# **ORGANOMETALLICS**

# Generation of Weakly Bound Al–N Lewis Pairs by Hydroalumination of Ynamines and the Activation of Small Molecules: Phenylethyne and Dicyclohexylcarbodiimide

Thorsten Holtrichter-Rößmann,<sup>‡</sup> Christian Rösener,<sup>†</sup> Johannes Hellmann,<sup>‡</sup> Werner Uhl,<sup>\*,†</sup> Ernst-Ulrich Würthwein,<sup>\*,‡</sup> Roland Fröhlich,<sup>‡</sup> and Birgit Wibbeling<sup>‡</sup>

<sup>†</sup>Institut für Anorganische und Analytische Chemie der Universität Münster, Corrensstraße 30, D-48149 Münster, Germany <sup>‡</sup>Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, D-48149 Münster, Germany

**Supporting Information** 

**ABSTRACT:** Treatment of aminoalkynes (ynamines), Me<sub>3</sub>Si-C=C-NR<sub>2</sub> [NR<sub>2</sub> = N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe, N(CHMe-CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>], with dialkylaluminum hydrides, H-AlR'<sub>2</sub> (R' = CH<sub>2</sub>tBu, *i*Bu, *t*Bu), afforded by hydroalumination the corresponding alkenyl derivatives R'<sub>2</sub>Al-(Me<sub>3</sub>Si)C=C(H)-NR<sub>2</sub> (**3** to **6**) in which the opposite Lewis functionalities adopted a *cis*-arrangement with the aluminum and nitrogen



atoms on the same side of the resulting C==C double bonds. Intramolecular Al–N interactions gave four-membered AlC<sub>2</sub>N heterocycles, but ring strain may cause relatively long Al–N distances of 2.07 to 2.15 Å. These compounds represent a new type of Lewis acid–base pairs, and we observed C–H bond activation by opening of the Al–N bond upon treatment with H-C==C- $C_6H_5$ . Compound 7 was isolated, which had the proton attached to nitrogen and the anionic ethynyl group bonded to aluminum. The formation of 7 is reversible in solution with an increasing dissociation into the starting compounds at elevated temperatures. Two different structural motifs were obtained upon reaction of the Lewis acid–base pairs with dicyclohexylcarbodiimide, which inserted selectively into the bond between the aluminum and the vinylic carbon atom. In the first compound (8) an amidinato ligand was formed, which coordinated the metal atom by both nitrogen atoms to give an AlCN<sub>2</sub> heterocycle. A six-membered heterocycle (9) resulted from the insertion of only one C==N double bond of the carbodiimide into the Al–C(vinyl) bond. 9 had an unchanged interaction of the metal atom with the  $\alpha$ -nitrogen atom of the former ynamine. The latter compound may be considered an intermediate, and rearrangement to yield an amidinato compound analogous to 8 was indeed observed with extended reaction time.

# INTRODUCTION

The activation of small molecules by frustrated Lewis pairs is a topic of considerable current interest.<sup>1</sup> A key discovery in this area was the heterolytic cleavage of the H-H bond of dihydrogen molecules by a boron-phosphorus compound in which the quench of the conflicting Lewis-acidic and -basic properties was prevented by steric shielding and a rigid perfluorinated phenylene backbone.<sup>2</sup> This finding initiated enormous research activities with the activation or fixation of further molecules such as carbon dioxide, alkynes, and ketones.<sup>3</sup> Most experiments have been conducted with compounds that had sterically shielded phosphorus atoms and highly Lewisacidic bis(pentafluorophenyl)boryl groups. In some cases the phosphanyl groups were replaced by other basic moieties such as carbenes,<sup>4</sup> thioethers,<sup>5</sup> etc.<sup>6</sup> Very few frustrated Lewis pairs were reported that had aluminum atoms as the Lewis-acidic centers.<sup>5,7-9</sup> They have the advantage that their Lewis acidity is relatively high and does not require activation by electronwithdrawing groups. They were able to activate carbon dioxide, C-H groups of terminal alkynes, or C $\equiv$ C triple bonds. We now report on the generation of a new class of active Lewis

pairs based on aluminum and nitrogen atoms and their application in some preliminary activation reactions.

# RESULTS AND DISCUSSION

Synthesis of Aluminum–Nitrogen Compounds by Hydroalumination of Ynamines. Hydroalumination<sup>10</sup> of the C $\equiv$ C triple bonds of alkynylphosphines proved to be a very efficient method for the generation of frustrated Lewis pairs based on phosphorus and aluminum atoms.<sup>8,9</sup> The addition of the Al–H bonds to the alkynyl groups is highly regio- and stereoselective and determined by charge distribution in the starting materials and by steric interactions in the products. The alkynyl carbon atoms bonded to phosphorus bear a relatively high negative partial charge and are preferably attacked by the electrophilic aluminum atoms, which results in geminal positions of the donor and acceptor functions. A *cis*arrangement of Al and H atoms in the resulting alkenyl groups characterizes the kinetically favored products. Rearrangement to give the thermodynamically favored *trans*-products with Al

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and H on different sides of the C=C double bonds seems to require intermolecular activation<sup>11</sup> and can be prevented by bulky substituents. The corresponding alkynylnitrogen starting compounds (ynamines) have an amino group attached to the C=C triple bond. They can be prepared by a facile route according to a literature procedure<sup>12</sup> by the reaction of the corresponding lithium amide with trichloroethene, subsequent treatment of the crude product with *n*-butyllithium and addition of chlorotrimethylsilane. Two new trimethylsilylethynylamines (1 and 2, eq 1) have been prepared in the course of

H-NR<sub>2</sub> + *n*-BuLi - *n*-BuH LiNR<sub>2</sub>  

$$\begin{array}{c} + Cl_2C=C(H)Cl \\ - LiCl \\ \hline \\ - DiCl \\$$

our investigations and applied for secondary hydroalumination reactions. These ynamines reveal a relatively low thermal stability and must be stored under argon at low temperatures (1, 2 °C; 2, -15 °C). However, they can easily be handled at room temperature for a short time.

Treatment of the ynamines 1 and 2 with dialkylaluminum hydrides,  $R_2AIH$  (R = CMe<sub>3</sub>, CH<sub>2</sub>CMe<sub>3</sub>, CH<sub>2</sub>CHMe<sub>2</sub>), afforded the corresponding alkenyl compounds 3 to 6 by selective hydroalumination reactions in 65–91% yields (eq 2).



Crystal structure determinations (Figures 1 and 4) showed that the aluminum atoms are bonded to those carbon atoms of the alkenyl moieties that are attached to the trimethylsilyl groups. This position may be preferred for essentially two reasons: (i) The corresponding carbon atom of the ynamine bears a relatively high negative partial charge, which favors the attack of the electrophilic aluminum atom. (ii) The negative partial charge induced in the products by the bonding to the electropositive aluminum atoms could be delocalized by hyperconjugation into the trimethylsilyl groups. Aluminum and hydrogen atoms are in a *trans*-arrangement on opposite sides of the C==C double bonds. This configuration allows an approach of the aluminum and nitrogen atoms and a significant



Figure 1. Molecular structure of 3. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Al(1)-C(7) 1.982(4), C(6)-C(7) 1.320(6), C(6)-N(1) 1.472(5), Al(1)-N(1) 2.144(3), C(6)-C(7)-Al(1) 91.6(3), C(6)-C(7)-Si(1) 121.9(3), Al(1)-C(7)-Si(1) 146.6(2), C(7)-C(6)-N(1) 116.8(4), C(6)-N(1)-Al(1) 81.4(2), C(7)-Al(1)-N(1) 70.3(2).



Figure 2. Molecular structure of 4. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Al(1)–C(11) 1.992(4), C(11)–C(12) 1.320(5), C(12)–N(1) 1.481(5), Al(1)–N(1) 2.103(3), C(12)–C(11)–Al(1) 90.7(3), C(12)–C(11)–Si(1) 119.5(3), Al(1)–C(11)–Si(1) 149.8(2), C(11)–C(12)–N(1) 116.1(3), C(12)–N(1)–Al(1) 82.2(2), C(11)–Al(1)–N(1) 70.9(1).

intramolecular bonding interaction between the Lewis-acidic and -basic centers. The resulting Al–N distances (2.073(2) (6), 2.103(3) (4), 2.144(3) (3), and 2.145(1) Å (5)) are in the upper range observed for adducts between neutral aluminum and nitrogen compounds.<sup>13</sup> They may reflect a relatively weak Al-N interaction between the tetracoordinated central atoms. The strain of the  $AINC_2$  heterocycles, which include a C=C double bond, becomes evident from an almost ideal rectangular arrangement of the C=C-Al groups with an average angle of 91.2°. These angles are much smaller than usually observed for products of hydroalumination or hydrogallation reactions with silylalkynes (110–120°) where no Lewis base is present in  $\beta$ position of the resulting alkenyl groups.<sup>11a,b,14,15</sup> In compounds 3 to 6 this situation leads to relatively narrow contacts of the metal atoms to the  $\beta$ -carbon atoms of the alkenyl moieties (240.8 pm on average). In contrast, the second endocyclic angle at the C=C double bonds (C=C-N) deviates less



Figure 3. Molecular structure of 5. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Al(1)-C(11) 1.982(2), C(11)-C(12) 1.323(2), C(12)-N(1) 1.480(2), Al(1)-N(1) 2.145(1), C(12)-C(11)-Al(1) 92.0(1), C(12)-C(11)-Si(1) 121.5(1), Al(1)-C(11)-Si(1) 146.5(1), C(11)-C(12)-N(1) 116.1(2), C(12)-N(1)-Al(1) 81.56(9), C(11)-Al(1)-N(1) 70.33(6).



Figure 4. Molecular structure of 6. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): AI-C(6) 1.993(2), C(6)-C(7) 1.322(3), C(7)-N(1) 1.483(2), AI-N(1) 2.073(2), C(7)-C(6)-AI 90.3(1), C(7)-C(6)-Si 123.5(2), AI-C(6)-Si 145.9(1), C(6)-C(7)-N(1) 115.2(2), C(7)-N(1)-AI 83.1(1), C(6)-AI-N(1) 71.27(7).

drastically from the ideal value (116.1° on average). The remaining angles of the heterocycles (C–Al–N, 70.7°, and C–N–Al, 82.1°) are very acute, which may be favored by the relatively high ionic character, in particular of the Al–N bond. Al–C (vinyl) (1.987 Å), C–N (1.479 Å), and C==C bond lengths (1.321 Å) of the central heterocycles are unexceptional and do not require a detailed discussion. The compounds 3, 4, and 5, which were obtained by hydroalumination of the ynamine 1, showed a different conformation of their 2,6-dimethylpiperidyl substituents. The bisaxial form (a,a) was observed for the neopentyl and *tert*-butyl derivatives 4 and 5, while the sterically less shielded *n*-butyl compound 3 had the bisequatorial arrangement (e,e) of both methyl groups. The e,e-form was calculated to be thermodynamically slightly favored

for the starting ynamines (see below for quantum-chemical calculations). Intramolecular repulsive interactions between the relatively bulky neopentyl or *tert*-butyl groups bonded to aluminum and the methyl groups of the piperidine substituent in **4** and **5** may help to stabilize the a,a-isomer in these cases.

The NMR data correspond to these molecular structures. The carbon atoms of the C=C double bonds have the expected chemical shifts in narrow ranges at  $\delta = 162$  (Al-C= C) and 148 (N-C=C) in the  ${}^{13}C$  NMR spectra.<sup>11</sup> The resonances of the vinylic hydrogen atoms were observed in the <sup>1</sup>H NMR spectra over a relatively broad range between  $\delta$  = 6.00 for the sterically less shielded compound 3 and  $\delta$  = 7.12 for the di(*tert*-butyl) derivative 5. The  ${}^{3}J_{Si-H}$  coupling constants across the C=C double bonds are usually very indicative of the configuration of the alkenyl groups, with values >20 Hz for the trans- and <12 Hz for the cis-arrangement of hydrogen and silicon atoms.<sup>11,15,16</sup> These coupling constants were difficult to determine for compounds 3 to 6, and only for 5 could a relatively small value of 6.4 Hz be detected with reasonable accuracy. The CH<sub>2</sub> hydrogen atoms of the neopentyl and isobutyl groups in 3, 4, and 6 are diastereotopic and gave two signals in the <sup>1</sup>H NMR spectra. Two resonances were also observed for the methyl carbon and hydrogen atoms of the isobutyl groups. These observations clearly indicate that the molecular structures detected in the solid state are retained in solution. A boron-phosphorus compound comparable to 3 to 6 that has the donor and acceptor atoms bridged by an ethylene group has recently been published, Mes<sub>2</sub>P-CH<sub>2</sub>CH<sub>2</sub>-B- $(C_6F_5)_2$ .<sup>17</sup> NMR spectroscopic characterization and quantum chemical calculations revealed an internal adduct formation via intramolecular B–P interactions, which is supported by  $\pi$ stacking between two aromatic rings. This compound was applied for the activation of small molecules such as dihydrogen. In order to check the propensity of our aluminum-nitrogen compounds to react in a similar way by opening of the Al-N bond and diminution of the ring strain, we treated them in a few preliminary experiments with phenylethyne and a carbodiimide.

Reaction of Compound 5 with the Terminal Alkyne H- $C \equiv C - C_6 H_5$ . Terminal alkynes showed two different kinds of activation upon treatment with frustrated Lewis pairs on the base of boron or aluminum and phosphorus atoms:  $^{3,8,9}$  (i) The C-H bonds were cleaved with the protons attached to the basic phosphorus atoms and the anionic ethynyl groups coordinated to the boron or aluminum atoms. (ii) The  $C \equiv C$ triple bonds were activated, and in some cases five-membered heterocycles with an endocyclic C=C double bond resulted by cycloaddition. Charge distribution determines the structures of the products also in these cases, and the carbon atoms attached to hydrogen are selectively bonded to boron or aluminum. We treated compound 5 with equimolar quantities of phenylethyne in cyclopentane and isolated reproducibly colorless crystals of 7 in quantitative yield (eq 3). Crystal structure determination (Figure 5) verified C-H bond cleavage. The proton of the former ethyne is bonded to the nitrogen atom, and the ethynyl group is attached with its electron-rich terminal carbon atom to the Lewis-acidic aluminum atom. Bond lengths and angles changed considerably upon coordination of the alkyne. The Al-C distance to the carbon atom of the C=C double bond is lengthened to 2.057(2) Å (1.982(2) Å in 5), which is in accordance with the increased coordination number of the metal atom. Interestingly also the Si-C bond length increased significantly from 1.855(2) to 1.895(1) Å in 7, which may be



Figure 5. Molecular structure of 7. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with the exception of N–H are omitted. Important bond lengths (Å) and angles (deg): Al(1)–C(11) 2.057(2), C(11)–C(12) 1.323(2), Al(1)–C(011) 2.008(2), C(011)–C(012) 1.209(2), Al(1)–C(11)–C(12) 127.3(1), Si(1)–C(11)–C(12) 108.7(1), Al(1)–C(11)–Si(1) 123.97(8), C(11)–C(12)–N(1) 126.1(1), C(11)–Al(1)–C(011) 104.97(6), Al(1)–C(011)–C(012) 174.0(1), C(011)–C(012)–C(013) 177.3(2).

influenced by steric crowding in this part of the molecule. The C-N bond is only slightly lengthened from 1.480(2) to 1.499(2) Å, and the C=C double bond is unaffected (1.323(2))Å). The angle Al–C=C is very acute in 5 (92.0(1)°), which verifies a considerable ring strain. In 7 this angle increased to 127.3(1)°. Steric repulsion may also cause the relatively large C=C-N angle of  $126.1(1)^{\circ}$  (116.1(3)° in 5). The angle Al(1)-C(11)-Si(1) of  $123.97(8)^{\circ}$  is larger than the ideal value, while the angle C=C-Si  $(108.7(1)^\circ)$  is smaller than expected. Both observations reflect the particular steric interactions in the molecule. The shortest Al-C bond length (2.008(2) Å) was observed to the sp-hybridized carbon atom of the alkynyl group (C(011)), which is in the normal range of distances between four-coordinate aluminum and sp-hybridized carbon atoms.<sup>18</sup> An interesting structural detail is the short contact between the  $\alpha$ -carbon atom of the alkyne and the proton attached to nitrogen (2.19 Å; N(1)···C(011) 3.000 Å), which indicates intramolecular N–H···C hydrogen bonding.<sup>19</sup> It may reflect an incomplete and reversible cleavage of the C-H bond and may help to understand the behavior of compound 7 in solution.

NMR spectroscopic characterization gave resonances similar to those of the aluminum-nitrogen compound **5** with only small changes of chemical shifts. The ethenyl carbon atoms were observed at  $\delta = 162.8$  and 138.0 in the <sup>13</sup>C NMR spectrum, and the <sup>29</sup>Si NMR resonance appeared at  $\delta = -3.6$  ( $\delta$ = -10.4 for 5). The most significant difference from the uncoordinated compound 5 occurred for the vinylic hydrogen atom, which had a chemical shift of  $\delta$  = 7.12 for 5 compared to  $\delta$  = 5.43 for 7. The resonance of 7 was split to a doublet by coupling with the proton bonded to the nitrogen atom  $({}^{3}J_{H-H} =$ 7.3 Hz). Further important resonances were observed in the  ${}^{1}$ H NMR spectrum at a very low field ( $\delta = 10.43$ , broad) for the N-H group and in the <sup>13</sup>C NMR spectrum at  $\delta = 118.1$  and 116.1 for the carbon atoms of the ethynyl group. Dissolution of single crystals of 7 in benzene afforded a mixture of compounds. Besides the resonances of 7 the characteristic resonances of the starting compounds 5 and phenylethyne were detected. The concentration of the latter substances increased with temperature in accordance with an increasing dissociation upon warming. In addition a strong broadening of the resonances was observed at elevated temperatures, indicating a fast exchange process. The ratio between the free compound 5 and its phenylethyne adduct 7 is about 1:6 at 10 °C, 1:2.5 at room temperature, and 1.4:1 at 35 °C. Further reactions of the aluminum-nitrogen compounds 3 to 6 with phenylethyne led to some changes in the chemical shifts of the starting compounds; however, we were not able to isolate another adduct in a pure and crystalline form.

**Reactions of Compounds 3 and 6 with Di(cyclohexyl)carbodiimide.** Treatment of the aluminum–nitrogen compound 3 with di(cyclohexyl)carbodiimide in *n*-hexane gave the complete consumption of the starting materials after stirring at room temperature for 2 h (eq 4). Compound 8 was formed almost quantitatively and isolated in 74% yield after crystallization from the concentrated reaction mixture. Crystal



structure determination (Figure 6) showed that a carbodiimide molecule was inserted selectively into the Al–C bond to the  $\alpha$ carbon atom of the vinyl group. Both nitrogen atoms of the



Figure 6. Molecular structure of 8. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Al(1)–N(01) 1.931(1), Al(1)–N(02) 1.933(1), N(01)–C(01) 1.341(2), N(02)–C(01) 1.346(2), C(01)–C(11) 1.484(2), C(11)–C(12) 1.359(2), N(01)–Al(1)–N(02) 68.83(5), N(01)–C(01)–N(02) 108.8(1), C(01)–C(11)–C(12) 1127.6(1), Si(1)–C(11)–C(12) 114.4(1), Si(1)–C(11)–C(01) 117.6(1), C(11)–C(12)–N(1) 133.8(1).

resulting amidinate coordinate to the metal atom in a chelating manner to form a four-membered AlN<sub>2</sub>C heterocycle with a delocalized  $\pi$ -electronic system across the N–C–N group (C– N 1.344 Å; Al-N 1.932 Å (average)). C-C bond formation between an enamine and a carbodiimide yielded a unique (Al)N<sub>2</sub>C-C=C(H)-NC<sub>2</sub> moiety with the second NC<sub>2</sub> group being part of the terminal dimethylpiperidine substituent. To the best of our knowledge, such reactions have not been reported previously for other enamines.  $\pi$ -Conjugation between the (Al)N<sub>2</sub>C heterocycle and the C=C double bond can be excluded by the almost perpendicular arrangement of both groups with torsion angles N(01)-C(01)-C(11)-C(12) and N(02)-C(01)-C(11)-C(12) of  $-115.6(2)^{\circ}$  and  $72.7(2)^{\circ}$ and the C–C bond length (C(01)-C(11) 1.484(2) Å), which is in the normal range of single bonds between sp<sup>2</sup>-hybridized carbon atoms.  $\pi$ -Conjugation between the C=C double bond and the nitrogen atom of the piperidine group (N(1)) is verified by an almost ideal planar environment of N(1) with the sum of the angles of 356.6°. Further evidence is provided by the short C(12)-N(1) bond (1.367(2) Å) and the slight lengthening of the C=C bond compared to the starting compound 3 (1.359(2) versus 1.320(6) Å). The torsion angles C(11)-C(12)-N(1)-C(13) and C(11)-C(12)-N(1)-C(12)-NC(17) (16.4(3)° and 175.5(2)°) verify the coplanar arrangement the these atoms. Insertion reactions of carbodiimides into the Al-C bonds of trialkylaluminum compounds and further amidinate complexes of aluminum have been reported previously.<sup>20</sup>

The NMR spectra are complicated. They reflect the particular constitution of compound 8 as derived from crystal structure determination. In the <sup>13</sup>C NMR spectrum the central carbon atom of the chelating NCN ligand ( $\delta = 177.4$ ) and the vinylic carbon atom attached to the nitrogen atom of the terminal piperidine group ( $\delta = 146.1$ ) have resonances in the

expected ranges. In contrast, the resonance of the second carbon atom of the C=C double bond has an unusual chemical shift of  $\delta$  = 90.4, which compared to the starting compound 3 is considerably shifted to higher field by more than 70 ppm. Only one resonance was observed at room temperature for the methyl groups of the piperidine group. This may indicate an accidental coincidence of the resonances or a fast rotation about the C–N bond despite the  $\pi$ delocalization in this part of the molecule as derived from the crystal structure (see above). Two different sets of resonances were observed for the isobutyl groups attached to aluminum, which indicates a hindered rotation about the C-C single bond of the central  $N_2C-C=C$  moiety. An isobutyl group is on the same side as the trimethylsilyl substituent, while the other one is parallel to the piperidine group. Steric interactions may prevent a fast rotation and an equilibration of the resonances. Temperature-dependent <sup>1</sup>H NMR experiments between -50 and +80 °C did not result in any significant alteration of the shape of the spectra. The resonances became expectedly a little broader at the lowest temperature.

The corresponding reaction of dicyclohexylcarbodiimide with compound 6, which has a piperazine instead of a piperidine group, was slower and gave another result in its first step. Stirring of the reaction mixture for 30 min at room temperature, concentration, and cooling yielded colorless crystals of compound 9 (eq 4), which showed completely different NMR spectra compared with 8. Two different sets of resonances of cyclohexyl groups showed that 9 contains two chemically different N-alkyl groups. The resonance of the inner carbon atom of the N=C-N group ( $\delta$  = 156.4) shows a considerable high-field shift compared to 6. The signal of the vinylic carbon atom that is attached to the silicon atom appears in a normal range ( $\delta$  = 138.0;  $\delta$  = 90.4 in 8). The isobutyl groups show two sets of resonances. Crystal structure determination revealed indeed a molecular structure that is completely different compared with that of 8 (Figure 7). A carbodiimide molecule has been inserted into the Al-C bond to the vinylic carbon atom, as before. However, the aluminum atom is coordinated to only one of its nitrogen atoms (N(01)), and the second one (N(02)) occupies a terminal position. The localized bonding situation results in different C-N bond lengths (C(01)-N(01) 1.372(2) and C(01)-N(02) 1.287(2)Å). The coordination sphere of the aluminum atom is completed by the central nitrogen atom of the piperazine group with an Al–N distance of 2.047(1) Å, in accordance with a dative bonding interaction (see above). The remaining distances are unexceptional (C(11)=C(12) 1.329(2), C(01)-C(11) 1.520(2), Al(1)-N(01) 1.871 Å) and do not require a detailed discussion.

Compound 9 represents the first step of the insertion of carbodiimides in the Al–C bond of the aluminum nitrogen compounds 3 to 6. Only a single C==N double bond inserts into the Al–C bond to the vinylic carbon atom, and the interaction of the aluminum atom to the  $\alpha$ -nitrogen atom of the piperazine ring is still intact. Rearrangement by opening of this Al–N bond and the chelating coordination of the metal atom by both nitrogen atoms of an amidinate ligand results in the formation of a compound analogous to 8. Such a secondary reaction was observed when the reaction mixture of 6 and dicyclohexylcarbodiimide was stirred for 2 d instead for only 30 min at room temperature. Single crystals of the product (10) could not be isolated, but the NMR spectroscopic characterization gave clear evidence that a compound analogous to 8 had



Figure 7. Molecular structure of 9. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms and methyl groups of the isobutyl substituents are omitted. Important bond lengths (Å) and angles (deg): Al(1)–N(01) 1.871(1), Al(1)–N(1) 2.047(1), N(01)–C(01) 1.372(2), C(01)–N(02) 1.287(2), C(01)–C(11) 1.520(2), C(11)–C(12) 1.329(2), C(12)–N(1) 1.466(2), N(01)–Al(1)–N(1) 94.17(6), Al(1)–N(01)–C(01) 122.0(1), N(01)–C(01)–C(11) 112.5(1), C(01)–C(11)–C(12) 121.5(1), C(11)–C(12)–N(1) 124.2(1), C(12)–N(1)–Al(1) 99.77(9).

been obtained. Only one set of resonances was observed for the cyclohexyl groups attached to nitrogen. Further, the chemical shifts of the central carbon atom of the NCN chelating ligand ( $\delta = 177.3$ ) and in particular of the carbon atom of the C=C double bond attached to silicon ( $\delta = 92.1$ ) are almost identical to those obtained for 8. Resonances of two chemically different isobutyl groups were detected, which is also in accordance with the results obtained for 8.

Quantum-Chemical Calculations. High-level quantumchemical calculations on the structures and reactivity of these novel compounds were performed by applying the GAUSSIAN 09 package of programs<sup>21</sup> (geometry optimizations) and the program TURBOMOLE<sup>22</sup> (B2PLYP-D single-point calculations<sup>23</sup>). Structure optimizations for three of the Lewis acidbase pairs (3, 5, and 6) were carried out with three different current DFT methods (B97- $D^{24}$ /def2-TZVP, M06- $2x^{25}$ /def2-TZVP, and B3LYP/6-311+G(d,p)) using basis sets<sup>26</sup> as implemented in the GAUSSIAN 09 package. The verification of the experimental Al-N distances was particularly important because they may have considerable influence on the specific reactivity of these Lewis pairs. The relatively best fit with the Xray data was obtained with the B97-D functional (Table 1), which indicates the importance of dispersion interactions for species with relatively weak interactions. Thus, in the following we mainly discuss geometries obtained at the B97-D/def2-TZVP level of theory with energies from single-point calculations at the B2PLYP-D/def2-QZVP//B97-D/def2-

Table 1. Al–N Distances [Å] Obtained by Three Computational Levels and Compared to the X-ray Data

	B97D/def2- TZVP	M06-2x/def2- TZVP	B3LYP/6- 311+G(d,p)	X-ray
3	2.158	2.127	2.240	2.143
5	2.158	2.113	2.263	2.145
6	2.116	2.071	2.148	2.073

TZVP level including zero-point corrections (at the B97-D/ def2-TZVP level).

The mechanism of the hydroalumination reaction of the ynamine 1 with di(*tert*-butyl)aluminum hydride to give the Lewis acid-base pair 5 was studied in detail by quantumchemical calculations (B2PLYP-D/def2-QZVP//M06-2x/def2-TZVP and B2PLYP-D/def2-QZVP//B97-D/def2-TZVP including zero-point correction) (Scheme 1). 1 can adopt two possible conformations with respect to the positions of the two

Scheme 1. Hydroalumination of 1-a,a and 1-e,e with HAltBu<sub>2</sub> and Formation of 5-a,a and 5-e,e (B2PLYP-D/def2-QZVP//B97-D/def2-TZVP+ZPE) [kcal/mol]



methyl groups of the piperidine subunit. As anticipated, the e.e. isomer is lower in energy by about 3.5 kcal/mol compared with the a,a-isomer. Treatment of 1 with dialkylaluminum hydrides yields the *cis*-addition products in the first step<sup>10,11</sup> (Zconfiguration at the C=C bond), which reflects the expected configuration from the generally accepted concerted reaction pathway of hydroalumination reactions.<sup>27</sup> These compounds exhibit  $\pi$ -delocalization of the lone pair at the nitrogen atom, which results in an almost ideally planar surrounding of nitrogen (sum of the angles: 356.6° (a,a) and 359.4° (e,e)), relatively short C-N bonds (1.377 and 1.374 Å, respectively), and slightly lengthened C=C bonds (1.371 and 1.370 Å, respectively). The delocalized  $\pi$ -system causes a coplanar arrangement of the alkenyl group and the average plane of the piperidine heterocycle. The addition of the Al-H bond is calculated to be quite exothermic, by 31-35 kcal/mol, with a slight preference for the a,a-product by ca. 3 kcal/mol, which may be caused by steric repulsion between the trimethylsilyl substituent and an in-plane piperidine methyl group in the e.e. derivative. *cis/trans*-Isomerization across the C=C bond yields the E-isomers (formal trans-addition of Al-H bonds) with Al and N atoms in neighboring positions. This isomerization process was often observed for hydroalumination reactions, and a possible pathway has been discussed in a previous

publication.<sup>11</sup> The *E*-isomers (**5-a**,**a** and **5-e**,**e**) are calculated to be lower in energy by 5-10 kcal/mol. Structural data calculated for the energetically preferred a,a-isomer (5-a,a) are similar to the experimental values obtained by X-ray diffraction of 5. The cis-arrangement of Al and N atoms allows a bonding interaction between the Lewis-acidic and -basic centers, which may contribute significantly to the comparably high stability of the molecules in their E-forms. The Al-N distances were calculated to be 2.159 (5-a,a; X-ray: 2.145(1)) and 2.249 Å (5-e,e), which indicates a weaker Al-N bonding interaction in the less thermodynamically stable e,e-isomer. The sum of the angles at the nitrogen atoms  $(340.7^{\circ} \text{ and } 332.3^{\circ})$  verifies their distorted tetrahedral coordination spheres. C=C(1.338 Å in both cases)and C-N bond lengths (1.468 (5-a,a) and 1.475 Å (5-a,a)) correspond to standard values and are in accordance with the absence of any  $\pi$ -delocalization in the C=C-N group (see the intermediate Z-isomers for comparison).

Phenylethyne reacted with the Lewis acid–base pair (*E*)-**5** by opening of the Al–N bond and C–H bond activation as described above (7, eq 3, Figure 5). Quantum-chemical calculations for the gas phase showed that in a first step a weakly bound primary van der Waals complex ( $E_{\rm rel} = 0.1$  kcal/ mol at B2PLYP-D/def2-QZVP//M06-2x/def2-TZVP without ZPE, no minimum at B97-D/def2-TZVP) is formed with a short contact of the acetylenic hydrogen atom to the amine nitrogen atom (1.839 Å, 1.809 Å at M06-2x) and a long  $\alpha$ alkynyl carbon–aluminum distance (2.450, 2.436 Å at M06-2x) (Scheme 2). Via a negligible barrier of only 0.3 kcal/mol (SCS-MP2/B3LYP; 0.1 kcal/mol at B2PLYPD/M06-2x) the final

# Scheme 2. Reaction of 5-a,a with Phenylethyne to Yield 6-e,e (B2PLYP-D/def2-QZVP//M06-2x/def2-TZVP) [kcal/mol]



product 7 is formed, which is exothermic compared with the starting compounds by -15.9 kcal/mol (-14.2, B2PLYPD/M06-2x). Cleavage of the acetylenic C–H bond results in the formation of a protonated amino group (N–H: 1.049; 1.041 Å M06) and a strong carbon–aluminum bond (2.022, 2.022 Å M06-2x; X-ray: 2.008(2) Å). The intramolecular hydrogen bond between the  $\alpha$ -carbon atom of the ethynyl group and the N–H proton was confirmed by a relatively short C…H distance of 1.929 Å (N…C 2.973 Å). The conformation of the dimethylpiperidine heterocycle in the minimum structures

changes from a,a in the starting compound 5 to e,e in 7, in accordance with the experimental observations. Rearrangement to the generally preferred e,e-form results already in the first step of this reaction with the formation of the transient van der Waals complex.

Two slightly different reaction pathways were found for the reactions of the Lewis acid—base pairs **3** and **6** with dicyclohexylcarbodiimide (B2PLYP-D/def2-QZVP//B97-D/def2-TZVP incl. ZPE) (cf. eq 4). The piperidinyl compound **3** gives a primary complex in which the aluminum atom is coordinated to one of the carbodiimide nitrogen atoms ( $E_{\rm rel} = -10.6$  kcal/mol) (Scheme 3). Interestingly, the piperidyl group (symbolized by NR<sub>2</sub> in the Scheme) is in a *cis*-position with

Scheme 3. Reaction of 3-e,e with Carbodiimide and Synthesis of the Amidinate Complex 8-a,a (B2PLYP-D/def2-QZVP//M06-2x/def2-TZVP) [kcal/mol]



respect to the trimethylsilyl group as a result of a simultaneous *cis/trans*-isomerization about the C==C bond. Carbon–carbon bond formation between the carbodiimide carbon atom and the vinylic carbon atom bearing the trimethylsilyl group starts via a cyclic transition state (-3.1 kcal/mol) and affords another intermediate (-21.9 kcal/mol) with a three-coordinate aluminum atom and a central chain of thee carbon atoms. A second *cis/trans*-isomerization about the C==C bond of the original Lewis pair and coordination of the piperidine nitrogen atom to aluminum result in the formation of a six-membered ring (-40.4 kcal/mol) with the bisaxial arrangement of the

piperidyl methyl groups (the e,e-form is energetically slightly less favored by -36.1 kcal/mol). Cleavage of the Al–N donor– acceptor bond to the piperidinyl nitrogen atom and rotation about the C–N bond afford the amidinate complex **8** as the final product (-58.7 kcal/mol), which has been obtained experimentally and characterized by crystal structure determination (eq 4; Figure 6). The Lewis pair **6**, which has a piperazine instead of a piperidine substituent, gives a slightly different reaction pathway upon treatment with carbodiimide. *cis/trans*-Isomerization does not occur parallel to the initial adduct formation (-14.8 kcal/mol) (Scheme 4). It is only observed for the second step, which comprises C–C bond

Scheme 4. Reaction of 6 with Dicyclohexylcarbodiimide and Formation of 10 via 9 (B2PLYP-D/def2-QZVP//B97D/ def2-TZVP+ZPE) [kcal/mol]



formation and cleavage of the Al–vinyl bond (-20.5 kcal/mol). The cyclic transition state is similar to that of the piperidine case (-0.5 kcal/mol). Rotation about the C–N bond, *cis/trans*isomerization, and coordination of the inner piperazine nitrogen atom to aluminum gives a six-membered heterocycle (-43.4 kcal/mol), which has been isolated and characterized by X-ray diffraction (9, Figure 7). Cleavage of the Al–N donor– acceptor bond and rotation about the C–N bond gives an amidinate complex (10), which, however, in this case is only slightly favored compared with 9 (-43.4 versus -45.6 kcal/mol). This low energetic driving force may cause the relatively long reaction times for the rearrangement of 9 to 10 and may facilitate the isolation and characterization of the intermediate compound 9.

### EXPERIMENTAL SECTION

All procedures were carried out under purified argon using standard Schlenk techniques. *n*-Hexane and cyclopentane were dried over LiAlH<sub>4</sub>; THF was dried over potassium. The starting compounds  $HAl(CH_2CMe_3)_2^{28}$  and  $HAl(CMe_3)_2^{29}$  were obtained according to

literature procedures. Trichloroethene, chlorotrimethylsilane, 2,6dimethylpiperidine, 1-methylpiperazine, and solutions of HAliBu<sub>2</sub> or n-butyllithium in n-hexane were applied as purchased. The chemical shifts of the NMR spectra were assigned on the basis of homo- and heteronuclear 2D NMR experiments (COSY, HSQC, HMBC, ROESY). NMR spectra were recorded at ambient probe temperature using the following Bruker instruments: Avance I (1H, 400.13; 13C, 100.62; <sup>29</sup>Si, 79.49 MHz) or Avance III (<sup>1</sup>H, 400.03; <sup>13</sup>C, 100.59; <sup>29</sup>Si, 79.47 MHz) and referenced internally to residual solvent resonances (chemical shift data in  $\delta$ ). <sup>13</sup>C NMR spectra were all protondecoupled. With the exception of compounds 1 and 2 IR spectra were recorded as a paraffin mull between KBr or CsI plates on a Shimadzu Prestige 21 spectrometer. Electron impact mass spectra were obtained on a Varian mass spectrometer. Elemental analysis was determined by the microanalytic laboratory of the Westfälische Wilhelms Universität Münster.

Synthesis of the Ynamines 1 and 2; General Procedure. A solution of one equivalent of the corresponding secondary amine (2,6-dimethylpiperidine, 1-methylpiperazine) in 30 mL of THF was treated with 1.2 equivalents of *n*-butyllithium in *n*-hexane at -78 °C. The solution was allowed to warm to room temperature and stirred for 1 h. It was slowly added to a solution of one equivalent of trichloroethene in 50 mL of THF at -78 °C. After stirring at room temperature for 1 h and cooling to -78 °C two equivalents of *n*-butyllithium were added. The solution was warmed to room temperature and stirred for a further 2 h. After cooling the mixture to -78 °C one equivalent of chlorotrimethylsilane in 10 mL of THF was added. The mixture was stirred at room temperature for 16 h and concentrated to ca. 20 mL under vacuum at room temperature. All ynamines were subsequently purified by vacuum distillation. They are air and moisture sensitive and must be stored under argon at low temperatures (1, 2 °C; 2, -15 °C).

**Characterization of 2,6-Dimethyl-1-(trimethylsilylethynyl)piperidine (1).** Yield: 32%; colorless liquid. Bp: 48 °C (4.8 × 10<sup>-2</sup> bar). Anal. Calcd for C<sub>12</sub>H<sub>23</sub>NSi (209.2): C, 68.9; H, 11.1; N, 6.7. Found: C, 68.7; H, 11.0; N, 6.6. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta$  2.54 (2 H, m, NCH), 1.44 (1 H, m, CH<sub>2</sub>), 1.25 (6 H, pseudo-d, N-CH-CH<sub>3</sub>), 1.20 (5 H, m, CH<sub>2</sub>), 0.25 (9 H, m, SiMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz):  $\delta$  105.7 (N-C=C), 67.5 (N-C=C), 56.7 (NCH), 32.2 (N-CH-CH<sub>2</sub>), 24.8 (N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 20.8 (N-CH-CH<sub>3</sub>), 1.3 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 60 MHz):  $\delta$  -20.5. IR (neat, cm<sup>-1</sup>): 2965 m, 2932 s, 2860 vw ν(CH); 2143 vs ν(C=C); 1447 m, 1375 m, 1356 m, 1314 m, 1246 s  $\delta$ (CH<sub>3</sub>); 1163 w, 1117 w, 1094 m, 1074 w, 1055 w ν(CC), ν(CN); 854 vs, 837 s ρ(CH<sub>3</sub>Si); 695 m, 635 vs ν(SiC). MS (EI, 20 eV, 25 °C): m/z (%): 209 (S7) [M]<sup>+</sup>, 194 (100) [M - CH<sub>3</sub>]<sup>+</sup>.

Characterization of 1-Methyl-4-(trimethylsilylethynyl)piperazine (2). Yield: 72%; colorless liquid. Bp: 45 °C (8 × 10<sup>-3</sup> bar). Anal. Calcd for C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>Si (196.1): C, 61.2; H, 10.3; N, 14.3. Found: C, 61.3; H, 10.2; N, 14.2. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): δ 2.89 (4 H, m, N-CH<sub>2</sub>-CH<sub>2</sub>-N-CH<sub>3</sub>), 2.00 (4 H, m, N-CH<sub>2</sub>-CH<sub>2</sub>-N-CH<sub>3</sub>), 1.92 (3 H, m, NCH<sub>3</sub>), 0.23 (9 H, m, SiMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz): δ 109.9 (N-C≡C), 62.2 (N-C≡C), 54.1 (N-CH<sub>2</sub>-CH<sub>2</sub>-N-CH<sub>3</sub>), 51.9 (N-CH<sub>2</sub>-CH<sub>2</sub>-N-CH<sub>3</sub>), 46.3 (N-CH<sub>3</sub>), 1.2 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 60 MHz): δ –20.1 ppm. IR (neat, cm<sup>-1</sup>): 2957 m, 2941 m, 2847 m, 2795 ν(CH); 2153 vs, 2139 sh ν(C≡C); 1452 m, 1371 m, 1287 m, 1248 m δ(CH<sub>3</sub>); 1209 w, 1144 m, 1007 w ν(CC), ν(CN); 854 s, 839 s, 758 w ρ(CH<sub>3</sub>Si); 690 w, 657 w, 633 vs ν(SiC). MS (EI, 20 eV, 25 °C): m/z (%) 196 (100) [M]<sup>+</sup>, 181 (47) [M – CH<sub>3</sub>]<sup>+</sup>, 168 (31) [M – C<sub>2</sub>H<sub>4</sub>]<sup>+</sup>, 123 (24) [M – SiMe<sub>3</sub>]<sup>+</sup>.

**Synthesis of Compound 3.** 2, 6-D im et hyl-1-(trimethylsilylethynyl)piperidine (1) (0.50 mL, 0.430 g, 2.06 mmol) was dissolved in 15 mL of *n*-hexane and treated with neat HAl*i*Bu<sub>2</sub> (0.37 mL, 0.292 g, 2.06 mmol) at room temperature. Stirring was continued for 2 h. Colorless crystals of **3** were obtained upon concentration of the reaction mixture and cooling to -28 °C. Yield: 0.593 g (82%). Mp (argon, sealed capillary): 47 °C. Anal. Calcd for C<sub>20</sub>H<sub>42</sub>AlNSi (351.3): C, 68.4; H, 12.1; N, 4.0. Found: C, 67.8; H, 11.8; N, 4.1. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  6.00 (1 H, s, br, N-CH= C), 2.13 (2 H, m, br, N-CH-CH<sub>3</sub>), 2.10 (2 H, septet, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, Al-CH<sub>2</sub>-CH), 1.37 and 1.06 (1 H, m, N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 1.34 (4 H, m, N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 1.21 and 1.19 (each 6 H, s, br, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (6 H, d,  ${}^{3}J_{H-H} = 6.5$  Hz, N-CH-CH<sub>3</sub>), 0.38 and 0.29 (2 H, m, Al-CH<sub>2</sub>-CH), 0.23 (s, 9 H, SiMe<sub>3</sub>).  ${}^{13}$ C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz):  $\delta$  162.3 (br, Al-C=C), 147.6 (br, Al-C=C), 62.2 (br, N-CH-CH<sub>3</sub>), 32.9 (br, N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 29.1 and 28.8 (Al-CH<sub>2</sub>-CHMe<sub>2</sub>), 27.1 (br, Al-CH<sub>2</sub>-CH), 26.9 (br, Al-CH<sub>2</sub>), 24.5 (br, N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 19.8 (N-CH-CH<sub>3</sub>), 0.1 (SiMe<sub>3</sub>).  ${}^{29}$ Si NMR (C<sub>6</sub>D<sub>6</sub>, 79 MHz):  $\delta$  –10.8. IR (CsI plates, paraffin); 1362 s, 1310 s, 1244 vs  $\delta$ (CH<sub>3</sub>); 1204 w, 1177 s, 1123 s, 1045 vs, 980 w  $\nu$ (CC),  $\nu$ (CN); 943 m, 914 w, 891 s, 845 s, 814 m, 789 w, 750 m  $\rho$ (CH<sub>3</sub>Si); 723 m (paraffin); 687 m, 671 m  $\nu_{as}$ (SiC); 615 s  $\nu_{s}$ (SiC); 598 s, 530 vs, 501 vs, 449 vs  $\nu$ (AlC),  $\nu$ (AlN). MS (EI, 20 eV, 30 °C): m/z (%) 296 (5), 295 (19), 294 (83) [M - *i*Bu]<sup>+</sup>, 239 (2), 238 (14) [M - *i*Bu - butene]<sup>+</sup>, 197 (14), 196 (100) [*i*BuAl-N{CH(Me)-CH<sub>2</sub>}<sub>2</sub>CH<sub>2</sub>]<sup>+</sup>, 98 (24) [H-C=C-SiMe<sub>3</sub>]<sup>+</sup>.

Synthesis of Compound 4. 2,6-Dimethyl-1-(trimethylsilylethynyl)piperidine (1) (0.270 mL, 0.233 g, 1.11 mmol) was dissolved in 5 mL of n-hexane and treated with HAl(CH<sub>2</sub>tBu)<sub>2</sub> (0.189 g, 1.11 mmol) in 10 mL of n-hexane at room temperature. Stirring was continued for 1 h. Colorless crystals of 4 were obtained upon concentration of the reaction mixture and cooling to -28 °C. Yield: 0.272 g (65%). Mp (argon, sealed capillary): 55 °C. Anal. Calcd for C<sub>22</sub>H<sub>46</sub>AlNSi (379.3): C, 69.7; H, 12.2; N, 3.7. Found: C, 69.3; H, 12.0; N, 3.7.  $^1\mathrm{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  6.84 (1 H, s, br, N-CH=C), 3.20 (2 H, m, br, N-CH-CH<sub>3</sub>), 1.54 and 1.12 (2 H, m, N-CH-CH2-CH2), 1.31 (18 H, s, CMe3), 0.94 (8 H, m, br, N-CH-CH3 and N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 0.68 and 0.49 (4 H, d,  ${}^{2}J_{H-H}$  = 13.8 Hz, Al-CH<sub>2</sub>), 0.31 (9 H, s, SiMe<sub>3</sub>).  ${}^{13}$ C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz):  $\delta$  164.3 (br, Al-C=C), 147.9 (Al-C=C), 54.5 (br, N-CH-CH<sub>3</sub>), 35.5 (Al-CH<sub>2</sub>-CMe<sub>3</sub>), 32.4 (br, Al-CH<sub>2</sub>), 32.2 (Al-CH<sub>2</sub>-C), 30.6 (N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 16.0 (N-CH-CH<sub>2</sub> and N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 0.6 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 79 MHz):  $\delta$  –9.8. IR (CsI plates, paraffin, cm<sup>-1</sup>): 1585 m, 1537 s ν(C=C); 1460 vs, 1377 s (paraffin); 1320 vw, 1310 vw, 1242 s  $\delta(CH_3)$ ; 1227 s, 1181 vw, 1123 s, 1098 m, 1022 vs, 976 m  $\nu(CC)$ ,  $\nu$ (CN); 885 w, 837 s, 752 m  $\rho$ (CH<sub>3</sub>Si); 721 (paraffin); 685 m  $\nu_{as}(SiC)$ ; 617 m  $\nu_{s}(SiC)$ ; 579 vw, 554 vw, 521 w, 494 m, 463 vs, 417 m  $\nu$ (AlC),  $\nu$ (AlN). MS (EI, 20 eV, 25 °C): m/z (%) 380 (0.2), 379 (1)  $[M]^+$ ; 310 (6), 309 (24), 308 (100)  $[M - CH_2 tBu]^+$ , 212 (2), 211 (18), 210 (45)  $[M - tBu - N{CH(Me)-CH_2}_2CH_2]^+$ .

Synthesis of Compound 5. 2,6-Dimethyl-1-(trimethylsilylethynyl)piperidine (1) (2.181 mL, 1.876 g, 8.97 mmol) was dissolved in 20 mL of n-hexane and treated dropwise (30 min) with a solution of HAltBu<sub>2</sub> (1.274 g, 8.97 mmol) in 70 mL of n-hexane at room temperature. Stirring was continued for 2 h. Colorless crystals were obtained upon concentration of the reaction mixture and cooling to -15 °C. Yield: 2.653 g (84%). Mp (argon, sealed capillary): 121 °C. Anal. Calcd for C20H42AlNSi (351.3): C, 68.4; H, 12.1; N, 4.0. Found: C, 68.2; H, 11.8; N, 4.0. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 400 MHz):  $\delta$  7.12 (1 H, s,  ${}^{3}J_{H-Si}$  = 6.4 Hz, N-CH=C), 3.36 (2 H, m, N-CH-CH<sub>3</sub>), 1.62 and 1.06 (2 H, m, N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 1.35 and 1.05 (each 1 H, m, N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 1.27 (18 H, s, CMe<sub>3</sub>), 0.94 (6 H, d,  ${}^{3}J_{\text{HH}} = 7,2 \text{ Hz}, \text{ N-CH-CH}_{3}, 0.27 (9 \text{ H}, s, \text{Si}Me_{3}).$   ${}^{13}\text{C} \text{ NMR} (C_{6}D_{6}, C_{6})$ 100 MHz): δ 160.8 (br, Al-C=C), 148.1 (Al-C=C), 54.1 (N-CH-CH<sub>3</sub>), 32.3 (CMe<sub>3</sub>), 29.3 (N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 18.0 (N-CH-CH<sub>3</sub>), 17.6 (br, CMe<sub>3</sub>), 12.7 (N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 0.10 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 79 MHz):  $\delta$  –10.4. IR (CsI plates, paraffin, cm<sup>-1</sup>): 1572 m, 1541 s  $\nu$ (C=C); 1464 vs, 1371 vs (paraffin); 1319 m, 1283 w, 1242  $\delta$ (CH<sub>3</sub>); 1174 m, 1128 s, 1091 m, 1061 m, 1020 s, 1001 s ν(CC), ν(CN); 939 sh, 887 m, 837 vs, 806 s, 748 s  $\rho$ (CH<sub>3</sub>Si); 719 vs (paraffin); 685 m  $\nu_{as}(SiC)$ ; 619 m  $\nu_{s}(SiC)$ ; 575 s, 559 s, 498 s, 449 s, 420 s  $\nu(AlC)$ ,  $\nu$ (AlN). MS (EI, 20 eV, 25 °C): m/z (%) 296 (4), 295 (14), 294 (69)  $[M - tBu]^+$ , 197 (11), 196 (100)  $[iBuAl-N{CH(Me)-CH_2}_2CH_2]^+$ , 98 (2) [H-C≡C-SiMe<sub>3</sub>]<sup>+</sup>.

Synthesis of Compound 6. 1-Methyl-4-(trimethylsilylethynyl)piperazine (2) (0.68 mL, 0.592 g, 3.02 mmol) was dissolved in 10 mL of *n*-hexane and treated dropwise with a solution of HAl*i*Bu<sub>2</sub> (1 M, 0.365 mL, 0.429 g, 3.02 mmol) in 5 mL of *n*-hexane at room temperature. Stirring was continued for 3 h. A colorless, waxy solid with some crystalline material embedded was obtained upon concentration of the reaction mixture and cooling to -28 °C. Yield: 0.927 g (91%); highly oxygen- and water-sensitive compound. Anal. Calcd for C<sub>18</sub>H<sub>39</sub>AlN<sub>2</sub>Si (338.3): C, 63.9; H, 11.6; N, 8.3. Found: C, 62.7; H, 11.4; N, 8.1. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): δ 6.14 (1 H, s, N-CH=C), 2.68 and 2.26 (each 2 H, m, C=CH-N-CH<sub>2</sub>), 2.21 and 1.88 (each 2 H, m, N-CH<sub>2</sub>-CH<sub>2</sub>-N-CH<sub>3</sub>), 2.13 (2 H, septet,  ${}^{3}J_{H-H} = 6.7$  Hz, Al-CH<sub>2</sub>-CH), 1.87 (3 H, s, N-CH<sub>3</sub>), 1.24 (12 H, d, <sup>3</sup>J<sub>H-H</sub> = 6.5 Hz, Al- $CH_2$ - $CHMe_2$ ), 0.39 and 0.26 (each 2 H, dd,  ${}^{3}J_{H-H} = 7.6$  Hz,  ${}^{2}J_{H-H} =$ 13.9 Hz, Al-CH<sub>2</sub>), 0.25 (9 H, s, SiMe<sub>3</sub>). <sup>13</sup>C NMR ( $C_6D_6$ , 100 MHz):  $\delta$  161.5 (br, Al-C=C), 148.3 (Al-C=C), 53.2 (N-CH<sub>2</sub>-CH<sub>2</sub>-N-CH<sub>3</sub>), 52.1 (N-CH<sub>2</sub>-CH<sub>2</sub>-N-CH<sub>3</sub>), 45.2 (N-CH<sub>3</sub>), 28.53 and 28.46 (Al-CH<sub>2</sub>-CHMe<sub>2</sub>), 26.7 (Al-CH<sub>2</sub>-CH), 23.1 (br, Al-CH<sub>2</sub>), -0.5 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR ( $C_6D_{64}$  79 MHz):  $\delta$  –10.6. IR (CsI plates, paraffin, cm<sup>-1</sup>): 1599 vs, 1549 vs  $\nu$ (C=C); 1462 vs (paraffin); 1400 m  $\delta$ (CH<sub>3</sub>); 1366 vs (paraffin); 1315 vs, 1290 vs, 1246 vs  $\delta$ (CH<sub>3</sub>); 1202 m, 1155 vs, 1107 s, 1057 vs, 1009 s, 978 s, 962 s  $\nu$ (CC),  $\nu$ (CN); 910 w, 841 vs, 754 s  $\rho$ (CH<sub>3</sub>Si); 727 s (paraffin); 632 vs  $\nu$ (SiC); 575 w, 523 s, 500 w, 478 w, 447 s  $\nu$ (AlC),  $\nu$ (AlN). MS (EI, 20 eV, 25 °C): m/z (%) 338 (0.1)  $[M]^+$ , 283 (7), 282 (30), 281 (65)  $[M - iBu]^+$ , 199 (15), 198 (100)  $[Me_3Si-C(H)] = C(H) - N(CH_2CH_2)_2 NMe]^+$  (hydrolysis?), 184 (13), 183 (100)  $[iBuAl-N(CH_2CH_2)_2NMe]^+$ , 98 (7)  $[H-C\equiv C-SiMe_3]^+$ .

Synthesis of the Phenylethyne Adduct 7. Compound 5 (0.950 g, 2.70 mmol) was dissolved in 30 mL of cyclopentane and treated with phenylethyne (0.297 mL, 0.276 g, 2.70 mmol) at room temperature. Stirring was continued for 2 h. Colorless crystals were obtained upon concentration of the reaction mixture and cooling to 2 °C. Yield: 1.216 g (99%); a temperature-dependent equilibrium between 7 and its constituents was observed in solution. Mp (argon, sealed capillary): 104 °C. Anal. Calcd for C<sub>28</sub>H<sub>48</sub>AlNSi (453.3): C, 74.2; H, 10.7; N, 3.1. Found: C, 73.4; H, 10.5; N, 3.0. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>-CD<sub>3</sub>, 400 MHz, 280 K): δ 10.43 (1 H, br, s, NH), 7.33 (2 H, pseudo-d, o-H of phenyl), 6.99 (2 H, m, m-H of phenyl), 6.96 (1 H, m, *p*-H of phenyl), 5.43 (1 H, d,  ${}^{3}J_{H-H} = 7.3$  Hz, N-CH=C), 1.64 (2 H, m, N-CH-CH<sub>3</sub>), 1.47 (18 H, s, Al-CMe<sub>3</sub>), 1.23 (6 H, br, N-CH-CH<sub>3</sub>), 1.21 and 0.99 (2 H, m, N-CH-CH2-CH2), 0.94 and 0.63 (1 H, m, N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 0.39 (9 H, s, SiMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>5</sub>-CD<sub>3</sub>, 100 MHz, 280 K): δ 162.8 (br, Al-C=C), 138.0 (Al-C=C), 131.8 (o-C of phenyl), 128.6 (m-C of phenyl), 127.5 (p-C of phenyl), 126.1 (ipso-C of phenyl), 118.1 (br, Al-C=C), 116.1 (Al-C=C), 60.5 (N-CH-CH<sub>3</sub>), 33.6 (Al-CMe<sub>3</sub>), 31.0 (N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 22.3 (N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 20.3 (N-CH-CH<sub>3</sub>), 16.1 (br, Al-CMe<sub>3</sub>), 1.8 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>5</sub>-CD<sub>3</sub>, 79 MHz, 280 K):  $\delta$  – 3.6. IR (CsI plates, paraffin, cm<sup>-1</sup>): 3319 w, 3179 w  $\nu$ (NH); 2922 vs, 2851 vs (paraffin); 2361 m, 2342 m  $\nu$ (C $\equiv$ C); 1884 w, 1593 vs, 1560 vs  $\nu$ (C=C), phenyl; 1462 vs (paraffin); 1400 m  $\delta$ (CH<sub>3</sub>); 1377 s (paraffin); 1352 m, 1306 m, 1244 s  $\delta$ (CH<sub>3</sub>); 1207 s, 1169 s, 1115 s, 1069 m, 1051 m, 1024 m, 1003 m, 988 w, 962 m  $\nu$ (CC),  $\nu$ (CN); 932 m, 918 w, 897 m, 878 m, 847 m, 829 m, 812 m, 785 w, 744 m 754 s  $\rho$ (CH<sub>3</sub>Si); 723 s (paraffin); 694 s  $\nu_{as}$ (SiC); 646 w, 625 w  $\nu_{\rm s}$ (SiC); 561 vs, 538 vs, 486 vs, 449 vs, 438 s, 410 m  $\nu$ (AlC),  $\nu$ (AlN). MS (EI, 20 eV, 60 °C): m/z (%) 296 (3), 295 (16), 294 (66)  $[M - PhCCH - tBu]^+$ , 197 (13), 196 (100)  $[iBuAl-N{CH(Me)} CH_2$ <sub>2</sub> $CH_2$ <sup>+</sup>, 102 (37) [Ph-C $\equiv$ C-H].

Synthesis of the Carbodiimide Insertion Product 8. The hydroalumination product 3 was generated in situ by the treatment of a solution of 2,6-dimethyl-1-(trimethylsilylethynyl)piperidine (1) (0.50 mL, 0.430 g, 2.06 mmol) in 15 mL of n-hexane with neat HAliBu<sub>2</sub> (0.365 mL, 0.292 g, 2.06 mmol) at room temperature. Stirring was continued for 2 h, and solid dicyclohexylcarbodiimide (0.424 g, 2.06 mmol) was added. The mixture was concentrated after 2 h at room temperature. Colorless crystals were obtained upon cooling of the solution to -45 °C. Yield: 0.850 g (74%). Mp (argon, sealed capillary): 94 °C. Anal. Calcd for C33H64AlN3Si (557.5): C, 71.1; H, 11.6; N, 7.5. Found: C, 70.6; H, 11.4; N, 7.6. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): δ 5.99 (1 H, s, N-CH=C), 3.57 (2 H, m, N-CH of piperidine), 3.17 (2 H, m, N-CH of cyclohexyl), 2.31 and 2.22 (each 1 H, septet, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, Al-CH<sub>2</sub>-CH), 1.95 and 1.35 (each 4 H, m, N-CH-CH<sub>2</sub> of cyclohexyl), 1.72 and 1.26 (each 4 H, m, N-CH-CH2-CH2 of cyclohexyl), 1.53 and 1.11 (each 2 H, m, N-CH-CH2-CH2-CH2 of cyclohexyl), 1.46 and 1.13 (each 2 H, m, N-CH-CH2-CH2 of piperidine), 1.45 and 1.25 (each 2 H, m, N-CH-CH<sub>2</sub> of piperidine), 1.33 and 1.30 (each 6 H, d,  ${}^{3}J_{H-H} = 6.4$  Hz, CH<sub>2</sub>-CHMe<sub>2</sub>), 1.03 (6 H, d,  ${}^{3}J_{HH}$  = 7,1 Hz, N-CH-CH<sub>3</sub>), 0.51 and 0.40 (each 2 H, d,  ${}^{3}J_{H-H}$  = 7.1

Hz, Al-CH<sub>2</sub>), 0.28 (9 H, s, SiMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz): δ 177.4 (N-C-N), 146.1 (N-C=C), 90.4 (N-C=C), 54.4 (N-CH of cyclohexyl), 51.4 (N-CH-CH<sub>3</sub>), 37.0 and 36.8 (N-CH-CH<sub>2</sub> of cyclohexyl), 30.9 (N-CH-CH<sub>2</sub> of piperidine), 29.3 (Al-CH<sub>2</sub>-CHMe<sub>2</sub>), 27.23 and 27.17 (Al-CH<sub>2</sub>-CH), 26.3 and 26.0 (N-CH-CH<sub>2</sub>-CH<sub>2</sub>e), of cyclohexyl), 26.1 (N-CH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub> of cyclohexyl), 24.1 and 23.9 (Al-CH<sub>2</sub>), 21.4 (N-CH-CH<sub>3</sub>), 14.1 (N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 1.1 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 79 MHz):  $\delta$  –4.2. IR (CsI plates, paraffin, cm<sup>-1</sup>): 1651 w, 1584 vs, br  $\nu$ (C=C),  $\nu$ (CN<sub>2</sub>); 1460 vs, 1375 s (paraffin); 1366 sh, 1342 w, 1312 w, 1290 w, 1248 m  $\delta$ (CH<sub>3</sub>); 1211 m, 1171 w, 1152 m, 1117 m, 1090 w, 1053 s, 1018 m, 982 m  $\nu$ (CC),  $\nu$ (CN); 945 w, 891 m, 839 s, 754 m  $\rho$ (CH<sub>3</sub>Si); 719 w (paraffin); 694 m, 669 m  $\nu_{as}$ (SiC); 644 m, 619 m  $\nu_{s}$ (SiC); 596 w, 563 w, 519 m, 451 m, 432 w  $\nu$ (AlC),  $\nu$ (AlN). MS (EI, 20 eV, 80 °C): *m/z* (%) 502 (38), 500 (100) [M - *i*Bu]<sup>+</sup>, 444 (1), 445 (4) [M - *i*Bu - butene]<sup>+</sup>.

Synthesis of the Carbodiimide Insertion Product 9. The hydroalumination product 6 was generated in situ. 1-Methyl-4-(trimethylsilyl)ethynylpiperazine (0.25 mL, 0.221 g, 1.13 mmol) was dissolved in 10 mL of n-hexane and treated dropwise with neat HAliBu<sub>2</sub> (0.20 mL, 0.160 g, 1.13 mmol) at room temperature. Stirring was continued for 1 h, and solid dicyclohexylcarbodiimide (0.232 g, 1.13 mmol) was added. Stirring was continued for 30 min, and compound 9 was obtained upon concentration of the reaction mixture and cooling to -15 °C. Yield: 0.375 (61%). Mp (argon, sealed capillary): 98 °C. Anal. Calcd for C31H61AlN4Si (544.4): C, 68.4; H, 11.3; N, 10.3. Found: C, 67.6; H, 11.0; N, 10.1. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>-CD<sub>3</sub>, 400 MHz): δ 5.64 (1 H, s, N-CH=C), 3.75 (1 H, m, C=N-CH of cyclohexyl), 3.49 and 2.91/2.98 and 2.43 (each 1 H, Al-N-CH<sub>2</sub> of piperazine), 3.34 (1 H, m, C-N-CH of cyclohexyl), 2.43 and 1.96/2.39 and 2.07 (each 1 H, m, C=N-CH-CH<sub>2</sub> of cyclohexyl), 2.15 and 2.07 (each 1 H, m, Al-CH<sub>2</sub>-CH), 2.00 and 1.88/2.00 and 1.81 (each 1 H, m, Al-N-CH<sub>2</sub>-CH<sub>2</sub> of piperazine), 1.93 and 1.39 (each 1 H, m, C=N-CH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub> of cyclohexyl), 1.88 and 1.37/1.87 and 1.69 (1 H, m, C=N-CH-CH<sub>2</sub>-CH<sub>2</sub> of cyclohexyl), 1.87 and 1.69/1.58 and 1.37 (each 1 H, m, C-N-CH-CH<sub>2</sub>-CH<sub>2</sub>), 1.81 (3 H, s, N-CH<sub>3</sub>), 1.81 and 1.37 (each 1 H, m, C-N-CH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub> of cyclohexyl), 1.70 and 1.36 (each 2 H, m, C-N-CH-CH<sub>2</sub> of cyclohexyl), 1.21 and 1.20 (each 6 H, d,  ${}^{3}J_{H-H} = 6.2$  Hz, Al-CH<sub>2</sub>-CHMe<sub>2</sub>), 0.45 and 0.14/0.12 and -0.01 (each 1 H, m, Al-CH<sub>2</sub>), 0.29 (9 H, s, SiMe<sub>3</sub>); unambiguous assignment was difficult owing to the overlap of resonances and the complicated splitting patterns. <sup> $I_3$ </sup>C NMR ( $C_6 D_5$ -CD<sub>3</sub>, 100 MHz):  $\delta$  156.4 (N-C-N), 138.6 (N-C(H)-C(Si)), 138.0 (N-C(H)=C(Si)), 56.9 (C-N-CH ofcyclohexyl), 56.4 (C=N-CH of cyclohexyl), 51.54 and 51.46 (Al-N-CH<sub>2</sub> of piperazine), 51.1 and 49.8 (Al-N-CH<sub>2</sub>-CH<sub>2</sub>), 45.7 (N-CH<sub>3</sub>), 36.9 and 36.5 C-N-CH-CH<sub>2</sub> of cyclohexyl), 33.8 and 31.8 (C=N-CH-CH2 of cyclohexyl), 29.0 and 28.7 (Al-CH2-CHMe3), 27.7 and 27.1 (C=N-CH-CH2-CH2 of cyclohexyl), 27.1 and 26.7 (C-N-CH-CH2-CH<sub>2</sub> of cyclohexyl), 27.0 and 26.8 (Al-CH<sub>2</sub>-CH), 25.3 (C-N-CH-CH<sub>2</sub>-CH2-CH2 of cyclohexyl), 24.9 (C=N-CH-CH2-CH2-CH2 of cyclohexyl), 23.0 and 22.1 (Al-CH<sub>2</sub>), 0.5 (SiMe<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>5</sub>-CD<sub>3</sub>, 79 MHz):  $\delta$  -4.1. IR (CsI plates, paraffin, cm<sup>-1</sup>): 1595 vs, br, 1551 s  $\nu$ (C=C); 1464 vs, 1375 vs (paraffin); 1315 m, 1292 s, 1248 vs  $\delta(CH_3)$ ; 1225 m, 1200 m, 1153 s, 1117 s, 1093 m, 1061 s, 1034 s, 1011 vs, 986 s, 970 m  $\nu$ (CC),  $\nu$ (CN); 951 m, 907 m, 889 s, 839 vs, 797 m, 775 w, 756 m  $\rho$ (CH<sub>3</sub>Si); 718 m (paraffin); 694 m, 665 m  $\nu_{\rm as}({\rm SiC})$ ; 633 s  $\nu_{\rm s}({\rm SiC})$ ; 588 w, 557 w, 523 s, 496 m, 478 w, 451 m, 437 m  $\nu$ (AlC),  $\nu$ (AlN). MS (EI, 20 eV, 40 °C): m/z (%) 489 (4), 488 (12), 487 (40)  $[M - butyl]^+$ , 334 (83), 335 (21), 336 (4)  $[M^+ \begin{array}{l} cyclohexene - butyl - butene - CH_3], 333 (3), 332 (13), 331 (55) \\ [M - SiMe_3 - cHex - butyl and M - 2butyl - N(CH_2CH_2)_2NMe]^+, \end{array}$ 307 (9), 306 (32), 305 (100)  $[M - AliBu_2 - cHex - Me]^+$ .

**Rearrangement of 9; Synthesis of 10.** The intermediates 6 and 9 were generated in situ. 1-Methyl-4-(trimethylsilyl)ethynylpiperazine (1.0 mL, 0.87 g, 4.44 mmol) was dissolved in 35 mL of *n*-hexane and treated dropwise with neat HAliBu<sub>2</sub> (0.787 mL, 0.630 g, 4.44 mmol) at room temperature. Stirring was continued for 2 h, and solid dicyclohexylcarbodiimide (0.914 g, 4.44 mmol) was added. Stirring was continued for 2 d. Compound 10 was obtained upon concentration of the reaction mixture and cooling to -28 °C. Yield: 2.162 g (89%). Mp (argon, sealed capillary): 98 °C. Anal. Calcd for C<sub>31</sub>H<sub>61</sub>AlN<sub>4</sub>Si (544.4): C, 68.4; H, 11.3; N, 10.3. Found: C, 68.2; H, 11.0; N, 10.2. <sup>1</sup>H NMR ( $C_6D_6$ , 400 MHz):  $\delta$  5.88 (1 H, s N-CH=C), 3.19 (2 H, m, N-CH of cyclohexyl), 3.05 (2 H, m, Al-N-CH<sub>2</sub> of piperazine), 2.29 and 2.22 (each 1 H, septet,  ${}^{3}J_{H-H} = 6.7$  Hz, Al-CH<sub>2</sub>-CH), 2.11 (4 H, m, Al-N-CH2-CH2 of piperazine), 1.99 (3 H, s, N-CH<sub>3</sub>), 1.94 and 1.38/1.91 and 1.40 (each 2 H, m, N-CH-CH<sub>2</sub> of cyclohexyl), 1.67 and 1.22 (each 4 H, m, N-CH-CH2-CH2 of cyclohexyl), 1.50 and 1.07 (each 2 H, m, N-CH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub> of cyclohexyl), 1.32 and 1.29 (each 6 H, d,  ${}^{3}J_{H-H}$  = 6.7 Hz, Al-CH<sub>2</sub>- $CHMe_2$ ), 0.50 and 0.46 (each 2 H, d,  ${}^{3}J_{H-H} = 7.1$  Hz, Al- $CH_2$ ), 0.25 (9 H, s, SiMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz): δ 177.3 (N-C-N), 145.2 (N-C=C), 92.1 (N-C=C), 55.3 (Al-N-CH<sub>2</sub>-CH<sub>2</sub> of piperazine), 54.2 (N-C of cyclohexyl), 49.3 (Al-N-CH<sub>2</sub> of piperazine), 46.1 (N-CH<sub>3</sub>), 36.9 and 36.3 (N-CH-CH<sub>2</sub> of cyclohexyl), 29.21 and 29.19 (Al-CH<sub>2</sub>-CHMe<sub>2</sub>), 27.18 and 27.15 (Al-CH<sub>2</sub>-CH), 26.11 and 26.06 (N-CH-CH2-CH2), 26.0 (N-CH-CH2-CH2-CH2), 23.9 and 23.2 (Al-CH2), 0.7  $(SiMe_3)$ . <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 79 MHz):  $\delta$  –4.8. IR (CsI plates, paraffin, cm<sup>-1</sup>): 1597 vs, br, 1557 sh  $\nu$ (C=C),  $\nu$ (CN<sub>2</sub>); 1460 vs, 1371 vs (paraffin); 1292 s, 1250 s  $\delta$ (CH<sub>3</sub>); 1225 w, 1200 s, 1165 s, 1140 s, 1070 m, 1030 s, 1009 vs  $\nu(CC)$ ,  $\nu(CN)$ ; 939 m, 891 m, 837 vs, 754 m  $\rho(CH_3Si)$ ; 669 s  $\nu_{as}(SiC)$ ; 637 s  $\nu_s(SiC)$ ; 523 m, 496 w, 451 m  $\nu$ (AlC),  $\nu$ (AlN). MS (EI, 20 eV, 60 °C): m/z (%) 490 (3), 488 (36)  $[M - butene]^+$ , 472 (1)  $[M - iBu - CH_3]^+$ , 332 (16), 331 (61)  $[M - iBu - CH_3]^+$  $SiMe_3 - cHex - iBu$  and  $M - 2iBu - N(CH_2CH_2)_2NMe]^+$ , 306 (34),  $305 (100) [M - AliBu_2 - cHex - Me]^+$ 

Crystal Structure Determinations. Single crystals were obtained by cooling of the reaction mixtures as described above. The crystallographic data were collected with a Bruker APEX diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97<sup>30</sup> by a full-matrix least-squares method based on  $F^2$ . Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Only the position of the N-H hydrogen atom of compound 7 was taken from a difference Fourier map and refined with isotropic U. The molecules of compounds 3 and 4 are localized on a crystallographic mirror plane. An isobutyl group of 6 was disordered; the atoms were refined on split positions with occupation factors of 0.86:0.14. An isobutyl group of 8 was disordered (C121); its atoms were refined on split positions (0.73:0.27). Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-865846 (3), -865847 (4), -865848 (5), -865849 (6), -865850 (7), -865851 (8), and -865852 (9).

#### ASSOCIATED CONTENT

#### **S** Supporting Information

CIF files giving the crystal data for compounds **3** to **9**. Results of quantum chemical calculations including optimized Cartesian coordinates (B97-D/def2-TZVP, M06-2x/def2-TZVP, and B3LYP/6-311+G(d,p) and single-point energies at the level B2PLYP-D/def2-QZVP//B97-D/def2-TZVP incl. ZPE). This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

#### **Corresponding Author**

\*Fax: +49-251-8336660. E-mail: uhlw@uni-muenster.de; wurthwe@uni-muenster.de.

## Notes

The authors declare no competing financial interest.

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# **REFERENCES**

(1) (a) Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. Angew. Chem. 2010, 122, 1444-1447; Angew. Chem., Int. Ed. 2010, 49, 1402-1405. (b) Ullrich, M.; Lough, A. J.; Stephan, D. W. Organometallics 2010, 29, 3647-3654. (c) Rokob, T. A.; Hamza, A.; Pápai, I. J. Am. Chem. Soc. 2009, 131, 10701-10710. (d) Jiang, C.; Blacque, O.; Berke, H. Organometallics 2010, 29, 125-133. (e) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. Angew. Chem. 2007, 119, 5056-5059; Angew. Chem., Int. Ed. 2007, 46, 4968-4971. (f) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. Angew. Chem. 2009, 121, 6770-6773; Angew. Chem., Int. Ed. 2009, 48, 6643-6646. (g) Berkefeld, A.; Piers, W. E.; Parvez, M. J. Am. Chem. Soc. 2010, 132, 10660-10661. (h) Ashley, A. E.; Thompson, A. L.; O'Hare, D. Angew. Chem. 2009, 121, 10023-10027; Angew. Chem., Int. Ed. 2009, 48, 9839-9843. (i) Otten, E.; Neu, R. C.; Stephan, D. W. J. Am. Chem. Soc. 2009, 131, 9918-9919. (j) Neu, R. C.; Otten, E.; Stephan, D. W. Angew. Chem. 2009, 121, 9889-9892; Angew. Chem., Int. Ed. 2009, 48, 9709-9712. (k) Bertini, F.; Lyaskovskyy, V.; Timmer, B. J. J.; de Kanter, F. J. J.; Lutz, M.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K. J. Am. Chem. Soc. 2012, 134, 201-204. (1) Marwitz, A. J. V.; Dutton, J. L.; Mercier, L. G.; Piers, W. E. J. Am. Chem. Soc. 2011, 133, 10026-10029.

(2) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. Science **2006**, 314, 1124–1126.

(3) (a) Stephan, D. W.; Erker, G. Angew. Chem. 2010, 122, 50-81; Angew. Chem. Int. Ed 2010, 49, 46-76. (b) Stephan, D. W. Dalton Trans. 2009, 3129-3136. (c) Stephan, D. W. Org. Biomol. Chem. 2008, 6, 1535-1539. (d) Erker, G. C. R. Chim. 2011, 14, 831-841.

(4) (a) Holschumacher, D.; Bannenberg, T.; Hrib, C. G.; Jones, P. G.; Tamm, M. Angew. Chem. 2008, 120, 7538–7542; Angew. Chem., Int. Ed. 2008, 47, 7428–7432. (b) Chase, P. A.; Stephan, D. W. Angew. Chem. 2008, 120, 7543–7547; Angew. Chem., Int. Ed. 2008, 47, 7433–7437. (c) Kronig, S.; Theuergarten, E.; Holschumacher, D.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. Inorg. Chem. 2011, 50, 7344–7359. (d) Theuergarten, E.; Schlüns, D.; Grunenberg, J.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. Chem. Commun. 2010, 8561–8563. (e) Holschumacher, D.; Bannenberg, T.; Ibrom, K.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. Dalton Trans. 2010, 39, 10590–10592. (f) Alcarazo, M.; Gomez, C.; Holle, S.; Goddard, R. Angew. Chem. 2010, 122, 5924–5927; Angew. Chem., Int. Ed. 2010, 49, 5788–5791.

(5) Dureen, M. A.; Brown, C. C.; Stephan, D. W. Organometallics 2010, 29, 6594-6607.

(6) (a) Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. Angew. Chem. 2008, 120, 6090-6092; Angew. Chem., Int. Ed.
2008, 47, 6001-6003. (b) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. J. Am. Chem. Soc. 2008, 130, 14117-14119. (c) Geier, S. J.; Stephan, D. W. J. Am. Chem. Soc. 2009, 131, 3476-3477. (d) Geier, S. J.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. Inorg. Chem. 2009, 48, 10466-10474.
(e) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. Angew. Chem. 2007, 119, 8196-8199; Angew. Chem., Int. Ed. 2007, 46, 8050-8053.
(f) Geier, S. J.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. Inorg. Chem. 2009, 48, 10466-10474. (g) Geier, S. J.; Chase, P. A.; Stephan, D. W. Chem. Commun. 2010, 46, 4884-4886. (h) Geier, S. J.; Dureen, M. A.; Ouyang, E. Y.; Stephan, D. W. Chem.—Eur. J. 2010, 16, 988-993.

(7) (a) Dureen, M. A.; Stephan, D. W. J. Am. Chem. Soc. 2009, 131, 8396-8397. (b) Ménard, G.; Stephan, D. W. J. Am. Chem. Soc. 2010, 132, 1796-1797. (c) Zhang, Y.; Miyake, G. M.; Chen, E. Y.-X. Angew. Chem. 2010, 122, 10356-10360; Angew. Chem., Int. Ed. 2010, 49, 10158-10162. (d) Menard, G.; Stephan, D. W. Angew. Chem. 2011, 123, 8546-8549; Angew. Chem Int. Ed. 2011, 50, 8396-8399. (e) Boudreau, J.; Courtemanche, M.-A.; Fontaine, F.-G. Chem. Commun. 2011, 47, 11131-11133.

(8) Westenberg, H.; Slootweg, J. C.; Hepp, A.; Kösters, J.; Roters, S.; Ehlers, A. W.; Lammertsma, K.; Uhl, W. *Organometallics* **2010**, *29*, 1323–1330.

(9) Appelt, C.; Westenberg, H.; Bertini, F.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. Angew. Chem. 2011, 123, 4011–4014; Angew. Chem., Int. Ed. 2011, 50, 3925–3928.

(10) Uhl, W. Coord. Chem. Rev. 2008, 252, 1540-1563.

(11) (a) Uhl, W.; Bock, H. R.; Claesener, M.; Layh, M.; Tiesmeyer, I.; Würthwein, E.-U. *Chem.—Eur. J.* **2008**, *14*, 11557–11564. (b) Uhl, W.; Claesener, M.; Haddadpour, S.; Jasper, B.; Tiesmeyer, I.; Zemke, S. Z. Anorg. Allg. Chem. **2008**, *634*, 2889–2896. (c) Uhl, W.; Claesener, M.; Hepp, A.; Jasper, B.; Vinogradov, A.; van Wüllen, L.; Köster, T. K.-J. Dalton Trans. **2009**, 10550–10562.

(12) Himbert, G.; Naßhahn, H.; Gerulat, O. Synthesis 1999, 293–294.

(13) (a) Hill, J. B.; Eng, S. J.; Pennington, W. T.; Robinson, G. H. J. Organomet. Chem. **1993**, 445, 11–11. (b) Gardiner, M. G.; Raston, C. L.; Cloke, F. G. N.; Hitchcock, P. B. Organometallics **1995**, 14, 1339–1353. (c) Mitzel, N. W.; Lustig, C. Z. Naturforsch. **2004**, 59b, 1532–1539. (d) Venugopal, A.; Kamps, I.; Bojer, D.; Berger, R. J. F.; Mix, A.; Willner, A.; Neumann, B.; Stammler, H.-G.; Mitzel, N. W. Dalton Trans. **2009**, 5755–5765. (e) Trepanier, S. J.; Wang, S. Organometallics **1994**, 13, 2213–2217. (f) Schumann, H.; Wassermann, B. C.; Schutte, S.; Heymer, B.; Nickel, S.; Seuß, T. D.; Wernik, S.; Demtschuk, J.; Girgsdies, F.; Weimann, R. Z. Anorg. Allg. Chem. **2000**, 626, 2081–2095.

(14) (a) Uhl, W.; Kovert, D.; Layh, M.; Hepp, A. Chem.—Eur. J. 2011, 17, 13553–13561. (b) Uhl, W.; Claesener, M.; Kovert, D.; Hepp, A.; Würthwein, E.-U.; Ghavtadze, N. Organometallics 2011, 30, 3075–3082. (c) Uhl, W.; Rohling, M.; Würthwein, E.-U.; Ghavtadze, N.; Bergander, K. Organometallics 2010, 29, 5236–5240. (d) Uhl, W.; Matar, M. J. Organomet. Chem. 2002, 664, 110–115.

(15) Uhl, W.; Bock, H. R.; Breher, F.; Claesener, M.; Haddadpour, S.; Jasper, B.; Hepp, A. Organometallics **2007**, *26*, 2363–2369.

(16) (a) Uhl, W.; Claesener, M. Inorg. Chem. 2008, 47, 729–735.
(b) Uhl, W.; Claesener, M. Inorg. Chem. 2008, 47, 4463–4470.
(c) Uhl, W.; Claesener, M.; Hepp, A. Organometallics 2008, 27, 2118–2122.
(d) Uhl, W.; Heller, D.; Rohling, M.; Kösters, J. Inorg. Chim. Acta 2011, 374, 359–365.

(17) (a) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072–5074. For a similar B–N compound see: (b) Schwendemann, S.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Sci.* **2011**, *2*, 1842–1849.

(18) (a) Uhl, W.; Er, E.; Matar, M. Main Group Chem. 2006, 5, 31– 40. (b) Uhl, W.; Er, E.; Hübner, O.; Himmel, H.-J. Z. Anorg. Allg. Chem. 2008, 634, 2133–2139. (c) Cui, C.; Schmidt, J. A. R.; Arnold, J. J. Chem. Soc., Dalton Trans. 2002, 2992–2994. (d) Schiefer, M.; Reddy, N. D.; Ahn, H.-J.; Stasch, A.; Roesky, H. W.; Schlicker, A. C.; Schmidt, H.-G.; Noltemeyer, M.; Vidovic, D. Inorg. Chem. 2003, 42, 4970–4976. (e) Schiefer, M.; Hatop, H.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. Organometallics 2002, 21, 1300–1303. (f) Zhu, H.; Chai, J.; Fan, H.; Roesky, H. W.; He, C.; Jancik, V.; Schmidt, H.-G.; Noltemeyer, M.; Merrill, W. A.; Power, P. P. Angew. Chem. 2005, 117, 5220–5223; Angew. Chem., Int. Ed. 2005, 44, 5090–5093. (g) Zhu, H.; Oswald, R. B.; Fan, H.; Roesky, H. W.; Ma, Q.; Yang, Z.; Schmidt, H.-G.; Noltemeyer, M.; Starke, K.; Hosmane, N. S. J. Am. Chem. Soc. 2006, 128, 5100–5108.

(19) (a) Kiely, A. F.; Nelson, C. M.; Pastor, A.; Henling, L. M.; Day, M. W.; Bercaw, J. E. Organometallics 1998, 17, 1324–1332.
(b) Dewhurst, R. D.; Hill, A. F.; Smith, M. K. Angew. Chem. 2004, 116, 482–484; Angew. Chem., Int. Ed. 2004, 43, 476–478.
(c) Viswamitra, M. A; Radharkrishnan, R.; Bandekar, J.; Desiraju, G. R. J. Am. Chem. Soc. 1993, 115, 4868–4869. (d) Steiner, T. Angew. Chem. 2002, 114, 50–80; Angew. Chem., Int. Ed. 2002, 41, 48–76.
(e) Desiraju, G. R. Acc. Chem. Res. 1996, 29, 411–449. (f) Braga, D.; Grepioni, F.; Desiraju, G. Chem. Rev. 1998, 98, 1375–1405.

(20) (a) Rowley, C. N.; DiLabio, G. A.; Barry, S. T. Inorg. Chem.
2005, 44, 1983–1991. (b) Lechler, R.; Hausen, H.-D.; Weidlein, J. J. Organomet. Chem. 1989, 359, 1–12. (c) Schmidt, J. A. R; Arnold, J. Organometallics 2002, 21, 2306–2313. (d) Chang, C.-C.; Hsiung, C.-S.; Su, H.-L.; Srinivas, B.; Chiang, M. Y.; Lee, G.-H.; Wang, Y. Organometallics 1998, 17, 1595–1601. (e) Coles, M. P.; Hitchcock, P.

B. Eur. J. Inorg. Chem. 2004, 2662–2672. (f) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. Jr. Organometallics 1997, 16, 5183–5194. (g) Kottmair-Maieron, D.; Lechler, R.; Weidlein, J. Z. Anorg. Allg. Chem. 1991, 593, 111–123. (h) Ergezinger, C.; Weller, F.; Dehnicke, K. Z. Naturforsch. 1988, 43b, 1621–1627. (i) Duchateau, R.; Meetsma, A.; Teuben, J. H. J. Chem. Soc., Dalton Trans. 1996, 223–224. (j) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. Jr. Organometallics 1998, 17, 4042–4048. (k) Kenney, A. P.; Yap, G. P. A; Richeson, D. S.; Barry, S. T. Inorg. Chem. 2005, 44, 2926–2933.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(22) TURBOMOLE V6.3, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, TURBOMOLE GmbH, 2010; available from http://www.turbomole.com.

(23) (a) Schwabe, T.; Grimme, S. Phys. Chem. Chem. Phys. 2007, 9,

3397-3406. (b) Grimme, S. J. Chem. Phys. 2006, 124, 034108.

(24) Grimme, S. J. Comput. Chem. 2006, 27, 1787-1799.

(25) Zhao, Y.; Truhlar, D. G. Theor. Chem. Acc. 2008, 120, 215–241.
(26) Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys. 2005, 7, 3297–3305; as taken from the EMSL basis set exchange (https://bse.pnl.gov/bse/portal).

(27) (a) Chey, J.; Choe, H.-S.; Chook, Y.-M.; Jensen, E.; Seida, P. R.; Francl, M. M. Organometallics 1990, 9, 2430–2436. (b) Bundens, J. W.; Francl, M. M. Organometallics 1993, 12, 1608–1615. (c) Gropen, O.; Haaland, A. Acta Chem. Scand., Ser. A 1982, 36, 435–438. (d) Bundens, J. W.; Yudenfreund, J.; Francl, M. M. Organometallics 1999, 18, 3913–3920.

(28) Beachley, O. T. Jr.; Victoriano, L. Organometallics **1988**, 7, 63–67.

(29) Uhl, W.; Cuypers, L.; Graupner, R.; Molter, J.; Vester, A.; Neumüller, B. Z. Anorg. Allg. Chem. 2001, 627, 607–614.

(30) SHELXTL-Plus, REL. 4.1; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1990. Sheldrick, G. M. SHELXL-97, Program for the Refinement of Structures; Universität Göttingen: Germany, 1997.