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STRUCTURAL CHARACTERIZATION OF A THERMALLY STABLE AMINOPHENYLALANE: X-RAY CRYSTAL STRUCTURE OF $\text{Ph}_3\text{Al}\cdot\text{N}(\text{H}_2)t\text{-Bu}$. A RARE Al-N MONOMER

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NOTE

STRUCTURAL CHARACTERIZATION OF A THERMALLY STABLE AMINOPHENYLALANE: X-RAY CRYSTAL STRUCTURE OF $\text{Ph}_3\text{Al}\cdot\text{N}(\text{H}_2)t\text{-Bu}$. A RARE Al-N MONOMER

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The X-ray crystal structure of $\text{Ph}_3\text{Al}\cdot\text{N}(\text{H}_2)t\text{-Bu}$, **I**, has been determined. The title compound was prepared in high yield from reaction of Ph_3Al with $\text{H}_2\text{N}(t\text{-Bu})$ in hexane. Refinement of 813 observed reflections converged at $R=0.086$. The Al-N bond distance is determined to be 1.98 (2)Å while the aluminium atom has a distorted tetrahedral geometry. Compound **I** represents the first structural characterization of a triarylaluminum-primary amine monomer. Moreover, the title compound exhibits unusual thermal stability.

KEY WORDS: Triphenylaluminium, alanes, amines, monomers, X-ray structure.

INTRODUCTION

Interest of this laboratory in the interactions of organoaluminium species with amines initially concerned macrocyclic amines.¹ More recently, workers have employed sterically demanding amines to assess the coordination and π -bonding ramifications about the aluminium metal centre.² It is interesting that the literature reveals a paucity of analogous studies involving sterically demanding organoaluminium groups. Indeed, the lack of aminoalane studies involving triarylaluminium derivatives constitutes a significant void in contemporary investigations. In an effort to assess this area, we endeavored to examine triphenylaluminium-amine, aminophenylalane, systems. Herein, we report the synthesis³ and molecular structure of $\text{Ph}_3\text{Al}\cdot\text{N}(\text{H}_2)t\text{-Bu}$, **I**, isolated from reaction of $\text{Ph}_3\text{Al}\cdot\text{OEt}_2$ ⁴ with $\text{H}_2\text{N}(t\text{-Bu})$ in hexane. This investigation represents the first structural examination of aminophenylalanes. Furthermore, **I**, a rare triarylaluminium-primary amine monomer which exhibits unusual thermal stability, is noteworthy as the first structurally characterized aminophenylalane monomer. The molecular structure of **I** is given in Figure 1.

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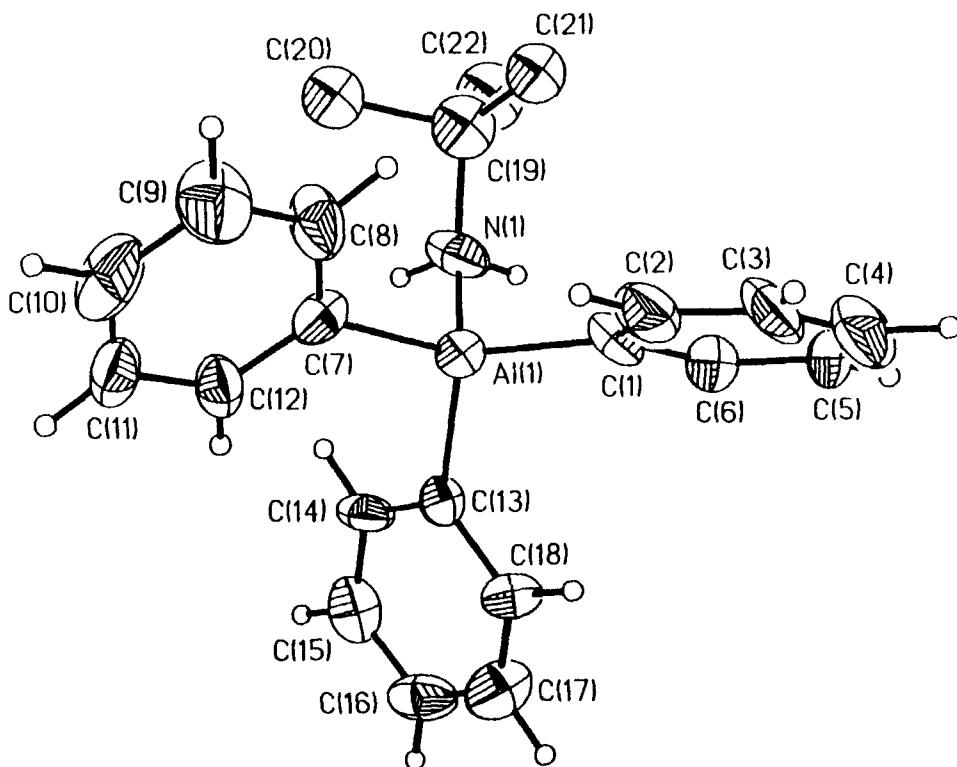
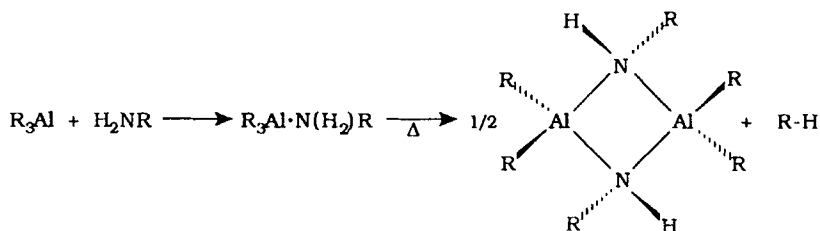


Figure 1 Thermal ellipsoid plot of $\text{Ph}_3\text{Al-N}(\text{H}_2)t\text{-Bu}$ showing the atom labelling scheme. Thermal ellipsoids show 50% probability levels.

X-ray intensity data for **I** were collected at $21 \pm 1^\circ\text{C}$ using an $\omega/2\theta$ scan technique on a Nicolet R3m single crystal diffractometer employing graphite-monochromated radiation ($\lambda = 0.71073 \text{ \AA}$). Calculations, structure solution, and refinement were performed using SHELXTL.⁵ A single crystal of **I** was mounted in a thin-walled glass capillary under argon. The structure was solved by direct methods and refined by full-matrix least-squares techniques. **I** crystallizes in the rhombohedral space group $R\bar{3}$ (No. 148; obverse, hexagonal) with unit cell dimensions $a = 21.060(4)$, $c = 25.451(7) \text{ \AA}$, $D_{\text{calcd}} = 1.013 \text{ g cm}^{-3}$, and $V = 9776(4) \text{ \AA}^3$, for $Z = 18$. The methyl carbon atoms of the *t*-butyl group were disordered over two sets of inequivalent sites.⁶ The full-occupancy non-hydrogen atoms were refined using anisotropic thermal parameters; the partial occupancy methyl carbon atoms were refined with isotropic thermal parameters. Hydrogen atoms were located by standard difference Fourier techniques for the ordered part of the structure, and were included in the structure factor calculation in idealized positions ($d_{\text{C-H}} = 0.96 \text{ \AA}$; $d_{\text{N-H}} = 0.90 \text{ \AA}$). A group thermal parameter ($U_{\text{iso}} = 0.10(1) \text{ \AA}^2$) was refined for all of the hydrogen atoms. The final cycle of refinement, based on 813 observed reflections with intensities $I > 3\sigma(I)$ in the range $3.5^\circ < 2\theta < 43.0^\circ$, converged at $R = 0.086$, $R_w = 0.092$.

Aminoalane chemistry was largely pioneered in the 1960's in a series of seminal studies.⁷ Reaction temperature was found to profoundly influence the nature of the

products isolated from these systems. Specifically, it was noted that 1:1 addition compounds, $R_3Al \cdot N(H_2)R'$ ($R = Me, Et$), would result from reaction of R_3Al with simple primary amines at ambient temperatures. At higher temperatures these $R_3Al \cdot N(H_2)R$ addition compounds reportedly eliminated alkane affording $[R_2Al \cdot N(H)R]_2$ dimers possessing characteristic Al_2N_2 four-membered rings. This preparative process is illustrated in Scheme 1.



Scheme 1

Dimeric aminoalanes of the sort shown in Scheme 1 are readily isolable. Indeed, the preparation of $[R_2Al \cdot N(H)R]_2$ dimers appears to be quite necessary along the reaction coordinate toward higher Al-N oligomers such as trimers,^{2a,c} tetramers,⁸ and hexamers.⁹ Similar behaviour has also been observed in the R_3Al -macrocyclic amine work of this laboratory where Al_2N_2 fragments have been shown to reside about the macrocyclic cavity.¹⁰ Thus, while Al_2N_2 dimers have become ubiquitous in organoaminoalane chemistry, it is noteworthy that the isolation of discrete monomeric $R_3Al \cdot N(H_2)R$ compounds is exceedingly rare. Compound I represents the first structurally characterized aminoalane monomer. Furthermore, I unexpectedly exhibits unusual thermal stability, resisting condensation, and the concomitant alkane elimination—even after 12 hours in refluxing hexane.

The aluminium atom in I adopts a reasonably distorted tetrahedral geometry with C(1)-Al-C(7) and N-Al-C(13) angles of 117.7 (9) and 100.0 (7)°, respectively. The Al-N bond distance is 1.98 (2)Å. Generally, Al-N distances in Al_2N_2 fragments range from 1.95 to 2.00Å while distances on the order of 1.78Å have been observed in compounds in which Al-N π -bonding is suspected.^{2c} A measure of perspective relative to the Al-N distance in the title compound may be acquired from an examination of the recently reported trimethylaluminium-thiomorpholine adduct, $Me_3Al \cdot N(H) \cdot C_4H_8S$.¹¹ The Al-N bond distance in this compound was determined to be 2.030 (4)Å. However, it is interesting to note that the ethyl analogue of $Me_3Al \cdot N(H) \cdot C_4H_8S$ was shown to afford the dimer $[Et_2Al \cdot NC_4H_8S]_2$ upon heating. The mean Al-C distance is determined to be 1.97 (2)Å.

Aside from the solid-state structure of Ph_3Al ,¹² which confirmed a dimeric structure similar to Al_2Me_6 , the literature reveals, to the best of our knowledge, only the triphenyl(η^5 -cyclopentadienyl)dicarbonyliron)aluminate anion, $[Ph_3Al \cdot Fe(CO)_2Cp]^-$ (Al-Fe: 2.510 (2)Å),¹³ as a structurally characterized Ph_3Al -based complex. The monomer I thus represents only the second such compound containing a Ph_3Al unit so characterized. Indeed, it is interesting that phenyl¹⁴ and cyclohexyl¹⁵ ligands have recently been brought to the fore in a series of novel organogallium compounds.

The fact that $Ph_3Al \cdot N(H_2)t-Bu$ does not undergo condensation is significant and worthy of particular note. As evidenced by the preparation of *cis*- $[Neo_2Al \cdot N(H)t-Bu]_2$,¹⁶ isolated from reaction of $H_2N(t-Bu)$ with Neo_3Al ($Neo = -CH_2CMe_3$),

t-butylamine is readily capable of undergoing condensation with R₃Al groups. In terms of the propensity of Ph₃Al to undergo condensation with primary amines (necessarily eliminating benzene), an examination of the early aminoalane literature provides meaningful insight. These investigations^{17,18} reported that adducts of Ph₃Al with methylamine, *n*-propylamine, benzylamine, and 2,6-dimethylaniline all readily eliminated benzene (upon heating) *en route* to [Ph₂Al-N(H)R]₂ dimers. Although no structural or spectroscopic data were provided, the triphenylaluminium-*t*-butylamine adduct was reportedly thermally stable, even in boiling benzene. However, reaction of Ph₃Al with 2-aminobiphenyl in this laboratory affords the condensation dimer [Ph₂Al-N(H)Bp]₂ (Bp = 2-aminobiphenyl).¹⁹

It would thus appear that the thermal stability of **I** has less to do with elimination of benzene or the observed lability of the hydrogen atoms of *t*-butylamine (in this given system) than it does with a synergic combination of steric and electronic factors.

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Supplementary Material

Full listings of crystallographic and refinement details, bond lengths and angles, atomic positions, temperature factors and observed and calculated structure factors are available from the authors upon request.

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- Dry argon was bubbled through a hexane (15 cm³) solution of H₂N(*t*-Bu) (0.15 cm³, 1.3 mmol) for *ca* 5 minutes. The reaction vessel containing the amine-hexane solution was taken into the dry box where Ph₃Al-OEt₂ (0.50 g, 1.5 mmol) was added. Reaction was immediate although not vigorous. A significant measure of material remained in the bottom of the reaction vessel. The system was removed from the dry box and heated in an oil bath (90°C) for 12 hours, resulting in a homogeneous solution. Slow cooling of the system for several hours afforded colourless, X-ray quality, rectangular crystals of Ph₃Al-N(H₂)-*t*-Bu in quantitative yield (based on Ph₃Al-OEt₂); m.p. 129–132°C. ¹H NMR (C₆D₆): δ 0.54 (s, 9H, CCH₃), 2.34 (s, 2H, NH₂), 7.36–7.97 (mult., 15H, C₆H₃). ¹³C NMR (C₆D₆): δ 30.0 [s, *t*-Bu], 33.0 [s, *t*-Bu], 138.5–138.9 [s (v br), Ph]. Anal.: (E + R Microanalytical Laboratories, Corona, NY) Found (Calcd) for C₂₂H₂₆AlN: C, 79.42 (79.73); H, 8.13 (7.91)%.
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- The *t*-Bu groups were found to be disordered over two possible sites related by rotation about the N-C bond. The major component atoms (C(20)-C(22)) were found to have an occupancy of 60% (by refinement of a multiplicity factor *m* in the early stages of refinement; *m* was held fixed in the final least-squares cycles); the minor component atoms (C(20A)-C(22A)) were set to an occupancy of 40%.
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