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$\mathrm{AlMe_2(BHT)NH_3}$: An Unusually Stable Organoaluminum–Ammonia Complex and Its Extended Coordination Sphere Solvate

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The elimination–condensation reaction sequence (eq 1) that occurs between an aluminum alkyl and a primary or secondary amine has been widely explored as a route to aluminum nitrogen ring and cluster compounds.[1] Similar condensation reactions have been recently exploited with ammonia as the nitrogen source for the low-temperature preparation of aluminum nitride (eq 2).[2,3]

$$\mathrm{AlR_3 + HNR'_2 \rightarrow [R_2AlNR'_2]_{\mathit{n}} + RH} \tag{1}$$

$$\mathrm{AlR_3 + NH_3 \xrightarrow[>400\ ^\circ C]{\Delta} AlN + 3RH} \tag{2}$$

Reaction of aluminum alkyls with ammonia results in the initial formation of the simple Lewis acid–base adducts (eq 3), which are ordinarily unstable with respect to condensation.[3-5] Furthermore, no organoaluminum–ammonia adducts have been structurally characterized.

$$\mathrm{AlR_3 + NH_3 \rightarrow R_3AlNH_3} \tag{3}$$

We have previously reported[6] that no condensation reactions are observed between primary and secondary amines and organoaluminum compounds of BHT (2,6-di-*tert*-butyl-4-methylphenoxide, BHT-H from the trivial name butylated hydroxytoluene). We have proposed that this lack of reactivity is due not to any steric hindrance but to the reduced nucleophilicity of the aluminum alkyls, as a consequence of π-donation from the aryloxide to aluminum.[6] We report herein the synthesis and structure of the thermally robust complex $\mathrm{AlMe_2(BHT)(NH_3)}$ (**1**) as well as its stable complex with excess ammonia.

The addition of excess $\mathrm{NH_3}$ to $\mathrm{AlMe_2(BHT)(OEt_2)}$[7] results in the quantitative formation of the Lewis acid–base complex $\mathrm{AlMe_2(BHT)(NH_3)}$ (**1**) (eq 4).[8] Compound **1** may also be synthesized[2] via the reaction of $\mathrm{[AlMe_2NH_2]_3}$[9] with BHT-H (eq 5). Given that the reaction of both aluminum alkyls, $\mathrm{(AlR_3)_{\mathit{n}}}$,

$$\mathrm{AlMe_2(BHT)(OEt_2) + NH_3\ (excess) \xrightarrow[pentane]{-78\ ^\circ C} \underset{\mathbf{1}}{AlMe_2(BHT)(NH_3)}} \tag{4}$$

$$\mathrm{\tfrac{1}{3}[AlMe_2NH_2]_3 + BHT\text{-}H \xrightarrow[pentane]{25\ ^\circ C} \mathbf{1}} \tag{5}$$

and amides, $\mathrm{[Al(NR_2)_3]_{\mathit{n}}}$, with alcohols has been extensively utilized for the synthesis of alkoxides,[10] it is perhaps contrary to expectations that the aluminum–nitrogen bond is the exclusive site of reactivity in the present case.

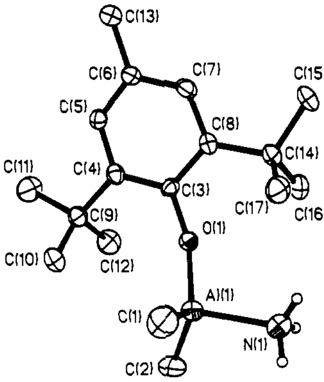

Figure 1. A view of the $\mathrm{AlMe_2(BHT)(NH_3)}$ molecule showing the atom-labeling scheme. Thermal ellipsoids show 40% probability levels. Hydrogen atoms, except those bonded to N(1), have been omitted.

The IR and multinuclear NMR spectra of **1** are consistent[11] with a 1:1 complex, the structure of which has been confirmed by X-ray crystallography.[12] The molecular structure of compound **1** is shown in Figure 1. The Al–N distance [2.015 (5) Å] is within the range observed for amine adducts of $\mathrm{AlMe_3}$ (1.88–2.09 Å),[13] while the aryloxide Al–O distance [1.743 (4) Å] and Al–O–C angle [149.6 (3)°] are in the ranges observed previously and are consistent with a small degree of π-bonding between oxygen and aluminum.[14]

In contrast to previously reported organoaluminum–ammonia complexes, compound **1** shows no propensity for alkane elimination, giving a parent ion in the mass spectrum,[15] and may be sublimed without decomposition at 130 °C (10^{-2} mmHg). Heating under an inert atmosphere beyond its melting point (170 °C)

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(8) To a rapidly stirred pentane (60 mL) solution of $\mathrm{AlMe_2(BHT)(OEt_2)}$ (1.00 g, 2.85 mmol) at −78 °C was added $\mathrm{NH_3}$ (excess) from a lecture cylinder. The reaction mixture was allowed to warm to room temperature, at which point a large amount of precipitate had formed. Removal of solvent in vacuo led to a white powder, which was crystallized from pentane/toluene. Yield: 60–80% isolated; mp = 170 °C.

(9) To a suspension of $\mathrm{[AlMe_2NH_2]_3}$ (0.50 g, 2.28 mmol) in pentane (40 mL) was added at room temperature BHT-H as a solid (1.51 g, 6.86 mmol). The reaction mixture was stirred for 36 h, after which the volatiles were removed under vacuum. Proton NMR of the crude material indicated **1** as the only product.

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(11) NMR (ppm, toluene-d_8): ^{1}H 7.15 (2 H, s, $\mathrm{C_6}\mathit{H}_2$), 2.34 (3 H, s, $\mathrm{C}\mathit{H}_3$), 1.44 [18 H, s, $\mathrm{C(C}\mathit{H}_3)_3$], 1.10 (3 H, br s, $\mathrm{N}\mathit{H}_3$), −0.55 (6 H, s, $\mathrm{AlC}\mathit{H}_3$); ^{13}C 155.22 (O*C*), 138.11 (*o*-*C*), 126.08 (*m*-*C*), 125.35 (*p*-*C*), 34.80 [$\mathit{C}\mathrm{(CH_3)_3}$], 31.12 [$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 21.45 ($\mathit{C}\mathrm{H_3}$), −6.09 ($\mathrm{Al}\mathit{C}\mathrm{H_3}$); ^{14}N 91 ($W_{1/2}$ = 4200 Hz); ^{27}Al 136 ($W_{1/2}$ = 4400 Hz). IR (cm^{-1}, Nujol, KBr): 3360, 3320, 3230, 3150 ν(N–H).

(12) Crystal data for $\mathrm{AlMe_2(BHT)(NH_3)}$ (**1**): monoclinic, $P2_1/n$, a = 9.287 (11) Å, b = 12.096 (5) Å, c = 16.836 (9) Å, β = 96.70 (7)°, V = 1878 (3) Å^3, Z = 4, D(calcd) = 1.297 g cm^{-3}, λ(Mo Kα) = 0.71073 Å (graphite monochromator), T = −80 °C. A Nicolet R3m/V diffractometer, equipped with an LT-1 low-temperature device, was used to collect 5163 reflections (4° $< 2\theta <$ 45°) on a colorless crystal 0.21 × 0.32 × 0.29 mm. Of these, 2456 were independent and 1666 observed [$F_o > 4\sigma F_o$]. A semiempirical absorption correction based on four ψ scans and Lorentz and polarization corrections were applied to the data. All the non-hydrogen atoms were located by direct methods, and they were refined anisotropically. The hydrogen atoms were included as idealized contributions. R = 0.083, R_w = 0.091, GOF = 0.90, final residual = 0.36 e Å^{-3}. All computations used SHELXTL-PLUS: Sheldrick, G., Nicolet XRD, Madison, WI, 1987.

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(15) Mass spectrum, 293 (M$^+$), 276 (M$^+$ − $\mathrm{NH_3}$), 261 [AlMe(BHT)].

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results in decomposition to multiple products including BHT-H.

Addition of excess NH_3 to a toluene-d_8 solution of **1** (3.4×10^{-2} M) at room temperature results in the formation of an apparent 1:2 complex, "$AlMe_2(BHT)(NH_3)_2$", as indicated by ^1H NMR spectroscopy. The chemical shift of the coordinated NH_3 proton is upfield of that observed for **1** [0.52 ppm vs 1.10 ppm (**1**)]. Given that uncoordinated NH_3 has a ^1H shift, in toluene-d_8 solution, of 6.98 ppm, this upfield shift is counter to that expected if a degenerate exchange between free and coordinated NH_3 were present in solution (eq 6). As the NMR sample is cooled to −40 °C, the resonance due to "coordinated" NH_3 broadens ($W_{1/2}$(max) = 216 Hz), increases in intensity, and moves further upfield. Between 10 and −5 °C the ^1H NMR spectrum indicates that an assembly of coordination complexes occurs, finally resulting in a single resonance ($W_{1/2}$(max) = 13 Hz) becoming sharper with a constant chemical shift (0.13 ppm) and an integration consistent with an extended coordination sphere complex $AlMe_2(BHT)(NH_3)_x$ ($13 \le x \le 15$).[16] This complex formation is irreversible, since no dissociation occurs upon warming to room temperature, although the resonance for the "coordinated" NH_3 becomes sharper ($W_{1/2}$ = 12 Hz). In fact the composition is retained for at least 24 h before significant decomposition of the sample occurs, primarily through formation of BHT-H. Removal of the solvent and excess NH_3 under vacuum results in the reisolation of **1**.

$$AlMe_2(BHT)(NH_3) + {}^*NH_3 \rightleftharpoons AlMe_2(BHT)({}^*NH_3) + NH_3 \quad (6)$$

We have previously shown that the ^1H NMR chemical shift of an aluminum–methyl group is a highly sensitive probe to changes in the coordination environment around aluminum.[17] In the present case, however, no change is observed for the Al–CH_3 of **1** in the presence of excess NH_3, at or below room temperature. This suggests that there is no change in the aluminum coordination number. Further conformation of this is demonstrated by the ^{27}Al NMR spectrum, which remains essentially constant, consistent with a four-coordinate aluminum. The ^{14}N NMR spectrum of **1** consists of a single resonance (91 ppm, $W_{1/2}$ = 4200 Hz). In the presence of excess NH_3, at room temperature, this is replaced by a broad resonance (136 ppm, $W_{1/2}$ = 1500 Hz), in addition to the peak for uncoordinated NH_3 (−385 ppm $W_{1/2}$ = 1000 Hz).

Given the above data, we propose the formation of a hydrocarbon-soluble extended coordination sphere complex, $AlMe_2(BHT)(NH_3)_x$, in which aggregation does not take place within the aluminum first coordination sphere.[18] We note that polyammonia solvates have been observed, especially in liquid NH_3,[19] but this is to our knowledge a rare example of such a complex which is formed in hydrocarbon solution and is stable at room temperature, although hydrogen-bonding outer sphere has previously been observed for a number of transition-metal coordination complexes.[20]

Acknowledgment. Financial support of this work is provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and bond distances and angles for **1** (3 pages); listing of observed and calculated structure factors for **1** (9 pages). Ordering information is given on any current masthead page.

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[18] The possibility exists that either the ammonia hydrogens in **1** are sufficiently acidic to protonate ammonia or a dissociation of **1** occurs, both of these resulting in a solvated ionic complex. In both cases, significant changes in the chemical environment of the aluminum and/or the BHT ligand would be observed. However, the unchanging nature of the aluminum–methyl, BHT, and ^{27}Al NMR resonances would tend to discount either possibility.

$$AlMe_2(BHT)(NH_3) + NH_3 \rightarrow \{[NH_4][AlMe_2(BHT)NH_2](NH_3)_x\}$$

$$AlMe_2(BHT)(NH_3) \xrightarrow{NH_3} \{[AlMe_2(NH_3)](BHT)(NH_3)_x\}$$

[19] The insoluble polyammonia complexes $EtAlCl_2{\cdot}(NH_3)_x$ and $Et_2AlCl(NH_3)_x$ (x = 2–5) have been isolated but shown to be ionic, for example $[Et_2Al(NH_3)_2]^+Cl^-$. (a) Cohen, M.; Gilbert, J. K.; Smith, J. D. *J. Chem. Soc.* **1965**, 1092. (b) Gilbert, J. K.; Smith, J. D. *J. Chem. Soc. A* **1968**, 233. The polyammonia complexes $AlI_3{\cdot}(NH_3)_x$ (x = 6, 20) have been reported, but with no spectroscopic characterization. (c) Franklin, E. C. *J. Am. Chem. Soc.* **1915**, *37*, 847.

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Catalytic Tail-to-Tail Dimerization of Methyl Acrylate Using Rh(III) Catalysts

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Adipic acid, an intermediate in nylon-66 production, is currently produced by oxidation of cyclohexane.[2] The catalytic tail-to-tail dimerization of acrylates (eq 1) represents an attractive alternate route to adipic acid from C_3 feedstocks and has received considerable attention.[3-5] The systems examined thus far exhibit one or more drawbacks including short catalyst lifetime (low total turnover numbers), low turnover frequencies, formation of branched (head-to-tail) dimers and oligomers, and a requirement for high temperatures. We report here a catalyst system that dimerizes methyl acrylate at ambient temperatures, even in the absence of solvent, with very high tail-to-tail selectivity, high total turnover numbers, and good turnover frequency.

$$CH_2{=}CHCO_2R \xrightarrow{cat.} \underset{\mathbf{1a}\ (trans);\ \mathbf{1b}\ (cis)}{RO_2CCH{=}CHCH_2CH_2CO_2R} + \underset{\mathbf{2a}\ (trans);\ \mathbf{2b}\ (cis)}{RO_2CCH_2CH{=}CHCH_2CO_2R} \quad (1)$$

Initial attempts to achieve acrylate dimerization were based on the observation that $Cp^*(P(OMe)_3)Rh(C_2H_4)(H)^+$ (**3**) (Cp^* = C_5Me_5) catalyzes ethylene dimerization.[6] Treatment of **3** with methyl acrylate (MA, 34 equiv) in CD_2Cl_2 (25 °C) results in initial formation of the cyclic complex $Cp^*(P(OMe)_3Rh(CH_2CH_2CO_2Me)^+$ (**4**)[7] followed by slow tail-to-tail dimerization of MA (50% conversion after 100 h). Complex **4** was synthesized

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