

indicating strong porphyrin – porphyrin conjugation. Comparing **13**, **15** and **16** shows that the thiophene unit leads to more conjugation than phenylene, but less than anthracene. It is remarkable that the 9,10-diethynylantracene bridge allows even more electronic communication than the simple butadiene link in **14**. This implies that longer oligomers of type **2/3** should have strong third-order NLO behavior.

Experimental Section

13: A solution of **12**^[9] (54 mg, 50 μ mol) in THF (8 mL) and pyridine (80 μ L) was treated with dimethylaminotrimethyltin (41 μ L, 250 μ mol) at 50 °C for 2 h, then evaporated. To the resulting waxy residue was added THF (8 mL), **8**^[11] (11 mg, 25 μ mol), tris(dibenzylideneacetone)dipalladium(0) (2.7 mg, 3 μ mol), and triphenylphosphane (3.1 mg, 12 μ mol) under argon. The mixture was stirred at 50 °C for 24 h. Purification by chromatography on silica (eluting with 50/2/1 petroleum ether (60–80 °C)/ethyl acetate/pyridine) and recrystallization from CH₂Cl₂/methanol yielded **13** as a brown solid (27 mg, 46 %).

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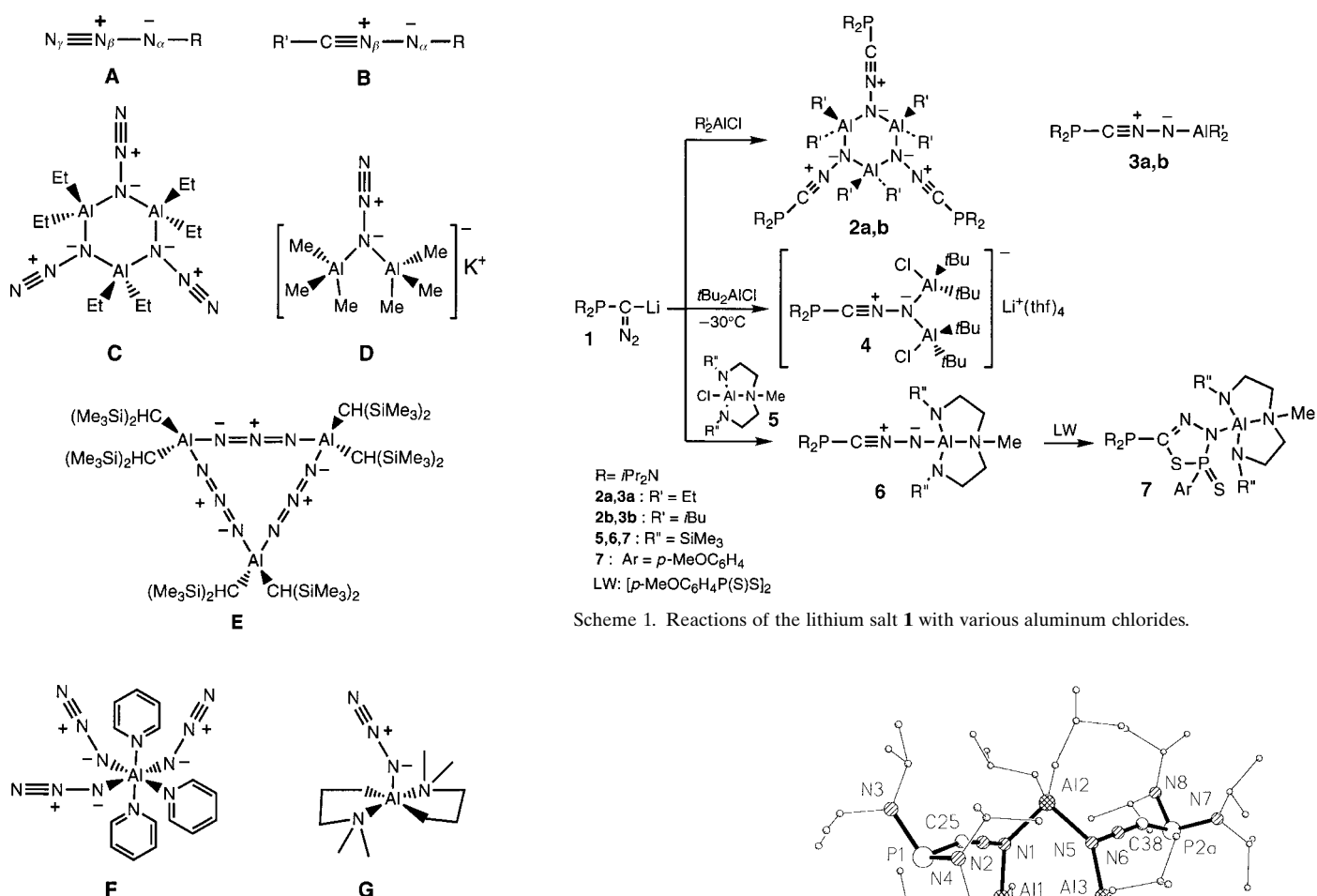
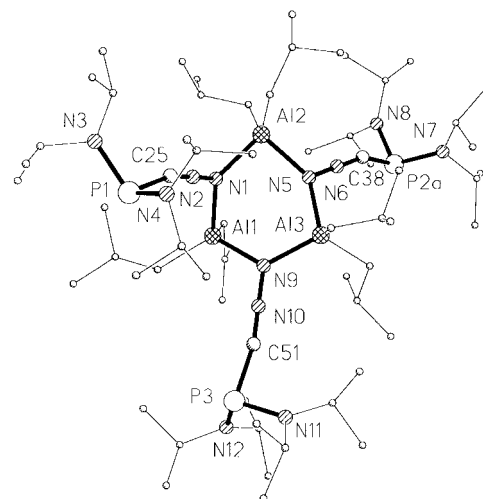
The Azide-Nitrilimine Analogy in Aluminum Chemistry**

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Covalent azides of type **A** are well-known 1,3-dipoles that have found widespread application in organic synthesis,^[1] and that are also of increasing importance in inorganic chemistry.^[2] Aluminum azides possess a rich structural diversity (derivatives **C**–**G**^[3]) and constitute valuable single-source

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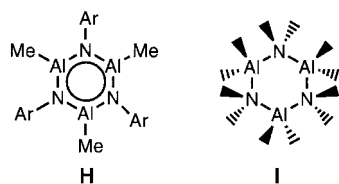
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 Scheme 1. Reactions of the lithium salt **1** with various aluminum chlorides.

 Figure 1. Molecular structure of **2b** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C25 1.804(7), C25–N2 1.144(7), N2–N1 1.287(6), N1–Al1 1.918(5), N1–Al2 1.893(5), P1–C25–N2 163.1(6), C25–N2–N1 177.9(6), N2–N1–Al1 114.5(4), N2–N1–Al2 119.2(4), Al1–N1–Al2 123.6(3), N1–Al1–N9 98.2(2).

precursors to AlN semiconducting phases.^[4] For many years, the development of the chemistry of the isolobal nitrilimines of type **B** was hampered because of their potential instability and the lack of suitable preparative methods. In recent years, efficient routes have been established for preparing stable nitrilimines^[5] and, just as for the azides, the $\text{N}_\alpha\text{--N}_\beta$ bond can be cleaved.^[6] Here we report the synthesis of various aluminum–nitrogen derivatives featuring the nitrilimine skeleton.

The lithium salt of the [bis(diisopropylamino)phosphanyl]diazomethane **1**^[7] was allowed to react in THF, at -78°C , with one equivalent of ClAlEt_2 and $\text{ClAl}(\text{iBu})_2$. After workup at room temperature, compound **2a** and **2b** were isolated in 85 and 90% yield,^[8] respectively (Scheme 1). The IR absorption at 2140 cm^{-1} , the ^{14}N chemical shift of the N_β center (**2a**: -203 ($\nu_{1/2} = 147\text{ Hz}$); **2b**: -203 ($\nu_{1/2} = 118\text{ Hz}$)), and the observation of doublet for the PC carbon atom (**2a**: 62.89 ($J_{\text{PC}} = 74.3\text{ Hz}$); **2b**: 63.21 ($J_{\text{PC}} = 62.5\text{ Hz}$)) in the ^{13}C NMR spectrum were consistent with nitrilimine structures **3a, b**. However, derivatives **2a, b** are inert toward the Lawesson's reagent, one of the most effective 1,3-dipolarophiles.^[9] Single crystals of **2b** suitable for an X-ray analysis^[10] were grown from a solution in pentane at -30°C (Figure 1). Compound **2b** is a trimer of nitrilimine **3b**, and is the first structurally characterized six-membered Al–N heterocycle in which the nitrogen and aluminum atoms possess different coordination numbers^[11] (an X-ray diffraction study performed of poor quality crystals

of **2a** also reveals a six-membered Al–N core). The central six-membered $(\text{AlN})_3$ heterocycle features a twisted conformation, in contrast to the planar geometry postulated from IR and Raman data for the analogous azide derivative **C**.^[3a] The mean endocyclic ring angles at the N_α (119.6°) and Al (109.6°) atoms reflect the sp^2 and sp^3 hybridization, respectively. The Al– N_α bond lengths ($1.89\text{--}1.93\text{ Å}$) are much longer than those observed for the only known aromatic alumazene **H** (1.78 Å),^[11] which contains three-coordinate Al and N centers, but are comparable to those of tris(aminoalanes) **I** (1.95 Å),^[12] which contain four-coordinate Al and N centers. The N–N–C fragments are almost linear ($177.5\text{--}179.7^\circ$), as are the P–C–N angles ($163.1\text{--}169.1^\circ$), reflecting the sp hybridization of the C and N_β atoms. The $\text{N}_\alpha\text{--N}_\beta$ bond



lengths (1.26–1.29 Å) are half way between those for a double and a single N–N bond, and the N_β –C bond lengths (1.14–1.16 Å) are typical for a C–N triple bond. Taken together, these data support a heteropropargylic canonical structure for the C–N–N fragment, in contrast to most of the known nitrilimines, which feature a cumulenic structure.^[13]

The same reaction was carried out with the more sterically hindered $\text{ClAl}(\text{tBu})_2$ in the hope of stabilizing a monomeric nitrilimine. After workup at below -30°C , highly air- and moisture-sensitive crystals of **4** (Scheme 1) suitable for an X-ray crystallographic study were obtained from the pentane solution at -30°C (Scheme 1; Figure 2).^[10] Compound **4** is a

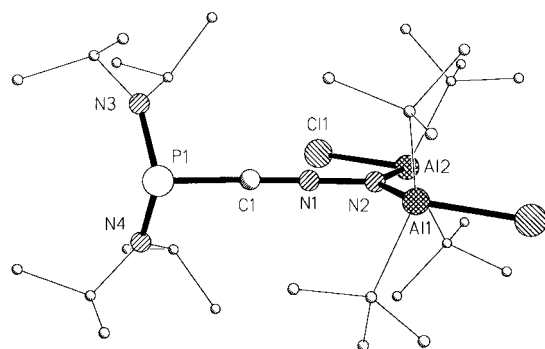


Figure 2. Molecular structure of the anion of **4** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.800(3), C1–N1 1.161(3), N1–N2 1.293(3), N2–Al1 1.954(3), N2–Al2 1.958(3); P1–C1–N1 168.9(3), C1–N1–N2 178.9(3), N1–N2–Al1 107.8(2), N1–N2–Al2 114.5(2), Al1–N2–Al2 137.7(1).

nitrilimine analogue of the azido complex **D**,^[3b] featuring a 1,1- μ - N_α bridging mode. In both cases, the $\text{Al}_2\text{N}_2\text{E}$ ($\text{E} = \text{C}$ or N) fragment is planar (maximum deviation: **4**: 0.006 Å; **C**: 0.01 Å), indicating an sp^2 hybridization for the bridging N_α nitrogen, while the N_β atom is sp -hybridized (**4**: C–N–N: 178.9° ; **C**: N–N–N: 178°). The Al–N distances lie in the same range (**4**: 1.96 and 1.95 Å; **C**: 2.03 Å), the N–N bond length (1.29 Å) lies between the values for a double and a single bond, and the C–N bond length (1.16 Å) is typical for a C–N triple bond. The P–C–N fragment is almost linear (168.9°). Again these data as a whole support a heteropropargylic canonical structure for the C–N–N fragment. Compound **4** is one of the very rare examples of a lithium salt featuring an Al–Cl bond;^[14] at temperatures above -20°C , it decomposes rapidly leading to a complicated mixture of products.

We have recently shown that the tridentate diamidoamine ligand $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{NR}]^{2-}$ allows the preparation of a variety of monomeric aluminum(III) derivatives.^[15] Therefore, the lithium salt of **1** was allowed to react with the aluminum chloride **5**. After workup at room temperature, nitrilimine **6**^[8] was isolated as an orange oil in 91 % yield (Scheme 1). The

^{31}P (48.51) and ^{13}C (61.17 (d, $J_{\text{PC}} = 83.5$ Hz)) NMR signals for the P–C–N–N skeleton are comparable to those observed for compounds **2a**, **b**, but the IR absorption is shifted to lower frequency ($\tilde{\nu} = 2076\text{ cm}^{-1}$; $\Delta\tilde{\nu} = 64\text{ cm}^{-1}/\mathbf{2a, b}$). The simplicity of the NMR spectra for the diamidoamine part is in agreement with a monomeric structure.^[15] Interestingly, in contrast to derivatives **2**, compound **6** reacted with the Lawesson's reagent,^[9] affording the expected [3+2] adduct **6** as an orange oil in 63 % yield.

The only example of four-coordinate “monomeric” aluminum azide features intermolecular hydrogen bonding involving the N_α and N_γ atoms in the solid state.^[3d] In contrast, the azide **8**,^[8] which is analogous to nitrilimine **6**, prepared in 85 % yield by treatment of the aluminum chloride **5** with NaN_3 , is monomeric as proved by a single-crystal X-ray diffraction study^[10] (Figure 3). These results clearly show that nitrilimines of type **B** can indeed exhibit a comparable coordination behavior to that of covalent azides **A**.

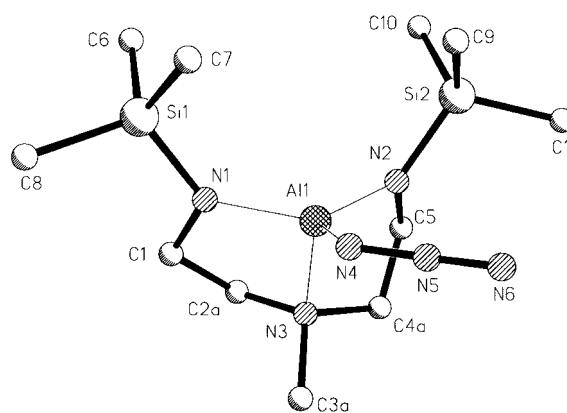


Figure 3. Molecular structure of **8** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1–N1 1.805(4), Al1–N2 1.807(4), Al1–N3 1.970(4), Al1–N4 1.837(5), N4–N5 1.212(6), N5–N6 1.137(6); Al1–N4–N5 129.9(4), N4–N5–N6 176.6(5).

Experimental Section

In a typical experiment a solution of Et_2AlCl (1M, 1.9 mL) in hexane was added dropwise at -78°C to a solution (10 mL) of **1** (prepared by addition at -78°C of a solution of BuLi (1.9 mmol) in hexane to the bis(diisopropylamino)phosphanyldiazomethane (0.52 g, 1.9 mmol)) in THF. The solution was allowed to warm to room temperature, stirred for 1 h, and the solvent was removed under vacuum. The residue was treated with pentane and filtered (10 mL). Compound **2a** was obtained from a pentane solution at -30°C as colorless crystals (0.64 g).

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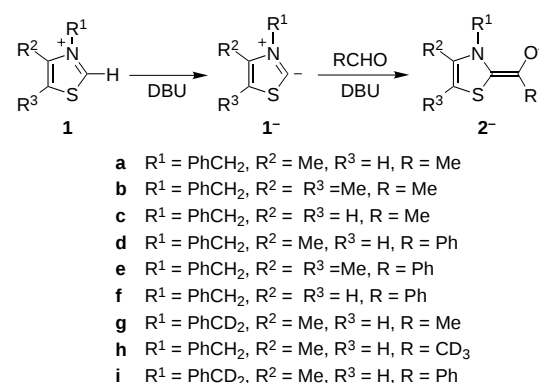
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Direct Observation of Radical Intermediates While Investigating the Redox Behavior of Thiamin Coenzyme Models**

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Thiamin diphosphate (ThDP) is the coenzyme for a number of important biochemical reactions, including the decarboxylation of pyruvic acid to acetaldehyde. The conjugate base of 2-hydroxyethyl-ThDP, which is an acyl carbanion equivalent and called an "active aldehyde", plays a key role in the catalysis of ThDP-dependent enzymes.^[1] The active aldehyde is able to reduce various physiological electron acceptors, for example the lipoamide in the pyruvate dehydrogenase multi-enzyme complex,^[2] the flavin adenine dinucleotide (FAD) in pyruvate oxidase,^[3] and the Fe₄S₄ cluster in pyruvate-ferredoxin oxidoreductase.^[4] Simple thiazolium ions have been studied extensively as models of the thiamin coenzyme, and valuable information about the elementary step of ThDP-dependent enzymatic reactions was provided.^[5–10] The active aldehyde, however, readily undergoes acyloin-type condensation with a second pyruvate or aldehyde molecule in the absence of oxidizing agents.^[1, 11] Such instability of the active aldehydes has precluded the direct determination of the most fundamental properties of the intermediates, such as oxidation potentials.^[12] Therefore, no direct observation of the radical intermediates derived from thiamin coenzyme models has been described so far. Here we report the direct observation of radical intermediates of active aldehydes **2**[•] with low-temperature cyclic voltammetry and EPR spectroscopy. Active aldehydes **2**[•] are derived from 3-benzylthiazolium salts **1** and simple aldehydes such as acetaldehyde and benzaldehyde in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

A cyclic voltammogram (CV) of the active aldehyde **2a**[•]—which is prepared in situ by adding neat DBU (1.0 × 10⁻² M) to a deaerated solution of 3-benzylthiazolium ion **1a** (5.0 ×



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