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Communications

Synthesis and Characterization of an Almost Linear, Quasi-Two-Coordinate, Cationic Diorganoaluminum Compound

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The preparation of low-coordinate cationic organoaluminum compounds as reactive alternatives to transition-metal catalysts for the polymerization of olefins or cyclic ethers has been reported by several groups in recent years.[1−4] Stable weakly coordinating anions such as $[B(C_6F_5)_4]^-$ were essential for the synthesis of these compounds. The stabilization of the more reactive alkyl-substituted cationic species required the employment of the more robust carborane ligands, as has been shown by Reed and co-workers for $[Et_2Al]^+[CB_{11}H_6X_6]^-$ (X = Cl, Br).[5] The Lewis acidity of the cationic aluminum center is sufficiently high, even in these compounds, that there were relatively close Al⋯X contacts leading to an essentially four-coordinate aluminum center and C−Al−C angles of 136.6 and 130.0°. These close contacts significantly decreased the reactivity of these species. As an alternative strategy to prepare and stabilize two-coordinate cationic aluminum compounds and at the same time minimize cation⋯anion contacts, we have investigated the potential of *m*-terphenyl substituents[6,7] as sterically shielding and protecting groups. Our recently reported successful synthesis of the first cationic diorganogallium compound, $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+[Li\{Al(OCH(CF_3)_2)_4\}_2]^-$ (Mes = 2,4,6-$Me_3C_6H_2$), which features a linear two-coordinate gallium center,[8] prompted us to prepare the corresponding more reactive and Lewis acidic aluminum analogues. We report here the synthesis of a novel cationic quasi-two-coordinate diterphenyl aluminum compound whose higher Lewis acidity is balanced by intramolecular Al⋯C contacts.

The ionic compound $[(2,6\text{-}Mes_2C_6H_3)_2Al]^+[B(C_6F_5)_4]^-$ (**1**)[9] was obtained in low isolated yield via hydride abstraction from $(2,6\text{-}Mes_2C_6H_3)_2AlH$ (**2**)[10] with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in benzene solution at room temperature (eq 1).

$$(2,6\text{-}Mes_2C_6H_3)_2AlH + [Ph_3C]^+[B(C_6F_5)_4]^- \rightarrow [(2,6\text{-}Mes_2C_6H_3)_2Al]^+[B(C_6F_5)_4]^- + Ph_3CH \quad (1)$$

Compound **1** crystallizes in two polymorphs: crystals obtained from benzene solution contain a benzene

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molecule per asymmetric unit, **1**·C_6H_6 (**1a**),[11] while it crystallizes from CH_2Cl_2 solution without incorporation of a solvent molecule (**1b**).[12] The overall features of both crystal structures are similar but show some significant differences in the aluminum coordination sphere. Both structures contain separate $[(2,6\text{-Mes}_2C_6H_3)_2Al]^+$ cations and $[B(C_6F_5)_4]^-$ anions. The closest contacts between cation and anion involve some methyl hydrogens of the terphenyl substituents and fluorine atoms of the anion with values of 2.46 Å for **1a** and 2.50 Å for **1b**. The closest Al···F contacts are 6.115 Å (Al(1)···F(4)) and 5.498 Å (Al(1)···F(9)), respectively. In **1a** the C−Al−C angle is wide at 159.17(5)° and approaches linearity. The Al−C bond lengths with values of 1.9379(12) and 1.9412(12) Å are on average 2.5% shorter than those in the precursor **2** but slightly longer than those found for other cationic aluminum compounds such as $[Et_2Al]^+[CB_{11}H_6Br_6]^-$ (1.926 Å average,[5] $[Me_2Al(OEt_2)_2]^+[MeB(C_{12}F_9)_3]^-$ (1.935 Å average),[13] and $[(^iPr_2\text{-ATI})AlEt(ClC_6H_5)]^+[B(C_6F_5)_4]^-$ (1.919(7) Å; $^iPr_2$-ATI = *N*,*N'*-diisopropylaminotroponiminate).[14] The geometric data for **1b** are similar to those for **1a** (see Figure 2). The strong Lewis acidity of the cationic aluminum center in **1** is manifested by the short Al···C contacts involving the flanking mesityl groups. In **1a** these contacts mainly involve the ipso carbons of the C(16) and C(33) mesityl groups with Al···C distances of 2.553(1) and 2.3532(12) Å. The latter value is only 0.28 Å longer than the sum of the Al and C covalent radii and is very similar to the Al···C(toluene) distance in the toluene complex $(C_6F_5)_3Al$·(toluene) (2.366(2) Å).[15] These close contacts lead to a significant bending of the terphenyl substituents toward the aluminum center. This is illustrated in the Al(1)−C(39)−C(34) and Al(1)−C(15)−C(14) angles with values of 97.67(8) and 103.72(8)°, respectively (see Figure 1). On the other hand, the Lewis acidity in **1b** is balanced by close contacts between the aluminum center and the ipso and one of the ortho carbons of two of the mesityl groups in an η^2 fashion (see Figure 2). Due to

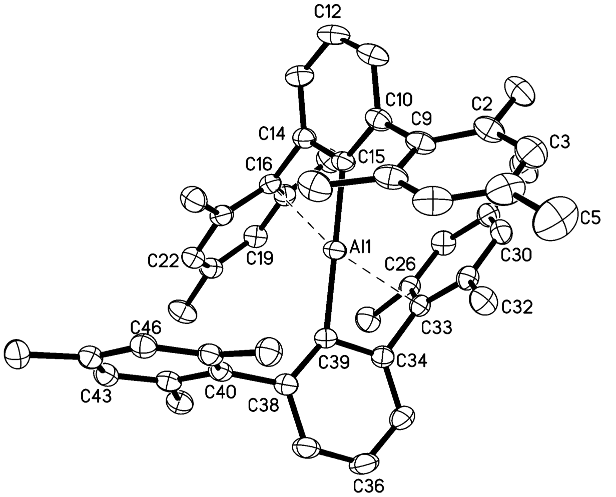

Figure 1. Structure of the cation in **1a**. Selected bond lengths (Å) and angles (deg): Al(1)−C(15) = 1.9379(12), Al(1)−C(39) = 1.9412(12), Al(1)···C(33) = 2.3532(12), Al(1)···C(16) = 2.553(1); C(15)−Al(1)−C(39) = 159.17(5), Al(1)−C(39)−C(34) = 97.67(8), Al(1)−C(15)−C(14) = 103.72(8).

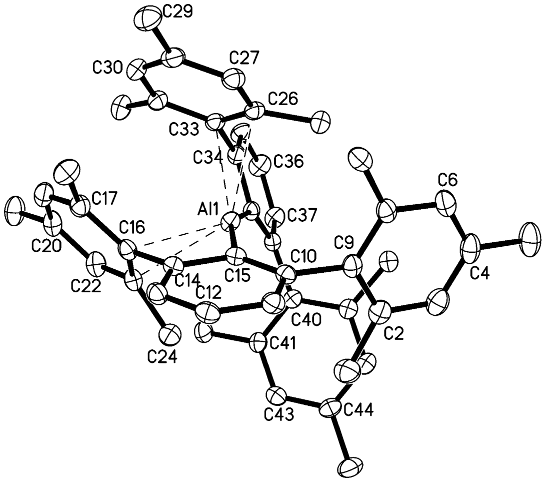

Figure 2. Structure of the cation in **1b**. Selected bond lengths (Å) and angles (deg): Al(1)−C(15) = 1.9407(13), Al(1)−C(39) = 1.9428(13), Al(1)···C(33) = 2.4852(13), Al(1)···C(16) = 2.619(1), Al(1)···C(26) = 2.563(1), Al(1)···C(23) = 2.571(1), Al(1)−H(24C) = 2.463(5); C(15)−Al(1)−C(39) = 156.54(6), Al(1)−C(39)−C(34) = 101.96(9), Al(1)−C(15)−C(14) = 105.71(9).

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(9) *Synthesis of **1***. A Schlenk flask was charged with $(2,6\text{-Mes}_2C_6H_3)_2AlH$ (**2**; 1.07 mmol, 0.71 g) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (1.07 mmol, 0.99 g) under an atmosphere of purified nitrogen. Benzene (15 mL) was added, and the mixture was stirred for a period of 1.5 days to afford a reddish solution, which upon settling separated into a pale red solution and a red, dense bottom layer. Decantation of the top layer, followed by concentration of this layer to 7 mL and cooling to 4 °C for 3 days, gave large yellow crystals of **1**·C_6H_6 (**1a**; 0.062 g). Repeated extraction of the bottom layer with benzene (ca. 10 mL each), concentration of the combined washings to ca. 20 mL, and crystallization at 4 °C afforded more product (**1a**). Recrystallization of this batch in methylene chloride at −30 °C yielded 0.266 g of **1b**. Combined yield: 23%. The physical data given were obtained from a sample of **1a**. Mp: 132−135 °C. Anal. Calc. for $C_{78}H_{56}AlBF_{20}$: C, 66.39; H, 4.00. Found: C, 66.09; H, 3.97. ^1H NMR (300 MHz, C_6D_6/C_6D_5Cl (3/1)): δ 7.09 (t, $J = 7.5$ Hz, *p*-H, 2H), 6.76 (s, *m*-H (Mes), 8H), 6.62 (d, $J = 7.5$ Hz, *m*-H, 4H), 2.09 (s, *p*-CH_3, 12H), 1.51(s, *o*-CH_3, 24H). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6/C_6D_5Cl (3/1)): δ 148.45, 141.65, 138.57, 137.52, 132.85, 132.03, 128.68, 21.72 (*o*-Me), 21.24 (*p*-Me). ^{19}F NMR (282.35 MHz, C_6D_6/C_6D_5Cl (3/1)): δ −131.7 (s, br, *o*-F, 8F), −162.1 (t, $J_{FF} = 21.4$ Hz, *p*-F, 4F), −166.0 (s, br, *m*-F, 8F).

(10) *Synthesis of **2***. A mixture of $2,6\text{-Mes}_2C_6H_3AlH_2\cdot OEt_2$[18] (1.07 g, 2.6 mmol) and $[2,6\text{-Mes}_2C_6H_3Li]_2$[19] (0.88 g, 1.4 mmol) was dissolved in benzene (20 mL) and heated to 70 °C for 0.5 h, after which time the solution became cloudy. The mixture was cooled to room temperature. After the LiH was allowed to settle out, the supernatant liquid was decanted, concentrated, and refrigerated to yield clear, colorless, X-ray-quality crystals of **2**. Yield: 52%. ^1H NMR (300 MHz, C_6D_6): δ 7.10 (t, $J = 7.5$ Hz, *p*-H, 2H), 6.85 (s, *m*-H (Mes), 8H), 6.69 (d, $J = 7.5$ Hz, *m*-H, 4H), 2.22 (s, *p*-CH_3, 12H), 1.85 (s, *o*-CH_3, 24H). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 150.56, 141.42, 136.86, 136.68, 129.88, 129.00, 127.47, 21.99 (*o*-Me), 21.44 (*p*-Me). FTIR (CsI plates, Nujol): ν(Al−H) 1862 cm^{-1}(m). Details of the X-ray crystal structure of **2** which is a rare example of a monomeric aluminum hydride, will be published elsewhere.

(11) Crystal data for **1**·C_6H_6 (**1a**): $C_{78}H_{56}AlBF_{20}$, FW = 1411.02, triclinic, space group $P\bar{1}$ (No. 2), $D_{calcd} = 1.450$ g cm^{-3}, $Z = 2$, $a = 11.5103(5)$ Å, $b = 16.5512(7)$ Å, $c = 17.7754(8)$ Å, $\alpha = 102.6760(10)°$, $\beta = 95.4220(10)°$, $\gamma = 99.1710(10)°$, $V = 3232.0(2)$ Å^3, $T = 120(2)$ K, Bruker ASX Apex diffractometer, λ(Mo Kα) = 0.710 73 Å, $\mu = 0.136$ mm^{-1}. Of 36 392 reflections measured, 13 974 were unique ($R_{int} = 0.0131$). Refinement on F^2 concluded with the values R1 = 0.0354 and wR2 = 0.0977 for 913 parameters and 12 610 data with $I > 2\sigma_I$.

(12) Crystal data for **1b**: $C_{72}H_{50}AlBF_{20}$, FW = 1332.91, orthorhombic, space group *Pbca* (No. 61), $D_{calcd} = 1.480$ g cm^{-3}, $Z = 8$, $a = 17.2959(8)$ Å, $b = 21.9714(10)$ Å, $c = 31.4784(15)$ Å, $V = 11962.3(10)$ Å^3, $T = 100(2)$ K, Bruker ASX Apex diffractometer, λ(Mo Kα) = 0.710 73 Å, $\mu = 0.142$ mm^{-1}. Of 129 036 reflections measured, 13 036 were unique ($R_{int} = 0.0308$). Refinement on F^2 concluded with the values R1 = 0.0372 and wR2 = 0.0977 for 859 parameters and 11 078 data with $I > 2\sigma_I$.

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the higher coordination number, these contacts are longer than those found for **1a**, with an average value of 2.560 Å compared to 2.453 Å for **1a**. The Al···C contacts also lead to a slight elongation of the $C_{ipso}-C_{ortho}$ bonds to 1.417 Å in **1a** and 1.420 and 1.415 Å in **1b**. For comparison, the corresponding $C_{ipso}-C_{ortho}$ bond distances in the noncoordinated mesityl groups average 1.405 Å in both compounds.

Compound **1** is slightly soluble in benzene, in which it forms a dense liquid clathrate[16] at higher concentration. It is soluble in dichloromethane and chlorobenzene. The ^{1}H and ^{13}C{^{1}H} NMR spectra show only one set of signals for the terphenyl substituents, indicating flexibility of the Al···C interactions. The ^{19}F NMR data are consistent with the presence of the free $[B(C_6F_5)_4]^-$ anion.[2]

Not too surprisingly, **1** is very sensitive toward moisture, traces of which immediately lead to cleavage of an Al−C bond and formation of the arene 1,3-$Mes_2C_6H_4$. In contrast to the gallium analogue, **1** shows reactivity toward olefins. Preliminary investigations showed that **1** reacts with 1-octene[17] and norbornene at room temperature in chlorobenzene solution to produce viscous oils. Interestingly, no reaction was observed between **1** and ethylene (room temperature, 1 atm). The yields of these oils were rather low, and the molecular weights of the oil from the 1-octene reaction were found to be 735 (M_n) and 822 (M_w), corresponding to the presence of mainly hexamers, heptamers, and octamers. Investigations of the nature of the active catalytic species are underway.

In summary, we have prepared an almost linear, quasi-two-coordinate, cationic diorganoaluminum compound and obtained the crystal structures of two polymorphs.

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Supporting Information Available: Crystallographic tables, numbering schemes, and unit cell plots for compounds **1a** and **1b**; data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Dry 1-octene (19.1 mmol, 3.0 mL) was added via syringe to a solution of **1b** (45 mg, 0.033 mmol) in chlorobenzene (10 mL) at room temperature. After it was stirred for 24 h, the reaction mixture was quenched with ethanol (5 mL), resulting in the formation of a dense bottom phase. Separation of this phase followed by removal of the volatile material in vacuo afforded a pale yellow viscous oil (0.26 g), which was analyzed by GPC vs polystyrene standards. Yield: 12%.

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