Synthesis and X-ray structure of the first 1,3,2,4-diazaphosphaaluminetidine

Stephan Schulz,* Tillmann Bauer and Martin Nieger

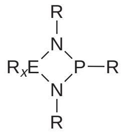
Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany.
E-mail: stephan@ac4010se.chemie.uni-bonn.de

Received (in Basel, Switzerland) 3rd March 1999, Accepted 2nd April 1999

Dehydrogenation reaction between $AlH_3{\leftarrow}NMe_3$ and $Bu^tP[N(H)Bu^t]_2$ leads to $Bu^tP(NBu^t)_2AlH{\leftarrow}NMe_3$, the first neutral 1,3,2,4-diazaphosphaaluminetidine.

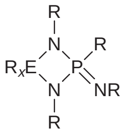
Four-membered heterocycles $RP(\mu\text{-}NR')_2ER''_x$ (E = main group element) have been studied extensively during the last two decades. Several neutral 1,3,2$\sigma^3\lambda^3$-diazaphosphatedines (type 1)[1] and 1,3,2$\sigma^4\lambda^5$-diazaphosphonatatedines (type 2)[2] have been synthesised and structurally characterised.

Type 1



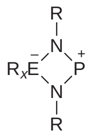
R_xE = RB,[1a] CO,[1b] R_2Si,[1c] RP,[1d] RAs,[1e] SO_2[1f]

Type 2



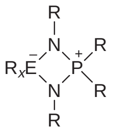
R_xE = RB,[2a] R_2Si,[1c, 2b] RP[2c]

Type 3



R_xE = R_2Al,[2b, 3a] R_2Ga[3b]

Type 4



R_xE = R_2Al,[3a, 4a, 4b] R_2Ga,[4a, 4c] R_2In[4a]

We became interested in the synthesis of neutral 1,3,2$\sigma^3\lambda^3$-diazaphosphatedines containing an element of group 13 due to the lack of structural information. Although 1,3,2,4-diazaphosphaboretidines $RP(\mu\text{-}NR')_2BR''$, synthesised by reactions of (a) aminoiminophosphanes $RN{=}P{-}NR_2'$ with BX_3 (X = Cl, Br),[1a,4] (b) dilithiated bis(amino)phosphanes $RP(NR'Li)_2$ with dichloroboranes $RBCl_2$,[1a] (c) iminoboranes $RN{=}BR'$ with dichlorophosphanes $RPCl_2$,[1a,3] (d) iminoboranes with aminoiminophosphanes,[1a,2] (e) aminoiminoboranes with PCl_3,[1a,3] and (f) aminoiminoboranes with aminoiminophosphanes,[1a,5] have been known for several years, to our knowledge, their solid state structures have not been determined. Investigations concerning the synthesis of 1,3,2,4-diazaphosphatidines of higher homologues of group 13 were not successful, because reactions (a) and (b) using Al, Ga or In compounds lead to zwitterionic complexes (type 3,[3] or 4[4]) and the analogous starting compounds for reactions (c)–(f), imino-alanes, -gallanes and -indanes $RN{=}ER'$ (E = Al, Ga, In), are, as yet, unknown.

We now report the synthesis and structural characterisation of the first neutral 1,3,2,4- diazaphosphaaluminatidine by a dehydrogenation reaction. $Bu^tP[N(H)Bu^t]_2$ was added to $AlH_3{\leftarrow}NMe_3$, which immediately led to gas evolution. The resulting viscous solid was subsequently heated to 115 °C until the gas evolution stopped. Cooling to room temperature led to a light yellow solid, which was dissolved in pentane and stored at −30 °C. Colourless crystalline **1** was obtained and characterised by ^{1}H, ^{13}C and ^{31}P NMR, IR and mass spectroscopy as well as single crystal X-ray analysis.‡

The ^{1}H NMR spectrum shows a doublet for the Bu^tP group and a singlet for the Bu^tN moieties, indicating that the two Bu^tN groups are equivalent. The ^{31}P NMR spectrum shows a singlet at δ 121.2, comparable to that (δ 126.6) found in $MeP(\mu\text{-}NBu^t)_2BMe$.[1a] The Al–H resonance was not observed in the ^{1}H NMR spectrum probably owing to broadening,[5] but the IR spectrum displays a typical Al–H stretching absorption band at 1793 cm^{-1}.

Crystals of **1** suitable for a single crystal X-ray structure determination were grown in pentane at −30 °C. The geometry at the P atom is pyramidal with an endocyclic N1–P1–N2 bond angle of 89.6° (Fig. 1). The average P–N bond length [1.732(2) Å] is comparable to those found in $(Bu^tN)Bu^tP(\mu\text{-}NBu^t)_2BBu^t$ [171.0(2) Å],[2a] $RP(\mu\text{-}NBu^t)_2SiMe_2$ [174.1(3) Å][1c] and $(Me_3Si)_2NP(\mu\text{-}NR')_2SiBu^t_2$ [176.9(2) Å][6] and reveals the absence of any double-bond character within the PN_2 fragment. The Al atom shows a distorted tetrahedral environment with an endocyclic N1–Al1–N2 bond angle of 83.3°. The average Al–N bond length within the non-planar ring [1.836(2) Å] is comparable to Al–N compounds with four-coordinate Al centers bound to three-coordinate N atoms.[7] The zwitterionic complexes $P(\mu\text{-}NAr)_2AlMe_2$ (Ar = $C_6H_2Bu^t_3$-2,4,6),[3a,4] $P(\mu\text{-}NSiMe_3)AlCl_2$[3a] (type 3) and $[(Ph_2P)\overline{NPPh_2N(SiMe_3)Al}Me_2]$[4b] (type 4) show significantly shorter P–N [average of 1.617(4), 1.614(6) and 1.613(1) Å, respectively] and longer Al–N bond lengths [average of 1.977(4), 1.890(6) and 1.947(2) Å,

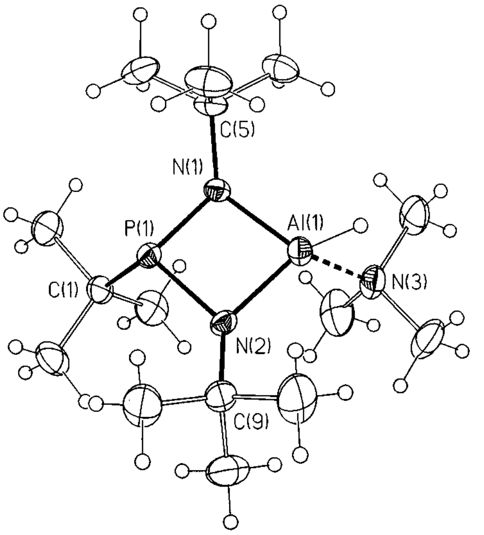


Fig. 1 The molecular structure of **1** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (°): C(1)–P(1) 1.902(2), P(1)–N(1) 1.732(2), P(1)–N(2) 1.732(1), Al(1)–N(1) 1.846(2), Al(1)–N(2) 1.826(2), Al(1)–N(3) 2.028(2), Al(1)–H(1) 1.478(5); N(1)–P(1)–N(2) 89.6(1), C(1)–P(1)–N(1) 105.0(1), C(1)–P(1)–N(2) 106.3(1), N(1)–Al(1)–N(2) 83.3(1), N(1)–Al(1)–N(3) 118.2(1), N(2)–Al(1)–N(3) 116.2(1), C(5)–N(1)–Al(1) 123.3(1), C(5)–N(1)–P(1) 120.7(1), C(9)–N(2)–P(1) 126.4(1), C(9)–N(2)–Al(1) 131.8(1), H(1)–Al(1)–N(1) 122.9(7), H(1)–Al(1)–N(2) 121.3(7), H(1)–Al(1)–N(3) 96.8(8).

respectively], while coordination of a Lewis base to a complex of type 3 as shown in P(μ-NSiMe$_3$)$_2$AlCl$_2$·quinuclidine[8] leads to comparable Al–N [average 1.855(10) Å] and less shortened P–N bond lengths [average of 1.673(10) Å]. The Al–H bond length [1.478(5) Å] and the terminal Al–N bond length [2.028(2) Å] in **1** are within the expected range.[5]

This work was supported by the DFG, Fonds der Chemischen Industrie and the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF). S. Schulz gratefully thanks Professor E. Niecke for financial support.

Notes and references

† **1**: mp 112 °C; yield 73%; NMR data: ^{1}H (C_6D_6, 25 °C) δ 1.20 (d, $^3J_{PH}$ 10.3 Hz, 9H, Bu^{t}P), 1.57 (d, $^4J_{PH}$ 0.7 Hz, 18H, Bu^{t}N), 1.99 (s, 9H, NMe$_3$); ^{13}C (C_6D_6, 25 °C) δ 27.99 (d, $^2J_{PC}$ 18.3 Hz, *Me*$_3$CP), 33.93 (d, $^1J_{PC}$ 45.4 Hz, Me$_3$*C*P), 35.56 (d, $^3J_{PC}$ 8.8 Hz, *Me*$_3$CN), 48.12 (s, NMe$_3$), 51.35 (d, $^2J_{PC}$ 17.2 Hz, Me$_3$*C*N); ^{31}P (C_6D_6, 25 °C) δ 121.2; IR (Nujol) ν/cm^{-1} 1793 (Al–H), 1205, 1007, 802, 736, 630, 577 cm^{-1}; EI-MS (20 eV, 150 °C) *m/z* (%): 317 (5) M$^+$, 258 (15) [M − NMe$_3$]$^+$, 201 (100) [M − NMe$_3$ − Bu^t]$^+$.

‡ *Crystal data* for **1**: $C_{15}H_{37}AlN_3P$, M = 317.4, orthorhombic, space group *Pbca* (no. 61), a = 12.8335(4), b = 16.7315(5), c = 18.6500(6) Å, V = 4004.6(2) Å^3, Z = 8, D_c = 1.053 g cm^{-3}, μ(Mo-Kα) = 0.178 mm^{-1}, $F(000)$ = 1408, 48091 reflections measured (4824 unique), R [$I > 2\sigma(I)$] = 0.050, *wR2* (all data) = 0.15357, GOF = 1.004 for 184 parameters and two restraints. Data were collected on a Nonius Kappa-CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[9] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[10] CCDC 182/1214. See http://www.rsc.org/suppdata/cc/1999/879/ for crystallographic files in .cif format.

1 (*a*) W. Jacksties, H. Nöth and W. Storch, *Chem. Ber*., 1985, **118**, 2030; P. Paetzold, C. von Plotho, E. Niecke and R. Rüger, *Chem. Ber*., 1983, **116**, 1678; K.-H. van Bonn, P. Schreyer, P. Paetzold and R. Boese, *Chem. Ber*., 1988, **121**, 1045; E. Niecke and W. Bitter, *Angew. Chem.*, 1975, **87**, 34; *Angew. Chem., Int. Ed. Engl*., 1975, **14**, 56; U. Wietelmann, *PhD Thesis*, 1986, München; (*b*) J. Breker and R. Schmutzler, *Chem. Ber*., 1990, **123**, 1307; (*c*) O. J. Scherer, M. Püttmann, C. Krüger and G. Wolmershäuser, *Chem. Ber*., 1982, **115**, 2076; W. Bitter and E. Niecke, *Chem. Ber*., 1976, **109**, 415; U. Klingebiel, *Chem. Ber*., 1978, **111**, 2735; (*d*) E. Niecke, W. Flick and S. Pohl, *Angew. Chem.*, 1976, **88**, 305; *Angew. Chem., Int. Ed. Engl*,. 1976, **15**, 309; E. Niecke, A. Nickloweit-Lüke and R. Rüger, *Phosphorus Sulfur*, 1981, **12**, 213; O. J. Scherer, *Chem. Ber*., 1976, **109**, 2996; (*e*) O. J. Scherer, *Z. Naturforsch. Teil B*, 1976, **31**, 142; (*f*) A. H. Cowley, S. K. Mehrota and H. W. Roesky, *Inorg. Chem*., 1981, **20**, 712.

2 (*a*) D. Gudat, E. Niecke, M. Nieger and P. Paetzold, *Chem. Ber*., 1988, **121**, 565; (*b*) R. Kröher, PhD Thesis, 1978, Göttingen; (*c*) R. Appel and M. Halstenberg, *J. Organomet. Chem*., 1975, **99**, C25.

3 (*a*) E. Niecke and R. Kröher, *Angew. Chem.*, 1976, **88**, 758; *Angew. Chem., Int. Ed. Engl*., 1976, **15**, 692; S. Pohl, *Chem. Ber*., 1979, **112**, 3159; S. Pohl, *Z. Naturforsch., Teil B*, 1977, **32**, 1342; P. B. Hitchcock, H. A. Jasim, M. F. Lappert and H. D. Williams, *J. Chem. Soc., Chem. Commun*., 1986, 1634; (*b*) R. Oberdörfer, M. Nieger and E. Niecke, *Chem. Ber*., 1994, **127**, 2397.

4 (*a*) H. Schmidbaur, K. Schwirten and H.-H. Pickel, *Chem. Ber*., 1969, **102**, 564; (b) P. Braunstein, R. Hasselbring and D. Stalke, *New J. Chem*., 1996, **20**, 337; (*c*) R. Oberdörfer, PhD Thesis, 1993, Bonn.

5 See for example: C. Jones, G. A. Koutsantonis and C. L. Raston, *Polyhedron*, 1993, **12**, 1829; M. G. Gardiner and C. L. Raston, *Coord. Chem. Rev*., 1997, **166**, 1.

6 J. Niesmann, U. Klingebiel, S. Rudolph, R. Herbst-Irmer and M. Noltemeyer, *J. Organomet. Chem*., 1996, **515**, 43.

7 B. Qian, D. L. Ward and M. R. Smith, III, *Organometallics*, 1998, **17**, 3070; S. L. Aeilts, M. P. Coles, D. C. Swenson and R. F. Jordan, *Organometallics*, 1998, **17**, 3265.

8 N. Burford, P. Losier, P. K. Bakshi and T. S. Cameron, *J. Chem. Soc., Chem. Commun*., 1996, 307.

9 G. M. Sheldrick SHELXS-90/96, Program for Structure Solution, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

10 G. M. Sheldrick SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, 1997.

Communication 9/01556F