Inorganic Chemistry
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On the Synthesis and Reactivity of Highly Labile Pseudohalogen Phosphenium Ions

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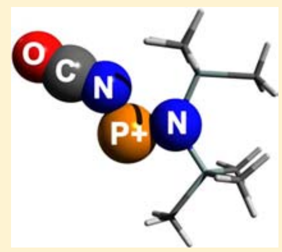
Supporting Information

ABSTRACT: The synthesis and characterization of salts bearing highly labile pseudohalogen-substituted aminophosphenium cations of the type $[(Me_3Si)_2NPX][GaCl_4]$ (X = NCO, NCS, $O(SiMe_3)$) and their respective reactivity toward Lewis bases (4-dimethylaminopyridine, dmap) and dienes (2,3-dimethyl-1,3-butadiene, dmb; 1,3-*cyclo*-hexadiene, chd) are described. As π-acidic species, aminophosphenium cations react with dmap at low temperatures to yield adduct salts of the type $[(Me_3Si)_2NP(dmap)X][GaCl_4]$ (X = Cl, N_3, NCO) which were fully characterized. In the reaction with dienes at −50 °C, salts bearing phospholenium cations were obtained that could be structurally characterized. The crystal structures of novel 7-phosphanorbornenium cations of the type $[(Me_3Si)_2NP(C_6H_8)X][GaCl_4]$ (X = Cl, N_3, NCO) are reported. All compounds were further investigated by means of density functional theory, and the bonding situation was accessed by Natural Bond Orbital (NBO) analysis.



INTRODUCTION

Phosphenium cations are phosphorus analogues of the carbenes, as they possess a dicoordinated, formally positively charged phosphorus atom, isolobally replacing the carbon. Consequently phosphenium cations of the type X-P-Y are stabilized best when X and Y are π-electron donors stabilizing the electron deficient phosphorus atom.[1] Schmidpeter suggested to categorize phosphenium cations into two groups which differ in the charge distribution in the π-electron system. On the one hand the positive charge of the cation is localized exclusively on the substituents, with a nucleophilic phosphorus (type A), and on the other hand the phosphorus is positively charged in the π-bond system and may be regarded as an ambiphilic center exhibiting both electrophilic and nucleophilic character (type B) (Scheme 1).[2] Dimroth and co-workers reported on the first phosphenium species in phosphamethine cyanines as early as 1964 (Figure 1, species **1**).[3] In 1975 the first acyclic phosphenium cations, $[(Me_2N)_2P]^+$ and $[(Me_2N)PCl]^+$, were prepared by Parry et al. utilizing halide ion abstraction from the precursor aminohalophosphines (Figure 1, species **2**).[4] Dimroth's phosphamethine cyanines represent type A cations, whereas aminophosphenium ions exemplify type B cations (Scheme 1). Also in the 1970s, $AlCl_3$ and $GaCl_3$ adducts of aminoiminophosphines have been synthesized as acyclic zwitterions which further cyclize to the four-membered ylidic rings by elimination of $Me_3Si{-}Cl$ (Figure 1, species **3**).[5]

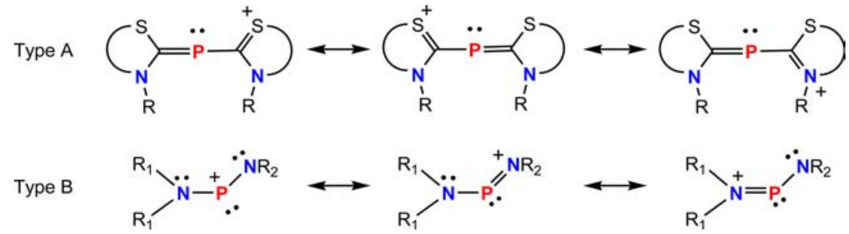
The first cationic phosphorus azide, a 1-azido-*cyclo*-1,3-diphospha-2,4-diazenium ion, $[Ter_2N_2P_2(N_3)]^+$ (**4**) (Ter = 2,6-mesityl-phenyl, with $[N_3(GaCl_3)_2]^-$ as counterion), was reported by Schulz et al. (Figure 1, species **4**).[6,7] Furthermore, diaminophosphenium species are known and have been observed in the aminolysis of phosphadiazonium salts by the group of Burford (Figure 1, species **5**).[8] Only recently, the terphenyl-substituted bisaminophosphenium phosphadiazonium ion (**5**, R = Ter) has been utilized as a powerful probe for cation−anion interactions in solution and in the solid state with a series of different anions.[9]

With their ambiphilic nature, type B phosphenium cations display a similar reactivity as electrophilic carbenoids. Therefore, the reaction of type B phosphenium cations with Lewis bases such as 4-dimethylaminopyridine (dmap) should lead to the formation of adduct cations, as carbenes are well-known to form true ylides in the reaction with pyridines.[10] Extending this concept, type B ions may also engage in chelotropic [4 + 1]-cycloaddition reactions with suitable dienes such as 2,3-dimethyl-1,3-butadiene (dmb) or 1,3-*cyclo*-hexadiene (chd).[11]

Phosphenium ions show a fascinating variety of structural motifs, and their unique solution and coordination chemistry has been reviewed frequently.[1,12] Following our interest in unusual bonding motifs in compounds bearing a binary NPn-core (Pn = P,[13] As,[14] Sb,[15] Bi[16]), we are concerned with the synthesis of low coordination phosphorus compounds. Despite the great structural variety of phosphenium species, structural data on acyclic phosphenium ions is scarcely found and only a few amino substituted examples are known: $[(iPr_2N)_2P]X$ (X = $[AlCl_4]^-$, $[GaCl_4]^-$, $[BPh_4]^-$).[17] The solid state structures of acyclic amino(chloro)phosphenium ions of the type $[R_2N{=}P{-}Cl]^+$ (R = $SiMe_3$,[18] Cy[19]) were not known until recently. Astonishingly, substitution of the chlorine atom in the cation of $[(Me_3Si)_2N{=}P{-}Cl][GaCl_4]$ (**6**) was achieved by treatment with $Me_3Si{-}N_3$ at −50 °C in methylene dichloride, and the first salt $[(Me_3Si)_2N{=}P{-}N_3][GaCl_4]$ (**7**) with an azide group

Received: January 17, 2013
Published: April 24, 2013

Scheme 1. Different Lewis Representations of (Top) Type A Phosphenium Cations, Displaying the Delocalization of the Positive Charge over the Substituent System in Addition to a Nucleophilic Phosphorus Center,[3] and of (Bottom) Type B Phosphenium Cations Displaying Their Ambiphilic Nature[4,18]



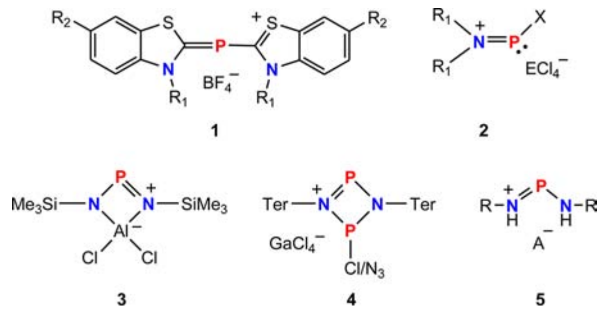


Figure 1. Different types of phosphenium salts: **1** phosphamethine cyanines,[3] **2** aminophosphenium tetrachloridometallates (R_1 = Me, *i*Pr, Cy and X = NR_2, Cl;[4,19] R_1 = $SiMe_3$ and X = Cl, N_3;[18] E = Al, Ga, Fe, **3** 4-membered zwitterionic rings with a phosphenium center,[5] **4** *μ*-chloro/azido-*cyclo*-1,3,-diphospha-2,4-diazenium tetrachloridogallate,[6] **5** aminoiminophosphenium salts (R = Mes*,[8] Ter;[9] A = Cl, OTf, $B(C_6F_5)_4$).

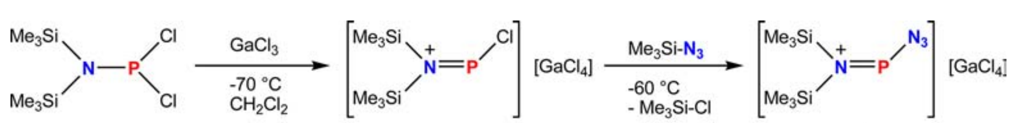
attached to a two-coordinate phosphorus was successfully isolated and structurally characterized (Scheme 2).[18]

7 is highly reactive and unstable in solution, but can be handled as a solid at temperatures below −30 °C. To the best of our knowledge pseudohalogen-substituted phosphenium salts have not been isolated or structurally characterized so far and can be expected to be highly reactive and unstable in solution.[20] Following the preparation of **7** we were intrigued by the idea to further extend this synthetic scope, by reacting **6** with other silylated pseudohalogens Me_3Si-X (X = NCO, NCS, NCSe, CN, CNO) to obtain the labile pseudohalogen phosphenium salts of the type $[(Me_3Si)_2N{=}P{-}X][GaCl_4]$. In this work we report on the synthesis, structure, and properties of such highly labile pseudohalogen substituted phosphenium salts. The ambiphilic nature of such cations was studied in reactions with (i) bases leading to the isolation of thermally stable *σ*-donor stabilized adduct cations of the type $[(Me_3Si)_2NP(base)X][GaCl_4]$ (X = Cl, N_3, NCO; base = dmap), and (ii) dienes resulting in the formation of pseudohalogen substituted phospolenium salts of the type $[(Me_3Si)_2NP(diene)X][GaCl_4]$ (X = Cl, N_3, NCO; diene = dmb, chd) in formal [4 + 1] chelotropic cycloaddition reactions. Moreover, the bonding situation in all these systems was investigated by density functional calculations.

■ RESULTS AND DISCUSSION

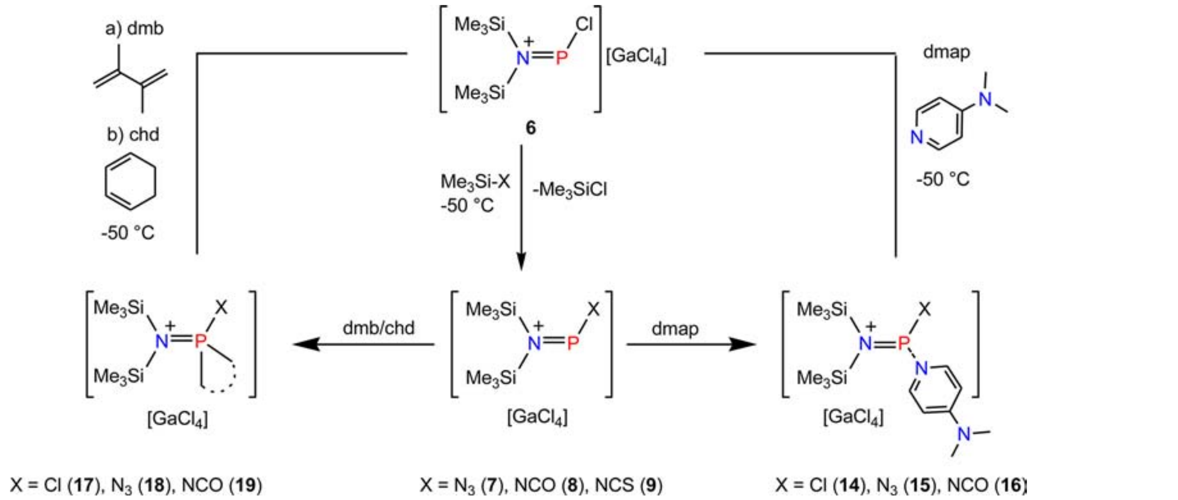
The starting material $[(Me_3Si)_2NPCl][GaCl_4]$ (**6**) can be prepared in situ, when $(Me_3Si)_2NPCl_2$ is reacted with $GaCl_3$ in CH_2Cl_2 at temperatures below −50 °C. Isolation of the amino(azido)phosphenium cation was achieved when $Me_3Si{-}N_3$ was added to **6** at −50 °C.[18] Since this synthetic route represents a high-yielding procedure, which allows for the isolation of **7** as crystalline solid, we were encouraged to react **1** with other trimethylpseudohalogenosilanes Me_3Si-X (X = NCO, NCS, NCSe, CNO, CN). Me_3Si-X (X = NCO, NCS) were added to a CH_2Cl_2 solution of **1** at −60 °C and subsequent concentration of the reaction mixture and storage at −40 °C for 24 h afforded the desired salts $[(Me_3Si)_2N{=}P\text{-}NCO][GaCl_4]$ (**8**) and $[(Me_3Si)_2N{=}P\text{-}NCS][GaCl_4]$ (**9**) as colorless crystalline solids (Scheme 3, middle). **8** and **9** are the first examples of structurally characterized acyclic phosphenium cations with an isocyanato or isothiocyanato group attached to a dicoordinated phosphorus atom. It should be noted that in 1987 Mazieres et al. reported on the spectroscopic detection of an $[iPr_2N{=}P\text{-}NCS]^+$ cation by ^{31}P NMR spectroscopy ($\delta(^{31}P)$ = 276 ppm); however, isolation of this compound was not achieved.[21] It is noteworthy that both salts can be prepared in good yields (**8**: 80%; **9**: 92%), but decomposition occurs even in the freezer of a high quality glovebox (<1 ppm O_2/H_2O) indicating their transient character. Isolated **9** was stable only 24 h in the freezer and decomposed to a brownish oil. In the IR spectrum, taken from cooled samples of **8** and **9**, the asymmetric stretching modes of the NCO and NCS functional groups are found at 2248 cm^{-1} and 1921 cm^{-1}, respectively, indicating that both groups are covalently attached to the phosphorus via the N atom (ν_{OCN}(KOCN) = 2130 cm^{-1}; ν_{SCN}(KSCN) = 2020 cm^{-1}).[22] In solution only traces of the cation in **8** could be detected ($\delta(^{31}P\{^1H\})$ = 338 ppm; cf. $\delta(^{31}P\{^1H\}$ = 363 ppm in $[(Me_3Si)_2N{=}P{-}N_3]^+$ at −70 °C). In the literature ^{31}P NMR data for differently substituted aminophosphenium salts can be found, which were mostly recorded at ambient temperatures.[4,12,21] This is in contrast to the bissilylamino-substituted systems, where only traces of the phosphenium cations can be detected in solution, which arises from two major facts: (i) The solubility of salts **8** and **9** in CH_2Cl_2 is rather low as both salts precipitate out even at −50 °C from highly diluted reaction mixtures. (ii) Trimethylsilyl

Scheme 2. Synthesis of Azidophosphenium Salt 7 Starting from $(Me_3Si)_2NPCl_2$



6 7

Scheme 3. Synthesis of Pseudohalogen-Substituted Phosphenium Salts (7, 8, 9), Adduct Stabilized Cationic Species (14, 15, 16), and Cyclic Phospholenium Salts (17−19 dmb/chd) in Chelotropic [4 + 1] Cycloaddition Reactions with dmb or chd, Respectively



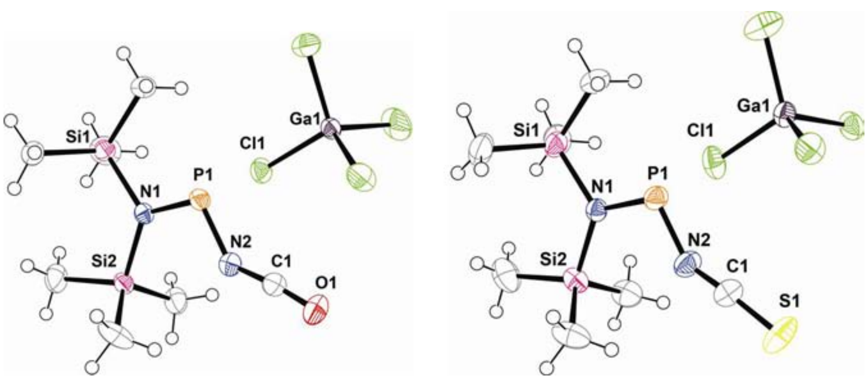


Figure 2. ORTEP drawing of **8** (left) and **9** (right). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg), (**8**): P1−N1 1.592(1), P1−N2 1.656(2), N1−Si 1.843(1), N1−Si2 1.846(1), N2−C1 1.211(2), O1−C1 1.155(2), P1−Cl1 3.1582(6); N1−P1−N2 103.65(7), O1−C1−N2 173.3(2); N2−P1−N1-Si1 −178.17. (**9**) P1−N1 1.593(1), P1−N2 1.651(2), N1−Si 1.835(2), N1−Si2 1.839(1), N2−C1 1.205(2), S1−C1 1.5421(2), P1−Cl1 3.0926(6); N1−P1−N2 103.79(8), S1−C1−N2 176.08; N2−P1−N1-Si2 −0.33.

groups are unstable in solution in the presence of $GaCl_3$ or other strong Lewis acidic centers such as phosphenium cations. Triggered by the action of the Lewis acid methyl exchange reactions might occur as previously reported by our group.[23] Furthermore, a dynamic equilibrium chemistry between $R_2NPClX/GaCl_3$ and $[R_2NPX][GaCl_4]$ is observed. This was also observed before by our group and the group of Weigand in solution ^{31}P NMR spectra of mixtures containing chlorophosphines and galliumtrichloride in different ratios.[18,19] However, **8** and **9** could be isolated at low temperatures nearly quantitatively since both salts are stabilized significantly in the solid state.

X-ray quality crystals of **8** were obtained directly from the reaction mixture at −40 °C, and crystals of **9** suitable for structural analysis were grown in a similar manner. **8** and **9** crystallize in the orthorhombic space groups $P2_12_12_1$ and *Pbca*, respectively, with four formula units per cell (Figure 2). The amino nitrogen atom sits in a planar environment in both cations indicating a formal sp^2 hybridization. Similarly to amino(azido)phosphenium species **7**, the NCO or NCS moieties nearly lie in the NPSi1Si2 plane, as only a minimal deviation from planarity is observed (**8**: Si1−N2−P1−N1 = −178.1°; **9**: −0.33°). The N_{amino}−P distance is in the typical range of a P−N double bond (**8** 1.592(1), **9** 1.593(1) Å) compared with the sum of the covalent radii (Σr_{cov}(P═N) = 1.60 Å).[24] The isocyanato moiety in **8** and the isothiocyanato group in **9** are slightly bent (∠NCO = 175°; ∠NCS = 174°). This trans-bent configuration was also observed in azido-species **7** and is a common feature for covalently bound triatomic pseudohalide groups. Furthermore, a rather short P−$N_{pseudohalogen}$ (**8** 1.656(2), **9** 1.651(2) Å) bond length is indicative of a partial double bond character (cf. Σr_{cov} (P═N) = 1.60 Å, (P−N) = 1.82 Å). As expected the C1−O1 and C1−S1 (**8** 1.155(2), **9** 1.5421(2) Å) distances are between a double and triple bond (cf. Σr_{cov} (C═O) = 1.24 Å, Σr_{cov} (C≡O) = 1.13 Å; (C═S) = 1.61, (C≡S) = 1.55), whereas the N1−C2 (**3** 1.211(2), **4** 1.205(2) Å) distances are indicative of a shortened double bond (cf. Σr_{cov} (C═N) = 1.27 Å, (C≡N) = 1.14). These values compare nicely with known phosphorus compounds that incorporate isocyanate (cf. P−N_{NCO} 1.673(3), N_{NCO}−C 1.168(4), C−O 1.146(4) Å in **10**, Figure 4)[25] or isothiocyanate (cf. P−N_{NCS} 1.707(7), N_{NCS}−C 1.165(9), S−C 1.551(9) Å; N_{NCS}−C−S 176.8(8)° in $P^{(III)}$ isothiocyanate **11**, Figure 4)[26] groups. Strong cation···anion interactions are observed for **8** and **9** in the crystal. For example, four contacts to neighboring chlorine atoms of the anion are detected in **8**

dx.doi.org/10.1021/ic4001285 | Inorg. Chem. 2013, 52, 5214−5225

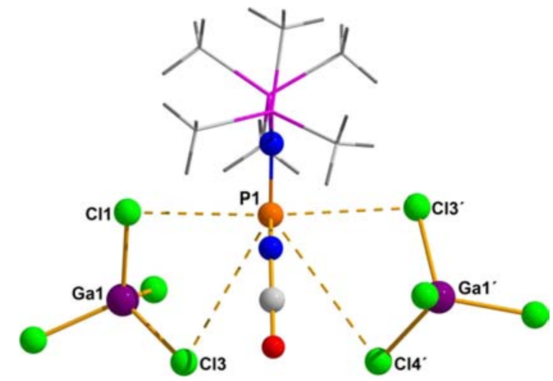
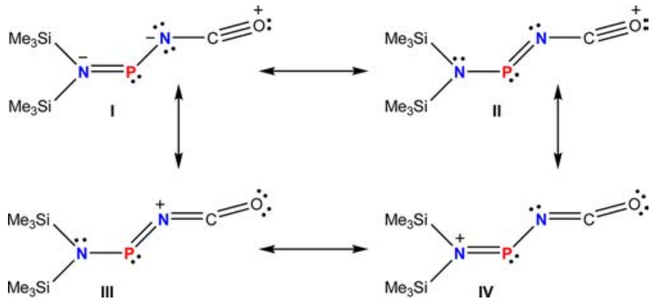


Figure 3. Ball and Stick drawing of the anion−cation interactions in amino(isocyanato)phosphenium salt **8**. Four close contacts are observed (distances in Å): P1−Cl1 3.1582(6), P1−Cl3 3.7630(7), P1−Cl3′ 3.273(7), P1−Cl4′ 4.0212(9).

whose lone pairs (LPs) offer effective donor sites. The three closest P−Cl distances (**8**: P1−Cl1 3.1582(6) Å, P1−Cl3′ 3.273(7) Å, P1−Cl3 3.7630(7) Å) are all in the range of the sum of the van der Waals radii (cf. Σr_{vdw}(P−Cl) = 3.70 Å). Therefore, electrostatic interactions, that stabilize the reactive phosphenium center, can be assumed (Figure 3). A similar situation is found in species **9**.

To access the bonding in these unique cations, we carried out Natural Bond Orbital (NBO) analyses and molecular orbital (MO) calculations for the salts **8** and **9** at the pbe1pbe/aug-cc-pVDZ level of density functional theory.[27] NBO analysis displays a localized p_π-p_π P−N_{amino} double bond, which is highly polarized, with 80% of the electron density being located on the nitrogen atom and a positive net charge on the phosphorus atom of +1.47*e* in **8** and 1.38*e* in **9**. This finding highlights the fact that pseudohalogen phosphenium ions are phosphorus-centered cations. An empty p-type orbital is found at the phosphorus atom, which is accessible for electron pair donors. The LPs located on the chlorine atoms of the anion can effectively interact with the positively charged phosphorus center and therefore a significant charge transfer (**8**: 0.11 and **9**: 0.12 *e*) from the anion to the cation is calculated. Thus the overall charge of the cation is significantly decreased ($q(X_{cat})$ = 0.89 and 0.88 *e* for the cations in **8** and **9**). The bonding situation in **8** and **9** is best described by at least four canonical Lewis formulas (Scheme 4) with formula I being the energetically favored Lewis representation according to NBO analysis. Lewis representation **I** of the cation in **8** shows two σ P−N single bonds and as described before an additional π P−N_{amino} bond. Two LPs are found on the N_{NCO} and N_{NCS} atoms, respectively, which are highly delocalized into the π* orbital of the P−N_{amino} bond and into the π* orbital of the C1−O1 bond,

Scheme 4. Resonance Scheme of Lewis Formulae for the Cation in 8 According to NBO Analysis



with hyperconjugative energies ($\Delta E^{(2)}$) of 41.9 and 115.9 kcal/mol, respectively. The postulated π-acidity of phosphenium cations is underlined by MO analysis, in which a lowest unoccupied MO (LUMO) with a large coefficient for a p-type orbital on the phosphenium center is found (Figure 5, top). Additionally, π bonding in the cation allows for delocalization of the positive charge, as shown by selected MOs of **8** and **9** (Figure 5).

Isolation and Characterization of a Siloxy Substituted Phosphenium Cation in [$(Me_3Si)_2N$=P-$OSiMe_3$][$GaCl_4$]. In a next series of experiments we were interested in the synthesis of the remaining pseudohalogen-substituted species [$(Me_3Si)_2N$=P−X][$GaCl_4$] (X = NCSe, CN, CNO). Treating **1** with Me_3Si-CNO led to an immediate color change and the deposition of colorless crystals, after concentrating the reaction mixture at −50 °C. Surprisingly, crystal structure analysis revealed the formation of an amino(trimethylsiloxy)-phosphenium salt [$(Me_3Si)_2N$=P-$OSiMe_3$][$GaCl_4$] (**12**) indicating decomposition of Me_3Si-CNO and the formal elimination of "CNCl" (Scheme 5). The crystalline material obtained in this reaction was found to be exclusively **12**, nevertheless byproducts of the reaction could not be identified. To date reactions employing Me_3Si-CNO as a $OSiMe_3$ transfer reagent remain elusive, and this reaction might open a new way to effectively transfer siloxy units. **12** is the first structurally characterized acyclic phosphenium cation with a siloxy moiety directly attached to the dicoordinated phosphorus atom. Crystals suitable for X-ray analysis were selected at −50 °C. It should be noted that only one aminooxyphosphenium [Mes*N(H)P-OMes*][$GaCl_4$] (Mes* = 2,4,6-tri-*tert*-butyl-phenyl) ion has been reported to date in the alcoholysis of an iminophosphenium salt.[28] Furthermore the structures of alkoxyphosphenium transition metal complexes are known; Muetterties and co-workers reported on an bisalkoxy phosphenium ligand in a cationic molybdenum complex {Mo[$P(OCH_3)_3$]$_5$[$P(OCH_3)_2$]}[PF_6] in 1978, and an aryloxy

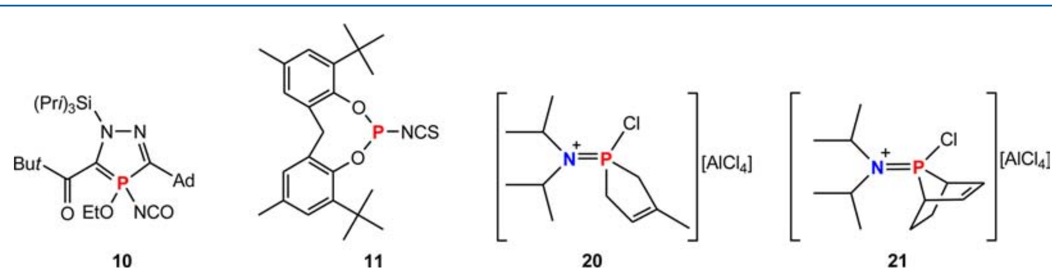


Figure 4. Structures of structurally characterized P-isothiocyanates and -isocyanates **10** and **11**.[25,26] Structures of phospholenium salts **20** and **21** prepared by Cowley et al.[11b].

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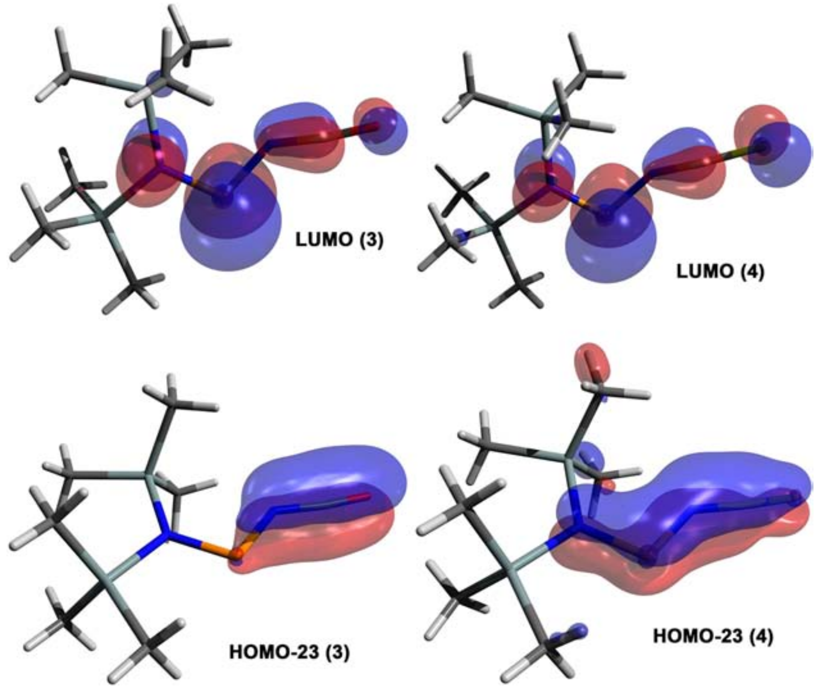
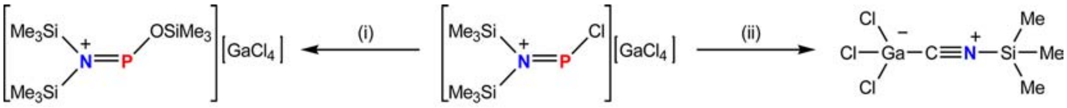


Figure 5. Top: LUMOs calculated for $[(Me_3Si)_2N{=}P\text{-}NCO]^+$ (left) and $[(Me_3Si)_2N{=}P\text{-}NCS]^+$ (right) at the pbe1pbe/aug-cc-pVDZ level of theory . Bottom: MOs displaying out-of-plane π delocalization in the cation in **8** (left) and over the whole N−P−N−C−S chain in **9** (right).

Scheme 5. Attempted Synthesis of Isoselenocyanato- and Cyano-Substituted Phosphenium Ions Starting from 1[a]



12 **6** **13**

[a]Left, formation of **12**; right, formation **13**. (i) Me_3Si-CNO at −50°C; −CNCl, -Me_3Si−Cl; (ii) Me_3Si-NCSe or Me_3Si-CN (decomposition products could not be identified).

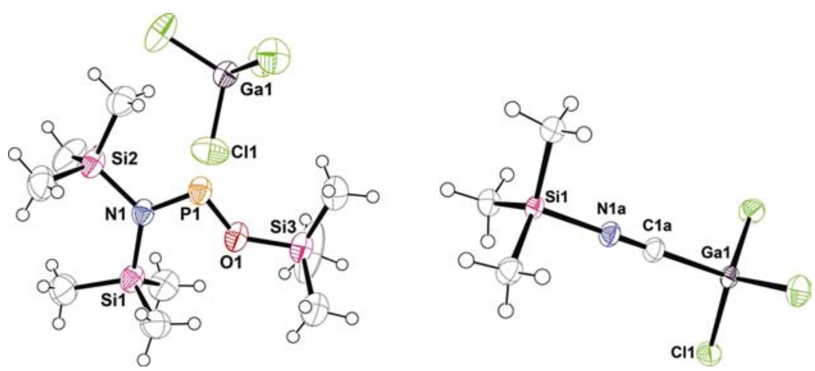


Figure 6. ORTEP drawing of **12** (left) and **13** (right). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): (**5**): P1−N1 1.600(3), P1−O1 1.557(3), N1−Si 1.825(3), N1−Si2 1.845(3), O1−Si3 1.715(3), P1−Cl1 3.133(2); N1−P1−O1 105.2(2); N1−P1−O1-Si3 175.2(2). (**6**) N1a-C1a 1.141(4), Si1−N1a 1.858(3), C1a-Ga1 2.029(4), Si1−C 1.836(2), Ga1−Cl 2.1452(5); Σ(∠Si) 343.7, Σ(∠Ga) 336.2; Si1−N1a−C1a−Ga1 180.

phosphenium stabilized in the coordination sphere of cobalt in $[Co(CO)_3(Mes^*O\text{-}PCp^*)]$ was reported by Lang et al. in 1996.[29] Aminosulfidophosphenium ions are also known; however, the sulfide groups were introduced prior to the formation of the cation, and the solid state structures were not reported. **12** crystallizes in the monoclinic space group $P2_1/n$ with four formula units per cell (Figure 6). The structural parameters found for **12** compare nicely with those of the other phosphenium species (**8**, **9**), as the $P{-}N_{amino}$ distance (**12** 1.600(3) Å) (cf. Σr_{cov} (P═N) = 1.60 Å) is a typical double bond and the NPO angle of 105.2(2)° is in the same range observed for the NPN angle in the cations of **8** and **9** ($\angle N_{amino}{-}P{-}N_{NCX}$ (deg): **8** 103.65(7), **9** 103.79(8); X = O, S). The P−O distance (**12** 1.557(3) Å) gives rise to a double bond (cf. Σr_{cov} (P═O) = 1.59 Å) with two LPs being located on oxygen as supported by NBO analysis. As observed in **7**−**9**, these LPs are highly delocalized into the π^* of the $P{-}N_{amino}$ bond ($\Delta E^{(2)}$ = 33.9 kcal mol^{-1}) and furthermore into the σ^*

dx.doi.org/10.1021/ic4001285 | Inorg. Chem. 2013, 52, 5214−5225

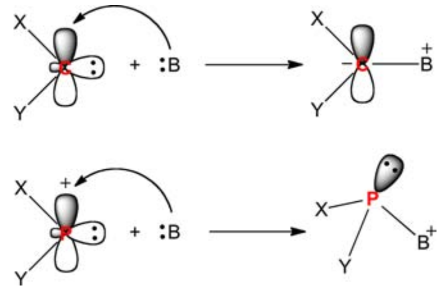
orbitals of the Si−C bonds in the trimethylsilyl group. Again close contacts to the anion are observed (P1···Cl1 = 3.133(2); Σr_{vdw}(P−Cl) = 3.70 Å). This kind of ion pairing seems to be a prominent feature in the structure of phosphenium cations with weakly coordinating anions. However, these weak cation−anion interactions cannot be neglected since they substantially contribute to the stability of phosphenium salts in the solid state. Nevertheless, all phosphenium salts discussed in this article are highly labile in solution, and **12** could not be detected in solution in the ^{31}P NMR spectrum, as precipitation occurs below −30 °C and above this temperature decomposition to unidentified products begins.

When trying to prepare the isoselenocyanato substituted phosphenium cation, the color of the reaction mixture changed to deep brown, but at no time was the formation of red selenium observed in the reaction vessel. Concentration of the reaction mixture after several days at −80 °C afforded small yellowish crystals, which decomposed when brought into an atmosphere of nitrogen at −50 °C for crystal selection. In this case red selenium formed, and the residual crystals were found to be a $GaCl_3$ adduct of *N*-trimethylisonitrilesilane (**13**) (Scheme 5). The same product was obtained and characterized by means of X-ray analysis in the attempted synthesis of the amino(cyano)phospheniun cation when **6** was treated with Me_3Si-CN. However, this adduct compound decomposes within 5 min at ambient temperatures in an argon atmosphere. Crystals suitable for structural analysis were collected at low temperatures, and the molecular structure could be determined. **13** crystallizes in the trigonal spacegroup *R*3 with three molecules in the unit cell (Figure 6). The linear Si1−N1−C1−Ga1 moiety lies on a 3-fold axis, and the bond lengths detected in **13** are indicative for the formulation of a dative bond between carbon and gallium (C1−Ga = 2.029(4) ; Σr_{cov} (C−Ga) = 1.99 Å). The nitrogen carbon distance is a typical triple bond (N1−C1 = 1.141(4) Å, cf. Σr_{cov} (C≡N) = 1.14 Å), and the sum of angles around silicon and gallium are in agreement with tetrahedrally coordinated centers (Σ(∠Si) 343.7°, Σ(∠Ga) 336.2°). It is noteworthy that the positions of the carbon and nitrogen atoms in **13** are found to be partially occupied by nitrogen and carbon respectively. Consequently **13** is best described as a mixture of Me_3Si-NC···$GaCl_3$ and Me_3Si-CN···$GaCl_3$. Astonishingly, the group of Mazieres reported a ^{31}P NMR chemical shift of 78 ppm for [*i*Pr_2N=P-CN]$^+$.[20] However, we were neither able to detect a similar signal at low temperature in ^{31}P NMR experiments nor could we find any further indications for the formation of [$(Me_3Si)_2$N=P-CN]$^+$.

Investigation of the Lewis Acidic Properties of Phosphenium Species 7−9. In earlier studies it was shown that phosphenium cations can be stabilized by the addition of Lewis bases that act as electron pair donors to the electron deficient *π*-acidic phosphenium center.[30] This reactivity is best understood in analogy to the carbenes which form ylides in the reaction with Lewis bases (Scheme 6).

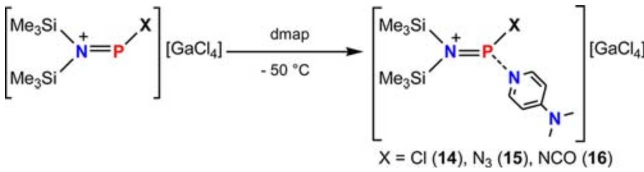
Bases usually employed for such reactions are phosphines, carbenes, or pyridine bases such as 4-dimethylaminopyridine (dmap) or 2,2′-bipyridine.[31] The catenation of phosphenium ions in the presence of phosphines is also well described and especially the group of Burford established a huge library of catena-phosphinophospenium salts in the past decade.[32] We therefore decided to add the strong pyridine base and *σ*-donor dmap to a solution of **6**, **7**, or **8** in CH_2Cl_2. It is well described in the literature that dmap can be utilized to remove $GaCl_3$ from mixtures as a dmap-adduct which does not dissolve in nonpolar solvents such as *n*-hexane.[23] Conclusively, two reaction channels are possible in this reaction: (i) The formation of adduct cations in salts of the type [$(Me_3Si)_2$NP(dmap)X][$GaCl_4$] or the removal of $GaCl_3$ as Cl_3Ga·dmap adduct along with the formation of the corresponding chlorophosphines $(Me_3Si)_2$NPClX (X = Cl, N_3, NCO) (Scheme 7 and Figure 7). Indeed both reaction pathways were observed. Upon addition of dmap at −50 °C to **6**, **7**, and **8** and subsequent concentration of the reaction mixture, colorless crystals of [$(Me_3Si)_2$NP(dmap)X][$GaCl_4$] (X = Cl (**14**), N_3 (**15**), NCO (**16**)) were isolated and structurally characterized (Figure 7, only structures of **14** and **15** are shown).

Scheme 6. Comparison of the Reactivity of Carbenes of the Type X−C−Y with the Isolobal [X−P−Y]$^+$ Ion in the Reaction with Lewis Bases[a]



[a]Carbenes (top) form ylides whereas phosphenium cations (bottom) form adduct cations. In both cases the LP located on the Lewis base interacts with an empty p-orbital of the Lewis acidic center (C or P).

Scheme 7. Synthesis of [$(Me_3Si)_2$NP(dmap)X][$GaCl_4$] (X = Cl (14), N_3 (15), NCO (16)) When dmap is Added to a Solution of 6 in CH_2Cl_2 at −50 °C



All cationic adduct salts (**14**, **15**, and **16**) are stable at room temperature, moisture and air sensitive. They can be stored over a long period of time in an inert atmosphere. Decomposition of these salts begins at around 100 °C nicely illustrating the ability of bases such as dmap to inhibit the reactivity of cationic Lewis acidic compounds by adduct formation.[33] As mentioned before, a second reaction channel is possible which is observed when **14**−**16** are redissolved in CD_2Cl_2 as demonstrated in ^{31}P NMR experiments. Accordingly in the ^{31}P NMR spectrum of **14** two resonances are detected (see Figure 8). A resonance at 163 ppm corresponds to the dmap adduct cations [$(Me_3Si)_2$NP(dmap)Cl]$^+$ whose chemical shift is in the typical range of neutral phosphines with two electronegative substituents on the phosphorus atom. Furthermore, a signal at 188 ppm, that corresponds to the starting material $(Me_3Si)_2NPCl_2$, is observed. Therefore, it can be concluded that there is an equilibrium in solution between $GaCl_3$-dmap and [$(Me_3Si)_2$NP(dmap)X]$^+$ (Figure 8).

Such an equilibrium is observed for all species **14**−**16**. It is noteworthy that in the crystal a substitutional disorder of the type [$(Me_3Si)_2$NP(dmap)Cl_yX_{1-y}]$^+$ (y = 0.14) is observed for **16**. This mixed compound gives the expected solution ^{31}P

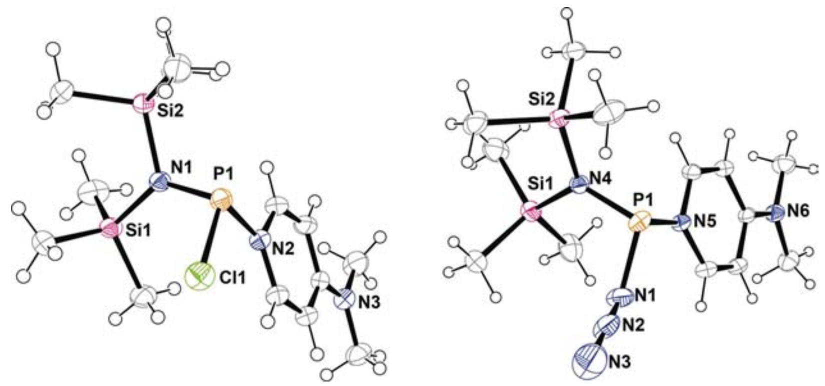


Figure 7. ORTEP drawings of the cations in **14** (left) and **15** (right). Ellipsoids are drawn at 50% probability, anions are omitted for clarity. Selected bond lengths (Å) and angles (deg): (**14**): P1−N1 1.641(1), P1−N2 1.829(1), P1−Cl1 2.0799(6), N1−Si 1.801(1), N1−Si2 1.817(1); N1−P1−O1 105.2(2); Σ(∠N1) 359.86, Σ(∠P1) 305.51; Si2−N1−P1-Cl1 129.46(6). (**15**) P1−N4 1.649(3), P1−N1 1.757(3), P1−N5 1.810(3), N1−N2 1.157(4), N2−N3 1.162(5), N1−Si 1.797(3), N1−Si2 1.808(3); N1−N2−N3 173.6(5), Σ(∠N4) 359.18, Σ(∠P1) 298.08; Si2−N4−P1−N1 138.5(2).

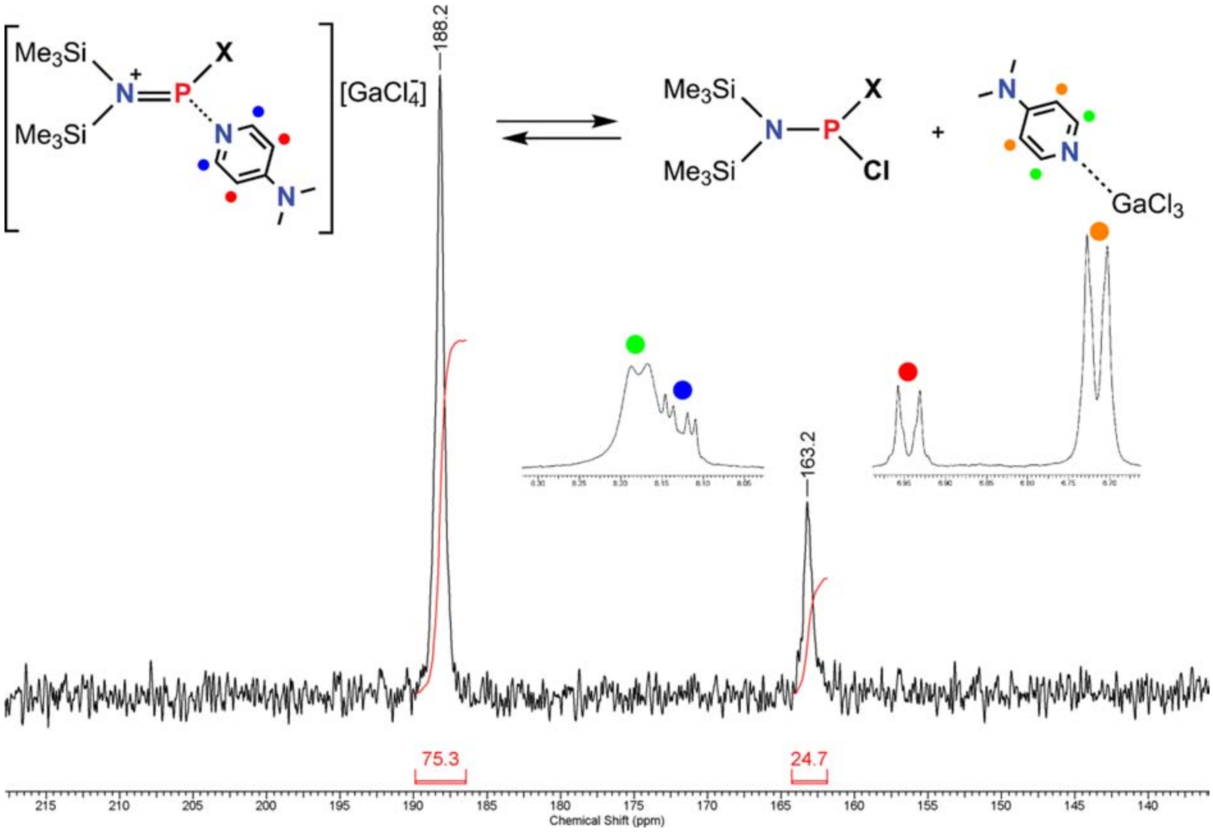


Figure 8. ^{31}P NMR (bottom) and ^{1}H NMR (top, proton positions indicated by colored dots) spectrum of a CD_2Cl_2 of **14** at room temperature, displaying the solution equilibrium between $[(Me_3Si)_2NP(dmap)X][GaCl_4]$ (X = Cl (**14**), N_3 (**15**), NCO (**16**)) and the corresponding chlorophosphine $(Me_3Si)_2NP(X)Cl$ in solution. The resonance in the ^{31}P NMR spectrum at 188 ppm corresponds to $(Me_3Si)_2NPCl_2$ and at 163 ppm the cation in **14** is detected.

NMR spectrum with four species present, $(Me_3Si)_2NPCl_2$, $[(Me_3Si)_2NP(dmap)Cl]^+$, $[(Me_3Si)_2NP(dmap)X]^+$, and $(Me_3Si)_2NPClX$. This kind of partial chlorine occupancy of a pseudohalogen position is a well-known phenomenon and regularly observed in binary azides when prepared in chlorinated solvents or from chlorine precursors.[14b,23c] Species **14**−**16** crystallize in the monoclinic space groups $P2_1/c$ (**14**, **16**) and $P2_1/n$ (**15**), respectively. In the molecular structures of the cations in **14**−**16** the P−N_{amino} distance is rather long (**14** 1.644(1), **15** 1.649(3), **16** 1.645(2) Å) compared with the phosphenium precursor ions and falls in the range of the starting material $(Me_3Si)_2NPCl_2$ (P−N_{amino} = 1.6468(8) Å). The dmap binds with its pyridine N atom, and the P−N_{dmap} distance (**14** 1.829(1), **15** 1.810(3), **16** 1.848(2) Å) is in the range of a typical P−N single bond (cf. Σr_{cov} (P−N) = 1.82 Å). The phosphine character of the adduct cation is also supported by the sum of angles around the central P atom (Σ∠(P): **14** 305.51, **15** 298.08, **16** 298.21°) and therefore in the typical range of a tricoordinated, trigonal pyramidal coordinated phosphorus in the oxidation state +III (cf. $(Me_3Si)_2NPCl_2$

$\Sigma\angle(P)$: 305.99°).[18] NBO analyses were carried out to gain insight into the bonding in these adduct cations, which show, that the positive charge is delocalized mainly over the π-system of the dmap moiety. The LP on the N_{amino} atom, located in a p-type orbital, is delocalized into the σ^* orbitals of the Si−C backbone and also negative hyperconjugation with the σ^* orbitals of the P−X bond contributes to the rather short P−N_{amino} distance and elongation of the P−X bond (**14** 2.0799(6), **15** 1.757(3), **16** 1.740(4) Å) underlining the phosphine character of these adduct cations (cf. Σr_{cov} (P−N) = 1.82, Σr_{cov} (P−Cl) = 2.04; $[Ter_2N_2P_2N_3]^+$ $d(P{-}N_{azide})$ = 1.706 (3) Å).[6] The natural charge on phosphorus is still positive with nearly 1.2−1.4 *e* (**14** 1.25, **15** 1.43, and **16** 1.45 *e*); however, no empty p orbital on phosphorus is found, and thus the adduct cations do not have any phosphenium characteristics, as dmap transfers electron density to the phosphenium fragment (e.g., $q_{charge\text{-}transfer}$ = 0.38 *e* in **14**).

Investigation of the Carbenoid Reactivity of 6−8. It is known that dienes such as dmb or chd can easily add to carbenes in chelotropic [4 + 1] cycloaddition reactions.[34] Therefore the formation of differently substituted phospholenium salts can be assumed when phosphenium ions are utilized instead of carbenes. Phosphenium species **6**−**8** are related to carbenes of the type X−C−Y and accordingly possess orbitals suitable for the [4 + 1] chelotropic cycloaddition with dienes (Figure 9 and 10).[10,11b] Computational studies were carried out to assess the bonding situation in the phosphenium cations which support the idea that these cycloadditions are symmetry allowed (Figure 10). Accordingly, addition of dmb to a freshly prepared solution of **6** in CH_2Cl_2 at −60 °C resulted in a clean conversion to one new phosphorus species as shown by ^{31}P NMR studies (Scheme 8).

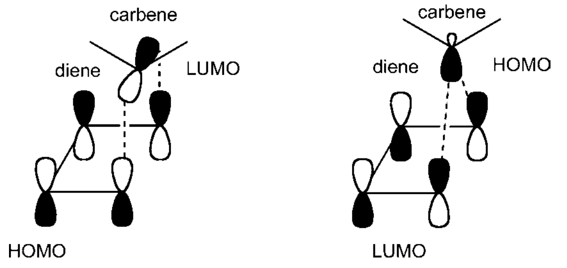


Figure 9. HOMO−LUMO interactions in a [4 + 1] chelotropic cycloaddition process.

Similar chelotropic [4 + 1] cycloaddition reactions have been utilized as early as 1983 when Soo and co-workers prepared the first phospholenium cations.[11a] They treated $[(Me_2N)_2P]^+$ with dmb in an attempt to optimize the McCormack reaction which is used to synthesize phosphorus-containing heterocycles.[35] The ^{31}P NMR chemical shifts of 95.9 ppm for $[(Me_3Si)_2NP(dmb)Cl][GaCl_4]$ (**17dmb**) compare well with similar literature values (cf. $\delta(^{31}P\{^1H\})$: **20** = 100.3, Figure 4).[11b] To grow X-ray quality crystals of **17dmb** a concentrated solution was stored in the freezer at −80 °C for 24 h. Structural analysis indeed revealed the formation of **17dmb**. To add to the diverse library of such salts and to investigate the possibility to synthesize room temperature stable derivatives of **7** and **8** we decided to additionally react **6** with 1,3-*cyclo*-hexadiene and treated **7** and **8** with both dmb and chd. According to ^{31}P NMR experiments the reaction of **6** with chd occurs immediately and $[(Me_3Si)_2NP(chd)Cl][GaCl_4]$ is formed. With respect to the position of the phosphorus LP, there are two possible conformers (*syn*/*anti*) in such 7-phosphanorbornenium cations (Figure 11).

The *anti* species of **17chd** is observed at 117 ppm, and the *syn* conformer is detected at 94 ppm in a 3:2 ratio. GIAO calculations of the magnetic field tensors were carried out to assign ^{31}P NMR shift of the *syn*- and *anti*-conformer of **17chd**.[36] In the ^1H NMR spectrum four different kinds of protons are detected for each conformer. As expected, two aromatic protons (multiplet at 6.67 ppm), two methine protons (multiplet at 3.8 ppm), and two sets of multiplets are observed for the CH_2-groups as both protons are magnetically inequivalent. All attempts to crystallize **17chd** directly from the reaction mixture in CH_2Cl_2 always resulted in the formation of microcrystalline material. Layering a CH_2Cl_2 solution of **17chd** with *n*-pentane and storage at −25 °C for 24 h yielded minimal amounts of crystals suitable for structural analysis. The *anti*-conformer of **17chd** is exclusively found in the solid state, which is in good agreement with the calculated structure of a similar, but neutral system, in *anti*-*i*Pr_2N-7-phosphanorbornene just recently reported by Cummins et al.[37] In addition the reactivity of metal phosphinidene complexes is well studied, and various examples of metal stabilized *anti*-7-phosphanorbornadienes have been structurally characterized.[38] Compound **17chd** is the first example of a structurally characterized 7-

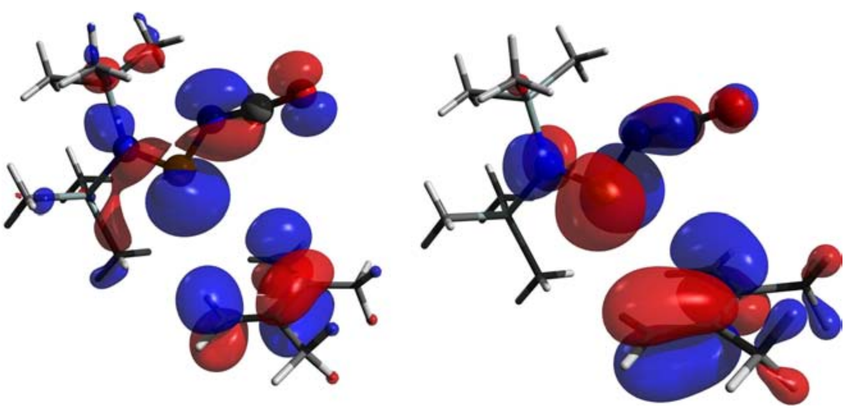
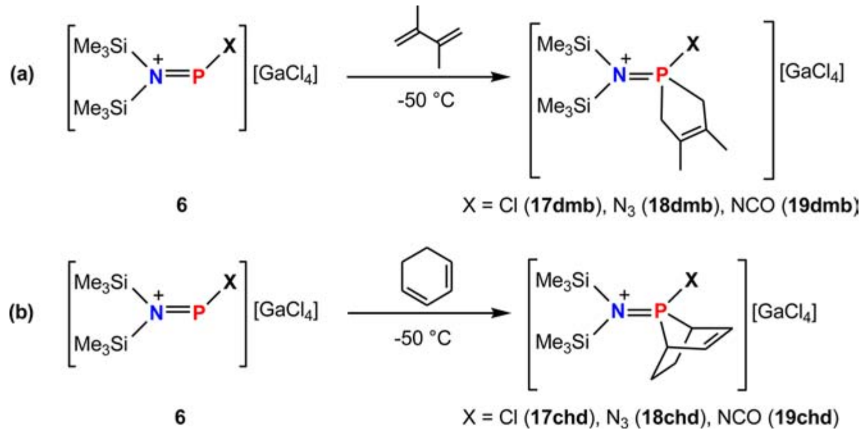
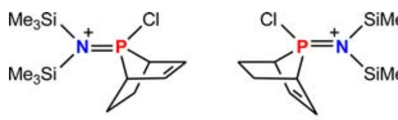


Figure 10. HOMO and LUMO combinations calculated for the cation in $[(Me_3Si)_2NPNCO]^+$ (**8**) and dmb (pbe1pbe/aug-cc-pVDZ) displaying the correct symmetry for chelotropic [4 + 1] cycloaddition. Left: Interaction of the HOMO-4 of **8** and the LUMO of dmb. Right: Interaction of the LUMO of **8** and the HOMO of dmb.

Scheme 8. Synthesis of Phospholenium Salts 17dmb−19dmb and 17chd−19chd[a]



[a](**a**) By addition of 2,3-dimethyl-1,3-butadiene to a solution of **1** in CH_2Cl_2 at −50 °C; (**b**) by addition of 1,3-*cyclo*-hexadiene to a solution of **1** in CH_2Cl_2 at −50 °C.



anti-**17chd** *syn*-**17chd**

Figure 11. *Syn*- and *anti*-conformers of 7-phosphanorbornenium salt **17chd**.

phosphanorbornenium cation obtained in the [4 + 1]-cycloaddition between chd and a phosphenium cation, underlining the assumption made by Cowley and co-workers that the sterically less encumbered configuration, that places the double bond on the same side as the chlorine atom, is indeed favored.[11b] Additionally, the ^{31}P NMR data reported for a mixture containing both *syn*- and *anti*-[$i$$Pr_2$NP(chd)Cl][$AlCl_4$] (**21**) (cf. δ(^{31}P{^{1}H}: syn-**21** = 98.7, anti-**21** = 117.2; Figure 4), correspond well with the values detected for **17chd.**[11b] Adopting the same synthetic procedure that yielded **17dmb** to **7** and **8** phosphapentene moieties containing phospholenium salts of these phosphenium salts have been prepared. [$(Me_3Si)_2$NP(dmb)N_3][$GaCl_4$] (**18dmb**) and [$(Me_3Si)_2$NP-(dmb)NCO][$GaCl_4$] (**19dmb**) could be prepared in moderate yields of nearly 50% and are, in contrast to their transient precursors, thermally stable up to 100 °C. In **18dmb** a partial chlorine occupancy (0.03) of the azide position was observed by means of X-ray crystallographic methods. Depending on tiny changes in the reaction conditions a slightly different, small contamination with chlorine was observed (see Supporting Information). Furthermore, the addition of chd to pseudohalogen-containing phosphenium salts **7** and **8** resulted, according to X-ray crystallographic methods, exclusively in the formation of *anti*-[$(Me_3Si)_2$NP(chd)N_3][$GaCl_4$] (**18chd**) and *anti*-[$(Me_3Si)_2$NP(chd)NCO][$GaCl_4$] (**19chd**). In the ^{31}P NMR spectrum also only one species is detected (Table 1). The molecular structures of dmb containing phospholenium salts **17dmb−19dmb** and chd-added species **17chd−19chd** are quite similar and will be discussed only briefly (Figure 12). The dmb derivative **17dmb** crystallizes in the monoclinic space group $P2_1/n$, whereas **18dmb**, **19dmb**, and **19chd** crystallize in the space group $P2_1/c$, respectively, all with four formula units in the unit cell. **17chd** and **18chd** crystallize in $P\bar{1}$ with two formula units in the cell. The NPCl(C_6H_8) moiety in **17chd** is disordered, and only the main part is shown. **18chd** crystallizes as a toluene solvate with one solvent molecule in the asymmetric unit. In **18dmb** a partial occupation of the azide position with chlorine is detected, a feature also detected in **16**. Interestingly upon reaction only modest changes within the [$(Me_3Si)_2$NPX]$^+$ moiety are observed. The most striking feature is that the group X (X = Cl, N_3, NCO) attached to the phosphorus atom is nearly perpendicular to the Si1−N_{amino}−Si2 plane, which is in contrast to the phosphenium

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Phospholenium Salts 17dmb−19dmb/17chd−19chd along with δ(^{31}P) NMR Shifts (ppm)[a]

	d(P1−N_{amino})	d(P1−X)[b]	d(P1−C)[c]	d(N_{amino}−Si)[c]	Σ∠P1	δ(^{31}P)
17dmb	1.6089(9)	2.0065(4)	1.801	1.824	333.98	95.9
18dmb	1.608(1)	1.683(2)	1.795	1.820	333.95	78.6
19dmb	1.612(2)	1.661(2)	1.792	1.819	333.5	66.2
17chd	1.592(2) /1.657(3)	1.994(2)[e]	1.822	1.824	322.83	116.6
11chd	1.609(2)	1.682(2)	1.826	1.815	322.01	91.4
12chd	1.612(2)	1.661(2)	1.792	1.819	320.87	83.7
8	1.592(1)	1.656(2)		1.844	103.65(7)	337
14	1.644(1)	2.0799(6)	1.829(1)[d]	1.809	305.51	163
$(Me_3Si)_2NPCl_2$	1.6468(8)	2.0834(5)[e]	2.1074(5)[f]	1.795	305.99	189

[a]In addition, the corresponding values for **8**, **14** and $(Me_3Si)_2NPCl_2$ are given for comparison. [b]X: **17** Cl, **18** N_3, **19** NCO. [c]Bond lengths are similar, therefore average value is presented. [d]d(P−N_{dmap}) is presented. [e]d(P−Cl1) in $(Me_3Si)_2NPCl_2$. [f]d(P−Cl2) in $(Me_3Si)_2NPCl_2$.

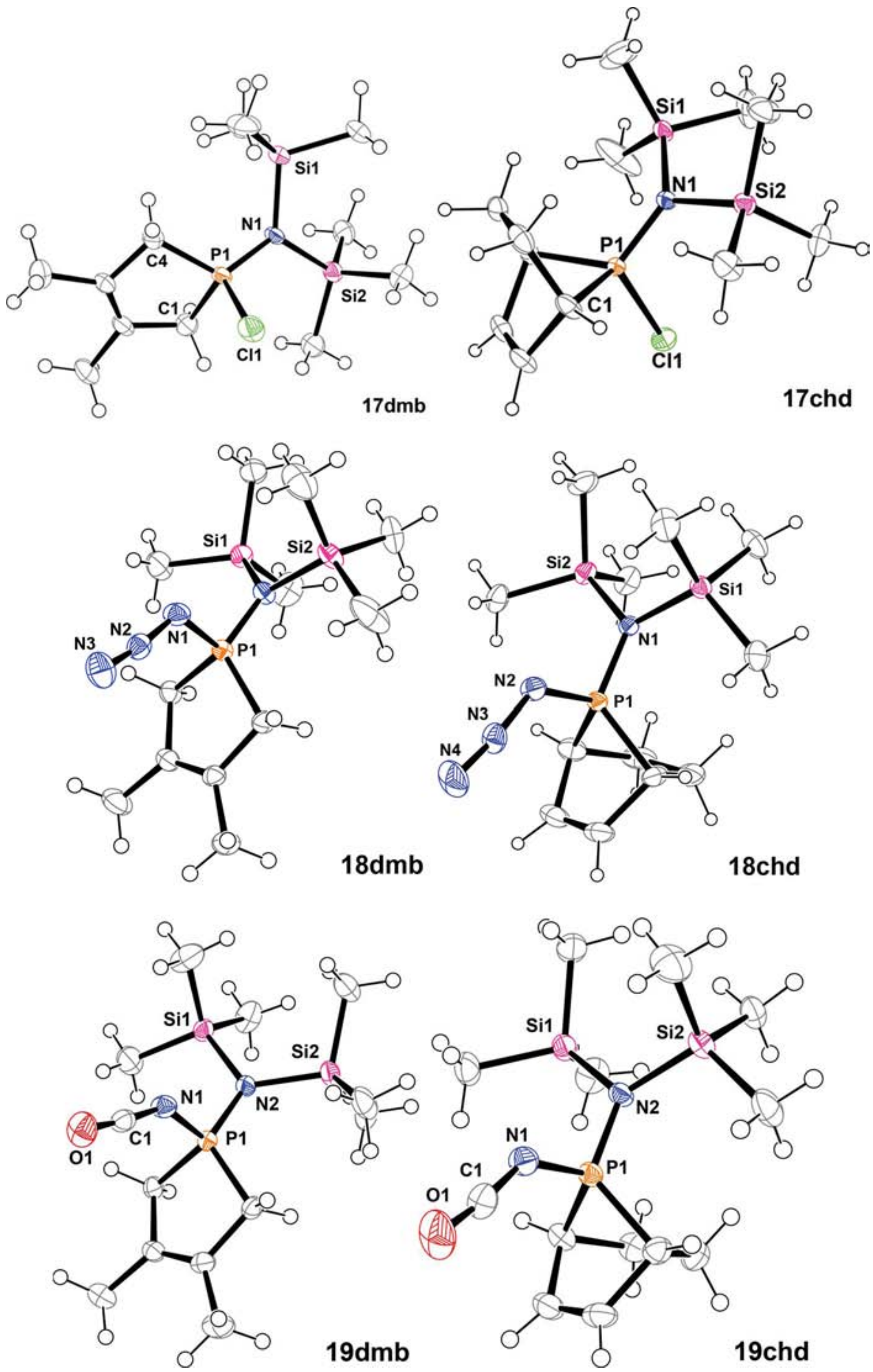


Figure 12. ORTEP drawings of the cations in **17dmb−19dmb** (left) and **17chd−19chd** (right). In **18dmb** a partial occupation of the azide position with chlorine is detected; the chlorine is omitted for clarity. Ellipsoids are drawn at 50% probability; anions are omitted for clarity. Selected bond lengths and angles are listed in Table 1.

cations and is similar to the situation in the dmap adducts **14−16**. As a result of this geometrical arrangement an interaction between the LP located in a p-type orbital at the N_{amino} and a σ*-orbital of the P−X bond is possible and therefore the P−N_{amino} bond is significantly shortened (1.60 Å, Table 1). Additionally, the P−X distance is longer than in the precursor cations. The phosphapentene moiety in **17dmb−19dmb** adopts an envelope conformation, and the C−C double bond points toward the group X (**17dmb**: N1−P1−C7−C8 = 146.19(7)°). A similar situation is found for the phosphapentene groups in **17chd−19chd**, in which the olefinic double bond is in a proximal arrangement with the group X and therefore the five-membered PC_4-ring also adopts an envelope conformation. The carbon distances within the phosphole unit are in the expected range for such compounds with a C−C double bond in the ring. The P−C distances represent short single bonds (Table 1, cf. Σr_{cov}(P−C) = 1.86, Σr_{cov}(P═C) = 1.69 Å). As a consequence of negative hyperconjugation between the LP on N_{amino} and the antibonding σ* Si−C orbitals the N_{amino}−Si distances are shortened which is clearly

dx.doi.org/10.1021/ic4001285 | Inorg. Chem. 2013, 52, 5214−5225

shown by NBO analysis. In contrast to the phosphenium cations **1−5**, in which contacts between anion and cation are detected, the phospholenium species can be considered as almost "naked" cations underlined by the overall natural charge of the cation of +0.99 *e* and by the fact that no short contacts to the counteranions are observed.

CONCLUSIONS

In this study we present for the first time the crystal structures of pseudohalogen-substituted phosphenium salts of the type $[R_2NPX][GaCl_4]$ (R = $SiMe_3$; X = NCO (**8**), NCS (**9**)) which are highly reactive and labile in solution. These salts are only stable below −40 °C; however, even at these low temperatures decomposition occurs within two weeks. Attempts to prepare $[R_2NPX][GaCl_4]$ (R = $SiMe_3$, X = CNO) resulted in the formation of $[(Me_3Si)_2NPO(SiMe_3)][GaCl_4]$ (**12**), the first salt with an oxygen atom directly attached to the phosphenium center. The reaction pathway gives rise to a trimethylsiloxy transfer from trimethylnitrileoxidosilane to the phosphorus, a reaction with no precedence in the literature so far. In subsequent reactions the ambiphilic nature of phosphenium cations was demonstrated as they react readily at low temperatures with σ-donors such as dmap to yield adduct cations in **14−16**. In solution these dmap adducts, which cannot be referred to as phosphorus centered cations, show a fascinating equilibrium chemistry that was studied by means of solution ^{31}P NMR spectroscopy. Moreover, phosphenium salts **6−8** were shown to react with dienes such as dmb and chd to afford 7-phosphanorbornenium salts **17dmb−19dmb/17chd−19chd** which are room temperature stable derivatives of the parent, transient phosphenium salts. We succeeded in the structural characterization of the first 7-phosphanorbornenium salts $[(Me_3Si)_2NPX(C_6H_8)][GaCl_4]$, which revealed the formation of the *anti*-conformer as the dominant species, when chd is added to the phosphenium salt. These findings are further supported by ^{31}P NMR data and DFT calculations. In future studies the potential of the phospholenium salts as starting materials for the synthesis of phosphaazenes will be investigated, and preliminary results show that interesting polymeric materials might be accessible.

ASSOCIATED CONTENT

Supporting Information

This material contains experimental and computational details, crystallographic information, and further experimental and theoretical data of all considered species. 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

Martin Ruhmann and Fabian Reiß (University of Rostock) are acknowledged for the measurement of Raman spectra. Financial support by the Fonds der chemischen Industrie (fellowship to C.H.) and the DFG are gratefully acknowledged.

REFERENCES

(1) (a) Fluck, E. *Top. Phosphorus Chem.* **1980**, *10*, 193. (b) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *I S*, 1148. (c) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.
(2) Schmidpeter, A. Multiple Bonds and Low Coordination Chemistry. In *Phosphorus Chemistry*; Regitz, M., Scherer, O., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; Vol. *D2*, p 149.
(3) Dimroth, K.; Hoffmann, P. *Angew. Chem.* **1964**, *76*, 433; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 384.
(4) (a) Kopp, R. W.; Bond, A. C.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3042. (b) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046.
(5) Niecke, E.; Kroher, R. *Angew. Chem.* **1976**, *88*, 758; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 692.
(6) Michalik, D.; Schulz, A.; Villinger, A.; Weding, A. *Angew. Chem.* **2008**, *120*, 6565−6568; *Angew. Chem., Int. Ed.* **2008**, *47*, 6465.
(7) Villinger, A.; Mayer, P.; Schulz, A. *Chem. Commun.* **2006**, 1236.
(8) Burford, N.; Cameron, T. S.; Clyburne, J. A. C.; Eichele, K.; Robertson, K. N.; Sereda, S.; Wasylishen, R. E.; Whitla, W. A. *Inorg. Chem.* **1996**, *35*, 5460.
(9) Reiss, F.; Villinger, A.; Schulz, A. *Eur. J. Inorg. Chem.* **2012**, *2*, 261.
(10) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
(11) (a) SooHoo, C. K.; Baxter, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 7443. (b) Cowley, A. H.; Kemp, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Whittlesey, B. R. *Inorg. Chem.* **1986**, *25*, 740.
(12) (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. (b) Sanchez, M.; Mazieres, M.-R.; Lamande, L.; Wolf, R. Phosphenium Cations. In *Multiple Bond and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O., Eds.; Georg Thieme: Stuttgart, Germany, 1990; Chapter 0.1, p 129. (c) Gudat, D. *Coord. Chem. Rev.* **1997**, *163*, 71.
(13) (a) Mayer, P.; Schulz, A.; Villinger, A. *Chem. Commun.* **2006**, 1236. (b) Mayer, P.; Schulz, A.; Villinger, A. *J. Organomet. Chem.* **2007**, *692*, 2839. (c) Beweries, T.; Kuzora, R.; Rosenthal, U.; Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 8974. (d) Kuprat, M.; Lehmann, M.; Schulz, A.; Villinger, A. *Inorg. Chem.* **2011**, *50*, 5784.
(14) (a) Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 603. (b) Michalik, D.; Schulz, A.; Villinger, A. *Inorg. Chem.* **2008**, *47*, 11798. (c) Schulz, A.; Villinger, A. *Inorg. Chem.* **2009**, *48*, 7359.
(15) (a) Lehmann, M.; Schulz, A.; Villinger, A. *Eur. J. Inorg. Chem.* **2010**, *35*, 5501. (b) Lehmann, M.; Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 5221. (c) Lehmann, M.; Schulz, A.; Villinger, A. *Eur. J. Inorg. Chem.* **2012**, *5*, 822.
(16) (a) Baumann, W.; Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9530. (b) Michalik, D.; Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 7575. (c) Lehmann, M.; Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 8087.
(17) Burford, N.; Losier, P.; Macdonald, C.; Kyrimis, V.; Bakshi, P. K.; Cameron. *Inorg. Chem.* **1994**, *33*, 1434.
(18) Hering, C.; Schulz, A.; Villinger, A. *Angew. Chem.* **2012**, *124*, 6345; *Angew. Chem., Int. Ed.* **2012**, *51*, 6241.
(19) Holthausen, M. H.; Weigand, J. J. *Z. Anorg. Allg. Chem.* **2012**, *638*, 1103.
(20) Mazieres, M. R.; Sanchez, M.; Bellan, J.; Wolf, R. *Phosphorus, Sulfur Relat. Elem.* **1986**, *26*, 97.
(21) Mazieres, M. P.; Roques, C.; Sanchez, M.; Majoral, J. P.; Wolf, R. *Tetrahedron* **1987**, *43*, 2109.
(22) (a) Miller, F. A.; Wilkins, C. H. *Anal. Chem.* **1952**, *24*, 1253. (b) Sowerby, D. B. *J. Inorg. Nucl. Chem.* **1961**, *22*, 205. (c) Oba, K.; Watari, F.; Aida, K. *Spectrochim. Acta* **1967**, *23A*, 1515.
(23) (a) Schulz, A.; Mayer, P.; Villinger, A. *Inorg. Chem.* **2007**, *46*, 8316. (b) Westenkirchner, A.; Villinger, A.; Karaghiosoff, K.; Wustrack, R.; Michalik, D.; Schulz, A. *Inorg. Chem.* **2011**, *50*, 2691−2702. (c) Hering, C.; Lehmann, M.; Schulz, A.; Villinger, A. *Inorg. Chem.* **2012**, *51*, 8212.
(24) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 12770.
(25) (a) Kerth, J.; Werz, U.; Maas, G. *Tetrahedron* **2000**, *56*, 35. (b) Hubner, T.; Gieren, A. *Z. Kristallogr.* **1986**, *174*, 95. (c) Ishmaeva, E. A.; Vereshchagina, Y. A.; Yarkova, E. G.; Burnaeva, L. M.; Litvinov,

I. A.; Krivolapov, D. B.; Gubaidullin, A. T.; Mironov, V. F.; Fattakhova, G. R. *Zh. Obshch. Khim.* **2002**, *72*, 1276.
(26) Kumaraswamy, S.; Kumar, K. S.; Kumar, N. S.; Swamy, K. C. *Dalton Trans.* **2005**, *10*, 1847.
(27) Weinhold, F.; Landis, C. *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: New York, 2005, and references therein.
(28) (a) Huang, T.; Liu, L.; Zhang, J.; Xu, X.; Huang, W.; Chen, R.; Wang, K.; Yu, X.; Liu, X. *Phosphorus, Sulfur and Silicon* **1998**, *140*, 183−193. (b) Burford, N.; Cameron, T. S.; Clyburne, J. A. C.; Eichele, K.; Robertson, K. N.; Sereda, S.; Wasylishen, R. E.; Whitla, W. A. *Inorg. Chem.* **1996**, *35*, 5460.
(29) (a) Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Abdel-Meguid, S.; Tavanaiepou, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056. (b) Lang, H.; Eberle, U.; Leise, M.; Zsolnai, l. *J. Organomet. Chem.* **1996**, *519*, 137.
(30) (a) Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916. (b) Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *Inorg. Chem.* **1983**, *22*, 3475. (c) Payrastre, C.; Madaule, Y.; Wolf, J. G. *Heteroat. Chem.* **1992**, *3*, 157. (d) Burford, N.; Cameron, T. S.; Ragogna, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 7947. (e) Burford, N.; Ragogna, P. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4307.
(31) (a) Davidson, J.; Weigand, J. J.; Burford, N.; Cameron, T. S.; Decken, A.; Zwanziger, W. *Chem. Commun.* **2007**, 4671. (b) Weigand, J. J.; Feldman, K.-O.; Henne, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 16321.
(32) Burford, N.; Dyker, C. A.; Decken, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2364.
(33) (a) Weiss, P.; Pomrehn, B.; Hampel, F.; Bauer, W. *Angew. Chem., Int. Ed.* **1995**, *34*, 1319. (b) Boomishankar, R.; Ledger, J.; Guilbaud, J.; Campbell, N. L.; Bacsa, J.; Bonar-Law, R.; Khimyak, Y. Z.; Steiner, A. *Chem. Commun.* **2007**, 5152.
(34) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: London, U.K., 1976, and references therein.
(35) W. B. McCormack, W. B.; Lewis, S. N.; Emmons, W. D. *Org. Synth.* **1973**, *5*, 787.
(36) The structures of *syn*- and *anti*-[$(Me_3Si)_2NP(C_6H_8)Cl$][$GaCl_4$] were optimized on the pbe1pbe/aug-cc-pVDZ level of density functional theory. Optimized structures were analyzed for being a minimum on the energy hyper surface and in the last step the magnetic field tensors were calculated with the GIAO-package implemented in GAUSSIAN09 using the NMR-command. For example: $\delta(^{31}P)_{anti,\,calc}$ = 79.15 ppm; $\delta(^{31}P)_{syn,\,calc}$ = 33.58 ppm.
(37) Velian, A.; Cummins, C. C. *J. Am. Chem. Soc.* **2012**, *134*, 13978.
(38) Lammertsma, K. *Top. Curr. Chem.* **2003**, *229*, 95.