hfip)_4^- > Al(pftb)_4^-$. The $Al(pftb)_4^-$ anion is one of the most weakly coordinating anions known to date and is comparable with $CB_{11}H_6Cl_6^-$, which currently claims the title "least coordinating anion".[1a] However, in contrast to the latter salt, $AgAl(OR_F)_4$ can easily be made in 20 g batches within two days. Moreover, H(HFIP) is cheap and therefore the $Al(hfip)_4^-$ anion should be of great interest for many applications, for example, cationic homogenous catalysis. The data presented here, suggest that the $Al(OR_F)_4^-$ anions are robust WCAs that may be introduced for the stabilisation of highly electrophilic cations. Silver metathesis reactions appear to be suitable for many purposes; however, special cations may need special strategies for ionisation, see for example, the silylium ion problem.[1a, 4, 45] Preliminary investigations showed that the $Al(OR_F)_4^-$ anions presented here also stabilise the Ph_3C^+ cation, but this will be subject to future communication.

Experimental Section

All manipulations were performed using standard Schlenk or dry-box techniques in an atmosphere of purified dinitrogen or argon (H_2O and $O_2 < 1$ ppm). All solvents were rigorously dried by standard procedures, distilled, degassed prior to use and stored under N_2. NMR spectra were recorded on a Bruker AC250 spectrometer and referenced against external $SiMe_4$ (^1H, ^{13}C), aqueous LiCl (^7Li), Cl_3CF (^{19}F), aqueous $AlCl_3$ (^{27}Al) and 85 % H_3PO_4 (^{31}P). Raman spectra were recorded on a Bruker IFS 66v spectrometer equipped with the Raman module FRA106 in sealed melting point capillaries. Mass spectra were recoreded on a Finnigan MAT711 spectrometer at 70 eV. Elemental analyses were performed by the analytical laboratory of the institute. Melting points were determined in sealed capillaries with a heating rate of 4° min^{-1} and melting points are given uncorrected.

$Al(hfip)_3(OEt_2)$ (1a-OEt₂): A cooled (–78 °C) solution of $LiAlH_4$ in OEt_2 (45.0 mL, 0.311 M, 14.0 mmol) was quickly added to a cooled (–78 °C) solution of freshly sublimed $AlCl_3$ (0.62 g, 4.7 mmol) in of Oet_2 (80 mL). The resulting clear solution was stirred for two minutes and then pure, liquid H(HFIP) (9.40 g, 5.89 mL, 55.9 mmol) was added over 10 min (strong gas evolution). The mixture was slowly warmed to ambient temperature (12 h) and all volatiles were removed in vacuo (3×10^{-2} mbar) leaving a colourless oil. Pentane (70 mL) was added and the resulting suspension was filtered. All volatiles were removed from the filtrate and the remaining colourless oil was distilled in a static vacuum giving a colourless liquid ($d = 1.492\ g\,mL^{-1}$) of **1a**-OEt_2. Yield: 8.84 g (90 %); b.p. 65–70 °C (1.5×10^{-2} mbar); ^1H NMR (250 MHz, C_6D_6, 25 °C): $\delta = 0.91$ (t, 6H; CH_3), 3.61 (q, 4H; CH_2), 4.50 (sept, $^3J(H,F) = 5.9$ Hz, 3H; CH); ^{13}C NMR (63 MHz, C_6D_6, 25 °C): $\delta = 13.2$ (s, CH_3), 70.9 (s, CH_2), 71.9 (sept, $^2J(C,F) = 33.3$ Hz; O–C), 123.5 (q, $J(C,F) = 283.4$ Hz; CF_3); ^{19}F NMR (235 MHz, C_6D_6, 25 °C): $\delta = -77.55$ (d, $^3J(F,H) = 5.8$ Hz; CF_3); ^{27}Al NMR (78 MHz, C_6D_6, 25 °C): $\delta = 54.5$ (s, $\nu_{1/2} = 1370$ Hz); MS (70 eV): m/z (%): = 582 (1.92) $[M - F]^+$, 532 (16.74) $[M - CF_3]^+$, 435 (75.76) $[M - OC(H)(CF_3)_2]^+$, 139 (100) $[F_2Al - OEt_2]^+$.

$LiAl(hfip)_4(OEt_2)$ (2a-OEt₂): Liquid **1a**-OEt_2 (1.11 g, 0.75 mL, 1.85 mmol) was added to solid LiHFIP[46] (0.32 g, 1.85 mmol), and the resulting suspension was treated for one hour with ultrasound at 40 °C to give a clear colourless liquid. This liquid was heated in a dynamic vacuum (2–3 h, 1×10^{-2} mbar) to about 150 °C, after which the liquid crystallised upon storage at ambient temperature. Yield: 1.43 g, 100 %; ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 0.91$ (t, CH_3), 1.12 (br, CH_3), 2.92 (q, CH_2), 3.38 (br, CH_2), 4.57 (sept, $^3J(H,F) = 5.6$ Hz; CH), 4.68 (br, CH); ^1H NMR (300 MHz, C_6D_6, 60 °C): $\delta = 0.88$ (t, 6H; CH_3), 3.10 (q, 4H; CH_2), 4.59 (sept, $^3J(H,F) = 5.6$ Hz; CH); ^7Li NMR (117 MHz, C_6D_6, 25 °C): $\delta = -0.6$ (s, 1Li), -0.9 (s, 1Li); ^7Li NMR (117 MHz, C_6D_6, 60 °C): $\delta = -0.8$ ($\nu_{1/2} = 330$ Hz); ^{13}C NMR (63 MHz, C_6D_6, 25 °C): $\delta = 13.8$ (s, CH_3), 66.7 (s, CH_2), 71.5 (sept, O–C, $^2J(C,F) = 33.3$ Hz), 123.2 (q, $J(C,F) = 283.5$ Hz; CF_3); ^{27}Al NMR (78 MHz, C_6D_6, 25 °C): $\delta = 57.1$ (s, $\nu_{1/2} = 770$ Hz).

General procedure for the synthesis of $LiAl(OR_F)_4$ [$OR_F = OCH(CF_3)_2$ (hfip), $OC(CH_3)(CF_3)_2$ (HFTB), $OC(CF_3)_3$ (PFTB)]: A solution of $LiAlH_4$ in Et_2O (containing 5 to 20 mmol $LiAlH_4$) was transfered into a Schlenk vessel. All volatiles were removed in vacuo (2–3 h, 5×10^{-3} mbar) until a constant weight was achieved (by increasing the temperature to about 80 °C). This purified $LiAlH_4$ was suspended in toluene (about 70 mL) and the alcohol $HO{-}R_F$ (4.1 equiv) was added at 0 °C temperature (1 h, gas evolution). The mixture was heated to reflux over night when a clear solution had formed. Cooling this solution for one hour to –20 °C lead to the precipitation of colourless $LiAl(OR_F)_4$. The supernatant solution was decanted and all the volatiles of the remaining solid were removed in vacuo (1 h, 5×10^{-2} mbar) yielding 66 to 80 % crude $LiAl(OR_F)_4$. This crude material was sufficient for the succeeding preparation of $AgAl(OR_F)_4$; however, it may be purified by sublimation at about 150 °C and 5×10^{-2} mbar.

$LiAl(hfip)_4$ (2a): $LiAlH_4$ (1.675 g, 44.10 mmol), H(HFIP) (30.38 g, 19.95 mL, 180.81 mmol); yield of crude [sublimed] material: 27.86 (90 %) [25.63 g (83 %)]; m.p. 120–125 °C; ^1H NMR (250 MHz, $CDCl_3$/5 % THF, 25 °C): $\delta = 4.19$ (sept, $^3J(H,F) = 6.2$ Hz; CH); ^7Li NMR (117 MHz, $CDCl_3$/5 % THF, 25 °C): $\delta = -1.1$; ^{13}C NMR (63 MHz, $CDCl_3$/5 % THF, 25 °C): $\delta = 70.4$ (sept, O–C, $^2J(C,F) = 32.3$ Hz), 122.7 (q, CF_3, $J(C,F) = 285.0$ Hz); ^{27}Al NMR (78 MHz, $CDCl_3$/5 % THF, 25 °C): $\delta = 59.9$ (s, $\nu_{1/2} = 230$ Hz); FT-Raman: $\tilde{\nu}$ (%) = 2955 (100), 1390 (15), 1295 (10), 1200 (11), 1129 (4), 1098 (7), 855 (82), 766 (28), 750 (18), 730 (7), 703 (10), 689 (9), 533 (16), 523 (15), 484 (4), 330 (41), 298 (10), 218 (13), 120 cm^{-1} (8).

$LiAl(hftb)_4$ (2b): $LiAlH_4$ (0.66 g, 17.4 mmol), H(HFTB) (13.03 g, 10.0 mL, 71.6 mmol); yield of crude [sublimed] material: 10.60 g (80 %) [10.20 g (77 %)]; m.p. 42–45 °C; ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.57$ (s, CH_3); ^7Li NMR (117 MHz, $CDCl_3$, 25 °C): $\delta = -1.0$; ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 17.2$ (s, CH_3), 75.8 (sept, $^2J(C,F) = 29.6$ Hz; O–C), 124.1 (q, $J(C,F) = 287.4$ Hz; CF_3); ^{27}Al NMR (78 MHz, $CDCl_3$, 25 °C): $\delta = 46.6$ (s, $\nu_{1/2} = 620$ Hz); FT-Raman: $\tilde{\nu}$ (%) = 2964 (32), 2862 (100), 774 (15), 543 (33), 332 (5), 247 cm^{-1} (4).

$LiAl(pftb)_4$ (2c): $LiAlH_4$ (0.53 g, 14.0 mmol), $HOC(CF_3)_3$ (13.52 g, 8.0 mL, 57.3 mmol); yield of crude [sublimed] material: 10.50 g (77 %) [9.03 g (66 %)]; m.p. 145–150 °C; ^7Li NMR (117 MHz, $CDCl_3$, 25 °C): $\delta = -0.9$; ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 120.9$ (q, $J(C,F) = 292.8$ Hz; CF_3);

^{19}F NMR (235 MHz, CDCl$_3$, 25 °C): $\delta = -76.9$ (s, CF$_3$); ^{27}Al NMR (78 MHz, CDCl$_3$, 25 °C): $\delta = 33.8$ (s, $\nu_{1/2} = 130$ Hz); FT-Raman: $\tilde{\nu}$ (%) = 801 (70), 745 (90), 571 (25), 538 (40), 326 (100), 234 cm^{-1} (20).

General procedure for the synthesis of AgAl(OR$_F$)$_4$ [OR$_F$ = OCH(CF$_3$)$_2$ (HFIP), OC(CH$_3$)(CF$_3$)$_2$ (HFTB), OC(CF$_3$)$_3$ (PFTB)]: The crude LiAl(OR$_F$)$_4$ (5 to 20 mmol) and an about 1.3 to 2.0 molar excess of AgF were mixed in a two-bulb fritplate vessel equipped with J. Young valves. After the addition of about CH$_2$Cl$_2$ (30 mL) the suspension was placed in an ultrasonic bath at 40 °C (12 h). Filtration and removal of the volatiles in vacuo (5×10^{-3} mbar) afforded the colourless, highly soluble CH$_2$Cl$_2$ adducts of AgAl(hftb)$_4$ and AgAl(pftb)$_4$, and unsolvated AgAl(hfip)$_4$ in almost quantitative yield. Replacing CH$_2$Cl$_2$ by 1,2-Cl$_2$C$_2$H$_4$ or 1,3-(CF$_3$)$_2$C$_6$H$_4$ gave the respective solvent adducts of AgAl(pftb)$_4$. We attempted to record FT-Raman spectra of all silver species; however, the samples decomposed in the Laser beam even at very low laser power.

AgAl(hfip)$_4$ (3a): Compound **2a** (11.41 g, 16.3 mmol), AgF (3.40 g, 27.9 mmol); yield: 12.17 g (93 %); m.p. 155–160 °C (decomp); ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): $\delta = 4.48$ (sept, ^3J(H,F) = 5.5 Hz; CH); ^{13}C NMR (63 MHz, CDCl$_3$, 25 °C): $\delta = 75.9$ (sept, ^2J(C,F) = 32.9 Hz; O–C), 122.1 (q, J(C,F) = 283.1 Hz; CF$_3$); ^{27}Al NMR (78 MHz, CDCl$_3$, 25 °C): $\delta = 58.0$ (s, $\nu_{1/2} = 255$ Hz); elemental analysis calcd (%) for C$_{12}$H$_4$AgAlF$_{24}$O$_4$ (803.01): C 17.95, H 0.50, Al 3.4; found C 18.14, H 0.69, Al 3.3.

[Ag(CH$_2$Cl$_2$)Al(hftb)$_4$] (3b-CH$_2$Cl$_2$): Compound **2b** (10.20 g, 13.5 mmol), AgF (2.02 g, 15.9 mmol); yield: 11.81 g (93 %) m.p. 137–145 °C (decomp); ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): $\delta = 1.59$ (s, CH$_3$, 12 H), 5.29 (s, CH$_2$Cl$_2$, 2 H); ^{13}C NMR (63 MHz, CDCl$_3$, 25 °C): $\delta = 17.7$ (s, CH$_3$), 75.9 (sept, ^2J(C,F) = 29.7 Hz; O–C), 123.8 (q, J(C,F) = 288.2 Hz; CF$_3$); ^{27}Al NMR (78 MHz, CDCl$_3$, 25 °C): $\delta = 45.2$ (s, $\nu_{1/2} = 270$ Hz); elemental analysis calcd (%) for C$_{17}$H$_{14}$AgAlCl$_2$F$_{24}$O$_4$ (944.05): Ag 11.4, Al 2.9; found Ag 11.9, Al 2.6.

[Ag(CH$_2$Cl$_2$)Al(pftb)$_4$] (3c-CH$_2$Cl$_2$): Compound **2c** (4.75 g, 4.9 mmol), AgF (1.09 g, 8.6 mmol); yield: 5.40 g (95 %); m.p. 97–100 °C (decomp); ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): $\delta = 5.34$ (s, CH$_2$Cl$_2$); ^{13}C NMR (63 MHz, CDCl$_3$, 25 °C): $\delta = 54.0$ (s, CH$_2$Cl$_2$), 121.2 (q, J(C,F) = 292.8 Hz; CF$_3$); ^{27}Al NMR (78 MHz, CDCl$_3$, 25 °C): $\delta = 34.1$ (s, $\nu_{1/2} = 39$ Hz); elemental analysis calcd (%) for C$_{17}$H$_2$AgAlCl$_2$F$_{36}$O$_4$ (1159.96): C 17.60, H 0.17; found C 16.82, H 0.02.

[Ag{C$_6$H$_4$(CF$_3$)$_2$}Al(pftb)$_4$] (3c-C$_6$H$_4$(CF$_3$)$_2$): Compound **2c** (4.80 g, 4.9 mmol), AgF (1.25 g, 9.9 mmol); yield: 5.63 g (97 %) of m.p. 87–92 °C (decomp); ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): $\delta = 7.63$ (t, 1 H), 7.83 (d, 2 H), 7.86 (s, 1 H); ^{13}C NMR (63 MHz, CDCl$_3$, 25 °C): $\delta = 121.8$ (q, J(C,F) = 292.9 Hz; OC(CF$_3$)$_3$), 122.9 (sept, ^3J(C,F) = 3.8 Hz; Ar-C2), 123.9 (q, J(C,F) = 272.5 Hz; Ar-CF$_3$), 129.1 (s, Ar-C4,6), 130.1 (s, Ar-C5), 132.0 (q, ^2J(C,F) = 33.5 Hz; Ar-C1,3); ^{27}Al NMR (78 MHz, CDCl$_3$, 25 °C): $\delta = 34.1$ (s, $\nu_{1/2} = 42$ Hz); elemental analysis calcd (%) for C$_{24}$H$_4$AgAlF$_{42}$O$_4$ (1289.14): C 22.36, H 0.31, Ag 8.4; found C 20.89, H 0.64, Ag 9.0.

X-ray crystal structure determinations: Data collection for X-ray structure determinations were performed on a STOE STADI4 four circle or a STOE IPDS diffractometer with graphite-monochromated Mo$_{K\alpha}$ (0.71073 Å) radiation. Single crystals were mounted in perfluoroether oil on top of a glass fiber and then brought into the cold stream of a low temperature device so that the oil solidified. All calculations were performed on PC's using the Siemens SHELX93 software package. The structures were solved by the Patterson heavy atom method and successive interpretation of the difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions by a riding model using fixed isotropic parameters. Relevant data concerning crystallographic data, data collection and refinement details are compiled in Table 6. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146439–146444. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit @ccdc.cam.ac.uk).

Computational details: All calculations have been performed by using the Gaussian 98[47] suite of programs. The geometries of the species related to Al(OR)$_4^-$ (OR = OCH$_3$, OCF$_3$) were fully optimised at the MPW1PW91/TZV[48, 49] and B3LYP/TZV[50, 51] levels, while those with OR = OC(CF$_3$)$_3$ were only optimised at the less expensive MPWPW91/SVP[49, 52] level. Due

Table 6. Crystallographic details of **3a**-(C$_2$H$_4$Cl$_2$)$_2$, **3b**-CH$_2$Cl$_2$, **3c**-(C$_2$H$_4$Cl$_2$)$_3$, **3c**-C$_6$H$_4$(CF$_3$)$_2$ and **4**.

	3a*(C$_7$H$_8$)$_2$	**3a**-(C$_2$H$_4$Cl$_2$)$_2$	**3b**-CH$_2$Cl$_2$	**3c**-(C$_2$H$_4$Cl$_2$)$_3$	**3c**-C$_6$H$_4$(CF$_3$)$_2$	**4**
crystal size [mm]	0.2 × 0.5 × 0.5	0.4 × 0.5 × 0.5	0.4 × 0.5 × 0.5	0.3 × 0.3 × 0.4	0.5 × 0.4 × 0.4	0.5 × 0.5 × 0.7
crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$C2$/c
a [Å]	10.983(2)	10.232(2)	11.814(2)	11.775(2)	12.008(2)	22.880(5)
b [Å]	14.841(3)	15.482(3)	15.698(3)	18.725(4)	16.216(3)	11.712(2)
c [Å]	22.436(5)	20.794(4)	16.720(3)	19.512(4)	20.092(4)	20.229(4)
α [°]	97.42(3)	90.00	90.00	90.00	90.00	90.00
β [°]	93.90(3)	94.28(3)	98.16(3)	90.00	104.10(3)	115.29(3)
γ [°]	101.91(3)	90.00	90.00	90.00	90.00	90.00
V [Å^3]	3531.6(12)	3284.6(11)	3069.4(11)	4302.1(15)	3794.7(13)	4901.4(17)
Z	2	4	4	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.857	2.024	2.043	2.118	2.256	2.090
μ [mm^{-1}]	0.755	1.128	1.031	1.051	0.979	1.231
abs. corr.	numerical	numerical	semiempirical	numerical	numerical	numerical
$I_{\text{min}}/I_{\text{max.}}$	0.635/0.762	0.581/0.665	0.521/0.662	0.782/0.913	0.621/0.869	0.685/0.816
$F(000)$	1936	1936	1832	2648	2472	2984
index range	$-13 \leq h \leq 13$	$-12 \leq h \leq 12$	$-14 \leq h \leq 10$	$-14 \leq h \leq 14$	$-14 \leq h \leq 14$	$-27 \leq h \leq 21$
	$-18 \leq k \leq 13$	$-18 \leq k \leq 18$	$0 \leq k \leq 18$	$-22 \leq k \leq 23$	$0 \leq k \leq 23$	$-13 \leq k \leq 0$
	$-21 \leq l \leq 27$	$-24 \leq l \leq 25$	$0 \leq l \leq 19$	$-23 \leq l \leq 23$	$0 \leq l \leq 23$	$-24 \leq l \leq 21$
max. 2θ [°]	51.84	51.98	50.00	51.84	51.62	50.04
T [K]	180	190	203	200	200	223
unique reflns	10286	6242	5065	8325	7218	4307
observed reflns [$I > 4\sigma(I)$]	8550	5064	3154	7453	3987	3828
parameters	1013	451	446	632	724	348
weighting scheme[a] x/y	0.1096	0.0575/2.1566	0.0439/9.7553	0.0993/1.5952	0.1955/12.5305	0.0684/14.8580
GOOF	1.096	1.044	1.233	1.042	1.155	1.097
final R [$I > 4\sigma(I)$]	0.0426	0.0390	0.0559	0.0491	0.1026	0.0424
final $wR2$	0.1320	0.1025	0.1127	0.1342	0.2899	0.1145
largest residual peak [e Å^3]	0.848	0.849	0.910	0.743	0.805	0.738

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

to the large size of the systems, frequency calculations were not performed and consequently zero-point energies were not included; however, the errors associated with this procedure are expected to be small due to error cancellation, especially in the isodesmic reactions [Eq. (6)].[41] Energies given (OR = OCH_3, OCF_3) were computed at the MPW1PW91/6–311 + G(2df,2p)//MPW1PW91/TZV and B3LYP/6–311 + G(2df,2p)//B3LYP/TZV levels, while those of the species with OR = $OC(CF_3)_3$ were obtained at the less expensive MPW1PW91/TZV//MPWPW91/SVP and B3LYP/TZV//MPWPW91/SVP levels. However, we found that for OR = OCF_3 the difference between the energies obtained with the TZV and the larger 6–311 + G(2df,2p) basis set was less than 21 kJ mol^{-1} and therefore we expect the energies calculated for the species with OR = $OC(CF_3)_3$ to be correct within an error of a similar size.

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