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Formation of Very Weakly Interacting Organometallic Cation−Anion Systems Using Pearson's HSAB Concept: Synthesis and Structures of $[Ag(Toluene)_3]^+$ $[\{((SiMe_3)_3C)_2Al_2F_5\}_2Li]^-$ and $[AlF_2(THF)_4]^+$ $[\{(SiMe_3)_3C\}_2Al_2F_5]^-$ †

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Summary: By using Pearson's HSAB principle $[Ag(Toluene)_3]^+$ $[\{((SiMe_3)_3C)_2Al_2F_5\}_2Li]^-$ *(**2**) has been synthesized from the reaction of* $[(SiMe_3)_3CAlF_2]_3$ *(**1**) with AgF and LiCl. Reaction of **1** with* AgF_2 *and* NH_4F *affords* $[AlF_2(THF)_4]^+$ $[\{(SiMe_3)_3C\}_2Al_2F_5]^-$ *(**3**) and* $[NH_4]^+$ $[(SiMe_3)_3CAlF_3]^-$ *(**4**), respectively. **2** and **3** have been structurally characterized.*

Introduction

Formation of host−guest type compounds by organometallic fluorides has been documented in literature.[1] For example, treatment of Cp^*TiF_3 with sodium or potassium fluoride affords $[(Cp^*{}_2Ti_2F_7)_2M]^-$ M^+ ($Cp^* = C_5Me_5$; M = Na or K). These are among the few examples of molecular recognition by nucleophilic host molecules which are formed in a template-controlled manner.[2] The formation of these molecular solids is due at least in part to the ability of fluorine to act as a bridging ligand and thereby assist in the assembly of large aggregates. Recently we have been involved in the synthesis of novel aluminum difluorides containing sterically hindered substituents on aluminum. To test the dependence of fluoride assisted cluster aggregate sizes on the type of organometallic fluoride involved, we chose to use $[(SiMe_3)_3CAlF_2]_3$ (**1**)[3] as the cluster-generating synthon. An additional point of synthetic interest was to be able to use Pearson's HSAB concept[4] for the selective incorporation of a metal ion in the organometallic cluster. We hoped that by adopting this concept it would be possible to generate an organometallic fluoride framework containing weakly interacting complex ion systems. The importance of these latter types of systems in Ziegler−Natta type catalysts has been commented upon.[5] In the following account we describe the synthesis and structure of $[Ag(Toluene)_3]^+$ $[\{((SiMe_3)_3C)_2Al_2F_5\}_2Li]^-$ (**2**) and $[AlF_2(THF)_4]^+$ $[\{(SiMe_3)_3C\}_2Al_2F_5]^-$ (**3**) and also the synthesis of $[NH_4]^+$ $[(SiMe_3)_3CAlF_3]^-$ (**4**).

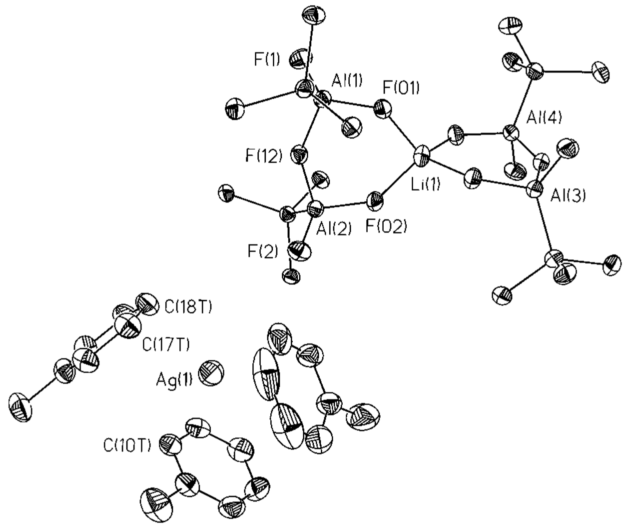

Figure 1. Molecular structure of the core of **2**. Significant bond lengths [Å] and angles [deg]: F(1)−Al(1) 1.657(2), F(12)−Al(1) 1.7914(19), F(01)−Al(1) 1.688(2), F(01)−Li(1) 1.854(6), Al(1)−C(01) 1.947(3); Al(1)−F(12)−Al(2) 144.64(11), Al(1)−F(01)−Li(1) 139.37(19), F(1)−Al(1)−F(01) 108.67(11), F(1)−Al(1)−F(12) 101.39(10), F(01)−Al(1)−F(12) 97.98(9), F(1)−Al(1)−C(01) 116.65(12), F(01)−Al(1)−C(01) 115.42(12), F(12)−Al(1)−C(01) 114.34(11), Ag(1)−C(10T) 2.396(3), Ag(1)−C(17T) 2.697(4), Ag(1)−C(18T) 2.408(4), C(10T)−Ag(1)−C(18T) 147.19(16).

Results and Discussion

Earlier results from this laboratory showed that treatment of Cp^*TiF_3 with an alkali metal or calcium difluoride generates a fluoride cluster with the incorporation of the alkali or alkaline earth metal ion within the cluster core.[1] Similarly it has also been shown that when Cp^*TiF_3 is reacted with metals, like sodium, magnesium, calcium, or aluminum, clusters are formed where again the cores contain the organometallic and the added metal in a fluoride network.[1,2,6] We thought that it would be interesting to assemble a cluster where the added metal ion is outside the core of the organo-

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† Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday.

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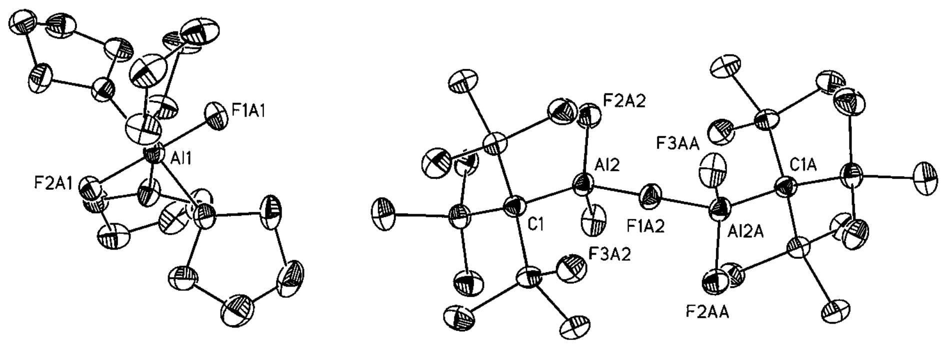

Figure 2. Molecular structure of **3**. Significant bond lengths [Å] and angles [deg]: Al(1)−F(2A1) 1.7006(14), Al(1)−O(1T3) 1.9435(17), Al(2)−F(2A2) 1.6692(16), Al(2)−F(1A2) 1.7795(7), Al(2)−C(1) 1.962(2); F(2A1)−Al(1)−F(1A1) 179.33(8), O(1T4)−Al(1)−O(1T3) 90.37(8), F(1A1)−Al(1)−O(1T2) 90.49(7), F(2A2)−Al(2)−F(3A2) 109.45(9), F(2A2)−Al(2)−F(1A2) 100.84(6), F(3A2)−Al(2)−F(1A2) 100.72(6), F(1A2)−Al(2)−C(1) 113.35(7).

metallic cluster with no fluoride interactions. We reasoned that this would require the choice of a soft metal ion in the synthetic strategy. Accordingly, compound **1** was reacted with AgF in the presence of LiCl. We expected the incorporation of Li^+ in the cluster framework in preference to Ag^+. This strategy was successful, and we were able to isolate compound **2** in 62% yield. The single-crystal X-ray analysis of **2** (Figure 1) shows that the cation Li^+ is coordinated to four fluorine atoms in approximately tetrahedral fashion and forms the $[\{((SiMe_3)_3C)_2Al_2F_5\}_2Li]^-$ anion. The cation Ag^+ on the other hand does not show any interaction with the fluorines and instead is surrounded by three toluene molecules.

The average terminal Al−F bond length [Al(1)−F(1) 1.657(2) Å] in **2** is similar to that in **1** (Al−F 1.67 Å).The mean Al−F bond length of lithium-bound fluorine is approximately 0.02 Å longer [Al(1)−F(01) 1.688(2) Å] than the terminal Al−F bond length in **1**. The bridging Al−F bond length [Al(1)−F(12) 1.7914(19) Å] is shorter (by approximately 0.03 Å) than that found in the ring of **1** (Al−F 1.81 Å). The aluminum−carbon bond length [Al(1)−C(01)1.947(3) Å] is comparable to that in **1** (Al−C 1.94 Å). The lithium−fluorine bond distance [F(01)−Li(1) 1.854(6) Å] is similar to that in $P(Si\mathit{t}Bu_2F)_2Li\cdot 2THF$ (F−Li 1.86 Å).[7] The ^1H NMR spectrum shows three signals (6.98−7.13, 2.10, and 0.51 ppm) in the ratio of 15:9:108 due to toluene protons and the $Si-CH_3$ protons, respectively. Apart from these, a low-intensity signal was observed (0.53 ppm) which may be due to the presence of a small amount of impurity in solution. Similarly, the ^{19}F NMR spectrum of the compound shows signals [−154.5 (2F), −158.6 (4F), and −158.8 (4F) ppm] due to Al−F−Al, Al−F−Li, and Al−F fluorine atoms, respectively. Here again a low-intensity signal was observed (−158 ppm) due to a minor impurity. Thus, the structural analysis confirms that, as expected, *hard* Li^+ is incorporated into the cluster and is coordinated to *hard* fluorines and Ag^+, being *soft*, is outside the cluster and shows no interaction with *hard* fluorine.

We were also interested in looking at the reaction of AgF_2 with **1**, because Ag^{2+} ion is harder then Ag^+ ion and it is expected that this ion may give an aggregated ion as in the case of Li^+. The reaction of AgF_2 with **1** in *n*-hexane yielded an *n*-hexane insoluble solid. The solid when treated with THF afforded $[AlF_2(THF)_4]^+ [\{(SiMe_3)_3C\}_2Al_2F_5]^-$ **3** in 21% yield (Figure 2). This shows that AgF_2 is a strong fluorinating agent, forming the AlF_2^+ ion, which is stabilized by four THF molecules. The crystal structure analysis confirms the presence of a discrete $[\{(SiMe_3)_3C\}_2Al_2F_5]^-$ ion. The terminal Al−F bond length [Al(2)−F(2A2) 1.6692(16) Å] is the same as that in **1**. The ring Al−F bond length in **1** is slightly longer than that found in **3** [Al(2)−F(1A2) 1.7795(7) Å]. The Al−C bond length [Al(2)−C(1) 1.962(2) Å] in **3** is slightly longer (by about 0.02 Å) compared to **1**. It may be mentioned that compound **3** slowly decomposes above 0 °C. NH_4^+ ion is a borderline cation, and we thought it worthwhile to study the reaction between ammonium fluoride and **1**. Thus a reaction between NH_4F and **1** in *n*-hexane was carried out, and we could isolate $[NH_4]^+ [(SiMe_3)_3CAlF_3]^-$ in very good yield (90%). The ^1H NMR (C_6D_6) shows two signals in the ratio 4:27 (0.37 and 5.45 ppm) due to $SiMe_3$ protons and NH_4 protons, respectively. ^{19}F NMR of the compound shows only one signal (−152.6 ppm). The IR (KBr, cm^{-1}) shows the N−H-stretching frequencies at 3183 and 3054 cm^{-1}.

Conclusion

It has been shown that it is possible to assemble organoaluminum fluoride clusters containing two different cations having different hardness, and the site occupancy of the added cations is determined by their hardness. Although, Ag^{2+} is comparatively hard, it is not possible to incorporate Ag^{2+} ion in the cluster.

Experimental Section

General Information. All experimental manipulations were carried out under a dry, prepurified nitrogen atmosphere, using Schlenk techniques and rigorously excluding moisture and air. The samples for spectral measurements were prepared in a drybox. Solvents were purified by conventional procedures and were freshly distilled prior to use. All ^1H and ^{19}F NMR spectra were recorded on a Bruker AM 200 instrument. The chemical shifts are reported in ppm with reference to $SiMe_4$ (external) for ^1H and to $CFCl_3$ (external) for ^{19}F nuclei. The upfield shifts from the reference are negative. IR spectra were recorded on a Bio-Rad Digilab FTS 7 spectrometer. Mass

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Table 1. Crystal Data and Structure Refinement Details for 2

empirical formula	$C_{61}H_{132}AgAl_4F_{10}LiSi_{12}$ + 0.5 C_5H_{12}
fw	1651.55
temp	133(2) K
λ	0.71073 Å
cryst syst	monoclinic
space group	$P2_1$
unit cell dimens	$a = 14.775(3)$ Å
	$b = 21.662(4)$ Å
	$c = 16.486(3)$ Å
	$\alpha = 90°$
	$\beta = 115.21(3)°$
	$\gamma = 90°$
Z	2
cell volume	4773.8(17) Å^3
D_c	1.149 Mg m^{-3}
μ	0.450 mm^{-1}
F(000)	1758
cryst dimens	0.60 × 0.60 × 0.40 mm
θ range	2.32−26.37°
index range	$-18 \le h \le 16$
	$-27 \le k \le 27$
	$-20 \le l \le 20$
no. of total reflns	67 312
no. of independent reflns	19 402 ($R_{int} = 0.0319$)
max and min transmission	0.8407 and 0.7742
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	19402/15/886
goodness-of-fit on F^2	1.110
R1, R2 [$I > 2\sigma(I)$]	R1 = 0.0367, wR2 = 0.0874
R1, R2 (all data)	R1 = 0.0497, wR2 = 0.0975
abs struct param	−0.045(15)
largest diff peak and hole	0.564 and −0.921 e/Å^3

Table 2. Crystal Data and Structure Refinement Details for 3

empirical formula	$C_{40}H_{94}Al_3F_7O_5Si_6$
fw	1037.63
temp	133(2) K
λ	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	
	$a = 22.1947(4)$ Å
	$b = 11.8950(2)$ Å
	$c = 22.1311(4)$ Å
	$\alpha = 90°$
	$\beta = 95.021(10)°$
	$\gamma = 90°$
cell volume	5820.32(18) Å^3
Z	4
D_c	1.184 Mg m^{-3}
μ	0.247 mm^{-1}
F(000)	2240
cryst dimens	0.70 × 0.70 × 0.60 mm
θ range	1.94−25.03°
index range	$-26 \le h \le 23$
	$-14 \le k \le 13$
	$-26 \le l \le 26$
no. of total reflns	71 715
no. of independent reflns	10 279 ($R_{int} = 0.0398$)
max and min transmission	0.8661 and 0.8463
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	10279/777/653
goodness-of-fit on F^2	1.107
R1, R2 [$I > 2\sigma(I)$]	R1 = 0.0412, wR2 = 0.0966
R1, R2 (all data)	R1 = 0.0560, wR2 = 0.1066
largest diff peak and hole	467 and −409 e/Å^3

spectra were obtained on a Finnigan MAT 8230 or a Varian MAT CH 5 mass spectrometer. Melting points were obtained on a HWS-SG 3000 instrument and are reported uncorrected. Elemental analyses were performed at the analytical laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Starting Materials. $[(SiMe_3)_3CAlF_2]_3$ (**1**) was prepared using literature procedure.[3] Other chemicals used were dried under high vacuum prior to use.

Synthesis of $[Ag(Toluene)_3]^+$ $[\{((SiMe_3)_3C)_2Al_2F_5\}_2Li]^-$ (2). To a mixture of **1** (1.00 g, 1.12 mmol), AgF (0.21 g, 1.67 mmol), and LiCl (0.036 g, 0.85 mmol) was added toluene (20 mL), and the mixture was stirred for 4 days at room temperature. This was then treated with 15 mL of *n*-hexane and cooled to 0 °C and then filtered. Upon removal of solvents in a vacuum, a yellow product **2** could be isolated [0.85 g; 62% (based on LiCl)]. Crystals for X-ray diffraction were grown from a toluene/*n*-hexane/*n*-pentane (10:1:1) mixture, mp ~126 °C (dec). ^{1}H NMR (200 MHz, C_6D_6, ppm): 6.98−7.13 (m, MePh−H, 15H); 2.10 (s, Ph−CH_3, 9H); 0.51 (s, Si−CH_3, 108H); 0.53 (s). ^{19}F NMR (188 MHz, C_6D_6, ppm): −154.5 (m, 2F), −158.0 (s, 1F), −158.6 (s, 4F), −158.8 (s, 4F). IR (KBr, Nujol, cm^{-1}): 1260, 1097, 1017, 862, 801, 676, 616, 464. Elemental analyses ($C_{61}H_{132}AgAl_4F_{10}LiSi_{12}$): calcd C, 45.35; H, 8.24; Ag, 6.68; Al, 6.68; F, 11.76; Si, 20.86; found C, 44.4; H, 8.3; Ag, 6.6; Al, 6.7, F, 10.6; Si, 21.2.

Synthesis of $[AlF_2(THF)_4]^+$ $[\{(SiMe_3)_3C\}_2Al_2F_5]^-$ (3). A suspension of **1** (0.44 g, 0.50 mmol) and AgF_2 (0.048 g, 0.33 mmol) in *n*-hexane was stirred at room temperature for 6 days. To the reaction mixture was then added THF, and the mixture was filtered. The filtrate upon standing at 0 °C afforded as a white crystalline product **3** (yield 0.150 g, 21%), whose X-ray-structure was determined. IR (KBr, Nujol, cm^{-1}): 1304, 1260, 1076, 1019, 866, 801, 676, 617, 465.

Synthesis of $[NH_4]^+$ $[(SiMe_3)_3CAlF_3]^-$ (4). A mixture of **1** (0.22 g, 0.25 mmol) and NH_4F (0.08 g, 2.16 mmol) was taken in *n*-hexane, and the mixture was stirred at room temperature for 3 days. The mixture was then filtered. The precipitate was treated with ether and filtered. A 0.22 g (90%) sample of **4** was isolated upon removal of the solvent in a vacuum, mp 282−286 °C. ^{1}H NMR (200 MHz, C_6D_6 ppm): 5.45 (s, 4H, NH_4); 0.37 (s, 27H, Si−CH_3). ^{19}F NMR (188 MHz, C_6D_6, ppm): −152.6 [s, $((SiMe_3)_3CAlF_3)$]. FAB *m/e* (%): 315.2 (100) [M − NH_4], 648.5 (6) [2M − NH_4] [M is $[NH_4]^+$ $[\{(SiMe_3)_3C\}_2Al_2F_5]^-$]. IR (KBr, cm^{-1}): 3183, 3054, 2975, 2956, 2903, 1430, 1259, 1097, 1020, 856, 675, 621. Elemental analyses ($C_{10}H_{31}AlF_3NSi_3$): calcd C, 36.0; H, 9.4; N, 4.2; found C, 35.4; H, 9.2; N, 3.9.

X-ray Structure Determination. Crystal data for **2** and **3** were collected on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens CCD area detector using ψ-scan mode. The structures were solved by direct methods (SHELXS-90/96)[8] and refined on all data by full-matrix least-squares on F^2.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in idealized positions and refined using a riding model. The crystal data and structure refinement details for **2** and **3** are given in Tables 1 and 2, respectively.

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Supporting Information Available: X-ray structural data for **2** and **3**, including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (26 pages). See any current masthead page for ordering and Internet access instructions.

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