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Synthesis of an Aluminum Spirocyclic Hybrid with an Inorganic B_2O_3 and an Organic C_3N_2 Core

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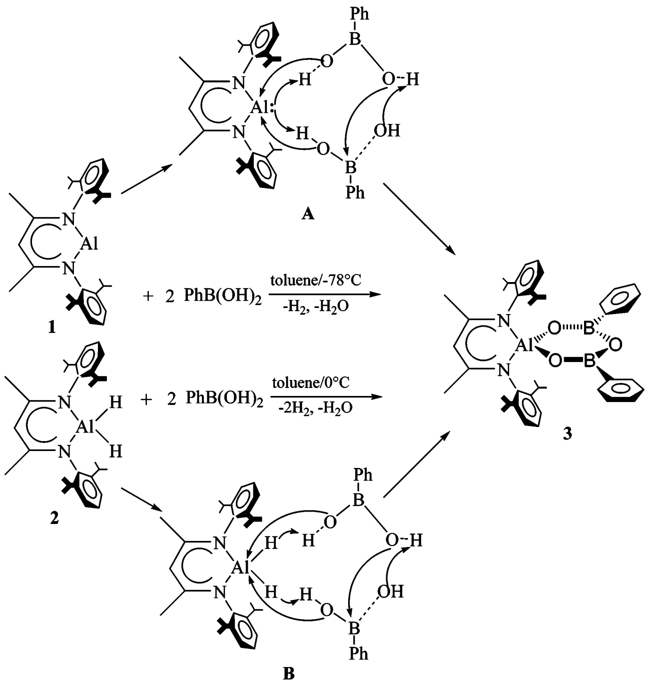
In recent years the synthesis of organic−inorganic hybrid materials has become an important target. This was impressively shown by I. Manners who discovered the ROP of silaferrocenophanes which provide access to poly(ferrocenylsilanes).[1] Today ferrocenophanes with different main group elements in the bridging position are known, including a ferrocenophane with aluminum.[2] Since then, aluminum containing organic−inorganic hybrid materials is a fascinating subject. Current ongoing research in our group showed that the germanium(II) compound $Ge[N(SiMe_3)_2]_2$ can be used to convert a proton to a hydride to generate the germanium(IV) cluster $[(RSiO_3GeH)_4]$.[3] As an alternative powerful reducing agent we introduced the aluminum(I) compound LAl (**1**) (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$)[4] to transfer two electrons to generate aluminum(III) species such as $(LAl)_2P_4$[5] and $(LAl)_2O_2$.[6] The easy formation of the latter compounds and the $[(RSiO_3GeH)_4]$ cluster prompted us to investigate the redox reaction of LAl and $PhB(OH)_2$ due to the easy electron transfer and the favorable formation of an Al−O−B bond. We investigated the reaction of $LAlH_2$ (**2**)[7] with $PhB(OH)_2$ to take advantage of the different polarity of the hydrogen atoms in both compounds, which should lead to an easy hydrogen elimination.

The reaction of **1** with $PhB(OH)_2$ in a 1:2 molar ratio (Scheme 1) resulted in an unprecedented formation of $LAl[(OBPh)_2O]$ (**3**). The color of the solution changes from red to colorless when the temperature of the solution is slowly raised to 20 °C. During the course of the reaction hydrogen gas evolution was observed. **3** separated after cooling as colorless crystals from the concentrated toluene solution. **3** is soluble in toluene, benzene, and trichloromethane.

3 was characterized by ^1H and ^{13}C NMR investigation in $CDCl_3$ solution, as well as by EI-MS, IR, and elemental analysis. The ^1H and ^{13}C NMR spectra both exhibit one set of resonances for the aryl groups both on boron and on the ligand, indicating a symmetric molecule. The EI mass spectrum shows the molecular ion of **3** (m/z 668) with 100% intensity. In the IR spectrum of **3**, there are no absorption bands above 3000 cm^{-1} which originate from the OH groups of the starting material (br, 3100−3400 cm^{-1}). **3** is thermally stable, as indicated by its melting point (338 °C). To support and understand the easy formation of **3** we also reacted $LAlH_2$ (**2**) with $PhB(OH)_2$. The reaction proceeds under elimination of hydrogen and water. Here, too, **3** is formed in a comparable yield.

Scheme 1. Synthesis of **3**



For the progress of the two reactions we assume two similar concerted mechanisms through the intermediate **A** (from **1**) or **B** (from **2**) shown in Scheme **1**. Proceeding from **1** to **3**, the aluminum(I) of **1** is oxidized to aluminum(III) (**3**) under formation of one equivalent of hydrogen resulting from two protons of the two molecules of $PhB(OH)_2$. The exothermic formation of the Al−O bonds is the driving force in this reaction. The increase of the proton acidity of the intermediate $LAl[OB(Ph)OH]_2$ leads to the elimination of water under AlO_3B_2 ring formation. The formation of **3** through the intermediate **B** is driven by the exothermic Al−O bond enthalpy. The H_2 elimination is favored through the hydridic (**2**) and protonic hydrogen ($PhB(OH)_2$) atoms. Compound **3** is an unique example of a spiro-centered aluminum atom, showing the inorganic AlO_3B_2 ring fused to the organic C_3N_2 part. There is only one inorganic spirocyclic aluminum compound known of composition $[(PhBO)_2Al(OBPh)_2Al_2Cl_4]$ which was prepared from $(PhBO)_3$ and $AlCl_3$, where both rings have the same composition.[8]

Single crystals of X-ray quality were obtained from a toluene solution of **3** at low-temperature, crystallizing in the triclinic space group $P\bar{1}$.[9] The structural analysis unambiguously ascertains the composition of **3**. Its molecular structure is shown in Figure 1. One aluminum atom, two boron atoms, and three oxygen atoms form a six-membered planar AlO_3B_2 ring. The central Al atom is located in the spirocyclic center of the two fused six-membered rings (C_3N_2-Al and AlO_3B_2). The Al−O bond length (av 1.750 Å) is longer than the terminal Al−OH bond distance (av 1.705 Å) in LAl(OH)$_2$.[10] The O−Al−O angle (104.7(3)°) is sharper than that in LAl(OH)$_2$ (115.38(8)°). The differences in bond length and bond angle of **3** with those in LAl(OH)$_2$ might be due to a certain strain within the six-membered rings of **3**. The B(2)−O(2) bond length (1.326(10) Å) adjacent to the aluminum atom is distinctly shorter than that of the B(2)−O(1) (1.415(11) Å) with the consequence

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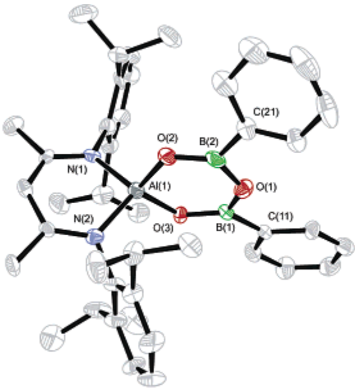

Figure 1. Molecular structure of **3**; thermal ellipsoids set at 50% probability. All hydrogen atoms and the toluene molecule are omitted for clarity. Selected bond lengths [Å] and angles [deg]: N(1)−Al(1) 1.877(6), N(2)−Al(1) 1.872(6), Al(1)−O(2) 1.754(5), Al(1)−O(3) 1.745(5), O(2)−B(2) 1.326(10), O(3)−B(1) 1.339(10), B(2)−O(1) 1.415(11), O(1)−B(1) 1.401(10), B(2)−C(21) 1.574(11), B(1)−C(11) 1.559(11); N(2)−Al(1)−N(1) 98.8(3), O(2)−Al(1)−O(3) 104.7(3), O(3)−Al(1)−N(2) 113.2(3), O(2)−Al(1)−N(2) 111.9(3), O(3)−Al(1)−N(1) 115.0(3), O(2)−Al(1)−N(1) 113.6(3), O(3)−B(1)−O(1) 122.4(7), B(2)−O(2)−Al(1) 121.7(5), O(2)−B(2)−O(1) 122.5(8), B(1)−O(3)−Al(1) 121.7(5).

Table 1. Calculated Bond Lengths and Angles

distance	[Å]	angle	[deg]
Al(1)−O(2)	1.7901	O(2)−Al(1)-O(3)	100.81
Al(1)−O(3)	1.7896	O(3)−B(1)-O(1)	119.65
B(2)−O(1)	1.4137	O(2)−B(2)-O(1)	119.37
B(2)−O(2)	1.3749	N(1)−Al(1)-N(2)	98.89

that the Al−O bond lengths in **3** increase when compared to those in $LAl(OH)_2$ and $(LAl)_2O_3AlMe$ (1.708−1.726 Å).[11] The wider O−B−O bond angles (122.4(7)°, 122.5(8)°) in comparison to the O−Al−O (104.7(3)°) are a consequence of the lower coordination number at boron compared to that at aluminum.

The ab initio calculations were performed with the aim of clarifying the bonding situation in the target molecule and giving further insight into the reaction mechanism. The calculations were performed at the well-established DFT level of theory making use of the B3LYP functional[12,13] as implemented in the Gaussian program package[14] making use of a basis-set termed 6-31G.[15−18] The analysis of the binding situation was performed at the calculated equilibrium geometry of the compound by means of a NBO analysis.[19−21] The determination of the reaction mechanism cannot be easily performed due to the fact there are three molecules involved and would surely go far beyond the scope of this work. The approach chosen here was to rule out further possible reaction pathways. As the two reactions result in the same product, herein we only investigated the reaction between **1** and $PhB(OH)_2$.

As clearly visible from Table 1 the resulting equilibrium structure agrees very well with the experimental X-ray data, thus giving the bond analysis a quite solid foundation. Both Al−N bonds are formed by overlapping a $sp^{3.04}$ hybrid orbital of aluminum with a $sp^{2.50}$ hybrid orbital of nitrogen with the main electronic contribution coming from nitrogen. These bonds are strengthened by a donor−acceptor interaction with the lone pair of nitrogen. The situation is quite similar for the Al−O bonds, but in this case the orbitals involved can be described as an $sp^{2.67}$ orbital on Al and an $sp^{2.70}$ orbital on O with most of the electronic density coming from oxygen. The formation of the Al−O bonds also has an effect on the Al−N bonds due to the stabilizing donor−acceptor interaction between antibonding Al−O orbitals and the Al−N bonds.

The investigation of the mechanism was performed by locating a transition-state structure on the potential hypersurface and also by taking a closer look at the possible alternative mechanism. The possible routes involving a two-step mechanism start with either hydrogen or water formation. Assuming that H_2 elimination is the first step of the reaction does not lead to the desired compound due to the rearrangement taking place in the Ph−B−OH unit (Figure S1, see Supporting Information). However the condensation as the first step looks quite promising as the transition state diagram indicates (Figure S2, see Supporting Information). But trying to reach the target molecule from this transition state is impossible due to the fact that the bond formation between aluminum and oxygen does not take place. Having ruled out this possible mechanistic explanation, it is quite reasonable that the calculated transition state shown in Figure S3 (see Supporting Information) is the crucial step in this reaction. The calculations indicate that the reason for the formation of the transition structures **A** and **B** proposed here is valid.

In summary the different reactions between $PhB(OH)_2$ with LAl(I) or $LAlH_2$(III) result in the same compound **3** in high yields.

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Supporting Information Available: Figures S1, S2, and S3; Experimental Section, including detailed synthetic procedures and analytical and spectral characterization data; CIF data for **3**; complete ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data for **2**: $C_{41}H_{51}AlB_2N_2O_3$, $M_r = 668.44$, triclinic, space group $P\bar{1}$, $a = 11.436(2)$ Å, $b = 12.091(2)$ Å , $c = 15.359(3)$ Å, $\alpha = 74.936(13)°$, $\beta = 76.052(13)°$, $\gamma = 74.564(13)°$, $V = 1.9428(6)$ nm^3, $Z = 2$, $\rho_{calcd} = 1.143$ Mgm^{-3}, $F(000) = 716$, $1.79 \leq \theta \leq 24.81°$. The R values are R1 = 0.0912 and wR2 = 0.1113 ($I > 2\sigma(I)$; the residual electron density: 0.234/−0.252 e Å^{-3}.
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