Synthesis and Characterization of Neutral and Cationic Intramolecularly Coordinated Aluminum Compounds. Structural Determination of $[(\mathrm{Pytsi})\mathrm{AlMe}]^+[\mathrm{MeB}(\mathrm{C_6F_5})_3]^-$ $[(\mathrm{Pytsi} = \mathrm{C}(\mathrm{SiMe_3})_2\mathrm{SiMe_2}(2\text{-}\mathrm{C_5H_4N})]$

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The synthesis and structure of neutral and cationic aluminum compounds equipped with the intramolecular donating $\mathrm{C(SiMe_3)_2SiMe_2(2\text{-}C_5H_4N)}$ ligand denoted by Pytsi is described. The compounds $(\mathrm{Pytsi})\mathrm{AlMe_2}$ (**1**), $(\mathrm{Pytsi})\mathrm{AlEt_2}$ (**2**), $[(\mathrm{Pytsi})\mathrm{AlMe}]^+[\mathrm{MeB(C_6F_5)_3}]^-$ (**3**), and $[(\mathrm{Pytsi})\mathrm{AlMe(thf)}]^+[\mathrm{MeB(C_6F_5)_3}]^-$ (**3·thf**) have been synthesized and characterized by standard methods, and the molecular structures of **1**, **2**, and **3** have been determined by single-crystal X-ray analyses. Compound **3** was obtained by an addition of 1 equiv of $\mathrm{B(C_6F_5)_3}$ to the dimethyl species **1**. The salt-like title compound **3** shows a methyl group in a bridging position between Al and B atoms consisting of a long Al−C distance of 2.380(2) Å and a B−C bond length of 1.681(3) Å.

Introduction

Cationic aluminum species with coordination numbers from 2 to 7 are known.[1] Those with low-coordinated Al centers are strong Lewis acids and are potentially useful as transition-metal-free olefin polymerization catalysts or initiators. Bochmann et al. reported in 1996 that the aluminocenium cation in $[\mathrm{Cp_2Al}]^+[\mathrm{MeB(C_6F_5)_3}]^-$ initiates polymerization of isobutene and isobutene−isoprene mixtures.[2] Three years earlier, the decamethyl derivative $\mathrm{Cp^*{}_2Al^+}$ was already characterized by Schnöckel et al.[3] From a formal viewpoint, aluminum in the aluminocenium cation is 2-fold coordinated; however, because of the pentahapto-coordinated Cp rings the coordination number in $[\mathrm{Cp_2Al}]^+$ is not well defined. Reed et al. reported the synthesis of $[\mathrm{Et_2Al}]^+[\mathrm{CB_{11}H_6X_6}]^-$ (X = Cl, Br).[4] On the basis of the X-ray structural analyses, the $\mathrm{Et_2Al^+}$ moiety is weakly coordinated to two halogen atoms of the carborane unit with C−Al−C angles of 130° (X = Br) and 137° (X = Cl). The salt-like species $[\mathrm{Et_2Al}]^+[\mathrm{CB_{11}H_6X_6}]^-$ has been shown to be an extremely efficient catalyst for polymerization of cyclohexene oxide.[4] Recently, a quasi-two-coordinated diorganoaluminum cation has been described by Wehmschulte et al.[5] The Al atom in $[(2,6\text{-}\mathrm{Mes_2C_6H_3})_2\mathrm{Al}]^+[\mathrm{B(C_6F_5)_4}]^-$ is shielded by very bulky *m*-terphenyl substituents with C−Al−C angles of 159° and 157° found in two different polymorphs. Jordan et al. reported in 1997 that three- and four-coordinated aluminum cations equipped with *N*,*N*′-dialkylamidinate ligands $\mathrm{RC(NR')_2}^-$ can be used for ethylene polymerization under mild conditions.[6] Comparable monoanionic *N*,*N*-bidentate ligands,[7−19] *O*,*N*-bidentate ligands,[20−25] and *C*,*N*-biden-

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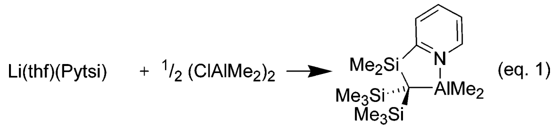
tate ligands[26] had been used to stabilize cationic Al centers with low coordination numbers.

Eaborn and Smith and others have shown that the sterically demanding trisyl ligand (trisyl = tris(trimethylsilyl)methyl, $C(SiMe_3)_3$; commonly denoted as Tsi) can be used to stabilize compounds with unusual low coordination numbers.[27] In addition to the bulkiness of the trisyl ligand, α silyl effects contribute to a stabilization of an attached metal center. Several trisyl derivatives in which one or more methyl groups are replaced by substituents with Lewis-base donor capabilities are known, among which the pytrisyl ligand, $C(SiMe_3)_2SiMe_2(2\text{-}C_5H_4N)$, is the most studied example.[28–33] Recently, we took advantage of the unique properties of the bulky and intramolecularly stabilizing pytrisyl ligand and synthesized [1]ferrocenophanes with aluminum[34] and gallium[35] in bridging positions.

Within this report we describe the synthesis and structural characterization of neutral and cationic pytrisyl alanes.

Results and Discussion

The dimethyl alane **1** is readily accessible by metathesis starting with the known Li(thf)(Pytsi)[28] and chlorodimethylalane (eq 1).



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Compound **1** had been described in a very recent publication by Hill and Smith.[33] The authors mentioned a disorder of **1** in the crystal lattice; however, the molecular structure of **1** was not described. We also found disordered molecules **1** in the crystal lattice, but could successfully model it. The structure of compound **1** is disordered about a plane of symmetry, bisecting the ring along the Si_2C plane in the $(Me_3Si)_2C$ moiety. One-half of the molecule reflects almost on top of the other half of molecule. Both halves of the compound **1**, one with a $SiMe_2$ group and the other with a Me_2Al group, have similar shapes and sizes, and a disorder as found for **1** is not unexpected. The diethyl alane **2**, which we synthesized similarly to compounds **1**, does not exhibit two similarly shaped molecular halves and, consequently, is not disordered in the crystal lattice (Figure 1, Table 1). To model the disorder in **1**, we used the structure of compound **2**. The terminal methyl groups on the two ethyl groups were replaced by H atoms, giving the same formula as **1**. A rigid model of the so modified molecule **2**, with occupancies set at 0.50, was used to refine the data for compound **1**, resulting in an *R* value of 7.9% with all atoms isotropic.

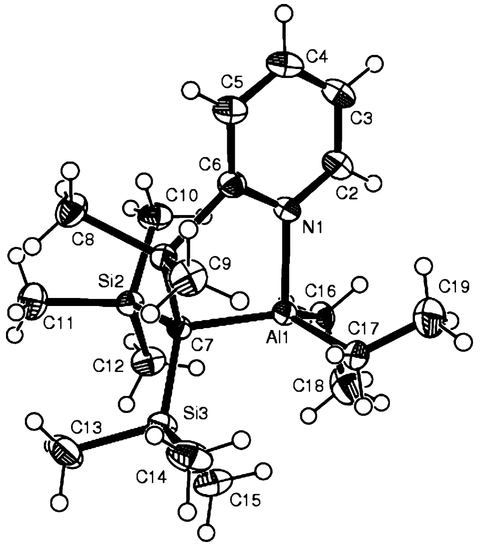

Figure 1. Molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Al1−N1 = 2.0034(18), Al1−C16 = 2.017(2), Al1−C17 = 1.994(2), Al1−C7 = 2.043(2), C7−Si1 = 1.865(2), C7−Si2 = 1.889(2), C7−Si3 = 1.884(2), N1−Al1−C7 = 96.02(8), N1−Al1−C16 = 103.66(9), N1−Al1−C17 = 102.73(9), C16−Al1−C7 = 123.29(10), C17−Al1−C7 = 116.10(10), C17−Al1−C16 = 110.47(10), Al1−C7−Si1 = 100.15(10), C7−Si1−C6 = 103.11(9), Si1−C6−N1 = 114.61(15), C6−N1−Al1 = 114.84(14).

One methyl substituent of **1** can be abstracted by the perfluorinated borane $B(C_6F_5)_3$, resulting in the salt-like compound $[(Pytsi)AlMe]^+[MeB(C_6F_5)_3]^-$ (**3**). Compound **3** crystallizes in the monoclinic space group *C*2/*c* with half a molecule of toluene in the asymmetric unit (Figure 2, Table 1). The most interesting part of the molecular structure of **3** is displayed by the Me group bridging the Al and B atoms. The positions of the hydrogen atoms of the bridging Me group were located in Δ*F* maps and refined. The nearly linear bridge [Al1−C17−B1 = 163.76(17)°] consists of a long Al1−C17 distance of 2.380(2) Å and a B1−C17 bond length of 1.681(3) Å. To the best of our knowledge, structures of salt-like compounds with a cationic Al center and methyl group bridging to a $B(C_6F_5)_3$ moiety are not described in the literature. However, the structural motif $L_nM\text{- - -}H_3C{-}B(C_6F_5)_3$ is known for transition metal species such as Ti,[36–38] Zr,[39–44] and Hf[45] com-

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Table 1. Crystal and Structural Refinement Data for Compounds 1, 2, and 3

	1	2	3·0.5toluene
empirical formula	$C_{16}H_{34}AlNSi_3$	$C_{18}H_{38}AlNSi_3$	$C_{37.50}H_{38}AlBF_{15}NSi_3$
fw	351.69	379.74	909.75
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	orthorhombic	triclinic	monoclinic
space group (No.)	*Pnma* (62)	$P\bar{1}$ (2)	*C*2/*c* (15)
Z	4	2	8
a, Å	12.7464(4)	8.8068(2)	21.4717(3)
b, Å	14.1803(4)	8.9623(2)	16.2706(2)
c, Å	12.1479(3)	17.2181(4)	25.7972(4)
α, deg	90	85.4238(8)	90
β, deg	90	75.5482(9)	113.1518(7)
γ, deg	90	62.6172(8)	90
vol, Å^3	2195.71(11)	1167.59(5)	8286.6(2)
d(calc), mg/m^3	1.064	1.080	1.458
temp, K	173(2)	173(2)	173(2)
abs coeff, mm^{-1}	0.252	0.241	0.233
θ range, deg	3.20−22.0	3.17−27.48	3.34−26.37
no. of reflns collected	2557	10 231	13 405
no. of indep reflns	1418	5339 [*R*(int) = 0.0458]	8451 [*R*(int) = 0.0329]
abs corr	none	none	none
ref method		full-matrix least-squares on F^2	
no. of data/restr/params	1418/0/38	5339/0/218	8451/57/563
goodness-of-fit on F^2	1.260	1.024	1.046
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0790, wR2 = 0.2044	R1 = 0.0472, wR2 = 0.1044	R1 = 0.0453, wR2 = 0.1043
R indices (all data)	R1 = 0.1105, wR2 = 0.2890	R1 = 0.0773, wR2 = 0.1173	R1 = 0.0704, wR2 = 0.1170
largest diff peak and hole, e Å^{-3}	0.702 and −0.946	0.389 and −0.302	0.474 and −0.409

pounds. A textbook example is $[Cp_2ZrMe]^+[MeB(C_6F_5)_3]^-$ with an Zr−μMe distance being 0.30 Å longer than the Zr−Me_{term} distance of 2.251(3) Å; the B−Me bond length is 1.667(3) Å.[42] In comparison, the Al1−C17 distance of 2.380(2) Å in **3** is 0.44 Å longer than that of the Al−Me_{term} bond [Al1−C16 = 1.943(3) Å]. This is a significant difference, and the Al1−C17 distance is far too long to be a covalent bond. Aluminum is 3-fold coordinated by the bidentate pytrisyl ligand and the remaining Me group plus weakly coordinated by the bridging Me group. This intermediate coordination is also reflected in the sum (342°) over the three angles between the C7, N1, and C16 and the central Al atom. This value is between the sum over the three corresponding angles in compound **2** with 4-fold coordination (323°) and the sum over three angles in an idealized trigonal planar arrangement (360°).

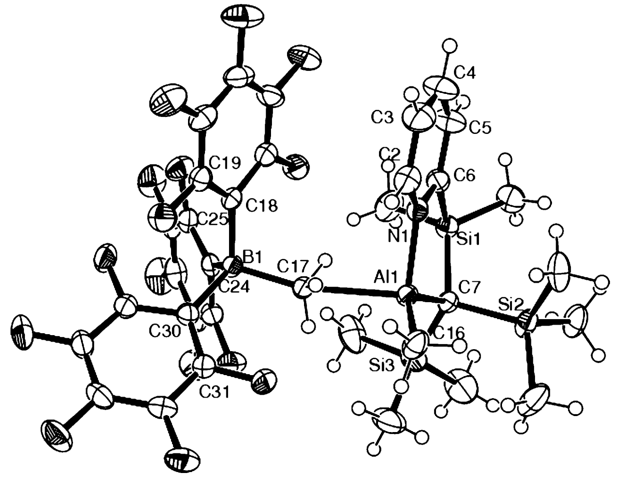

Figure 2. Molecular structure of **3** with thermal ellipsoids drawn at the 50% probability level. Solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al1−N1 = 1.9485(18), Al1−C16 = 1.943(3), Al1−C17 = 2.380(2), Al1−C7 = 1.975(2), C7−Si1 = 1.875(2), C7−Si2 = 1.912(2), C7−Si3 = 1.893(2), B1−C17 = 1.681(3), N1−Al1−C7 = 100.58(9), N1−Al1−C16 = 111.49(10), N1−Al1−C17 = 93.91(8), C16−Al1−C7 = 129.77(10), C17−Al1−C7 = 112.38(10), C17−Al1−C16 = 103.11(10), Al1−C7−Si1 = 101.83(10), C7−Si1−C6 = 102.42(10), Si1−C6−N1 = 115.93(15), C6−N1−Al1 = 113.66(15).

We intended to characterize compound **3** in solution by NMR spectroscopy. The reaction batch that we used to obtain single crystals showed the typical pattern of a pytrisyl ligand exhibiting a mirror plane on time average in the ^1H NMR spectrum. Unfortunately, we could not measure a proton NMR spectrum of **3** free of byproducts. However, if in an NMR tube a 1:1 mixture of the solid starting materials **1** and $B(C_6F_5)_3$, cooled to −78 °C, is dissolved in precooled toluene-d_8 (−78 °C), low-temperature ^1H, ^{11}B, ^{19}F, and ^{13}C NMR spectra of compound **3**, nearly free of byproducts, can be obtained (see Experimental Section and Supporting Information). For example, the ^1H NMR spectra show one singlet for each of the AlMe, $SiMe_2$, $C(SiMe_3)_2$, and BMe moieties and four singlets for the pyridyl group. The chemical shift of the Me group of the anion is temperature dependent. It changes from δ 1.47 at −78 °C to δ 1.35 at −18 °C and is broadened at higher temperatures before it disappears in the baseline at 12 °C. For the AlMe group only insignificant changes of the chemical shift can be observed in the range −78 to −18 °C, but at higher temperatures, it behaves similar to the BMe group and is also hidden in the baseline at 12 °C. At temperatures above −8 °C new ^1H NMR peaks appeared, and prolonged exposure of the flame-sealed NMR tube to ambient temperatures resulted in ^1H NMR

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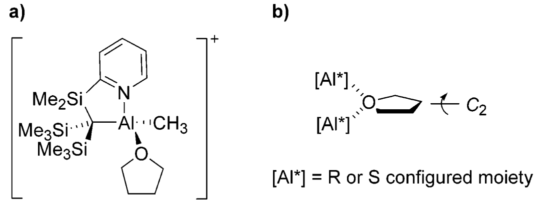
Chart 1. (a) Cation of 3·thf; (b) NMR Time-Averaged Molecular Symmetry of the Cation of 3·thf



spectra with numerous signals; we could neither identify a byproduct nor isolate one. This temperature sensitivity prevented a complete uncovering of the dynamic behavior of **3** in solution. Similar dynamic behavior had been observed for other salt-like species, e.g., [{HC(CMeNAr)$_2$}AlMe][MeB(C$_6$F$_5$)$_3$],[11] and it was proposed that an exchange of the Me groups occurs in solution as illustrated in eq 2. We assume that such an equilibrium also exists for compound **3**.

$$\mathrm{LAlMe_2} + \mathrm{B(C_5F_6)_3} \rightleftharpoons [\mathrm{LAlMe}]^+ + [\mathrm{MeB(C_5F_6)_3}]^- \quad \text{(eq. 2)}$$

L = chelating ligand

The chemical shift of the Me group of [MeB(C$_6$F$_5$)$_3$]$^-$ for **3** is significantly downfield from those of salts of the type A[MeB(C$_6$F$_5$)$_3$], with A$^+$ being an "innocent" cation. Jordan et al. chose [NBu$_3$Bz][MeB(C$_6$F$_5$)$_3$] (δ 1.09; toluene-d_8)[11] as a reference compound. We found a chemical shift of δ 0.99 (toluene-d_8) for the thf adduct of compound **3**, [(Pytsi)AlMe(thf)][MeB(C$_6$F$_5$)$_3$], which is discussed below. The downfield shift is indicative of ion-pairing in solution and shows that compound **3**, dissolved in toluene, exhibits a molecular structure with an Al-Me-B moiety, similar as that found in the crystal lattice.

If the synthesis of compound **3** is performed in the presence of 1 equiv of thf, a new compound, [(Pytsi)AlMe(thf)][MeB(C$_6$F$_5$)$_3$] (**3**·thf), is formed. The ^{1}H NMR spectrum reveals an asymmetric pytrisyl ligand: two singlets for the C(SiMe$_3$)$_2$ moiety and two singlets for the SiMe$_2$ group. These NMR data are consistent with the formation of the expected cation shown in Chart 1a.

The cation of the salt **3**·thf exhibits C_1 point group symmetry. Therefore, all H and C atoms of the coordinated thf molecule are nonequivalent and, in principle, should give one resonance each. The coordinated thf moiety, however, shows only two ^{13}C NMR peaks at δ 24.75 and 74.69 and three multiplets in the ^{1}H NMR spectrum at δ 1.35 (4H), 3.08 (2H), and 3.34 (2H). This result can be interpreted as being due to the well-known inversion of the envelope conformation of thf, resulting in a time-averaged C_2 symmetry of the cation (Chart 1b).

The NMR data show that the thf molecule does not dissociate and reassociate fast on the NMR time scale; a process like this would be accompanied by an inversion at the Al atom. However, if 2 equiv of thf-d_8 are added to a NMR sample of **3**·thf in toluene-d_8, two new multiplets appear, unequivocally indicating noncoordinated thf. In addition, the relative intensity of the sets of signals of coordinated thf decreased respectively, revealing that added thf-d_8 replaces coordinated thf in **3**·thf. At ambient temperature the free thf resonates at δ 1.48 and 3.48, which is downfield with respect to those of the coordinated thf at δ 1.35 (4H), 3.08 (2H), and 3.34 (2H). By increasing the temperature the chemical shifts of the coordinated thf move closer to those of the noncoordinated thf, so that at 100 °C (500 MHz) the signals at higher field coalesced to one signal at δ 1.53 (CH_2CH$_2$O) and that at lower field still appeared as two broad signals (δ 3.54 and 3.34). Coalescence phenomena can be observed for the two sets of singlets for the diastereotopic methyl group in SiMe$_2$ and C(SiMe$_3$)$_2$, respectively, which broaden with increasing temperature, and at 100 °C only two very broad singlets are present. These NMR results show that a fast exchange of the coordinated thf and noncoordinated thf occurs, resulting in an inversion of the Al atom.

Conclusions

We have shown that one methyl group of the dimethylalane **1** can be abstracted by the perfluorinated borane B(C$_6$F$_5$)$_3$, resulting in the salt-like compound [(Pytsi)AlMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (**3**). The molecular structure of **3** in the solid state shows a methyl group in a bridging position between aluminum and boron with a long Al−C distance of 2.380(2) Å. Compound **3** is not stable in solution at ambient temperature; however, a stable thf adduct can be obtained. These initial results show that the pytrisyl ligand is capable of stabilizing an aluminum cation with a low coordination number. We started to change compound **3** systematically by using different weakly coordinating anions, by exchanging the remaining methyl group at aluminum by a sterically more demanding group, and by increasing the steric bulk of the pytrisyl ligand by introducing sterically demanding groups in position 6 of the pyridine ring. By fine-tuning compound **3**, we hope to control the reactivity of cationic pytrisyl alanes and make use of them in catalytic processes such as olefin polymerization.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques. Solvents were dried using a Braun solvent purification system and stored under nitrogen over 4 Å molecular sieves. All solvents for NMR spectroscopy were degassed prior to use and stored under nitrogen over 4 Å molecular sieves. Li(thf)(Pytsi)[28] [Pytsi = C(SiMe$_3$)$_2$SiMe$_2$-(2-C$_5$H$_4$N)] and B(C$_6$F$_5$)$_3$[46] were synthesized as described in the literature. Me$_2$AlCl and Et$_2$AlCl were purchased from Aldrich and used as received. ^{1}H, ^{13}C, ^{11}B, ^{27}Al, and ^{19}F NMR spectra were recorded on a Bruker 500 MHz Avance. ^{1}H (500 MHz) and ^{13}C (125.8 MHz) chemical shifts were referenced to the residual protons of the deuterated solvents. In the case of toluene-d_8, the peak of the Me group was used as a reference (^{1}H NMR δ 2.09; ^{13}C NMR δ 20.40). Other nuclei were referenced to an external standard dissolved in C$_6$D$_6$: ^{27}Al NMR (130.3 MHz; [Al(acac)$_3$]), ^{11}B NMR (165.5 MHz, BF$_3$-OEt$_2$), ^{19}F NMR (470.5 MHz, CFCl$_3$). Samples were dissolved in C$_6$D$_6$, and NMR spectra were obtained at ambient temperature unless noted differently. We could not detect the ^{13}C NMR signal of the pytrisyl C atom directly bound to Al for compounds **1**, **2**, and **4**. Mass spectra were measured on a VG 70SE, and signals of the most abundant ions are listed. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer using V$_2$O$_5$ to promote complete combustion.

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(46) Lancaster, S. *SyntheticPage* **2003**, 215.

(Pytsi)AlMe$_2$ (1). A solution of Me$_2$AlCl (4.9 mL, 1 M in hexanes) was added dropwise to a stirred solution of Li(thf)(Pytsi) (1.828 g, 4.9 mmol) in hexane (20 mL) at −78 °C. The resulting solution was stirred for 20 min at −78 °C and then allowed to warm to ambient temperature. After the reaction mixture was stirred for 16 h, the solid was filtered off and washed with hexane (3 × 5 mL). Removal of the solvent left a light yellow solid, which was sublimed at 90 °C and high vacuum to give the colorless crude product. Crystallization from hexane (10 mL) at −30 °C resulted in colorless crystals, suitable for single-crystal X-ray structural determination (1.184 g, 69%). Compound **1** was first described in ref 33. Our spectroscopic data were identical to those given earlier, but we consider that amendments are required to assignments of ^{1}H and ^{13}C resonances from the pyridine moiety. Our assignments were confirmed by ^{1}H−^{1}H COSY and HMQC experiments. ^{1}H NMR: δ −0.21 (s, 6H, AlMe$_2$), 0.27 (s, 18H, SiMe$_3$), 0.40 (s, 6H, SiMe$_2$), 6.34 (pst, 1H, 5-H), 6.79 (pst, 1H, 4-H), 6.92 (d, 1H, 3-H), 7.93 (d, 1H, 6-H). ^{13}C{^{1}H} NMR: δ −3.16 (br, AlMe$_2$), 4.35 (SiMe$_2$), 6.57 (SiMe$_3$), 124.39 (5-C), 129.22 (3-C), 138.37 (4-C), 145.88 (6-C), 174.05 (*ipso*-C). ^{27}Al NMR: δ 176 ($w_{1/2} = 2850$ Hz). MS: *m/z* 336 (100, M − Me$^+$), 264 (52, $C_{12}H_{22}NSi_3^+$), 248 (20, $C_{11}H_{18}NSi_3^+$). Anal. Calcd for $C_{16}H_{34}NAlSi_3$ (351.691): C, 54.64; H, 9.74; N, 3.98. Found: C, 54.67; H, 10.11; N, 3.75.

(Pytsi)AlEt$_2$ (2). Li(thf)(Pytsi) (3.206 g, 8.6 mmol) was dissolved in hexane (40 mL) at ambient temperature and cooled with an acetone−dry ice bath. Et$_2$AlCl (8.6 mL, 1 M in hexane) was added over a period of 10 min using a syringe and a septum, and the resulting solution was stirred for another 20 min, before the dry ice bath was removed. The reaction mixture was stirred overnight at ambient temperature. The solution was filtered, and the solid was washed with hexane (3 × 10 mL). After the solvent was removed from the filtrate in high vacuum, pale yellow crystals were obtained by sublimation at 140 °C in high vacuum. The sublimed compound was dissolved in hexane (25 mL), and crystallization at ca. −20 °C resulted in colorless compound **2** (2.281 g, 70%). ^{1}H NMR: δ 0.26 (s, 18H, SiMe$_3$), 0.31 (d/q, 2H, $^2J_{HH} = 14.3$ Hz, $^3J_{HH} = 8.1$ Hz, AlCH$_2$), 0.39 (s, 6H, SiMe$_2$), 0.50 (d/q, 2H, $^2J_{HH} = 14.3$ Hz, $^3J_{HH} = 8.1$ Hz, AlCH$_2$), 1.37 (d/d, 6H, $^3J_{HH} = 8.1$ Hz, AlCH$_2$CH_3), 6.34 (pst, 1H, 5-H), 6.78 (pst, 1H, 4-H), 6.92 (d, 1H, 3-H), 8.10 (d, 1H, 6-H). ^{13}C{^{1}H} NMR: δ 4.09 (SiMe$_2$), 4.19 (br, AlCH$_2$), 6.32 (SiMe$_3$), 10.49 (AlCH$_2$CH$_3$), 123.61 (5-C), 129.15 (3-C), 138.09 (4-C), 146.09 (6-C), 173.83 (ipso-C). ^{27}Al NMR: δ 173 ($w_{1/2} = 2400$ Hz). MS (70 eV) *m/z* (%) 364 (7, M − Me$^+$), 350 (100, M − $C_2H_5^+$), 295 (12) [PytsiH$^+$], 280 (36, $C_{13}H_{26}NSi_3^+$, 264 (18, $C_{12}H_{22}NSi_3^+$), 248 (8, $C_{11}H_{18}NSi_3^+$). Anal. Calcd for $C_{18}H_{38}AlNSi_3$ (379.745): C, 56.93; H, 10.09; N, 3.69. Found: C, 56.37; H, 9.47; N, 3.12.

(Pytsi)AlMe$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (3). A NMR tube, charged with **1** (0.0176 g, 0.0500 mmol) and B(C$_6$F$_5$)$_3$ (0.0256 g, 0.0500 mmol), was cooled to −78 °C, precooled toluene-d_8 (1 mL, −78 °C) was added with a syringe, and the tube was carefully shaken in such a way that a significant increase of the temperature was avoided. The NMR tube containing a clear and colorless solution was inserted into a cooled NMR probe head (see Supporting Information for NMR spectra). ^{1}H NMR (225 K, toluene-d_8): δ −0.12 (s, 18H, SiMe$_3$), −0.09 (s, 3H, AlMe), 0.04 (s, 6H, SiMe$_2$), 1.40 (s, 3H, BMe), 6.40 (m, br, 1H, 4-H or 5-H), 6.51 (d, 1H, 3-H), 6.83 (m, 1H, 5-H or 4-H), 7.58 (d, 1H, 6-H). ^{13}C{^{1}H} NMR: δ −4.98 (AlMe), 1.16 (C(SiMe$_3$)$_2$), 2.57 (SiMe$_2$), 4.63 (SiMe$_3$), 12.1 (br, BMe), 125.65 (4-C or 5-C), 130.46 (3-C), 136.94 (d/m, $^1J_{CF} = 241$ Hz, m-C$_6$F$_5$), 141.36 (5-C or 4-C), 144.69 (6-C), 148.30 (d/m, $^1J_{CF} = 241$ Hz, o-C$_6$F$_5$), 171.96 (ipso-C$_5$H$_4$N); peaks for ipso-C$_6$F$_5$ and p-C$_6$F$_5$ are hidden by the solvent signals. ^{11}B NMR: δ −14.80 (s). ^{19}F NMR: δ −133.55 (d, 6F, o-F), −159.95 (m, 3F, p-F), −164.34 (m, 6F, m-F); small amounts of B(C$_6$F$_5$)$_3$ were detected at δ −128.66 (d, 6F, o-F), −140.43 (m, 3F, p-F), −159.75 (m, 6F, m-F) (see ref 11).

Single crystals of **3** were obtained as follows (see Results and Discussion). B(C$_6$F$_5$)$_3$ (0.716 g dissolved in 10 mL of toluene, 1.4 mmol) was added via a cannula to a solution of **1** (0.492 g, 1.4 mmol) in toluene (10 mL), and the resulting reaction mixture was stirred for 1 h. The solvent was removed in high vacuum from the clear, colorless solution, resulting in a formation of a white wax. Trituration with hexane (2 × 20 mL) gave **3** as a white solid (0.938 g, 78%). Toluene (10 mL) was added, and the flask was placed in the freezer (ca. −20 °C), resulting in the formation of two liquid layers and some colorless crystals. The two liquid layers were syringed off, and all remaining volatiles were removed in high vacuum. X-ray analysis of the crystals revealed the desired compound.

(Pytsi)AlMe(thf)$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (3·thf). B(C$_6$F$_5$)$_3$ (0.472 g dissolved in 10 mL of toluene, 0.921 mmol) was added via a cannula to a stirred solution of **1** (0.324 g, 0.921 mmol) and thf (0.08 mL, ~0.921 mmol) in toluene (10 mL). The reaction mixture was stirred for 30 min, resulting in the formation of two layers. All volatiles were removed in high vacuum. Trituration with hexane (2 × 20 mL) did not result in the formation of a solid, but gave a colorless sticky foam after the remaining solvent was removed in high vacuum (0.789 g, 92%). ^{1}H NMR (toluene-d_8): δ −0.50 (s, 3H, AlMe), −0.17 (s, 9H, SiMe$_3$), 0.00 (s, 9H, SiMe$_3$), 0.10 (s, 3H, SiMe), 0.29 (s, 3H, SiMe), 0.99 (s, 3H, BMe), 1.35 (m, 4H, CH_2CH$_2$O), 3.08 (m, 2H, CH$_2$O), 3.34 (m, 2H, CH$_2$O), 7.00 (pst, 1 H, 5-H), 7.24 (d, 1H, 3-H), 7.38 (pst, 1H, 4-H), 7.80 (d, 1H, 6-H). ^{13}C{^{1}H} NMR (toluene-d_8): δ −7.89 (AlMe), 2.04 (SiMe), 4.01 (SiMe), 5.15 (SiMe$_3$), 5.59 (SiMe$_3$), 11.3 (br, BMe), 24.75 (CH$_2$CH$_2$O), 74.69 (CH$_2$O), 126.53 (5-C), 130.1 (br, *ipso*-C$_6$F$_5$), 131.27 (3-C), 137.1 (d/m, $^1J_{CF} = 245$ Hz, m-C$_6$F$_5$), 138.1 (d/m,$^1J_{CF} = 245$ Hz, p-C$_6$F$_5$), 142.22 (4-C), 145.46 (6-C), 149.21 (d/m, $^1J_{CF} = 239$ Hz, o-C$_6$F$_5$), 173.69 (ipso-C$_5$H$_4$N). ^{11}B NMR (CDCl$_3$): δ −15.1 (s, br). ^{19}F NMR (CDCl$_3$): δ −137.29 (d, 6 F, o-F), −168.90 (m, 3 F, p-F), −171.61 (m, 6 F, m-F).

X-ray Structural Analysis. For all three structures **1**, **2**, and **3**, data were collected at −100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program.[47] Cell refinement and data reductions used the programs DENZO and SCALEPACK.[48] SIR97[49] was used to solve the structure, and SHELXL97[50] was used to refine the structure. Except for the bridge methyl protons in **3**, H atoms were placed in calculated positions with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom for aromatic protons and 1.5 times U_{eq} of the carrier atoms for methyl and methylene hydrogen atoms.

Because of the disorder of compound **1**, the structure of compound **2** was used as a model for compound **1** (see Results and Discussion). A rigid model of the modified molecule **2**, with occupancies set at 0.50, was used to refine the data for compound **1**. Since the reflected half of **1** has atoms very close to the other half of **1**, it was not possible to allow the positions to refine independently and it was also not possible to refine the atoms anisotropically, because strong correlations result in meaningless thermal ellipsoids. The crystal only diffracted to 22 degrees. Only 38 parameters (6 to define the position and orientation of the rigid molecule, temp factor on 21 non-H atoms, and rotation of the 10 methyl groups plus scale) were refined against 1418 reflections (1138 observed). For further information see the Supporting Information.

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Supporting Information Available: ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra of **3** (225 K, toluene-d_8) and crystallographic data for **1**, **2**, and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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