Inorganica Chimica Acta
LETTER

Reaction of diisobutylaluminum hydride with a macrocyclic tetradentate secondary amine. Synthesis and molecular structure of $[Al(i\text{-}Bu)]_2[C_{10}H_{20}N_4][Al(i\text{-}Bu)_3]_2$: evidence of an unusual disproportionation of $(i\text{-}Bu)_2AlH$

Mark F. Self, William T. Pennington
and **Gregory H. Robinson***
Department of Chemistry, Clemson University, Clemson, SC 29634-1905 (U.S.A.)

(Received April 23, 1990)

Organoaluminum chemistry is currently experiencing considerable activity. While the impact of aluminum compounds on the production of semiconductor material has played a significant role in this resurgence, the last few years have also witnessed increased activity in fundamental aspects of organoaluminum chemistry. Indeed, recent seminal reports have described the synthesis and molecular structure of rare six-coordinate aluminum alkyls [1, 2] and an optically active five-coordinate organoaluminum complex [3]. The increased interest in organoaluminum chemistry notwithstanding, relatively few studies have concerned diisobutylaluminum hydride. As the literature reveals a paucity of reports concerning the association of alkylaluminum hydrides, we decided to explore this area of organoaluminum chemistry. Herein we report the synthesis and molecular structure of $[Al(i\text{-}Bu)]_2[C_{10}H_{20}N_4][Al(i\text{-}Bu)_3]_2$, isolated from reaction of diisobutylaluminum hydride with the macrocyclic tetradentate amine 1,4,8,11-tetraazacyclotetradecane (cyclam), $C_{10}H_{24}N_4$, in chlorobenzene. The isolation of the title compound is significant as it appears to have resulted from a disproportionation of diisobutylaluminum hydride, necessarily proceeding through an interesting mixed alkyl-hydride bridged species. The suggested disproportionation is particularly noteworthy in that the widely accepted trimeric mode of association of diisobutylaluminum hydride does not appear to have played a significant role. The X-ray crystal structure of the title compound is given in Fig. 1.

Experimental

Synthesis

A 50-ml reaction vessel was charged with $C_{10}H_{24}N_4$ (1.25 mmol) and admitted to the dry box where chlorobenzene (25 ml) was added. Diisobutylaluminum hydride (95%), generously donated by Ethyl Corp., (4.98 mmol) was slowly added to the reaction vessel via syringe. The solution immediately began to turn pale yellow. The reaction was quite exothermic and vigorous. The tube was capped, removed from the drybox and heated in a fluidizing sand bath at 150 °C for 12 h. Upon cooling to room temperature the solution was filtered via cannula into a 100-ml Schlenk flask and concentrated *in vacuo*. Allowing the flask to stand overnight at room temperature resulted in the formation of clear, rectangular, air-sensitive crystals; 84% yield (based on $C_{10}H_{24}N_4$). Melting point: 223 °C dec. ^1H NMR (Bruker 300 MHz) ($CDCl_3$): δ −0.146 (d, 16 H, $(CH_3)_2CHCH_2Al$), 0.509 (m, 4 H, $NCH_2CH_2CH_2N$), 0.896 (d, 24 H, $(CH_3)_2CHCH_2Al$), 0.953 (d of d, 8 H, NCH_2CH_2N, $^3J(CH_2–CH_2) = 1.43$, 6.40 Hz), 1.064 (d of d, 8 H, $NCH_2CH_2CH_2N$, $^3J(CH_2–CH_2) = 6.47$, 9.57 Hz), 1.830 (quint, 8 H, $(CH_3)_2CHCH_2Al$). ^{27}Al NMR ($CDCl_3$), $Al(NO_3)_3$ external reference: δ 78.82 (bs).

Crystal data

X-ray data were collected on a Nicolet R3m/V diffractometer using an $\omega/2\theta$ scan technique with Mo Kα radiation ($\lambda = 0.71073$ Å) at 21 °C. A single crystal of $[Al(i\text{-}Bu)]_2[C_{10}H_{20}N_4][Al(i\text{-}Bu)_3]_2$ was mounted in a thin-walled glass capillary under an inert atmosphere of argon. Cell parameters and an

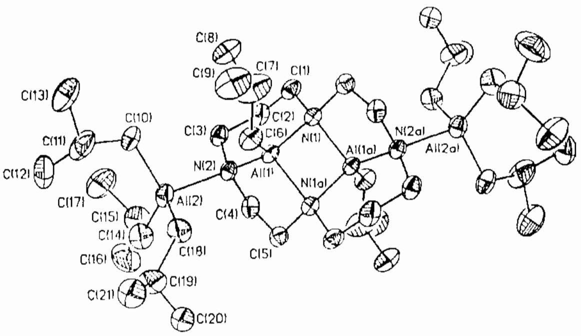

Fig. 1. A view of the molecule showing the atom-labeling scheme. Thermal elipsoids show 25% probabilty levels. Hydrogen atoms have been omitted. Only the major component atoms of the disordered isobutyl group are shown.

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*Author to whom correspondence should be addressed.

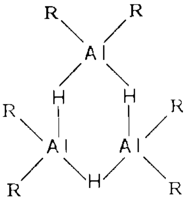
0020-1693/90/$3.50

orientation matrix from the setting angles of 50 carefully centered reflections in the range $24.2 < 2\theta < 32.5°$ corresponded to a triclinic cell belonging to space group $P\bar{1}$ (No. 2) with unit cell dimensions $a = 10.443(2)$, $b = 10.562(2)$, $c = 12.443(3)$ Å, $\alpha = 79.43(2)$, $\beta = 82.16(2)$, $\gamma = 68.06(2)°$, $V = 1247.6(5)$ Å^3, and $D_{calc} = 1.01$ g cm^{-3} for $Z = 1$. Full-matrix least-squares refinement based on 1987 observed reflections with intensities ($I > 3\sigma(I)$) in the range $3.50 < 2\theta < 45.0°$ using SHELXTL [4] converged at $R = 0.083$ ($R_w = 0.106$). Positional and anisotropic thermal parameters were refined for all of the non-hydrogen atoms except carbon atoms representing disordered methyl groups of one isobutyl group*, which were refined isotropically. Hydrogen atoms of the macrocycle were located from difference Fourier maps and were placed in idealized positions. An isotropic group thermal parameter ($U = 0.074(7)$ Å^2) was refined for all of these hydrogen atoms.

Results and discussion

Several points are worthy of note regarding structure and bonding in $[Al(i\text{-}Bu)]_2[C_{10}H_{20}N_4][Al(i\text{-}Bu)_3]_2$. The title compound resides about a crystallographic center of symmetry with a planar Al_2N_2 ring occupying the central cavity of the macrocycle. The Al–N–Al and N–Al–N bond angles are 91.1(2)° and 88.9(2)°, respectively. Moreover, it is important to note that the Al(1)–N(2) 'out of plane' bond distance of 1.912(7) Å is considerably shorter than the Al(1)–N(1) and Al(1)–N(1a) 'in plane' distances of 1.938(5) and 1.955(5) Å, respectively. The most prominent feature of $[Al(i\text{-}Bu)]_2[C_{10}H_{20}N_4][Al(i\text{-}Bu)_3]_2$, however, is the absence of diisobutylaluminum hydride units and the presence of the triisobutylaluminum units.

Definite X-ray crystallographic studies have confirmed that aluminum alkyls [5, 6] and alkylaluminum halides [7, 8] exist as discrete dimers containing μ-dialkyl or μ-dihalide bridges, respectively. Unlike these organoaluminum compounds, cryoscopic molecular weight measurements [9, 10], NMR [11], and spectral data [12] all suggest that diiosobutylaluminum hydride is a trimeric species containing an Al_3H_3 six-membered core (I).



I

A mixture of hydride bridged dimers and trimers, however, has been observed for diisobutylaluminum hydride in the gas phase [13].

As can be seen from the X-ray structure of $[Al(i\text{-}Bu)]_2[C_{10}H_{20}N_4][Al(i\text{-}Bu)_3]_2$, the title compound contains two isobutylaluminum units and two triisobutylaluminum units. The presence of triisobutylaluminum and isobutylaluminum units and the corresponding absence of diisobutylaluminum hydride units, may be accounted for by examining the associative behavior of diisobutylaluminum hydride. Ziegler [14] demonstrated that the presence of a Lewis base can profoundly effect the associative behavior of dialkylaluminum halides by favoring a mixed alkyl-halide bridged dimer (instead of the more frequently observed dihalide bridged dimer). In this way, the strongest available Lewis acid species, $RAlX_2$, could readily be provided upon bridge cleavage of the dimer. This laboratory recently observed similar behavior in the reaction of dialkylaluminum halides with $C_{10}H_{24}N_4$ [15]. Contamination of diisobutylaluminum hydride with triisobutylaluminum does not appear to be an attractive explanation for the high yield isolation of the title compound as triisobutylaluminum has been shown to undergo facile conversion to diisobutylaluminum hydride at 50 °C [16, 17]. It is therefore proposed that the presence of the macrocyclic Lewis base effectively serves to sufficiently shift the equilibrium of diisobutylaluminum hydride so as to favor the stronger Lewis acid species, $(i\text{-}Bu)AlH_2$. Necessarily, this would proceed via a mixed alkyl-hydride bridged dimer as shown in Fig. 2. Cleavage of such a dimer could provide $i\text{-}Bu_3Al$ and $i\text{-}BuAlH_2$. The title compound could thus be prepared by the stronger Lewis acid

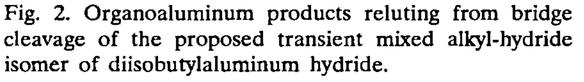


Fig. 2. Organoaluminum products reluting from bridge cleavage of the proposed transient mixed alkyl-hydride isomer of diisobutylaluminum hydride.

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*Most of the atoms of the isobutyl groups exhibit a high degree of thermal motion, indicating possible disorder. However, a model involving partially occupied sites could only be resolved for one of these groups. Atoms C(20) and C(21) represent methyl groups of a major orientation (occupancy = 0.67). The occupancy factors were arrived at by refinement, in the late stages of the least-squares, of a group occupation factor (x) for the major orientation; the occupancy of the minor component was set to a value of $(1 - x)$. In the final cycles of least-squares the group occupation factor was not refined. Atoms C(20), C(20a), C(21), and C(21a) represent partial occupancy atoms of the disordered isobutyl group.

species, i-BuAlH$_2$, preferentially reacting with the N–H bonds of the macrocycle eliminating dihydrogen. The two triisobutylaluminum units could then react with the remaining two nitrogen atoms of the macrocycle (eqn. (1)).

$$2(\text{i-Bu})\text{AlH}_2 + \text{C}_{10}\text{H}_{24}\text{N}_4 \longrightarrow [\text{Al}(\text{i-Bu})]_2[\text{C}_{10}\text{H}_{20}\text{N}_4] + 4\text{H}_2$$

$$[\text{Al}(\text{i-Bu})]_2[\text{C}_{10}\text{H}_{20}\text{N}_4] + 2\text{Al}(\text{i-Bu})_3 \longrightarrow [\text{Al}(\text{i-Bu})]_2[\text{C}_{10}\text{H}_{20}\text{N}_4][\text{Al}(\text{i-Bu})_3]_2 \quad (1)$$

Studies concerning the reaction of organoaluminum species with secondary amines have been under investigation in this laboratory for some time [18, 19]. A high degree of Al–N association and the elimination of alkane is characteristic of these systems. In the same way that this laboratory previously demonstrated that the presence of a Lewis base effects the associative properties of alkylaluminum halides, the same appears to be true of alkylaluminum hydrides. Future contributions from this laboratory will address other aspects of the associative properties of diisobutylaluminum hydride.

Supplementary material

Summary of data collection and refinement, plots of molecules, tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (11 pages); a listing of observed and calculated structure factors (14 pages) are available from the authors upon request.

Acknowledgement

We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554).

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