ORGANOMETALLICS

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An Alkynylaminomethylaluminum Species with a Six-Membered Chair Conformation $Al_2C_2N_2$ Framework: A New Path to Geminal N/Al Frustrated Lewis Pairs

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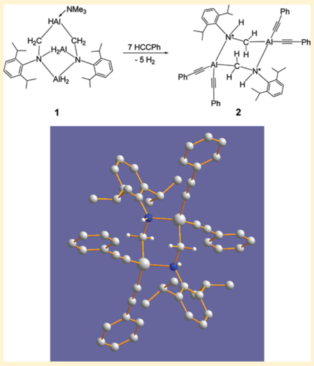
S *Supporting Information*

ABSTRACT: The hydroalumination of the fused pentahydride aminocarbaaluminum species $[(C_6H_3(i\text{Pr}_2\text{-}2,6)N(\mu\text{-}AlH_2)CH_2)_2(\mu\text{-}AlH)NMe_3]$ (**1**) with phenylacetylene resulted in the unexpected dimer $[C_6H_3(i\text{Pr}_2\text{-}2,6)(^*N)HCH_2Al(CCPh)_2]_2$ (**2**) with chiral centers at the nitrogen atoms. Compound **2** was characterized by X-ray structural analysis and contains geminal frustrated Lewis pairs.



Organometallic complexes of the type $[R_mMCH_2XR'_n]_x$ with heteroatoms in positions geminal to the metals (R, R′ = organic groups; M = B, Al, Ga, In, Li, Mg; X = N, P, S, O)[1] have been demonstrated to present carbenoid reactivity[2] and have shown potential as new reagents for synthetic applications.[3] By the metathesis reaction of Me_2NCH_2Li (or $MeSCH_2Li$) with Me_2MCl (M = Al, Ga, In), a series of geminal dimethylaminomethyl and methylthiomethyl compounds of aluminum, gallium, and indium with the formulas $(Me_2NCH_2MMe_2)_2$ and $(MeSCH_2MMe_2)_2$ have been prepared by Mitzel and co-workers, respectively.[1b−d] These compounds, investigated by X-ray diffraction analysis, present exclusively dimeric cyclohexane-like chair conformations in the solid state. Further investigations showed that the dimers seemed to be retained in all phases; however, M−S bond cleavage in the six-membered rings of $(MeSCH_2MMe_2)_2$ occurred to give monomers bound to the Lewis base via the metal atom by the addition of Lewis bases stronger than Me_2S.[1b] Recently, the synergic action of sterically hindered geminal frustrated Lewis pairs (FLPs) such as $(R_2PCH_2AlMe_2)_2$ and $R_2PCH_2CH_2B(C_6F_5)_2$ have attracted great interest in activating CO_2, H_2, and many small organic molecules in the varied organic transformations.[4] For example, the stable Lewis adducts $(R_2PCH_2AlMe_2)_2$ (R = Me, Ph) reacted with CO_2 to afford the corresponding aluminum carboxylates,[4d] while $(C_6F_5)_2PCH_2CH_2B(C_6F_5)_2$ underwent 1,2-addition reactions to an alkene (alkyne) or a 1,3-addition reaction to mesityl azide, respectively, to give the corresponding addition products.[4e] Therefore, an investigation of the synthetic strategies of the geminal group 13 element frustrated Lewis pairs as well as the related structural conformations seemed to be required for advances in this area. Herein we report the synthesis and structural characterization of the dimeric alkynylaminomethylaluminum frustrated Lewis pair $[C_6H_3(i\text{Pr}_2\text{-}2,6)(^*N)HCH_2Al(CCPh)_2]_2$ (**2**) with two chiral centers at nitrogen atoms stabilized with bulky $C_6H_3(i\text{Pr}_2\text{-}2,6)$ groups, which was prepared by the hydroalumination of the fused aminocarbaaluminum hydride $[(C_6H_3(i\text{Pr}_2\text{-}2,6)N(\mu\text{-}AlH_2)CH_2)_2(\mu\text{-}AlH)\cdot NMe_3]$ (**1**)[5] with phenylacetylene.

■ RESULTS AND DISCUSSION

The synthetic chemistry is shown in Scheme 1. The reaction of dry phenylacetylene with **1**[5] gave, after workup, the unexpected dimeric alkynyl aminomethylaluminum compound $[C_6H_3(i\text{Pr}_2\text{-}2,6)(N^*)HCH_2Al(C{\equiv}CPh)_2]_2$ (**2**) (N* = chiral center) as a moisture- and oxygen-sensitive colorless white solid in 65% isolated yield as well as the known aluminum acetylide complex $[(PhC{\equiv}C)_3Al\cdot NMe_3]$ (**3**).[6] Complex **2** is readily soluble in THF, DMSO, warm toluene, and benzene but is sparingly soluble in *n*-hexane.

The solid-state structure determined by X-ray diffraction analysis showed that the structure of **2** adopts a dimeric $Al_2C_2N_2$ ring configuration (Figure 1),[7] which is similar to those found in $(Me_2NCH_2MMe_2)_2$ and $(MeSCH_2MMe_2)_2$ previously reported by Mitzel et al. (M = Al, Ga, In).[1b−d] The dimeric **2** has a crystallographic inversion center at the

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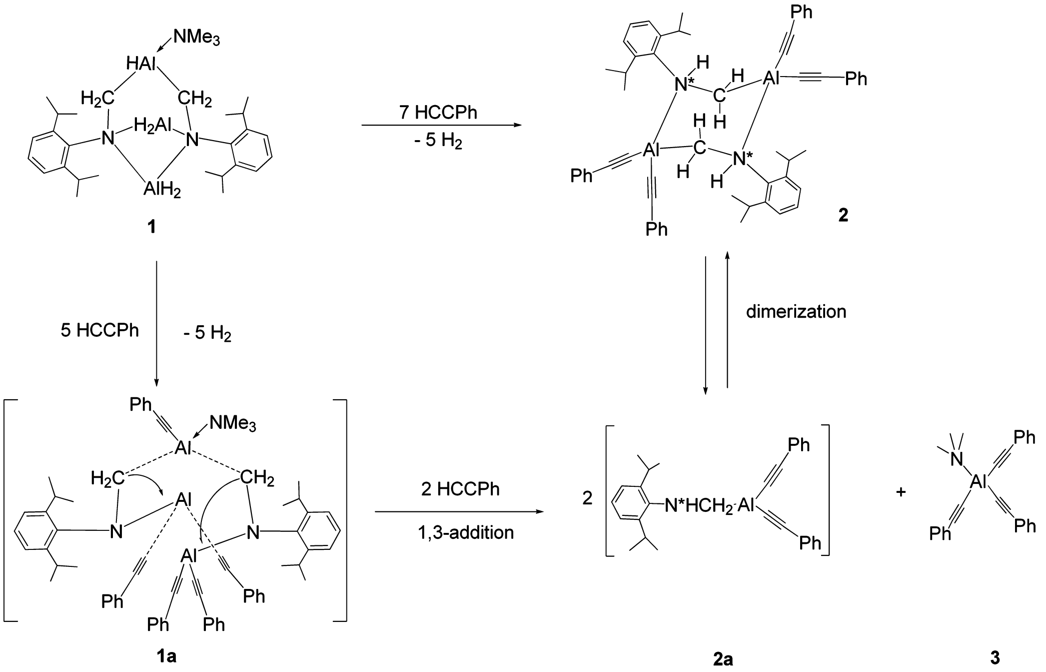
Scheme 1. Preparation of the Dimeric Alkynylaminomethylaluminum Frustrated Lewis Pair $[C_6H_3(i\mathrm{Pr}_2\text{-}2,6)N^*HCH_2Al(CCPh)_2]_2$ (2)[a]



[a] N* = chiral center.

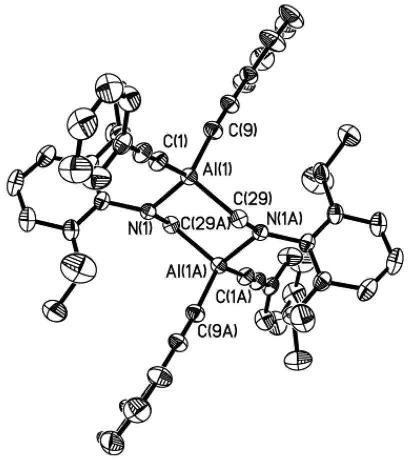


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−C(1) = 1.918(2), Al(1)−C(9) = 1.926(2), Al(1)−N(1) = 1.990(2), Al(1)−C(29) = 1.996(2), N(1)−C(17) = 1.477(3), N(1)−C(29A) = 1.530(2); C(1)−Al(1)−C(9) = 118.21(11), C(1)−Al(1)−N(1) = 107.26(9), C(9)−Al(1)−N(1) = 110.35(9), C(1)−Al(1)−C(29) = 111.82(9), C(9)−Al(1)−C(29) = 105.51(10), N(1)−Al(1)−C(29) = 102.60(8), C(17)−N(1)−C(29A) = 116.16(15), C(17)−N(1)−Al(1) = 123.00(13), C(29A)−N(1)−Al(1) = 109.30(12), C(17)−N(1)−H(1) = 101.4(14), C(29A)−N(1)−H(1) = 104.7(14), Al(1)−N(1)−H(1) = 98.3(15). Symmetry code: (A) −*x*, −*y* + 2, −*z* + 1.

middle of the six-membered $Al_2C_2N_2$ ring formed by Al−N donor−acceptor bonds. The ring adopts a chair conformation in the solid state with the bulky $C_6H_3(i\mathrm{Pr}_2\text{-}2,6)$ groups on the nitrogen atoms being in equatorial positions. The arrangement of the six-membered-ring conformation being significantly different from that found in **1**[5] suggests that the molecular rearrangement occurred during the transformation. In the six-membered $Al_2C_2N_2$ core of **2**, the aluminum atoms are connected exclusively to carbon and nitrogen atoms, and the coordination environments of aluminum are almost identical. The acetylide groups at aluminum atoms display a terminal feature which is comparable to that found in the complex $[(3,5\text{-}t\mathrm{Bu}_2\mathrm{pz})(\mu_4\text{-}Al(C{\equiv}CPh)_2)]_2$.[8] The most interesting finding is that one hydrogen atom is located on each nitrogen atom and the nitrogen centers thereby become chiral in **2**. Thus, the hydrogen atoms at the adjacent two prochiral carbon atoms must be diastereotopic. The Al−C bond distance (1.996(2) Å) within the ring is somewhat shorter than those reported in $(i\mathrm{Pr}_2NCH_2AlMe_2)_2$ (Al−C = 2.007(2) Å)[1d] but is quite comparable to that found in the complex $(Me_2NCH_2AlMe_2)_2$ (Al−C= 1.980(1) Å),[1c] whereas the Al−C bond lengths in the Al−C≡CPh groups are within the range of 1.918(2)−1.926(2) Å, close to those found in $[(3,5\text{-}t\mathrm{Bu}_2\mathrm{pz})(\mu_4\text{-}Al(C{\equiv}CPh)_2)]_2$ (1.913(3)−1.929(3) Å).[8] The Al(1)−N(1) (1.990(2) Å) and N(1)−C(29A) bond lengths (1.530(2) Å) are close to the Al−N and N−C distances associated with $(i\mathrm{Pr}_2NCH_2AlMe_2)_2$ (Al−N = 2.042(1) Å; N−C = 1.521(2) Å), indicative of N−C single-bond character.[1d] The N−C−Al (113.64(13)°) and C−N−Al angles (109.29(13)°) of the core are more acute than those found in $(Me_2NCH_2AlMe_2)_2$ (N−C−Al = 121.0(1)°, C−N−Al = 110.7(1)°)[1c] but are somewhat larger than those found in **1** (C−N−Al (108.68(10)° (av)) and the ideal tetrahedral angle, likely due to a somewhat strain-free environment of the six-membered ring.

The elemental analysis results are in good agreement with the formula of **2**. The ^1H NMR (C_6D_6, 23 °C) spectrum of **2** exhibits four sharp doublets at δ 1.56 (6 H, ^1J = 4.0 Hz), 1.41 (6 H, ^1J = 4.0 Hz), 1.31 (6 H, ^1J = 8.0 Hz), and 1.17 (6 H, ^1J = 8.0 Hz) for the $-CH_3$ units of the isopropyl groups and two septets at δ 4.76 and 4.10 ppm for $CH(CH_3)_2$ groups, probably indicating the molecular asymmetry at the exocyclic groups and a hindered rotation about the exocyclic N−C bond in the solution. Notably, only a single doublet at δ 2.43 (4 H) was observed, which is probably attributable to the two diastereotopic hydrogen atoms at the prochiral carbon ($-CH_2$) of the core. This observation is reminiscent of the signals found in **1** as well as in the previously reported polyhedral aluminum species [{(μ_3-AlH)(μ_3-CH$_2$N*t*Bu)}$_4$] (**4**),[9] where two sets of coupled doublets are observed at δ 2.569 (2 H) and 2.430 (2 H) (^1J = 13.60 Hz, ratio 1:1) for **1** and at δ 1.61 (4 H) and 1.85 (4 H) (^1J = 12.65 Hz, ratio 1:1) for **4**,[9] respectively. The two doublets for **1** and for **4** had been tentatively assigned to the two nonequivalent hydrogen atoms CH^aH^b (a ≠ b) of the carbon due to the constraint of the three rings of **1**[5] and the ring of the polyhedral **4**.[9] However, the single doublet for **2**, as a reviewer suggested, is more likely due to diastereotopic hydrogen atoms at the adjacent prochiral carbon $-CH^aH^b$ (a ≠ b) of the core rather than the constraint of the ring.[5,9] According to the integration, the single doublet for $-CH^aH^b$ observed for **2** is likely due to two sets of overlapped doublets with a small difference of chemical shifts. We attempted to elucidate preliminary information regarding the occurrence of a single doublet for the $-CH_2$ groups from variable-temperature ^{1}H NMR spectra from −60 to +60 °C in toluene-d_6. Coalescence of the diastereotopic hydrogen atoms of **2** was, however, not observed, as the NMR chemical shift and the contour do not change significantly, similar to what is observed for **4**.[9] From the variable-temperature ^{1}H NMR spectra of **2** and **4**, it may be assumed that compounds **2** and **4** dissociate or partially dissociate into **2a** (Scheme 1) and monomeric {(μ_3-AlH)(μ_3-CH$_2$(*N)*t*Bu)} in solution, where the diastereotopic hydrogen atoms at the prochiral carbon are thus nonequivalent due to the chiral nitrogen centers (the electron lone pair on the nitrogen atom can be viewed as a substituted group). The resonance at δ 3.60 (t, 2 H) in the ^{1}H NMR (C_6D_6, 23 °C) spectrum is attributable to the N−*H* groups in **2**, which is further evidenced by a medium-intensity band (at about 3227 cm^{-1}) in the range of N−*H* stretching frequencies in the IR spectrum.

The mechanism for the formation of **2** is currently not clear and seems complicated.[10] After the metathesis reaction of **1** with phenylacetylene, the resulting aluminum species probably undergoes dissociation into the intermediate **1a** having two intramolecular three-membered rings (CNAl) formed by weak Al···C interactions,[1c] followed by hydrogen addition of phenylacetylene to the amino groups of **1a**, as shown in Scheme 1.[11] It seems more likely that in the dissociated species the three-coordinated aluminum and nitrogen are the more reactive sites for the addition reaction with hydrogen of phenylacetylene to aluminum and nitrogen, where the Al−N bond is opened, the terminal proton of the alkyne is added to nitrogen, and the alkynido group is coordinated to aluminum.[11] It is also possible that the reaction alternatively precedes a path similar to those recently reported for Al/P and B/P systems, in which the hydrogen atom of phenylacetylene bridges between nitrogen and aluminum atoms (N···AlNMe$_3$) of **1a** as an intermediate following 1,3-addition to give **2**.[4c,12]

In summary, the hydroalumination of the fused pentahydride aminocarbaaluminum species [(C$_6$H$_3$(*i*Pr$_2$-2,6)N(μ-AlH$_2$)-CH$_2$)$_2$(μ-AlH)NMe$_3$] (**1**) with phenylacetylene resulted in the unexpected dimeric [C$_6$H$_3$(*i*Pr$_2$-2,6)(*N)HCH$_2$Al-(CCPh)$_2$]$_2$ (**2**) with chiral centers at the nitrogen atoms. The hydroalumination in this case is probably via a process of initial multistep intramolecular rearrangement followed by an 1,3-addition of terminal phenylacetylene to nitrogen and aluminum atoms. The successful preparation of **2** seems to open a route to a series of sterically hindered geminal alkynylaminomethylaluminum frustrated Lewis pairs by simply optimizing the substituted groups at isocyanides[5] and acetylenes. In addition, compound **2** is expected to be suitable for further applications such as activating small organic molecules[4] and acting as a cocatalyst in organic transformations.[3c] Work is proceeding along these lines.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under a nitrogen atmosphere under anaerobic conditions using standard Schlenk, vacuum line, and glovebox techniques. The solvents were thoroughly dried, deoxygenated and distilled in a nitrogen atmosphere prior to use. C_6D_6 was degassed and dried with CaH_2 for 24 h before use. Phenylacetylene was dried over molecular sieves for several days before use. The ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX-400 spectrometer. IR measurements were carried out on a Nicolet 360 FT-IR spectrometer from Nujol mulls prepared in a drybox. Melting points were measured in sealed nitrogen-filled capillaries without temperature correction with a Reichert-Jung apparatus Type 302102. Elemental analyses were carried out on an Elemental Vario EL3 (Germany) elemental analyzer.

Preparation of [C$_6$H$_3$(*i*Pr$_2$-2,6)(*N)HCH$_2$Al(CCPh)$_2$]$_2$ (2). To a solution of **1** (0.52 g, 1.0 mmol)[5] in toluene (30 mL) was slowly added phenylacetylene (0.80 mL, 7.2 mmol) via a syringe at room temperature. After gas evolution ceased, the volatile components were removed under reduced pressure (0.01 mbar). The resulting residue was dissolved in warm toluene (50 mL). The solution was concentrated to afford **2** as white crystals at room temperature (0.54 g, 65% based on **1**). Mp: 203−205 °C dec. ^{1}H NMR (C_6D_6, 23 °C): δ 7.62 (d, 6 H, Ph ring), 7.10 (m, 12 H, Ph ring), 6.80 (m, 8 H, Ph ring), 4.76 (septet, 2 H, C*H*), 4.10 (septet, 2 H, C*H*), 3.60 (t, 2 H, N*H*), 2.43 (d, 2 H, C*H*$_2$), 1.56 (d, ^3J = 4.0 Hz, 6 H, C*H*$_3$), 1.41 (d, ^3J = 4.0 Hz, 6 H, C*H*$_3$), 1.31 (d, ^3J = 4.0 Hz, 6 H, C*H*$_3$), 1.17 (d, ^3J = 4.0 Hz, 6 H, C*H*$_3$), ^{13}C{^{1}H} NMR (C_6D_6, 23 °C): δ 132.4, 132.3, 132.2, 128.5, 127.3, 126.8, 125.3, 124.9, 124.8, 124.0 (*C*(Ph)), 44.4 (*C*H$_2$), 29.3, 28.8 (*C*(iPr)), 25.6, 25.3, 24.8, 24.5 (*C*H$_3$); IR (Nujol mull, cm^{-1}): 3227 (m), 2124 (m), 1944 (w), 1873 (w), 1801 (w), 1737 (w), 1665 (w), 1597 (m), 1312 (m), 1261 (m), 1216 (m), 1161 (w), 1085 (s), 1024 (s), 921 (m), 882 (w), 802 (s), 755 (m), 728 (m), 691 (m), 603 (w). Anal. Calcd for $C_{58}H_{60}Al_2N_2$: C, 83.02; H, 7.21; N, 3.34. Found: C, 82.87; H, 7.36; N, 3.23. The mother liquor was further concentrated to give **3** as white crystals. The physical data of **3** are identical with those reported in the literature.[6]

X-ray Crystallography. Suitable single crystals were sealed under N_2 in thin-walled glass capillaries. X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo Kα radiation, φ−ω-scan technique, λ = 0.710 73 Å). The intensity data were integrated by means of the SAINT program.[13] SADABS[14] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the SHELXTL package.[15] The hydrogen atoms attached to nitrogen atoms were calculated on ideal positions. Crystallographic parameters for compound **2** along with details of the data collection and refinement are contained in the Supporting Information.[7]

Crystal Data for 2: $C_{58}H_{60}Al_2N_2$, M_r = 839.04, triclinic, space group $P\bar{1}$, a = 11.055(5) Å, b = 11.533(5) Å, c = 11.605(5) Å, α = 75.055(5) °, β = 87.816(5)°, γ = 62.785(5)°, V = 1265.9(9) Å^3, Z = 1, ρ_{calcd} = 1.101 Mg m^{-3}, crystal size 0.20 × 0.12 × 0.10 mm^3, $F(000)$ = 448, μ(Mo Kα) = 0.095 mm^{-1}, GOF = 0.920, 4856 independent reflections (R_{int} = 0.0296). The final R indices were R1 = 0.0639 ($I > 2\sigma(I)$) and wR2 = 0.1690 (all data).

ASSOCIATED CONTENT

Supporting Information

Tables and a CIF file giving X-ray crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) See the Supporting Information (S-2).

(11) It has been evidenced that aluminum hydride and terminal acetylene is prone to undergo a metathesis reaction by the elimination of hydrogen rather than an addition reaction; see ref 6a.

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