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Lewis Superacids

Simple Access to the Non-Oxidizing Lewis Superacid $PhF\rightarrow Al(OR^F)_3$ ($R^F = C(CF_3)_3$)

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Dedicated to Professor Heinrich Nöth on the occasion of his 80th birthday

The design of very strong molecular Lewis acids has invoked the interest of many research groups. Such Lewis acids are commonly used in rearrangement reactions, catalysis, and ionization and bond heterolysis reactions.[1,2] Several procedures have been developed to evaluate the strengths of a Lewis acid.[2,3] However, since the pioneering work of N. Bartlett et al.[4] it is known that the fluoride ion affinity (FIA) is a reliable measure of the Lewis acidity, combining the strength of a Lewis acid $A_{(g)}$ with the energy that is released upon binding a fluoride ion F^- [Eq. (1)].[4–6a]

$$A_{(g)} + F^-_{(g)} \xrightarrow{\Delta H = -\mathrm{FIA}} AF^-_{(g)} \qquad (1)$$

The FIA is defined as the negative of the enthalpy ΔH [Eq. (1)], and the strength of a Lewis acid thus corresponds to the absolute value of the FIA. From recent work[6a] it is evident that Lewis acids stronger than SbF_5 are now available as compounds in the bottle, for example, $As(OTeF_5)_5$,[7] $B(OTeF_5)_3$,[8] 1,2-$((C_6F_5)_2B)_2C_6F_4$[9] and others (Table 1). To account for the special properties of these new and very strong Lewis acids, it appears reasonable and useful to define the term Lewis superacid:[10]

"*Molecular Lewis acids, which are stronger than monomeric SbF_5 in the gas phase, are Lewis Superacids.*"

We propose using the FIA as a quantitative measure for Lewis acidity (Table 1).[11] This definition may be seen in analogy to Brønsted acids: Brønsted superacids are stronger than the strongest conventional Brønsted acid, 100% H_2SO_4.[12] Analogously, SbF_5 is commonly viewed as the strongest conventional Lewis acid. Lewis acidity, in this case the FIA, can be assessed by several means.[4–6,13] However, the simplest and most general access to reliable FIA values now comprises the use of quantum chemical calculations in isodesmic reactions.[5] Table 1 shows the calculated FIAs of a representative set of strong neutral Lewis acids.

Inspection the FIA values in Table 1 shows that apart from monomeric $AlBr_3$ and AlI_3, SbF_5 is the strongest conventional Lewis acid, that is, easily accessible, stable under normal conditions, and employed in technical applications[19]. Solid, liquid, and gaseous AlX_3 shows a strong tendency towards aggregation, which diminishes the Lewis acidity more effectively than the aggregation in SbF_5 (see values in brackets in Table 1). Thus, the basis for our definition above is reasonable. Lewis superacids such as $As(OTeF_5)_5$[7] or AuF_5[20] are stronger than SbF_5, but are elusive entities that are rarely used. Further compounds such as $Sb(OTeF_5)_5$,[21] $CB_{11}F_{11}$, or $B(CF_3)_3$[22] are unstable and have only been determined computationally. None of the Lewis superacids collected in Table 1 is accessible in bulk quantities or used in commercial applications. $Al(C_6F_5)_3$ even has a reputation of being explosive.[23] It is likely that the amorphous Lewis acids ACF (aluminum chlorofluoride) and ABF (aluminum bromofluoride) are an exception;[24] however, these extended solid-state compounds are impossible to compare to molecular Lewis acids as collected in Table 1, and thus are not considered. All of the very strong Lewis acids given in Table 1 have drawbacks in that they are either highly oxidizing (AsF_5, SbF_5, $M(OTeF_5)_5$, etc.) and/or often easily hydrolyze with formation of anhydrous HF (aHF). This does not hold for the organometallic boron acids $B(Ar^F)_3$ ($Ar^F = C_6F_5$, etc.);[25] however, apart from the chelating 1,2-$((C_6F_5)_2B)_2C_6F_4$,[9] they are all weaker and thus not Lewis superacids. Thus, a simple access to a non-oxidizing Lewis superacid that does not hydrolyze with formation of hazardous chemicals such as aHF would be desirable. Herein we present the simple and direct synthesis of a compound which, based on experiment and theory, can be classified as a non-oxidizing Lewis superacid.

Based on the following observations from Table 1, it appeared reasonable to prepare an aluminum Lewis acid bearing the bulky perfluorinated alkoxy ligand OR^F ($R^F = C(CF_3)_3$): a) the FIA values of small gaseous aluminum Lewis acids such as monomeric AlX_3 (X = F, Cl, Br, I; FIA = 457–499 kJ mol^{-1}) are close to or even higher than that of monomeric SbF_5 (489 kJ mol^{-1}); and b) the replacement of monoatomic ligands like F by electronegative polyatomic ligands such as $OTeF_5$, CF_3, or C_6F_5 leads to a large increase in Lewis acidity. In principle, the resulting compound should be

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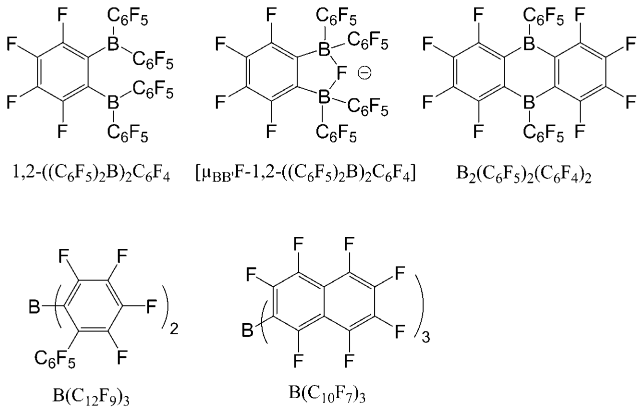
Table 1: Representative overview of known strong Lewis acids and their corresponding fluoride complexes.[a] [14]

Lewis acid/anion	FIA	Lewis acid/anion	FIA
$CB_{11}F_{11}$/$CB_{11}F_{12}^{-}$	716	AlF_3[e]/$[FAlF_3]^-$	467
$Sb(OTeF_5)_5/[FSb(OTeF_5)_5]^-$	633	$AlCl_3$[e]/$[FAlCl_3]^-$	457 [332][b,f]
$As(OTeF_5)_5/[FAs(OTeF_5)_5]^-$	593	GaI_3[e]/$[FGaI_3]^-$	454[b]
AuF_5/$[AuF_6]^-$	556[b] [15]	$BI_3/[FBI_3]^-$	448[b]
$B(CF_3)_3$/$[FB(CF_3)_3]^-$	552	$B(C_{12}F_9)_3/[FB(C_{12}F_9)_3]^-$[c]	447[b]
$B(OTeF_5)_3/[FB(OTeF_5)_3]^-$	550	$Ga(C_6F_5)_3/[FGa(C_6F_5)_3]^-$	447[b]
$Al(OR^F)_3/[FAl(OR^F)_3]^-$	537	$B(C_6F_5)_3/[FB(C_6F_5)_3]^-$	444
$Al(C_6F_5)_3/[FAl(C_6F_5)_3]^-$	530[b]	$GaBr_3$[e]/$[FGaBr_3]^-$	436[b]
1,2-$((C_6F_5)_2B)_2C_6F_4/[\mu_{BB'}F$-1,2-$((C_6F_5)_2B)_2C_6F_4]^-$[c]	510	$BBr_3/[FBBr_3]^-$	433[b]
$PhF \rightarrow Al(OR^F)_3/[FAl(OR^F)_3]^- + PhF$[d]	505[b]	$GaCl_3$[e]/$[FGaCl_3]^-$	432[b]
AlI_3[e]/$[FAlI_3]^-$	499 [393][b,f]	GaF_3[e]/$[FGaF_3]^-$	431[b]
$AlBr_3$[e]/$[FAlBr_3]^-$	494[393][b,f]	$AsF_5/[AsF_6]^-$	426
		$BCl_3/[FBCl_3]^-$	405[b]
$SbF_5/[SbF_6]^-$	489 [434][f]	$OCB(CF_3)_3/[FB(CF_3)_3]^- + CO$[g]	404[b]
$B_2(C_6F_5)_2(C_6F_4)_2/[FB_2(C_6F_5)_2(C_6F_4)_2]^-$[c]	471	$PF_5/[PF_6]^-$	394
$B(C_6H_3(CF_3)_2)_3/[FB(C_6H_3(CF_3)_2)_3]^-$	471	$BF_3/[BF_4]^-$	338
$B(C_{10}F_7)_3/[FB(C_{10}F_7)_3]^-$[c]	469[b]		

[a] Unstable and hitherto unknown Lewis acids that have only been determined theoretically are shown in *italics* (stability refers to standard conditions: 298 K, 1013 mbar). The empty row marks the border between normal and Lewis superacids. If not otherwise stated, FIA values [kJ mol^{-1}] are taken from Ref. [6a] or were calculated as part of this work using the same methodology as in [6a]. [b] This work. [c] For molecular structures, see Scheme 1. [d] $R^F = C(CF_3)_3$. [e] Monomeric EX_3 (E = Al, Ga). [f] Values in brackets are with respect to the standard state of the Lewis acid, that is, solid for AlX_3,[16] and liquid for SbF_5.[17] We are aware that for higher aggregates such as Sb_nF_{5n} and Al_nX_{3n} the calculated FIA values reach much higher numbers, but the gas-phase value of 489 kJ mol^{-1} gives a reasonable approximation of the average Lewis acidity of monomers and oligomers present in the condensed or liquid phase. [g] $OCB(CF_3)_3$ reacts with F^- to give $[F(O)CB(CF_3)_3]^-$.[18]



Scheme 1. Molecular structures for Table 1, footnote [c].

a stronger acid than monomeric AlX_3. The bulky ligands should also prevent the alane from dimerization. Quantum chemical calculations give the FIA of $Al(OR^F)_3$ as 537 kJ mol^{-1} (Table 1), that is, assign it as a Lewis superacid. Synthesis according to Equation (2) from AlR_3 (R = Me, Et) was investigated.

$$AlR_3 + R^FOH \xrightarrow[273\,K,\ -3\,RH\uparrow]{Solvent} Al(OR^F)_3 \qquad (2)$$

However, isolation of solid $Al(OR^F)_3$ from toluene, dichloromethane, pentane or hexane at ambient conditions was very difficult, because of self-decomposition with C–F activation and formation of aluminum fluorides. The DFT-optimized structure of $Al(OR^F)_3$ shows the reason for the C–F activation. Owing to the high Lewis acidity of the three-coordinate aluminum atom, it also binds two fluorine atoms of the CF_3 groups with an average distance of 2.13 Å (Figure 1).

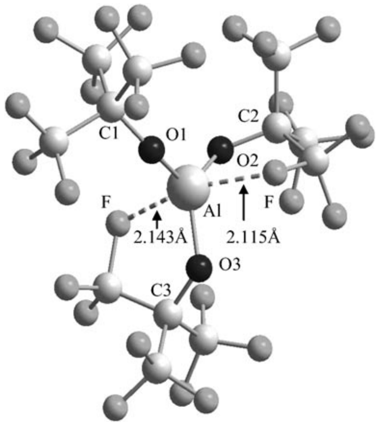


Figure 1. DFT-optimized structure of $Al(OR^F)_3$ ($R^F = C(CF_3)_3$) at the BP86/SV(P) level.

We interpret this result as the first step towards C–F bond cleavage and decomposition. To avoid this internal coordination, we changed solvents and performed the reaction given in Equation (2) in fluorobenzene, from which the crystalline adduct $PhF \rightarrow Al(OR^F)_3$ **1** formed in 98% yield. In the ^{19}F NMR spectrum, the singlet of the equivalent CF_3 groups occurs at $\delta^{19}F = -75.2$ ppm, and that of the coordinated fluorobenzene (Ph*F*→Al) is found at −144.0 ppm (calculated −138.6 ppm; BP86/SV(P)). The ^{27}Al NMR spectrum has one broad signal at 38 ppm ($\Delta_{1/2} = 2350$ Hz). Compound **1** is highly soluble in fluorobenzene at 273 K (stock solutions with concentrations of up to 828 $\mathrm{g\,L^{-1}}$, i.e., 1.0 $\mathrm{mol\,L^{-1}}$, were prepared). A dilute fluorobenzene solution of **1** in a sealed tube was stable for days at room temperature, as shown by NMR spectroscopy. However, we recommend storage and use of the solution at temperatures under 273 K. Large single crystals of **1** form upon cooling to 253 K, may be isolated, and are stable for weeks at or below 273 K. We also stored solid **1** in pentane or hexane at 243 K. These stock systems form clear solutions at about 268 K and may be used in situ for the preparation of $[\mathrm{FAl(OR^F)_3}]^-$ and $[\mathrm{(R^FO)_3AlFAl(OR^F)_3}]^-$ salts.[26] The crystal structure of **1** is shown in Figure 2.[27]

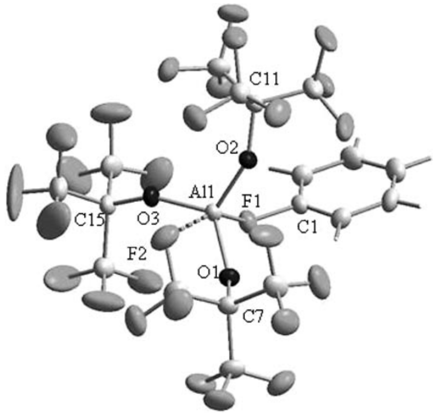


Figure 2. Molecular structure of $[\mathrm{PhF\rightarrow Al(OR^F)_3}]$ (**1**; $\mathrm{R^F = C(CF_3)_3}$) at 103.1 K with thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: Al1-O3 1.685(2), Al1-O2 1.693(2), Al1-O1 1.706(2), Al1-F1 1.864(2), Al1-F2 2.770(8), O1-C7 1.369(3), O2-C11 1.365(3), O3-C15 1.364(3), F1-C1 1.447(3); O3-Al1-O2 115.83 (10), O3-Al1-O1 121.43(10), O2-Al1-O1 113.22(10), O3-Al1-F1 102.83(9), O2-Al1-F1 103.01, O1-Al1-F1 95.30(9), C7-O1-Al1 138.08(18), C11-O2-Al1 150.16(19), C15-O3-Al1 151.56(19), C1-F1-Al1 129.99(15).

Compound **1** is the first neutral Lewis acid that coordinates the weak nucleophile fluorobenzene via the fluorine atom. The only available example of a fluorine-bound fluorobenzene complex is cationic $[(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Ti}\leftarrow\mathrm{FPh}]^+$.[28] The geometry about the central aluminum ion Al1 can be described as distorted tetrahedral or 4(+1). The fifth contact opposite to the coordinating fluorobenzene molecule derives from a $\mathrm{CF_3}$ group but is quite long (2.770(8) Å), which illustrates the improved stability of the adduct complex compared to the calculated data from free $\mathrm{Al(OR^F)_3}$, with $\mathrm{CF_3}$ contacts of about 2.13 Å (see above). The influence of the Lewis acid on the coordinated fluorobenzene molecule is noteworthy, indicated by a C–F bond elongation of 0.09 Å (C1-F1 1.447 Å; free fluorobenzene, 1.356 Å).[29]

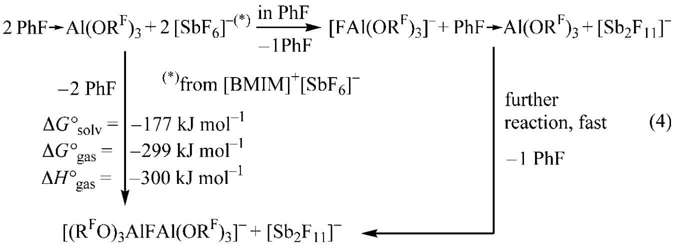
Nevertheless, some other features show the fluorobenzene to be only loosely bound and liable to substitution. The Al1–F1 bond (1.864(2) Å) is much longer than the Al–F bonds of coordinating fluorides in $[\mathrm{CPh_3}][\mathrm{FAl(OR^F)_3}]$ (1.66 Å)[30] and $[\mathrm{(R^FO)_3AlFAl(OR^F)_3}]^-$ (1.77 Å).[31] This bond is also longer than the Al1–O bonds from the alkoxides (av. 1.695 Å), which in fact are shortened by 0.03 Å compared to the corresponding homoleptic $[\mathrm{Al(OR^F)_4}]^-$ anion.[32] Furthermore, the average Al1-O-C angle (150.9°) of two out of three $\mathrm{OC(CF_3)_3}$ groups indicates an ionic Al1–O bond character and high electron deficiency at the aluminum atom.[33] In agreement with this, the sum of the O-Al-O angles of 350.5° is closer to a trigonal coordination (360°) than to the ideal tetrahedral (328.5°).

The weak coordination of fluorobenzene to $\mathrm{Al(OR^F)_3}$ may further be anticipated from the low calculated complexation enthalpy $\Delta_r H^\circ_{gas}$ of only $-32\ \mathrm{kJ\,mol^{-1}}$ [Eq. (3)]. As calculated and experimental Al–F bond lengths differ by +0.11 Å, this value appears to be a lower limit. As further confirmation, exchange between deuterated and nondeuterated fluorobenzene in fluorobenzene solution was observed by ^{19}F NMR experiments. This result validates a reversible coordination of fluorobenzene, and testifies that access to free $\mathrm{Al(OR^F)_3}$ is accessible in fluorobenzene solution. However, when **1** is dissolved in dichloromethane at 298 K, the adduct is not stable. An analysis of the equilibrium shows how the stability of **1** depends on the concentration of fluorobenzene [Eq. (3)].

$$\mathrm{PhF} + \mathrm{Al(OR^F)_3} \xrightleftharpoons{\mathrm{C_6D_5F}} \mathrm{PhF} \rightarrow \mathrm{Al(OR^F)_3} \quad K = \frac{[\mathrm{PhFAl(OR^F)_3}]}{[\mathrm{PhF}][\mathrm{Al(OR^F)_3}]} \qquad (3)$$

The concentration of fluorobenzene in dichloromethane is equal to that of free $\mathrm{Al(OR^F)_3}$, and thus large enough to allow decomposition of the free Lewis acid by C–F activation (see Figure 1). As a solvent, the concentration of fluorobenzene is much larger. Therefore, the concentration of $\mathrm{Al(OR^F)_3}$ has to be much lower, and thus $\mathrm{PhF\rightarrow Al(OR^F)_3}$ is fairly stable in fluorobenzene. From the solvent dependence of the equilibrium given in Equation (3), we suggest that ΔG°_{solv} must be close to $0\ \mathrm{kJ\,mol^{-1}}$ ($K = 0.01$–100).

For experimental confirmation of the postulated superacidity of $\mathrm{PhF\rightarrow Al(OR^F)_3}$ (see Table 1), the reaction of **1** with a suitable source of $[\mathrm{SbF_6}]^-$, for example, the ionic liquid $[\mathrm{BMIM}][\mathrm{SbF_6}]$ ($[\mathrm{BMIM}]^+$ = 1-butyl-3-methylimidazolium), was performed [Eq. (4)].



(4)

The formation of $[\mathrm{FAl(OR^F)_3}]^-$ confirms fluoride abstraction from $[\mathrm{SbF_6}]^-$; however, the intermediate Lewis acid $\mathrm{SbF_5}$ generated further reacts with another $[\mathrm{SbF_6}]^-$ ion to form $[\mathrm{Sb_2F_{11}}]^-$,[34] which was assigned reproducibly from the NMR spectra of several reactions: $[\mathrm{Sb_2F_{11}}]^-$: $\delta^{19}\mathrm{F(C_6D_5F)} = -99.9$, -115.7, and -133.6 ppm; compare with: $\delta^{19}\mathrm{F(HF)} = -90.4$, -116.7, and -138.7 ppm[35] and δ^{19}F(calcd, BP86/SV(P)) = -90.2, -95.5, and -126.3 ppm. Similarly to $\mathrm{SbF_5}$, the Lewis acid $\mathrm{PhF\rightarrow Al(OR^F)_3}$ reacts further with the fluoride complex $[\mathrm{FAl(OR^F)_3}]^-$, giving the fluoride-bridged anion, as confirmed by NMR spectroscopy and an X-ray structure analysis of $[\mathrm{BMIM}][\mathrm{(R^FO)_3AlFAl(OR^F)_3}]$.[36] The course of reaction in Equation (4) is in agreement with calculations at the BP86/SV(P) level, in which the first half of the reaction is exergonic by $\Delta_rG^\circ_{solv} = -102\ kJ\,mol^{-1}$ and the entire reaction (4) by $\Delta_rG^\circ_{solv} = -177\ kJ\,mol^{-1}$.

Overall we anticipate that the non-oxidizing Lewis superacid $PhF{\rightarrow}Al(OR^F)_3$ will find widespread application where maximum hard Lewis acidity is required, but oxidative conditions are not tolerated.

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[15] The FIA has been previously calculated with a different method.[20b] In contrast to those results, the FIA values presented herein were calculated at the BP86/SV(P) level of theory to allow comparison.

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[27] Suitable crystals of **1** were formed by cooling a fluorobenzene solution to 253 K. Data was collected on a Bruker Diffraction Apex II using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 106 K. A single crystal was mounted in perfluoroether oil on top of glass fiber and then placed in the cold stream of low-temperature device so that the oil solidified. The structure was solved with direct methods in SHELXS and successive interpretation of the difference Fourier maps using SHELXL-97 (G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**). Refinement against F^2 was carried out with SHELXL-97. All non-hydrogen atoms were included anisotropically in the refinement. Crystal structure determination of $PhF{\rightarrow}Al(OR^F)_3$ (**1**): $T = 173(2)$ K, Lorentz, polarization, and numerical absorption corrections, $P2_1/n$, $Z = 4$, $a = 10.6289(4)$, $b = 21.3339(8)$, $c = 11.8219(5)$ Å, $\beta = 96.733(2)^\circ$, $V = 2662.20(18)$ Å^3, $\mu = 0.297\ mm^{-1}$, $\rho_{calc} = 2.066\ Mg\,m^{-3}$, $\theta_{max} = 26.61^\circ$, reflections: 72201 collected, 5486 unique ($R_{int} = 0.0497$), $R1 = 0.0445$, $wR2$(all data) = 0.1016, $GOF = 1.064$. CCDC-662085 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[33] Owing to the weak internal Al1–F2 interaction (2.778 Å) one of the OR^F ligands adopts a smaller Al-O-C angle (138.1°).

[34] This assignment is further supported by a reaction of SbF_5 with fluorobenzene: liquid SbF_5 was added to liquid fluorobenzene at room temperature in a glove box; an oxidation occurs, and the solution turns an intense green. In reactions according to Equation (4), the green coloration was never observed. This suggests that the fluoride ion is removed from $[SbF_6]^-$ in an associative process, that is: $[(R^FO)_3Al{-}F{\cdots}SbF_5{\cdots}SbF_6]^{2-} \rightarrow [(R^FO)_3AlF]^- + [Sb_2F_{11}]^-$.

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[36] Unfortunately, the quality of the structure is not good owing to twinning and disorder. Selected details of the refinement: *P*1; cell constant: 11.3443, 11.3787, 12.8865 Å; 109.202, 97.371, 118.639°; $R1 = 26.1\,\%$; 39402 reflections, completeness: 98 %, θ: 28°, 11493 data, 852 parameters.