Lewis Pairs

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An Aluminum–Nitrogen Based Lewis Pair as an Effective Catalyst for the Oligomerization of Cyanamides: Formation of Acyclic C–N Oligomers Instead of Thermodynamically Favored Cyclic Aromatic Trimers**

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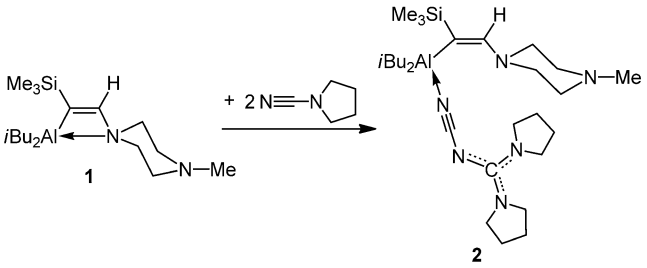
Polyethyne with a chain of conjugated C=C bonds is the base of an extraordinarily important class of substances which upon doping with halogens give electric conducting materials.[1] Its air-sensitivity prevents a wider application, but its outstanding properties initiated intense research activities for the exploration of stable derivatives. The comparatively unexplored polynitriles with alternating carbon and nitrogen atoms in a chain of conjugated C=N double bonds are promising alternatives.[2] But apart from some incompletely characterized polymers[3] only a few oligomers with relatively short chains were reported. The oligomers were obtained by Lewis-acid catalyzed ring-opening reactions or by linear organic synthesis to yield N-acylated monodisperse di- to pentameric formula units.[4] An unprecedented catalytic oligomerization of cyanamides (aminocarbonitriles) in the presence of an Al/N based Lewis pair (**1**) opened the facile access to acyclic amino-substituted oligonitriles.

Compound **1** was obtained by hydroalumination of an ynamine[5] and had Al and N atoms (Scheme 1) in vicinal positions. Al–N interaction gave an AlC_2N heterocycle with a relatively long Al–N distance (207 pm) and an Al-C=C angle of 90.3°. Ring strain facilitated Al–N bond cleavage which resulted in a reactivity similar to that of frustrated Lewis pairs (FLPs).[6] Terminal alkynes gave C–H bond cleavage and carbodiimides novel insertion reactions.[5] B/P or Al/P based FLPs have been applied in several catalytic reactions, such has hydrogenation,[7] dehydrogenation,[8] hydrosilylation,[9] ring-opening polymerization,[9,10] or phase transfer.[11]



Scheme 1. Synthesis of compound **2**.

We treated **1** with two equivalents of pyrrolidine carbonitrile. Compound **2** precipitated and was isolated in 58% yield (Scheme 1). It consists of an adduct of **1** (Figure 1) with a unique dimeric cyanamide[12] which is formed by the insertion of a nitrile moiety into the NC–N single bond of a second molecule. The C≡N nitrogen atom N01 (C≡N

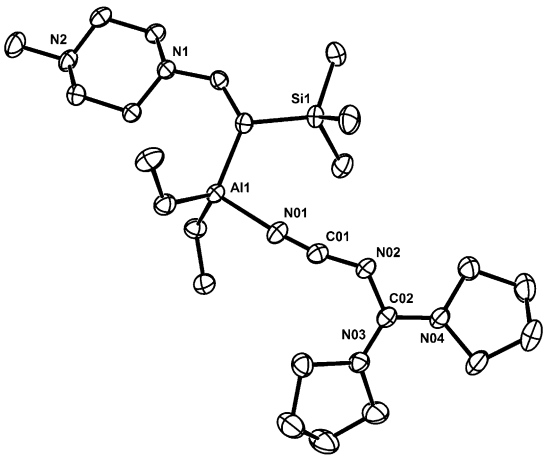


Figure 1. Molecular structure of **2**, thermal ellipsoids set at 40% probability; hydrogen atoms are omitted. Important bond lengths [pm] and angles [°]: Al1-N01 195.0(1), N01-C01 115.9(2), C01-N02 128.4(2), N02-C02 133.9(2), C02-N03 134.4(2), C02-N04 133.2(2), C01-N02-C02 128.6(2).

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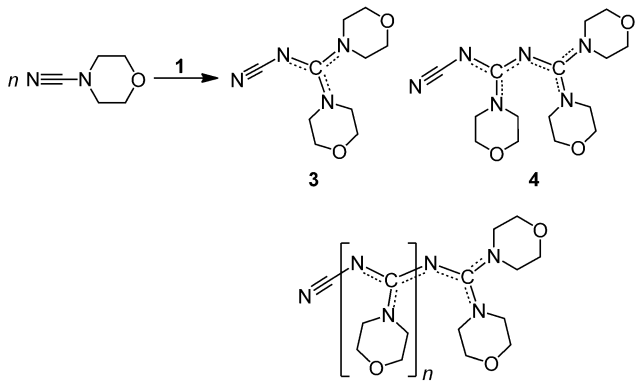
115.9(2) pm) is coordinated to the Al atom with a short Al–N bond (195.0(1) pm).[13] C–N bond lengths of 128.4(2) (C01–N02) and 133.6(av) pm (C02–N03, C02–N04) and the planarity of the nitrogen atoms N03 and N04 verify π-delocalization. The resonance signal of the carbon atom C02 was observed at $\delta = 156.6$ ppm in the ^{13}C NMR spectrum. The *cis*-arrangement of Al and N atoms at the C=C double bond is unchanged ($^3J_{Si\text{-}H} = 11.4$ Hz).[14] An adduct of **1** with a monomeric cyanamide was not detected even with a stoichiometric 1:1 ratio of the reagents.

The release of the dimer from **2**, the formation of higher oligomers, and the application of **1** in catalytic processes were the focus of further investigations. Treatment of **1** with three equivalents of 4-morpholine carbonitrile in toluene or *n*-hexane (Scheme 2) yielded a colorless solid, while compound



Scheme 2. Generation of oligocyanamides.

1 was identified in the supernatant solution by NMR spectroscopy. Solutions of the solid in CD_2Cl_2 showed a complicated ^1H NMR spectrum, but resonance signals of trimethylsilyl groups were not observed. Recrystallization from $CHCl_3$ gave colorless crystals of the dimeric nitrile **3** in 82% yield. The same reaction was observed in homogeneous phase in CH_2Cl_2. Structural parameters of **3** (Figure 2) are closely related to those of **2** (C3≡N4 115.4(3), C3–N2 131.6(3) pm).[12] The C–N distances to the planar morpholine nitrogen atom (133.4(3)–135.8(3) pm) indicate delocalized π bonding. The N4≡C3–N2 group is almost linear (172.6(2)°; 169.7(2)° in **2**), while the C3-N2-C1 group has an angle of 122.4(2)° (128.6(2)° in **2**). The ^{13}C NMR resonances at $\delta =$ 165.1 and 116.2 ppm are characteristic of imine and nitrile carbon atoms.[15] Oligomerization of dialkylated cyanamides has not been observed previously. Self-condensation of the unsubstituted compound N≡C–NH_2 or its tautomeric form yielded dicyandiamide or the trimeric melamine.[16] Lewis-pair **1** is clearly well suited to catalyze the unprecedented oligomerization of alkylated species.

Even a hundredfold excess of cyanamide gave almost complete conversion, with a yellowish solid of the oligomers formed in 93% yield after 6 days at room temperature. MALDI spectra showed a continuous series of oligomers with up to 24 monomeric units (2690.4 au). Very weak mass peaks indicated even higher oligomers. MS-MS spectra of selected masses (1122, 1234, 1346, and 1570 au; 10, 11, 12, or

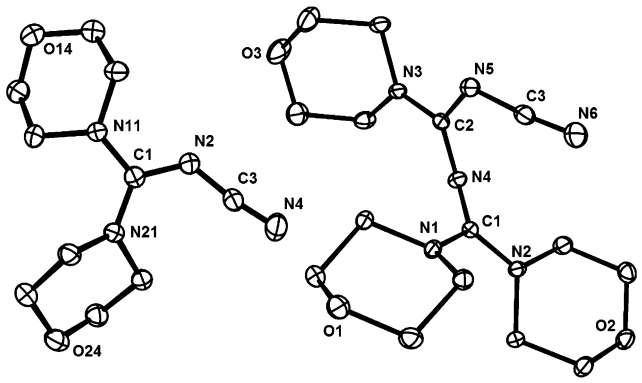


Figure 2. Molecular structures of **3** (left) and **4** (right), thermal ellipsoids set at 40% probability; hydrogen atoms are omitted. Important bond lengths [pm] and angles [°]; **3**: C3-N4 115.4(3), C3-N2 131.6(3), C1-N2 133.4(3), C1-N11 134.6(3), C1-N21 135.8(3); **4**: C3-N6 115.9(1), C3-N5 132.0(1), C2-N5 133.8(1), C2-N4 135.9(1), C1-N4 132.3(1), N4-C2-N5 126.12(9), C2-N5-C3 117.50(9), C1-N4-C2 121.89(8), C1-N4-C2-N5 44.5(1).

14 monomers) showed a similar degradation with fragments consisting of four to six and eight cyanamide units. A mass of 586 au ($C_{26}H_{40}N_{11}O_5$) was detected which may result from a cation with two triazine groups connected by a C–N bond and five morpholine groups attached to the five remaining ring carbon atoms [1-(4,6-dimorpholino-1,3,5-triazin-2-yl)-2,4,6-trimorpholino-1,3,5-triazinium]. In preliminary experiments reversed-phase HPLC (hexyl-phenyl columns) with solutions of the crude products in aqueous ammonia (1%) and acetonitrile allowed the separation of oligomers (detected by UV and MS). A sample obtained with a 20-fold excess of the cyanamide at 50°C (3 days) in toluene gave a composition of 55, 13, 5, and 2% of the dimer to pentamer, respectively. A mixed fraction of higher oligomers was isolated (4%), but could not be separated.

Treatment of the crude product with THF, filtration, and addition of small quantities of *n*-pentane yielded reproducibly a few colorless crystals of an acyclic trimer of morpholine carbonitrile (**4**, Figure 2)[2] with an unsaturated chain of alternating four nitrogen and three carbon atoms. The C≡N bond has the standard length of 115.9(1) pm. The remaining C–N bonds (132.0(1) to 136.4(1) pm) are in accordance with a helical π-system.[4a] The N≡C–N group is almost linear (174.5(1)°), the other angles of the chain vary between 117.50(9) to 126.12(9)°. The formation of the acyclic trimer **4** is unique because trimerization of nitriles usually gives cyclic triazines.[3,17] It is clearly the specific cooperative influence of Lewis pair **1** which favors the chain oligomerization over cyclization. Oligomers were not obtained with AlR_3 derivatives (R = *t*Bu, *i*Bu), which afford simple adducts instead, for example, $tBu_3Al \leftarrow N{\equiv}C\text{-}N(CH_2CH_2)_2O$.

Quantum chemical calculations (M062x/6-311 + G-(d,p))[18] revealed that the formation of the dimer and the acyclic trimer of pyrrolidinyl carbonitrile is exothermic with −25.1 (including zero point energy) and −51.5 kcal mol^{-1} (Figure 3). The formation of the cyclic trimer is strongly favored over the chain form by 36.5 kcal mol^{-1}. This observation underscores the efficacy of our catalyst to form the

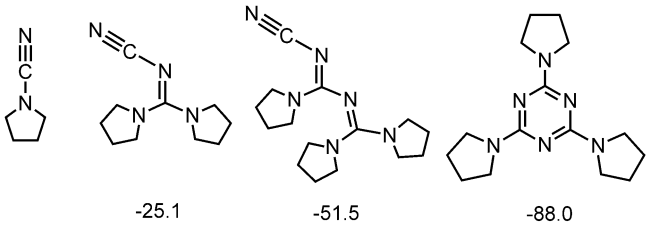


Figure 3. Relative energies [kcal mol^{-1}] of the monomer, dimer, acyclic and cyclic trimer of pyrrolidine carbonitrile (M062x/6-311+G(d,p) including ZPE).

acyclic oligomers. Several 1:1 complexes of cyanamide and FLP **1** have been considered as intermediates. The lowest energy was calculated for **A** (Figure 4) which has the

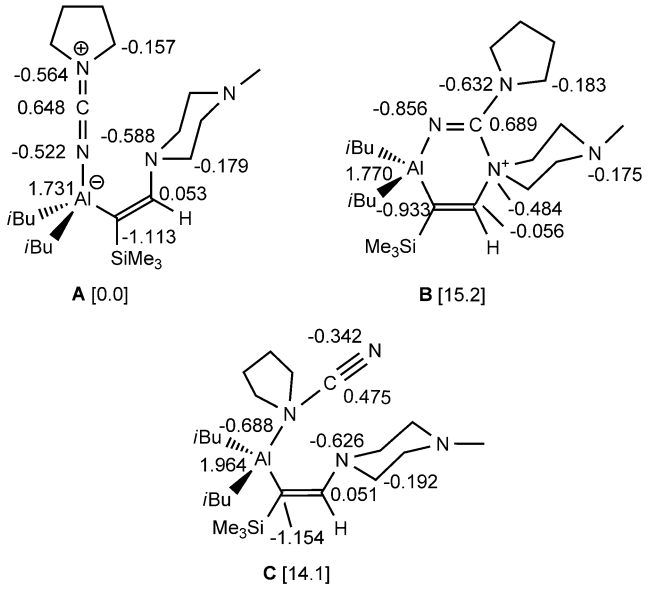
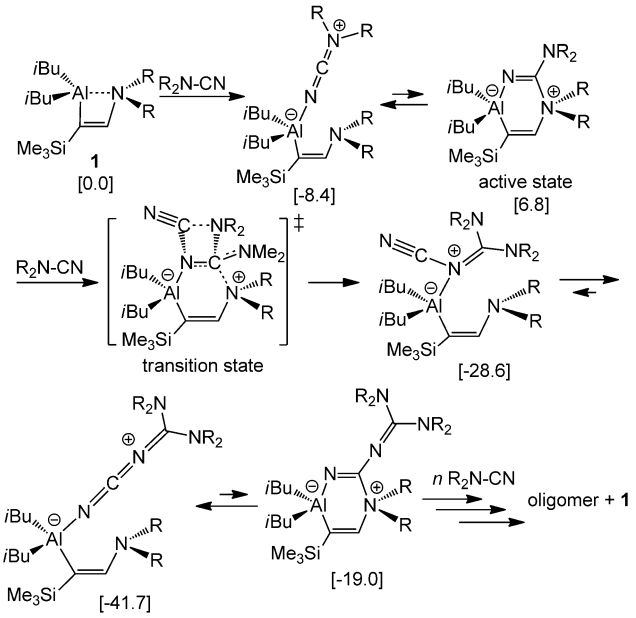


Figure 4. Adducts of pyrrolidine carbonitrile and **1**; NBO charges and relative energies [kcal mol^{-1}] (M062x/6-311+G(d,p)).

cyanamide coordinated by its nitrile nitrogen atom and a linear Al-N=C=N group ($E_{rel} = 0.0$ kcal mol^{-1}, -8.4 kcal mol^{-1} based on the free constituents). The charge distribution according to the NBO analysis of the cyanamide subunit is almost the same as in catalytically inactive AlR_3 complexes (Supporting Information). Ring-chain tautomerism gave the cyclic species **B** which is 15.2 kcal mol^{-1} higher in energy. Species **B** has a highly polarized alternating NBO charge distribution along the cyanamide chain with a high negative charge at the nitrile nitrogen atom attached to aluminum and a positive charge at the nitrile carbon atom. The increased polarity may be the key feature in catalysis. Species **C** results from the coordination of aluminum to the nitrogen atom of the pyrrolidine ring of the cyanamide. It has $E_{rel} = 14.1$ kcal mol^{-1} with respect to **A** and shows a normal charge distribution along the CN subunit. Alternatives, such as dissociated cyanamide with coordination of the cyano/isocyano group and the NR_2 moiety to Al or N recombine upon geometry optimization to **A**, **B**, and **C**. Species **B** and **C** are higher in energy than their components by +6.8 and +5.7 kcal mol^{-1} indicating the facile release of cyanamide or its respective oligomers.

The key step in a preliminary mechanism (Scheme 3) involves a formal [2+2]-cycloaddition of the incoming cyanamide with the activated intermediate **B** to form the chain (**A**) or cyclic (**B**) derivative of the FLP-dimer complex.



Scheme 3. Proposed mechanism for the formation of oligomeric cyanamides with energies relative to the sum of **1** and two molecules of pyrrolidine carbonitrile. Energy values [kcal mol^{-1}].

Addition of a third cyanamide may afford the trimer. Since the binding energy is not high, release of the dimer may recover the Lewis pair **1** as an alternative route. Higher molecular species may be formed by living oligomerization in which the coordination of oligomers to **1** enables subsequent insertion steps.

In conclusion, in an unprecedented reaction Lewis pair **1** catalyzes selectively the oligomerization of cyanamides and the assembly of chains of alternating nitrogen and carbon atoms. The formation of the thermodynamically strongly favored cyclic trimer is suppressed.[17] Separation of the mixtures and isolation of specific oligomers will allow the detailed study of their physical properties, in particular of their redox behavior. Further modification of the Lewis pair, the nitrile substituents, and the reaction conditions may allow the formation of higher oligomers or even polymers with properties such as electric conductivity or charge transfer after doping.

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[12] CCDC 928075 (**2**), CCDC 928076 (**3**) and CCDC 928077 (**4**) contain 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.

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