DOI: 10.1002/ejic.200800726

New Bis(amino)cyclodiphosph(III)azane Complexes of Aluminum

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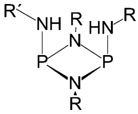
Keywords: Aluminum / Chelates / Cage compounds / N,P ligands

The reaction of the bis(amino)cyclodiphosph(III)azane *cis*-{(tBuNH)$_2$(PNtBu)$_2$} with AlEt$_3$, AlBrEt$_2$, AlBr$_2$Et, and AlBr$_3$ was investigated. The less Lewis acidic compound AlEt$_3$ forms the adduct *cis*-[(tBuNH)$_2$(PNtBu){P(·AlEt$_3$)NtBu}], in which the aluminum atom is exclusively coordinated to one phosphorus atom. No ethane elimination was observed. By using the more Lewis acidic compounds AlBr$_2$Et and AlBr$_3$ the *N*-coordinated complexes *cis*-[(tBuNH)(PNtBu)(tBuN·AlBr$_2$Et){P(H)NtBu}] and *cis*-[(tBuNH)(PNtBu)(tBuN·AlBr$_3$)-{P(H)NtBu}] were obtained, in which the aluminum atoms are *N*-coordinated by a tBuN=PH unit. Upon coordination of the aluminum compounds, a concomitant 1,2-H shift from the nitrogen atom onto the phosphorus atom within the *cis*-{(tBuNH)$_2$(PNtBu)$_2$} ligand was observed.

Introduction

Even though organoaluminum compounds are known for more than a century,[1] it is only since the 1950s that organoaluminum compounds have gained a significant application, triggered by the pioneering work of Karl Ziegler.[2] Today, organoaluminum compounds have attracted much attention due to their applications, including organic syntheses, industrial catalytic methods, and chemical vapor deposition (CVD) processes.[3] Moreover, organoaluminum compounds are used as activators of group 4 complexes in Ziegler–Natta catalysis or related systems and are known to act as ethylene oligomerization and polymerization catalysts.[4] Trialkylaluminum compounds, which usually are dimeric in condensed phase are typical Lewis acids, which combine with donors such as amines, phosphanes, ethers, and thioethers to give tetrahedral tetracoordinated species.[5] The reaction of alkylaluminum compounds with primary and secondary amines gives adducts initially, which can further react to eliminate alkane and to give oligomers that have Al–N–Al units.[5,6]

Recently, we were attracted by the bis(amino)cyclodiphosph(III)azanes as ligands for alkylaluminum compounds (Scheme 1). They are usually prepared by treating *cis*-(ClPNtBu)$_2$ with excess of a free amine[7,8] and have been widely used as dianionic chelating N-donor ligands. Today, cyclodiphosph(III)azanes are well established as anionic *N*-donor ligands in main group[8,9] and early transition metal chemistry.[10,11] Moreover, in group 4 chemistry, compounds of this ligand were used in ethylene polymerization in the presence of MAO.[10d,10e]



Scheme 1.

Whereas the coordination of alkylaluminum compounds to other P–N compounds is well established,[12–14] there were only a few reports about [cyclodiphosph(III)azane]aluminum chlorides in the literature,[15] before we recently reported on the reaction of the bis(amino)cyclodiphosph(III)azane *cis*-{(tBuNH)$_2$(PNtBu)$_2$} with AlMe$_3$, AlClMe$_2$, AlCl$_2$Me, and AlCl$_3$.[16] It was shown by us, that the less Lewis acidic compound AlMe$_3$ forms the adduct *cis*-[(tBuNH)$_2$(PNtBu){P(·AlMe$_3$)NtBu}] (**1**), in which the aluminum atom coordinates to one phosphorus atom (Scheme 2). At elevated temperature, AlMe$_3$ underwent a dynamic exchange between the two phosphorus atoms, but no methane elimination was observed. In contrast, by using the more Lewis acidic compound AlClMe$_2$ the *P*-coordinated compound *cis*-[(tBuNH)$_2$(PNtBu){P(·AlClMe$_2$)-NtBu}] (**2**) was obtained at low temperature (Scheme 2). This complex rearranged irreversibly to a product, in which the AlClMe$_2$ group was coordinated by one exocyclic nitrogen atom. A concomitant 1,2-H shift from this nitrogen atom onto the phosphorus atom was observed. The *N*-coordinated rearrangement product slowly decomposed by a P–N bond cleavage in solution. Reaction of the even more Lewis acidic compounds AlCl$_2$Me and AlCl$_3$ finally led to stable adducts of composition *cis*-[(tBuNH)(PNtBu)-(tBuN·AlCl$_2$Me){P(H)NtBu}] (**3**) and *cis*-[(tBuNH)-

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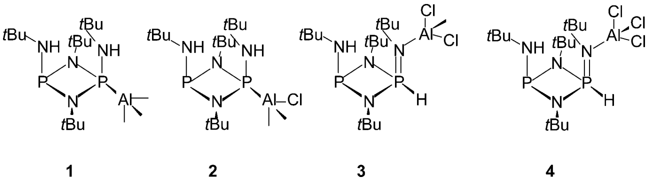
(PN*t*Bu)(*t*BuN·$AlCl_3$){P(H)N*t*Bu}] (**4**), in which the aluminum atoms were *N*-coordinated by a *t*BuN=PH unit (Scheme 2). Thus, in dependence on the Lewis acidity, the aluminum compound we observe shows either P or N coordination and no methane elimination.

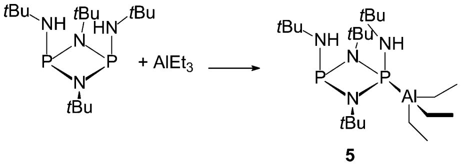


Scheme 2.

Upon reporting of these results, we were questioned frequently, if the observed behavior is limited to methylaluminum chloride compounds only or if the observed results can be more generalized. Therefore, we investigated the reaction of *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} now with the ethylaluminum bromide compounds $AlEt_3$, $AlBrEt_2$, $AlBr_2Et$, and $AlBr_3$.

Results and Discussion

Treatment of the *tert*-butyl-substituted *cis*-bis(amino)-cyclodiphosph(III)azane *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$}[8] in a 1:1 molar ratio with $AlEt_3$ in toluene resulted in the Lewis acid–base adduct of composition *cis*-[(*t*BuNH)$_2$(PN*t*Bu)-{P(·$AlEt_3$)N*t*Bu}] (**5**), in which the aluminum atom binds to one phosphorus atom (Scheme 3). Even at elevated temperature, no ethane elimination was observed. Complex **5** was characterized by standard analytical/spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction (Figure 1).



Scheme 3.

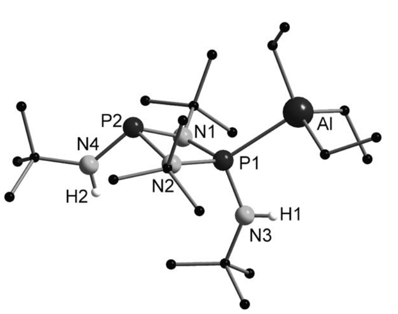


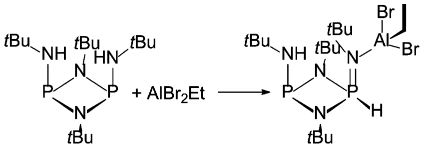
Figure 1. Solid-state structure of **5** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] and angles [°]: N1–P1 1.696(2), N1–P2 1.746(2), N2–P1 1.690(2), N2–P2 1.745(2), N3–P1 1.652(2), N4–P2 1.654(2), Al–P1 2.5348(8); Al–P1–N1 122.34(6), Al–P1–N2 120.84(6), Al–P1–N3 104.89(7), N1–P1–N2 82.61(8), N1–P1–N3 112.89(9), N2–P1–N3 112.48(9), N1–P2–N2 79.60(7), N1–P2–N4 105.18(9), N2–P2–N4 105.42(9).

Compound **5** crystallizes in the monoclinic space group $P2_1/n$ having four molecules in the unit cell. The structure clearly shows that the aluminum atom is coordinated by the phosphorus atom. This unusual coordination mode was also observed for compound **1**, but in general, even though there are some P–Al Lewis acid–base adducts known,[17] the coordination of the aluminum atom to the softer phosphorus atom in P–N compounds is rare,[13,14] and to the best of our knowledge the coordination of an aluminum atom to a phosphorus atom of a protic P–N–H compound was not reported by other groups. Due to the coordination of the $AlEt_3$ molecule, there is a steric repulsion between the aluminium compound and the N*t*Bu group resulting in an *endo*/*exo* arrangement of the N*t*Bu groups of the *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} ligand. Moreover, as a result of the $AlEt_3$ coordination, the heterocycle is distorted. The N1–P1 [1.696(2) Å] and N2–P1 [1.690(2) Å] distances are significantly shorter than the corresponding N1–P2 [1.746(2) pm] and P2–N2 [1.745(2) Å] bonds. 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 1.652(2) Å, P2–N4 1.654(2) Å vs. 1.664(2) Å in *cis*-[(*t*BuNH)$_2$(PN*t*Bu)$_2$]}.[8] The P1–Al bond length of 2.5348(8) Å is in the range of those of compound **1** [2.5201(9) Å] and Me_3AlPPh_2(N-P*i*Pr$_3$) [2.5190(11) Å].[13] The Al–P1–N1 [122.34(6)°] and Al–P1–N2 [120.84(6)°] bond angles are almost in the same range, wheraes the Al–P1–N3 angle [104.89(7)°] is significantly smaller.

Even though compounds **1** and **5** seem to be quite similar in the solid-state, there is a significantly different behavior in solution. Whereas compound **1** shows two broad signals in the $^{31}P\{^1H\}$ NMR spectrum at room temperature and a point of coalescence at elevated temperature, for compound **5** only one signal at δ = 87.4 ppm at room temperature is seen. This signal is close to the one observed in the starting material *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} (δ = 88.5 ppm).[8] Obviously, the $AlEt_3$ molcule is only weakly coordinated to the ligand.

Similar differences can also be seen by comparing the reactions of *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} and $AlClMe_2$ and $AlBrEt_2$, respectively. For the reaction of $AlClMe_2$ with *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} we observed the formation of the *P*-coordinated compound **2** at room temperature, which in solution rearranged to an *N*-coordinated *cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN·$AlClMe_2$){P(H)N*t*Bu}] product that rapidly decomposed to a number of further products.[16] Performing the same reaction with $AlBrEt_2$ resulted immediately in decomposition, and no coordination compound could be isolated.

In contrast to the examples described above, the reaction of the more Lewis acidic $AlBr_2Et$ with *cis*-{(*t*BuNH)$_2$-(PN*t*Bu)$_2$} in a 1:1 molar ratio in toluene resulted in the *N*-coordinated product *cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN·$AlBr_2Et$){P(H)N*t*Bu}] (**6**) (Scheme 4). Obviously, upon coordination of the $AlBr_2Et$ molecule onto one exocyclic nitrogen atom a 1,2-H shift from this nitrogen atom onto the phosphorus atom of the *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} ligand forming a *t*BuN=PH subunit takes place. Similar H-shifts on a P–N backbone were previously observed.[12] Complex **6** is almost insoluble in benzene. As a result of this low solubility, no useful NMR spectroscopic data was obtained. Compound **6** was characterized by elemental analysis, and the solid-state structure of **6** was established by single-crystal X-ray diffraction (Figure 2).



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Scheme 4.

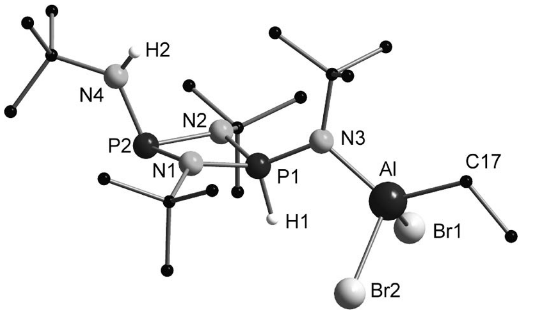
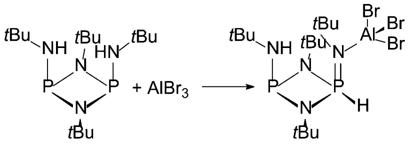


Figure 2. Solid-state structure of **6** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] and angles [°]: Al–N3 1.930(3), Al–Br1 2.332(2), Al–Br2 2.3484(14), N1–P1 1.654(3), N1–P2 1.758(3), N2–P1 1.651(3), N2–P2 1.768(3), N3–P1 1.595(3), N4–P2 1.640(4); N3–Al–Br1 108.46(12), N3–Al–Br2 105.72(11), N3–Al–C17 121.1(2), Br1–Al–Br2 103.67(6), Br1–Al–C17 107.4(2), Br2–Al–C17 109.10(2), N1–P1–N2 85.8(2), N1–P1–N3 123.9(2), N2–P1–N3 124.1(2), N1–P2–N2 79.28(15), N1–P2–N4 106.1(2), N2–P2–N4 105.7(2).

Compound **6** crystallizes in the triclinic space group $P\bar{1}$ having two molecules in the unit cell. In contrast to compound **5** the alkylaluminum molecule is now attached to a nitrogen atom (N3). The coordination polyhedron of the aluminum atom is a distorted tetrahedron showing bonding angles of N3–Al–Br1 108.46(12)°, N3–Al–Br2 105.72(11)°, N3–Al–C17 121.1(2)°, Br1–Al–Br2 103.67(6)°, Br1–Al–C17 107.4(2)°, and Br2–Al–C17 109.10(2)°. The Al–N3 bond length is in the expected range of 1.930(3) Å, which is consistent with those of comparable complexes such as compound **3** [1.928(2) Å], [(*i*Pr$_2$N)$_2$P(H)N(H)Al(Me)$_3$] [1.928(6) Å][12a] and [(Cy$_2$N)$_2$P(H)N(H)AlMe$_3$] [1.941(2) Å].[12b] The hydrogen atoms H1 and H2 were freely refined upon solving the structure, thus confirming the rearrangement. Moreover as a result of the P=N double bond, the N3–P1 distance of 1.595(3) Å is shorter than the corresponding N4–P2 bond of 1.640(4) Å. As observed for compounds **5**, the P$_2$N$_2$ heterocycle is distorted. Within this cycle the N1–P1 [1.654(3) Å] and N2–P1 [1.651(3) Å] bonds are shorter than N1–P2 [1.758(3) Å] and N2–P2 [1.768(3) Å]. The distortion is obviously a result of the aluminum coordination to the heterocycle.

To complete the series, AlBr$_3$ was treated with *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} in a 1:1 molar ratio in toluene. Out of the reaction mixture the expected product of composition *cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN·AlBr$_3$){P(H)N*t*Bu}] (**7**) precipitated as crystalline material in good yields (Scheme 5). As observed for compound **6**, compound **7** is also insoluble in benzene, and no useful NMR spectroscopic data could be collected. Thus, compound **7** was characterized by elemental analysis and single-crystal X-ray crystallography (Figure 3) only. Compound **7** crystallizes in the monoclinic space group $P2_1/n$ having four molecules in the unit cell. As observed in compound **6**, the *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} ligand rearranged to form *t*BuN=PH, to which the AlBr$_3$ molcule is coordinated through the nitrogen atom. The hydrogen atoms H1 and H2 were freely refined upon solving the structure confirming the rearrangement. The N3–Al bond of 1.901(4) Å is slightly shorter than that in **6** [1.930(3) Å], which may be a result of the higher Lewis acidity of AlBr$_3$ compared with AlBr$_2$Et. Concomitant with AlBr$_3$ coordination, a distortion of the P$_2$N$_2$ heterocycle is observed [N1–P1 1.648(3) Å and N2–P1 1.646(4) Å vs. N1–P2 1.760(4) Å and N2–P2 1.765(4) Å]. The difference between the *N*-coordinated aluminum chloride and bromide compounds can already be seen in the solid state. The aluminum chloride compounds **3** and **4** show comparable metrics of the crystal lattice, which is a result of the similar size of the methyl group and the chlorine atom.[16] In contrast, compounds **6** and **7** show significantly different lattice parameters.



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Scheme 5.

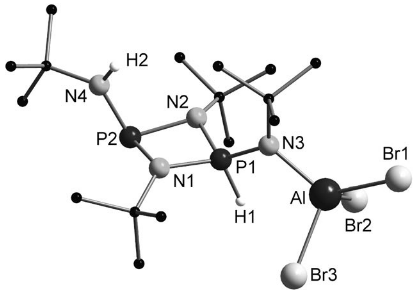

Figure 3. Solid-state structure of **7** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] and angles [°]: N1–P1 1.648(3), N1–P2 1.760(4), N2–P1 1.646(4), N2–P2 1.765(4), N3–P1 1.607(3), N3–Al 1.901(4), N4–P2 1.646(4), Al–Br1 2.2827(14), Al–Br2 2.3133(14), Al–Br3 2.2990(13); Br1–Al–Br2 105.85(5), Br1–Al–N3 118.40(12), Br1–Al–Br3 107.22(5), Br2–Al–Br3 107.92(6), Br2–Al–N3 108.51(12), Br3–Al–N3 108.51(12), N1–P1–N2 85.9(2), N1–P1–N3 124.7(2), N2–P1–N3 123.5(2).

Conlusions

We investigated in a systematic manner the reaction of the bis(amino)cyclodiphosph(III)azane *cis*-{(*t*BuNH)$_2$-(PN*t*Bu)$_2$} with $AlEt_3$, $AlBrEt_2$, $AlBr_2Et$, and $AlBr_3$ and compared the results with the coordination of $AlMe_3$, $AlClMe_2$, $AlCl_2Me$, and $AlCl_3$ onto this ligand.[16] Two coordination patterns were observed. The less Lewis acidic compound $AlMe_3$ and $AlEt_3$ exclusively coordinate to one phosphorus atom in the solid state, but $AlEt_3$ is more weakly coordinated in solution. In both cases, alkane elimination was not observed. The weaker coordination of the ethylaluminum compounds is also seen by comparing the reactivity of $AlBrEt_2$ with that of $AlClMe_2$. For $AlClMe_2$ a *P*-coordination was observed at low temperature, along with an irreversible rearrangement of the $AlClMe_2$ group onto one exocyclic nitrogen atom concomitant with a 1,2-H shift from this nitrogen atom onto the phosphorus atom. The *N*-coordinated rearrangement product slowly decomposed by a P–N bond cleavage in solution. In contrast, by using $AlBrEt_2$ as reagent, an immediate decomposition was observed. With the more Lewis acidic compounds $AlCl_2Me$, $AlBr_2Et$, $AlCl_3$, and $AlBr_3$, stable *N*-coordinated adducts were obtained, in which the aluminum atoms are 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 in 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 mbH or Euriso-Top GmbH (all ≥99 atom-% D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded with 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). IR spectra were obtained with a Bruker Vertex 70 spectrometer. Elemental analyses were carried out with an Elementar Vario EL III. $AlEt_3$ (1 M in hexane) and $AlBr_3$ (Aldrich) were used as purchased. $AlEtBr_2$ was prepared form $AlBr_3$ and $AlEt_3$. *cis*-{(*t*BuNH)$_2$(PN*t*Bu)$_2$} was prepared according to literature procedures.[8]

***cis*-[(*t*BuNH)$_2$(PN*t*Bu){P(·AlEt$_3$)N*t*Bu}] (5):** 1 mL of a 1 M solution of $AlEt_3$ in hexane was added dropwise to a solution of 0.348 g (1.0 mmol) of *cis*-[(*t*BuNH)$_2$(PN*t*Bu)$_2$] in 5 mL of toluene at 0 °C. The mixture was then crystallized at –20 °C. Yield: 0.255 g (55%) (colorless crystals). ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): δ = 0.08 [q, ^3J(H,H) = 8.11 Hz, 6 H, CH_2], 1.21 (s, 18, *t*Bu), 1.31 [t, ^3J(H,H) = 8.11 Hz, 9 H, CH_3], 1.40 (s, 18 H, *t*Bu), 2.57 (br., 2 H, NH) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 161.7 MHz, 20 °C): δ = 87.4 (s) ppm. $C_{22}H_{53}AlN_4P_2$ (462.61): calcd. C 57.12, H 11.55, N 12.11; found C 57.17, H 12.12, N 11.68.

***cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN·AlBr$_2$Et){P(H)N*t*Bu}] (6):** 2 mL of a 0.5 M solution of $AlBrEt_2$ in toluene was added dropwise to a solution of 0.348 g (1.0 mmol) of *cis*-[(*t*BuNH)$_2$(PN*t*Bu)$_2$] in 5 mL of toluene at 0 °C. The mixture was then crystallized at –20 °C. Yield: 0.101 g (18%) (colorless crystals). IR (KBr): $\tilde{\nu}$ = 601 (m), 740 (m), 878 (s), 997 (s), 1030 (m), 1221 (s), 1360 (s), 1370 (s), 1464 (m), 2867 (s), 2965 (s, νCH), 3197 (m, νC=C–*H*), 3335 (m) cm^{-1}. $C_{18}H_{43}AlBr_2N_4P_2$ (564.30): calcd. C 38.31, H 7.68, N 9.93; found C 38.37, H 7.82, N 9.23.

***cis*-[(*t*BuNH)(PN*t*Bu)(*t*BuN·AlBr$_3$){P(H)N*t*Bu}] (7):** A solution of 0.131 g (0.37 mmol) of *cis*-[(*t*BuNH)$_2$(PN*t*Bu)$_2$] in 10 mL of toluene was added dropwise to a solution of 0.1 g (0.37 mmol) of $AlBr_3$ in 10 mL of toluene at 0 °C. The mixture was then crystallized at –20 °C. Yield: 0.117 g (51%) (colorless crystals). IR (KBr): $\tilde{\nu}$ = 625 (w), 765 (w), 898 (s), 1012 (s), 1040 (m), 1203 (s), 1228 (s), 1371 (m), 1370 (s), 1470 (m), 2867 (s), 2972 (vs, νCH), 3185 (m, νC=C–*H*), 3311 (m) cm^{-1}. $C_{16}H_{38}AlBr_3N_4P_2$ (615.14): calcd. C 31.24, H 6.23, N 9.11; found C 31.41, H 6.49, N 8.63.

X-ray Crystallographic Studies of 5, 6 and 7: Crystals of **5**, **6** and **7** were grown at –20 °C from mother solutions. Suitable crystals were covered in mineral oil (Aldrich) and mounted onto glass fibers. The crystals were transferred directly to the –73 °C N_2 cold stream of a Stoe IPDS II T diffractometer. Subsequent computations were carried out with an Intel Pentium IV PC. All structures were solved by direct methods (SHELXS-97[18]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively, using the program SHELXL-97.[19] The hydrogen atom contributions were calculated, but not refined. 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-693094 (for **5**), -693095 (for **6**), -693096 (for **7**) 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.

5: $C_{22}H_{53}AlN_4P_2$, monoclinic, $P2_1/n$ (no. 14); lattice constants: a = 10.3545(7), b = 17.9205(11), c = 16.8964(11) Å, β = 94.151(5)°; V = 2979.0(3) Å^3, Z = 4; μ(Mo-K_α) = 0.190 mm^{-1}; $\theta_{max.}$ = 25; 5251 (R_{int} = 0.0482) independent reflections measured, of which 4033 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.421/–0.288 e/A^{-3}; 286 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0417; wR_2 (all data) = 0.1069.

6: $C_{18}H_{43}AlBr_2N_4P_2$, triclinic, $P\bar{1}$ (no. 2); lattice constants: a = 9.668(3), b = 9.100(2), c = 16.314(4) pm, α = 81.20(2), β = 78.23(2), γ = 86.20(2)°; V = 1387.6(6) Å^3, Z = 2; μ(Mo-K_α) = 3.079 mm^{-1}; $\theta_{max.}$ = 25; 4879 (R_{int} = 0.0517) independent reflections measured, of which 3368 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.430/–0.178 e/A^{-3}; 265 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0459; wR_2 (all data) = 0.0919.

7: $C_{16}H_{38}AlBr_3N_4P_2$, monoclinic, $P2_1/n$ (no. 14); lattice constants: a = 10.1004(7), b = 19.2509(12), c = 13.9558(9) Å, β = 94.125(5)°; V = 2706.6(3) 10^6 pm^3, Z = 4; μ(Mo-K_α) = 4.631 mm^{-1}; $\theta_{max.}$ = 25; 4769 (R_{int} = 0.0758) independent reflections measured, of which 3781 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.620/–0.622 e/A^{-3}; 255 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0433; wR_2 (all data) = 0.1045.

Acknowledgments

This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

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Received: July 23, 2008