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Synthesis and single crystal X-ray structure of the first imido analog of an eight-membered aluminophosphinate heterocycle†

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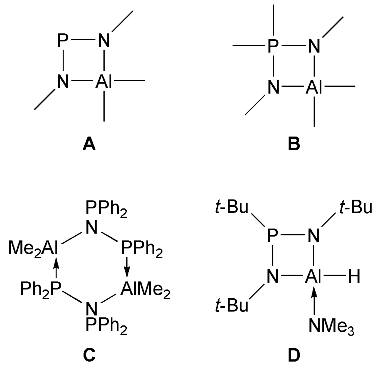
The equimolar reaction of *t*-BuP(NH$_2$)$_2$ and Et$_2$AlH yields [*t*-Bu(H)P(NH)$_2$AlEt$_2$]$_2$ 1, a novel eight-membered heterocycle containing an AlNP-backbone.

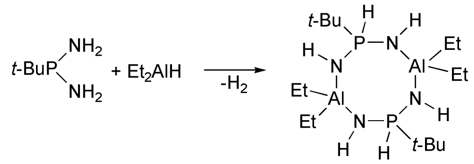
Group 13/15 heterocycles have been synthesized and structurally characterized in large numbers. The great interest in such compounds is based on both their interesting structural chemistry and on their potential application to serve as single source precursors for the preparation of the corresponding binary materials. In contrast, heterocycles containing a backbone of one group 13 and two different group 15 elements have been studied to a far lesser extent and are almost limited to compounds showing an AlNP moiety (Scheme 1). Zwitterionic heterocycles of type **A** and **B** have been synthesized by reaction of alanes and iminophosphanes and -phosphoranes, respectively, while **C** was formed by reaction of (Ph$_2$P)$_2$NH and AlMe$_3$.[1]



Scheme 1 AlNP heterocycles known to date.

We only recently became interested in such compounds and reacted alanes with amino- and alkylaminophosphanes (R$_2$N)$_2$PNH$_2$ and RP(NHR′)$_2$, respectively, yielding the first neutral four-membered heterocycle **D**.[2] These promising results prompted our interest toward bisaminophosphanes RP(NH$_2$)$_2$, which were expected to be much more reactive than the alkyl-substituted derivatives. *t*-BuP(NH$_2$)$_2$ is the only stable compound of the desired type known to date, most likely a consequence of their lability toward consecutive condensation reactions. However, its chemical reactivity has not been explored in detail, so far.[3] This is very surprising because the high functionality (P^{III}-center, two NH$_2$ groups) and thermal stability renders it a very promising reagent in preparative inorganic chemistry.

We now report on the equimolar reaction of *t*-BuP(NH$_2$)$_2$ and Et$_2$AlH, yielding [*t*-Bu(H)P(NH)$_2$AlEt$_2$]$_2$ **1** in good yield. **1** was characterized by elemental analysis, mass, IR and multinuclear NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{31}P)† as well as by single crystal X-ray diffraction.‡



The ^{31}P-NMR spectrum of **1** obtained from the reaction solution shows two resonances of equal intensity at 46.7 and 47.6 ppm, indicating the formation of both the *cis*- and *trans*-isomer of **1** in solution. Almost pure **1** (*trans*-isomer; ^{31}P-NMR 46.7 ppm) was obtained after recrystallization from hexane at −30 °C (5% *cis*-isomer). ^{1}H and ^{13}C-NMR spectra of as-formed **1** show resonances due to the organic ligands (Et, *t*-Bu, H). As was observed in the ^{31}P NMR spectrum, they also show the presence of the *cis*-isomer in about 5% yield. The IR spectrum clearly indicates the presence of N–H and P–H moieties due to bands at the typical positions: (3358 (NH), 2376 (PH) cm^{-1}). The central eight-membered ring of **1** is stable in the gas phase, as is indicated by the mass spectrum showing a peak at *m*/*z* 349 ([M − *t*-Bu −H$_2$]$^+$) in 100% intensity.

Single crystals of **1** suitable for a X-ray structure determination were obtained from a solution in hexane at 0 °C. **1** crystallizes in the monoclinic space group *P*2$_1$/*c* (no. 14)(Fig. 1).

The central feature of **1** is the eight-membered ring adopting a chair-like conformation, the first structurally characterized heterocycle of this type containing an AlNP backbone. However, this structural motif was previously observed in isoelectronic alumino- and gallophosphinates, -phosphonates and -phosphates,[4] which are of interest due to their potential to form microporous materials with possible applications as molecular sieves or in catalysis.[5] **1** is the first aluminonitridophosphinate. In contrast to structurally characterized P–O

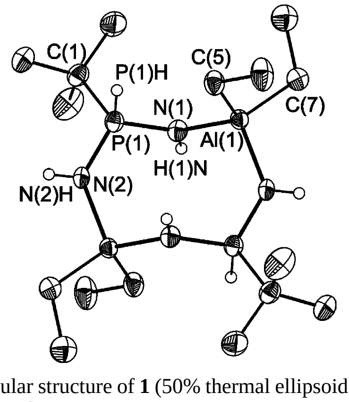


Fig. 1 The molecular structure of **1** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (°):P(1)–N(1) 1.609(2), P(1)–N(2) 1.599(2), P(1)–C(1) 1.821(2), P(1)–P(1)H 1.374(14), Al(1)–N(1) 1.895(2), Al(1)–N(2)′ 1.892(2), N(1)–H(1)N 0.826(15), N(2)–H(2)N 0.799(2); N(1)–P(1)–N(2) 113.2(1), N(1)–Al(1)–N(2)′ 106.4(1), P(1)–N(1)–Al(1) 127.1(1), P(1)–N(2)–Al(1)′ 129.0(1).

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† Electronic supplementary data (ESI) available: preparation and spectroscopic data of **1**, crystallographic data of **1**, xyz-coordinates and absolute energies of all computed species. See http://www.rsc.org/suppdata/cc/b2/b203590a/

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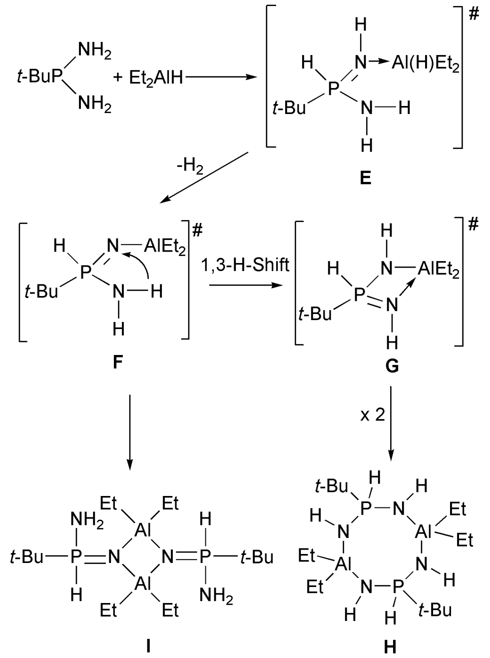
compounds,[4] which unexceptionally show alkoxy- or Ph-substituted P-center, **1** contains a P–H functionality. The Al–N distances (1.892(2), 1.895(2) Å) are typical for fourfold-coordinated Al and threefold-coordinated N centers. The P–N bond lengths (1.599(2) and 1.609(2) Å) clearly indicate the multiple bond character within the PN_2 fragment. Both the Al–N and P–N bonds are elongated compared to P–O and M–O bonds in aluminophosphinates,[4] in accordance with the different atomic radii of N and O. The coordination sphere of each N atom is completed by a H atom. Both N centers are almost planar coordinated as is indicated by their bond angular sums (358.6° N(1), 359.8° N(2)). The Al–C, N–H, P–H and P–C bond distances as observed in **1** are within the expected ranges. The same holds for the exocyclic C–Al–C, C–P–H, C–P–N and C–Al–N bond angles. The endocyclic P–N–Al bond angles (127.1(1), 129.0(1)°) are significantly larger than the N–P–N (113.2(1)°) and N–Al–N angles (106.4(1)°), as was observed in aluminophosphinates.

The formation of **1** is unexpected with respect to the observations made for reactions of $(Cy_2N)_2PNH_2$ (Cy = cyclohexane) and dialkylalanes R_2AlH, leading to compounds of the type $[(Cy_2N)_2P(H)NAlR_2]_2$ containing a central four-membered Al_2N_2 heterocycle.[2a] Obviously, the reaction occurs through a different mechanism. Scheme 2 describes the most likely reaction sequence for the formation of **1**.

In a first step, *t*-$BuP(NH_2)_2$ reacts with Et_2AlH under adduct formation. Simultaneously, a 1,2-H shift from the N to the P atom occurs (N(H)–P(H) tautomerization) to give compound **E**. The equilibrium between the thermodynamically more stable N(H)-phosphanylamido form and the P(H)-iminophosphorane form is known to be influenced by substituent effects: coordination of strong Lewis acids favours the formation of the P(H)-iminophosphorane form.[6] **E** consequently reacts under H_2-elimination to give compound **F**, which stabilizes under 1,3-H shift to yield **G**. Finally, **G** dimerizes to give **H** (= **1**) The proposed reaction pathway was calculated in order to obtain reliable information on the structures of **E**–**H** and their absolute energies.[7] The formation of **E** is exothermic by about 66 kJ mol^{-1}. Interestingly, the observed formation of **F** is entropy-controlled, since the reaction is endothermic by 26 kJ mol^{-1}. However, through the liberation of H_2 entropy drives the reaction to the right hand side. The transformation of **F** into hypothetical **I** is strongly exothermic (245 kJ mol^{-1}), however, the alternative formation of **H** (310 kJ mol^{-1}) is thermodynamically more favoured by about 60 kJ mol^{-1}. The key step clearly is the 1,3-H shift leading to **G**, which is accompanied by an energy gain of 85 kJ mol^{-1}. The calculated structure of **H** is in good agreement with the experimental data as obtained for **1**. The P–N distances of **G** (1.636, 1.642 Å) clearly show the multiple bond character within the PN_2 moiety and the calculated Al–N bond lengths are also equal (1.992, 1.981 Å) and, therefore, intermediate between an Al–N dative and an Al–N σ-bond.



Scheme 2 Proposed reaction mechanism for the formation of **1** (= **H**).

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Notes and references

‡ *Crystal data* for **1**: $C_{16}H_{44}Al_2N_4P_2$, M = 408.5, space group $P2(1)/c$ (No.14), monoclinic, a = 11.5332(6), b = 9.4303(5), c = 12.2830(8) Å, β = 109.5(1)°, V = 1259.3(2) Å^3, Z = 2, D_c = 1.077 g cm^{-3}, μ (Mo$_{K\alpha}$) = 0.249 mm^{-1}, $F(000)$ = 448, 5688 reflections measured (2221 unique), $R(\text{for } I > 2\sigma(I))$ = 0.0351, $wR2$ (all data) = 0.0954, GOF = 1.045 for 117 parameters and 9 restraints (N–H, P–H and disordered Et). H atoms were localized by difference electron density determination and refined using a riding model (*t*-Bu, Et); H at N and P were refined free with restraints to the bond distance. CCDC 184045. See http://www.rsc.org/suppdata/cc/b2/b203590a/ for crystallographic data in .cif or other electronic format.

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7 All computations were done with the program TURBOMOLE, Version 5; current version: http://www.chemie.uni-karlsruhe.de/PC/TheoChem.). Geometries of all species were optimised at the BP86 level with the split valence polarisation SVP basis set (for references see ESI).