$GaCl_3$-assisted [2 + 3] cycloaddition: A route to tetrazaphospholes†

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The $GaCl_3$-assisted [2 + 3] cycloaddition of Mes*–N=P–Cl (Mes* = 2,4,6-$^tBu_3C_6H_2$) with trimethylsilylazide (TMS–N_3) results in the formation of the first tetrazaphosphole, stabilized as a $GaCl_3$ adduct in high yields (>96%).

Pentazole and pentaphosphole rings are the full iso(valence)electronic nitrogen and phosphorus analogues of the cyclopentadienylide anion and the final members of the azaphosphole series (Fig. 1). While pentaphosphole derivatives are unknown, aryl derivatives of pentazoles have been known since 1957.[1] Pentazoles were prepared at low temperatures by coupling diazonium salts with azide ions following the procedure of Huisgen and Ugi.[2]

Recently, we reported on the successful preparation of the first binary member of the azaphosphole series, the 4-bis(trimethylsilyl)amino-1,2,4,3,5-triazadiphosphole (**1**), which was synthesized in a $GaCl_3$-induced trimethylsilylchloride (TMS–Cl) elimination in *N*,*N*′,*N*′-tris(trimethylsilyl)]hydrazino(dichloro)phosphane ($(TMS)_2N(TMS)N–PCl_2$) followed by a [2 + 3] cycloaddition reaction.[3]

To prepare a tetrazaphosphole (aryl–N_4P), another member of the azaphosphole series (Fig. 1), it seemed quite promising to apply the $GaCl_3$-assisted elimination of TMS–Cl to the reaction of aryl–N=P–Cl (aryl = Mes* = 2,4,6-$^tBu_3C_6H_2$) with trimethylsilylazide (TMS–N_3) in an 1,3-dipolar cycloaddition reaction (Scheme 1). Reacting an alkyl-substituted azide (R–N_3 (R = ^tBu, CEt_3)) with [Mes*–N=P^+][$AlCl_4^-$] results in the formation of tetrazaphospholium salts, first described by Niecke *et al.*[4] However, the idea of a $GaCl_3$-assisted [2 + 3] cycloaddition to synthesize new azaphospholes can only work when suitably substituted 1,3-dipoles (*e.g.* TMS–N_3) are used, so that in the [2 + 3] cycloaddition, small molecules such as TMS–Cl can be eliminated (Scheme 1). Otherwise, only the formation of a tetrazaphospholium tetrachlorogallate would be observed.[4,5a]

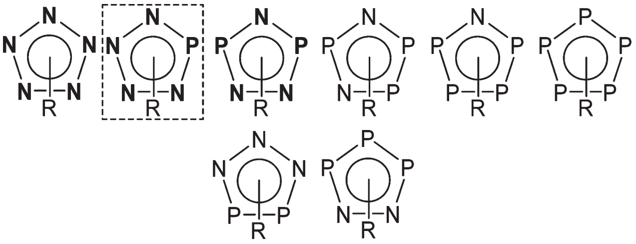
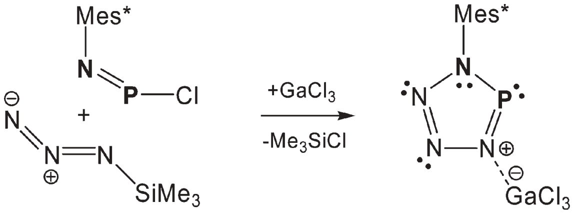


Fig. 1 P(III)–N five-membered rings. **Bold** marked species are known and fully characterized, the novel tetrazaphosphole is marked by a dashed rectangle (R = organic or inorganic group).



Scheme 1 Synthesis of **3**.

Herein, we wish to report (i) a new high-yielding synthetic procedure and (ii) a full experimental (Raman, ^1H, ^{13}C, ^{31}P (MAS) NMR, MS, X-ray) characterization of the first aryl-tetrazaphosphole (**2**), stabilized as $GaCl_3$ adduct (**3**), combined with DFT calculations.

Adding TMS–N_3 to the red solution of Mes*–N=P–Cl[5b] in benzene results in a slight brightening of the red colouration. ^{31}P NMR experiments displayed a new phosphorus resonance (singlet at $\delta[^{31}P]$ = 245.1 ppm) after one hour reaction time at ambient temperature, besides the resonance of the starting material Mes*–N=P–Cl (singlet at $\delta[^{31}P]$ = 135.1 ppm; *cf.* **1**: 317.2 and 292.1 ppm, trizaphosphole (R_2N_3PC, R = Ph):[6] 245 ppm). The best yield of Mes*–N_4P is obtained after one hour reaction time (intensity ratio of 1.00 (Mes*–N=P–Cl) : 0.17 (Mes*–N_4P)). Noticeable decomposition is observed with longer reaction times. Based on the excellent agreement between experiment and theory ($\delta_{calc}[^{31}P]$ = 243.5 ppm), this new resonance, which lies within the typical range of dicoordinated phosphorus(III) compounds, could be assigned to 1-(2,4,6-tri-*tert*-butylphenyl)tetrazaphosphole (**2**). Upon adding one equiv. of $GaCl_3$ to this reaction mixture, the red colour immediately vanishes and both ^{31}P NMR resonances disappear, while only one new singlet resonance at $\delta[^{31}P]$ = 228.8 ppm is observed, which could be assigned to the $GaCl_3$ adduct of **2** (*cf.* theory: $\delta_{calc}[^{31}P]$ = 229.5 ppm). ^{31}P MAS NMR experiments (which revealed only a single resonance at $\delta_{iso}[^{31}P]$ = 223(15) ppm) proved the existence of the same molecule in the solid state as that observed in the solvent NMR study.

Removal of the solvent results in a colourless polycrystalline powder.‡ Pure, dry **3** is unstable at ambient temperature, is heat and shock sensitive and decomposes slowly in the solid state and in solvents, releasing N_2 gas (detected by ^{14}N NMR and MS experiments). Colourless crystals of **3** rapidly become yellow when traces of water or oxygen are present. The intrinsic N_2 release is reduced under pressure and at low temperatures. Hence, **3** can be handled for a short period in the solid state and in common

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† Electronic Supplementary Information (ESI) available: Crystallographic data for **3** (Tables S1–S3), experimental and computational details (calculated structural and vibrational data of all described species (B3LYP)) (Tables S4–S6). See DOI: 10.1039/b517459g.

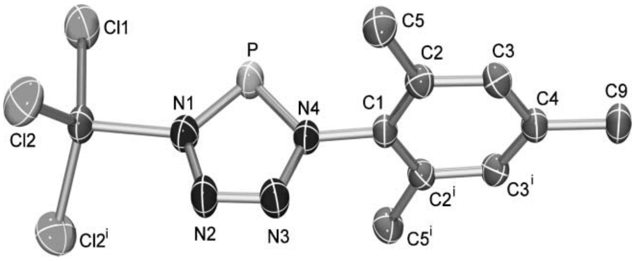

Fig. 2 ORTEP drawing of the molecular structure of **3** in the crystal. Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms and the disordered ^{t}Bu groups omitted for clarity). Selected bond lengths (Å) and angles (°)]: Ga–Cl1 2.146(1), Ga–Cl2 2.136(1), Ga–N1 1.990(4), P–N1 1.631(4), P–N4 1.664(3), N1–N2 1.374(5), N2–N3 1.286(5), N3–N4 1.355(5) and N4–C1 1.460(5); Cl1–Ga–Cl2 114.28(3), Cl1–Ga–N1 101.9(1), Cl1–Ga–Cl2^i 114.28(3), Cl2–Ga–N1 105.00(6), Cl2–Ga–Cl2^i 114.56(6), N1–P–N4 88.2(2), Ga–N1–P 129.7(2), Ga–N1–N2 116.1(3), P–N1–N2 114.3(3), N1–N2–N3 111.8(4), N2–N3–N4 111.5(3), P–N4–N3 114.2(3), P–N4–C1 128.0(3) and N3–N4–C1 117.8(3). Symmetry code: i = *x*, ½ − *y*, *z*.

organic solvents (*e.g.* benzene, CH_2Cl_2, ether, *etc.*) when cooled ($T < -5$ °C) and stored in the dark. **3** is easily prepared in bulk and in high yields (>96%).

X-Ray quality crystals were obtained from a saturated CH_2Cl_2 solution of **3** at −5 °C, and the single crystal X-ray study revealed an intriguing $GaCl_3$-stabilized 1-(2,4,6-tri-*tert*-butylphenyl)tetrazaphosphole. **3** crystallizes in colourless needles in the monoclinic space group $P2_1/m$ with two units per cell.§ As depicted in Fig. 2, the PN_4 ring is planar, like in the pentazoles and the triazadiphosphols.[3,7] The PN_4 ring is however slightly distorted, with two larger N–N bond lengths (d(N1–N2) = 1.374(5) and d(N3–N4) = 1.355(5) Å) and one very short N–N distance (d(N2–N3) = 1.286(5) Å; *cf.* N–N distances between 1.307–1.338 Å in phenylpentazole and 1.380(5) Å in **1**). These N–N distances between 1.28–1.38 Å are substantially shorter than the sum of the covalent radii (d_{cov}(N–N) = 1.48 and d_{cov}(N=N) = 1.20 Å),[8] which indicates partial double bond character for all the N–N bonds, with the N2–N3 bond being close to having a bond order of two. Hence, the release of molecular nitrogen seems to be predisposed. However, upon $GaCl_3$ adduct formation, the "naked" PN_4 ring becomes sandwiched between the large aryl and large $GaCl_3$ moieties, leading to an astonishing kinetic stability for **3** (Fig. 3).

A similar bond situation is found for the two P–N bonds (1.631(4) and 1.664(3) Å) of the PN_4 ring, which also lie in the range between a single and double bond (d_{cov}(N–P) = 1.8 and d_{cov}(N=P) = 1.6 Å). The Ga–N bond length of 1.990(4) Å is in the typical range found for other $GaCl_3$ adducts, *cf.* 1.978(3) in **1** and 2.003(5) Å in $Cl_3Ga{\cdot}NMe_2SiMe_2NMe_2$.[3,9] The N–P–N angle of 88.2(2)° is rather small compared to the P–N–N (114–115°) and N–N–N angles (111–112°). In the crystal, all molecules are parallel to each other and the aryl groups are superimposed (Fig. 4). 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 bond orbital analysis).[10]

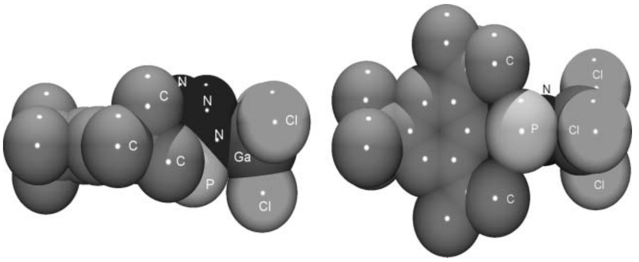

Fig. 3 Space-filling models of **3** (left: N_4P ring in plane, right: 90° out of plane).

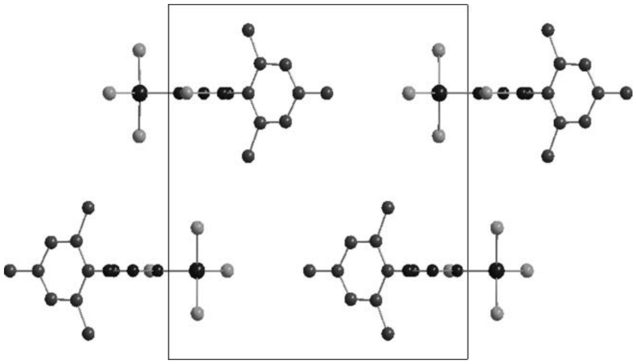

Fig. 4 View along the a-axis in the crystal of **3**.

Adducts such as **3** are typical charge transfer complexes, and the bond between the $GaCl_3$ and the azaphosphole can be regarded as a donor–acceptor bond.[3] The calculated adduct formation ((gas phase): Mes*–N_4P + $GaCl_3$ → **3**) is exergonic (ΔG_{298} = −2.1 and ΔH_{298} = −12.7 kcal mol^{-1}).† According to NBO analysis, the charge transfer is about 0.15e in **3** (*cf.* 0.16e in **1**). The P–N σ- and π-bonds are highly polarized and almost ideally covalent between the adjacent nitrogen atoms of the ring in **2** and **3**.

In summary, **3** represents a $GaCl_3$-stabilized tetrazaphosphole, with an electronic structure that is related to those of aromatic hydrocarbons that have $(4n + 2)$ π-electrons and therefore formally obey the Hückel rule. **3** can formally be regarded as the [2 + 3] cycloaddition product of Mes*–P=N$^+$ and N_3^- ions.

Caution: Like pentazoles, tetrazaphospholes and their adducts are explosives and thermally unstable species; appropriate safety precautions should be taken.

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Notes and references

‡ A solution of TMS–N_3 (0.115 g, 1.0 mmol) in benzene (10 mL) was added dropwise to a stirred solution of Mes*NPCl (0.326 g, 1.0 mmol) in benzene (10 mL) at 5 °C. To the red solution, $GaCl_3$ (0.194 g, 1.1 mmol) in benzene (20 mL) was quickly added *via* syringe, resulting in a colourless solution. Removal of the solvent *in vacuo* yielded **3** as fine, colourless, needle-like crystals, yield 0.498 g, 0.98 mmol, 98%; mp 145–150 °C (dec.). Anal. calc. % (found): C, 42.52 (42.06); H, 5.75 (5.35); N, 11.02 (10.61). NMR (CD_2Cl_2): ^{1}H 1.05 (s, 18 H), 1.37 (s, 9 H) and 7.66 (s, 2 H); $^{13}C\{^1H\}$ 30.9 (s, C9 ($CH_3)_3$), 32.9 (d, $^5J_{PC}$ = 3.8 Hz, C5 ($CH_3)_3$), 35.4 (s, C9), 37.0 (s, C5), 124.8 (s, C3), 127.9 (d, $^2J_{PC}$ = 6.9 Hz, C2), 147.1 (d, $^3J_{PC}$ = 3.1 Hz, C1) and 154.6 (s, C4) (Fig. 2). $^{31}P\{^1H\}$ 226.7 (s) (in C_6D_6: 228.8). ^{31}P MAS NMR (25 °C, ω_{rot} = 15 kHz): δ_{iso} 223 (s). *m*/*z* (%): 332 (0.3) [**2**]$^+$, 287 (0.8) [**2** − NP]$^+$, 261 (4.0) [Mes*NH_2]$^+$, 259 (4.6) [Mes* + Me]$^+$, 258 (7.9) [**2** − N_3P]$^+$, 246 (11.9) [Mes*]$^+$, 245 (7.3) [Mes* − H]$^+$, 244 (37.8) [Mes* − 2 H]$^+$, 228 (1.8), 202 (2.1) [Mes* − C_3H_5]$^+$, 188 (4.4) [Mes* − ^{t}Bu]$^+$, 132 (6.4)

[Mes* − 2^{t}Bu − 2H]$^+$, 56 (16.4) [^{t}Bu]$^+$, 41 (30.8) [C_3H_5]$^+$, 39 (10.4) [C_3H_3]$^+$, 36 (4.9) [HCl]$^+$ and 28 (100) [N_2]$^+$.

§ A suitable single crystal of [Mes*N_4P](GaCl$_3$) (**3**) was mounted in Kel-F oil on the end of a glass fiber and transferred to the N_2 cold stream of a Nonius Kappa CCD diffractometer (graphite-monochromated MoKα radiation with λ = 0.71073 Å). *Crystal data*: $N_4P_1Ga_1Cl_3C_{18}H_{29}$, FW = 508.5, monoclinic, V = 1200.47(6) Å^3, a = 6.0103(2) Å , b = 14.8760(4) Å, c = 13.4368(4) Å, α = 90°, β = 92.2260(13)°, γ = 90°, T = 200 K, space group $P21/m$ (No. 11), Z = 2, μ(Mo-Kα) = 1.557 mm^{-1}, 22291 reflections measured, 2857 unique (R_{int} = 0.119). The final R_1 was 0.048 and wR_2= 0.124. CCDC 292916. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517459g

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