Notes

Tris(pentafluorophenyl)alane: A Novel Aluminum Organyl

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Introduction

Aluminum organyls, AlR_3, are of great interest due to their high reactivity with compounds such as amines, alcohols, and lithium alkyls and also in industrial processes as starting materials for catalytic reactions.[1,2] $AlMe_3$ and $AlEt_3$ are prepared using Al, RCl, NaCl, and Na as starting materials; furthermore, the other alkyls are prepared using $(i\text{-Bu})_3Al$.[3]

On the laboratory scale are mainly three synthetic routes known for preparing aluminum organyls:[4] (i) the thermal reaction of HgR_2 with Al; (ii) the Grignard reaction of RMgCl compounds with $AlCl_3$; (iii) the reaction of alkenes with $AlH_3{\cdot}Et_2O$.

An alternative route for preparing tris(aryl)alanes is the metathesis of mixed aluminum organyls of the type $R'AlR_2$, where R′ is an aromatic and R an aliphatic substituent.[5] This reaction affords the two pure aluminum organyls AlR_3 and AlR'_3.

Herein we report the preparation of tris(pentafluorophenyl)alane $(C_6F_5)_3Al$, (**1**) by treatment of Me_2AlCl with LiC_6F_5 leading to $Me_2AlC_6F_5$ as an intermediate. Thermal decomposition affords **1** and $AlMe_3$ as shown in Scheme 1.

Experimental Section

All manipulations were carried out in an atmosphere of dry nitrogen, using standard Schlenk tube techniques. The solvents were freshly distilled under nitrogen from the appropriate drying agents.

Safety Notes. C_6F_5Li decomposes explosively above −40 °C. Tris(pentafluorophenyl)alane (**1**) tends to explode under circumstances not exactly determined.

Synthesis of 1. To a freshly prepared solution of C_6F_5Li (55 mmol) in *n*-hexane (30 mL) at −78 °C was added slowly an equimolar amount of Me_2AlCl (1 M in *n*-hexane, 55 mmol). After warming up to room temperature the reaction mixture was stirred overnight, and the precipitated LiCl was separated from the solution by filtration. The solvent was removed in *vacuo* followed by slowly heating the intermediate $Me_2AlC_6F_5$ in *vacuo* (1×10^{-3} pa) up to 180 °C. $AlMe_3$ was distilled off and collected in a cooling trap held at −196 °C. The pyrolysis was finished when $AlMe_3$ evolution had ceased. Recrystallization of the pale yellow residue yielded 11.0 g (64%) of the tris(pentafluorophenyl)aluminum thf adduct **1** with melting point 197 °C. IR (Nujol): 1759 (m), 1643 (vs), 1511 (vs), 1357 (s), 1273 (vs), 1069 (vs), 1057 (vs), 1012 (m), 992 (m), 956 (vs), 861 (m), 848 (s), (740) (m), 667 (m) cm^{-1}. ^{19}F-NMR (C_6D_6, 75.39 MHz, external $CFCl_3$): δ −120.1 (m, 6 F, *o*-F), −153.8 (m, 3 F, *p*-F), −160.1 (m, 6 F, *m*-F)ppm. MS (70 eV): *m*/*e* (%) 600 (15) [M], 168 (100) [C_6F_5H]. Anal. Calcd for $C_{22}H_8AlF_{15}O$: C, 44.3, H, 1.9. Found: C, 43.5, H, 1.9%.

Scheme 1

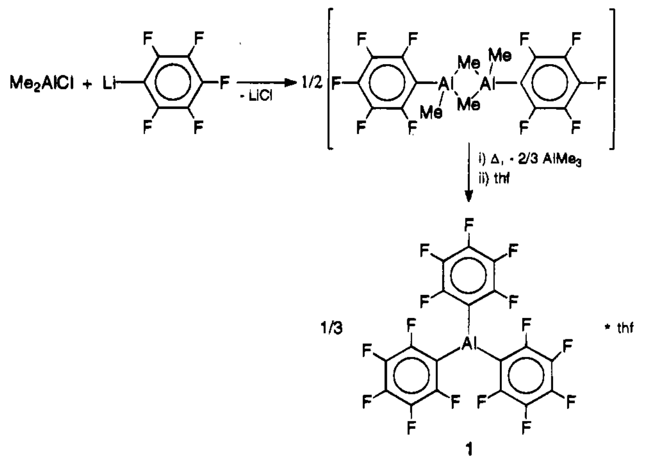

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Table 1. Crystallographic Data for **1**

formula	$C_{22}H_8AlF_{15}O$	*V*, Å^3	1079.4(6)
fw	600.26	*Z*	2
cryst system	triclinic	ϱ_{calcd}, Mg m^3	1.847
space group	$P\bar{1}$ (No. 2)	θ-range, deg	3.51−22.51
a, Å	10.449(3)	μ, mm^{-1}	0.239
b, Å	10.853(3)	reflcns	2914
c, Å	10.901(4)	restraints	0
α, deg	112.57(2)	params	352
β, deg	90.350(10)	$R\ [I > 2\sigma(I)]$[a]	0.0347
γ, deg	107.340(10)	w*R*2 (all reflcns)[b]	0.0944

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$ $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [F_o^2 + 2F_c^2]/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1**

Al(1)−O(11)	1.860(2)	Al(1)−C(41)	1.989(2)
Al(1)−C(21)	1.997(3)	Al(1)−C(31)	2.000(3)
O(11)−Al(1)−C(41)	102.77(9)	O(11)−Al(1)−C(21)	106.30(9)
C(41)−Al(1)−C(21)	116.50(10)	O(11)−Al(1)−C(31)	105.88(9)
C(41)−Al(1)−C(31)	114.14(10)	C(21)−Al(1)−C(31)	110.09(10)

Crystallography. Data were collected at −120 °C on a SIEMENS-STOE AED2 four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), using the $\theta-\omega$ scan technique in the θ range from 3.51 to 22.51°. Details of crystal data, measurements of intensities, and data processing are summarized in Table 1. The structure was solved by full matrix direct methods supplied in the SHELXTL system and refined by least-squares methods against 2118 F^2-values.[6] $R1 = 0.0372$ [$F_o^2 > 2\sigma(F_o^2)$]; $wR2 = 0.0944$ (all data).

Results and Discussion

Tris(pentafluorophenyl)alane (**1**) was recrystallized from boiling thf, yielding the thf adduct of the aluminum organyl as a pale yellow solid. Single crystals of **1** were obtained from thf, suitable for a structure determination by X-ray diffraction.[6] Selected bond lengths and angles are given in Table 2, and atomic coordinates and equivalent isotropic displacement coefficients are given in the supplementary material.

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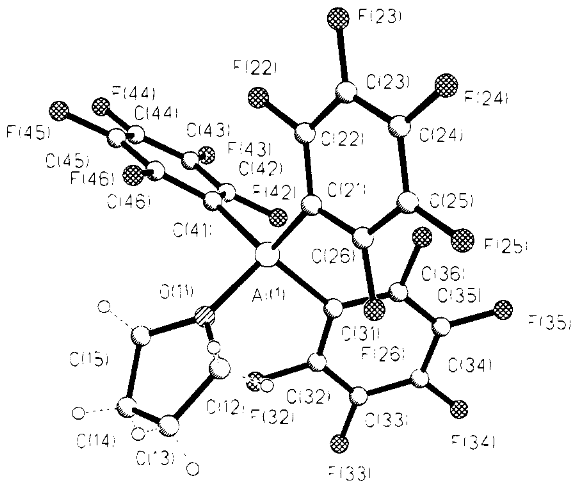

Figure 1. Crystal structure of the tris(pentafluorophenyl)alane thf adduct **1**.

The tris(pentafluorophenyl)alane thf adduct **1** crystallizes in the triclinic space group $P\bar{1}$ in the form of cuboids. The geometry at the aluminum atom is slightly tetrahedrally distorted as seen from the angles at aluminum ranging from 102.8(9) to 116.5(10)°. The average bond length between aluminum and carbon is 1.995 Å comparable to other aluminum aryl compounds (e. g. Mes_3Al (1.995(8) Å))[7] or corresponding to the Al−C distances of the $AlMe_3$ monomer in the gas phase.[8]

The ^{19}F-NMR of **1** shows the significant signals of the pentafluorophenyl ligand, and also the mass spectra and elemental analysis confirm the composition of **1**.

Not only the general validity but also the easy performance makes this metathesis reaction an alternative in the synthesis of tris(aryl)alanes. The analogous boron compound $B(C_6F_5)_3$ is used as cocatalyst in the field of metallocene-catalyzed olefine polymerization, e. g. with $Cp^*_2ZrH_2$,[9] so that **1** can be expected to act as cocatalyst in these systems.

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Supporting Information Available: Tables giving details of the crystallographic data collection, complete bond lengths and angles, anisotropic displacement coefficients, and complete atomic coordinates and displacement coefficients of **1** (5 pages). Ordering information is given on any current masthead page.

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