Inorganic Chemistry

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Azidophosphenium Cations: Versatile Reagents in Inorganic Synthesis

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Supporting Information

ABSTRACT: This work describes the synthesis and characterization of a series of iminophosphorane-substituted phosphenium cations of the type $[R_2NPNP(Cl)_2NPNR'_2][GaCl_4]$ [R = *i*Pr; R′ = *i*Pr (**7**[**GaCl$_4$**]), $SiMe_3$ (**8**)], which are directly derived from azidophosphenium salt $[iPrNPN_3][GaCl_4]$ (**2*i*Pr**[**GaCl$_4$**]) and the corresponding chlorophosphane R_2NPCl_2. The reactivity of **7**[**GaCl$_4$**] toward 2,3-dimethylbutadiene (dmb) and 2,2′-bipyridine (bipy) was investigated, resulting in the formation of **7-dmb**[**GaCl$_4$**] and **7-Cl**. In addition, self-condensation of $[(Me_3Si)_2NPN_3][GaCl_4]$ (**2SiMe$_3$**[**GaCl$_4$**]) was studied in detail, and $[(Me_3Si)_2NPNP(XY)N(SiMe_3)_2][GaCl_4]$ [X = Cl; Y = Cl (**13**), N_3 (**14**)] were determined as products on the basis of ^{31}P NMR spectroscopy. The reaction of **2SiMe$_3$**[**GaCl$_4$**] with $[(Me_3Si)_2NPCl][GaCl_4]$ (**1SiMe$_3$**[**GaCl$_4$**]) yielded an unprecedented bicyclic 1,3,2λ^3,4λ^5-diazadiphosphetidine (**15**), which was formed via a $GaCl_3$-assisted Me_3SiCl elimination starting from **13**. Furthermore, cations of the type $[R_2NPNPR'_3][GaCl_4]$ [R = *i*Pr; R′ = *c*Hex (**19**)] were obtained by the effective combination of **2R**[**GaCl$_4$**] (R = *i*Pr, $SiMe_3$) with PR'_3 (R′ = Ph, *c*Hex). Azidochlorophosphanes $R_2NP(N_3)Cl$ [R = *i*Pr, $SiMe_3$ (**20R**)] are shown to be accessible when **2R**[**GaCl$_4$**] was combined with bipy. All new compounds were fully characterized by means of X-ray, vibrational spectroscopy, CHN analysis, and NMR experiments. All compounds were further investigated by means of density functional theory, and the bonding situation was accessed by natural bond orbital analysis.

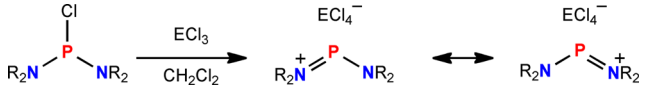
INTRODUCTION

Dimroth and Hoffmann reported on the synthesis of the first low-valent dicoordinated phosphorus compounds in phosphamethine cyanines in 1964.[1] The term "phosphenium cation" indicates a positively charged divalent phosphorus atom, which formally possesses an empty p orbital and a lone pair (LP) of electrons and thus can be considered as a main-group carbenoid, in which the central carbon atom is replaced by an isovalent P^+. These highly reactive species $[R^1{-}P{-}R^2]^+$ are stabilized best when R^1 and R^2 are π-electron-donating groups, such as amino functions NR_2 (R = Me, *i*Pr). The first examples of acyclic aminophosphenium salts of the type $[(R_2N)_2P][AlCl_4]$ and $[R_2NPCl][AlCl_4]$ [R = Me, Et, *i*Pr (**1R**[**AlCl$_4$**])] were prepared by Parry et al. by the effective combination of chlorophosphane and halogen-abstracting reagent ECl_3 (E = Al, Ga, Fe) in CH_2Cl_2 (Scheme 1).[2] Since then, the reactivity and coordination properties of these species have been studied in detail and reviewed regularly.[3−5] Nevertheless, the molecular structure of chlorophosphenium cations of the type $[R_2NPCl]^+$ remained unknown until recently [R = $SiMe_3$ (**1SiMe$_3$**$^+$),[6] *c*Hex[7]].

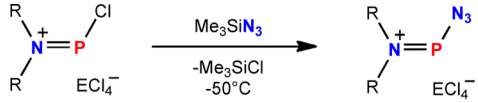
In 1984, Wolf et al. reported for the first time that $[R_2NPCl]^+$ [R = Me, *i*Pr (**1*i*Pr**$^+$)] can be further functionalized on the phosphenium center by treatment with pseudohalogensilanes such as Me_3SiN_3, whereupon Me_3SiCl is liberated (Scheme 2).[8]

In the absence of X-ray crystal structures, the intermediate formation of azidophosphenium cation $[R_2NPN_3]^+$ [R = Me, *i*Pr (**2*i*Pr**$^+$)] was established by ^{31}P NMR spectroscopy.[9]

Scheme 1. Synthesis of Bis(aminophosphenium) Salts by the Combination of Chlorophosphane (R = Me, Et, *i*Pr) and ECl_3 (E = Al, Ga, Fe) as a Halogen-Abstracting Reagent



Scheme 2. Synthesis of Azidophosphenium Salts Starting from Chlorophosphenium Salts in the Reaction with Me_3SiN_3 at −50 °C, Whereupon Me_3SiCl Is Released [E = Al (R = Me, *i*Pr), Ga (R = $SiMe_3$)]



R = Me, *i*Pr (**1*i*Pr**$^+$), $SiMe_3$ (**1SiMe$_3$**$^+$) R = Me, *i*Pr (**2*i*Pr**$^+$), $SiMe_3$ (**2SiMe$_3$**$^+$)

E = Al, Ga

Received: February 11, 2014
Published: March 21, 2014

   dx.doi.org/10.1021/ic500332s | *Inorg. Chem.* 2014, 53, 3880−3892

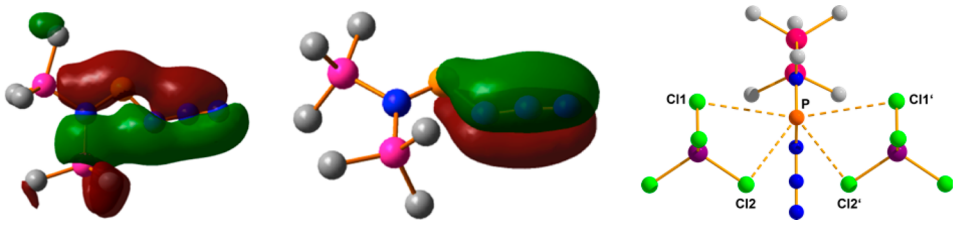
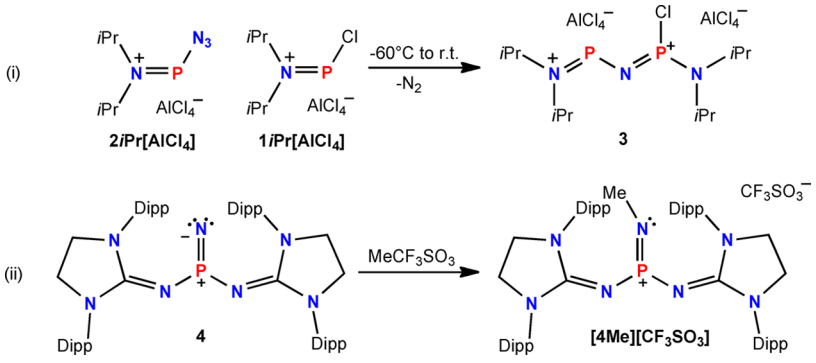
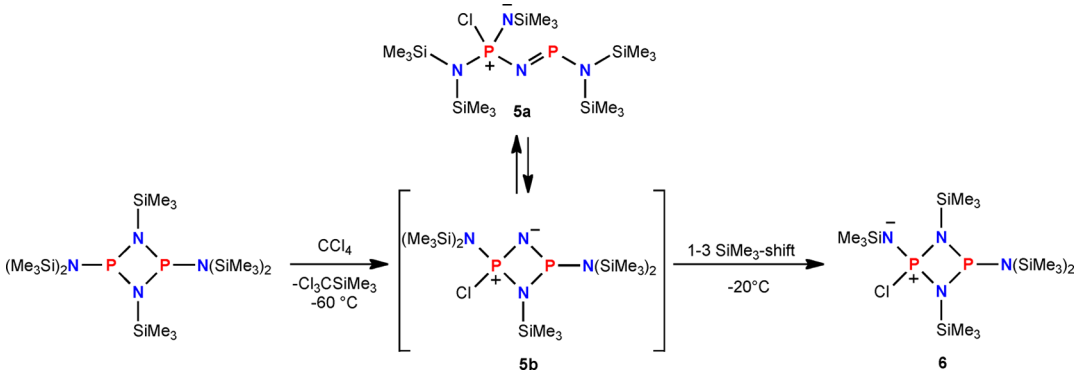


Figure 1. Depiction of selected Kohn–Sham orbitals calculated for the azidophosphenium cation $\mathbf{2SiMe_3}^+$ (left, middle). Ball-and-stick drawing of the anion···cation interactions in the azidophosphenium salt $\mathbf{2SiMe_3[GaCl_4]}$ (right). Four close contacts are observed (distances in angstroms): P1–Cl1 3.1582(6), P1–Cl3 3.7630(7), P1–Cl3′ 3.273(7), P1–Cl4′ 4.0212(9).

Scheme 3. (i) Formation of the Phosphenium–Phosphonium Dication 3^{2+} as a $AlCl_4^-$ Salt According to Early Studies by Wolf et al.[6,7,16] and (ii) Preparation of the First Isolable Iminophosphorane Cation $[4Me][CF_3SO_3]$[14,15]



Scheme 4. Formation of Iminophosphorane–Iminophosphanes 5 and Rearrangement in a 1–3-Trimethylsilyl Shift toward Diazadiphosphetidines 6 According to Studies by Boeske et al.[17,18]



Azidophosphenium ions are considered highly labile and only of transient nature because they can decompose in a Staudinger reaction.[10] In the classical Staudinger reaction, organic azides react with P^{III} compounds in an oxidative coupling between phosphorus and nitrogen, in which phosphorus is oxidized to P^V and dinitrogen is liberated, affording a great variety of iminophosphoranes, which are an important class of substances in organic synthesis and can be further hydrolyzed to give amines.[11]

Nevertheless, our group succeeded in the isolation of an azidophosphenium cation in the salt $[(Me_3Si)_2NPN_3][GaCl_4]$ ($\mathbf{2SiMe_3[GaCl_4]}$) at −50 °C, which, as an isolated crystalline solid, is stable below −30 °C for at least 1 year.[6] This astonishing stability stems from delocalization of the positive charge and formal π-electron density along the NPN_3 skeleton (Figure 1, left) as well as from four close van der Waals contacts to chlorine atoms of the $GaCl_4^-$ anion (Figure 1, right). Furthermore, we succeeded in isolation of the analogous pseudohalogen-substituted salts $[(Me_3Si)_2NPX][GaCl_4]$ (X = NCO, NCS, $OSiMe_3$), which were shown to react with Lewis bases such as 4-(*N*,*N*-dimethylamino)pyridine and as dienophiles with dienes such as 2,3-dimethyl-1,3-butadiene (dmb) or 1,3-*cyclo*-hexadiene.[12]

However, in solution, only traces of $\mathbf{2SiMe_3[GaCl_4]}$ [$\delta(^{31}P)$ = 368.6 ppm, at −65 °C] were detected by means of low-temperature ^{31}P NMR techniques because the salt readily precipitates from cold CH_2Cl_2 solutions. At room temperature, only the resonances of unidentified decomposition products could be detected. A thorough search of the literature revealed that Wolf and co-workers investigated the reactivity of $\mathbf{2}i\mathbf{Pr[AlCl_4]}$, which they assumed to self-condense, affording polymers and phosphenium–phosphonium salts of the type $[i\mathrm{Pr_2NPNP(Cl)N}i\mathrm{Pr_2}][AlCl_4]_2$ (**3**; Scheme 3, reaction i). In accordance with the proposed molecular structure of $\mathbf{3}^{2+}$, an AX spin system was observed in the $^{31}P\{^1H\}$ NMR spectrum with distinct resonances for the phosphenium phosphorus and phosphonium center (cf. $[i\mathrm{Pr_2NPNP(Cl)N}i\mathrm{Pr_2}]^+$ $\delta_{\mathrm{phosphenium}}(^{31}P)$ = 311 ppm, $\delta_{\mathrm{phosphonium}}(^{31}P)$ = 26 ppm,

dx.doi.org/10.1021/ic500332s | Inorg. Chem. 2014, 53, 3880–3892

$J(^{31}P-^{31}P)$ = 111.5 Hz; Scheme 3). However, the formation of a tricoordinated iminophosphonium species is unlikely. Because of the high electrophilicity of the phosphorus center in such iminophosphorane cations, the counterion usually binds covalently to the phosphorus center.[13] Just recently, the first isolable cationic iminophosphorane cation ([**4Me**][CF_3SO_3]) was prepared by methylation of an isolable $\sigma^3\lambda^5$-nitridophosphorane [**4**; also $\sigma^3\lambda^5$-nitridophosphane(V)], which is stabilized by bulky imidazolin-2-iminato substituents, therefore effectively denying interaction with the anion (Scheme 3, reaction ii).[14,15]

Systems that are related to the phosphenium−phosphonium species **3** are iminophosphane−iminophosphoranes of the type $(Me_3Si)_2NP(Cl)(NSiMe_3)NPN(SiMe_3)_2$ (**5a**), which possesses similar ^{31}P NMR shifts for the dicoordinated P^{III} and tetracoordinated P^V atoms, respectively (cf. **5a** $\delta(^{31}P)$ = 341.1 (P^{III}) and −10.6 (P^V) ppm, J(P−P) = 79.9 Hz; Scheme 4).[17] Moreover, they display an N−P−N−P−N backbone similar to that found in $\mathbf{3}^{2+}$. Furthermore, **5a** was shown to be in equilibrium with its cyclic form **5b**, which undergoes a 1,3-trimethylsilyl migration to yield a cyclic 1,3,2λ^3,4λ^5-diazadiphosphetidine (**6**; Scheme 4).[18]

Herein, by utilizing **2*i*Pr**[$GaCl_4$] as a model compound, we describe the decomposition products of azidophosphenium species **2SiMe$_3$**[$GaCl_4$]. The work of Wolf and co-workers has been reevaluated, the missing solid-state structures of **1*i*Pr**$^+$ and **2*i*Pr**$^+$ have been determined, and self-condensation products of **2*i*Pr**[$AlCl_4$] need to be revised on the basis of our findings. Furthermore, **2*i*Pr**[$GaCl_4$] is shown to be a versatile starting material for the formation of complex cations with an N−P−N−P−N backbone. Starting from **2SiMe$_3$**[$GaCl_4$], we succeeded in isolating a unique bicyclic system bearing a P_2N_2 ring, which is connected to a NGa_2Cl four-membered ring representing the first structurally characterized 1,3-diaza-2λ^3,4λ^5-diphosphetidine.

RESULTS AND DISCUSSION

Phosphenium salts of the type [R_2NPCl][$GaCl_4$] [R = *i*Pr, $SiMe_3$ (**1R**[$GaCl_4$])] are most efficiently generated by the combination of dichlorophosphane R_2NPCl_2 and $GaCl_3$ in CH_2Cl_2 at −80 °C. Concentration of the respective reaction mixtures at −50 °C yielded colorless crystalline materials, which in the case of **1*i*Pr**[$GaCl_4$] are stable at ambient temperatures for at least 1 h (vide infra). In contrast to **1*i*Pr**[$GaCl_4$], **1SiMe$_3$**[$GaCl_4$] decomposes in isolated form even at temperatures below −30 °C by thermal elimination of Me_3SiCl. The dynamic solution chemistry of **1*i*Pr**[$GaCl_4$] and **1SiMe$_3$**[$GaCl_4$] was extensively studied by means of variable-temperature ^{31}P NMR spectroscopy, and a dynamic equilibrium between R_2NPCl_2 and $GaCl_3$ and the respective phosphenium salt [R_2NPCl][$GaCl_4$] is characteristic for these species.[7,19] Although **1*i*Pr**[$AlCl_4$] was first reported in 1976 by Parry and co-workers, its solid-state structure has not been reported so far.[2,20] Crystal structures have just been reported for products in which **1*i*Pr**$^+$ was incorporated by means of the oxidative addition of substrates to the phosphenium center (**A**,[21] **B**,[22] and **C**;[23] Figure 2).

Treating iPr_2NPCl_2 with $GaCl_3$ in a CH_2Cl_2 solution at −80 °C and letting the mixture stand overnight at −80 °C afforded crystals of **1*i*Pr**[$GaCl_4$] suitable for X-ray analysis. **1*i*Pr**[$GaCl_4$] crystallizes solvent free in the monoclinic space group $P2_1/c$ with four formula units in the unit cell (Figure 3, left). The short P−N_{amino} distance [1.591(3) Å] is best described as a P−N $p_\pi p_\pi$ double bond [cf. P−N_{amino} of **1SiMe$_3$**[$GaCl_4$] (avg)

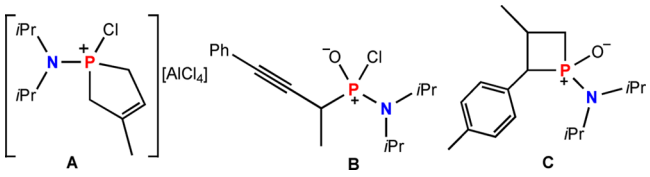


Figure 2. Crystallographically determined structures of molecules formally incorporating **1*i*Pr**$^+$.

1.590 Å; $\sum r_{cov}$(P=N) = 1.60 Å], in accordance with natural bond orbital (NBO) analysis.[19,24] The P−Cl bond is shortened with respect to the sum of the covalent radii [2.003(1) Å; $\sum r_{cov}$(P−Cl) = 2.04 Å; cf. [$(Me_3Si)_2NPCl$][$GaCl_4$] 2.019(4) Å].[19,24] The $GaCl_4^-$ counteranion significantly interacts with the electron-deficient phosphenium center because two P1−Cl_{anion} contacts are detected within the sum of the respective van der Waals radii of phosphorus and chlorine [3.014(1) Å; $\sum r_{vdW}$(P−Cl) = 3.55 Å].[25] Hence, a significant charge transfer of 0.15e from the anion to the cation further enhances its stability by ion pairing. Salt formation is also visualized in the Raman spectrum, which reveals a sharp band at 347 cm^{-1} for the A_1 asymmetric Ga−Cl stretching mode, whereas free $GaCl_3$ is not observed.[26]

For the first time, Wolf and co-workers discussed the existence of an azidophosphenium salt of the type [iPr_2NPN_3][$AlCl_4$] (**3**) in 1984. They reported that **1*i*Pr**[$AlCl_4$] reacts with Me_3SiN_3 to intermediately yield **2*i*Pr**[$AlCl_4$], which self-condenses to yield phosphorus bis(cations) (Scheme 3, reaction i).[8,9] However, the solid-state structure of such phosphenium azides remained unknown until our group uncovered the molecular structure of [$(Me_3Si)_2NPN_3$][$GaCl_4$] (**2SiMe$_3$**[$GaCl_4$]).[19] **2SiMe$_3$**[$GaCl_4$] can be prepared at −50 °C by treating a CH_2Cl_2 solution of **1SiMe$_3$**[$GaCl_4$] with Me_3SiN_3. Nevertheless, **2SiMe$_3$**[$GaCl_4$] is only stable in the solid state below −30 °C and decomposes rapidly in a CH_2Cl_2 solution as vigorous gas evolution is observed upon thawing.[6]

Following the synthetic protocol that yielded **2SiMe$_3$**[$GaCl_4$], **2*i*Pr**[$GaCl_4$] was prepared in good yield (81%) and its structure was determined by X-ray crystallographic measurements. **2*i*Pr**[$GaCl_4$] possesses two major advantages compared to **2SiMe$_3$**[$GaCl_4$]: (i) **2*i*Pr**[$GaCl_4$] cannot be engaged in chlorine/methyl exchange reactions in the presence of $GaCl_3$, which is common for silylated aminopnictanes;[27−30] (ii) **2*i*Pr**[$GaCl_4$] is not sensitive toward the thermal release of Me_3SiCl, which is well documented for silylated aminopnictanes in the presence of $GaCl_3$.[19,31,32] Moreover, **2*i*Pr**[$GaCl_4$] is thermally stable up to 78 °C. Therefore, we envisaged **2*i*Pr**[$GaCl_4$] as a model system for thermal decomposition reactions of azidophosphenium salts. **2*i*Pr**[$GaCl_4$] crystallizes solvent-free in the monoclinic space group $C2/c$ with eight formula units in the unit cell (Figure 3, right). The geometry of the NPN_3 skeleton resembles that of the azidophosphenium ion in **2SiMe$_3$**[$GaCl_4$] with a N_{amino}−P1 double bond [**2*i*Pr**$^+$ 1.6003(9) Å; cf. **2SiMe$_3$**$^+$ 1.597(3) Å][19] and a short P1−N_{azide} distance [1.665(1) Å; cf. $\sum r_{cov}$(P=N) = 1.60, $\sum r_{cov}$(P−N) 1.82 Å].[24] The N−P−N angle [100.57(5)°; cf. **2SiMe$_3$**$^+$ 101.03(9)°][6] is rather acute, and the azide group shows the typical trans-bent configuration (regarding the phosphorus atom, P1−N1−N2−N3 180°) with an N1−N2−N3 angle of 171.4(2)°, with a formally sp^2-hybridized N_α atom [P1−N1−N2 121.19(9)°]. The closest P1−Cl_{anion} contact [3.0448(4) Å] is shorter than the sum of the respective van der

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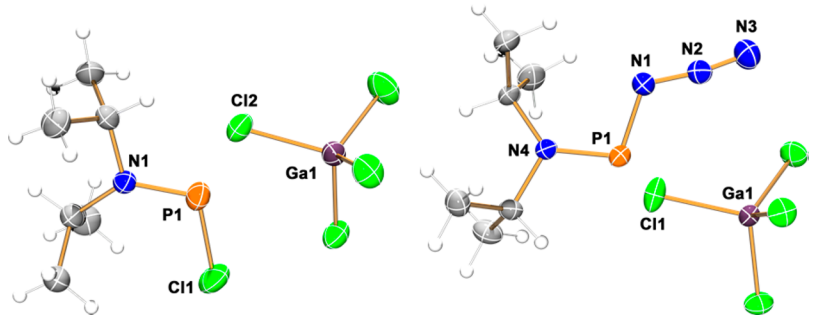
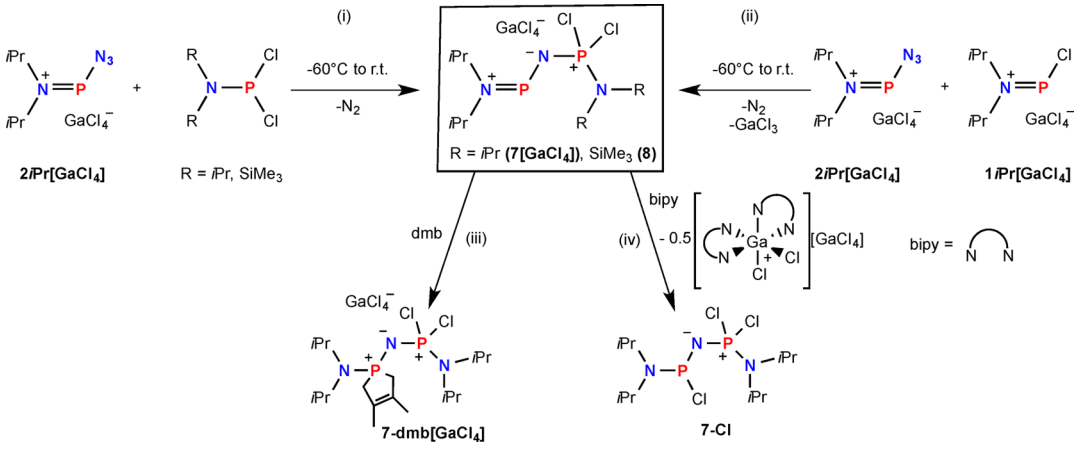


Figure 3. ORTEP drawings of the molecular structures of **1*i*Pr**[$GaCl_4$] (left) and **2*i*Pr**[$GaCl_4$] (right). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): **1*i*Pr**[$GaCl_4$], P1−N1 1.591(3), P1−Cl1 2.003(1), P1−Cl2 3.014(1), N1−C1 1.502(4), N1−C4 1.520(4); N1−P1−Cl1 106.9(1); Σ(<N1) 360.0; C1−N1−P1−Cl1 −0.6(3), C1−N1−P1−Cl2 94.9(3); **2*i*Pr**[$GaCl_4$], P1−N4 1.6003(9), P1−N1 1.665(1), N1−N2 1.248(1), N2−N3 1.114(2), N4−C1 1.509(1), N4−C4 1.504(1); N1−P1−N4 100.57(5), N1−N2−N3 171.4(1); Σ(<N4) 359.97; C4−N4−P1−N1 2.8(1), P1−N1−N2−N3 171.6(9).

Scheme 5. Different Pathways for the Preparation of 7[$GaCl_4$] (Reactions i and ii) and Examples of Transformations Starting from 7[$GaCl_4$] (Reactions iii and iv)



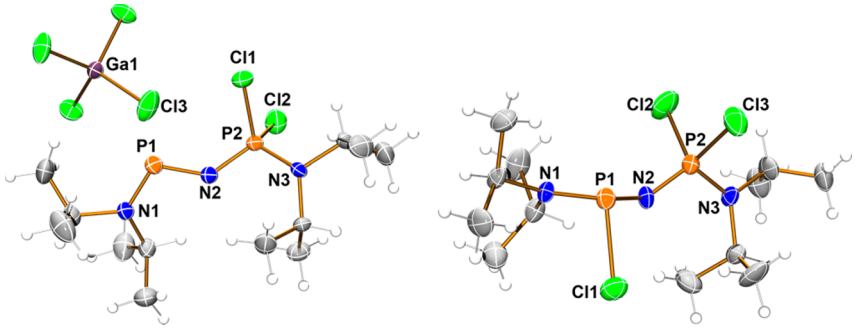


Figure 4. ORTEP drawings of the molecular structures of 7[$GaCl_4$] (left) and **7-Cl** (right). Ellipsoids are drawn at 50% probability at −100 °C. Selected bond lengths (Å) and angles (deg): 7[$GaCl_4$], P1−N1 1.1611(2), P1−N2 1.597(2), P2−N2 1.557(2), P2−N3 1.597(2), P2−Cl1 1.9987(8), P2−Cl2 2.0055(8), P1−Cl5 3.532(1); N1−P1−N2 104.97(9), P2−N2−P1 129.4(1), N2−P2−N3 112.4(1), ∑(<P2) 334.58; ∑(<N1) 359.95; ∑(<N3) 359.88; N2−P1−N1−C4 178.0(2), N1−P1−N2−P2 176.6(2), N3−P2−N2−P1 −165.0(2), N2−P2−N3−C10 178.6(2); **7-Cl**, P1−N1 1.640(4), P1−N2 1.660(4), P2−N2 1.504(2), P2−N3 1.603(4), P1−Cl1 2.207(2), P2−Cl2 2.020(2), P2−Cl3 2.038(2); N1−P1−N2 101.8(2), P2−N2−P1 138.1(3), N2−P2−N3 114.7(2), ∑(<P1) 301.1, ∑(<P2) 333.3, ∑(<N1) 358.6, ∑(<N3) 359.1; N2−P1−N1−C4 28.4(4), N3−P2−N2−P1 149.7(4).

Waals radii [$\sum r_{vdw}$(P−Cl) = 3.55 Å].[25] Additionally, three more contacts between chlorine atoms from the anion and the phosphenium center are found, a geometrical arrangement that is in accordance with other pseudohalogen-substituted phosphenium salts (e.g., Figure 1).[12] This implicates a small charge transfer from the anion to the phosphenium ion, which was calculated by means of NBO analysis and amounts to only 0.08 e; therefore, the cation can be considered almost "naked".[33]

In a first series of experiments, we followed the procedure described by Wolf et al., in which they carried out the reaction of **2*i*Pr**[$GaCl_4$] with 1 equiv of the chlorophosphenium salt **1*i*Pr**[$GaCl_4$], which resulted according to their interpretation in the formation of a bis(cation) ($\mathbf{3}^{2+}$) on the basis of ^{31}P NMR spectroscopy (Scheme 3, reaction i).[8] Treating **2*i*Pr**[$GaCl_4$]

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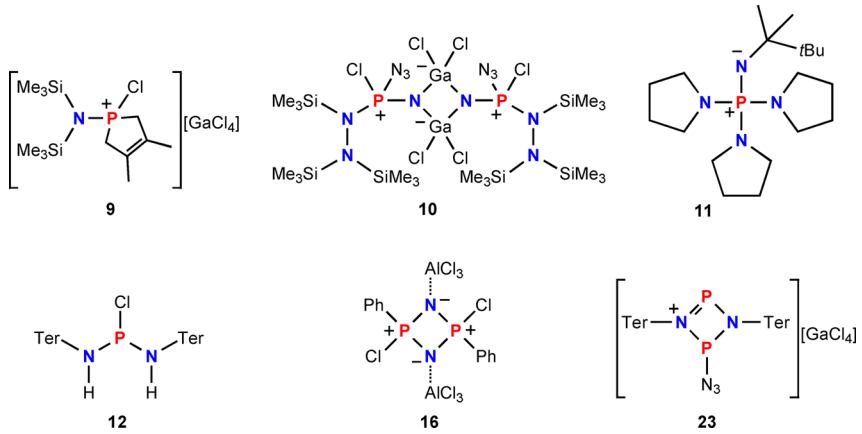


Figure 5. Structures of phospholenium salt **9**, Staudinger product **10**, triaminoiminophosphorane **11**, terphenyl-substituted aminochlorophosphane **12**, cyclodiphospha(V)diazene **16**, and *cyclo*-diphospha(III)diazenium salt **23**.

with equimolar amounts of **1*i*Pr**[**GaCl$_4$**] in CH_2Cl_2 at −50 °C and subsequent warming to room temperature led to vigorous gas evolution, and after workup and recrystallization from CH_2Cl_2, phosphenium species [*i*Pr$_2$NPNP(Cl)$_2$N*i*Pr$_2$][GaCl$_4$] (**7**[**GaCl$_4$**]) could be isolated (Scheme 5, reaction ii; Figure 4, left). The formation of **7**[**GaCl$_4$**] was unequivocally proven by X-ray crystallographic analysis and is best described as a Staudinger reaction between the azide **2*i*Pr**[**GaCl$_4$**] and the parent phosphine *i*Pr$_2$NPCl$_2$, which is present in solutions of **1*i*Pr**[**GaCl$_4$**] according to ^{31}P NMR experiments (vide infra). Hence, in this reaction, 1 equiv of $GaCl_3$ must remain in the mixture.

7[**GaCl$_4$**] is a thermally robust (T_{dec} = 125 °C) colorless crystalline solid that dissolves in polar solvents such as CH_2Cl_2 and C_6H_5F and is insoluble in *n*-hexane and benzene. **7**[**GaCl$_4$**] features an AX spin system in the ^{31}P NMR spectrum with two distinct doublets for the phosphenium phosphorus and the iminophosphorane moiety [**7**[**GaCl$_4$**]; $\delta_{phosphenium}(^{31}P)$ = 311.2, $\delta_{iminophosphorane}(^{31}P)$ = 27.4; $^2J(^{31}P-^{31}P)$ = 111.5 Hz], which lies in the typical range of four-coordinate P^V compounds [cf. $\delta(^{31}P)$ = 33.4 ppm for (*i*Pr)$_2$NP(Cl)(N$_3$)N(Ph)·AlCl$_3$].[34] In the ^{1}H spectrum, four sets of signals are detected for the *i*Pr groups, with one of the septets of the methine protons being split into a septet of doublets, indicating interaction of that proton with the phosphenium phosphorus atom, which results in deshielding and therefore a rather strong downfield-shifted signal.

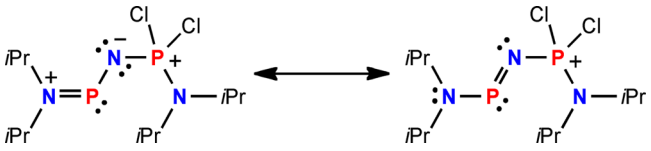
To render the formation of **7**[**GaCl$_4$**] stoichiometrically, **2*i*Pr**[**GaCl$_4$**] and an equimolar amount of *i*Pr$_2$NPCl$_2$ were combined at −50 °C and allowed to slowly warm to room temperature, which was accompanied by the evolution of dinitrogen (Scheme 5, reaction i). **7**[**GaCl$_4$**] is the sole product and can be crystallized by gradually cooling the saturated reaction mixture to −24 °C overnight (isolated yield 63%). The formation of **7**[**GaCl$_4$**] underlines the Staudinger-type reactivity of azidophosphenium species with phosphanes. In the Staudinger reaction, organic azides typically react with PPh_3 in an oxidative addition to yield iminophosphoranes as an intermediate, which can be further hydrolyzed to give amines and phosphane oxides.[10] In the case of **2*i*Pr**[**GaCl$_4$**] in the first reaction step, either the phosphenium cation **1*i*Pr**$^+$ or *i*Pr$_2$NPCl$_2$ adds with its phosphorus atom to the N_{azide} atom while eliminating dinitrogen and forming the corresponding iminophosphorane-substituted phosphenium cation. The dicationic structure proposed by Wolf and co-workers was not observed;[8] even if such a species was formed transiently, it can be assumed that it forms the iminophosphorane moiety by abstracting a chloride from the $GaCl_4^-$ anion.[13]

Adding (Me$_3$Si)$_2$NPCl$_2$ instead of *i*Pr$_2$NPCl$_2$ to a solution of **2*i*Pr**[**GaCl$_4$**] at −50 °C and warming to room temperature yielded after workup a colorless solid, which was recrystallized from fluorobenzene (C_6H_5F) at 5 °C and found to be the addition product of (Me$_3$Si)$_2$NPCl$_2$ to **2*i*Pr**[**GaCl$_4$**], the iminophosphorane−phosphenium salt [*i*Pr$_2$NPNP(Cl$_2$)N-(SiMe$_3$)$_2$][GaCl$_4$] (**8**). **8** displays the expected AX spin system in the ^{31}P NMR spectrum, with the phosphenium center resonating at 311.3 ppm (cf. **7**[**GaCl$_4$**] 311.2 ppm), whereas the P^V atom is detected at 30.4 ppm, which is downfield-shifted compared to that of **7**[**GaCl$_4$**] (27.4 ppm). The compound was characterized by X-ray analysis, and a representation of the molecular structure of **8** is shown in Figure 6 (right). Owing to their similarity, the molecular structures of **7**[**GaCl4**] and **8** are discussed in one context.

7[**GaCl$_4$**] crystallizes in the monoclinic space group $P2_1/c$ with eight formula units in the cell and thus two independent formula units in the asymmetric unit, whereas **8** crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell. The discussion of the structure is led for one independent formula unit, respectively. The cations in **7**[**GaCl$_4$**] and **8** possess both a dicoordinated phosphenium phosphorus atom P1 with a P1−N$_{amino}$ double bond [**7**[**GaCl$_4$**] 1.611(2) Å; **8** 1.612(4) Å] and a phosphonium phosphorus atom P2, which is also bound to another amino group with a short P2−N3 distance [**7**[**GaCl$_4$**] 1.597(3) Å, **8** 1.588(5) Å; cf. **9** P−N 1.6089(8) Å,[12] **10** P^V−N$_{amino}$ 1.634(5) Å; Figure 5],[35] which can be considered a P^V−N single bond. The imino−nitrogen phosphorus distances N2−P1 [**7**[**GaCl$_4$**] 1.557(2) Å; **8** 1.597(4) Å] and N2−P2 [**7**[**GaCl$_4$**] 1.597(2) Å; **8** 1.550(4) Å] are rather short (cf. **10** P^V−N$_{imino}$ 1.558(4) Å],[35] with both distances being shorter than the sum of the respective covalent radii for a P−N double bond [$\sum r_{cov}$(P=N) = 1.60 Å],[24] indicating a certain degree of π delocalization along the N_2P_2 moiety, which is further underlined by the two canonical Lewis formulas for **7**[**GaCl$_4$**] shown in Scheme 6. Overall, N_3P_2 is W-shaped, with a rather acute N1−P1−N2 angle [**7**[**GaCl$_4$**] 104.97(9)°; **8** 105.0(2)°], a slightly larger N2−P2−N3 angle [**7**[**GaCl$_4$**] 112.4(1)°; **8** 113.6(2)°], and a typical P1−N2−P2 angle (**7**[**GaCl$_4$**] 129.4(1)°; **8** 133.2(3)°] for the sp^2-hybridized imino nitrogen, with a LP of electrons on the nitrogen site according to NBO analysis. The closest contacts between

dx.doi.org/10.1021/ic500332s | *Inorg. Chem.* 2014, 53, 3880−3892

Scheme 6. Two Canonical Lewis Formulas of the Cation in 7[GaCl$_4$] Displaying π Delocalization along the N−P−N−P−N Backbone in 7$^+$



phosphorus and GaCl$_4^-$ [7[**GaCl$_4$**] 3.532(1) Å; **8** 3.289(2) Å] are in the range of the respective van der Waals radii of phosphorus and chlorine [$\sum r_{vdw}$(P−Cl) = 3.55 Å].[25] Therefore, the anion and cation are well separated, which is supported by the calculated charge transfer.[33] Overall, P2 is distorted tetrahedrally coordinated, which is in accordance with a four-coordinate phosphonium phosphorus.

To test the reactivity of 7[**GaCl$_4$**] as a dienophile, we added 2,3-dimethyl-1,3-diene (dmb) because phosphenium cations, which might be regarded as nucleophilic carbenes with respect to the reactivity, are known to react with suitable dienes in chelotropic [4 + 1] cycloaddition reactions. This reaction resulted in the formation of the expected phospholenium species **7-dmb**[**GaCl$_4$**] (Scheme 5, reaction iii), which was crystallographically characterized (Figure 5, left). **7-dmb**-[**GaCl$_4$**] crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell. Upon the addition of dmb, the P−N$_{amino}$ [1.624(2) Å] and N$_{imino}$−P1 [1.618(2) Å] bonds elongate, whereas the P2−N$_{imino}$ [1.533(2) Å] bond shortens significantly compared to 7[**GaCl$_4$**] (cf. **11** 1.511 Å; Figure 5).[36] The anion and cation are well separated, and no contacts are observed between them. The phosphole moiety is almost planar and slightly bent toward the P^{V}Cl$_2$ fragment.

Furthermore, we wanted to set free the parent chlorophosphane *i*Pr$_2$NPClNP(Cl)$_2$N*i*Pr$_2$ (**7-Cl**). Therefore, GaCl$_3$ needs to be removed from the reaction mixture, which can easily be achieved by adding 2,2′-bipyridine (bipy) to a CH$_2$Cl$_2$ solution of 7[**GaCl$_4$**] because GaCl$_3$ is known to form a chelating complex with bipy in [GaCl$_2$(bipy)$_2$][GaCl$_4$], which is hardly soluble in CH$_2$Cl$_2$ and can be removed by filtration (Scheme 5, reaction iv).[37,38] In the course of this reaction, chlorine is back-substituted to the phosphenium phosphorus and **7-Cl** is obtained by extracting the crude reaction mixture with *n*-hexane and identified by ^{31}P and ^{1}H NMR spectroscopy. As expected, the tricoordinated P^{III} resonates in the ^{31}P NMR spectrum at 156.2 ppm (cf. **12** 129.9 ppm; Figure 5),[17,18,39] whereas P^V is high-field-shifted compared to the starting material 7[**GaCl$_4$**] [δ_{P^V}(^{31}P) = −6.4; cf. 7[**GaCl$_4$**] 27.4 ppm], indicating the loss of positive charge. **7-Cl** crystallizes in the monoclinic space group $P2_1$ with two molecules in the unit cell (Figure 6, right). Upon chlorine back-substitution, the N1−P1 [1.640(4) Å] and N2−P1 [1.660(4) Å] distances elongate significantly toward values typical for N−P single bonds in chlorophosphanes [cf. **12** (avg) 1.644 Å; Figure 5].[39] The N2−P2 [1.504(4) Å] bond is found to be shorter than that in the parent cation 7$^+$, indicating a localized P^V−N double bond, whereas the P2−N3 [1.603(4) Å] distance can still be considered a P^V−N single bond. The P^{III} atom P1 is trigonal-pyramidally coordinated, whereas P2 exhibits the expected distorted tetrahedral environment. The striking structural feature of **7-Cl** is the P−Cl bond [2.207(2) Å], which is significantly elongated with respect to the respective sum of the covalent radii of phosphorus and chlorine [cf. $\sum r_{cov}$(P−Cl) = 2.10 Å]. Therefore, it is plausible to discuss a certain degree of phosphenium character due to strong hyperconjugative effects, which is underlined by a calculated positive charge of 0.43e for the isolated 7$^+$ cation, which is only slightly more positive than the formal cation in [(Me$_3$Si)$_2$NPCl][Cl] with a cationic charge of 0.34e.[19]

Having fully characterized 7[**GaCl$_4$**], we turned back to our initial starting point to uncover the decomposition products of azidophosphenium salt **2SiMe$_3$**[**GaCl$_4$**] (Scheme 7). In a first series of experiments, a CH$_2$Cl$_2$ solution of **2SiMe$_3$**[**GaCl$_4$**] was allowed to slowly warm to room temperature and the reaction was followed by ^{31}P NMR spectroscopy. At −40 °C, only minimal amounts of the parent azidophosphenium cation **2SiMe$_3^+$** were present in solution (green, Figure 7). In addition, two broad doublets could be detected in the downfield region of the spectrum at 357.6 and 354.4 ppm, respectively, with a splitting of 90.8 and 79.9 Hz and a corresponding second set of doublets at 29.3 and 22.1 ppm, respectively, supportive of a species that contains both a phosphenium phosphorus atom and a four-coordinated P^V. Alongside these three species, impurities are detected in the high-field region, which could not be identified. Hence, these data are supportive of the formation

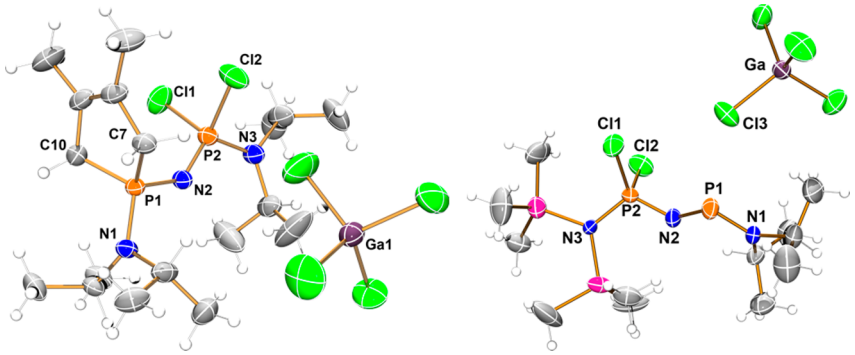
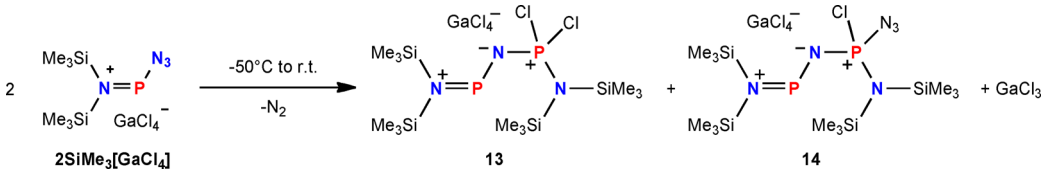


Figure 6. ORTEP drawings of the molecular structures of **7-dmb**[**GaCl$_4$**] (left) and **8** (right). Ellipsoids are drawn at 50% probability at −100 °C, and only the major part is displayed. Selected bond lengths (Å) and angles (deg): **7-dmb**[**GaCl$_4$**], P1−N1 1.624(2), P1−N2 1.618(2), P2−N2 1.533(2), P2−N3 1.607(2), P2−Cl1 2.0207(9), P2−Cl2 2.0073(9), P1−C7 1.799(2), P1−C10 1.796(2); P2−N2−P1 137.7(1), N2−P2−N3 114.1(1); Σ(<P1) 335.26, Σ(<P2) 335.62, Σ(<N1) 358.76, Σ(<N3) 360; N2−P1−N1−C1 79.8(2), P1−C7−C8−C11 −164.9(2); **8**, P1−N1 1.612(4), P1−N2 1.597(4), P2−N2 1.550(4), P2−N3 1.588(5), P2−Cl1 1.996(2), P2−Cl2 2.010(2), P1−Cl3 3.289(2); N1−P1−N2 105.0(2), P2−N2−P1 133.2(3), N2−P2−N3 113.6(2); Σ(<P1) 337.64, Σ(<N1) 359.9, Σ(<N3) 359.4; N2−P1−N1−C4 178.0(2), N1−P1−N2−P2 9.4(4), N3−P2−N2−P1 −130.5(4), Cl2−P2−N3−Si1 120.8(3).

dx.doi.org/10.1021/ic500332s | Inorg. Chem. 2014, 53, 3880−3892

Scheme 7. Self-Condensation via a Staudinger Reaction in Azidophosphenium Species $2SiMe_3[GaCl_4]$



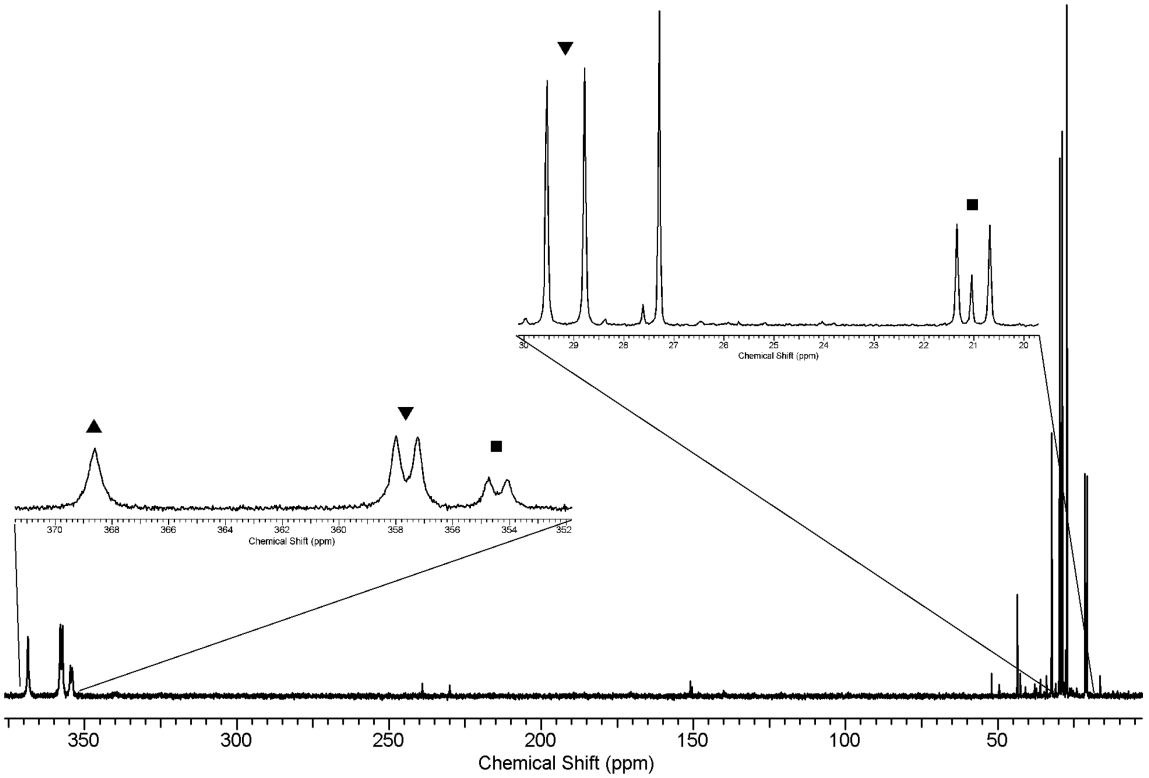
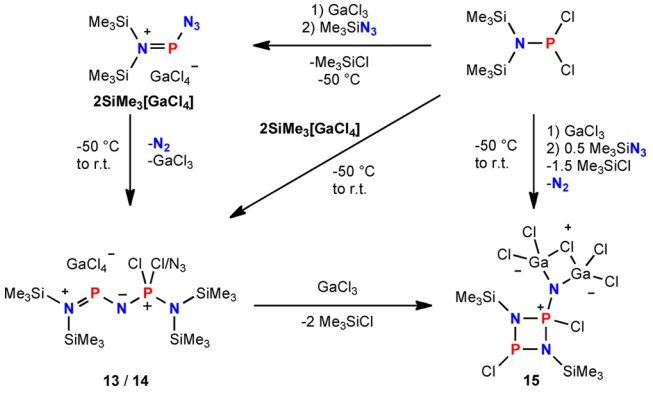


Figure 7. ^{31}P NMR spectrum of a CH_2Cl_2 solution of $2SiMe_3[GaCl_4]$ recorded at −40 °C. The signal at 368.6 ppm (▲) corresponds to the cation $2SiMe_3^+$, and the doublets correspond to 13^+ (▼) and 14^+ (■), respectively, and unidentified impurities.

of $[(Me_3Si)_2NPNP(Cl)_2N(SiMe_3)_2][GaCl_4]$ (**13**) as the major product [$\delta_{phosphenium}(^{31}P)$ = 357.6 ppm, $\delta_{P^V}(^{31}P)$ = 29.3 ppm; Figure 7]. However, the second set of doublets indicates the formation of mixed species $[(Me_3Si)_2NPNP(Cl)(N_3)N(SiMe_3)_2][GaCl_4]$ (**14**; $\delta_{phosphenium}(^{31}P)$ = 354.3 ppm, $\delta_{P^V}(^{31}P)$ = 22.1 ppm; Figure 7 and Scheme 7). In analogy to the formation of $7[GaCl_4]$, $2SiMe_3[GaCl_4]$ was treated with an equimolar amount of $(Me_3Si)_2NPCl_2$, which afforded **13** in a higher purity according to ^{31}P NMR experiments. However, traces of **14** are still present in the reaction mixture, indicating a dynamic solution chemistry of $2SiMe_3[GaCl_4]$, $GaCl_3$, and $(Me_3Si)_2NP(N_3)Cl$ with respect to chlorine/azide scrambling, which is regularly observed in CH_2Cl_2 solutions.[40] Neither crystals of **13** nor **14** could be grown because in all cases oily residues remained and showed no propensity to become solid.

Interestingly, treating $1SiMe_3[GaCl_4]$ with 0.5 equiv of Me_3SiN_3 at −50 °C in CH_2Cl_2 and warming the mixture to room temperature over a period of 2 h yielded after concentration and storage at −24 °C under exclusion of light for 48 h a colorless crystalline solid. The compound was characterized by X-ray crystallography as the unprecedented bicyclic compound $[(Me_3Si)_2N_2P_2Cl_2N(Ga_2Cl_5)]$ (**15**; Scheme 8 and Figure 8, left). The formation of **15** is best understood as $GaCl_3$-assisted elimination of two molecules of Me_3SiCl from

Scheme 8. Comprehensive Solution Chemistry of $(Me_3Si)_2NPCl_2$ in the Presence of $GaCl_3$ and Me_3SiN_3



13 and rearrangement of the naked $[(Me_3Si)_2N_3P_2Cl_2]^-$ fragment to a cyclic intermediate, which is subsequently stabilized by adduct formation with a $Ga_2Cl_5^+$ fragment. Intermediates of this transformation could not be observed. To test this hypothesis, we added $GaCl_3$ to a solution containing **13** and followed the reaction with ^{31}P NMR spectroscopy, which clearly indicated the formation of **15**. The stabilization of anionic intermediates by a $Ga_2Cl_5^+$ fragment has

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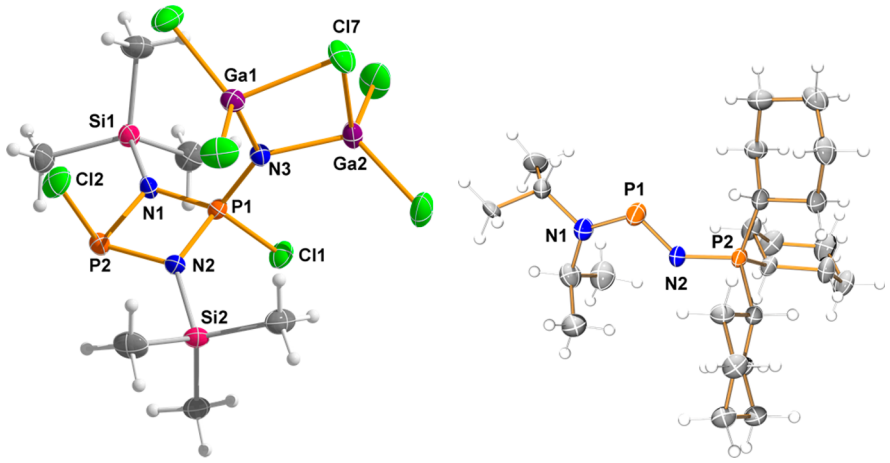
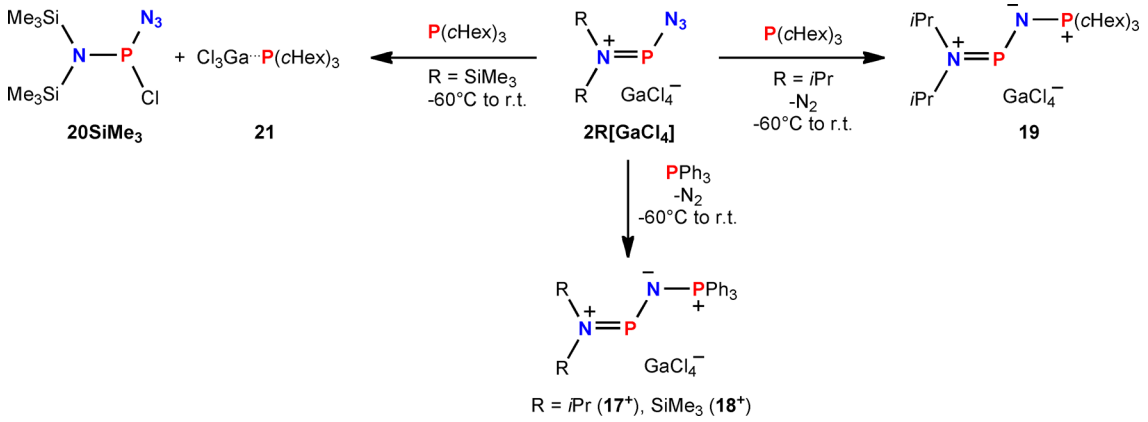


Figure 8. ORTEP drawings of **15** (left) and **19**$^+$ (right). The anion is omitted for clarity. Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): **15**, P1−N1 1.634(2), C1−P1 1.773(3), N1−C4 1.504(3), N1−Si1 1.769(2), C1−C2 1.518(3), C2−C3 1.331(3), P1−C7 1.801(3), P1−C10 1.797(3), C7−C8 1.498(4), C8−C9 1.322(4); Σ(<N1) 359.26, Σ(<P1) 324.63; Si1−N1−P1−C7 59.5(2), C4−N1−P1−C10 115.27(19), C2−C1−P1−N1 51.2, C4−N1−P1−C1 −7.0(2); **5**, P2−N2 1.643(2), P2−C23 1.812(3), P2−C26 1.824(3), P2−C29 1.833(3), N2−C20 1.539(3), N2−Si2 1.790(2), C20−C21 1.499(4), C21−C22 1.328(4), C26−C27 1.538(5), C27−C28 1.298(5); Σ(<N2) 356.74, Σ(<P2) 340.59. Selected bond lengths and angles of **19**$^+$ are listed in Table 1

Scheme 9. Different Reactivities Observed in the Reaction of 2R[GaCl$_4$] with Phosphanes PPh$_3$ and P*c*Hex$_3$



been previously described in the reaction of HypN(SiMe$_3$)PCl$_2$ (Hyp = Si(SiMe$_3$)$_3$) with GaCl$_3$.[41] In the ^{31}P NMR spectrum of isolated **15**, two resonances were detected for the NP(Cl)N group at 142.6 ppm, in good agreement with other strained NP^{III} heterocyclic compounds [cf. **6** $\delta(^{31}P)$ = 102.5 ppm; Scheme 4],[18] and for the tetracoordinated P^V at 23.9 ppm, with both signals being split into doublets with a $^2J(^{31}P-^{31}P)$ coupling of 64.5 Hz, which is in good agreement with the few examples of 1,3,2λ^3,4λ^5-diazaphosphetidines, which were shown to form by a 1,3-SiMe$_3$ shift from iminophosphane−iminophosphoranes (Scheme 4).[17,18] **15** crystallizes in the orthorhombic space group *Pbca* with eight molecules in the cell (Figure 8, left). The characteristic structural feature of **15** is the (Me$_3$Si)$_2$N$_2$P$_2$Cl$_2$ four-membered ring with two long P2−N$_{amino}$ bonds [1.733(2) and 1.736(2) Å] and two significantly shorter P1−N$_{amino}$ distances [1.640(2) and 1.636(2) Å], in accordance with related systems that also incorporate a four-coordinated phosphorus atom [cf. **16** P−N 1.665(2) Å; Figure 5].[42] The N1−P2−N2 angle [83.5(1)°] is rather acute, whereas the N1−P1−N2 angle is close to 90°. The exocyclic SiMe$_3$ groups are attached to the amino nitrogen by single bonds [1.789(2) and 1.786(2) Å; $\sum r_{cov}$(Si−N) = 1.87 Å][24] and lie below a plane that is formed by the central P$_2$N$_2$ ring. The exocyclic NGa$_2$Cl ring is attached to the central P$_2$N$_2$ moiety via the nitrogen atom N3 with a comparably short P1−N3 [1.565(2) Å] distance, which can be regarded as a P^V−N single bond, with a partial charge on N3 of −1.87e according to NBO analysis and an overall negative charge of the [(Me$_3$Si)$_2$N$_3$P$_2$Cl$_2$] fragment of −0.95e. The charge is compensated for via the unusual Ga$_2$Cl$_5$ fragment, which is covalently bound to N3 with Ga−N single bonds [1.903(2) and 1.906(2) Å; $\sum r_{cov}$(Ga−N) = 1.92 Å, cf. **10** Ga−N$_{imino}$ 1.946 Å; Figure 5].[35] Within the Ga$_2$Cl$_5$ moiety, two long Ga−Cl bonds are detected between Ga and the bridging chlorine atom Cl7 [2.3273(8) and 2.3450(7) Å, $\sum r_{cov}$(Ga−Cl) = 2.23 Å],[24] whereas the exocyclic Ga−Cl distances can be considered as typical polar covalent single bonds (avg 2.121 Å). In agreement with this observation is the calculated partial charge of −0.40e for Cl7, which is less negative than the other chlorine atoms at −0.47e.

Having prepared 7[**GaCl$_4$**], we wanted to investigate the possibility of utilizing azidophosphenium cations as building blocks for the generation of cations with multiple phosphorus atoms. Reacting **2*i*Pr**[**GaCl$_4$**] or **2SiMe$_3$**[**GaCl$_4$**] with phosphanes of the type PR$_3$ (R = *c*Hex, Ph) should yield iminophosphorane-substituted phosphenium cations of the type [R$_2$NPNPR′$_3$][GaCl$_4$] (Scheme 9). In the earlier studies

dx.doi.org/10.1021/ic500332s | *Inorg. Chem.* 2014, 53, 3880−3892

Table 1. Selected Structural Data (Distances in Å and Angles in deg) and ^{31}P NMR Data (Chemical Shifts in ppm) of Aminophosphenium Species 1*i*Pr$^+$, 2*i*Pr$^+$, 2SiMe$_3^+$, 7[GaCl$_4$], 8, 15, 7-dmb[GaCl$_4$], and 7-Cl

	P−N1	P−X[a]	N2−P2	P2−N3	N$_{amino}$−P−X[a]	P1−N$_{imino}$−P2	Σ(<P2)	^{31}P P1	^{31}P P2
1*i*Pr$^+$	1.591(3)	2.003(1)			106.8(1)			294.7	
2*i*Pr$^+$	1.6003(9)	1.665(2)			100.57(5)			310.9	
2SiMe$_3^+$								367.5	
7[GaCl$_4$]	1.611(2)	1.597(2)	1.557(2)	1.597(2)	104.97(9)	129.4(1)	334.58	311.2	27.4
7-dmb[GaCl4]	1.624(2)	1.618(2)	1.533(2)	1.607(2)	112.4(1)	137.7(1)	335.26	48.1	−4.4
7-Cl	1.640(4)	1.660(4)					333.26	156.2	−6.4
8	1.612(4)	1.597(4)	1.550(4)	1.588(5)	105.0(2)	133.2(3)	335.62	311.3	30.4
15	1.62[b]	1.573(3)	1.628(3)		107.6(4)	128.3(2)	327.48	303.8	49.1

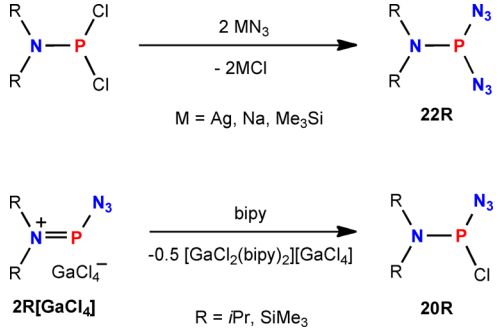
[a]X = Cl (1), N$_{azide}$ (2*i*Pr$^+$, 2SiMe$_3^+$), N$_{imino}$ (8−15). [b]N*i*Pr moiety disordered; therefore, averaged P−N distance.

by Wolf and co-workers, such cations were prepared in the reaction of 2*i*Pr[AlCl$_4$] with PBu$_3$ and PPh$_3$, whereas at low temperatures, PBu$_3$ formed a Lewis acid base adduct with a phosphenium cation, as indicated by the characteristic ^{31}P NMR shifts for these adducts and a large P−P coupling constant [cf. [4···PBu$_3$][AlCl$_4$] $\delta_{phosphenium}(^{31}P)$ = 102.3 ppm, $\delta_{PBu_3}(^{31}P)$ = 20 ppm, $J(^{31}P-^{31}P)$ = 327 Hz].[43] We therefore treated 2*i*Pr[GaCl$_4$] and 2SiMe$_3$[GaCl$_4$] with PR$_3$ (R = Ph, *c*Hex) at −50 °C, and the mixtures were rapidly warmed to room temperature, resulting in vigorous gas evolution. The ^{31}P NMR spectra showed a species with an AX spin system supportive of a iminophosphorane-substituted phosphenium salt of the type [*i*Pr$_2$NNPPPh$_3$][GaCl$_4$] [17[GaCl$_4$]; $\delta_{phosphenium}(^{31}P)$ = 310.9 ppm, $\delta_{PBu_3}(^{31}P)$ = 28.8 ppm, $J(^{31}P-^{31}P)$ = 68 Hz] because Wolf et al. reported identical values for [*i*Pr$_2$NNPPPh$_3$][AlCl$_4$] (17[AlCl$_4$]), indicating that there is no electronic effect upon a change in the anion from GaCl$_4^-$ to AlCl$_4^-$. 2SiMe$_3$[GaCl$_4$] as a starting material yielded [(Me$_3$Si)$_2$NPNPPh$_3$][GaCl$_4$] (18[GaCl$_4$]) with a more deshielded phosphenium phosphorus atom because the resonance for this atom at 361.5 ppm is 50 ppm downfield-shifted compared to 17[GaCl$_4$], which clearly shows that the (Me$_3$Si)$_2$N substituent is more electron-withdrawing than *i*Pr$_2$N (vide infra). However, the molecular structure of 17[GaCl$_4$] and 18[GaCl$_4$] could not be determined. The introduction of P(*c*Hex)$_3$ as a base in the reaction with 2*i*Pr[GaCl$_4$] in CH$_2$Cl$_2$ resulted after concentration of the reaction mixture in the deposition of colorless crystals, which were identified by a single-crystal structure determination as [*i*Pr$_2$NNP(*c*Hex)$_3$][GaCl$_4$] (19). 19 crystallizes in the monoclinic space group $P2_1/c$ with two formula units and one molecule of CH$_2$Cl$_2$ in the asymmetric unit. In one cation, the *i*Pr$_2$NP group is disordered and split into two parts. In the other independent cation, one N*i*Pr moiety is found to be disordered. Because the molecular geometry is similar in both formula units, just one of the two cations is discussed. The metrical parameters are in the expected range and compare well with the values in 7$^+$ and 8$^+$ (Table 1). The bond distances N1−P1 (avg 1.62 Å), P1−N2 [1.573(3) Å], and N2−P2 [1.628(3) Å] are supportive of a phosphonium formulation similar to that discussed for 9$^+$.

In contrast, the addition of P(*c*Hex)$_3$ to a CH$_2$Cl$_2$ of 2SiMe$_3$[GaCl$_4$] was not accompanied by gas evolution, and in the ^{31}P NMR spectrum of the reaction mixture, two species were detected. On the one hand, the azidochlorophosphane (Me$_3$Si)$_2$NP(N$_3$)Cl (20SiMe$_3$) and, on the other hand, the GaCl$_3$ adduct of P(*c*Hex)$_3$ (*c*Hex)$_3$P···GaCl$_3$ (21),[44] which crystallize from concentrated reaction mixtures (Scheme 9), were observed. The main reason for the different reactivities observed supposedly lies in the steric congestion that stems from the N(SiMe$_3$)$_2$ moiety in 2SiMe$_3^+$, which effectively denies the formation of an iminophosphorane-substituted phosphenium salt.

The formation of 20SiMe$_3$ prompted us to investigate the possibility of using 2*i*Pr[GaCl$_4$] and 2SiMe$_3$[GaCl$_4$] as precursors for azido(chloro)phosphanes because these species cannot be prepared using standard routes such as the addition of 1 equiv of AgN$_3$, Me$_3$SiN$_3$, or NaN$_3$ because in all cases a mixture of mono- and disubstituted azidophosphanes was obtained. In contrast, in the presence of an excess of Me$_3$SiN$_3$, complete conversion to *i*Pr$_2$NP(N$_3$)$_2$ (22*i*Pr) and (Me$_3$Si)$_2$NP(N$_3$)$_2$ (22SiMe$_3$) was accomplished. It is worth noting that the synthesis of 22R can also be achieved by addition of 2 equiv of AgN$_3$ or NaN$_3$ in CH$_2$Cl$_2$ and workup from *n*-hexane (Scheme 10).

Scheme 10. Attempted Synthesis of Azidochlorophosphanes Resulting in the Formation of Diazides 22R (R = *i*Pr, SiMe$_3$) and Synthetic Access to 20R via bipy-Induced Chlorine Back-substitution to Azidophosphenium Species 2R[GaCl$_4$]



To circumvent these drawbacks, to a CH$_2$Cl$_2$ solution of 2R[GaCl$_4$] (R = iPr, SiMe$_3$) was added a stoichiometric amount of bipy to remove GaCl$_3$ and obtain the chloride-back-substituted chlorophosphane. Removal of the solvents in vacuo and extraction of the residues with *n*-hexane afforded in the case of 2*i*Pr[GaCl$_4$] a mixture of chlorophosphanes *i*Pr$_2$NP(N$_3$)Cl (20*i*Pr) [20*i*Pr $\delta(^{31}P)$ 155.1 ppm] and *i*Pr$_2$NPCl$_2$ (in an analogous procedure, 20SiMe$_3$ is obtained; 20SiMe$_3$ $\delta(^{31}P)$ 173.4 ppm). This mixture solidifies at ca. −25 °C, crystals suitable for X-ray analysis were selected at −50 °C, and the molecular structure was successfully determined (Figure 9). The crystal structure revealed, in good accordance with the ^{31}P NMR data, a mixture of both 20*i*Pr and *i*Pr$_2$NPCl$_2$ in an occupational disorder of 0.79/0.21 (Figure 9). 20*i*Pr crystallizes

dx.doi.org/10.1021/ic500332s | Inorg. Chem. 2014, 53, 3880−3892

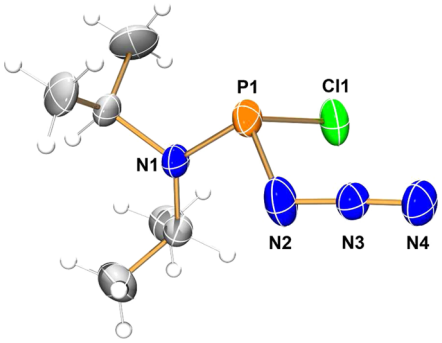


Figure 9. ORTEP drawing of the molecular structure of **20*i*Pr**. Ellipsoids are drawn at 50% probability, and just the main part of the mixed phosphane is shown because **20*i*Pr** crystallizes as a mixture of the general formula $iPr_2NPCl(N_3)_{0.79}(Cl)_{0.21}$. Selected bond lengths (Å) and angles (deg): P1−N1 1.658(1), N2−P1 1.76(3), N2−N3 1.24(1), N3−N4 1.125(4), P1−Cl1 2.1075(9); Σ(<N1) 359.26, Σ(<P1) 324.63; N2−N3−N4 177.3; N2−P1−N1−C4 −44.9.

in the monoclinic space group $P2_1/m$ with two molecules in the unit cell. **20*i*Pr** lies on a crystallographically imposed mirror plane, which results in disorder of the whole molecule. The P−N_{amino} bond [1.658(1) Å] is in the expected range for a P−N single bond in chlorophosphanes [cf. $(Me_3Si)_2NPCl_2$ 1.6468(8) Å],[19] with the azido group bound to the phosphorus via a P−N_{azide} [1.76(3) Å] single bond [cf. **10**[35] P−N_{azide} 1.698(5) Å, **23**[32] P−N_{azide}1.706(3) Å; Figure 5]. Conclusively, chlorine back-substitution with the aid of bipy is a viable route toward chlorophosphanes starting from phosphenium precursors, but in the presence of an azide substituent, scrambling of the substituents might result in mixed phosphanes.[40]

CONCLUSION

Azidophosphenium cations **2R**[$GaCl_4$] (R = *i*Pr, $SiMe_3$) were shown to be susceptible to the loss of dinitrogen in the presence of phosphanes. Starting from **2*i*Pr**[$GaCl_4$] or **2SiMe$_3$**[$GaCl_4$], different iminophosphorane-substituted polyphosphorus salts **7**[$GaCl_4$], **8**, **13**, and **14** could be obtained from Staudinger reactions with different chlorophosphanes, and the comprehensive chemistry of **7**[$GaCl_4$] was studied in detail. This study clearly demonstrates a misinterpretation of data published by Wolf and co-workers. In an effort to develop a route toward chlorophosphanes, phosphenium cations were shown to be transformed to chlorophosphanes by the addition of bipyridine as the chelating ligand, which effectively removes $GaCl_3$ from $GaCl_4^-$ salts. The new topology of the NPNPN cations formulated in this work might result in the formation and design of new polyphosphorus ligands for transition-metal fragments.

EXPERIMENTAL SECTION

Synthesis of [*i*Pr$_2$NPCl][$GaCl_4$] (1*i*Pr[$GaCl_4$]). A CH_2Cl_2 (2 mL) solution of $GaCl_3$ (0.189 g, 1.07 mmol) was added dropwise to a stirred solution of iPr_2NPCl_2 (0.213 g, 1.05 mmol) in CH_2Cl_2 (3 mL) at −75 °C. The clear colorless mixture was allowed to stir for 15 min and concentrated to incipient crystallization at −50 °C. Standing overnight at −80 °C yielded, after removal of the supernatant solution, 0.203 g (0.53 mmol, 51%) of **1*i*Pr**[$GaCl_4$] as colorless crystals.

Mp: 51 °C. Anal. Calcd (found): C, 19.06 (19.10); H, 3.73 (3.70); N, 3.70 (3.72). ^{1}H NMR (25 °C, CD_2Cl_2, 500.13 MHz): δ 1.49−1.59 (m, 12H, $CH(CH_3)_2$), 4.41−4.63 (m, 2H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 125.76 MHz): δ 23.48 (d, $J(^{31}P-^{13}C)$ = 8.25 Hz, $CH(CH_3)_2$), 56.24−57.74 (m, $CH(CH_3)_2$), 58.19 (d, $J(^{31}P-^{13}C)$ = 8.25 Hz, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 202.46 MHz): δ 294.7 (br s, NPCl). Raman (100 mW, 25 °C, 3 scans, cm^{-1}): 3305(1), 3237(1), 3181(1), 2976(1), 2944(1), 1459(2), 1399(2), 1360(2), 1320(2), 1263(2), 1201(2), 1163(2), 1131(2), 1121(2), 1032(5), 927(2), 884(2), 634(3), 567(5), 506(3), 479(3), 397(3), 374(4), 360(3), 345(10), 265(3), 201(4).

Synthesis of [*i*Pr$_2$NPN$_3$][$GaCl_4$] (2*i*Pr[$GaCl_4$]). A CH_2Cl_2 (5 mL) solution of $GaCl_3$ (0.283 g, 1.61 mmol) was added dropwise to a stirred solution of iPr_2NPCl_2 (0.325 g, 1.61 mmol) in CH_2Cl_2 (2 mL) at −75 °C. The clear colorless mixture was allowed to stir for 30 min at this temperature and treated with a CH_2Cl_2 solution (5 mL) of Me_3SiN_3 (0.186 g, 1.61 mmol) afterward. The yellowish solution was concentrated to incipient crystallization, whereas the temperature was maintained below −30 °C. Standing overnight in a freezer (−80 °C) afforded, after removal of the supernatant liquid, 0.460 g (1.20 mmol, 75%) of **2*i*Pr**[$GaCl_4$] as colorless crystals.

Mp: 78 °C (dec). Anal. Calcd (found): C, 18.73 (19.32); H, 4.21 (3.90); N, 14.56 (14.30). ^{1}H NMR (−20 °C, CD_2Cl_2, 500.13 MHz): δ 1.44−1.57 (m, 12H, $CH(CH_3)_2$), 4.31−4.44 (m, 2H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (0 °C, CD_2Cl_2, 125.76 MHz): δ 20.20 (s, $CH(CH_3)_2$), 21.70−22.24 (m, $CH(CH_3)_2$), 50.29−50.44 (m, $CH(CH_3)_2$), 51.01 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (−20 °C, CD_2Cl_2, 202.46 MHz): δ 310.93 (s, NPN_3). IR (ATR, 25 °C, 32 scans, cm^{-1}): 3174 (w), 3101 (w), 2981 (w), 2939 (w), 2899 (w), 2879 (w), 2505 (w), 2159 (s), 1574 (w), 1468 (m), 1460 (w), 1411 (m), 1391 (w), 1373 (m), 1558 (s), 1207 (s), 1181 (m), 1165 (s), 1154 (s), 1139 (s), 1111 (s), 1020 (s), 965 (s), 909 (m), 885 (m), 848 (s), 754 (m), 638 (m), 569 (s), 552 (s), 542 (s). Raman (100 mW, 25 °C, 3 scans, cm^{-1}): 2988(1), 2969(1), 2947(1), 2896(1), 2873(1), 2733(1), 2174(10), 2166(4), 1464(3), 1441(3), 1413(3), 1372(3), 1307(3), 1207(3), 1167(3), 1023(6), 967(3), 886(3), 759(3), 639(3), 554(3), 543(3), 469(3), 398(3), 362(3), 347(7), 275(4), 241(3), 203(4).

Synthesis of [*i*Pr$_2$NPNP(Cl)$_2$N*i*Pr$_2$][$GaCl_4$] (7[$GaCl_4$]). *Procedure 1.* A CH_2Cl_2 (5 mL) solution of $GaCl_3$ (0.283 g, 1.6 mmol) was added dropwise to a stirred solution of iPr_2NPCl_2 (0.325 g, 1.6 mmol) in CH_2Cl_2 (2 mL) at −80 °C. The colorless mixture was allowed to stir for 30 min at this temperature. Afterward, a CH_2Cl_2 solution (2.5 mL) of Me_3SiN_3 (0.093 g, 0.8 mmol) was added at −60 °C, and the mixture was allowed to slowly warm to ambient temperature and stirred for 2 h. The mixture attained a yellow color, and gas evolution could be observed. After removal of the solvent in vacuo, a yellow oil is obtained as the crude product, from which colorless crystals grew. The crude mixture was taken up in fresh CH_2Cl_2 (0.5 mL) and placed in a freezer (−24 °C) for 12 h. After removal of the supernatant liquid, 0.394 g (0.71 mmol, 44%) of **7**[$GaCl_4$] was isolated as colorless crystals.

Procedure 2. A CH_2Cl_2 (3 mL) solution of $GaCl_3$ (0.186 g, 1.06 mmol) was added dropwise to a stirred solution of iPr_2NPCl_2 (0.213 g, 1.05 mmol) in CH_2Cl_2 (3 mL) at −80 °C. The colorless mixture was allowed to stir for 30 min at this temperature. Afterward, a CH_2Cl_2 solution (2.5 mL) of Me_3SiN_3 (0.123 mg, 1.05 mmol) was added at −60 °C, and the mixture was stirred for another 30 min, followed by the addition of another 1 equiv of iPr_2NPCl_2 (0.213 g, 1.05 mmol). Subsequently, the mixture was rapidly warmed to room temperature, which was accompanied by vigorous gas evolution. After stirring for 1 h and removal of the solvent in vacuo, a yellow oil was obtained as the crude product, which was washed with *n*-hexane (1 mL). The crude mixture is redissolved in CH_2Cl_2 (0.5 mL) and placed in a freezer (−24 °C) for 12 h. After removal of the supernatant liquid, 0.370 g (0.66 mmol, 63%) of **7**[$GaCl_4$] was isolated as colorless crystals.

Mp: 122−123 °C. Anal. Calcd (found): C, 25.79 (25.69); H, 5.05 (5.13); N, 7.52 (7.59). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 1.41 (d, $J(^1H-^1H)$ = 6.80 Hz, 12H, $CH(CH_3)_2$), 1.44 (d, $J(^1H-^1H)$ = 6.99 Hz, 6H, $CH(CH_3)_2$), 1.61 (d, $J(^1H-^1H)$ = 6.80 Hz, 6H, $CH(CH_3)_2$), 3.91 (sept, $J(^1H-^1H)$ = 6.80 Hz, $CH(CH_3)_2$), 4.03 (sept, $J(^1H-^1H)$ = 6.80 Hz, $CH(CH_3)_2$), 4.08−4.25 (sept, $CH(CH_3)_2$), 4.88−4.98 (sept, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.48 MHz): δ 22.16 (d, $J(^{31}P-^{13}C)$ = 2.20 Hz, $CH(CH_3)_2$), 22.31 (d, $J(^{31}P-^{13}C)$ = 2.75 Hz, $CH(CH_3)_2$), 27.09 (d, $J(^{31}P-^{13}C)$ = 11.55 Hz, $CH(CH_3)_2$), 51.67 (d, $J(^{31}P-^{13}C)$ = 5.50 Hz, $CH(CH_3)_2$), 52.63 (d, $J(^{31}P-^{13}C)$ = 27.51 Hz, $CH(CH_3)_2$), 54.23 (d, $J(^{31}P-^{13}C)$ = 11.00 Hz,

dx.doi.org/10.1021/ic500332s | Inorg. Chem. 2014, 53, 3880−3892

$CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6, 121.51 MHz): δ 27.40 (d, $J(^{31}P-^{31}P)$ = 111.5 Hz, $NPCl_2N$), 311.16 (d, $J(^{31}P-^{31}P)$ = 111.5 Hz, NPN). IR (ATR, 25 °C, 16 scans, cm^{-1}): 3167 (w), 2976 (w), 2935 (w), 2874 (w), 2164 (w), 1454 (w), 1413 (m), 1400 (w), 1390 (w), 1375 (m), 1282 (m), 1251 (m), 1237 (s), 1203 (m), 1170 (m), 1146 (s), 1122 (m), 1109 (s), 1027 (s), 989 (s), 968 (s), 887 (w), 859 (m), 797 (m), 738 (w), 659 (m), 754 (m), 636 (w), 607 (w), 564 (s), 551 (s). Raman (12 mW, 25 °C, 3 scans, cm^{-1}): 3238(1), 2984(1), 2940(1), 2456(1), 1456(1), 1444(1), 1415(1), 1318(1), 1205(1), 1168(1), 1144(1), 1123(1), 1031(1), 969(1), 945(1), 893(2), 861(1), 799(1), 756(1), 706(1), 660(1), 637(1), 570(1), 554(1), 504(2), 485(1), 469(1), 406(1), 378(1), 346(10), 326(1), 300(1), 289(1), 252(1), 220(1), 202(1).

Synthesis of $[i\mathrm{Pr_2NPNP(Cl)_2N(SiMe_3)_2}][\mathrm{GaCl_4}]$ (8). To a cooled sample of $\mathbf{2}i\mathbf{Pr}[\mathbf{GaCl_4}]$ (0.326 g, 0.85 mmol) at −50 °C was added a CH_2Cl_2 (3 mL) solution of $(Me_3Si)_2NPCl_2$ (0.223 g, 0.85 mmol) at that temperature, and the mixture was slowly warmed to room temperature over a period of 2 h. At ca. −30 °C, vigorous gas evolution was observed. Removal of the solvents in vacuo resulted in an oily colorless residue, which was washed with *n*-hexane (1 mL). The residual oil was redissolved in minimal amounts of C_6H_5F, and standing at 5 °C for 12 h afforded colorless crystals of **8** (0.280 g, 0.45 mmol, 53%).

Anal. Calcd (found): C, 23.29 (23.59); H, 5.21 (4.92); N, 6.79 (7.32). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 1.38 (d, $^3J(^1H-^1H)$ = 6.8 Hz, 6H, $C(CH_3)_2$), 1.61 (d, $^3J(^1H-^1H)$ = 6.8 Hz, 6H, $C(CH_3)_2$), 4.1 (sept, $^3J(^1H-^1H)$ = 6.8 Hz = 1H, $CH(CH_3)_2$), 5.03 (sept, d, $^3J(^1H-^1H)$ = 6.8 Hz, $J(^{31}H-^1H)$ = 2.8 Hz, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2/CH_2Cl_2, 121.51 MHz): δ 311.3 (d, $^2J(^{31}P-^{31}P)$ = 111.5 Hz, $NPNiPr_2$), 30.4 (d, $NP(Cl)_2N$). Raman (100 mW, 25 °C, 4 scans, cm^{-1}): 2986(3), 2970(2), 2944(2), 2906(4), 2732(1), 1459(3), 1361(2), 1331(2), 1168(2), 1142(2), 1136(2), 1033(3), 1011(2), 972(2), 969(2), 892(3), 862(2), 773(2), 659(6), 641(5), 576(2), 554(2), 500(3), 471(2), 451(3), 419(2), 402(2), 370(3), 345(10), 290(2), 213(2).

Synthesis of $[i\mathrm{Pr_2NP(dmb)NP(Cl)_2N}i\mathrm{Pr_2}][\mathrm{GaCl_4}]$ (7-dmb-$[\mathrm{GaCl_4}]$). A CH_2Cl_2 (5 mL) solution of dmb (0.071 g, 0.86 mmol) was added dropwise to a CH_2Cl_2 solution of $\mathbf{7}[\mathbf{GaCl_4}]$ (0.200 g, 0.36 mmol) at −20 °C. The colorless mixture was allowed to slowly warm to room temperature over a period of 2 h. Afterward, the solvent was removed in vacuo, and the white solids were washed with *n*-hexane, taken up in CH_2Cl_2 (0.5 mL), and placed in a freezer (−40 °C) for 12 h. After removal of the supernatant liquid, 0.100 g (0.16 mmol, 44%) of $\mathbf{7\text{-}dmb}[\mathbf{GaCl_4}]$ was isolated as colorless crystals.

Mp: 156 °C. Anal. Calcd (found): C, 33.73 (33.53); H, 5.98 (5.36); N, 6.56 (6.46). ^1H NMR (25 °C, CD_2Cl_2, 300.14 MHz): δ 1.34 (d, $J(^1H-^1H)$ = 6.80 Hz, 24H, $CH(CH_3)_3$), 1.84 (s, 6H, CCH_3), 2.87–3.18 (m, 4H, $PCCH_2$), 3.64 (sept, $J(^1H-^1H)$ = 6.80 Hz, $CH(CH_3)_3$), 3.69 (sept, $J(^1H-^1H)$ = 6.80 Hz, $CH(CH_3)_3$), 3.79 (sept, $J(^1H-^1H)$ = 6.80 Hz, $CH(CH_3)_3$), 3.89 (sept, $J(^1H-^1H)$ = 6.80 Hz, $CH(CH_3)_3$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.48 MHz): δ 16.88 (d, $J(^{31}P-^{13}C)$ = 15.41 Hz, CCH_3), 21.89 (d, $J(^{31}P-^{13}C)$ = 2.20 Hz, $CH(CH_3)_2$), 23.32 (d, $J(^{31}P-^{13}C)$ = 3.30 Hz, $CH(CH_3)_2$), 38.64 (d, $J(^{31}P-^{13}C)$ = 3.30 Hz, $PCCH_2$), 39.79 (d, $J(^{31}P-^{13}C)$ = 3.30 Hz, $PCCH_2$), 49.87 (d, $J(^{31}P-^{13}C)$ = 2.20 Hz, $CH(CH_3)_2$), 50.73 (d, $J(^{31}P-^{13}C)$ = 6.05 Hz, $CH(CH_3)_2$), 128.22 (d, $J(^{31}P-^{13}C)$ = 12.11 Hz, $C_2C{=}CC_2$). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.51 MHz): δ −4.35 (d, $J(^{31}P-^{31}P)$ = 5.87 Hz, $NPCl_2N$), 48.08 (d, $J(^{31}P-^{31}P)$ = 5.87 Hz, NPC_2N). IR (ATR, 25 °C, 32 scans, cm^{-1}): 2981 (w), 2937 (w), 2913 (w), 2877 (w), 2856 (w), 2168 (w), 1468 (w), 1441 (w), 1412 (m), 1391 (m), 1375 (m), 1288 (s), 1215 (m), 1206 (m), 1192 (w), 1175 (m), 1153 (m), 1136 (m), 1112 (m), 1082 (w), 1018 (s), 990 (s), 949 (w), 926 (w), 894 (w), 866 (w), 852 (m), 841 (m),796 (m), 742 (w), 709 (m), 658 (m), 646 (w), 547 (s), 527 (m). Raman (100 mW, 25 °C, 4 scans, cm^{-1}): 2990(1), 2971(1), 2945(1), 2930(1), 2907(1), 2737(1), 2722(1), 1667(1), 1468(1), 1445(1), 1416(1), 1405(1), 1385(1), 1326(1), 1311(1), 1292(1), 1210(1), 1180(1), 1154(1), 1137(1), 1127(1), 1117(1), 1033(1), 1000(1), 946(1), 928(1), 895(3), 854(1), 842(1), 797(1), 720(1), 711(1), 660(1), 647(1), 551(1), 527(1), 493(1), 456(3), 429(1), 408(3), 377(1), 347(10), 296(1), 254(1), 201(2).

Synthesis of $[i\mathrm{Pr_2NP(Cl)NP(Cl)_2N}i\mathrm{Pr_2}][\mathrm{GaCl_4}]$ (7-Cl). A CH_2Cl_2 (5 mL) solution of 2,2′-bipyridine (0.157 g, 1.01 mmol) was dropwise added to a CH_2Cl_2 solution of $\mathbf{7}[\mathbf{GaCl_4}]$ (0.559 g, 1.00 mmol) at 0 °C. The obtained suspension was allowed to stir at room temperature over a period of 2 h, the solvent was removed in vacuo afterward, and the residues were extracted with *n*-hexane and filtered. Removal of *n*-hexane in vacuo yielded 0.283 g (0.74 mmol, 74%) of **7-Cl** as a colorless crystalline solid.

Mp: 60 °C (dec). Anal. Calcd (found): C, 37.66 (38.091); H, 7.37 (7.31); N, 10.98 (11.30). ^1H NMR (25 °C, CD_2Cl_2, 300.14 MHz): δ 1.09–1.43 (m, 24H, $CH(CH_3)_3$), 3.76 (sept, $J(^1H-^1H)$ = 6.80 Hz, $2CH(CH_3)_3$), 3.86 (sept, $J(^1H-^1H)$ = 6.80 Hz, $2CH(CH_3)_3$). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.51 MHz): δ 156.2 (d, $J(^{31}P-^{31}P)$ = 140.85 Hz, NPClN), −6.4 (d, $J(^{31}P-^{31}P)$ = 140.85 Hz, $NPCl_2N$). IR (ATR, 25 °C, 32 scans, cm^{-1}): 2971 (m), 2932 (w), 2871 (w), 2835 (w), 2760 (w), 2722 (w), 1463 (w), 1407 (m), 1395 (w), 1367 (m), 1315 (s), 1273 (m), 1199 (m), 1173 (s), 1150 (s), 1116 (s), 1021 (m), 991 (s), 972 (s), 880 (m), 857 (m), 725 (m), 653 (m), 634 (m), 551 (s), 528 (s). Raman (632 nm, 100 mW, 25 °C, 5 scans, cm^{-1}): 2973(5), 2957(5), 2946(7), 2934(7), 2896(4), 2874(4), 2725(2), 2715(2), 1463(4), 1455(4), 1408(2), 1391(2), 1380(3), 1372(3), 1323(3), 1315(3), 1200(2), 1174(2), 1142(2), 1120(2), 1031(2), 1023(2), 992(2), 974(3), 944(2), 936(2), 924(1), 892(4), 880(3), 858(1), 655(2), 634(5), 552(2), 504(4), 494(2), 453(7), 407(5), 398(3), 386(3), 366(2), 337(2), 318(1), 287(10), 235(2).

Decomposition of $[(\mathrm{Me_3Si})_2\mathrm{NPN_3}][\mathrm{GaCl_4}]$. A CH_2Cl_2 solution of freshly prepared $\mathbf{2SiMe_3}[\mathbf{GaCl_4}]$ in CH_2Cl_2 (5 mL) at −75 °C was allowed to slowly warm to room temperature over a period of 4 h, resulting in a yellowish reaction mixture, while gas evolution was observed. The solvents were removed in vacuo, and the oily residues were washed with *n*-hexane (1 mL). The residual yellowish oil was redissolved in CH_2Cl_2 (2 mL) and concentrated to a volume of 0.3 mL. Crystallization attempts from CH_2Cl_2 and C_6H_5F and vapor diffusion of *n*-hexane into a saturated CH_2Cl_2 solution failed in all cases, and the products were identified by ^{31}P NMR spectroscopy.

$^{31}P\{^1H\}$ NMR (−40 °C, CD_2Cl_2, 121.49 MHz): for $\mathbf{2Si\text{-}Me_3}[\mathbf{GaCl_4}]$, 368.6 (s); $\mathbf{13}^+$), 357.6 (d, $J(^{31}P-^{31}P)$ = 90.8 Hz), 29.3 (d, $J(^{31}P-^{31}P)$ = 90.8 Hz); for $\mathbf{14}^+$, 354.4 (d, $J(^{31}P-^{31}P)$ = 79.9 Hz), 22.1 (d, $J(^{31}P-^{31}P)$ = 79.9 Hz).

Synthesis of $[(\mathrm{Me_3Si})_2\mathrm{N_2P_2Cl_2N(Ga_2Cl_5)}]$ (15). A CH_2Cl_2 solution (4 mL) of $GaCl_3$ (0.177 g, 1.00 mmol) was dropwise added to a stirred solution of $(Me_3Si)_2NPCl_2$ (0.263 g, 1.00 mmol) in CH_2Cl_2 (2 mL) at −75 °C. The resulting colorless solution was maintained at that temperature for 30 min and treated with a CH_2Cl_2 (2 mL) solution of Me_3SiN_3 (0.060 g, 0.52 mmol) afterward. The colorless clear mixture was slowly warmed to room temperature, with bubbling setting in at −20 °C. Stirring at room temperature for 1 h resulted in a yellowish solution, from which the solvents were removed in vacuo and the oily residues were washed with *n*-hexane (1 mL). The residual yellowish oil was redissolved in CH_2Cl_2 and concentrated to incipient crystallization. After standing at −24 °C for 72 h, colorless crystalline plates of **15** were obtained but could not be effectively separated from the supernatant oil.

Anal. Calcd (found): C, 11.30 (12.63); H, 2.84 (3.13); N, 6.59 (5.61). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 0.50 (s, 18H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.48 MHz): δ 0.37 (dd, $J(^{31}P-^{13}C)$ = 2.7 Hz, $J(^{31}P-^{13}C)$ = 3.7 Hz, $Si(CH_3)_3$). INEPT ^{29}Si NMR (25 °C, CD_2Cl_2, 59.62 MHz): δ 16.09 (s, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.49 MHz): δ 23.86 (d, $J(^{31}P-^{31}P)$ = 64.5 Hz), 142.64 (d, $J(^{31}P-^{31}P)$ = 64.5 Hz).

Synthesis of $[\mathrm{R_2NPNPPh_3}][\mathrm{GaCl_4}]$ [R = $i\mathrm{Pr_2}$ (17), $\mathrm{SiMe_3}$ (18)]. A CH_2Cl_2 solution of $GaCl_3$ (0.174 g, 0.99 mmol) was dropwise added to a stirred solution of R_2NPCl_2 (R = *i*Pr, $SiMe_3$) (0.202 or 0.263 g, 1 mmol) in CH_2Cl_2 (2 mL) −75 °C. The resulting colorless solution was maintained at that temperature for 30 min and treated with a CH_2Cl_2 (2 mL) solution of Me_3SiN_3 (113 mg, 0.98 mmol) afterward, resulting in the formation of a colorless crystalline solid that precipitates from the reaction mixture. Subsequently, a CH_2Cl_2 (5 mL) solution of PPh_3 (263 mg, 1.0 mmol) was dropwise added at −50 °C and the mixture rapidly warmed to ambient temperature, which

dx.doi.org/10.1021/ic500332s | Inorg. Chem. 2014, 53, 3880–3892

was accompanied by vigorous gas evolution. Stirring for 1 h resulted in a yellowish solution, from which the solvent was removed in vacuo, and the oily residues were washed with *n*-hexane (1 mL). Crystallization attempts from CH_2Cl_2 and C_6H_5F and vapor diffusion of *n*-hexane into a saturated CH_2Cl_2 solution failed in all cases, and the products were identified by ^{31}P NMR spectroscopy.

[*i*Pr$_2$NPNPPh$_3$][GaCl$_4$] (**17**). ^1H NMR (25 °C, CD_2Cl_2/CH_2Cl_2, 300.13 MHz): δ 1.47 (d, $J(^1H-^1H)$ = 6.80 Hz, 6H, CH(CH_3)$_2$), 1.52 (d, $J(^1H-^1H)$ = 6.80 Hz, 6H, CH(CH_3)$_2$), 4.08 (sept, $J(^1H-^1H)$ = 6.80 Hz, C*H*(CH$_3$)$_2$), 4.77−4.88 (m, C*H*(CH$_3$)$_2$), 7.57−7.70 (m, 12H, *m*-C*H*, *o*-C*H*), 7.76−7.82 (m, 3H, *p*-C*H*). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2/CH_2Cl_2, 121.51 MHz): δ 28.82 (d, $J(^{31}P-^{31}P)$ = 67.5 Hz, N*P*Ph$_3$), 310.85 (d, $J(^{31}P-^{31}P)$ = 67.5 Hz, N*P*N).

[(Me$_3$Si)$_2$NPNPPh$_3$][GaCl$_4$] (**18**). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 0.47 (d, $J(^{31}P-^1H)$ = 1.51 Hz, 18H, Si(CH_3)$_3$), 7.52−7.70 (m, 12H, *o*-C*H*, *m*-C*H*), 7.75−7.84 (m, 3H, *p*-C*H*). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.51 MHz): δ 30.09 (d, $J(^{31}P-^{31}P)$ = 59 Hz, N*P*Ph$_3$), 361.50 (d, $J(^{31}P-^{31}P)$ = 59 Hz, N*P*N).

Synthesis of [*i*Pr$_2$NPNP*c*Hex$_3$][GaCl$_4$] (19). A CH_2Cl_2 solution of $GaCl_3$ (0.174 g, 0.99 mmol) was dropwise added to a stirred solution of *i*Pr$_2$NPCl$_2$ (0.263 g, 1.0 mmol) in CH_2Cl_2 (2 mL) at −75 °C. The resulting colorless solution was maintained at that temperature for 30 min and was treated with a CH_2Cl_2 (2 mL) solution of Me_3SiN_3 (113 mg, 0.98 mmol) afterward, resulting in the formation of a colorless crystalline solid that precipitates from the reaction mixture. Subsequently, a CH_2Cl_2 (4 mL) solution of P*c*Hex$_3$ (278 mg, 0.99 mmol) was added dropwise at −60 °C and the mixture rapidly warmed to ambient temperature, which was accompanied by vigorous gas evolution. Stirring for 1 h resulted in a yellowish solution from which the solvents were removed in vacuo, and the oily residues were washed with *n*-hexane (1 mL). The residual yellowish oil was redissolved in CH_2Cl_2 and concentrated to incipient crystallization. After standing for 48 h at −24 °C, colorless crystals of **19** were obtained (0.275 g, 0.41 mmol, 41%).

Mp: 159−164 °C (dec). Anal. Calcd (found): C, 43.80 (43.58); H, 7.06 (6.98); N, 4.09 (3.78). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 1.23−1.52 (m, 14H, P(C$_6$H$_{11}$)$_3$), 1.37 (d, $J(^1H-^1H)$ = 6.80 Hz, 6H, CH(CH_3)$_2$), 1.48 (d, $J(^1H-^1H)$ = 6.80 Hz, 6H, CH(CH_3)$_2$), 1.76−1.83 (m, 3H, P(C$_6$H$_{11}$)$_3$), 1.87−1.98 (m, 12H, P(C$_6$H$_{11}$)$_3$), 2.11−2.27 (m, 4H, P(C$_6$H$_{11}$)$_3$), 4.00 (sept, $J(^1H-^1H)$ = 6.80 Hz, C*H*(CH$_3$)$_2$), 4.60−4.74 (m, C*H*(CH$_3$)$_2$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.46 MHz): δ 19.90 (s, P(C$_6$H$_{11}$)$_3$), 22.24 (d, $J(^{31}P-^{13}C)$ = 2.20 Hz, P(C$_6$H$_{11}$)$_3$), 25.49 (s, P(C$_6$H$_{11}$)$_3$), 26.11 (d, $J(^{31}P-^{13}C)$ = 1.10 Hz, CH(*C*H$_3$)$_2$), 26.25 (s, P(C$_6$H$_{11}$)$_3$), 26.61 (s, P(C$_6$H$_{11}$)$_3$), 26.78 (s, P(C$_6$H$_{11}$)$_3$), 26.83−27.06 (m, P(C$_6$H$_{11}$)$_3$), 28.48 (s, P(C$_6$H$_{11}$)$_3$), 28.61 (d, $J(^{31}P-^{13}C)$ = 3.85 Hz, P(C$_6$H$_{11}$)$_3$), 34.75 (d, $J(^{31}P-^{13}C)$ = 55 Hz, P(C$_6$H$_{11}$)$_3$), 49.62 (s, *C*H(CH$_3$)$_2$), 49.85−50.17 (m, *C*H(CH$_3$)$_2$), 50.54 (s, *C*H(CH$_3$)$_2$). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2/CH_2Cl_2, 121.51 MHz): δ 49.1 (d, $J(^{31}P-^{31}P)$ = 23.5 Hz, N*P*(C$_6$H$_{11}$)$_3$), 303.81 (s, N*P*N). IR (ATR, 25 °C, 32 scans, cm^{-1}): 3183 (w), 2973 (w), 2933 (s), 2856 (s), 2725 (w), 2674 (w), 2092 (w), 1591 (w), 1447 (s), 1408 (w), 1397 (w), 1386 (w), 1371 (m), 1296 (m), 1260 (s), 1228 (m), 1202 (s), 1174 (s), 1157 (m), 1116 (s), 1041 (m), 1004 (s), 981 (s), 919 (m), 889 (s), 850 (s), 824 (m), 773 (m), 760 (m), 739 (m), 693 (w), 636 (w), 578 (w), 540 (s), 530 (s). Raman (12 mW, 25 °C, 3 scans, cm^{-1}): 3237(1), 2977(1), 2941(1), 2904(1), 2877(1), 2858(1), 2398(1), 1445(1), 1389(1), 1381(1), 1354(1), 1331(1), 1294(1), 1284(1), 1217(1), 1206(1), 1174(1), 1119(1), 1087(1), 1051(1), 1023(2), 1005(1), 982(1), 942(1), 887(1), 848(1), 818(2), 792(1), 774(1), 761(1), 740(1), 694(1), 687(1), 637(2), 556(2), 541(1), 518(1), 506(1), 469(1), 444(1), 421(1), 375(2), 343(10), 321(1), 309(1), 298(1), 220(3).

Synthesis of R$_2$NP(Cl)N$_3$ (20*i*Pr, 20SiMe$_3$). To a solution of **2*i*Pr**[**GaCl$_4$**] (0.385 g, 1.0 mmol) in CH_2Cl_2 (4 mL) was added dropwise a solution of bipy (0.157 g, 1.0 mmol) at −75 °C, and the resulting colorless suspension was allowed to warm to ambient temperatures, which resulted in a color change to orange. After stirring at room temperature for 1 h, the solvent was removed in vacuo, and the residual solids were extracted with *n*-hexane (5 mL). The colorless filtrate was concentrated to incipient crystallization and stored at −40 °C for 4 days, resulting in the deposition of colorless crystals of **20*i*Pr**. At room temperature, crystals of **20*i*Pr** rapidly melt, whereas only NMR data could be collected for this compound. **20SiMe$_3$** can be obtained in an analogous procedure.

^1H NMR (25 °C, CD_2Cl_2, 500.13 MHz): δ 1.19 (d, $J(^1H-^1H)$ = 6.94 Hz, 6H, CH(CH_3)$_2$), 1.28 (d, $J(^1H-^1H)$ = 6.62 Hz, 6H, CH(CH_3)$_2$), 3.76 (sept, $J(^1H-^1H)$ = 6.94 Hz, C*H*(CH$_3$)$_2$), 3.92 (sept, $J(^1H-^1H)$ = 6.62 Hz, 6H, C*H*(CH$_3$)$_2$). $^{13}C\{^1H\}$ NMR: δ 23.56 (d, $J(^{31}P-^{13}C)$ = 11.00 Hz, CH(*C*H$_3$)$_2$), 24.25 (d, $J(^{31}P-^{13}C)$ = 3.67 Hz, CH(*C*H$_3$)$_2$), 48.12 (d, $J(^{31}P-^{13}C)$ = 11.91 Hz, *C*H(CH$_3$)$_2$), 48.94 (d, $J(^{31}P-^{13}C)$ = 13.75 Hz, *C*H(CH$_3$)$_2$). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 202.46 MHz): δ 155.12 (s, N*P*ClN$_3$), 173.4 (s, N*P*ClN$_3$) (**20SiMe$_3$**).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, general information, structure elucidation, synthesis, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Dr. Dirk Michalik is gratefully acknowledged for his help with variable-temperature ^{31}P NMR experiments. Financial support by the Fonds der chemischen Industrie (fellowship to C.H.) and the DFG (Grant SCHU 1170/8-1) is gratefully acknowledged.

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