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N- Versus *P*-Coordination in Bis(amino)cyclodiphosph(III)azane Complexes of Aluminum

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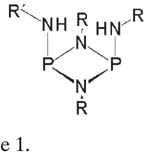
Abstract: The reaction of the bis(amino)cyclodiphosph(III)azane, *cis*-{(tBuNH)$_2$(PNtBu)$_2$}, with $\mathrm{AlMe_3}$, $\mathrm{AlClMe_2}$, $\mathrm{AlCl_2Me}$, and $\mathrm{AlCl_3}$ is reported. The less Lewis acidic compound $\mathrm{AlMe_3}$ forms the adduct *cis*-[(tBuNH)$_2$(PNtBu){P(·$\mathrm{AlMe_3}$)NtBu}] (**1**), in which the aluminum atom is exclusively coordinated to one phosphorus atom. At elevated temperatures $\mathrm{AlMe_3}$ undergoes migratory exchange between the two phosphorus atoms, but no methane elimination is observed. By using the more Lewis acidic compound $\mathrm{AlClMe_2}$ the *P*-coordinated compound *cis*-[(tBuNH)$_2$(PNtBu){P(·$\mathrm{AlClMe_2}$)NtBu}] (**2**) can be obtained at low temperatures. Compound **2** rearranges irreversibly to a product in which the $\mathrm{AlClMe_2}$ group is coordinated by one exo-cyclic nitrogen atom. A concomitant 1,2-H shift from this nitrogen atom onto the phosphorus atom is observed. The *N*-coordinated rearrangement product slowly decomposes via a P–N bond cleavage in solution. Reaction of the even more Lewis acidic compounds $\mathrm{AlCl_2Me}$ and $\mathrm{AlCl_3}$ finally led to stable adducts, *cis*-[(tBuNH)(PNtBu)(tBuN·$\mathrm{AlCl_2Me}$){P(H)NtBu}] (**3**), and *cis*-[(tBuNH)(PNtBu)(tBuN·$\mathrm{AlCl_3}$){P(H)NtBu}] (**4**), in which the aluminum atoms are *N*-coordinated by a tBuN=PH unit.

Keywords: aluminum · cage compounds · chelates · N,P ligands

Introduction

Organoaluminum compounds have attracted much attention owing to their applications that include organic syntheses, industrial catalytic methods, and chemical vapor deposition (CVD) processes.[1] Aluminum alkyls are employed as activators of group 4 complexes in Ziegler–Natta catalysis or related systems and are known to act themselves as ethylene oligomerization and polymerization catalysts.[2] Recently several aluminum compounds, which include bidentate, monoanionic, and nitrogen-based ligands, such as amidinates,[3] guanidinates,[4] aminotroponiminates,[5,6] diiminophosphinates[7] and β-diiminates (β-diketiminates) were reported.[8] Some of these ligands were used to stabilize the low oxidation states of aluminum[8,9] and aluminum cations. These cations that have weak counterion interactions, were used for catalytic olefin polymerization.[3,4,5,10] Bidentate, dianionic nitrogen-based ligands derived from diamines and triamines were used in aluminum chemistry to form Lewis acidic catalysts.[11,12,13,14]

In this context we were attracted by the bis(amino)cyclodiphosph(III)azanes (Scheme 1), which are known to act as dinegative chelating N-donor ligands. Cyclodiphosph(III)azanes have been known for more then a century,[15] but were only fully characterized in the 1970s.[16,17] Their preparation is usually based on the reaction of *cis*-(ClPNtBu)$_2$ with an excess of a free amine.[18,19] Today, cyclodiphosph(III)azanes are well established as anionic *N*-donor ligands in main group[19,20] and early transition metal chemistry.[21,22] Group 4 compounds of this ligand have shown high activity in the polymerization of ethylene in the presence of methylaluminoxane (MAO).[21d,e]



Scheme 1.

Whereas the coordination of aluminum alkyls to other P–N compounds is well estab-

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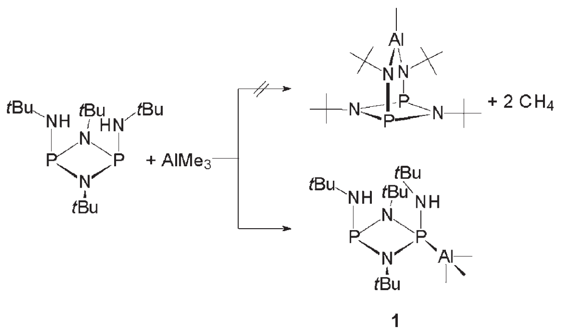
lished,[23,24,25] there are few reports about cyclodiphosph(III)azane aluminum chlorides, and none for aluminum alkyls.[20] The first bis(amido)cyclodiphosph(III)azane complex of aluminum, $[(Me_3SiN)_2(PNSiMe_3)_2AlCl_2]^-$, is the product of a condensation reaction between a zwitterionic diazaphosphoniaaluminatacyclobutane and $(Me_3Si)_2NPNSiMe_3$.[26] The neutral aluminum compounds *cis*-$[(t\mathrm{BuN})_2(\mathrm{PN}t\mathrm{Bu})_2\mathrm{AlCl}]$ and *cis*-$[(\mathrm{PhN})_2(\mathrm{PN}t\mathrm{Bu})_2\mathrm{AlCl}]$ were obtained by means of a metathesis reaction of $AlCl_3$ with the corresponding lithium salts *cis*-$[(t\mathrm{BuNLi{\cdot}THF})_2(\mathrm{PN}t\mathrm{Bu})_2]$ and *cis*-$[(\mathrm{PhNLi{\cdot}THF})_2(\mathrm{PN}t\mathrm{Bu})_2]$, respectively.[20] In contrast the oxidized cyclodiphosph(V)azane compounds *cis*-$[(t\mathrm{BuNH})_2\{\mathrm{P(E)N}t\mathrm{Bu}\}_2]$ (E = O, S, Se) react with 2 equivalents of $AlMe_3$ to afford, through methane elimination, the bis(dimethylaluminum) complexes *cis*-$[\{(t\mathrm{BuNAlMe_2})_2\{\mathrm{P(E)N}t\mathrm{Bu}\}_2\}]$, in which the aluminum atoms are coordinated through an E-P-N-heteroallylic moiety onto the cyclodiphosph(V)azane backbone.[27]

In this contribution we report a systematic study of the reaction of bis(amino)cyclodiphosph(III)azanes with $AlMe_3$, $AlClMe_2$, $AlCl_2Me$, and $AlCl_3$. In dependence on the Lewis acidity, the aluminum compound we observe has either *P* or *N*-coordination and no methane elimination occurs.

Results and Discussion

Our original intention in aluminum chemistry was the synthesis of a methyl aluminum cyclodiphosph(III)azane complex of composition *cis*-$[(t\mathrm{BuN})_2(\mathrm{PN}t\mathrm{Bu})_2\mathrm{AlMe}]$ (Scheme 2).



Scheme 2.

To obtain this product we treated the *t*butyl substituted *cis*-bis(amino)cyclodiphosph(III)azane, *cis*-$\{(t\mathrm{BuNH})_2(\mathrm{PN}t\mathrm{Bu})_2\}$,[19] in a 1:1 molar ratio with $AlMe_3$ in toluene. To our surprise, even at elevated temperatures we did not observe methane elimination, and the desired complex was not obtained. Instead, a Lewis acid base adduct of composition *cis*-$[(t\mathrm{BuNH})_2(\mathrm{PN}t\mathrm{Bu})\{\mathrm{P}({\cdot}\mathrm{AlMe_3})\mathrm{N}t\mathrm{Bu}\}]$ (**1**), in which the aluminum atom binds to one phosphorus atom, was isolated (Scheme 2). Increasing the amount of $AlMe_3$ did not yield a bimetallic complex of composition *cis*-$[(t\mathrm{BuNH})_2\{\mathrm{P}({\cdot}\mathrm{AlMe_3})\mathrm{N}t\mathrm{Bu}\}_2]$. Complex **1** has been characterized by using standard analytical/spectroscopic techniques and the solid-state structure was established by using single crystal X-ray diffraction (Figure 1).

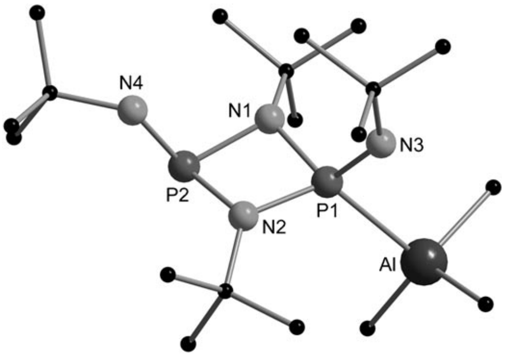
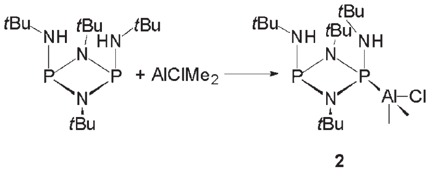


Figure 1. Solid-state structure of **1** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [pm] or angles [°]: Al–P1 252.01(9), P1–N1 169.5(2), P1–N2 169.0(2), P2–N1 174.6(2), P2–N2 174.6(2), P1–N3 165.2(2), P2–N4 165.0(2), Al–P1–N3 100.40(8), N1–P1–N2 82.57(9), N1–P2–N2 79.56(8), N3–P1–N1 113.42(10), N3–P1–N2 114.23(11), N4–P2–N1 106.06(11), N4–P2–N2 105.38(11).

Compound **1** crystallizes in the monoclinic space group $P2_1$ and has two molecules in the unit cell. The structure clearly shows that the aluminum atom is coordinated by the phosphorus atom. Even though there are some P–Al Lewis acid base adducts known,[28] the coordination of aluminum to the softer phosphorus atom in P–N compounds is rare,[24,25] and to the best of our knowledge, the coordination of aluminum to a phosphorus atom in a protic P–N–H compound is unknown. In contrast to the starting material *cis*-$\{(t\mathrm{BuNH})_2(\mathrm{PN}t\mathrm{Bu})_2\}$,[19] an endo/exo arrangement of the N*t*Bu groups is observed in the solid state. This arrangement is most probably a result of the steric repulsion of the *t*Bu group and the coordinated Me_3Al. A similar arrangement is observed in *cis*-$\{(\mathrm{Ph_2CHNH})_2(\mathrm{PN}t\mathrm{Bu})_2\}$[29] and in the phosphorus(V) compound *cis*-$[(t\mathrm{BuNH})_2\{\mathrm{P(S)N}t\mathrm{Bu}\}_2]$.[30] The P1–Al bond length is in the expected range (252.01(9) pm); for example, 251.90(11) pm in $\mathrm{Me_3AlPPh_2(NP}i\mathrm{Pr_3)}$).[24] The P–N distances of the N*t*Bu groups exocyclic to the $(PN)_2$ heterocycle are in the range of the starting material (P1–N3 165.2(2) pm, and P2–N4 165.0(2) pm versus 166.4(2) pm in *cis*-$\{(t\mathrm{BuNH})_2(\mathrm{PN}t\mathrm{Bu})_2\}$).[19] As a result of the $AlMe_3$ coordination the heterocycle is distorted. The P1–N1 (169.5(2) pm) and P1–N2 (169.0(2) pm) distances are shorter then the corresponding P2–N1 (174.6(2) pm) and P2–N2 (174.6(2) pm) bond lengths.

In solution, compound **1** shows a dynamic behavior at room temperature. Thus, two broad signals are observed in the $^{31}P\{^1H\}$ NMR spectrum. The signal at $\delta = 88.6$ ppm is close to the one observed in the starting material *cis*-$\{(t\mathrm{BuNH})_2(\mathrm{PN}t\mathrm{Bu})_2\}$[19] ($\delta = 88.5$ ppm) and can be assigned to the non-coordinating phosphorus atom, whereas the high field shifted signal at $\delta = 62.7$ ppm is the resonance of the P–Al function. The dynamic process can be interpreted as a move of the $AlMe_3$ molecule between the two phosphorus atoms of the heterocycle. To study the dynamic behavior, the variable temperature $^{31}P\{H\}$ NMR spectra of **1** were recorded in $[D_8]$toluene. In accordance with the solid state structure at low temperature, (223 K) two sharp signals for the phosphorus atoms are observed. These signals start to coalesce on increasing the temperature, to reveal a coalescence temperature of about $T_c = 309$ K. At higher temperatures (up from 323 K) the signals appear as broad singlets. The coalescence temperature ($T_c = 309$ K) and the separation ($\Delta\nu = 4640.5\ \mathrm{s}^{-1}$, 161.70 MHz NMR) of the two coalescing signals were used to calculate the free energy for the exchange of $AlMe_3$ between the two phosphorus atoms to be $\Delta G_{Tc}^{\neq} = 52.03 \pm 0.8\ \mathrm{kJ\,mol^{-1}}$.[31] The whole process is reversible. Thus, even in boiling toluene no methane elimination and no *N*-coordination was observed.

To further investigate the coordination behavior of aluminum alkyls we increased the Lewis acidity of the aluminum atom by substituting, in a stepwise fashion, the methyl groups on the aluminum center by chlorine atoms.[32] Thus, we treated *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} in a 1:1 molar ratio with $AlClMe_2$ in toluene. At low temperature we obtained *cis*-[(*t*BuNH)$_2$(PN*t*Bu){P(•AlClMe$_2$)N*t*Bu}] (**2**) (Scheme 3), which is analogous to compound **1**. Thus, the aluminum atom is coordinated by one phosphorus atom. The solid state structures of compounds **1** and **2**, including the metrics of the unit cell, are almost identical. Accordingly, compound **2** also crystallizes in the monoclinic space group $P2_1$ and has two molecules in the unit cell (Figure 2). Again, an endo/exo arrangement of the N*t*Bu groups of the P_2N_2 heterocycle is observed in the solid state. As a result of the increased Lewis acidity, the P1–Al bond length of compound **2** (Al–P1 247.74(13) pm) is significantly shorter than observed in compound **1** (252.01(9) pm). The geometry of the P_2N_2 heterocycle is distorted again and the metrics within the heterocycle vary only slightly from those observed in **1**.



Scheme 3.

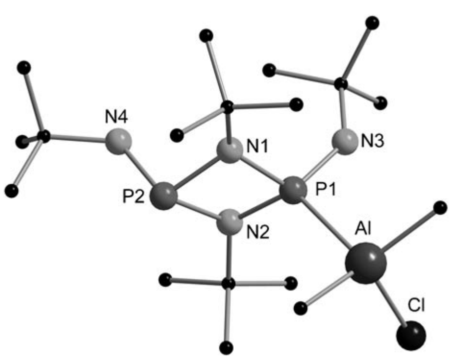
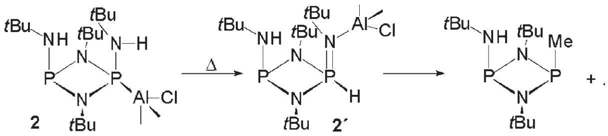


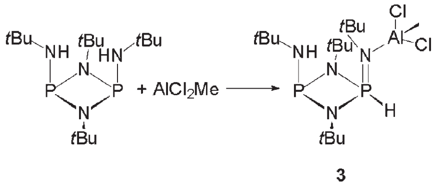
Figure 2. Solid-state structure of **2** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [pm] or angles [°]: Al–P1 247.74(13), P1–N1 167.9(3), P1–N2 169.0(3), P2–N1 173.6(3), P2–N2 174.8(3), P1–N3 164.0(3), P2–N4 165.3(3), Al-P1-N3 105.30(12), N1-P1-N2 82.70(13), N1-P2-N2 79.43(13), N3-P1-N1 115.54(15), N3-P1-N2 114.11(14), N4-P2-N1 106.01(14), N4-P2-N2 106.87(14).

Complex **2** has also been characterized by using NMR techniques. At room temperature we observed two processes. Firstly, as seen previously for complex **1**, two broad signals are observed in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 49.2$ and 88.1 ppm, which again can be interpreted as a shifting of the $AlClMe_2$ between the two phosphorus atoms of the heterocycle. The second process is an irreversible shifting of the $AlClMe_2$ group onto one exo-cyclic nitrogen atom concomitant with a 1,2-H shift from this nitrogen atom onto the phosphorus atom (Scheme 4). Similar H-shifts have been observed previously on a P–N backbone.[23] Single crystals of the rearrangement product could be obtained, but the single crystal X-ray structure could not be fully refined. Based on the $^{31}P\{^1H\}$ NMR spectra we suggest that the rearrangement product is *cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN•AlClMe$_2$){P(H)N*t*Bu}] (**2′**) (Scheme 4). This suggestion is consistent with the data we could extract from the single crystal X-ray structure. *cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN•AlClMe$_2$){P(H)N*t*Bu}] rapidly decomposes to a number of products. Within this decomposition process the *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} ligand is partly destroyed. As one of the first decomposition products the P-methylated species *cis*-{(*t*BuNH)(Me)(PN*t*Bu)$_2$} could be identified by using NMR techniques (Scheme 4).



Scheme 4.

In contrast to the examples described above, reaction of the more Lewis acidic $AlCl_2Me$ with *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} in a 1:1 molar ratio in toluene results in the *N*-coordinated product *cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN•AlCl$_2$Me){P(H)N*t*Bu}] (**3**) (Scheme 5), which is the analogue of the first rearrangement product **2′** of complex **2**. Thus, the $AlCl_2Me$ molecule binds onto one exo-cyclic nitrogen atom of a rearranged *t*BuN=PH unit. Complex **3** was characterized after analysis of the ^1H and $^{31}P\{^1H\}$ NMR spectra and by using elemental analysis. The solid-state structure of **3** was established by using single crystal X-ray diffraction



Scheme 5.

(Figure 3). The ^{1}H NMR spectrum of compound **3** shows the expected sharp singlet for the Al–CH_3 group at $\delta = 0.30$ ppm. The signal on the *t*butyl group, which is attached to N3 ($\delta = 0.91$ ppm) is, as a result of the coupling to P1, split into a doublet ($^{4}J_{(\mathrm{P,H})} = 1.6$ Hz). The corresponding signal of the *t*butyl group at N4 is a singlet at $\delta = 1.50$ ppm. The signal of the P–H group is observed at $\delta = 8.18$ ppm, and has a coupling constant of $^{1}J_{(\mathrm{P,H})} = 613$ Hz. Two signals are observed in the ^{31}P{^{1}H} NMR spectrum at $\delta = 6.8$ and 76.2 ppm. The signal at high field is assigned to the P–H group, which is consistent with compounds reported earlier, $[(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{P(H)N(H)Al(Me)}_3]$ ($\delta = 13.7$ ppm)[23a] and $[(\mathrm{Cy}_2\mathrm{N})_2\mathrm{P(H)N(H)Al}(t\mathrm{Bu})_3]$ ($\delta = 15.9$ ppm).[23b]

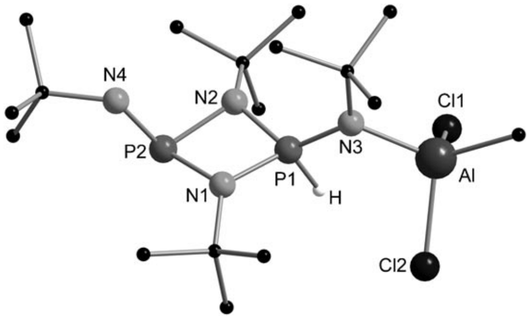
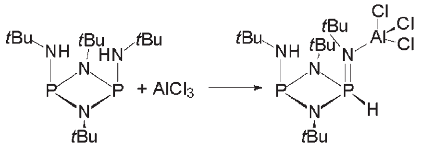


Figure 3. Solid-state structure of **3** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [pm] or angles [°]: Al–N3 192.6(2), P1–N1 165.3(2), P1–N2 165.2(2), P2–N1 176.3(2), P2–N2 176.2(2), P1–N3 159.5(2), P2–N4 164.4(2), Al-N3-P1 114.74(10), N1-P1-N2 85.92(11), N1-P2-N2 79.45(10), N3-P1-N1 123.40(10), N3-P1-N2 124.53(11), N4-P2-N1 105.82(11), N4-P2-N2 106.49(11).

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ and has four molecules in the unit cell. The solid state structure (Figure 3) is consistent with the NMR data. An $AlCl_2Me$ molecule is attached to N3. The Al–N3 bond length is in the expected range of 192.8(2) pm, consistent with comparable complexes such as $[(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{P(H)N(H)Al(Me)}_3]$ (192.8(6) pm)[23a] and $[(\mathrm{Cy}_2\mathrm{N})_2\mathrm{P(H)N(H)AlMe}_3]$ 194.1(2) pm.[23b] As a result of the partial P=N double bond the P1–N3 distance of 159.4(3) pm is shorter than the corresponding P2–N4 bond length of 164.4(2) pm. As observed for compounds **1** and **2**, the P_2N_2 heterocycle is distorted. Within this cycle the P1–N1 (165.3(2) pm) and P1–N2 bond (165.2(2) pm) distances are shorter than P2–N1 (176.3(2) pm) and P2–N2 (176.2(2) pm). The distortion is clearly a result of the of the $AlCl_2Me$ coordination to the heterocycle.

To complete the series, $AlCl_3$ was treated with *cis*-$\{(t\mathrm{BuNH})_2(\mathrm{PN}t\mathrm{Bu})_2\}$ in a 1:1 molar ratio in toluene. Out of the reaction mixture the expected product of composition *cis*-$[(t\mathrm{BuNH})(\mathrm{PN}t\mathrm{Bu})(t\mathrm{BuN}{\cdot}\mathrm{AlCl}_3)\{\mathrm{P(H)N}t\mathrm{Bu}\}]$ (**4**) precipitates as crystalline material in good yield (Scheme 6). Compound **4** is almost insoluble in benzene. As a result of this low solubility no useful NMR data was obtained. Thus, compound **4** was characterized by using elemental analysis and single crystal X-ray crystallography (Figure 4) only. Compound **4** crystallizes in the monoclinic space group $P2_1/n$ and has four molecules in the unit cell. As observed for compounds **1** and **2**, compounds **3** and **4** also show comparable metrics within the crystal lattice. Consistent with the observations described above, the $AlCl_3$ molecule is attached to the exocyclic nitrogen atom of a *t*BuN=PH unit. The Al–N3 bond length of 190.9 (3) pm is slightly shorter than in **3** (192.8(2) pm), which may be a result of the higher Lewis acidity of $AlCl_3$ compared with $AlCl_2Me$. As a result of the $AlCl_3$ coordination, a distortion of the P_2N_2 heterocycle is observed (P1–N1 164.7(3) pm and P1–N2 164.2(3) pm versus P2–N1 176.7(3) pm and P2–N2 176.6(3) pm).



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Scheme 6.

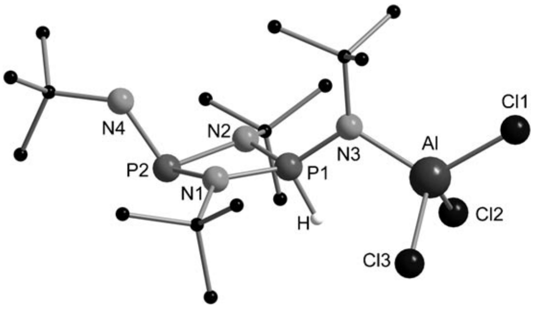

Figure 4. Solid-state structure of **4** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [pm] or angles [°]: Al–N3 190.9(3), P1–N1 164.7(3), P1–N2 164.2(3), P2–N1 176.7(3), P2–N2 176.6(3), P1–N3 160.0(2), P2–N4 164.8(3), Al-N3-P1 113.58(14), N1-P1-N2 86.36(13), N1-P2-N2 79.15(12), N3-P1-N1 124.23(13), N3-P1-N2 123.64(12), N4-P2-N1 106.29(14), N4-P2-N2 106.09(13).

Conclusion

We present a systematic study of the reaction of the bis(amino)cyclodiphosph(III)azanes, *cis*-$\{(t\mathrm{BuNH})_2(\mathrm{PN}t\mathrm{Bu})_2\}$, with $AlMe_3$, $AlClMe_2$, $AlCl_2Me$, and $AlCl_3$. Basically two coordination patterns were observed. The less Lewis acidic compound $AlMe_3$ exclusively coordinates to one phosphorus atom. At elevated temperatures an exchange of $AlMe_3$ between the two phosphorus atoms occurs, but no methane elimination was observed. By using the more Lewis acidic compound $AlClMe_2$ a *P*-coordination was seen at low temperatures and an irreversible rearrangement of the $AlClMe_2$ group onto one exo-cyclic nitrogen atom, concomitant with a 1,2-H shift from this nitrogen atom onto the phosphorus atom was observed. The *N*-coordinated rearrangement product slowly decomposes via a P−N bond cleavage in solution. Use of the increasingly Lewis acidic compounds $AlCl_2Me$ and $AlCl_3$ led to stable *N*-coordinated complexes that contain aluminum atoms coordinated by a rearranged *t*BuN=PH unit.

Experimental Section

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line, or in an argon-filled MBraun glove box. Toluene was distilled under nitrogen from $LiAlH_4$. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft or Euriso-Top (all = 99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded by using a JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and external 85 % phosphoric acid (^{31}P NMR). Elemental analyses were carried out by using an Elementar vario EL. *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$}[19] was prepared according to literature procedures.

***cis*-[(*t*BuNH)$_2$(PN*t*Bu){P(·AlMe$_3$)N*t*Bu}] (1)**: A 0.5 mL aliquot of a solution of $AlMe_3$ (2 M) in toluene was added dropwise to a solution of 0.348 g of *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} (1.0 mmol) in 2 mL of toluene at 0 °C. The mixture then crystallized at −20 °C. Yield: 0.270 g (64 %, colorless crystals); ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): $\delta = -0.16$ (s, 9H; $AlMe_3$), 1.14 (s, 18H; *t*Bu), 1.42 (s, 18H; *t*Bu), 2.96 ppm (br, 2H; NH); $^{31}P\{^1H\}$ NMR (C_6D_6, 161.7 MHz, 20 °C): $\delta = 62.7$ (br), 88.6 ppm (br); elemental analysis calcd (%) for $C_{19}H_{47}AlN_4P_2$ (420.53): C 54.27, H 11.27, N 13.32; found: C 54.03, H 11.27, N 13.53.

***cis*-[(*t*BuNH)$_2$(PN*t*Bu){P(·AlClMe$_2$)N*t*Bu}] (2)**: A 1 mL aliquot of a solution of $AlClMe_2$ (1 M) in hexane was added dropwise to a solution of 0.348 g of *cis*-[(*t*BuNH)$_2$(PN*t*Bu)$_2$] (1.0 mmol) in 2 mL of toluene at 0 °C. The mixture then crystallized at −20 °C. Yield: 0.189 g (43 %, colorless crystals); ^{1}H NMR (C_7D_8, 400 MHz, 20 °C): $\delta = -0.14$ (s, 6H; $AlMe_2Cl$), 1.14 (s, 18H; *t*Bu), 1.39 (s, 18H; *t*Bu), 3.12 ppm (br, 2H; NH); $^{31}P\{^1H\}$ NMR (C_7D_8, 161.7 MHz, 20 °C): $\delta = 49.2$ (br), 88.1 ppm (br); elemental analysis calcd (%) for $C_{18}H_{44}AlClN_4P_2$ (440.95): C 49.03, H 10.06, N 12.71; found: C 48.69, H 10.66, N 12.69.

***cis*-{(*t*BuNH)(Me)(PN*t*Bu)$_2$} (2′)**: ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): $\delta =$ 3.08 (br d, 1H; NH, $^2J_{(P,H)} = 9$ Hz), 1.32 (d, $^2J_{(P,H)} = 6.6$ Hz, 3H; Me), 1.28 (t, $^4J_{(P,H)} = 0.4$ Hz, 18H; *t*Bu), 1.19 ppm (d, $^4J_{(P,H)} = 1.2$ Hz, 9H; *t*Bu); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.61 MHz, 20 °C): $\delta = 54.1$ (P2NC), 51.4 (NHC), 34.1 (d, J(P,C) = 48 Hz, PMe), 32.7 (NHCC3), 31.0 ppm (P2NCC3); ^{31}P NMR (C_6D_6, 161.7 MHz, 20 °C): $\delta = 134.6$ (br, N2P−N), 118.5 ppm (d, ^2J(P,P) = 7.9 Hz, N2PMe); ^{15}N NMR (C_6D_6, 40.56 MHz, 20 °C): $\delta =$ −302.4 (N-ring), −255.4 ppm (NH).

***cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN·AlCl$_2$Me){P(H)N*t*Bu}] (3)**: A 1 mL aliquot of a solution of $AlCl_2Me$ (1 M) in toluene was added dropwise to a solution of 0.348 g of *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} (1.0 mmol) in 2 mL of toluene at 0 °C. The mixture then crystallized at −20 °C. Yield: 0.228 g (49 %, colorless crystals); ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): $\delta = 0.30$ (s, 3H; $AlMeCl_2$), 0.91 (d, $^3J_{(P,H)} = 1.6$ Hz, 9H; *t*Bu), 1.30 (s, 18H; *t*Bu), 1.50 (s, 9H; *t*Bu), 1.65 (s, 1H; NH), 8.18 ppm (dd, $^1J_{(P,H)} = 612$ Hz, $^3J_{(P,H)} =$ 4.18 Hz, 1H; PH); ^{31}P NMR (C_6D_6, 161.7 MHz, 20 °C): $\delta = -6.8$ (d, $^1J_{(P,H)} = 612$ Hz), 76.2 ppm (s); elemental analysis calcd (%) for $C_{17}H_{41}AlCl_2N_4P_2$ (461.37): C 44.26, H 8.96, N 12.14; found: C 43.85, H 8.94, N 12.82.

***cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN·AlCl$_3$){P(H)N*t*Bu}] (4)**: A solution of 0.131 g of *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} (0.37 mmol) in 10 mL of toluene was added dropwise to a solution of 0.050 g of $AlCl_3$ (0.37 mmol) in 10 mL of toluene at 0 °C. The mixture was then crystallized at −20 °C. Yield: 0.092 g (52 %, colorless crystals); elemental analysis calcd (%) for $C_{16}H_{38}AlCl_3N_4P_2$ (481.79): C 39.89, H 7.95, N 11.63; found: C 38.45, H 8.09, N 10.82.

X-ray crystallographic studies of 1, 2, 3 and 4: Crystals of **1**, **2**, **3** and **4** were grown at −20 °C from mother solutions. Crystals of **1**–**4** were obtained from cold toluene. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C N_2 cold stream of a Stoe IPDS 2T diffractometer. Subsequent computations were carried out by means of an Intel Pentium IV PC.

All structures were solved by using direct methods (SHELXS-97[33]). The remaining non-hydrogen atoms were located after successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o\text{-}F_c)^2$, the weight is defined as $4F_0^2/2(F_o^2)$, and F_o and F_c are the observed and calculated structure factor amplitudes by using the program SHELXL-97.[34] Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. CCDC-628159–628162 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.

*Complex **1***: $C_{19}H_{47}AlN_4P_2$, monoclinic, $P2_1$ (no. 4); lattice constants $a =$ 930.26(8), $b = 1625.92(9)$, $c = 964.74(8)$ pm, $\beta = 113.293(6)°$; $V =$ $1340.2(2) \times 10^6$ pm^3, $Z = 2$; $\mu(Mo_{K\alpha}) = 0.309$ mm^{-1}; $\theta_{max} = 25$; 4550 [$R_{int} =$ 0.0273] independent reflections measured, of which 4218 were considered observed with $I > 2\sigma(I)$; max residual electron density 0.248 and −0.233 e A^{-3}; 262 parameters, Flack parameter 0.02(9), $R1$ [$I > 2\sigma(I)$] = 0.0348; w$R2$ (all data) = 0.0836.

*Complex **2***: $C_{18}H_{44}AlClN_4P_2$, monoclinic, $P2_1$ (no. 4); lattice constants $a =$ 903.40(10), $b = 1724.24(12)$, $c = 940.85(10)$ pm, $\beta = 115.795(8)°$; $V =$ $1319.5(2) \times 10^6$ pm^3, $Z = 2$; $\mu(Mo_{K\alpha}) = 0.205$ mm^{-1}; $\theta_{max} = 25$; 4596 [$R_{int} =$ 0.0448] independent reflections measured, of which 3747 were considered observed with $I > 2\sigma(I)$; max residual electron density 0.253 and −0.178 e A^{-3}; 258 parameters, Flack parameter 0.08(9), $R1$ [$I > 2\sigma(I)$] = 0.0428; w$R2$ (all data) = 0.0917.

*Complex **3***: $C_{17}H_{41}AlCl_2N_4P_2$, monoclinic, $P2_1/n$ (no. 14); lattice constants $a = 993.95(7)$, $b = 1917.09(12)$, $c = 1371.00(10)$ pm, $\beta = 94.608(6)°$; $V =$ $2604.0(3) \times 10^6$ pm^3, $Z = 4$; $\mu(Mo_{K\alpha}) = 0.415$ mm^{-1}; $\theta_{max} = 25$; 4549 [$R_{int} =$ 0.0794] independent reflections measured, of which 3570 were considered observed with $I > 2\sigma(I)$; max residual electron density 0.473 and −0.337 e A^{-3}; 256 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0456; w$R2$ (all data) = 0.1245.

*Complex **4***: $C_{16}H_{38}AlCl_3N_4P_2$, monoclinic, $P2_1/n$ (no. 14); lattice constants $a = 995.57(6)$, $b = 1904.1(2)$, $c = 1374.98(8)$ pm, $\beta = 94.590(5)°$; $V =$ $2598.1(3) \times 10^6$ pm^3, $Z = 4$; $\mu(Mo_{K\alpha}) = 0.519$ mm^{-1}; $\theta_{max} = 29$; 6983 [$R_{int} =$ 0.0786] independent reflections measured, of which 4536 were considered observed with $I > 2\sigma(I)$; max residual electron density 0.493 and −1.047 e A^{-3}; 250 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0614; w$R2$ (all data) = 0.1783.

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