Treatment of Tetramethylpyrazole and 3,5-Diphenylpyrazole with Dialkylaluminum Hydrides - Hydroalumination *versus* Deprotonation

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Treatment of tetramethylpyrazole, $N_2C_3Me_4$, with equimolar quantities of di(*tert*-butyl)aluminum hydride leads to the addition of an Al–H bond to one of the C=N double bonds. The dimeric product (**1**) contains a central six-membered Al_2N_4 ring in which two $^tBu_2Al^+$ units are bridging two N_2C_3 heterocycles. In the zwitterionic, non-centrosymmetric compound one aluminum atom is coordinated by two imino nitrogen atoms, while the second one is bonded to two amide nitrogen atoms. No double hydroalumination occurs upon treatment of tetramethylpyrazole with two equivalents of the hydride. Instead, an adduct (**2**) of the monomeric hydroalumination product with di(*tert*-butyl)aluminum hydride was isolated in which the two aluminum atoms are connected by a 3c-2e Al–H–Al bond. A unique trinuclear compound (**3**) is obtained upon reaction of tetramethylpyrazole with an excess of the sterically less shielded diethylaluminum hydride. It contains two different N_2C_3 heterocycles: One still contains a C=N double bond similar to that in compounds **1** and **2**, while the second one is completely reduced by double hydroalumination to give a saturated heterocycle. The two rings are bridged by three $AlEt_2$ groups. Deprotonation results upon treatment of 3,5-diphenylpyrazole, $N_2C_3H_2(C_6H_5)_2$, with di(*tert*-butyl)aluminum hydride.

Key words: Organoelement Compounds, Aluminum, Hydrazides, Heterocycles, Hydroalumination

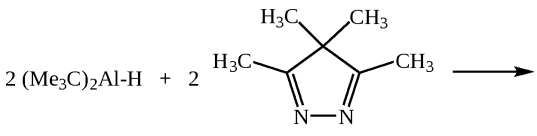
Introduction

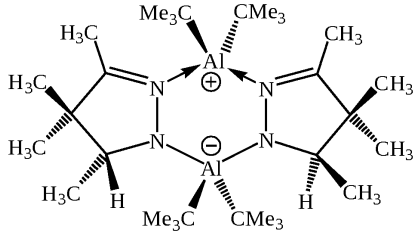
Organoaluminum, -gallium or -indium hydrazides [1] show a fascinating coordination chemistry similar to that of hydroxylamides [2] or peroxides [3] which results from the singular arrangement of two adjacent donor atoms in the ligands. The synthesis of these hydrazides was accomplished *via* several different and efficient routes such as salt elimination, release of hydrogen or alkanes [1]. The latter method comprises the treatment of the corresponding trialkylaluminum or -gallium compounds with hydrazines having at least one N-H function. We preferred this procedure in our recent investigations, because the starting compounds are easily available, and volatile alkanes are formed as the only by-products in usually very selective reactions. Adducts are formed in the first step which could be isolated and characterized in several cases [1, 4 – 6]. Steric interactions are determining their structures, and in most cases the less shielded nitrogen atoms coordinate to the metal atoms. Only one compound, $Me_3Ga{\leftarrow}NH(Me)\text{-}NH_2$ [5], has the more basic alkylated nitrogen atom attached to the metal atom. The release of alkanes from these adducts with the almost quantitative formation of the corresponding hydrazides takes place spontaneously below room temperature or upon slight warming. The products contain a monoanionic hydrazido ligand and are dimeric with four-, five- or six-membered heterocycles [1, 6 – 8]. Further reactions gave very interesting oligocyclic or cage-like compounds which have dianionic hydrazinediido groups [1, 5, 7, 9]. The latter were also accessible by twofold hydroalumination of tetramethyl-2,3-diazabutadiene. However, complete reduction to yield a hydrazinediide occurred only with AlH_3 [10], while even an excess of dialkylaluminum hydrides or gallium hydrides gave hydrazone derivatives with an intact C=N double bond [11]. In continuation of these investigations we also applied cyclic diaza compounds and treated pyrazole derivatives with dialkylaluminum hydrides.

Results and Discussion

Reactions of tetramethylpyrazole with $(Me_3C)_2$Al-H

Tetramethylpyrazole was dissolved in toluene and treated with an equimolar quantity of di(*tert*-





(1)

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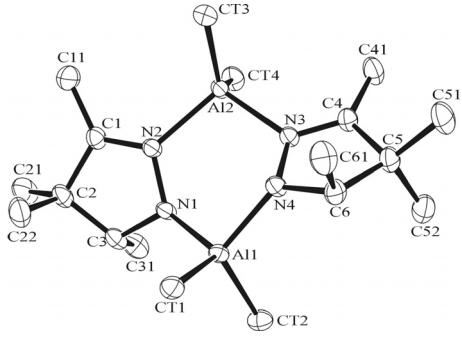
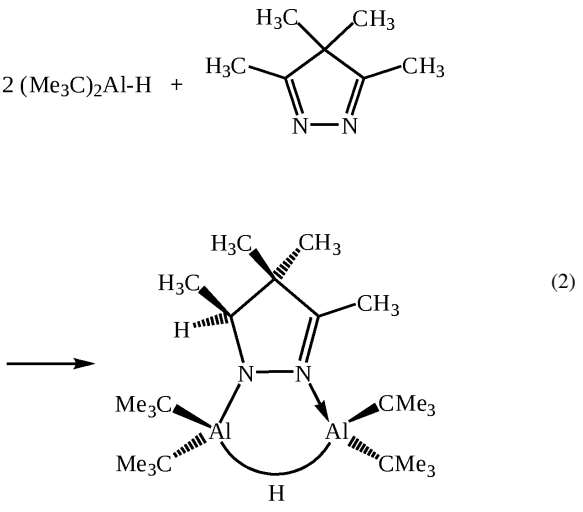


Fig. 1. Molecular structure of **1**. The ellipsoids are drawn at the 40 % probability level; hydrogen atoms and methyl groups of CMe_3 are omitted. Selected bond lengths (pm) and angles (deg): Al1–N1 190.2(2), Al1–N4 190.4(2), Al2–N2 198.9(2), Al2–N3 198.6(2), N1–N2 140.1(2), N3–N4 139.9(2), N1–C3 149.2(3), N2–C1 130.2(3), N3–C4 130.0(3), N4–C6 149.1(3); N1–Al1–N4 100.56(8), N2–Al2–N3 101.46(8), Al1–N1–N2 124.4(1), Al1–N4–N3 124.2(1), Al2–N2–N1 118.3(1), Al2–N3–N4 118.9(1).

butyl)aluminum hydride at room temperature. The color of the solution changed from yellow to orange. Concentration of the reaction mixture and cooling to +3 °C afforded colorless crystals of the product (**1**, Eq. 1) in 34 % yield. Crystal structure determination (Fig. 1) revealed a dimeric formula unit in the solid state in which two aluminum atoms bridge two C_3N_2 heterocycles to give a central six-membered Al_2N_4 ring. Only one C=N double bond of each pyrazole unit was reduced by the addition of an Al–H bond which results in markedly different endocyclic C–N bond lengths of 130.1 (C=N, average value) and 149.2 pm (average C–N single bond). The carbon atoms C1 and C4 are sp^2-hybridized with the adjacent atoms almost ideally in a common plane, while C2, C3, C5 and C6 have a distorted tetrahedral surrounding. The N–N bond length (140.0 pm) is in the lower range of N–N single bonds of simple hydrazines (141 – 149 pm) [1, 12]. The Al_2N_4 ring deviates considerably from planarity and adopts a *twist*-conformation [13] (torsion angles: +55.2, −25.8, −26.7, +54.4, −28.6, and −30.7°; clockwise, starting with Al1–N1–N2–Al2). Caused by this arrangement the normals of the five-membered rings enclose an angle of 58.7°. Interestingly, the molecular symmetry is not centrosymmetric. One aluminum atom is coordinated by two imino and the second one by two amido nitrogen atoms. This bonding situation results in different Al–N distances (Al2–N 198.8 and Al1–N 190.3 pm, respectively) which are in accordance with previous observations [1, 4 – 9]. The Al–C distances (203.0 pm on average) are not influenced by the different coordination of the metal atoms. However, the smaller C–Al–C angle at Al1 (114.1 *versus* 123.5°) may indicate a stronger steric stress at this position. The N–Al–N angles are similar at both aluminum atoms (100.6 *versus* 101.5°), but the Al–N–N angles are different with the larger ones at the negatively charged amido nitrogen atoms (124.3 *versus* 118.6°).

The NMR data of **1** are in accordance with the molecular structure found in the solid state. We observe two resonances of *tert*-butyl groups and four signals for the chemically different methyl groups attached to the C_3N_2 heterocycle. One of the latter signals is split into a doublet by coupling with the ring hydrogen atom ($^3J_{H\text{-}H}$ = 6.6 Hz) which also leads to a quartet at δ = 3.86. These NMR data verify the existence of dimeric formula units also in solution. Owing to the occurrence of two chiral carbon atoms in the dimeric molecules of **1** four different stereoisomers may be formulated. Two of these have a head-to-head (symmetry C_2 according to the structure in the solid state or C_s), the other ones a head-to-tail arrangement (C_2 or C_i) of the heterocycles. The C_s structure should give NMR resonances of four different *tert*-butyl groups and can clearly be ruled out. The NMR data do not allow to distinguish between the three remaining structures, however, a strong rearrangement compared to the situation in the solid state is necessary to form the head-to-tail isomers, hence, their formation seems to be relatively implausible. An equilibrium between two possible forms in solution was detected for dimeric 2-dimethylaluminumpyridine [14]. In this case warming of the solution gave rearrangement and



(2)

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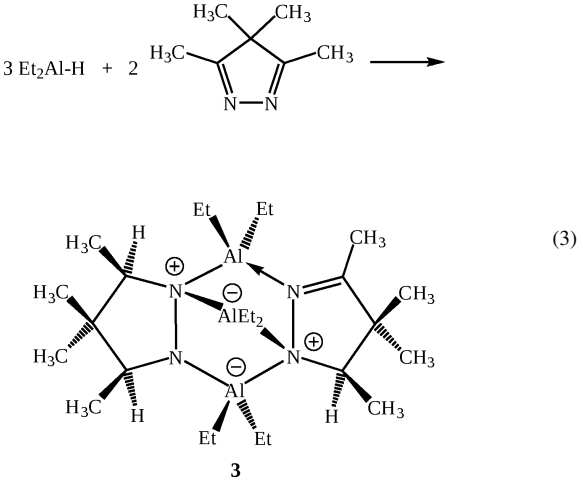
complete formation of the centrosymmetric form. We do not have any indication of such an equilibrium for compound **1**, and heating of **1** in boiling toluene did not result in any alteration of the NMR spectra.

The hydroalumination of both C=N double bonds in each heterocycle could not be achieved even when an excess of the hydride was reacted with tetramethylpyrazole. Reactions in the ratio 2 : 1 gave an adduct in 72 % yield in which a monomeric fragment of **1** is coordinated by an intact molecule of di(*tert*-butyl)aluminum hydride *via* a 3c-2e Al–H–Al bond and an interaction of the metal atom with one of the nitrogen atoms of the C_3N_2 heterocycle (**2**, Eq. 2). Longer reaction times or warming did not result in any secondary process. The constitution of the yellow compound **2** could unambiguously be assigned from the ^{1}H NMR data. We observed four different resonances of *tert*-butyl groups which are caused by the different coordination of the aluminum atoms to imino or amido nitrogen atoms and the chirality of the carbon atom bearing a hydrogen atom and a methyl group. Further, we detected four resonances of methyl groups attached to the C_3N_2 ring. Two of the latter resonances are split into doublets. One coupling constant (6.7 Hz) is characteristic of a $^3J_{H\text{-}H}$ coupling to the hydrogen atom added to the pyrazole ring by hydroalumination. The resonance belongs to the methyl group bonded to the C-H fragment of the ring. The occurrence of a second doublet reflects a long-range coupling ($^5J_{H\text{-}H}$ = 1.0 Hz) between the ring hydrogen atom and the methyl group attached to the C=N double bond. Caused by these different couplings the ring hydrogen atom gives a quartet of quartets with an expected chemical shift of δ = 3.43. A broad resonance at δ = 2.97 is indicative of a hydrogen atom bridging the two aluminum atoms. The occurrence of a C=N double bond is in accordance with a resonance at δ = 155.9 in the ^{13}C NMR spectrum (δ = 66.6 for the sp^3-hybridized carbon atom bonded to the nitrogen atom). We were not able to determine the structure of **2** by X-ray diffraction in sufficient accuracy because all crystals obtained from different solvents (*n*-pentane, cyclopentane, toluene, 1,2-difluorobenzene, diethyl ether *etc.*) were of very poor quality. The positions of the carbon, nitrogen and aluminum atoms could be found. They have verified the structure of **2** given schematically in Eq. 2, but the parameters could not be refined satisfactorily.

Reaction of tetramethylpyrazole with Et_2Al-H

Hydroalumination of both C=N double bonds of the heterocycle could not be achieved in the reactions of excess di(*tert*-butyl)aluminum hydride with tetramethylpyrazole. A reason may be the steric shielding by the bulky *tert*-butyl groups which prevents the second addition reaction. Therefore we reduced the steric demand of the substituents attached to aluminum and treated the pyrazole with two equivalents of diethylaluminum hydride in toluene/*n*-pentane at r. t. (Eq. 3). The color of the mixture changed from yellow to dark red. Concentration and cooling of the solution to +3 °C afforded yellow crystals of compound **3** in 67 % yield. A crystal structure determination revealed an interesting and unprecedented molecular structure (Fig. 2) which contains two different five-membered



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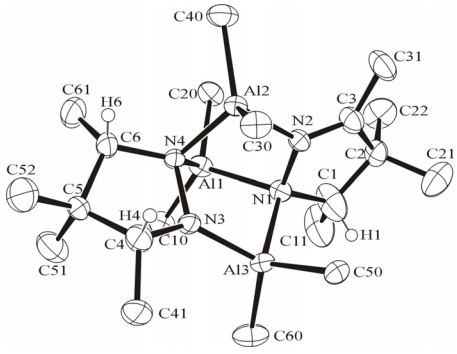


Fig. 2. Molecular structure of **3**. The ellipsoids are drawn at the 40 % probability level; methyl groups of CH_2CH_3 and hydrogen atoms with the exception of C-H of the heterocycle are omitted. Selected bond lengths (pm) and angles (deg): Al1–N1 200.3(2), Al1–N4 196.0(2), Al2–N2 200.0(2), Al2–N4 193.5(2), Al3–N1 201.8(2), Al3–N3 185.7(2), N1–N2 145.3(3), N3–N4 150.9(3), N1–C1 150.5(4), N2–C3 128.6(3), N3–C4 145.1(3), N4–C6 151.3(3); N1–Al1–N4 86.79(8), N2–Al2–N4 89.10(9), N1–Al3–N3 89.80(9).

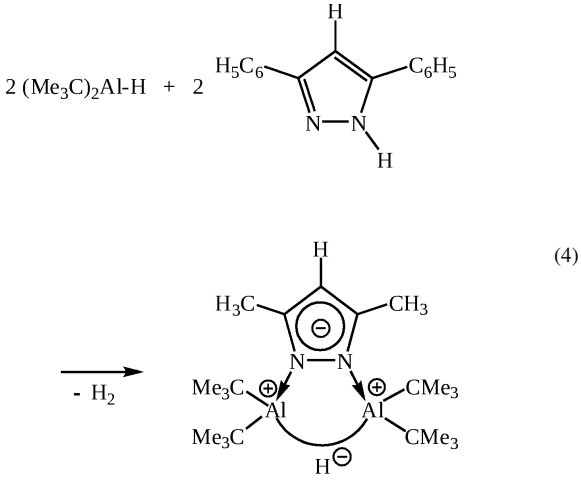
C_3N_2 heterocycles. One has still a C=N double bond similar to the situation in compounds **1** and **2** as generated in a single hydroalumination step. The second ring is completely saturated and results from twofold hydroalumination as originally intended. The first heterocycle is planar and has quite different C–N bond lengths of 128.6 (N2–C3) and 150.5 pm (N1–C1) corresponding to the different bond orders, while the second one adopts a twist conformation with both C–N bond lengths in the range characteristic of single bonds (N3–C4, 145.1 pm; N4–C6, 151.3 pm). The small difference is caused by the different coordination numbers of three and four at the nitrogen atoms N4 and N3, respectively. These heterocycles are bridged by three diethylaluminum groups. Two metal atoms (Al2 and Al3) bridge the C_3N_2 rings in a manner similar to that in compound **1** to give a six-membered Al_2N_4 ring in a *twist*-conformation. The third aluminum atom (Al1) bridges this ring to give a bicyclic, norbornane-like molecular structure. All aluminum atoms have a coordination number of four. The Al–N distances differ markedly. The shortest distance (185.7 pm) occurs between Al3 and the negatively charged, tricoordinated nitrogen atom N3 (sum of the angles 359.2°). The distance between the sp^2-hybridized imino nitrogen atom N2 (sum of the angles 359.6°), and Al2 (200.0 pm) is considerably longer. All other Al–N bond lengths between tetracoordinated aluminum and nitrogen atoms are in the range of 193.5 to 201.8 pm. The ring hydrogen atoms, which have resulted from the hydroalumination of the C=N bonds, are on the same side of the heterocyclic ring system and opposite to the $AlEt_2$ group bridging the central Al_2N_4 ring.

The results of the NMR spectroscopic characterization are in complete agreement with the solid-state molecular structure and the different degrees of hydroalumination of the pyrazole rings. However, very complicated spectra result in accordance with the molecular symmetry. The ethyl substituents gave broad multiplets in the ^{1}H NMR spectrum between $\delta = -0.14$ and +0.58 for their CH_2 and between $\delta =$ 1.36 and 1.46 for their CH_3 groups which could not be resolved and assigned to particular positions in the molecule. However, in the ^{13}C NMR spectrum the expected six resonances of the ethyl CH_3 groups were observed in the narrow range between $\delta = 10.4$ and 10.9. Three doublets were identified in the ^{1}H NMR spectrum for the methyl groups attached to the C(H) atoms of the C_3N_2 heterocycles (C1, C4 and C6, according to Fig. 2). Four singlets resulted for the chemically different methyl groups at the carbon atoms C2 and C5, and three quartets with equal intensity are characteristic of the hydrogen atoms attached to C1, C4 and C6. A resonance at $\delta = 175.8$ (C3) in the ^{13}C NMR spectrum is indicative of the remaining N=C double bond, while the sp^3-hybridized carbon atoms in the C_3N_2 rings which were generated by hydroalumination (C1, C4, C6) have resonances at $\delta = 63.4$, 64.2 and 64.7.

Compound **3** is formally formed by the reaction of the starting compounds in a molar ratio of 3 : 2 (aluminum hydride *versus* pyrazole). However, when the reaction is conducted with exactly this stoichiometric ratio at r. t. the resonances of **3** could not be detected in the NMR spectra. Heating in toluene for several days is required to form **3** under these conditions. Complete hydroalumination of all C=N double bonds was not achieved when the solutions were stirred for longer periods or heated under reflux (111 °C). Even a large excess of the hydride (up to a ratio of 9 : 1) yielded compound **3** as the only product.

Reaction of 3,5-diphenylpyrazole with $(Me_3C)_2$Al-H

Hydrogen atoms bonded to a pyrazole ring can be redistributed to produce a tautomeric form which contains an N-H group and a C=C beside a C=N double bond. The N-H function is relatively acidic, and treatment with dialkylaluminum hydride therefore may not result in hydroalumination as described before,



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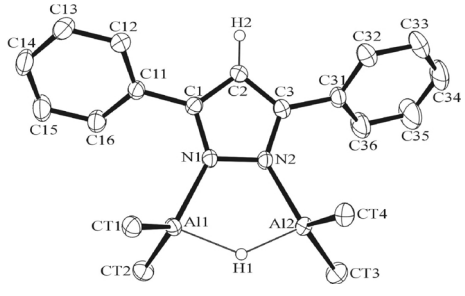

Fig. 3. Molecular structure of **4**. The ellipsoids are drawn at the 40 % probability level; methyl groups and phenyl hydrogen atoms are omitted. Selected bond lengths (pm) and angles (deg): Al1–N1 195.1(2), Al2–N2 195.3(2), Al1–H1 177(2), Al2–H1 169(2), N1–N2 138.3(2), N1–C1 135.1(3), N2–C3 135.1(3), C1–C2 138.6(3), C2–C3 138.3(3); Al1–N1–N2 117.5(1), Al2–N2–N1 116.2(1).

but lead to deprotonation and release of hydrogen. We observed such a reaction when we treated 3,5-diphenylpyrazole with di(*tert*-butyl)aluminum hydride (Eq. 4). Complete consumption of the starting compounds was only observed for a molar ratio of 2 : 1 (hydride *versus* pyrazole). Colorless crystals of the product (**4**) were isolated after concentration of the reaction mixture and cooling to −15 °C in 60 % yield. The molecular structure of compound **4** (Fig. 3) consists of two aluminum atoms which have two terminal *tert*-butyl substituents and are bridged by a pyrazole ring and a hydrogen atom *via* a 3c-2e Al–H–Al bridge. **4** is clearly formed by hydrogen release and coordination of a second molecule of the starting hydride. Each nitrogen atom of the pyrazole ring is coordinated to an aluminum atom with almost indistinguishable Al–N distances of 195.1(2) and 195.3(2) pm. The complete delocalization of the π electron density and the aromatic character of the pyrazole ring is evident from the quite similar C–N [C1–N1 and C3–N2 135.1(3) pm], N–N [138.3(2) pm] and C–C bond lengths [C1–C2 138.6(3) and C2–C3 138.3(3) pm] [15]. The Al_2N_2H ring is almost ideally planar with a maximum deviation of an atom from the average plane of only 6 pm. The normals of both heterocycles enclose an angle of 17.4°. The benzene rings are tilted with respect to the pyrazole plane by 41.1 and 48.4°. All NMR data are in complete agreement with the solid-state molecular structure, and no detailed discussion is required. A similar compound has been obtained previously by the corresponding reaction with diisobutylaluminum hydride [16]. Its constitution analogous to that of **4** was not established by crystal structure determination, but by NMR spectroscopy and structures of secondary products.

Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-pentane and *n*-hexane over $LiAlH_4$, toluene over Na/benzophenone). Tetramethylpyrazole [17], 3,5-diphenylpyrazole [18], di(*tert*-butyl)- [19] and diethylaluminum hydride [20] were obtained according to literature procedures.

Reaction of tetramethylpyrazole with di(tert-butyl)aluminum hydride in a molar ratio of 1 : 1; synthesis of ***1***

$(Me_3C)_2AlH$ (0.200 g, 1.41 mmol), dissolved in 20 mL of *n*-pentane was added to a solution of tetramethylpyrazole (0.175 g, 1.41 mmol) in 20 mL of toluene at r. t. The color changed from yellow to orange red. The solution was stirred at r. t. for 18 h and concentrated. Colorless crystals of **1** precipitated upon cooling to +3 °C. Yield: 0.126 g (34 %). – M. p. (under argon, sealed capillary): 220 °C (dec.). – IR (paraffin; CsBr plates): ν = 1580 m, 1560 m ν(C=N); 1462 vs, 1377 vs (paraffin); 1314 m, 1287 w $\delta(CH_3)$; 1163 m, 1059 s, 1042 s, 1016 m, 997 m, 949 s, 928 m, 806 s ν(CC), ν(CN); 723 s (paraffin); 687 m, 629 w, 611 m, 581 m, 563 m, 542 m, 476 cm^{-1} s ν(AlC), ν(AlN), δ(CC). – ^{1}H NMR (400 MHz, C_6D_6): d = 3.86 (q, $^3J_{H\text{-}H}$ = 6.6 Hz, 2H, NCH), 1.70 (s, 6H, N=C-CH_3), 1.40 and 1.11 (each s, 18H, CMe_3), 1.09 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H, N-CH-CH_3), 1.03 and 0.73 (each s, 6H, CMe_2). – ^{13}C NMR (100 MHz, C_6D_6): δ = 159.0 (N=C), 65.2 (N-C), 49.3 (CMe_2), 33.0 and 32.0 (CMe_3), 25.2 and 19.5 (CMe_2), 19.1 (N-CH-CH_3), 17.2 and 15.7 (CMe_3), 13.5 (N=C-CH_3). – MS (EI, 20 eV, 70 °C): *m/z* (%) = 475 (100), 476 (30) $[M–t\text{Bu–butene}]^+$.

Reaction of tetramethylpyrazole with di(tert-butyl)aluminum hydride in a molar ratio of 1 : 2; synthesis of ***2***

$(Me_3C)_2AlH$ (0.444 g, 3.13 mmol), dissolved in 20 mL of *n*-pentane, was added to a solution of tetramethylpyrazole (0.194 g, 1.56 mmol) in 20 mL of toluene at r. t. The color changed from yellow to deep red. The solution was stirred at +50 °C for 12 h. Yellow crystals of **2** precipitated after concentration and cooling to +3 °C. Yield: 0.457 g (72 %). – M. p. (under argon, sealed capillary): 143 °C. – IR (paraffin; CsBr plates): ν = 1585 m ν(C=N); 1458 vs, 1377 vs (paraffin); 1323 m, 1310 m, 1271 w $\delta(CH_3)$; 1169 s, 1144 m, 1103 m, 1076 s, 1061 s, 1030 m, 1016 m, 1001 s, 951 s, 935 s, 841 w, 812 vs, 779 w ν(CC), ν(CN); 723 vs (paraffin); 708 vs, 615 m, 575 w, 540 w, 495 w, 457 cm^{-1} s ν(AlC), ν(AlN), δ(CC). – ^{1}H NMR (400 MHz, C_6D_6): δ = 3.43 (qq, $^3J_{H\text{-}H}$ = 6.7 Hz, $^5J_{H\text{-}H}$ = 1.0 Hz, 1H, NCH), 2.97 (s, br., 1H, AlH), 1.49 (d, $^5J_{H\text{-}H}$ = 1.0 Hz, 3H, N=C-CH_3), 1.28, 1.26, 1.183 and 1.177 (each s, 9H, CMe_3), 0.98 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 3H, N-CH-C*H*$_3$), 0.63 and 0.48 (each s, 3H, CMe_2). – ^{13}C NMR (100 MHz, C_6D_6): δ = 155.9 (N=C), 66.6 (N-C), 50.0 (*C*Me_2), 32.0, 31.7, 31.3 and 31.2 (C*Me*$_3$), 22.9 and 15.7 (C*Me*$_2$), 17.3, 16.3 and 15.6 (two resonances coincide) (*C*Me_3), 12.7 (N-CH-*C*H_3), 12.4 (N=C-*C*H_3). – MS (EI, 20 eV, 30 °C): *m/z* (%) = 351 (100), 352 (22) [M–*t*Bu]$^+$.

Reaction of tetramethylpyrazole with diethylaluminum hydride in a molar ratio of 1 : 2; synthesis of ***3***

Et_2AlH (0.5 mL, 0.400 g, 4.65 mmol), dissolved in 10 mL of *n*-pentane, was added to a solution of tetramethylpyrazole (0.285 g, 2.30 mmol) in 20 mL of toluene at r. t. The color changed from yellow to deep red. The solution was stirred at r. t. for 12 h. Yellow crystals of **2** precipitated after concentration and cooling to +3 °C. Yield: 0.387 g (67 %). – M. p. (under argon, sealed capillary): 186 °C. – IR (paraffin; CsBr plates): ν = 1556 m ν(C=N); 1460 vs, 1377 vs (paraffin); 1304 m $\delta(CH_3)$; 1192 m, 1109 m, 1088 w, 1026 w, 986 m, 955 m, 918 m, 891 m, 773 m ν(CC), ν(CN); 721 s (paraffin); 689 m, 642 s, 573 w, 548 w cm^{-1} s ν(AlC), ν(AlN), δ(CC). – ^{1}H NMR (400 MHz, C_6D_6): δ = 3.36 (q, $^3J_{H\text{-}H}$ = 6.8 Hz, 1H, NCH of the unsaturated ring), 3.150 (q, $^3J_{H\text{-}H}$ = 6.6 Hz, 1H, NCH of the saturated ring), 3.146 (q, $^3J_{H\text{-}H}$ = 6.4 Hz, 1H, NCH of the saturated ring), 1.53 (s, 3H, N=C-CH_3), 1.46 to 1.36 (m, 18H, CH_3 of ethyl), 1.18 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 3H, N-CH-C*H*$_3$ of the saturated ring), 1.14 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 3H, N-CH-C*H*$_3$ of the saturated ring), 1.06 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 3H, N-CH-C*H*$_3$ of the unsaturated ring), 0.77 and 0.71 (each s, 3H, CMe_2 of the saturated ring), 0.55 and 0.50 (each s, 3H, CMe_2 of the unsaturated ring), 0.58 to −0.14 (m, 12H, CH_2 of ethyl). – ^{13}C NMR (100 MHz, C_6D_6): δ = 175.8 (N=C), 64.2 and 64.7 (N-C of the saturated ring), 63.4 (N-C of the unsaturated ring), 53.5 (*C*Me_2 of the unsaturated ring), 46.2 (*C*Me_2 of the saturated ring), 25.0 and 18.5 (C*Me*$_2$ of the unsaturated ring), 23.8 and 14.8 (C*Me*$_2$ of the saturated ring), 14.9 and 14.8 (N-CH-*C*H_3 of the saturated ring), 14.6 (N-CH-*C*H_3 of the unsaturated ring), 12.8 (N=C-*C*H_3), 10.92, 10.88, 10.63, 10.53, 10.40 and 10.39 (CH_3 of ethyl), 3.6, 2.7, 1.9 and 0.2 (broad resonances of $AlCH_2$). – MS (EI, 20 eV, 60 °C): *m/z* (%) = 506 (3) [M]$^+$, 477 (67), 478 (16) [M–Et]$^+$, 391 (43) [M–EtH–$AlEt_2$]$^+$.

Table 1. Crystal data, data collection, and structure refinement.

	1·toluene	**3**	**4**
Crystal data			
Empirical formula	$C_{37}H_{70}Al_2N_4$	$C_{26}H_{57}Al_3N_4$	$C_{31}H_{48}Al_2N_2$
M_r	624.93	506.70	502.67
Crystal system	— monoclinic —		
Space group [22]	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, pm	1206.32(5)	1006.67(3)	902.00(6)
b, pm	2231.1(1)	1748.18(6)	4565.8(3)
c, pm	1456.69(6)	1764.62(6)	819.76(4)
β, deg	95.112(3)	95.600(1)	113.228(4)
V, $\times 10^{-30}$ m^3	3905.0(3)	3090.6(2)	3102.4(3)
ρ_{calc}, g cm^{-3}	1.06	1.09	1.08
Z	4	4	4
F(000), e	1384	1120	1096
μ, mm^{-1}	0.9 (CuK_α)	0.1 (MoK_α)	1.0 (CuK_α)
Data collection			
T, K	153(2)	153(2)	153(2)
Radiation	CuK_α	MoK_α	CuK_α
Unique reflections	7345	7079	5841
Reflections $I \geq 2\sigma(I)$	5743	5479	4701
Refinement			
Refined parameters	411	332	332
Final R $[I \geq 2\sigma(I)]$[a]	0.062	0.064	0.056
Final $wR2$[b] (all data)	0.176	0.181	0.144
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	0.92 / −0.34	1.08 / −0.65	0.46 / −0.26

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program.

Reaction of 3,5-diphenylpyrazole with di(tert-butyl)-aluminum hydride; synthesis of ***4***

$(Me_3C)_2AlH$ (0.482 g, 3.39 mmol), dissolved in 10 mL of *n*-hexane, was added to a suspension of 3,5-diphenylpyrazole (0.373 g, 1.69 mmol) in 20 mL of toluene at −30 °C. The solid dissolved readily, and a clear, yellow solution resulted. The solution was warmed to r. t. over a period of 12 h. Colorless crystals of **4** precipitated after concentration and cooling to −15 °C. Yield: 0.513 g (60 %). – M. p. (under argon, sealed capillary): 134 °C. – IR (paraffin; CsBr plates): ν = 1558 w, 1543 m phenyl, pyrazole; 1462 vs, 1377 s (paraffin); 1300 w, 1275 w $\delta(CH_3)$; 1182 w, 1157 w, 1098 m, 1069 m, 1003 m, 972 w, 934 w, 916 w, 812 m, 758 s ν(CC), ν(CN); 723 w (paraffin); 698 s phenyl; 671 w, 579

w, 556 w, 451 cm^{-1} m ν(AlC), ν(AlN), δ(CC). – ^{1}H NMR (400 MHz, C_6D_6): δ = 7.48 (m, 4H, *ortho*-H of phenyl), 7.16 (m, 4H, *meta*-H of phenyl), 7.09 (m, 2H, *para*-H of phenyl), 6.35 (s, 1H, pyrazole), 3.41 (s, br., 1H, AlHAl), 1.17 (s, 36H, CMe_3). – ^{13}C NMR (100 MHz, C_6D_6): δ = 156.1 (NC of pyrazole), 131.4 (*ipso*-C of phenyl), 130.1 (*para*-C of phenyl), 129.6 (*meta*-C of phenyl), 127.8 (*ortho*-C of phenyl), 106.9 (CH of pyrazole), 31.2 (CMe_3), 16.8 (CMe_3). – MS (EI, 20 eV, 30 °C): *m/z* (%) = 445 (100), 446 (29) $[M–tBu]^+$.

Crystal structure determinations

Single crystals were obtained upon cooling of the reaction mixtures as described above. Data collections were performed on Bruker SMART APEX-II (MoK_α radiation) and Bruker SMART 6000 (CuK_α radiation) diffractometers. The structures were solved by Direct Methods and refined by full-matrix least-squares calculations based on F^2 [21]. Hydrogen atoms with the exception of Al-H were calculated on ideal positions and refined by the riding model. Crystal data, data collection parameters and details of the structure refinement are given in Table 1. The crystals of **1** enclosed a molecule of toluene per formula unit of the tricyclic compound. The methyl group of an ethyl substitutent (C60) of **3** was disordered over three positions; the atoms were refined with occupation factors of 0.33.

CCDC 767773 (**1**), 767772 (**3**) and 767774 (**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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