

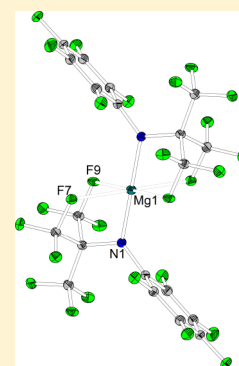
The New NH-Acid $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ and Its Crystalline and Volatile Alkaline and Earth Alkaline Metal Salts

Julius F. Kögel, Lars H. Finger, Nicolas Frank, and Jörg Sundermeyer*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35043 Marburg, Germany

Supporting Information

ABSTRACT: Herein we report on the new NH-acid *N*-(2,3,4,5,6-pentafluorophenyl)-*N*-nonafluoro-*tert*-butylamine, $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$, bearing two different sterically demanding and strongly electron-withdrawing perfluorinated amine substituents. The title compound and seven of its alkaline and alkaline earth metal salts were synthesized and investigated concerning their thermal, spectroscopic, and structural properties. The Li, Na, K, Cs, and Mg salts were investigated by single-crystal XRD analysis. The molecular structures reveal interesting motifs such as manifold fluorine metal secondary interactions. The lithium and magnesium compounds exhibit a remarkable thermal stability and an unexpectedly high volatility. We believe that this report will provoke investigations to apply the corresponding anion in ionic liquids, in lithium electrolytes, and as a weakly electron-donating ligand in the preparation of highly Lewis-acidic main group, rare earth, or transition metal complexes.



INTRODUCTION

Highly Brønsted acidic amines or imides HNRR' with two electron-withdrawing perfluorinated alkyl, aryl, or acid functionalities, so-called NH-acids, have attracted considerable scientific interest during the last decades. In particular, the most prominent representative bis(trifluoromethylsulfonyl) imide, $\text{HN}(\text{SO}_2\text{CF}_3)_2$,¹ has found widespread use: Its corresponding anion has been used as a component of ionic liquids² or electrochemical devices³ due to its weakly coordinating nature. Exhibiting a higher acidity in the gas phase than hydrogen iodide, $\text{HN}(\text{SO}_2\text{CF}_3)_2$ has been the subject of manifold experimental and theoretical investigations on its acidic behavior.⁴ The extraordinary acidity allows the use of bis(trifluoromethylsulfonyl)imide as a Brønsted acid catalyst in imine amidation reactions,⁵ hetero-Michael additions,⁶ and enantioselective Diels–Alder⁷ or cyclization reactions of siloxyalkynes with arenes and alkenes.⁸ Furthermore, various metal complexes of $\text{HN}(\text{SO}_2\text{CF}_3)_2$ have been applied to reactions catalyzed by Lewis acids, which was recently reviewed by Antonietti et al.⁹ The weakly donating property of the corresponding anion was used to design copper and silver complexes $[\text{M}(\text{L})\text{N}(\text{SO}_2\text{CF}_3)_2]$ with high binding affinity toward arenes and olefins L .¹⁰

Although being less acidic than $\text{HN}(\text{SO}_2\text{CF}_3)_2$ by several orders of magnitude, bis(pentafluorophenyl)amine first reported by Brooke et al. has also been a subject of research.¹¹ Metal amido complexes of $\text{HN}(\text{C}_6\text{F}_5)_2$ show interesting metal fluorine interactions in many cases since this ligand offers only aromatic fluorine atoms as possible donors besides the nitrogen atom. For example, this has been observed for the lithium salts $\text{LiN}(\text{C}_6\text{F}_5)_2 \cdot \text{Et}_2\text{O}$ and $\text{LiN}(\text{C}_6\text{F}_5)_2 \cdot \text{THF}$ ¹² and the neodymium complex $(\eta^6\text{-toluene})\text{Nd}[\text{N}(\text{C}_6\text{F}_5)_2]_3$.¹³ Recently Yin et al. reported the preparation of the homoleptic cerium and

lanthanum complexes stabilized by $\text{M} \cdots \text{F}$ interactions.¹⁴ $[\text{N}(\text{C}_6\text{F}_5)_2]^-$ is also found as a ligand for the transition metals titanium, zirconium, vanadium, iron, cobalt,¹⁵ and tungsten.¹⁶

The two unsymmetrical hybrids of bis(perfluoroalkylsulfonyl)imide and bis(pentafluorophenyl)amine, $\text{HN}(\text{C}_6\text{F}_5)(\text{SO}_2\text{CF}_3)$ and $\text{HN}(\text{C}_6\text{F}_5)(\text{SO}_2\text{C}_4\text{F}_9)$, have also been applied to the preparation of imidazolium- and phosphonium-based ionic liquids in the same way as their parent compound $\text{HN}(\text{C}_6\text{F}_5)_2$.¹⁷ Furthermore, their corresponding lithium salts were studied as electrolytes in lithium ion batteries.¹⁸

Perfluorinated alcohols, in particular those with a sterically demanding nonafluoro-*tert*-butyl group, have been used by Krossing et al. to prepare the Lewis superacidic aluminum complex $\text{Al}(\text{OC}(\text{CF}_3)_3)_3$.¹⁹ Corresponding perfluorinated secondary amines and their complexes containing the electron-withdrawing $\text{C}(\text{CF}_3)_3$ group have not been thoroughly investigated so far. Therefore we set out to synthesize one example of such an acidic amine, in particular the title compound $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ and its basic group 1 and 2 amido metal coordination compounds. It is expected that the two different sterically demanding N-substituents are competing in their specific secondary $\text{C}-\text{F} \cdots \text{M}$ interactions next to the primary $\text{N}-\text{M}$ interaction. Other points of interest of such metal perfluoramides are their thermal stability, their solubility in organic solvents, and their ability to form crystalline perfluoramido metal Lewis acids.

SYNTHESES

The synthesis of *N*-(2,3,4,5,6-pentafluorophenyl)-*N*-nonafluoro-*tert*-butylamine, $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$, starts with the

Received: January 22, 2014

Published: March 17, 2014

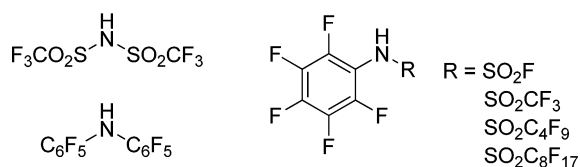


Figure 1. Examples of symmetric and unsymmetric NH-acids.

reaction of pentafluoroaniline with hexafluoroacetone followed by the addition of phosphoryl chloride, giving *N*-pentafluorophenyl-2-iminohexafluoroacetone with a yield of up to 87%.²⁰ The transfer of a trifluoromethyl group to the imine carbon atom is achieved by trifluoromethyltrimethylsilane, the so-called Ruppert's reagent,²¹ in the presence of 1.2 equivalents of cesium fluoride in THF following a protocol by Petrov used for other derivatives.²² In our case, the cesium salt was isolated and extensively dried to remove traces of THF. Protonation with 10% aqueous hydrochloric acid yielded pure $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ as a colorless oil (Scheme 1).

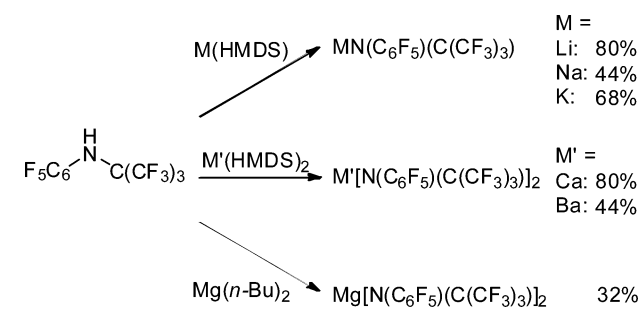
The lithium, sodium, and potassium salts were obtained by deprotonation of $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ with the corresponding bis(trimethylsilyl)amides in hexane or toluene. $\text{Ca}[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]_2$ and $\text{Ba}[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]_2$ were prepared in an analogous manner, whereas the corresponding magnesium salt was obtained from the reaction of the NH-acid with di-*n*-butylmagnesium.

SPECTROSCOPIC AND ACIDIC PROPERTIES

All compounds described herein were analyzed by ^1H , ^{13}C , and ^{19}F NMR spectroscopy, IR spectroscopy, and elemental analysis. The proton NMR spectrum of $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ shows a singlet, whereas its chemical shift is strongly solvent dependent, as it has already been observed for related NH-acids. The ^{13}C NMR signals of carbon atoms carrying fluorine atoms show large $^1J_{\text{FC}}$ coupling constants between 251.3 and 292.2 Hz. For most compounds studied herein, only the $^1J_{\text{FC}}$ coupling constant can be determined, whereas $^2J_{\text{FC}}$ and $^3J_{\text{FC}}$ coupling constants remain unresolved. A triplet with a chemical shift of -69.6 ppm in benzene- d_6 and a coupling constant of 7.1 Hz is observed for the CF_3 groups in the ^{19}F NMR spectrum of $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$, which can be referred to a coupling through space with the aromatic *ortho*-fluorine atoms. The IR spectrum shows an absorption band for the NH stretch vibration at 3406 cm^{-1} ($\text{HN}(\text{C}_6\text{F}_5)_2$: 3423 cm^{-1} ,^{11b} $\text{HN}(\text{C}(\text{CF}_3)_3)_2$: 3454 cm^{-1}).²² Furthermore, the molecular ion peak of $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]^-$ was detected in the (-)-ESI mass spectrum.

All of the reported complexes are slightly soluble in toluene, the solvent that was mainly used for the metalation of the perfluorinated amine title compound. This underlines a certain molecular nature of the complexes. Their latent ionic character is manifested in strongly donating solvents such as DMSO- d_6 : Independently of the cation, the ^{13}C and ^{19}F NMR spectra exhibit nearly identical chemical shifts and the ^{13}C NMR signals

Scheme 2. Preparation of Alkaline and Earth Alkaline Metal Salts of $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$



show almost equal $^1J_{\text{CF}}$ coupling constants, suggesting that a complete dissociation into solvated cations $[\text{M}(\text{dms})_x]^{+2}$ and anions $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)(\text{dms})_y]^-$ is occurring. The ^{19}F NMR signals for the anion solvated in DMSO- d_6 show a considerable high-field shift compared to the solvated NH-acid that is especially distinct for the *para*-fluorine atoms (e.g., -185.0 ppm in the case of $\text{Li}(\text{dms})_x\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ compared to -153.0 ppm for the NH-acid).

A qualitative competition experiment versus bis-(pentafluorophenyl)amine (gas phase acidity: 316.5 kcal/mol)^{4a} in DMSO solution was performed to estimate the acidity of $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ and the electron-withdrawing character of the perfluorinated *tert*-butyl group.

The observation that $\text{HN}(\text{C}_6\text{F}_5)_2$ fully protonates $\text{LiN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ (1:1 molar ratio) suggests that the symmetric NH-acid is more acidic in DMSO than $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ by at least 1 order of magnitude.²³ Furthermore, we could show that the strong acid $\text{HN}(\text{SO}_2\text{CF}_3)_2$ (gas phase acidity: 286.5 kcal/mol)^{4b} is not able to protonate the amine $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ in DMSO to form an ammonium salt.

STRUCTURAL FEATURES

The molecular structures of the lithium, sodium, and potassium salts (Figures 2–5) display dinuclear molecular complexes: Two metal atoms are bridged by the nitrogen atoms of two $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]^-$ moieties ($d(\text{Li}-\text{N})$ 2.08(1) and 2.10(1) Å; $d(\text{Na}-\text{N})$ 2.477(2) and 2.442(2) Å; $d(\text{K}-\text{N})$ 2.822(1) and 2.904(1) Å). As expected, the nonbonding $\text{N}\cdots\text{N}$ distances within the dimers increase when advancing from the small lithium ion (3.234(8) Å) to the larger sodium (3.481(2) Å) and potassium (3.744(1) Å) ions. Furthermore, the small size of the lithium atom results in a small $\text{Li}-\text{N}-\text{Li}$ angle of $78.7(5)^\circ$ and a large $\text{N}-\text{Li}-\text{N}$ angle of $101.3(5)^\circ$, whereas the corresponding values invert with increasing size of the metal ion ($\text{Na}-\text{N}-\text{Na}$ $89.58(5)^\circ$; $\text{N}-\text{Na}-\text{N}$ $90.42(5)^\circ$; $\text{K}-\text{N}-\text{K}$ $98.36(3)^\circ$; $\text{N}-\text{K}-\text{N}$ $81.64(3)^\circ$). In addition to the coordination of the metal atoms by nitrogen donors, the formation of several metal fluorine contacts is observed (illustrated as dashed lines in Figures 2–8). The lithium salt shows three particularly short $\text{Li}\cdots\text{F}$ distances between 2.02(1) and 2.12(1) Å and three additional

Scheme 1. Preparation of $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ Starting from Pentafluoroaniline

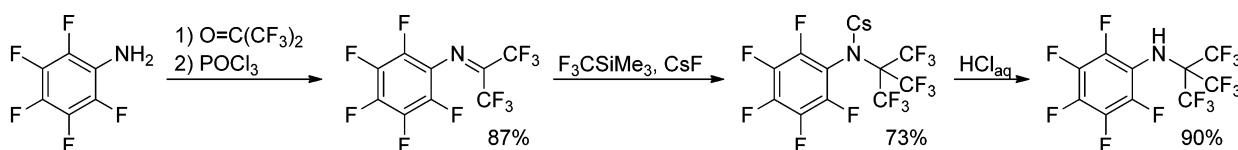


Table 1. Crystal Data and Experimental Conditions

	LiN(C ₆ F ₅)(C ₄ F ₉)	NaN(C ₆ F ₅)(C ₄ F ₉)	KN(C ₆ F ₅)(C ₄ F ₉)	CsN(C ₆ F ₅)(C ₄ F ₉)	Mg[N(C ₆ F ₅)(C ₄ F ₉) ₂]
empirical formula	C ₁₀ F ₁₄ LiN	C ₁₀ F ₁₄ NaN	C ₁₀ F ₁₄ KN	C ₁₀ F ₁₄ CsN, C ₇ H ₈	C ₂₀ F ₂₈ MgN ₂
mol weight [g mol ⁻¹]	407.05	423.10	439.21	625.15	824.53
cryst habit	colorless block	colorless needle	colorless plate	colorless plate	colorless block
cryst size [mm ³]	0.11 × 0.10 × 0.10	0.35 × 0.11 × 0.10	0.25 × 0.23 × 0.07	0.32 × 0.10 × 0.07	0.26 × 0.22 × 0.16
cryst system	orthorhombic	triclinic	monoclinic	monoclinic	triclinic
space group	<i>Pccn</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P121/m1</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	18.685(3)	6.9421(5)	15.9930(5)	10.0049(9)	6.785(5)
<i>b</i> [Å]	10.6119(12)	9.8740(6)	13.9077(6)	20.860(2)	10.022(5)
<i>c</i> [Å]	12.2994(16)	10.4269(6)	11.7967(4)	10.3310(10)	10.497(4)
α [deg]	90	64.0980(17)	90	90	61.91(3)
β [deg]	90	75.0294(19)	95.485(3)	112.852(3)	85.492(11)
γ [deg]	90	74.6100(20)	90	90	74.112(5)
volume [Å ³]	2438.8(6)	611.46(7)	2611.88(16)	1986.8(3)	604.6(6)
<i>Z</i>	8	2	8	4	1
density [g cm ⁻³]	2.217	2.298	2.234	2.090	2.265
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)	100(2)
absorp coeff [mm ⁻¹]	0.281	0.318	0.584	1.997	0.310
θ range [deg]	2.2 to 25.0	2.2 to 26.2	1.9 to 26.8	2.2 to 27.2	2.2 to 26.0
index ranges	-22 ≤ <i>h</i> ≤ 19, -12 ≤ <i>k</i> ≤ 11, -14 ≤ <i>l</i> ≤ 12	-8 ≤ <i>h</i> ≤ 8, -12 ≤ <i>k</i> ≤ 12, -12 ≤ <i>l</i> ≤ 11	-20 ≤ <i>h</i> ≤ 20, -17 ≤ <i>k</i> ≤ 17, -14 ≤ <i>l</i> ≤ 14	-12 ≤ <i>h</i> ≤ 12, -26 ≤ <i>k</i> ≤ 26, -13 ≤ <i>l</i> ≤ 13	-8 ≤ <i>h</i> ≤ 8, -12 ≤ <i>k</i> ≤ 12, -12 ≤ <i>l</i> ≤ 12
reflns collected	6827	12 094	17 992	31 732	5614
indep reflns	2162 [<i>R</i> (int) = 0.1524]	2457 [<i>R</i> (int) = 0.0596]	2775 [<i>R</i> (int) = 0.0409]	4535 [<i>R</i> (int) = 0.0406]	2368 [<i>R</i> (int) = 0.0849]
absorp corr	multiscan	multiscan	multiscan	multiscan	multiscan
max. and min. transmn	0.9719 and 0.9673	0.969 and 0.959	0.9645 and 0.8222	0.7455 and 0.6153	1.2918 and 0.6145
data/restraints/ params	2162/2/205	2457/0/235	2775/0/235	4535/6/314	2368/0/232
goodness-of-fit on <i>F</i> ²	0.488	1.059	1.029	1.203	0.981
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0417	<i>R</i> 1 = 0.0350	<i>R</i> 1 = 0.0214	<i>R</i> 1 = 0.0235	<i>R</i> 1 = 0.0460
<i>R</i> indices (all data)	w <i>R</i> 2 = 0.0727	w <i>R</i> 2 = 0.0956	w <i>R</i> 2 = 0.0537	w <i>R</i> 2 = 0.0704	w <i>R</i> 2 = 0.1217
larg diff peak/ hole [e Å ⁻³]	0.34/-0.29	0.54/-0.35	0.36/-0.26	0.72/-0.47	0.57/-0.51
treatment of H atoms				constr	

Li...F contacts exhibiting lengths between 2.94(1) and 3.14(1) Å, which are only slightly below the sum of the van der Waals radii of lithium and fluorine.²⁴ The bigger sodium ion allows the coordination of eight fluorine atoms and shows a broad range of Na...F distances from 2.336(2) to 3.348(1) Å. The potassium is coordinated by seven fluorine atoms with K...F distances between 2.7255(8) and 2.9939(8) Å. Plenio, who reviewed the field of interactions between metals and organically bound fluorine atoms, reported a maximum between 2.45 and 2.75 Å in the distribution of Na...F distances and between 2.85 and 3.05 Å in the case of K...F contacts.²⁵ Thus, most of the corresponding values observed for KN(C₆F₅)(C(CF₃)₃) are comparably short, which can be referred to the fact that the ligand exhibits only one nitrogen donor atom beside the fluorine atoms. The crystal structures of LiN(C₆F₅)(C(CF₃)₃), NaN(C₆F₅)(C(CF₃)₃), and KN(C₆F₅)(C(CF₃)₃) reveal the interaction of neighboring dimers *via* M...F contacts. The fact that single crystals of LiN(C₆F₅)(C(CF₃)₃) were obtained *via* sublimation at 120 °C and 1.3 × 10⁻³ mbar is in accord with only weak Li...F contacts between the dimers. Furthermore, this unexpected behavior proves the remarkable thermal stability of LiN(C₆F₅)(C(CF₃)₃) with respect to LiF elimination. We could show that LiN(C₆F₅)₂ readily eliminates

lithium fluoride during attempts to sublime it.¹⁸ A high volatility is known for fluorinated alkoxides that are used for chemical vapor deposition²⁶ and for alkaline metal bistrimethylsilylamides, but it is unique for lithium (and magnesium, see below) amides with perfluorinated ligands.

In the case of the sodium salt the formation of two-dimensional chains can be observed in the crystal structure (Figure 4), whereas the lithium and the potassium salts form complicated three-dimensional networks. Dimeric substructures revealing metal fluorine contacts were also found for LiN(C₆F₅)₂·Et₂O (*d*(Li–N) between 2.09(1) and 2.12(1) Å, *d*(Li...Li) 2.67(1) Å, N–Li–N 100.7(4)° and 101.4(4)°, Li–N–Li 78.4(4)° and 79.1(4)°) and LiN(C₆F₅)₂·THF (*d*(Li–N) between 2.080(6) and 2.178(6) Å, *d*(Li...Li) 2.675(8) Å, N–Li–N 103.2(3)° and 99.2(3)°, Li–N–Li 79.2(2)° and 77.8(2)°), which exhibit similar N–Li and Li...Li distances as well as N–Li–N and Li–N–Li angles to the lithium salt discussed herein.¹² The shortest Li...F contact observed in these structures is longer than in the solvent-free lithium salt discussed herein (LiN(C₆F₅)₂·Et₂O: 2.196(9) Å, LiN(C₆F₅)₂·THF: 2.098(6) Å).

The crystal structure of (η⁶-toluene)CsN(C₆F₅)(C(CF₃)₃) (Figure 6) also reveals nitrogen-bridged dimers, but addition-

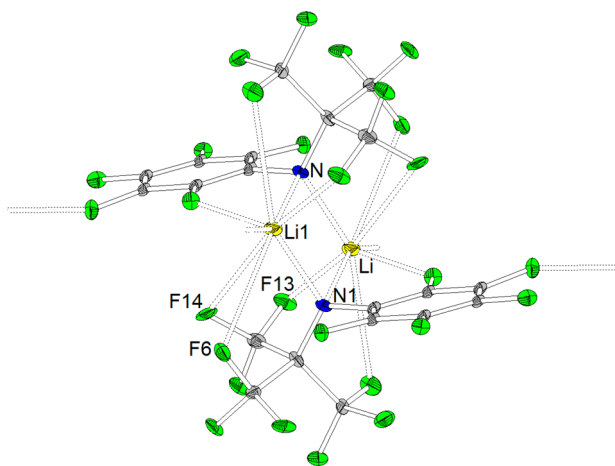


Figure 2. Molecular structure of $\text{LiN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ (ellipsoids with 30% probability). Selected bond lengths (Å) and angles (deg): Li1-N1 2.10(1), $\text{Li1-N}(1-x, -y, 1-z)$ 2.08(1), $\text{Li1}\cdots\text{F1}(1-x, -y, 1-z)$ 2.02(1), $\text{Li1}\cdots\text{F2}(x, 0.5-y, -0.5+z)$ 2.06(1), $\text{Li1}\cdots\text{F6}$ 3.10(1), $\text{Li1}\cdots\text{F11}(1-x, -y, 1-z)$ 3.14(1), $\text{Li1}\cdots\text{F13}(1-x, -y, 1-z)$ 2.12(1), $\text{Li1}\cdots\text{F14}$ 2.94(1), $\text{Li1}\cdots\text{Li}(1-x, -y, 1-z)$ 2.65(2), $\text{Li1-N1-Li}(1-x, -y, 1-z)$ 98.36(3).

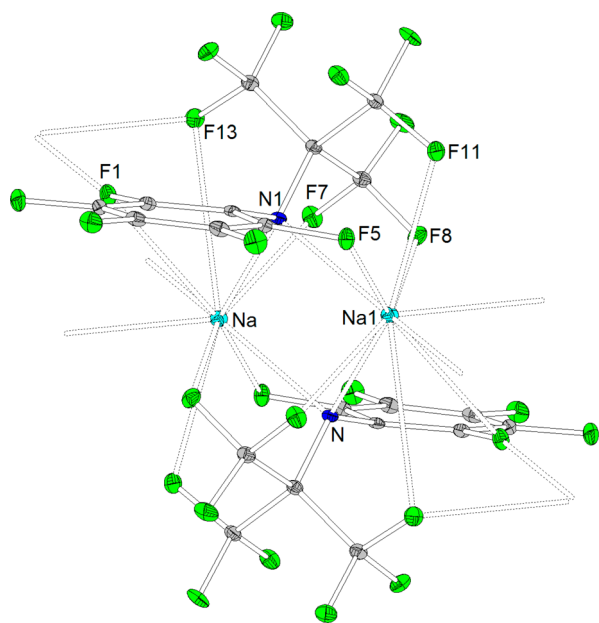


Figure 3. Molecular structure of $\text{NaN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ (ellipsoids with 30% probability). Selected bond lengths (Å) and angles (deg): Na1-N1 2.477(2), $\text{Na1-N}(1-x, -y, 1-z)$ 2.442(2), $\text{Na1}\cdots\text{F1}(1+x, y, z)$ 2.336(2), $\text{Na1}\cdots\text{F1}(1-x, -y, 1-z)$ 3.117(1), $\text{Na1}\cdots\text{F5}$ 2.483(2), $\text{Na1}\cdots\text{F7}(1-x, -y, 1-z)$ 2.558(1), $\text{Na1}\cdots\text{F8}$ 2.420(1), $\text{Na1}\cdots\text{F11}$ 2.804(1), $\text{Na1}\cdots\text{F13}(1+x, y, z)$ 2.688(1), $\text{Na1}\cdots\text{F13}(1-x, -y, 1-z)$ 3.348(1), $\text{Na1}\cdots\text{Na}(1-x, -y, 1-z)$ 3.466(1), $\text{Na1-N1-Na}(1-x, -y, 1-z)$ 89.58(5).

ally contains a toluene molecule showing η^6 -coordination to two cesium atoms, which emphasizes the soft Lewis-acidic character of this metal center (distance between Cs and the center of toluene: 3.4092(4) Å). The $\text{Cs}\cdots\text{C}_{\text{Ar}}$ distances are between 3.625(2) and 3.739(2) Å and thus lie within the range from 3.3 to 3.8 Å that was reported for cesium arene interactions.²⁷ The toluene ligands link two vicinal dimers in each case (Figure 7). Each cesium atom shows interactions with three $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]^-$ units. Two of these provide their

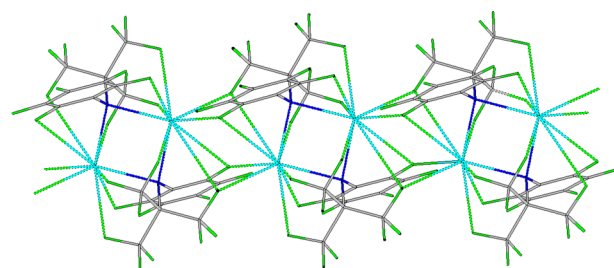


Figure 4. Two-dimensional chains observed in the crystal structure of $\text{NaN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$.

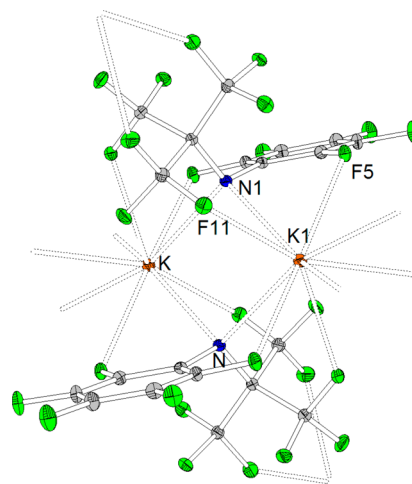


Figure 5. Molecular structure of $\text{KN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ (ellipsoids with 30% probability). Selected bond lengths (Å) and angles (deg): K1-N1 2.904(1), $\text{K1-N}(1.5-x, 0.5-y, 2-z)$ 2.822(1), $\text{K1}\cdots\text{F1}(1.5-x, 0.5-y, 2-z)$ 2.8259(9), $\text{K1}\cdots\text{F4}(2-x, y, 2.5-z)$ 2.9939(8), $\text{K1}\cdots\text{F5}$ 2.7978(7), $\text{K1}\cdots\text{F7}(1.5-x, 0.5-y, 2-z)$ 2.7633(8), $\text{K1}\cdots\text{F9}(x, 1-y, 0.5+z)$ 2.9865(9), $\text{K1}\cdots\text{F11}$ 2.7255(8), $\text{K1}\cdots\text{F12}(x, 1-y, 0.5+z)$ 2.9865(9), $\text{K1}\cdots\text{K}(1.5-x, 0.5-y, 2-z)$ 4.3337(4), $\text{K1-N1-K1}(1.5-x, 0.5-y, 2-z)$ 78.7(5).

nitrogen atoms, two fluorine atoms belonging to CF_3 groups, and one aromatic fluorine atom as donor atoms. The third $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]^-$ moiety coordinates with one *meta*- and the *para*-fluorine atom of a C_6F_5 moiety to the metal center. The distances between the cesium atom and coordinating fluorine atoms range from 3.054(1) to 3.653(2) Å. Plenio reported a maximum in the distribution between 3.20 and 3.40 Å for weakly bonding $\text{Cs}\cdots\text{F}$ contacts.²⁵ The M-N-M ($96.07(5)^\circ$) and the N-M-N angles ($83.93(5)^\circ$) in $(\eta^6\text{-toluene})\text{CsN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ are similar to the corresponding values found in the potassium salt ($98.36(3)^\circ$ and $81.64(3)^\circ$). As expected, the cesium salt shows the largest M-N bond lengths (3.212(2) and 3.330(2) Å) and nonbonding $\text{N}\cdots\text{N}$ distance (4.375(2) Å) among the structures studied herein.

A different coordination mode is found for the magnesium compound (Figure 8) in which a distorted octahedron formed by two $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]^-$ moieties is observed, whereas the asymmetric unit contains only half of the octahedron. Neighboring octahedra interact via π -stacking of C_6F_5 moieties. The fact that single crystals of $\text{Mg}[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]_2$ were obtained by sublimation at 115 °C and atmospheric pressure suggests comparably weak intermolecular interactions and a remarkable thermal stability. The magnesium atom is coordinated by two nitrogen atoms *trans* to each other ($d(\text{Mg-N})$ 1.981(2) and 1.981(2) Å) and four fluorine

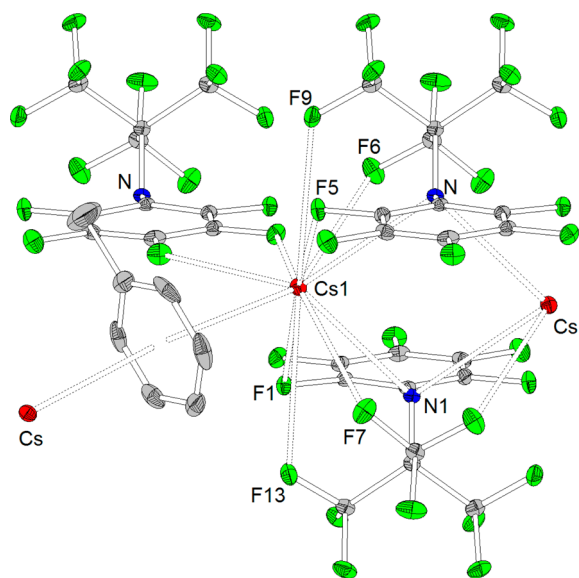


Figure 6. Molecular structure of $(\eta^6\text{-toluene})\text{CsN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ (ellipsoids with 30% probability). $\text{Cs}\cdots\text{F}$ contacts are shown only for Cs1. Selected bond lengths (Å) and angles (deg): Cs1–N1 3.212(2), Cs1–N1(1– x , 1– y , 1– z) 3.330(2), Cs1···F1 3.082(2), Cs1···F2(2– x , 1– x , 1– z) 3.454(2), Cs1···F3(2– x , 1– x , 1– z) 3.303(2), Cs1···F5(1– x , 1– y , 1– z) 3.054(1), Cs1···F6 3.079(2), Cs1···F7 3.140(2), Cs1···F9 3.356(2), Cs1···F13 3.653(2), Cs1···Cs1(1– x , 1– y , 1– z) 4.8648(4), Cs1–N1–Cs1(1– x , 1– y , 1– z) 96.07(5).

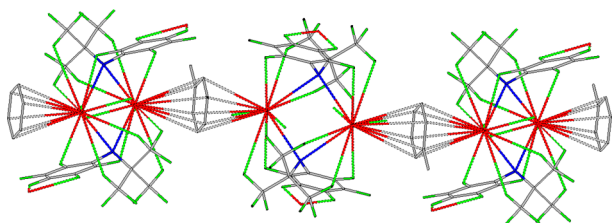


Figure 7. Connection of dimers by η^6 -coordinated toluene molecules in $(\eta^6\text{-toluene})\text{CsN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$.

atoms that are part of *tert*-butyl moieties ($d(\text{Mg}\cdots\text{F})$ 2.186(2) and 2.223(1) Å). It seems that the harder cation Mg^{2+} favors the interaction with sp^3 C–F donors of the *tert*-butyl moiety, while the softer alkali cations M^+ are much less specific in their competitive sp^2 C–F vs sp^3 C–F interaction and in their coordinative configuration. The linear N–Mg–N axis is tilted toward the plane formed by the four coordinating fluorine atoms by $15.57(5)^\circ$. The F–Mg–F angle of fluorine atoms belonging to the same $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]^-$ unit is $72.14(5)^\circ$, whereas this value is $107.86(5)^\circ$ for fluorine atoms of different $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]^-$ moieties. The C–F distances involving coordinating fluorine atoms (1.388(3) and 1.385(3) Å) are considerably longer compared to noncoordinating fluorine atoms bound to aliphatic carbon atoms (ranging from 1.313(3) to 1.333(3) Å). Whereas literature-known alkaline earth metal complexes of HNPh_2 such as $(\text{thf})_2\text{Mg}(\text{NPh}_2)_2$, $(\text{dme})_2\text{Ca}(\text{NPh}_2)_2$, $(\text{thf})_4\text{Sr}(\text{NPh}_2)_2$, and $(\text{thf})_4\text{Ba}(\text{NPh}_2)_2$ reveal the coordination of ether molecules to the metal center,²⁸ the magnesium complex reported herein is a rare example of a solvent-free group II metal amide coordinated only by organically bound fluorine atoms in addition to two nitrogen donors. The two diphenylamide ligands and the two THF molecules in $(\text{thf})_2\text{Mg}(\text{NPh}_2)_2$ form a distorted tetrahedron

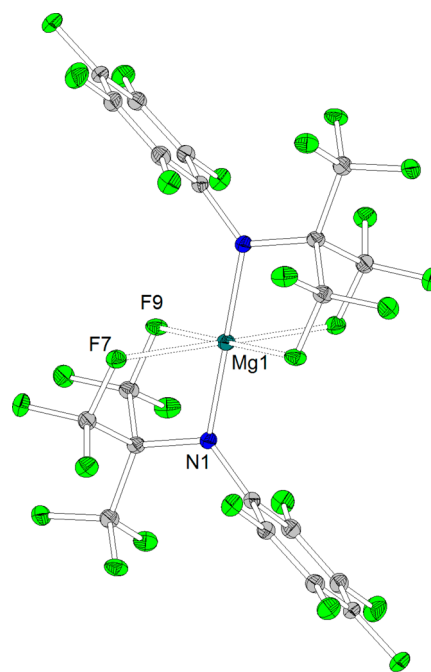


Figure 8. Molecular structure of $\text{Mg}[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]_2$ (ellipsoids with 30% probability). Selected bond lengths (Å) and angles (deg): Mg1–N1 1.981(2), Mg1···F7 2.186(2), Mg1···F9 2.223(1), N1–Mg–N1 180, F9–Mg1–F7 72.14(5).

and a longer Mg–N distance of 2.013(3) Å than found for $\text{Mg}[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]_2$. Similar Mg···F distances of 2.200(2) and 2.199(3) Å to the magnesium complex studied herein were found in a literature-known magnesium amide with a cyclam ligand.²⁹ An octahedral coordination of a magnesium atom involving Mg···F contacts was also observed for the homoleptic magnesium complex of $\text{HN}(\text{C}_6\text{F}_5)((\text{CH}_2)_2\text{NMe}_2)$ showing Mg···F distances of 2.431(3) Å.³⁰

Generally, we notice a trend that more fluorine atoms belonging to CF_3 groups than to aromatic fluorine atoms are involved in $\text{M}\cdots\text{F}$ contacts.³¹ This can be explained by the higher flexibility of the aliphatically bound fluorine atoms due to rotation around the N– C_{tert} and the C_{tert} –C bonds, allowing a less constrained alignment of the fluorine lone pairs to the metal center. However, we have to be aware that some of the longer $\text{M}\cdots\text{F}$ contacts originate from the inevitable vicinity of the metal cations and fluorine atoms caused by the extremely bulky perfluorinated ligands or packing effects rather than solely from an energetically favorable interaction. Thus, the higher number of $\text{M}\cdots\text{F}$ contacts involving CF_3 groups might also be a result of the higher number of aliphatic compared to aromatic fluorine atoms.

CONCLUSION AND OUTLOOK

We have presented the synthesis of a new secondary amine with strongly electron-withdrawing and sterically demanding perfluorinated phenyl and *tert*-butyl substituents. *N*-(2,3,4,5,6-Pentafluorophenyl)-*N*-nonafluoro-*tert*-butylamine, $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$, was obtained *via* a CF_3 -group transfer reaction from trifluoromethyltrimethylsilane to the corresponding imine precursor. This NH-acid was fully characterized and used for the synthesis of the alkaline metal salts of lithium, sodium, potassium, and cesium. In addition, the homoleptic complexes of the earth alkaline metals magnesium, calcium, and barium were prepared. We observed a rather unusual volatility for the

Table 2. Selected Structural Features of the Crystal Structures of $\text{LiN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$, $\text{KN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$, $\text{CsN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$, and $\text{Mg}[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]_2$ ^a

	N–M	M···F contacts	coordinating $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]^-$ units	CN	M···F _{Ar}	M···F _{Al}	N···N	N–M–N	M–N–M
$\text{LiN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$	2.08(1)	6	3	8	2.02(1)	2.12(1)	3.234(8)	101.3(5)	78.7(5)
	2.10(1)				2.06(1)	2.94(1)			
$\text{NaN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$	2.442(2)	8	3	10	2.336(2)	2.420(1)	3.481(2)	90.42(5)	89.58(5)
	2.477(2)				2.483(2)	2.558(1)			
					3.117(1)	2.688(1)			
						2.804(1)			
$\text{KN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$	2.822(1)	7	4	9	2.7978(7)	2.7255(8)	3.744(1)	81.64(3)	98.36(3)
	2.904(1)				2.8259(9)	2.7633(8)			
					2.9939(8)	2.7930(8)			
						2.8831(8)			
$\text{CsN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$	3.212(2)	8	3	10	3.054(1)	3.079(2)	4.375(2)	83.93(5)	96.07(5)
	3.330(2)				3.082(1)	3.140(2)			
					3.303(2)	3.356(2)			
					3.454(2)	3.653(2)			
$\text{Mg}[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]_2$	1.981(2)	4	2	6	2.186(2)	2.186(2)	3.962(3)	180.0	
	1.981(2)				2.186(1)	2.186(1)			
					2.223(1)	2.223(1)			

^aBond lengths in Å, angles in deg, CN = coordination number, F_{Ar} = aromatic fluorine atoms, F_{Al} = fluorine atoms of CF₃ groups.

lithium and the magnesium salts, which reveal certain covalent character. This was used to grow single crystals via sublimation. Molecular structures of the lithium, sodium, potassium, cesium, and magnesium salts reveal interesting coordination motifs with manifold labile metal fluorine contacts. Due to its low basicity, we anticipate that the anion $[\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)]^-$ is a promising rather weakly coordinating ligand for the generation of highly Lewis-acidic main group, rare earth, or transition metal complexes. The alkaline metal salts reported herein could serve as starting materials for the synthesis of such Lewis superacids via salt elimination reactions, or they could prove to be valuable precursors for the preparation of highly hydrophobic electrolyte systems.

EXPERIMENTAL SECTION

Reactions were carried out under an inert atmosphere using standard Schlenk techniques. Moisture- and air-sensitive substances were stored in a conventional nitrogen-flushed glovebox. Solvents were purified according to literature procedures and kept under an inert atmosphere. *N*-Pentafluorophenyl-2-iminohexafluoropropane was prepared as described above.²⁰ The metal precursors $\text{LiN}(\text{SiMe}_3)_2$,³² $\text{NaN}(\text{SiMe}_3)_2$,³² $\text{KN}(\text{SiMe}_3)_2$,³³ $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$,³⁴ and $\text{Ba}[\text{N}(\text{SiMe}_3)_2]_2 \cdot \text{THF}$ ³⁵ were synthesized according to literature procedures. Spectra were recorded on the following spectrometers. NMR: Bruker ARX300, Bruker DRX400, Bruker DRX500. IR: ATR-FT-IR. MS: LTQ-FT or QStarPulsar i (Finnigan). Elemental analysis: CHN-Rapid (Heraeus).

Synthesis of $\text{CsN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$. A mixture of *N*-pentafluorophenylbis(trifluoromethyl)methyleneimine (5.37 g, 16.23 mmol, 1.0 equiv) and trifluoromethyltrimethylsilane (2.54 g, 17.85 mmol 1.1 equiv) was added dropwise to a suspension of cesium fluoride (2.98 g, 19.47 mmol, 1.2 equiv) in 40 mL of THF over 30 min. The reaction mixture changed color to yellow and turned red after stirring overnight. The suspension was filtered over Celite, and the filtrate was evaporated to dryness *in vacuo*. The red residue was washed with 40 mL of hexane, and the remaining solid was excessively dried *in vacuo* to remove traces of THF and obtain $\text{CsN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$

(6.34 g, 11.89 mmol, 73%) as a red solid. Single crystals suitable for structure determination were obtained by slowly cooling a saturated solution of $\text{CsN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ in toluene from 90 °C to –30 °C. ¹³C NMR (101 MHz, DMSO-*d*₆): δ 142.7 (d, ¹J_{FC} = 231.2 Hz, *o*-C_{Ar}), 137.6 (dm, ¹J_{FC} = 239.4 Hz, *m*-C_{Ar}), 133.2 (t, ²J_{FC} = 12.1 Hz, *ipso*-C_{Ar}), 128.1 (dt, ¹J_{FC} = 231.5 Hz, ²J_{FC} = 14.5 Hz, *p*-C_{Ar}), 123.0 (q, ¹J_{FC} = 297.0 Hz, –CF₃), 76.1 ppm (dec, ²J_{FC} = 25.4 Hz, C(CF₃)₃). ¹⁹F NMR (282 MHz, DMSO-*d*₆): δ –68.8 (t, ¹J_{FF} = 9.7 Hz, 9F, –CF₃), –156.7 (br s, 2F, *o*-F_{Ar}), –170.1 (t, ³J_{FF} = 21.7 Hz, 2F, *m*-F_{Ar}), –184.1 ppm (br s, 1F, *p*-F_{Ar}). IR: $\tilde{\nu}$ 1615 (w), 1507 (m), 1481 (m), 1412 (m), 1279 (m), 1234 (s), 1214 (s), 1190 (s), 1112 (w), 1072 (s), 1025 (w), 972 (s), 930 (s), 771 (w), 756 (w), 721 (s), 673 (m), 582 (w), 556 (w), 537 (w), 497 (w), 449 cm^{–1} (w). (–)-ESI-MS (MeCN): *m/z* (%) 400 (32) [M][–], 219 (100) [M – C₆F₅N][–], 180 (8) [M – C₄F₉][–], 167 (18) [M – C₄F₉N][–]. HRMS ((–)-ESI): *m/z* calcd for C₁₀F₁₄N[–] 399.9813 [M][–]; found 399.9817. Anal. Calcd (%) for C₁₀CsF₁₄N (533.00): C 22.53, H 0.00, N 2.63. Found: C 22.29, H 0.19, N 2.78.

Synthesis of $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$. A suspension of $\text{CsN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ (1000 mg, 1.876 mmol) in 50 mL of dichloromethane was extracted with 40 mL of hydrochloric acid (10%). The aqueous phase was additionally extracted twice with 75 mL of dichloromethane, and the combined organic phases were dried over MgSO₄. The solvent was removed at the rotary evaporator, and the remaining oily residue was distilled at 74 °C and 57 mbar to give $\text{HN}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)$ (675 mg 1.687 mmol, 90%) as a colorless oil, which was stored under an inert atmosphere. ¹H NMR (300 MHz, benzene-*d*₆): δ 2.58 ppm (s, 1H, NH). ¹³C NMR (101 MHz, benzene-*d*₆): δ 146.4 (dm, ¹J_{FC} = 251.3 Hz, C_{Ar}), 141.3 (dm, ¹J_{FC} = 256.1 Hz, *p*-C_{Ar}), 137.7 (dm, ¹J_{FC} = 251.3 Hz, C_{Ar}), 121.0 (q, ¹J_{FC} = 292.2 Hz, –CF₃), 113.8 (t, ²J_{FC} = 14.8 Hz, *ipso*-C_{Ar}), 69.0 ppm (dec, ²J_{FC} = 28.4 Hz, C(CF₃)₃). ¹⁹F NMR (282 MHz, benzene-*d*₆): δ –69.6 (t, ¹J_{FF} = 7.1 Hz, 9F, –CF₃), –143.2 to –143.3 (m, 2F, F_{Ar}), –153.0 (t, ³J_{FF} = 22.2 Hz, 1F, *p*-F_{Ar}), –162.9 ppm (t, ³J_{FF} = 19.6 Hz, 2F, F_{Ar}). IR: $\tilde{\nu}$ 3406 (w, $\nu(\text{N–H})$), 1522 (s), 1243 (s), 1114 (m), 1018 (s), 989 (s), 959 (s), 757 (w), 726 (s), 686 (w), 667 (m), 540 (m), 473 cm^{–1} (w). (–)-ESI-MS (MeCN): *m/z* (%) 400 (2) [M][–], 167 (8) [C₆F₅N][–]. HRMS ((–)-ESI): *m/z* calcd for C₁₀F₁₄N[–] 399.9813 [M][–]; found 399.9815. Anal. Calcd (%) for

$C_{10}HF_{14}N$ (401.10): C 29.94, H 0.25, N 3.49. Found: C 30.55, H 0.39, N 4.03.

Synthesis of $LiN(C_6F_5)(C(CF_3)_3)$. A solution of LiHMDS (1.137 g, 6.79 mmol, 1.0 equiv) in 30 mL of hexane was added dropwise to a solution of $HN(C_6F_5)(C(CF_3)_3)$ (2.727 g, 6.79 mmol, 1.0 equiv) in 30 mL of hexane. A colorless solid precipitated, and the reaction mixture was stirred for 2 h at room temperature. The precipitate was separated by centrifugation and washed twice with 20 mL of pentane. It was dried *in vacuo* to give $LiN(C_6F_5)(C(CF_3)_3)$ (2.222 g, 5.45 mmol, 80%) as a white solid. Single crystals suitable for structure determination were obtained by sublimation of $LiN(C_6F_5)(C(CF_3)_3)$ at 120 °C and 6.3×10^{-3} mbar. ^{13}C NMR (101 MHz, DMSO- d_6): δ 142.5 (dm, $^1J_{FC} = 230.9$ Hz, *o*- C_{Ar}), 137.5 (dm, $^1J_{FC} = 239.0$ Hz, *m*- C_{Ar}), 133.5 (t, $^2J_{FC} = 13.0$ Hz, *ipso*- C_{Ar}), 127.7 (dm, $^1J_{FC} = 230.7$ Hz, *p*- C_{Ar}), 123.0 (q, $^1J_{FC} = 297.1$ Hz, $-CF_3$), 76.2 ppm (dec, $^2J_{FC} = 25.3$ Hz, $C(CF_3)_3$). ^{19}F NMR (376 MHz, DMSO- d_6): δ -69.0 (t, $^3J_{FF} = 10.6$ Hz, 9F, $-CF_3$), -157.1 to -157.3 (m, 2F, *o*- F_{Ar}), -170.5 (t, $^3J_{FF} = 23.3$ Hz, 2F, *m*- F_{Ar}), -185.0 ppm (tt, $^3J_{FF} = 24.1$ Hz, $^4J_{FF} = 11.6$ Hz, 1F, *p*- F_{Ar}). IR: $\tilde{\nu}$ 1516 (m), 1490 (m), 1427 (w), 1285 (m), 1250 (m), 1228 (m), 1196 (m), 1165 (m), 1125 (w), 1074 (s), 991 (s), 972 (s), 948 (s), 874 (w), 793 (w), 758 (w), 723 (m), 685 (m), 668 (w), 631 (w), 599 (w), 563 (w), 538 (w), 516 (m), 483 (w), 467 (w), 446 cm^{-1} (w). (–)-ESI-MS (MeCN): *m/z* (%) 400 (8) $[M]^-$, 167 (100) $[C_6F_5]^-$. HRMS ((–)-ESI): *m/z* calcd for $C_{10}F_{14}N^-$ 399.9813 $[M]^-$; found 399.9811. Anal. Calcd (%) for $C_{10}LiF_{14}N$ (407.03): C 29.51, H 0.00, N 3.44. Found: C 29.15, H 0.00, N 3.74.

Synthesis of $NaN(C_6F_5)(C(CF_3)_3)$. A solution of NaHMDS (104 mg, 0.567 mmol, 1.0 equiv) in 10 mL of toluene was added dropwise to a solution of $HN(C_6F_5)(C(CF_3)_3)$ (226 mg, 0.567 mmol, 1.0 equiv) in 10 mL of toluene. A gray solid precipitated, and the reaction mixture was stirred overnight at room temperature. The precipitate was separated by centrifugation and washed twice with 10 mL of hexane. It was dried *in vacuo* to give $NaN(C_6F_5)(C(CF_3)_3)$ (106 mg, 0.251 mmol, 44%) as a light gray solid. Single crystals suitable for structure determination were obtained by the slow diffusion of a solution of $HN(C_6F_5)(C(CF_3)_3)$ in pentane into a solution of NaHMDS in toluene. ^{13}C NMR (101 MHz, DMSO- d_6): δ 142.5 (dt, $^1J_{FC} = 231.2$ Hz, $^2J_{FC} = 8.4$ Hz, *o*- C_{Ar}), 137.6 (dm, $^1J_{FC} = 239.4$ Hz, *m*- C_{Ar}), 133.6 (t, $^2J_{FC} = 13.2$ Hz, *ipso*- C_{Ar}), 127.8 (dt, $^1J_{FC} = 230.9$ Hz, $^2J_{FC} = 14.7$ Hz, $^3J_{FC} = 4.8$ Hz, *p*- C_{Ar}), 123.1 (q, $^1J_{FC} = 297.0$ Hz, CF_3), 76.2 ppm (dec, $^2J_{FC} = 25.4$ Hz, $C(CF_3)_3$). ^{19}F NMR (282 MHz, DMSO- d_6): δ -69.3 (t, $^3J_{FF} = 10.3$ Hz, 9F, $-CF_3$), -157.5 to -157.8 (m, 2F, *o*- F_{Ar}), -170.9 (t, $^3J_{FF} = 23.0$ Hz, 2F, *m*- F_{Ar}), -185.4 ppm (tt, $^3J_{FF} = 24.2$ Hz, $^4J_{FF} = 11.9$ Hz, 1F, *p*- F_{Ar}). IR: $\tilde{\nu}$ 1516 (m), 1480 (m), 1420 (w), 1180 (br), 1076 (m), 965 (s), 934 (s), 774 (w), 721 (m), 668 (w), 538 cm^{-1} (w). (–)-ESI-MS (MeCN): *m/z* (%): 219 (10) $[C_4F_9]^-$, 167 (25) $[C_6F_5]^-$. HRMS ((–)-ESI): *m/z* calcd for $C_{10}F_{14}N^-$ 399.9813 $[M]^-$; found 399.9813. Anal. Calcd (%) for $C_{10}NaNF_{14}N$ (423.08): C 28.39, H 0.00, N 3.31. Found: C 28.59, H 0.29, N 3.46.

Synthesis of $KN(C_6F_5)(C(CF_3)_3)$. A solution of KHMDS (644 mg, 3.22 mmol, 1.0 equiv) in 20 mL of toluene was added dropwise to a solution of $HN(C_6F_5)(C(CF_3)_3)$ (1292 mg, 3.22 mmol, 1.0 equiv) in 15 mL of hexane. A colorless solid precipitated, and the reaction mixture was stirred for 2 h at room temperature. The precipitate was separated by centrifugation and washed twice with 20 mL of hexane. It was dried *in vacuo* to give $KN(C_6F_5)(C(CF_3)_3)$ (956 mg, 2.18 mmol, 68%) as a white solid. Single crystals suitable for structure determination were obtained by layering a saturated solution of $KN(C_6F_5)(C(CF_3)_3)$ in toluene with hexane. ^{13}C NMR (63 MHz, DMSO- d_6): δ 142.5 (dt, $^1J_{FC} = 231.3$ Hz, $^2J_{FC} = 8.9$ Hz, *o*- C_{Ar}), 137.6 (dm, $^1J_{FC} = 239.3$ Hz, *m*- C_{Ar}), 133.6 (t, $^2J_{FC} = 12.6$ Hz, *ipso*- C_{Ar}), 127.8 (dt, $^1J_{FC} = 230.9$ Hz, $^2J_{FC} = 14.6$ Hz, $^3J_{FC} = 4.8$ Hz, *p*- C_{Ar}), 123.1 (q, $^1J_{FC} = 297.1$ Hz, $-CF_3$), 76.2 ppm (dec, $^2J_{FC} = 25.4$ Hz, $C(CF_3)_3$). ^{19}F NMR (376 MHz, DMSO- d_6): δ -69.0 (t, $^3J_{FF} = 9.9$ Hz, 9F, $-CF_3$), -157.1 to -157.3 (m, 2F, *o*- F_{Ar}), -170.5 (t, $^3J_{FF} = 23.3$ Hz, 2F, *m*- F_{Ar}), -185.5 ppm (tt, $^3J_{FF} = 24.1$ Hz, $^4J_{FF} = 11.6$ Hz, 1F, *p*- F_{Ar}). IR: $\tilde{\nu}$ 1642 (w), 1496 (s), 1465 (s), 1341 (m), 1256 (w), 1120 (w), 1018 (s), 997 (s), 972 (s), 817 (w), 729 (w), 708 (m), 645 (m), 564 (m),

477 cm^{-1} (w). Anal. Calcd (%) for $C_{10}KF_{14}N$ (439.19): C 27.35, H 0.00, N 3.19. Found: C 27.21, H 0.14, N 3.39.

Synthesis of $Mg[N(C_6F_5)(C(CF_3)_3)]_2$. A solution of di-*n*-butylmagnesium (1 mol/L in heptane, 0.722 mL, 0.722 mmol, 1.0 equiv) was added dropwise to a solution of $HN(C_6F_5)(C(CF_3)_3)$ (401 mg, 1.444 mmol, 2.0 equiv) in 20 mL of toluene. A gray solid precipitated, and the reaction mixture was stirred overnight at room temperature. The precipitate was separated by centrifugation and washed with 15 mL of hexane. It was dried *in vacuo* to give $Mg[N(C_6F_5)(C(CF_3)_3)]_2$ (192 mg, 0.233 mmol, 32%) as a light gray solid. Single crystals suitable for structure determination were obtained by sublimation of $Mg[N(C_6F_5)(C(CF_3)_3)]_2$ at 117 °C and 1 mbar. ^{13}C NMR (101 MHz, DMSO- d_6): δ 142.7 (d, $^1J_{FC} = 231.4$ Hz, *o*- C_{Ar}), 137.5 (dm, $^1J_{FC} = 240.4$ Hz, *m*- C_{Ar}), 132.9 (t, $^2J_{FC} = 12.9$ Hz, *ipso*- C_{Ar}), 128.3 (dt, $^1J_{FC} = 232.1$ Hz, $^2J_{FC} = 14.1$ Hz, *p*- C_{Ar}), 123.0 (q, $^1J_{FC} = 296.9$ Hz, $-CF_3$), 75.9 ppm (dec, $^2J_{FC} = 25.4$ Hz, $C(CF_3)_3$). ^{19}F NMR (282 MHz, DMSO- d_6): δ -68.8 (t, $^3J_{FF} = 10.5$ Hz, 18F, $-CF_3$), -156.9 to -157.2 (m, 4F, *o*- F_{Ar}), -170.3 (t, $^3J_{FF} = 23.1$ Hz, 4F, *m*- F_{Ar}), -184.8 ppm (tt, $^3J_{FF} = 23.9$ Hz, $^4J_{FF} = 11.8$ Hz, 2F, *p*- F_{Ar}). IR: $\tilde{\nu}$ 1513 (m), 1495 (w), 1260 (br), 1181 (m), 1083 (s), 984 (s), 932 (s), 730 (m), 532 (w), 433 cm^{-1} (w). Anal. Calcd (%) for $C_{20}F_{28}MgN_2$ (824.49): C 29.13, H 0.00, N 3.40. Found: C 29.32, H 0.32, N 3.46.

Synthesis of $Ca[N(C_6F_5)(C(CF_3)_3)]_2$. A solution of $HN(C_6F_5)(C(CF_3)_3)$ (470 mg, 1.170 mmol, 2.0 equiv) in 15 mL of toluene was added dropwise to a solution of $Ca(HMDS)_2$ (211 mg, 0.585 mmol, 1.0 equiv) in 15 mL of toluene. A brown solid precipitated, and the reaction mixture was stirred overnight at room temperature. The precipitate was separated by centrifugation and washed twice with 15 mL of hexane. It was dried *in vacuo* to give $Ca[N(C_6F_5)(C(CF_3)_3)]_2$ (300 mg, 0.373 mmol, 64%) as a beige solid. ^{13}C NMR (101 MHz, DMSO- d_6): δ 142.5 (d, $^1J_{FC} = 231.3$ Hz, *o*- C_{Ar}), 137.6 (dm, $^1J_{FC} = 239.1$ Hz, *m*- C_{Ar}), 133.6 (t, $^2J_{FC} = 14.2$ Hz, *ipso*- C_{Ar}), 127.7 (dm, $^1J_{FC} = 230.9$ Hz, *p*- C_{Ar}), 123.0 (q, $^1J_{FC} = 297.3$ Hz, $-CF_3$), 76.0 ppm (dec, $^2J_{FC} = 24.9$ Hz, $C(CF_3)_3$). ^{19}F NMR (282 MHz, DMSO- d_6): δ -68.8 (t, $^3J_{FF} = 10.3$ Hz, 18F, $-CF_3$), -156.9 to -157.1 (m, 4F, *o*- F_{Ar}), -170.3 (t, $^3J_{FF} = 22.9$ Hz, 4F, *m*- F_{Ar}), -184.6 ppm (s, 2F, *p*- F_{Ar}). IR: $\tilde{\nu}$ 1517 (m), 1482 (m), 1421 (w), 1224 (br), 1076 (s), 974 (s), 941 (s), 816 (s), 758 (s), 561 cm^{-1} (w). Anal. Calcd (%) for $C_{20}F_{28}CaN_2$ (840.26): C 28.59, H 0.00, N 3.33. Found: C 28.38, H 0.22, N 3.56.

Synthesis of $Ba[N(C_6F_5)(C(CF_3)_3)]_2 \cdot THF$. A solution of $HN(C_6F_5)(C(CF_3)_3)$ (190 mg, 0.474 mmol, 2.0 equiv) in 10 mL of toluene was added dropwise to a solution of $Ba(HMDS)_2 \cdot THF$ (126 mg, 0.237 mmol, 1.0 equiv) in 10 mL of toluene. The reaction mixture was stirred overnight at room temperature, and all volatiles were removed *in vacuo*. The remaining residue was washed twice with 15 mL of hexane. It was dried *in vacuo* to give $Ba[N(C_6F_5)(C(CF_3)_3)]_2 \cdot THF$ (110 mg, 0.109 mmol, 46%) as a light brown solid. 1H NMR (300.1 MHz, DMSO- d_6): δ 3.60 (br s, 4H, OCH_2), 1.76 ppm (br s, 4H, OCH_2CH_2). ^{13}C NMR (125.8 MHz, DMSO- d_6): δ 142.5 (dt, $^1J_{FC} = 231.0$ Hz, $^2J_{FC} = 7.7$ Hz, *o*- C_{Ar}), 137.5 (dm, $^1J_{FC} = 238.8$ Hz, *m*- C_{Ar}), 133.5 (t, $^2J_{FC} = 13.8$ Hz, *ipso*- C_{Ar}), 127.7 (dt, $^1J_{FC} = 231.2$ Hz, $^2J_{FC} = 14.7$ Hz, $^3J_{FC} = 4.7$ Hz, *p*- C_{Ar}), 123.0 (q, $^1J_{FC} = 297.2$ Hz, $-CF_3$), 76.2 (dec, $^2J_{FC} = 25.5$ Hz, $C(CF_3)_3$), 66.9 (OCH_2), 25.0 ppm (OCH_2CH_2). ^{19}F NMR (282.4 MHz, DMSO- d_6): δ -69.6 (t, $^3J_{FF} = 10.4$ Hz, 18F, $-CF_3$), -157.7 to -158.0 (m, 4F, *o*- F_{Ar}), -171.1 (t, $^3J_{FF} = 23.0$ Hz, 4F, *m*- F_{Ar}), -185.6 ppm (tt, $^3J_{FF} = 23.9$ Hz, $^4J_{FF} = 11.8$ Hz, 2F, *p*- F_{Ar}). IR: $\tilde{\nu}$ 1508 (m), 1483 (m), 1440 (w), 1200 (br), 1076 (s), 982 (s), 935 (s), 873 (m), 804 (m), 719 (m), 665 (w), 538 cm^{-1} (w). Anal. Calcd (%) for $C_{24}H_8BaF_{28}N_2O$ (1009.62): C 28.55, H 0.80, N 2.77. Found: C 27.93, H 1.64, N 2.21.

■ ASSOCIATED CONTENT

Supporting Information

Supporting Information contains the bond valence analyses of the Mg–N and Mg...F interactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jsu@staff.uni-marburg.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Fonds der Chemischen Industrie (doctoral scholarship for J.F.K. and L.H.F.) for support of this work. We thank Dr. Klaus Harms and Fabian Schröder for their valuable support with crystal structure refinement. We thank Felicia Weber for her synthetic contribution.

■ REFERENCES

- (1) (a) Foropoulos, J.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720–3723. (b) DesMarteau, D. D.; Witz, M. J. *Fluorine Chem.* **1991**, *52*, 7–12. (c) Rey, I.; Johansson, P.; Lindgren, J.; Lassègues, J. C.; Grondin, J.; Servant, L. *J. Phys. Chem. A* **1998**, *102*, 3249–3258.
- (2) (a) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, Md. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593–16600. (b) Fujii, K.; Fujimori, T.; Takamuku, T.; Kanzaki, R.; Umebayashi, Y.; Ishiguro, S. *J. Phys. Chem. B* **2006**, *110*, 8179–8183. (c) Williams, D. B.; Stoll, M. E.; Scott, B. L.; Costa, D. A.; Oldham, W. J. *Chem. Commun.* **2005**, *11*, 1438–1440. (d) Jin, H.; O'Hare, B.; Dong, J.; Arzhantsev, S.; Baker, G. A.; Wishart, J. F.; Benesi, A. J.; Maroncelli, M. *J. Phys. Chem. B* **2008**, *112*, 81–92.
- (3) (a) MacFarlane, D. R.; Huang, J.; Forsyth, M. *Nature* **1999**, *402*, 792–794. (b) Howlett, P. C.; MacFarlane, D. R.; Hollenkamp, A. F. *Electrochem. Solid-State Lett.* **2004**, *7*, A97–A101. (c) Matsumoto, H.; Sakaebe, H.; Tatsumi, K.; Kikuta, M.; Ishiko, E.; Kono, M. *J. Power Sources* **2006**, *160*, 1308–1313. (d) Borgel, V.; Markevicha, E.; Aurbacha, D.; Semraub, G.; Schmidt, M. *J. Power Sources* **2009**, *189*, 331–336.
- (4) (a) KoppeI, I. A.; Taft, R. W.; Anvia, F.; Zbu, S.-Z.; Hu, L.-Q.; Sung, K.-S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Ignat'ev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasov, V. M.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc.* **1994**, *116*, 3047–3057. (b) Leito, I.; Raamat, E.; Kütt, A.; Saame, J.; Kipper, K.; Koppel, I. A.; Koppel, I.; Zhang, M.; Mishima, M.; Yagupolskii, L. M.; Garlyauskayte, R. Y.; Filatov, A. A. *J. Phys. Chem. A* **2009**, *113*, 8421–8424. (c) Kütt, A.; Rodima, T.; Saame, J.; Raamat, E.; Mäemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2011**, *76*, 391–395.
- (5) Rowland, G. B.; Zhang, H.; Rowland, E. B.; Chennamadhavuni, S.; Wang, Y.; Antilla, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 15696–15697.
- (6) Wabnitz, T. C.; Spencer, J. B. *Org. Lett.* **2003**, *5*, 2141–2144.
- (7) Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 6388–6390.
- (8) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 10204–10205.
- (9) Antoniotti, S.; Dalla, V.; Dunach, E. *Angew. Chem.* **2010**, *122*, 8032–8060; *Ang. Chem., Int. Ed.* **2010**, *49*, 7860–7888 and references therein.
- (10) Stricker, M.; Oelkers, B.; Rosenau, C. P.; Sundermeyer, J. *Chem.—Eur. J.* **2013**, *19*, 1042–1057.
- (11) (a) Brooke, G. M.; Burdon, J.; Stacey, M.; Tatlow, J. C. *J. Chem. Soc.* **1960**, 1768–1771. (b) Koppang, R. *Acta Chem. Scand.* **1971**, *25*, 3067–3071.
- (12) Khvorost, A.; Shutov, P. L.; Harms, K.; Lorberth, J.; Sundermeyer, J.; Karlov, S. S.; Zaitseva, G. S. *Z. Anorg. Allg. Chem.* **2004**, *630*, 885–889.
- (13) Click, D. R.; Scott, B. L.; Watkin, J. G. *Chem. Commun.* **1999**, 633–634.
- (14) Yin, H.; Lewis, A. J.; Carroll, P.; Schelter, E. J. *Inorg. Chem.* **2013**, *52*, 8234–8243.
- (15) Giesbrecht, G. R.; Gordon, J. C.; Clark, D. L.; Hijar, C. A.; Scott, B. L.; Watkin, J. G. *Polyhedron* **2003**, *22*, 153–163.
- (16) Peryshkov, D. V.; Schrock, R. R. *Organometallics* **2012**, *31*, 7278–7286.
- (17) Linder, T.; Sundermeyer, J. *Chem. Commun.* **2009**, *20*, 2914–2916.
- (18) (a) Sundermeyer, J.; Roling, B.; Linder, T.; Froemling, T.; Huber, B. *Eur. Pat. Appl.* EP 2314572 A1, 20110427, 2011. (b) Sundermeyer, J.; Roling, B.; Linder, T.; Huber, B.; Froemling, T. *PCT Int. Appl.* WO 2011048152 A1, 20110428, 2011. (c) Huber, B.; Linder, T.; Hormann, K.; Frömling, T.; Sundermeyer, J.; Roling, B. *Z. Phys. Chem.* **2012**, *212*, 377–390.
- (19) (a) Müller, L. O.; Himmel, D.; Stauffer, J.; Steinfeld, G.; Slattery, J.; Santiso-Quinones, G.; Brecht, V.; Krossing, I. *Angew. Chem.* **2008**, *120*, 7772–7776; *Angew. Chem., Int. Ed.* **2008**, *47*, 7659–7663. (b) Kraft, A.; Trapp, N.; Himmel, D.; Böhler, H.; Schlüter, P.; Scherer, H.; Krossing, I. *Chem.—Eur. J.* **2012**, *18*, 9371–9380.
- (20) Petrov, V. A.; DesMarteau, D. D. *J. Fluorine Chem.* **1996**, *77*, 175–181.
- (21) Singh, R. P.; Shreeve, J. M. *Tetrahedron* **2000**, *56*, 7613–7632.
- (22) Petrov, V. A. *Tetrahedron Lett.* **2000**, *41*, 6959–6963.
- (23) The exact pK_a value in acetonitrile solution was determined in the group of Ivo Leito and will probably be published soon as a part of an acidity ladder.
- (24) We are aware that the use of the sum of the van der Waals radii as the upper limit for a M...F interaction is problematic since we deal with metal ions. This issue is addressed in a review on M...F contacts by Plenio (ref 25).
- (25) (a) Plenio, H. *Chem. Rev.* **1997**, *97*, 3363–3384. (b) Plenio, H. *ChemBioChem* **2004**, *5*, 650–655.
- (26) (a) Samuels, J. A.; Chiang, W.-C.; Yu, C.-P.; Apen, E.; Smith, D. C.; Baxter, D. V.; Caulton, K. G. *Chem. Mater.* **1994**, *6*, 1684–1692. (b) Chou, T.-Y.; Chi, Y.; Huang, S.-F.; Liu, C.-S.; Carty, A. J.; Scoles, L.; Udachin, K. A. *Inorg. Chem.* **2003**, *42*, 6041–6049. (c) Matthews, J. S.; Rees, W. S., Jr. *Adv. Inorg. Chem.* **2000**, *50*, 173–192. (d) Liu, Y.-H.; Cheng, Y.-C.; Tung, Y.-L.; Chi, Y.; Chen, Y.-L.; Liu, C.-S.; Peng, S.-M.; Lee, G.-H. *J. Mater. Chem.* **2003**, *13*, 135–142.
- (27) (a) Smith, J. D. *Adv. Organomet. Chem.* **1998**, *43*, 267–348. (b) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Zhang, S. *Organometallics* **2000**, *19*, 1190–1193.
- (28) Gärtner, M.; Fischer, R.; Langer, J.; Görls, H.; Walther, D.; Westerhausen, M. *Inorg. Chem.* **2007**, *46*, 5118–5124.
- (29) Alves, L. G.; Martins, A. M.; Duarte, M. T. *J. Mol. Struct.* **2012**, *1026*, 168–173.
- (30) Deacon, G. B.; Junk, P. C.; Kelly, R. P. *Aust. J. Chem.* **2013**, *66*, 1288–1296.
- (31) Bond valence analyses were performed for the M...F interactions in the crystal structures reported herein. The results are in accordance with the corresponding M...F distances and are presented as Supporting Information. (a) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192–197. (b) Brown, I. D. *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*; Oxford University Press, 2002.
- (32) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; Ferdinand Enke Verlag: Stuttgart, 1975; pp 712–713.
- (33) Aahman, J.; Somfai, P. *Synth. Commun.* **1995**, *25*, 2301–2303.
- (34) Brady, E. D.; Hanusa, T. P.; Pink, M.; Young, V. G. *Inorg. Chem.* **2000**, *39*, 6028–6037.
- (35) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 121–125.