Chemistry with the Lewis Superacid $Al(OC(CF_3)_3)_3$

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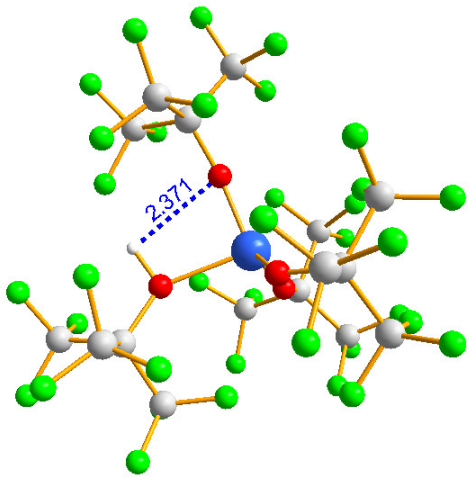
The design of particularly strong molecular Lewis acids are of great interest for applied and fundamental chemistry. These Lewis acids are often used in rearrangement reactions, ionizations, catalysis and bond heterolysis reactions. In analogy to Brønsted superacids, which are stronger than the strongest conventional Brønsted acid, 100% H_2SO_4, we defined the Lewis superacids as molecular compounds, which are stronger than monomeric SbF_5 in the gas phase.[1]
Following N. Bartlett the strength of a Lewis acid is evaluated by the fluoride ion affinity (FIA).[2] It combines the strength of a Lewis acid $LS_{(g)}$ with the energy that is released upon binding a fluoride ion F^-. Quantum chemical calculations of isodesmic reactions allow the simplest and most general access to FIA values. Lewis superacids are defined by a FIA higher than that of monomeric SbF_5 (489 kJ/mol), which is the strongest conventional Lewis acid.[1] In our group we synthesized the Lewis superacid $Al(OC(CF_3)_3)_3$ with a FIA of 537 kJ/mol.

In analogy to the HF/SbF_5 system[3] we created on the basis of the Lewis superacid $Al(OC(CF_3)_3)_3$ a Brønsted acidic system by synthesizing the protonated weakly coordinating anion $H^+[Al(OC(CF_3)_3)_4]^-$. IR, Raman and NMR studies indicate that the system might be better described as an $HOC(CF_3)_3/Al(OC(CF_3)_3)_3$ adduct. Nevertheless experiments (reaction with SbF_6^- and SO_2) as well as calculated studies reveal a more Lewis acidic system than SbF_5. Protonation of diethylether or aromats like mesitylene were achieved.



$$Ar + HX + AlX_3 \longrightarrow [ArH]^+[AlX_4]^-$$

In dependence of the polarity of the solvent (hexane, perfluorohexane or dichloromethane) we isolated only $H^+[Al(OC(CF_3)_3)_4]^-$ (figure), $[HMes]^+[Al(OC(CF_3)_3)_4]^-$ or $[HMes]^+[((CF_3)_3CO)_3Al\text{-}F\text{-}Al(OC(CF_3)_3)_3]^-$.
We will provide an overview about the stability, reactivity and problems with the new acidic system. It is an impressive example for the synthesis of a non-oxidizing Brønsted superacid using the Lewis superacidity of $Al(OC(CF_3)_3)_3$.

[1] L. O. Müller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quinones, V. Brecht, I. Krossing, *Angew. Chem.* **2008**, *120*, 7772.
[2] T. E. Mallouk, G. L. Rosenthal, G. Mueller, R. Brusasco, N. Bartlett, *Inorg. Chem.* **1984**, *23*, 3167.
[3] G. A. Olah, *J. Am. Chem. Soc.* **1965**, 1103.