A Rearrangement of Azobenzene upon Interaction with an Aluminum(I) Monomer LAl {L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$}

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Reaction of LAl (**1**) or [LAl{η^2-$C_2(SiMe_3)_2$}] (**2**) {L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$} with azobenzene affords a five-membered ring compound [LAl{N(H)-*o*-C_6H_4N(Ph)}] (**3**). In the formation of **3** a three-membered intermediate [LAl(η^2-N_2Ph_2)] (**A**) is suggested by a [1 + 2] cycloaddition reaction; **A** is not stable and further rearranges to **3**. DFT calculations on similar compounds with modified L′ {L′ = HC[(CMe)(NPh)]$_2$} show that the complexation energy of the reaction of L′Al with azobenzene to form [L′Al(η^2-N_2Ph_2)] is about –39 kcal mol^{-1}, and the best estimate of the energy difference between [L′Al(η^2-N_2Ph_2)] and [L′Al{N(H)-*o*-C_6H_4N(Ph)}] is –76 kcal mol^{-1}.

Introduction

The reactions of Group 13 metal(I) tetramers (RM)$_4$ (R = organic group, M = Al, Ga, In) with unsaturated molecules [$H_2C{=}C(Me){-}C(Me){=}CH_2$, PhC(O)–C(O)Ph, RN=C(H)–C(H)=NR, R = Me, *i*Pr][1–3] allow the trapping of the corresponding monomer RM, and are also an interesting oxidative addition of compounds with unsaturated bonds to low-valent metal centers.[4] This leads to heterocyclic compounds containing novel heavier main-group elements that have potential applications in pharmaceutical, agrochemical, and materials science.[5] We have recently prepared the aluminum(I) monomer LAl {**1**, L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$}, which has a singlet carbene character.[6] The reductive coupling reaction of LAlI$_2$ with potassium in the presence of alkynes follows a [1 + 2] cycloaddition pathway to yield the aluminacyclopropene [LAl{η^2-C_2(R)(R′)}] (R = R′ = SiMe$_3$, Ph; R = Ph, R′ = SiMe$_3$).[7] A direct coupling reaction between LAl and alkyne ($Me_3SiC{\equiv}CC{\equiv}CSiMe_3$) is subsequently realized to form [LAl{η^2-$C_2(SiMe_3)(C{\equiv}CSiMe_3)$}].[8] In this context, we are interested in the interaction of the Al^{I} center with compounds containing an N=N double bond. The reaction of **1** or [LAl{η^2-$C_2(SiMe_3)_2$}] (**2**) with azobenzene unexpectedly resulted in the formation of the five-membered ring complex [LAl{N(H)-*o*-C_6H_4N(Ph)}] (**3**). Compound **3** contains an N(H)-*o*-C_6H_4N(Ph) moiety which is formed by an isomerization of azobenzene. Obviously, a rearrangement of azobenzene is occurring upon interaction with LAl.

Results and Discussion

Upon stirring of a toluene solution of **1** and azobenzene at elevated temperature (80 °C) for 5 h, the red color changed to orange. Partial removal of the solvent in vacuo and addition of *n*-hexane led to the crystallization of **3**, at 4 °C, as orange crystals in good yield. An alternative route to **3** was investigated by treating **2** with azobenzene in the temperature range from –50 °C to room temperature. The result indicated that **2** could be used as a good precursor for **1**.

Compound **3** is thermally stable, as indicated by its high melting point (260–261 °C) and its most intense molecular ion peak {*m*/*z* (%) = 626 (100) [M$^+$]} found in the EI mass spectrum. Complex **3** has been fully characterized by spectroscopic, analytical, and X-ray single-crystal measurements.

The molecular structure of **3** is shown in Figure 1. The central Al atom is involved as part of two fused five- (AlN$_2$C$_2$) and six-membered (AlN$_2$C$_3$) rings. The corresponding AlN$_4$ core appears in a distorted tetrahedral geometry. The Al–N bond lengths within the AlN$_2$C$_2$ ring are 1.807(2) Å [Al–N(H)] and 1.847(1) Å [Al–N(Ph)], and are similar to those of the AlN$_4$ ring complex [1.815(2), 1.851(2) Å].[9] The Al–N$_{\beta\text{-diketiminato}}$ bond lengths [1.893(1) and 1.862(1) Å] fall in the range [1.874(1)–1.959(3) Å] observed for other four-coordinate (β-diketiminato)aluminum compounds,[7,10] although one bond is a little shorter than these values. The AlN$_2$C$_2$ ring is nearly planar (Δ = 0.0719 Å) and this planar character can be extended to the

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adjacent disubstituted phenyl group (Δ = 0.0816 Å). It is interesting to note that, within the AlN_2C_2 ring, the C(31)–C(36) bond [1.429(2) Å] is longer than the remaining ones of the phenyl ring [1.382(2)–1.393(2) Å]. This obviously contributes to the AlN_2C_2 ring formation. The phenyl groups involved in different structural environments [disubstituted C_6H_4, N(Ph), Ar] exhibit diverse resonances for their aromatic protons in the ^1H NMR spectrum of **3**. An unambiguous assignment of the resonances was not possible. The NH proton resonates at δ = 3.06 (s) ppm and in the IR spectrum the absorption at 3220 cm^{-1} is assignable to ν_{NH}.

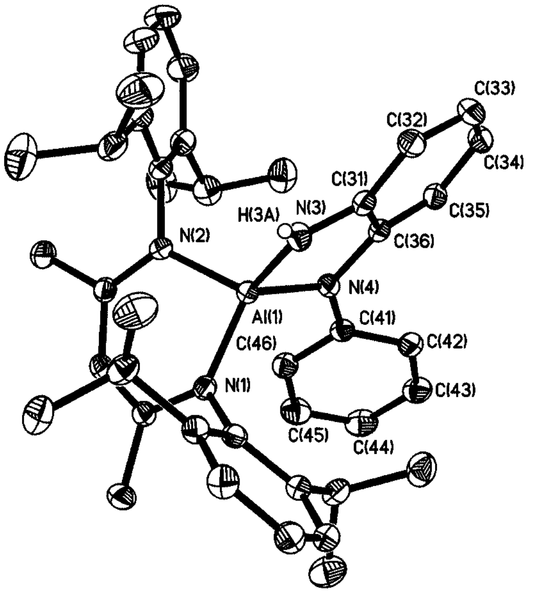
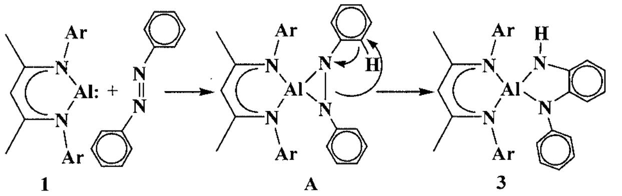


Figure 1. Molecular structure of compound **3**. The hydrogen atoms of the C–H bonds have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.862(1), Al(1)–N(2) 1.893(1), Al(1)–N(3) 1.807(2), Al(1)–N(4) 1.847(1), N(3)–C(31) 1.386(2), C(31)–C(36) 1.429(2), C(36)–N(4) 1.420(2); N(1)–Al(1)–N(2) 97.68(6), N(3)–Al(1)–N(4) 90.39(6), Al(1)–N(3)–C(31) 109.86(10), N(3)–C(31)–C(36) 115.57(14), C(31)–C(36)–N(4) 113.40(10), C(36)–N(4)–Al(4) 108.44(10).

The reaction of **1** with azobenzene may initially proceed through an [LAl(η^2-N_2Ph_2)] (**A**) intermediate, which is formed by a [1 + 2] cycloaddition reaction. **A** is not stable due to the highly strained, metal-containing, three-membered AlN_2 ring, and therefore rearranges by cleaving the N–N bond, with migration of a hydrogen atom from the *ortho* position of one adjacent phenyl ring to yield **3** (Scheme 1). Compounds with similar structures to **A** are known for transition and lanthanide metals, for which different electronic interaction modes (π-bonds and one-electron transfer) have been discussed.[11–13] A three-membered AlN_2 heterocycle bearing an exocyclic N=C double bond at one of the two N atoms has also been reported.[14] Correspondingly, an easy cleavage of the N–N bond and the rearrangement of the adjacent *ortho*-phenyl hydrogen atom of azobenzene have also been observed in the reaction of an FeH-containing active site with azobenzene,[15,16] and in a cyclometalation[17,18] and a substitution[19] reaction.



Ar = 2,6-$iPr_2C_6H_3$

Scheme 1. Proposed formation of **3** from the reaction of **1** and PhNNPh.

A further insight into this proposed mechanism can be gained from theoretical calculations.[20] The computed results show that the complexation energy of the initial reaction of L′Al with azobenzene to form [L′Al(η^2-N_2Ph_2)] {L′ is HC[(CMe)(NPh)]$_2$ for simplicity of calculation} is about –39 kcal mol^{-1}. This indicates a reasonable possibility that **A** is an intermediate in the reaction of **1** with azobenzene. The value of –39 kcal mol^{-1} is even lower than that calculated for the complexation energy of LAl with alkyne (ca. –21 kcal mol^{-1}) using the same method.[10] When [L′Al(η^2-N_2Ph_2)] is further converted into [L′Al{N(H)-*o*-C_6H_4N(Ph)}], a best estimate of the energy difference between these two isomers is –76 kcal mol^{-1}. This suggests an energetically favored stable rearrangement, and is also in agreement with the rearrangement of a three- to a five-membered ring. Furthermore, the D_{298}(Al–η^2-N_2) value is comparable to that of the Al–N bond strength in donor–acceptor $H_3Al{\cdot}NH_3$ species predicted by ab initio studies with a zero-point vibrational energy correction [D_{298}(Al–N) = 26 kcal mol^{-1}].[21] This implies a reasonably strong Al–η^2-N_2 bonding. Therefore, the cleavage of the corresponding N–N bond in the rearrangement of **A** to **3** is highly favored, although no such bond dissociation energy data are available for comparison.[22]

Conclusions

In summary, we have investigated the reaction of aluminum(I) monomer LAl (**1**) with azobenzene. The formation of a five-membered AlN_2C_2 ring containing product **3** is different to the [1 + 2] cycloaddition product formed in the reaction of LAl with alkyne, and indicates an interesting rearrangement of azobenzene via a possible three-membered AlN_2 intermediate (**A**) upon interaction with LAl.

Experimental Section

General: All manipulations were carried out under purified nitrogen using Schlenk techniques. The solvents were dried by standard methods. Chemicals were purchased from Aldrich or Fluka and were used as received. LAl (**1**)[6] and [LAl{η^2-$C_2(SiMe_3)_2$}] (**2**)[7] were prepared as described in the literature. Elemental analyses were performed by the Analytisches Laboratorium des Instituts für Anorganische Chemie der Universität Göttingen. ^1H (300.13 MHz) and ^{13}C (125.76 MHz) NMR spectra were recorded with a Bruker AM 300 spectrometer and IR spectra with a Bio-Rad Digilab FTS-7 spectrometer. EI mass spectra were recorded with a Finnigan

MAT 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes and are not corrected.

Synthesis of [LAl{N(H)-*o*-C_6H_4N(Ph)}] (3). Method A: A toluene solution (30 mL) of LAl (**1**, 0.22 g, 0.5 mmol) and PhNNPh (0.09 g, 0.5 mmol) was stirred and heated slowly to 80 °C for 5 h. The color of the solution changed from red to orange. The volume of the solution was reduced in vacuo (ca. 10 mL) and *n*-hexane was added (10 mL). Upon keeping this solution at 4 °C for one week, orange X-ray quality crystals of **3** were obtained (0.15 g) and collected. The mother liquor was concentrated again (ca. 4 mL) and *n*-hexane added (8 mL). Another crop of orange crystals (0.10 g) was obtained by keeping the solution at –26 °C for 24 h. Total yield: 0.25 g (81%). M.p. 260–261 °C. ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ = 0.90 [d, $^3J_{H,H}$ = 6.8 Hz, 2×3 H, CH(CH_3)$_2$], 0.92 [d, $^3J_{H,H}$ = 6.8 Hz, 2×3 H, CH(CH_3)$_2$], 1.07 [d, $^3J_{H,H}$ = 6.8 Hz, 2×3 H, CH(CH_3)$_2$], 1.23 [d, $^3J_{H,H}$ = 6.8 Hz, 2×3 H, CH(CH_3)$_2$], 1.47 (s, 2×3 H, β-CH_3), 3.05 [sept, $^3J_{H,H}$ = 6.8 Hz, 2×1 H, CH(CH$_3$)$_2$], 3.06 (s, 1 H, NH), 3.14 [sept, $^3J_{H,H}$ = 6.8 Hz, 2×1 H, CH(CH$_3$)$_2$], 5.12 (s, 1 H, γ-CH), 6.31–6.34 (m, 1 H), 6.58–6.66 (m, 2 H), 6.82–6.92 (m, 3 H), 6.94–7.02 (m, 4 H), 7.22–7.30 (m, 4 H), 7.48–7.52 (m, 15 H, Ar-H and Ph-H) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6, 298 K): δ = 23.4, 24.2, 24.5, 24.9, 25.1, 28.3, 29.2 [CH(CH$_3$)$_2$, β-CH$_3$], 99.2 (γ-C), 112.3, 114.0, 115.1, 118.8, 124.0, 125.1, 127.9, 128.2, 129.0, 139.5, 143.1, 143.7, 145.3, 148.8 (Ar-C, Ph-C), 171.5 (CN) ppm. IR (Nujol mull): $\tilde{\nu}$ = 3220 (NH) cm^{-1}. EI-MS: *m*/*z* (%) = 626 (100) [M$^+$]. $C_{41}H_{51}AlN_4$ (626.87): calcd. C 78.56, H 8.20, N 8.14; found C 78.23, H 8.18, N 8.24. **Method B:** A toluene solution (5 mL) of PhNNPh (0.18 g, 1 mmol) was added to a toluene solution (20 mL) of [LAl{η^2-$C_2(SiMe_3)_2$}] (**2**; 0.62 g, 1 mmol) at –50 °C. The mixture was allowed to warm to room temperature whilst being stirred. The solution changed from black to orange. After continuing the stirring for 12 h, the solution was concentrated to dryness in vacuo and washed with *n*-hexane (10 mL) to afford an orange crystalline solid, which was characterized as **3** by m.p. and EI mass measurements.

X-ray Structure Determination and Refinement: The crystallographic data for compound **3** were collected with a Stoe IPDS II array detector system with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-96)[23] and refined against F^2 using SHELXL-97.[24] All non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically; hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atoms. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 1. CCDC-253931 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for compound **3**.

	3
Empirical formula	$C_{41}H_{51}AlN_4$
Formula mass	626.84
T [K]	133(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	11.704(3)
b [Å]	12.612(2)
c [Å]	12.980(4)
α [°]	86.460(2)
β [°]	77.11(2)
γ [°]	86.40(2)
V [Å^3]	1861.7(7)
Z	2
$\rho_c$alcd. [Mg m^{-3}]	1.118
μ [mm^{-1}]	0.087
F(000)	676
θ range [°]	1.61–24.88
Index ranges	$-13 \le h \le 13$
	$-14 \le k \le 14$
	$-15 \le l \le 15$
No. of reflections collected	27600
No. of independent reflections (R_{int})	6396 (0.0536)
No. of data/restraints/parameters	6396/0/424
GoF/F^2	1.015
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0391, 0.0915
R_1,[a] wR_2[b] (all data)	0.0539, 0.0979
Largest diff peak/hole [e Å^{-3}]	0.210/–0.235

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

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