

# GaCl<sub>3</sub>-assisted [3+2] cycloaddition: A route to new binary PN-heterocycles

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## Abstract

Starting from a [3+2] synthetic tool kit, new PN-heterocycles may be isolated according to a new synthetic approach called GaCl<sub>3</sub>-assisted [3+2] cycloaddition. According to this concept the dipolarophile Mes<sup>\*</sup>-N=P-Cl (Mes<sup>\*</sup> = 2,4,6-tri-*tert*-butylphenyl) was reacted with the 1,3-dipole (TMS)<sub>2</sub>N-N(TMS)-PCl<sub>2</sub> (TMS = trimethylsilyl) yielding the kinetically stabilized [3+2] cycloaddition product triazadiphosphole, Mes<sup>\*</sup>N<sub>3</sub>P<sub>2</sub>, stabilized as GaCl<sub>3</sub> adduct. Synthesis, structure and bonding are discussed.

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## 1. Introduction

Over the past 50 years only a very small number of planar five-membered ring molecules and ions containing only the elements phosphorus(III) and/or nitrogen have been isolated and fully characterized. Only three are known: the neutral pentazole derivatives, RN<sub>5</sub>, [1] the pentaphosphacyclopentadienide anion, P<sub>5</sub><sup>-</sup> [2] and the 1-alkyl-4-aryl-tetraazaphospholium cations (as tetrachloroaluminate), R<sub>2</sub>N<sub>4</sub>P<sup>+</sup> [3]. Recently, the first two binary PN species of the neutral class have been isolated and fully characterized by our group: triazadiphospholes, RN<sub>3</sub>P<sub>2</sub>, [4] (R = (TMS)<sub>2</sub>N) and tetrazaphospholes, Mes<sup>\*</sup>N<sub>4</sub>P (Mes<sup>\*</sup> = 2,4,6-tri-*tert*-butylphenyl), which were isolated on the search for a phosphorus analogue of covalent azides [5,6].

The synthesis of these new binary PN heterocycles (triazadiphospholes and tetrazaphospholes) was achieved by a GaCl<sub>3</sub>-assisted [3+2] cycloaddition reaction starting from “disguised” dipolarophiles and 1,3-dipole species such as the ambivalent hydrazino(dichloro)phosphane,

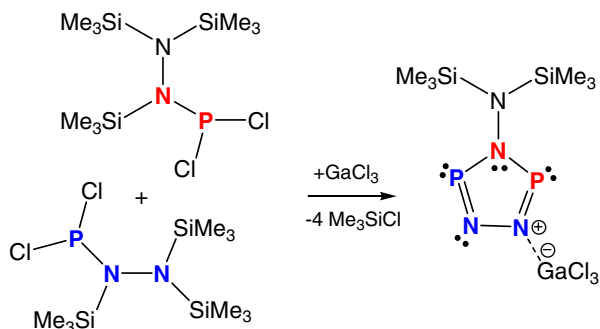
(TMS)<sub>2</sub>N-N(TMS)-PCl<sub>2</sub>, which can react as dipolarophile and 1,3-dipole [4]. This reaction *only* occurs when GaCl<sub>3</sub> is added to (TMS)<sub>2</sub>N-N(TMS)-PCl<sub>2</sub> (Scheme 1) since GaCl<sub>3</sub> induces TMS-Cl elimination.

Formally, the formation of the P<sub>2</sub>N<sub>3</sub> ring in the triazadiphosphole might be regarded as a [3+2] cycloaddition of NNP<sup>-</sup> and R-NP<sup>+</sup> ions (R = N(TMS)<sub>2</sub>) or a dimerization of the phosphorus azide analogue TMS-NNP which has been stabilized by cycloaddition followed by a 1,4-shift of one TMS group. Quantum chemical studies revealed that the GaCl<sub>3</sub> adduct formation kinetically and thermodynamically stabilizes PN-heterocycles [4,5]. Starting from a [3+2] synthetic tool kit which contains binary PN dipolarophiles (R-N=P-Cl R = Mes<sup>\*</sup>, (TMS)<sub>2</sub>N-N(TMS)-PCl<sub>2</sub>) and 1,3-dipols (e.g. TMS-N<sub>3</sub>, (TMS)<sub>2</sub>N-N(TMS)-PCl), new PN heterocycles may be isolated according to the new synthetic approach called GaCl<sub>3</sub>-assisted [3+2] cycloaddition [7].

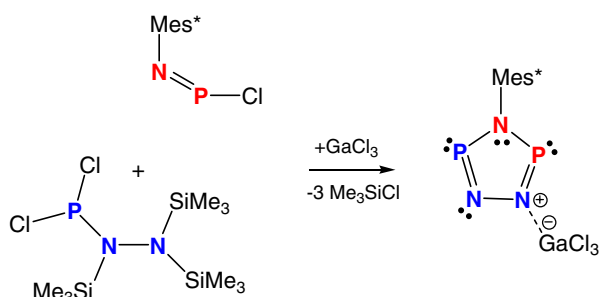
To prove our idea of a GaCl<sub>3</sub>-assisted [3+2] cycloaddition we reacted the kinetically stabilized iminophosphane (Mes<sup>\*</sup>-N=P-Cl), a good dipolarophile, with the hidden 1,3-dipole (TMS)<sub>2</sub>N-N(TMS)-PCl<sub>2</sub> leading finally to the formation of a new triazadiphosphole (Scheme 2).

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Scheme 1. GaCl<sub>3</sub>-assisted [3+2] cycloaddition with the ambivalent hydrazino(dichloro)phosphane, (TMS)<sub>2</sub>N-N(TMS)-PCl<sub>2</sub>, which can react as dipolarophile and/or 1,3-dipole leading to triazadi-phospholes.



Scheme 2. GaCl<sub>3</sub>-assisted [3+2] cycloaddition with the kinetically stabilized iminophosphane (R-N=P-Cl) as dipolarophile and the 1,3-dipole (TMS)<sub>2</sub>N-N(TMS)-PCl<sub>2</sub> leading to triazadi-phospholes.

## 2. Results and discussion

Immediately after adding a benzene solution of (TMS)<sub>2</sub>N-N(TMS)-PCl<sub>2</sub> to a solution of GaCl<sub>3</sub> and Mes\*<sub>2</sub>N=P-Cl (forming [Mes\*<sub>2</sub>N≡P<sup>+</sup>][GaCl<sub>4</sub><sup>-</sup>]) in benzene at 5 °C a reaction could be observed which is finished after 2 h according to <sup>31</sup>P NMR studies. Only one species was observed in solution ( $\delta^{[31\text{P}]}$  = 311 and 287 ppm) which corresponds to the formation of a low-coordinated phosphorus species, a 1-(2,4,6-tri-*tert*-butylphenyl)-1,2,4,3,5-triazadi-phosphole (**1**, cf. 317 and 292 ppm in RN<sub>3</sub>P<sub>2</sub> with R = (TMS)<sub>2</sub>N). Interestingly, only broad resonances without coupling were observed which can be attributed to coalescence due to the fast exchange of the GaCl<sub>3</sub> along the N-N unit in the P<sub>2</sub>N<sub>3</sub> ring. The GaCl<sub>3</sub>-induced [3+2] cycloaddition (Scheme 2) at 5 °C represents a fast and clean high-yielding reaction (>95%) leading to the second triazadi-phosphole stabilized as GaCl<sub>3</sub> adduct (Fig. 1). After removal of the benzene a yellowish crystalline powder could be isolated. As expected <sup>31</sup>P MAS studies also displayed two resonances at  $\delta^{[31\text{P}]}$  = 299 and 292 ppm.

Compound **1** is air and moisture sensitive but stable under argon atmosphere in solid and in common organic solvents (e.g. benzene, CH<sub>2</sub>Cl<sub>2</sub>, ether, etc.). Furthermore, **1** is easily prepared in bulk and is unlimitedly stable in a sealed tube when cooled and stored dark. It is thermally stable up to over 125 °C. At this temperature slow decom-

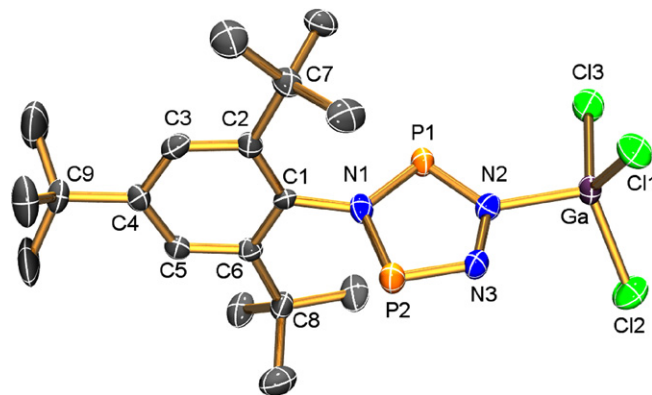


Fig. 1. ORTEP drawing of the molecular structure of one independent molecule of **1** in the crystal. Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ga1–Cl1 2.1501(6), Ga1–Cl2 2.1359(6), Ga1–Cl3 2.1550(7), Ga1–N2 1.9830(5), P1–N1 1.6706(4), P1–N2 1.6355(4), P2–N3 1.6079(4), P2–N1 1.7014(4), N2–N3 1.3760(4); C1–N1 1.4698(4); C1–Ga1–Cl2 113.92(7), C1–Ga1–Cl3 112.02(1), C1–Ga1–N2 103.84(1), Ga1–N2–N3 112.14(3), N1–P1–N2 93.48(2), P1–N2–N3 120.05(3), N1–P2–N3 96.86(3), P2–N3–N2 114.05(3).

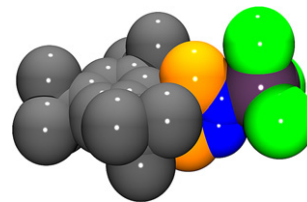


Fig. 2. Space-filling model of **1** displaying the kinetic stabilization by sandwich formation (N blue, P orange, C dark grey, Cl green, Ga violet). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

position starts accompanied by a slow TMS-Cl elimination and oligomerization (MS experiments). Above 235 °C immediate decomposition (explosion) with a large gas release is observed. This remarkable stability can be attributed to a large kinetic stabilization since the P<sub>2</sub>N<sub>3</sub> ring sits in a sandwich formed by the large supermesityl group and the GaCl<sub>3</sub> molecule upon adduct formation (Fig. 2).

Compound **1** crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in the unit cell consistent with the <sup>31</sup>P MAS NMR data (see before). The perspective view of **1** is depicted in Fig. 1. The planar five-membered P<sub>2</sub>N<sub>3</sub> ring (dihedral angles within the ring are smaller than 1.6°) is almost perpendicular to the supermesityl ring ( $\angle$ C–C–N–P angles between 78° and 99°). Interestingly, bond lengths and angles within the P<sub>2</sub>N<sub>3</sub> ring of **1** are almost identical compared to the (TMS)<sub>2</sub>N stabilized species. Upon GaCl<sub>3</sub> adduct formation the C<sub>2v</sub> symmetry of the “naked” P<sub>2</sub>N<sub>3</sub> ring is slightly distorted with two smaller P–N bond lengths ( $d(\text{P1–N2}) = 1.6355(4)$ ,  $d(\text{P2–N3}) = 1.6079(4)$  Å) and two longer P–N distances ( $d(\text{P1–N1}) = 1.6706(4)$ ,  $d(\text{P2–N1}) = 1.7014(4)$  Å). These P–N distances between 1.63 and 1.70 Å are substantially shorter than the sum of the covalent radii ( $d_{\text{cov}}(\text{N–P}) = 1.8$ ,  $d_{\text{cov}}(\text{N=P}) = 1.6$  Å) [8,9]

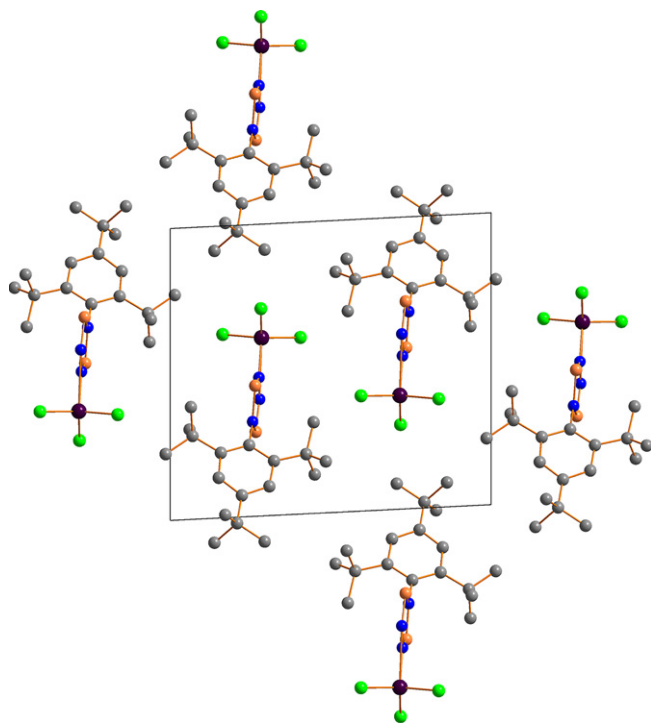


Fig. 3. View along *a*-axis in **1** (N blue, P orange, C dark grey, Cl green, Ga violet). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

which indicates partial double bond character for the P–N bonds. A similar situation is found for the N2–N3 bond (1.3760(4) Å) of the P<sub>2</sub>N<sub>3</sub> ring which also lies in the range between a single and a double bond ( $d_{\text{cov}}(\text{N–N}) = 1.4$ ,  $d_{\text{cov}}(\text{N}=\text{N}) = 1.2$  Å). The Ga–N bond length of 1.9830(5) Å (Ga1–N2) is slightly shorter than those found for the adducts Cl<sub>3</sub>Ga · NMe<sub>2</sub>SiMe<sub>2</sub>NMe<sub>2</sub> [2.003(5)] [10]. In the crystal all P<sub>2</sub>N<sub>3</sub> rings are piled up parallel to each other and also the aryl groups, perpendicular to the P<sub>2</sub>N<sub>3</sub> rings (Fig. 3).

The short P–N and N–N bond distances together with the planarity indicate the presence of a strongly delocalized 6π-electron system which is supported by MO and NBO calculations (NBO = natural orbital analysis) [11]. GaCl<sub>3</sub> adducts of triazadiphospholes are typical charge transfer complexes and the bond between the GaCl<sub>3</sub> and the RP<sub>2</sub>N<sub>3</sub> fragment can be coined as a donor–acceptor bond and hence can be regarded as partially bound system [12]. According to NBO analysis, the charge transfer between the ring and GaCl<sub>3</sub> is about 0.16*e* and the P–N σ- and π-bonds are highly polarized and almost ideally covalent between the adjacent N–N.

In summary, a new GaCl<sub>3</sub>-assisted [3+2] synthetic tool kit has been developed and successfully applied to the synthesis of neutral binary triazadiphospholes and tetraza-phospholes. Because of the astonishing stability of these species in solution as well as in solid, such compounds may have great synthetic potential, for example, as a source for binary PN or ternary PNGa species and as ligands in organometallic chemistry. Furthermore, it is interesting

to see if the heavier analogues show similar cycloaddition reactions.

### 3. Experimental

A solution of Mes\*NPCL (0.326 g, 1.0 mmol) in 10 mL benzene is added to a solution of GaCl<sub>3</sub> (0.194 g, 1.1 mmol) in 15 mL benzene at 5 °C. After adding a solution of *N,N',N'*-[tris(trimethylsilyl)]hydrazino(dichloro)phosphane (0.349 g, 1.0 mmol) in 10 mL benzene the reaction mixture was allowed to stir for 2 h. After removal of the solvent a yellowish powder of **1** is obtained 0.503 g (96%): mp 235 °C (decomp.). Raman (200 mW, 25 °C, cm<sup>-1</sup>): 2971 (65), 2908 (69), 2783 (8), 2718 (9), 1599 (73), 1406 (51), 1395 (46), 1367 (39), 1295 (36), 1268 (27), 1233 (27), 1216 (35), 1200 (38), 1181 (31), 1136 (53), 1118 (27), 1073 (57), 991 (45), 927 (26), 898 (26), 822 (53), 781 (29), 672 (51), 586 (41), 528 (90), 361 (100), 345 (80), 256 (58), 194 (55), 155 (51). <sup>1</sup>H NMR (25 °C, CD<sub>2</sub>Cl<sub>2</sub>): δ 1.18 (s, 18H), 1.36 (s, 9H), 7.66 (s, 2H). <sup>13</sup>C NMR (25 °C, CD<sub>2</sub>Cl<sub>2</sub>, for numbering see Fig. 1): δ 30.9 (s, C9(CH<sub>3</sub>)<sub>3</sub>), 33.8 (dd, <sup>5</sup>J<sub>CP</sub> = 3.8 Hz, C7/8(CH<sub>3</sub>)<sub>3</sub>), 35.3 (s, C9), 37.1 (s, C7/8), 125.2 (s, C3/5), 128.3 (s, C2/6), 146.3 (dd, <sup>2</sup>J<sub>CP</sub> = 2.7 Hz, C1), 153.0 (s, C4). <sup>31</sup>P NMR (25 °C, CD<sub>2</sub>Cl<sub>2</sub>): δ 287.2 (s), 311.1 (s). <sup>31</sup>P MAS NMR (25 °C, ω<sub>rot</sub> = 25 kHz): δ<sub>iso</sub> 299.1 (s), 292.9 (s). MS (FAB<sup>+</sup>, Xenon, 6 keV, m-NBA matrix): 290 [Mes\*NP]<sup>+</sup>, 262 [Mes\*NH<sub>3</sub>]<sup>+</sup>, 261 Mes\*NH<sub>2</sub><sup>+</sup>, 234 [Mes\*NP-*t*-Bu]<sup>+</sup>. MS (EI, 70 eV, >5%) *m/z* (%): 350 [1+H]<sup>+</sup> (3), 349 [1]<sup>+</sup> (1), 348 [1-H]<sup>+</sup> (4). C<sub>18</sub>H<sub>29</sub>N<sub>3</sub>P<sub>2</sub>GaCl<sub>3</sub> (524.47): Anal. Calc. C, 41.22; H, 5.38; N, 8.01. Found: C, 39.93; H, 5.98; N, 6.65%.

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### Appendix A. Supplementary material

CCDC 617320 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.024.

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