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The Reactivity of Silylated Amino(dichloro)phosphanes in the Presence of Silver Salts

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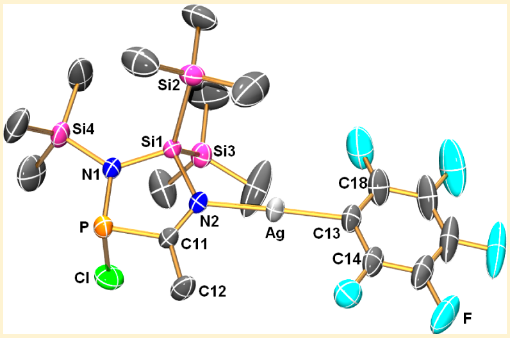
Supporting Information

ABSTRACT: New cyclic and acylic phosphorus−nitrogen compounds have been synthesized in reactions of Hyp−N(SiMe$_3$)PCl$_2$ (hypersilyl = Hyp = (Me$_3$Si)$_3$Si) with silver salts of the perfluorinated anions [CF$_3$CO$_2$]$^-$, [CF$_3$SO$_3$]$^-$, and [C$_6$F$_5$]$^-$. Depending on the choice of the silver salt, not only AgCl but also Me$_3$SiCl elimination could be observed, leading to a transient highly reactive 1,3 dipole molecule. This 1,3 dipole molecule was found to be a key species, which can undergo [3 + 2] cyclization, when a dipolarophile such as acetonitrile is present. Also, dimerization or even *cyclo*-tetramerization are observed. The occurrence of different reaction channels demonstrates that the hypersilyl moiety can act as a highly reactive functional group. All new compounds have been characterized by single-crystal X-ray diffraction studies.



INTRODUCTION

Me$_3$Si−Cl elimination can be observed for compounds containing Me$_3$Si groups in the presence of chloride even at low temperatures due to the high bond energy of the silicon chlorine bond (ΔH_{298} = 95 kcal·mol^{-1}); however, often high activation barriers prevent Me$_3$SiCl elimination.[1] A Lewis acid, such as GaCl$_3$, decreases the activation barrier and is additionally responsible for product stabilization by adduct formation after the elimination reaction.[2,3]

For example, (Me$_3$Si)$_2$NPCl$_2$, which is capable of releasing two equivalents of Me$_3$SiCl, is shown to be a suitable starting material to prepare highly reactive PN intermediates by successive elimination of Me$_3$SiCl. Me$_3$SiCl elimination can either be triggered thermally and/or by addition of a Lewis acid such as GaCl$_3$, thus leading to the formation of a highly labile amino(chloro)phosphenium cation in [(Me$_3$Si)$_2$NPCl][GaCl$_4$] and iminophosphenium salt [Me$_3$Si−N≡P][GaCl$_4$] upon warming to ambient temperatures (Scheme 1, top).[4]

Thermal elimination of Me$_3$SiCl from (Me$_3$Si)$_2$NPCl$_2$ results in the formation of Me$_3$Si−N═P−Cl in the first step, as was previously shown by photoelectron spectroscopy.[5] There is just one report of Me$_3$Si−N═P−Cl being generated in solution when a phosphoranimine was reductively dechlorinated by a tertiary phosphine.[6] This iminophosphane is likely to be highly reactive, prone to polymerize to oligophosphazanes, and could be detected only as transient species by ^{31}P NMR spectroscopy. In contrast to Me$_3$Si−N═P−Cl, Niecke and Flick prepared a stable iminophosphane (Me$_3$Si)$_2$N−P═N(SiMe$_3$) by eliminating Me$_3$SiF from (Me$_3$Si)$_2$NP(F)N(SiMe$_3$)$_2$ at ambient temperature.[7]

The bulky hypersilyl group (hypersilyl = Hyp = (Me$_3$Si)$_3$Si), first introduced by Gilman and Smith,[8] exhibits high steric demand (cone angle: 199°), good solubility in organic solvents, and the property to react as both σ-acceptor and π-donator. Therefore, we were interested in utilizing the Hyp group to stabilize reactive PN intermediates and to study the analogous Hyp−Cl elimination reaction triggered by the action of the Lewis acid GaCl$_3$.[9] However, in contrast to the Me$_3$Si−Cl elimination, Hyp−Cl eliminations are not as straightforward as expected. For example, reaction of Hyp−N(SiMe$_3$)PCl$_2$ (**1**) with GaCl$_3$ does not lead to Hyp−N═P−Cl, but a surprising heterobicycle could be isolated (Scheme 1), while for the analogous (Me$_3$Si)$_2$NPCl$_2$, Me$_3$SiCl elimination was observed upon the addition of GaCl$_3$ at ambient temperatures (→ [Me$_3$Si−N═P][GaCl$_4$] + Me$_3$SiCl).[10] Interestingly, also in the case of the Hyp group, only Me$_3$Si−Cl elimination instead of Hyp−Cl was observed in a rather complex reaction. The present work has focused on the reactions of **1** with Ag$^+$ ions as Lewis acid and perfluorinated anions such as AgTFA (TFA = OCOCF$_3$ = trifluoroacetate), AgOTf (OTf = trifluorosulfonate), AgC$_6$F$_5$, and AgC$_6$F$_5$·CH$_3$CN, providing enormous opportunities for adjusting the Lewis acidity of the Ag$^+$ ions in solution and thus allowing the examination of the product distribution as a function of the utilized anion.

RESULTS AND DISCUSSION

Syntheses. Treatment of **1** with AgTFA over the course of 3 h at −75 °C in toluene resulted in the formation of a new compound with a ^{31}P NMR resonance of 147.7 ppm (cf. **1**: 177.0 ppm).[9] After extraction with *n*-pentane, the doubly TFA-substituted product Hyp−N(SiMe$_3$)P(OCOCF$_3$)$_2$ (**2**, Scheme

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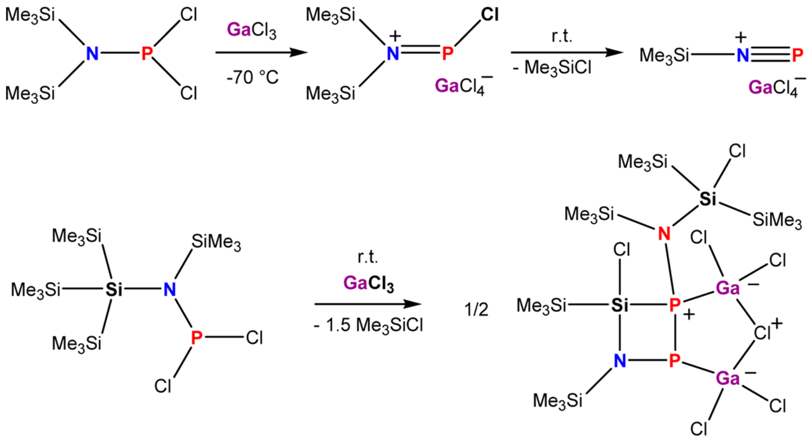
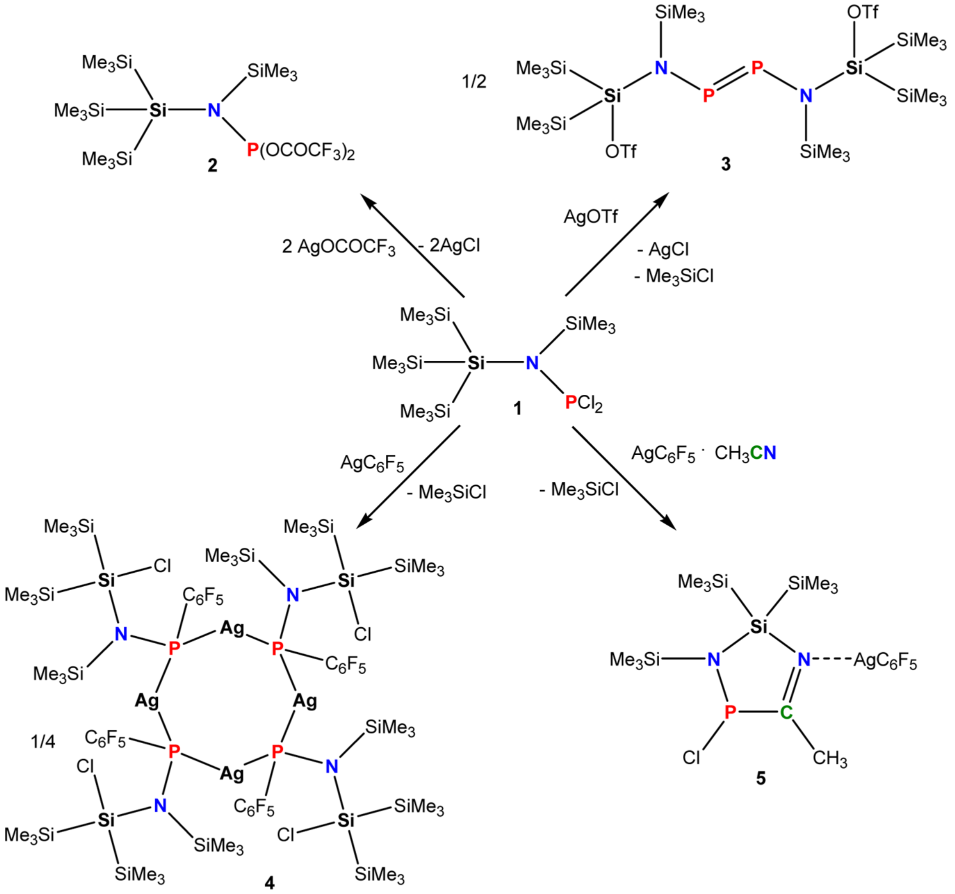
Scheme 1. Different Reaction Channels for $(Me_3Si)_2NPCl_2$ (top) and $Hyp(Me_3Si)NPCl_2$ (bottom)



Scheme 2. Products 2−5 Obtained by Treatment of 1 with Perfluorinated Silver Salts



2) was obtained. Product **2** was crystallized from *n*-pentane at −40 °C (Figure 1). The formation of a covalent P−O bond in reactions of P−Cl containing moieties with AgTFA was already observed due to a high P−O bond energy of $\Delta H_{298} = 97$ kcal·mol^{-1}, e.g. in the reaction of bis(terphenylamino)-chlorophosphane $(TerNH)_2PCl$ with AgTFA (terphenyl = Ter = 2,6-(2,4,6-trimethylphenyl)phenyl).[1,11]

A completely different reaction channel was observed when **1** was treated with AgOTf, which afforded in an unusual reaction the diaminodiphosphene $(TfO)(Me_3Si)_2Si{-}N(SiMe_3)P{=}P{-}N(SiMe_3)Si(SiMe_3)_2(OTf)$ (**3**, Scheme 2) in rather good yields (76%). This compound displays a strongly downfield shifted ^{31}P NMR signal at 505.7 ppm, which lies in the expected range for a P=P bond (cf. $(Me_3Si)N(t\text{-}Bu)P{=}PN(t\text{-}Bu)(SiMe_3)$ at 499.0 ppm, $Mes^*P{=}PN(SiMe_3)_2$ at 501.5 ppm).[12,13] Compound **3** was formed over a period of 1 h at −60 °C. After extraction with *n*-hexane and recrystallization from toluene at −25 °C, pure orange crystals of **3** suitable for single crystal X-ray studies were isolated (Figure 2). Whereas in the reaction of **1** with AgTFA only AgCl was precipitated, in the reaction with AgOTf the diaminodiphosphene **3** was formed upon elimination of AgCl and Me_3SiCl. Astonishingly, at the end of the reaction sequence, one Me_3Si group of the Hyp moiety

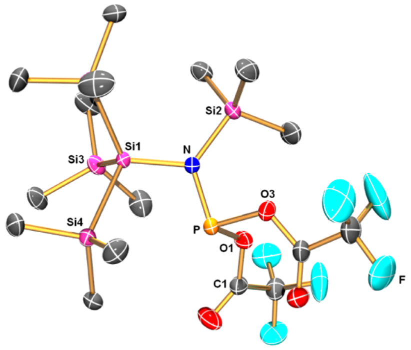


Figure 1. ORTEP drawing of the molecular structure of **2** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: P–N 1.633(1), P–O1 1.712(1), P–O3 1.721(1), Si1–N,1.803(1); N–P–O1 101.62(6), N–P–O3 98.36(6), O1–P–O3 91.90(6), P–N–Si1 124.77(8), P–N–Si2 111.77(7), Si1–N–Si2 123.46(7).

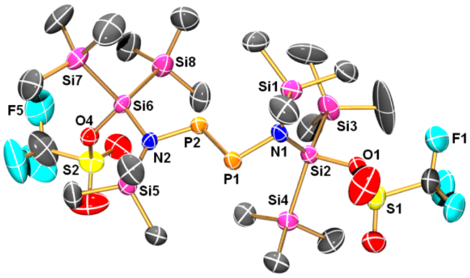


Figure 2. ORTEP drawing of the molecular structure of **3** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms and disorder omitted for clarity). Selected bond lengths [Å] and angles [deg]: P1–N1 1.704(4), P2–N2 1.747(3), P1–P2 2.050(2); N1–P1–P2–N2 178.9(2), P2–P1–N1–Si1 1.5(3), P1–P2–N2–Si6 89.6(2).

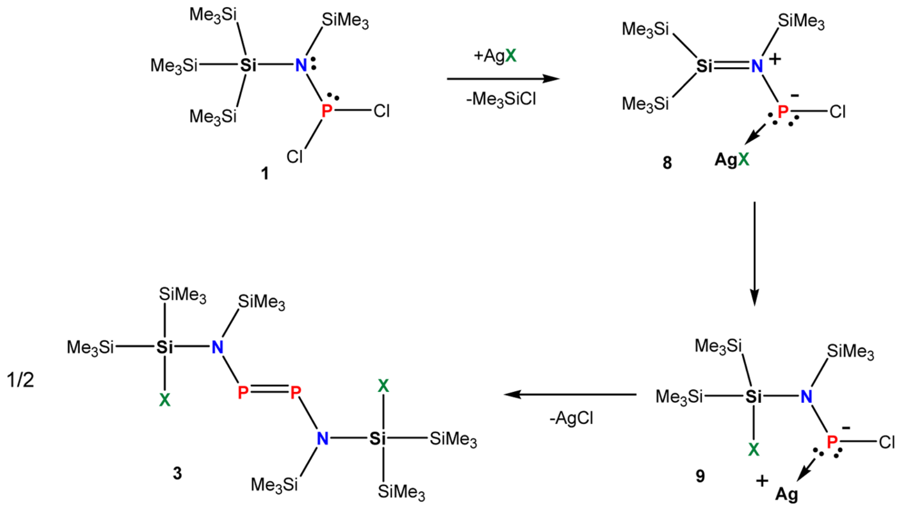
was substituted by an OTf unit (Scheme 3), and in addition a P–P linkage occurred (see also section Reaction Mechanism).

The first diphosphene was reported by Yoshifuji et al., who introduced the bulky 2,4,6-tri-*tert*-butylphenyl group (supermesityl, Mes*) as a substituent in 1981.[14] The reduction of supermesityldichlorophosphine with elemental magnesium resulted in the formation of crystalline Mes*–P=P–Mes*. In general, dehalogenative coupling of halophosphines can be realized by utilization of reducing agents such as pure metals (e.g., magnesium), sodium naphthalenide, organolithium compounds, bis(trimethylsilyl)mercury, divalent germanium and tin compounds, or electron-rich olefins. Also, the elimination of hydrogen halides, salts, or trimethylsilyl halides provides other methods for diphosphene synthesis.[15] We reported the titanocene-mediated coupling of dichlorophosphines to give stable diphosphenes in 2008.[16]

In a next series of experiments, the reactions of **1** with pure AgC_6F_5 and the solvate $AgC_6F_5 \cdot CH_3CN$ were investigated. Due to its sparing solubility, AgC_6F_5 was added at −70 °C as a solid to a solution of **1** in CH_2Cl_2. The reaction mixture was stirred over 3 h and subsequently warmed up to ambient temperature. Extraction with *n*-hexane and concentration of the solution to incipient crystallization resulted in the deposition of colorless crystals of **4** which could be isolated in a good yield of 72%. Single crystal X-ray studies revealed the formation of an eight-membered macrocycle of the type $Ag_4(PR_2)_4$ in tetrameric phosphide-bridged, multinuclear silver complex **4**. In this complex, four silver and four phosphorus atoms are bound alternately; the latter exhibit both C_6F_5 and $N(SiMe_3)Si(SiMe_3)_2Cl$ substituents (Scheme 2, Figure 3). Moreover, one Me_3Si unit of the Hyp moiety was exchanged by a Cl atom. The ^{31}P NMR spectrum shows an upfield shifted signal at −13.2 ppm (cf. $[Ag_4(PPh_2)_4(PMe_3)_4]$ −94 ppm).[17] Complex **4** can be regarded as the formal tetramer of the corresponding mononuclear silver(I) phosphanido complexes (Scheme 4, species **10**, vide infra) $[Ag–PR^1R^2]$ ($R^1 = C_6F_5$, $R^2 = N(SiMe_3)Si(SiMe_3)_2Cl$), which, however, could neither be detected nor isolated. Similar eight-membered rings with an Ag_4P_4 heterocycle have been reported before. Fenske et al.[17] obtained $[Ag_4(Ph_2)_4(PMe_3)_4]$ in the reaction of AgCl and Ph_2PSiMe_3 in the presence of PMe_3. Hey-Hawkins et al. described the reaction of $[AgCl(PCyp_3)]_4$ or $[AgCl(PPh_3)_2]$ with $[Na\{$*cyclo*-$(P_5(t\text{-}Bu)_4)\}]$ yielding $[Ag_4\{$*cyclo*-$(P_4(t\text{-}Bu_3))P\text{-}(t\text{-}Bu)\}_4]$.[18]

To proof the idea of the presence of a highly reactive mononuclear silver(I) phosphanido complex bearing a Si–N double bond (species **8**, Scheme 4), discussed as a key intermediate in the section Reaction Mechanism (see below),

Scheme 3. Proposed Reaction Mechanism for the Generation of Species 3 (X = OTf)



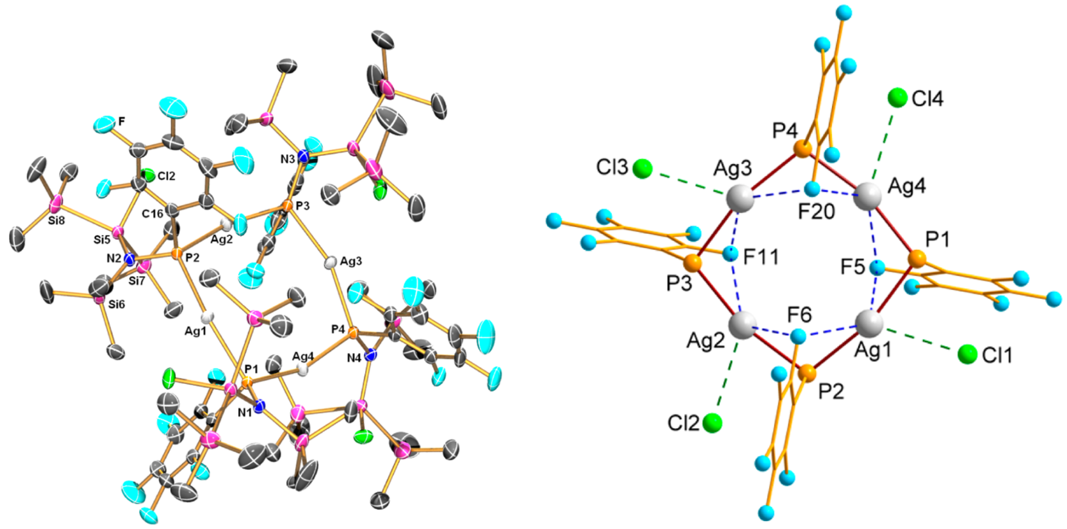
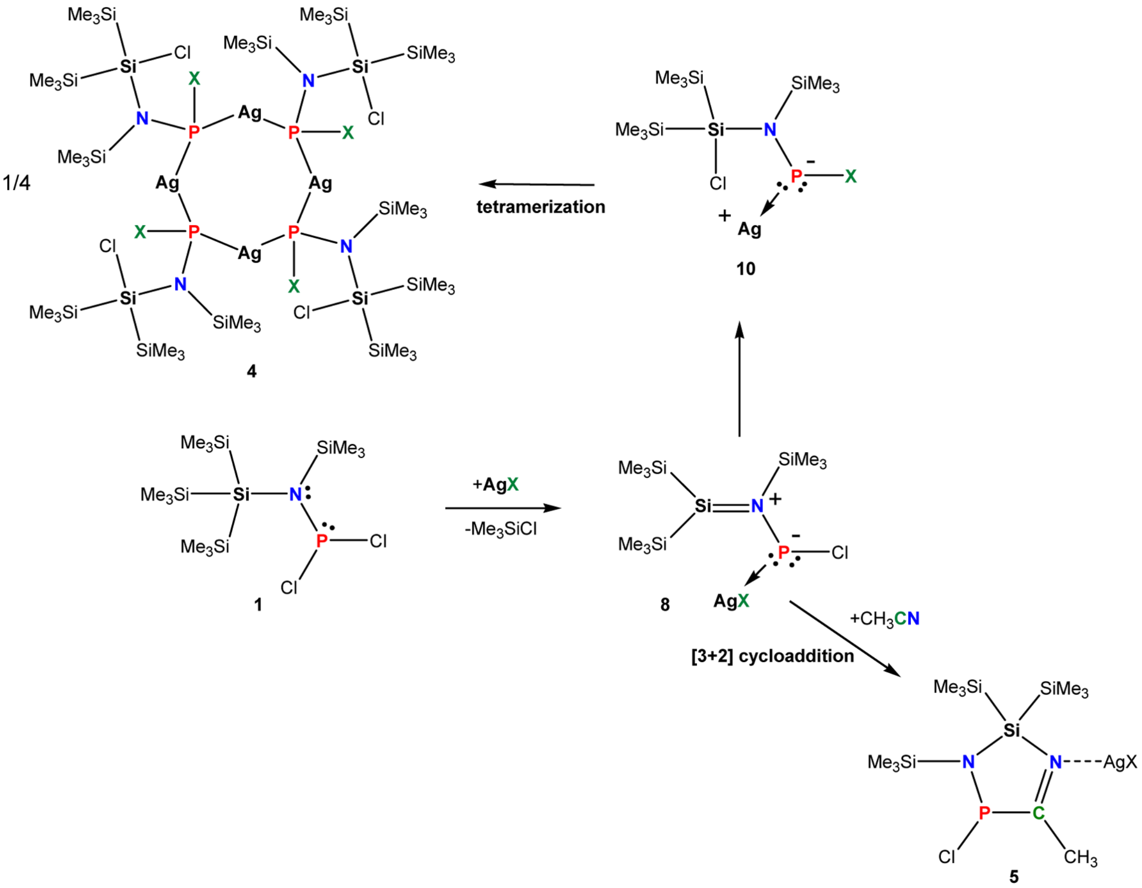


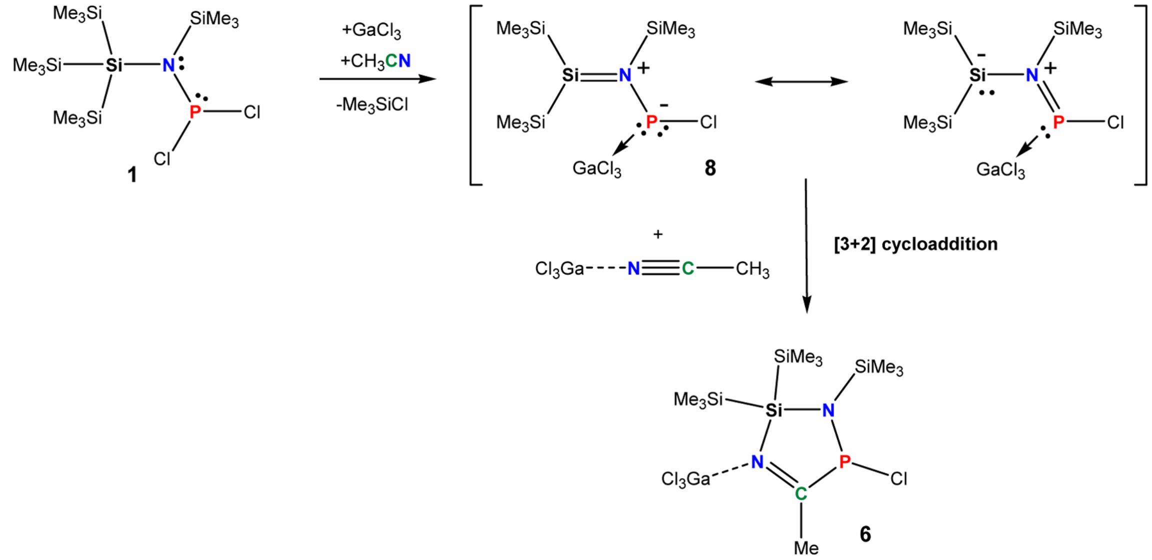
Figure 3. Left: ORTEP drawing of the molecular structure of **4** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ag1–P2 2.4158(7), Ag1–P1 2.4259(7), Ag2–P3 2.4182(6), Ag2–P2 2.4266(6), Ag3–P4 2.4150(7), Ag3–P3 2.4245(7), Ag4–P1 2.4162(6), Ag4–P4 2.4271(6), P2–Ag1–P1 160.38(2), P3–Ag2–P2 160.96(2), P4–Ag3–P3 160.78(2), P1–Ag4–P4 160.33(2), Ag4–P1–Ag1 105.61(2), Ag3–P4–Ag4 105.39(2), Ag1–P2–Ag2 104.99(2), Ag2–P3–Ag3 105.09(2). Right: Ball-and-stick representation of the Ag_4P_4 core and the Ag···X van der Waals interactions (X = Cl, F): Ag1···Cl1 3.1774(7), Ag2···Cl2 3.1764(7), Ag3···Cl3 3.1844(9), Ag4···Cl4, 3.1902(7); Ag1···F5 3.314(2), Ag1···F6 3.199(2), Ag2···F6 3.365(2), Ag2···F11 3.211(2), Ag3···F11 3.351(2), Ag3···F20 3.183(2), Ag4···F20 3.300(2), Ag4···F5 3.176(2).

Scheme 4. Proposed Reaction Mechanism for the Generation of Species 4 and 5 (X = C_6F_5)



we used the solvate $AgC_6F_5{\cdot}CH_3CN$ instead of AgC_6F_5, thus providing a dipolarophile (CH_3CN), which should be capable of trapping reactive 1,3 dipole species **8** in a [3 + 2] cycloaddition. The solvate $AgC_6F_5{\cdot}CH_3CN$ was added as a solid to **1** at −80 °C, which was dissolved in CH_2Cl_2. The reaction mixture was slowly warmed up to ambient temperature over a period of 8 h. The ^{31}P NMR spectrum displayed only one new resonance at 177.0 ppm. Extraction with *n*-hexane and

Scheme 5. Reaction of 1 with CH_3CN and $GaCl_3$ (Including Proposed Intermediates) Leading to the Formation of Heterocyclus 6



removal of solvent resulted indeed in the formation of a new five-membered N−Si−N−C−P heterocyclic compound **5**, stabilized as the AgC_5F_5 adduct. To the best of our knowledge, no such heterocycle has been reported before, and **5** can formally be regarded as the [3 + 2] cycloaddition product of species **8** and MeCN. Compound **5** was crystallized from *n*-hexane at −30 °C. After 30 min at this temperature, the decomposition of **5** occurred, detected by additional signals in ^{31}P NMR spectra. Therefore, **5** could only be characterized by X-ray analysis and low temperature NMR spectroscopy.

The formation of the five-membered heterocycle as the AgC_6F_5 adduct (**5**) prompted us to use $GaCl_3$ as a Lewis acid, which would be another proof for the Lewis acid induced Me_3SiCl elimination yielding a 1,3 dipole species. Furthermore, **5** was only stable at low temperatures, which we attributed to the fact that at higher temperatures, AgC_6F_5 underwent further reactions triggered by the elimination of AgCl. Thus, avoiding AgC_5F_6 should lead to a more stable heterocycle if stabilized by $GaCl_3$. Therefore, **1** was treated with CH_3CN and $GaCl_3$ in a molar ratio of 1:1:1 in CH_2Cl_2 at −40 °C (Scheme 5). The ^{31}P NMR spectrum of the light orange solution displayed immediately one resonance at 147.4 ppm (cf. **5**: 177.0 ppm). Removal of the solvent led to a red solid, which was unequivocally shown to be the five-membered heterocycle stabilized as the $GaCl_3$ adduct (**6**) by single crystal X-ray crystallography (Figure 5) after recrystallization from CH_2Cl_2 at ambient temperature. It should be noted that, besides **6**, small amounts of the dimeric condensation product **7** could be isolated as side product (Scheme 6). The presence of **7** can be best explained by HCl elimination between the P−Cl bond of one molecule and the acidic $H{-}C_{\mathrm{methyl,acetonitrile}}$ bond of another molecule as depicted in Scheme 6. In contrast to **5**, the synthesis of **6** is simple and almost quantitative (yield: 95%).

Species **1**, **2**, **4**, and **6** are air- and moisture-sensitive; however, they are stable under an argon atmosphere over a long period as solids, when stored in sealed tubes and kept cool at 5 °C, as well as in common organic solvents (benzene, CH_2Cl_2, diethyl ether).

Reaction Mechanisms. The different reaction products obtained in the reaction of **1** with several AgX (X = $OCOCF_3$, OTf, C_6F_5, and $C_6F_5{\cdot}CH_3CN$) salts provoked a few questions regarding the reaction mechanisms. While the reaction of **1** with AgTFA is a simple anion exchange reaction (Scheme 2), all other silver salts display rather unusual reaction pathways. So far, we are not able to isolate any intermediates as displayed in Schemes 3−5; however, in the light of similar products, which could be isolated and fully characterized for X = OTf, C_6F_5, and $C_6F_5{\cdot}CH_3CN$, we believe that highly reactive 1,3 dipole species **8** seems to be the key intermediate in all of these reactions. The formation of intermediate **8** is triggered by the action of the Lewis acid, either Ag^+ or $GaCl_3$, which induces Me_3SiCl elimination. Interestingly, the Me_3Si group of the Hyp moiety and not that attached to the N atom is involved in this elimination, which therefore can be referred to as a 1.3 elimination, thus leading to the reactive phosphanide species **8** bearing a Si═N double bond. Presumably, **8** is stabilized in solution by adduct formation with the Lewis acids AgX or $GaCl_3$.

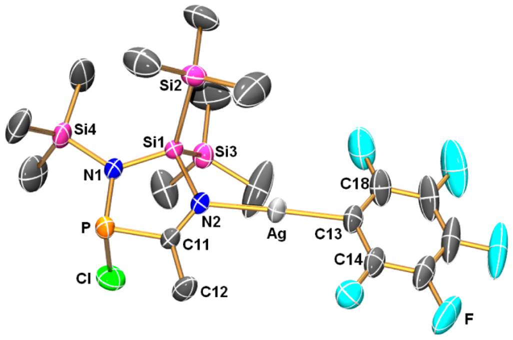


Figure 4. ORTEP drawing of the molecular structure of **5** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms and disorder of the C_6F_5 group omitted for clarity). Selected bond lengths [Å] and angles [deg]: Si1−N1 1.769(3), Si1−N2 1.797(2), P1−N1 1.672(3), P1−C11 1.864(3), Ag1−N2 2.127(2), N2−C11 1.270(4), N1−P1−C11 95.18(1), N1−Si1−N2 96.27(1), N2−C11−P1 117.4(2), P1−N1−Si1 115.12(1), C11−N2−Si1 115.58(2), N1−Si1−N2−C11 3.9(2), Si1−N2−C11−P1−0.3(3), N1−P1−C11−N2−3.6(3), C11−P1−N1−Si1 6.1(2).

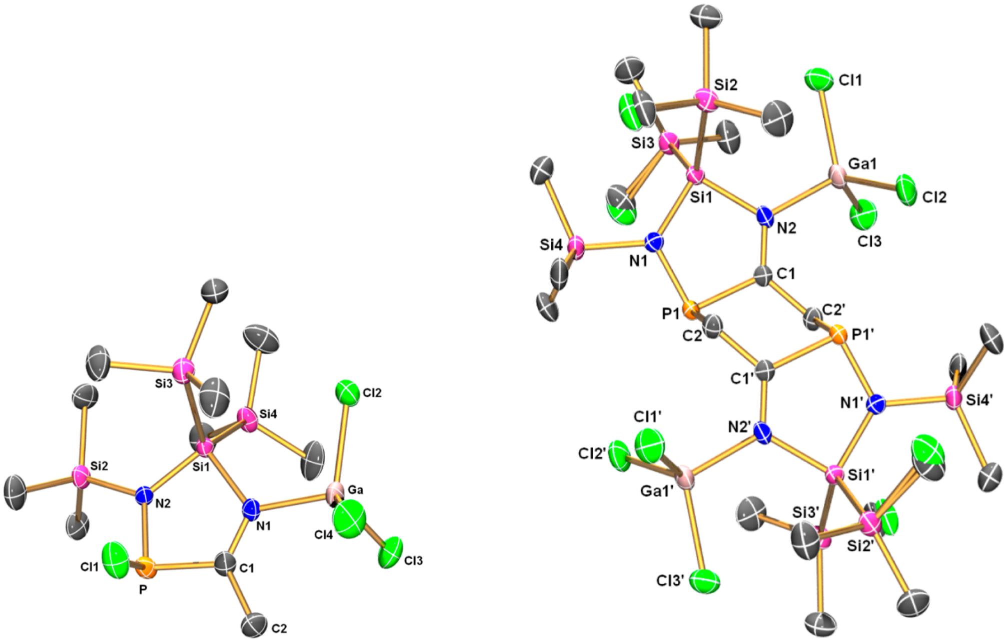
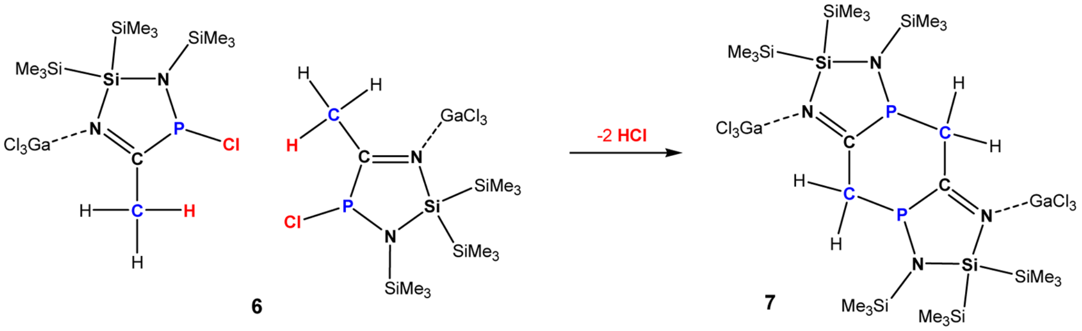


Figure 5. ORTEP drawings of the molecular structures of **6** (left) and the dimer **7** (right) in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). In Si bounded Me_3Si moieties of **7**, the positions of Me groups are partially occupied by Cl atoms (0.83 Cl atoms per molecule). Selected bond lengths [Å] and angles [deg], **6**: P1−N2 1.664(4), P1−C1 1.862(5), Ga1−N1 1.971(4), Si1−N2 1.776(4), Si1−N1 1.843(4), N1−C1 1.284(6), N2−P1−C1 95.2(2), N2−Si1−N1 94.9(2), C1−N1−Si1 114.8(4), P1−N2−Si1 116.3(2), N1−C1−P1 117.7(4), N2−Si1−N1−C1−4.1(4), C1−P1−N2−Si1−10.1(3), N1−Si1−N2−P1 9.5(3), Si1−N1−C1−P1−1.9(5), N2−P1−C1−N1 7.4(5). **7**: N1−P1 1.683(3), N1−Si1 1.773(3), N2−C1 1.295(4), N2−Si1 1.842(3), N2−Ga1 1.984(3), P1−C1 1.844(3), P1−C2 1.918(3), C1−C2′ 1.479(4), P1−N1−Si1 115.8(2), C1−N2−Si1 114.9(2), N1−P1−C1 96.0(1), N1−Si1−N2 95.4(1), N2−C1−P1 117.7(2), Si1−N1−P1−C1 3.2(2), P1−N1−Si1−N2−2.2(2), C1−N2−Si1−N1−0.5(2), Si1−N2−C1−P1 2.7(3), N1−P1−C1−N2−3.7(2).

Scheme 6. Condensation Reaction of 6 Leading to Tricyclus 7



In the case of the AgOTf reaction, an intramolecular transfer of the OTf group to the Si atom, which is involved in the SiN double bond, occurs, while AgCl precipitates, forming phosphene **9**. Finally, **9** dimerizes, affording diphosphene **3**. Obviously, in this case, no stable monomeric or tetrameric silver(I) phosphanido complex is formed.

When AgC_6F_5 is utilized, the Cl atom is transferred to the Si atom, while the C_6F_5 group is shifted from the Ag center to the P atom, yielding silver phosphanide species **10** (Scheme 4), which is the formal monomer of **4**. Now, the silver(I) phosphanido complex **4** is formed in a tetramerization step. Indirect experimental evidence for the transient presence of species **8** was obtained by the reaction of $AgC_6F_5{\cdot}CH_3CN$ with **1**, since now acetonitrile can act as a dipolarophile in a [3 + 2] cycloaddition reaction[19] forming five-membered heterocycle **5** stabilized as the AgC_6F_5 adduct (Scheme 4). To generalize the idea of Lewis acid triggered Me_3SiCl elimination, we also used $GaCl_3$ in the reaction with **1** and CH_3CN, which should also form species **8**. Again, heterocycle **5** was observed, but this time stabilized as the $GaCl_3$ adduct. It should be noted that without the use of a Lewis acid no [3 + 2] cycloaddition can be observed. Therefore, this reaction can be referred to as Lewis acid assisted [3 + 2] cycloaddition.

The concept of a $GaCl_3$ assisted [3 + 2] cycloaddition, in which the added Lewis acid $GaCl_3$ decreases the activation barrier to Me_3SiCl elimination and stabilizes the [3 + 2] heterocycle by adduct formation at the end of the reaction sequence, was shown in a series of other reactions, involving even other heteroelements such as arsenic.[20−22] For instance, the reaction of the kinetically stabilized iminophosphane Mes*−N=P−Cl (Mes* = 2,4,6-tri*tert*-butylphenyl), a good dipolarophile, with $(Me_3Si)_2N{-}N(SiMe_3){-}PCl_2$, a “disguised” 1,3-dipole, yielded a triazadiphosphole (RN_3P_2, R = Mes*).[3,23] The first tetrazaphosphole,[24] RN_4P (R = Mes*), was also obtained by a $GaCl_3$-assisted [3 + 2] cycloaddition of Mes*−N=P−Cl with $Me_3Si{-}N_3$. The same reaction with the heavier

Table 1. Crystallographic Details of 2−4

	2	3	4
chem. formula	$C_{16}H_{36}F_6NO_4PSi_5$	$C_{20}H_{54}F_6N_2O_6P_2S_2Si_8$	$C_{60}H_{108}Ag_4Cl_4F_{20}N_4P_4Si_{16}$
fw [g mol^{-1}]	591.88	883.43	2412.10
color	colorless	orange	colorless
cryst. syst.	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/n$	$P\bar{1}$
a [Å]	16.9769(5)	9.7411(4)	14.7631(2)
b [Å]	9.3993(3)	17.2317(9)	14.7767(2)
c [Å]	37.984(1)	27.196(1)	24.6511(4)
α [deg]	90.00	90.00	73.796(1)
β [deg]	93.495(2)	91.248(2)	88.587(1)
γ [deg]	90.00	90.00	89.952(1)
V [Å^3]	6049.9(3)	4564.0(4)	5162.3(1)
Z	8	4	2
ρ_{calcd} [g cm^{-3}]	1.300	1.286	1.552
μ [mm^{-1}]	0.347	0.453	1.17
$\lambda_{MoK\alpha}$ [Å]	0.710 73	0.710 73	0.710 73
T [K]	173(2)	173(2)	173(2)
measured reflns	69 902	40 065	173 195
independent reflns	9209	10 412	37 217
reflns with $I > 2\sigma(I)$	7148	7287	22 342
R_{int}	0.0410	0.0475	0.051
$F(000)$	2480	1856	2432
R_1 ($R[F^2 > 2\sigma(F^2)]$)	0.0412	0.0612	0.046
wR_2 (F^2)	0.0984	0.1931	0.085
GOF	1.040	1.077	1.017
params	310	580	1045
CCDC #	980 648	980 649	980 650

Table 2. Crystallographic Details of 5−7

	5	6	7
chem. formula	$C_{17}H_{30}AgClF_5N_2PSi_4$	$C_{11}H_{30}Cl_4GaN_2PSi_4\cdot CH_2Cl_2$	$C_{21.17}H_{55.52}Cl_{6.83}Ga_2N_4P_2Si_8\cdot 4(CH_2Cl_2)$
fw [g mol^{-1}]	644.08	630.15	1374.18
color	colorless	yellow	yellow
cryst syst	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
a [Å]	8.8451(5)	28.748(1)	9.8121(7)
b [Å]	12.1525(6)	13.1009(4) Å	11.6925(8)
c [Å]	13.8638(8)	15.2495(6) Å	15.072(1)
α [deg]	90.811(3)	90	75.135(5)
β [deg]	104.190(3)	90	74.483(4)
γ [deg]	99.590(3)	90	69.088(4)
V [Å^3]	1422.2(1)	5743.3(4)	1531.3(2)
Z	2	8	2
ρ_{calcd} [g cm^{-3}]	1.504	1.458	1.490
μ [mm^{-1}]	1.07	1.74	1.76
$\lambda_{MoK\alpha}$ [Å]	0.710 73	0.710 73	0.710 73
T [K]	173(2)	173(2)	173(2)
measured reflns	44 724	52 470	43 123
independent reflns	10 064	10 837	8464
reflns with $I > 2\sigma(I)$	6531	7500	5284
R_{int}	0.043	0.096	0.069
$F(000)$	652	2576	699
R_1 ($R[F^2 > 2\sigma(F^2)]$)	0.050	0.050	0.056
wR_2 (F^2)	0.134	0.089	0.134
GOF	1.016	1.011	1.004
params	348	515	216
CCDC #	980 652	980 653	980 651

arsenic analogue led to the first tetrazarsole.[21b] All studied $GaCl_3$ assisted [3 + 2] cycloadditions are fast, high-yielding (>90%), and clean reactions. These cyclizations can be carried out even at low temperatures or ambient temperatures (−30 to

25 °C), whereas classical triazole-forming reactions require elevated temperatures. The concept of $GaCl_3$ assisted [3 + 2] cycloaddition reactions can now be extended to Lewis acids such as AgX salts (X = OTf, C_6F_5).

X-Ray Structure Analysis. The solid-state structures of compounds **2**, **3**, **4**, **5**, **6**, and **7** are displayed in Figures 1−5, along with selected bond lengths and angles. Crystallographic details for all compounds are given in Tables 1 and 2. X-ray quality crystals of all species considered were selected in a Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer or on a Bruker-Nonius Apex X8 CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073). The structures were solved by direct methods (*SHELXS-97*)[25] and refined by full-matrix least-squares procedures (*SHELXL-97*).[26] Semiempirical absorption corrections were applied (SADABS).[27] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the refinement at calculated positions using a riding model.

Compound **2** (Figure 1) crystallizes in the monoclinic space group *C*2/*c* with eight formula units per cell. The observed molecular structure exhibits the expected trigonal pyramidal environment around the P atom and trigonal planar around the N atom along with a short P−N distance (1.633(1) Å; cf. **1**: 1.6451(9) Å;[9] d_{cov}(N−P) = 1.82 and d_{cov}(P═N) = 1.62 Å),[28] indicating partial double bond character for this highly polarized P−N bond due to hyperconjugation.[29,30]

Diphosphene **3** (Figure 2) crystallizes in the monoclinic space group $P2_1/n$ with four formula units per cell. The position of the molecule is disordered with the exception of the Me_3Si moieties on the Si atoms Si1, Si3, Si4, Si5, and Si7. The P1−P2 bond length amounts to 2.050(2) Å, which lies in the typical range of a typical P═P bond (Σr_{cov}(P═P) = 2.02 Å),[28] such as in $(Me_3Si)_2N(Me_3Si)NP{=}PN(SiMe_3)N(SiMe_3)_2$ (2.038(1) Å) and $(Me_2(t\text{-Bu})Si)_2N{-}P{=}P{-}N(Si(t\text{-Bu})Me_2)_2$ (2.034 Å).[12,16] The P1−N1 and P2−N2 bond lengths are shorter (1.704(4) and 1.747(3) Å, cf. 1.700(2) Å in $(Me_3Si)_2N(Me_3Si)N{-}P{=}P{-}N(SiMe_3)N(SiMe_3)_2$) than a typical P−N single bond (Σr_{cov}(P−N) = 1.80 Å, Σr_{cov}(P═N) = 1.61 Å) but a little elongated compared to that in **1** with P−N 1.633(1) Å, still indicating partial double bond character. The *trans* bent N1−P1−P2−N2 skeleton is almost planar with a dihedral angle of −178.9(2)°. While Si1 and Si2 lie in this plane, Si5 and Si6 are orthogonally arranged with respect to this plane (Si6−N2−P2−P1−89.6(2)°).

The eight-membered heterocycle **4** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The most prominent structural feature of **4** is the eight-membered heterocycle with alternating tricoordinated P and dicoordinated Ag atoms and shows along the Ag1−Ag3 axis a slightly folded arrangement (Ag1−Ag2−Ag3−Ag4 15.724(6)°), similar to the situation found for the complex $[Ag_4\{cyclo\text{-}P_4t\text{-}Bu_3)Pt\text{-}Bu\}_4]$.[18] All eight Ag−P bond lengths are almost equally long and are in the range between 2.415(7) and 2.427(6) Å, indicating a strong dative bond (Σr_{cov}(Ag−P) = 2.39 Å).[28] As expected for dicoordinated Ag units, the P−Ag−P angles deviate slightly from linearity and lie between 160.33(2) and 160.96(2)°, while the Ag−P−Ag angles only amount to 104.99(2)−105.61(2)°. In addition, as depicted in Figure 3 (right), intramolecular Ag···X interactions (X = F, Cl) must be considered (three per Ag center) and might be the reason for the absence of any coordinating solvent molecule around the Ag centers. The Ag···Cl distances between 3.1764(7) and 3.1902(7) Å are significantly shorter than the sum of van der Waals radii of both atoms (Σr_{vdW}(Ag···Cl) = 3.47 Å)[31] but significantly longer than the sum of the covalent radii (Σr_{cov}(Ag−Cl) = 2.27 Å).[28] Two short Ag···F distances ranging between 3.176(2) and 3.365(2) are found per Ag center, which also might be indicative for weak van der Waals interactions (Σr_{vdW}(Ag···F) = 3.19 Å).[31] Interestingly, AgCl does not precipitate, indicating that the Ag^+ ions are strongly fixed within the formal [2 + 3] coordination mode. The shortest Ag···Ag distance amounts to 3.8416(3) Å, which is considerably longer than the sum of van der Waals radii of two silver atoms, 3.42 Å.[31]

Again all four terminal P−N bond lengths (1.720(2)−1.724(2) Å) are rather short, and the N atoms sit in an almost trigonal planar environment.

Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The C_6F_5 and methyl groups of one Me_3Si moiety are disordered. The five-membered nonaromatic heterocycle is almost planar with torsion angles between 0.3 and 6.1°. Both N atoms adopt a distorted trigonal planar coordination geometry (Σ(N) = 360°) in contrast to the P atom (Σ(P) = 201.9°). The P−Cl bond is nearly perpendicular to the ring system (C11−P1−Cl1 90.95(1)°; N1−P1−Cl1 105.73(1)°), similar to the situation found for *P*-chlorodiazaphospholenes synthesized by Gudat et al.[32] Both Si−N distances (1.797(2) and 1.769(3) Å) and P−C (1.864(3) Å) are in the range of single bonds (cf. Σr_{cov}: Si−N 1.87, P−C 1.86 Å),[28] while the C−N bond length of 1.270(4) Å represents a typical CN double bond. Again, due to strong hyperconjugative effects the P−N bond length (1.672(3) Å) is rather short (e.g., compared to the P−C bond), displaying some double bond character. The N−Ag−C unit is almost linear (N−Ag−C 177.48°), connecting the five-membered diazasilaphosphole with the C_6F_5 ring, which is slightly tilted to the five-membered ring (Si1−N2−C13−C18−11.47°, C11−N2−C13−C14−7.52°). The bond between the Lewis acid AgC_6F_5 and the N atom of the heterocycle can be considered as a donor−acceptor bond with a Ag−N bond length of 2.127(2) Å (cf. Σr_{cov}(Ag−N) = 1.99 Å, AgNCO: Ag−N 2.115 Å).[28,33] Moreover, the Ag−N distance is considerably shorter compared to that in the starting material $AgC_6F_5{\cdot}CH_3CN$ (Ag−N 2.392 Å), displaying a stronger donor−acceptor interaction in **5**.[34]

Compound **6**·CH_2Cl_2 crystallizes in the orthorhombic space group $Pna2_1$ with eight formula units per cell. Two independent heterocycles **6** and two CH_2Cl_2 solvent molecules, which are both disordered, are found in the asymmetric unit. The dimer **7** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The asymmetric unit consists of a half molecule, which lies on a two-fold crystallographic axis with the whole molecule generated by the symmetry operation −*x* + 1, −*y* + 1, −*z* as depicted in Figure 5 (right). In Si bound Me_3Si moieties of **7**, the positions of Me groups are partially occupied by Cl atoms (0.83 Cl atoms per molecule). This partial Cl/C occupation is in line with the arguments given in the section Reaction Mechanism in accord with the proposed transient presence of species **8** in Scheme 5.

Since all metrical parameters of **6** are very similar to those found for **5**, we will focus on the structure and bond discussion of **7** and the differences between **6** and **7**. In **7**, two heterocycles are bridged by two CH_2 moieties, and the C2−P1−C1−C2′−P1′−C1′ six-membered ring exists in the chair conformation. Both **6** and **7** are typical charge transfer complexes, and the bond between the $GaCl_3$ and the N atom of the heterocycle can be described as a donor−acceptor bond (see structure elucidation of **5**) with Ga−N bonds of 1.971(4) in **6** and 1.983(3) Å in **7**, respectively (Σr_{cov}(Ga−N) = 1.96 Å).[28] These Ga−N distances are in accord with those in the triazadiphospholes $(\mathrm{Me_3Si})_2\mathrm{N{-}N_3P_2{\cdot}GaCl_3}$ (1.978(3) Å)[22] and Mes*−$\mathrm{N_3P_2{\cdot}GaCl_3}$ (1.9830(5) Å, Mes* = 2,4,6-tri-*tert*-butylphenyl)[3] but shorter than those found for the adducts $\mathrm{Cl_3Ga{\cdot}NMe_2SiMe_2NMe_2}$ (2.003(5) Å) and $\mathrm{MeCl_2Ga{\cdot}H_2N{-}NH}$(*t*-Bu) (2.023(7) Å), respectively.[35,36] According to NBO analysis (NBO = natural bond orbital),[37] the charge transfer amounts to 0.16 in **6** and 0.19*e* in **7**, in agreement with values found for triazadiphosphole or tetrazaphosphole $\mathrm{GaCl_3}$ adducts.[3,22,24] Emanated from NBO calculations all bonds in the heterocycles of **6** and **7** are highly polarized. The N atoms exhibit a high negative partial charge (**6**: $Q_{\mathrm{N1}} = -1.00$, $Q_{\mathrm{N2}} = -1.57$; **7**: $Q_{\mathrm{N1}} = -1.60$, $Q_{\mathrm{N2}} = -1.01e$). The lower values of the $\mathrm{GaCl_3}$ coordinated N atoms can be attributed to the influence of the electrophilic Lewis acid.

■ CONCLUSIONS

The reactions of Hyp−N(SiMe$_3$)PCl$_2$ with AgTFA, AgOTf, $\mathrm{AgC_6F_5}$, and $\mathrm{AgC_6F_5{\cdot}CH_3CN}$ were shown to result in the formation of diverse products. While the reaction of **1** with AgTFA is a simple anion exchange, all other silver salts display rather unusual reaction pathways, which can be explained by the presence of a highly reactive intermediate (**8**) exhibiting a dicoordinated P atom and a Si−N double bond. The formation of **8** is triggered by the action of the Lewis acid, either $\mathrm{Ag^+}$ or $\mathrm{GaCl_3}$, which induces $\mathrm{Me_3SiCl}$ elimination. Astonishingly, the $\mathrm{Me_3Si}$ group of the Hyp group and not that attached to the N atom is involved in this elimination. Starting from the intermediate formation of 1,3 dipole molecule **8**, (i) the reaction with AgOTf finally gives a new diphosphene, and (ii) the reaction with $\mathrm{AgC_6F_5}$ yields an eight-member heterocycle; while the reaction with $\mathrm{AgC_6F_5{\cdot}CH_3CN}$ forms in a formal [3 + 2] cycloaddition, the new five-membered heterocycle **5** stabilized as the $\mathrm{AgC_6F_5}$ adduct (Scheme 4). The same heterocycle was obtained with $\mathrm{GaCl_3}$, thus extending the concept of Lewis acid assisted [3 + 2] cycloadditions.

■ EXPERIMENTAL DETAILS

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure,[38] dried over $\mathrm{P_4O_{10}}$, and freshly distilled prior to use. Toluene was dried over Na/benzophenone and freshly distilled prior to use. Acetonitrile was dried over $\mathrm{P_4O_{10}}$ and freshly distilled prior to use. *N*-hexane and *n*-pentane were dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. Silvertrifluoroacetate,[39] silvertriflate,[39] *N*-[tris(trimethylsilyl)silyl]-*N*-trimethylsilyl-amino-dichlorophosphane $(\mathrm{Me_3Si})_3\mathrm{Si{-}N(SiMe_3)PCl_2}$ (**1**),[9] and pentafluorophenylsilver[34] have been reported previously and were prepared according to a literature procedure. Gallium trichloride (99.999%, Sigma-Aldrich) was used as received.

NMR. $^{31}\mathrm{P}\{^1\mathrm{H}\}$, $^{13}\mathrm{C}\{^1\mathrm{H}\}$, ^{29}Si-INEPT, and $^{19}\mathrm{F}\{^1\mathrm{H}\}$ and ^{1}H NMR spectra were recorded on Bruker AVANCE 300 and AVANCE 500 spectrometers, respectively. The ^{1}H and ^{13}C chemical shifts were referenced to solvent signals ($\mathrm{C_6D_6}$: δ ^1H = 7.15, δ ^{13}C = 128.0; $\mathrm{CD_2Cl_2}$: δ ^1H = 5.31, δ ^{13}C = 54.0). The ^{1}H and ^{13}C NMR signals were assigned by DEPT and two-dimensional correlation spectra (HSQC and HMBC) using standard pulse sequences (standard Bruker software). The ^{19}F, ^{29}Si, and ^{31}P chemical shifts are referred to $\mathrm{CFCl_3}$, TMS, and $\mathrm{H_3PO_4}$ (85%), respectively. $\mathrm{CD_2Cl_2}$ was dried over $\mathrm{P_4O_{10}}$.

IR. A Nicolet 380 FT-IR with a Smart Orbit ATR device was used.

Raman. A Bruker VERTEX 70 FT-IR with a RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm), was used.

CHN Analyses. An Analysator Flash EA 1112 from Thermo Quest or a C/H/N/S-Mikroanalysator TruSpec-932 from Leco was used.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). The heating rate was 20 °C/min (clearing points are reported).

DSC. A DSC 823e from Mettler-Toledo (Heating-rate 5 °C/min) was used.

MS. A Finnigan MAT 95-XP from Thermo Electron was used.

Synthesis of $(\mathrm{Me_3Si})_3\mathrm{SiN(SiMe_3)P(OCOCF_3)_2}$ (2). To a solution of $(\mathrm{Me_3Si})_3\mathrm{SiN(SiMe_3)PCl_2}$ (**1**; 0.437 g, 1.00 mmol) in toluene (5 mL) at −70 °C was added a solution of AgTFA (0.453 g, 2.05 mmol) dropwise under stirring over a period of 15 min. The colorless suspension was warmed to room temperature and stirred for 1 h. The solvent was removed *in vacuo*, resulting in a yellowish residue which was extracted with *n*-pentane (10 mL). After filtration, the colorless solution was concentrated to incipient crystallization *in vacuo* and stored at −40 °C, resulting in the deposition of colorless crystals. Removal of the supernatant by syringe and drying *in vacuo* yields 0.450 g (0.760 mmol, 76%) of **2** as colorless crystals. Mp: 101 °C. Anal. calcd % (found) for $\mathrm{C_{16}H_{36}F_6NO_4PSi_5}$ (591.85): C, 32.47 (32.00); H, 6.13 (6.30); N, 2.37 (2.41). ^{1}H NMR (25 °C, $\mathrm{CD_2Cl_2}$, 300.13 MHz): δ 0.29 (d, 27 H, $^5J(^{31}\mathrm{P}{-}^1H$ = 1.3 Hz, $^1J(^{13}\mathrm{C}{-}^1H$ = 121 Hz, $\mathrm{Si(Si(C}H_3)_3)_3$), 0.35 (s, 9 H, $^2J(^{29}\mathrm{Si}{-}^1\mathrm{H})$ = 6.6 Hz, $\mathrm{N(Si(C}H_3)_3)$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 75.47 MHz): δ 2.24 (d, $^4J(^{31}\mathrm{P}{-}^{13}\mathrm{C})$ = 5.3 Hz, $^1J(^{29}\mathrm{Si}{-}^{13}\mathrm{C})$ = 46 Hz, $\mathrm{Si(Si(CH_3)_3)_3}$), 3.79 (s, $^1J(^{29}\mathrm{Si}{-}^{13}\mathrm{C})$ = 57 Hz, $\mathrm{N(Si(CH_3)_3)}$), 114.7 (dq, $^3J(^{31}\mathrm{P}{-}^{13}\mathrm{C})$ = 4.3 Hz, $^1J(^{19}\mathrm{F}{-}^{13}\mathrm{C})$ = 286.5 Hz, $\mathrm{CF_3}$), 155.4 (dq, $^2J(^{31}\mathrm{P}{-}^{13}\mathrm{C})$ = 6.8 Hz, $^2J(^{19}\mathrm{F}{-}^{13}\mathrm{C})$ = 43.7 Hz, OCO). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 282.4 MHz): δ −76.0 (s). ^{29}Si NMR (25 °C, $\mathrm{CD_2Cl_2}$, 59.63 MHz): δ −26.0 (m, $^2J(^{31}\mathrm{P}{-}^{29}\mathrm{Si})$ = 44 Hz, *Si*(SiMe$_3$)$_3$)), −12.6 (m, Si(*Si*Me$_3$), 14.8 (m, $^2J(^{31}\mathrm{P}{-}^{29}\mathrm{Si})$ = 1.9 Hz, N(*Si*Me$_3$)). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 121.49 MHz): δ 147.7 (s). IR (ATR, 32 scans): 2950 (m), 2894 (m), 1787 (s), 1774 (s), 1441 (w), 1398 (w), 1360 (m), 1260 (m), 1245 (m), 1219 (s), 1169 (s), 1149 (s), 1108 (s), 981 (s), 824 (s), 791 (m), 774 (m), 748 (m), 727 (s), 682 (s), 656 (m), 622 (s), 566 (m). Raman (200 mW, 1049 scans, 25 °C, cm^{-1}): 2994 (2), 2952 (5), 2896 (10), 1789 (1), 1776 (1), 1418 (1), 1265 (1), 1241 (1), 1108 (1), 1050 (1), 985 (1), 863 (1), 751 (1), 686 (2), 645 (1), 627 (3), 509 (2), 485 (1), 464 (1), 450 (1), 433 (1), 402 (1), 364 (1), 333 (1), 301 (1), 176 (2), 119 (1). MS (CI$^+$, isobutane): 478 $[\mathrm{M} - \mathrm{CF_3CO_2}]^+$, 518 $[\mathrm{M} - \mathrm{SiMe_3}]^+$, 592 $[\mathrm{M} - \mathrm{H}]^+$.

Synthesis of $(\mathrm{TfO})(\mathrm{SiMe_3})_2\mathrm{SiN(SiMe_3)P{=}PN(SiMe_3)Si(SiMe_3)_2(OTf)}$ (3). To a solution of $(\mathrm{Me_3Si})_3\mathrm{SiN(SiMe_3)PCl_2}$ (**1**; 0.873 g, 2.00 mmol) in toluene (10 mL) at −60 °C was added a solution of AgOTf (1.028 g, 4.00 mmol) in toluene (10 mL) dropwise over a period of 25 min. The brown solution was warmed to room temperature and stirred for 1 h. The solvent was removed *in vacuo*, and the resulting brown residue was extracted with *n*-hexane (10 mL). After filtration (F4), the solvent was removed *in vacuo*, and the brown solid was solved in toluene (2 mL). The brown solution was concentrated to incipient crystallization *in vacuo* and stored at −25 °C for 12 h, resulting in the deposition of orange crystals. Removal of the supernatant by syringe and drying *in vacuo* yield 1.340 g (1.520 mmol, 76%) of **3** as orange crystals. Mp: 134 °C. Anal. calcd % (found) for $\mathrm{C_{20}H_{54}F_6N_2O_6P_2S_2Si_8}$ (883.4): C 27.19 (26.90), H 6.16 (6.25), N 3,17 (3.06). ^{1}H NMR (25 °C, $\mathrm{CD_2Cl_2}$, 300.13 MHz): δ 0.32 (s, 36 H, $^2J(^{29}\mathrm{Si}{-}^1H$ = 6.5 Hz, $^1J(^{13}\mathrm{C}{-}^1H$ = 121 Hz, $\mathrm{Si(Si(C}H_3)_3)_2$, 0.45 (s, 18 H, $^2J(^{29}\mathrm{Si}{-}^1\mathrm{H})$ = 6.2 Hz, $\mathrm{N(Si(C}H_3)_3)$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 75.47 MHz): δ 0.51 (s, $\mathrm{Si(Si(CH_3)_3)_2}$), 2.61 (t, $^3J(^{31}\mathrm{P}{-}^{13}\mathrm{C})$ = 8.2 Hz, $\mathrm{N(Si(CH_3)_3)}$), 119.1 (q, $^1J(^{19}\mathrm{F}{-}^{13}C$ = 317.8 Hz, $\mathrm{S(CF_3)}$). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 282.4 MHz): δ −76.8 (s). ^{29}Si NMR (25 °C, $\mathrm{CD_2Cl_2}$, 59.63 MHz): δ −14.9 (m, Si(*Si*Me$_3$)$_2$), 13.1 (m, N*Si*Me$_3$), 25.0 (m, *Si*(SiMe$_3$)$_2$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 121.49 MHz): δ 505.7 (s). IR (ATR, 32 scans): 2955 (m), 2897 (m), 1383 (s), 1244 (s), 1199 (s), 1149 (s), 1072 (m), 1031 (m), 950 (m), 918 (m), 878 (m), 828 (s), 792 (s), 749 (m), 689 (m), 624 (s), 599 (w), 565 (m), 537 (m).

Synthesis of $Ag_4P[(C_6F_5)N(SiMe_3)Si(SiMe_3)_2Cl]_4$ (4). To a solution of $(Me_3Si)_3SiN(SiMe_3)PCl_2$ (**1**) (0.253 g, 0.58 mmol) in CH_2Cl_2 (10 mL) at −70 °C was added AgC_6F_5 (0.193 g, 0.61 mmol). The brown solution is warmed to ambient temperature over a period of 3 h. The solvent was removed *in vacuo*, and the brown solid was extracted with *n*-hexane (10 mL). After filtration (F4), the solvent was removed *in vacuo*, and the brown solid was solved in toluene (2 mL). The brown solution was concentrated to incipient crystallization *in vacuo* and stored at 5 °C for 12 h, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying *in vacuo* yield 0.216 g (0.35 mmol, 72%) of **4** as colorless crystals. Mp: 79 °C (dec.). Anal. calcd % (found) for $C_{60}H_{108}Ag_4Cl_4F_{20}N_4P_4Si_{16}$ (2412.04): C, 29.88 (30.15); H, 4.51 (4.59); N, 2.32 (2.46). ^1H NMR (−70 °C, CD_2Cl_2, 300.13 MHz): δ 0.16 (s, 18H, $Si(CH_3)_3$, 0.27 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (−70 °C, CD_2Cl_2, 75.5 MHz): δ 0.1 (s, $Si(CH_3)_3$), 3.0 (s, $Si(CH_3)_3$), 143.9 (m, *i*-C), 147.4 (m, CF), 165.3 (m, CF), 185.0 (m, CF). $^{19}F\{^1H\}$ NMR (−70 °C, CD_2Cl_2, 282.4 MHz): δ −163.5 (m, 2F, *m*-CF), −159.2 (t, 1F, $^3J(^{19}F-^{19}F) = 20$ Hz, *p*-CF), −129.7 (br, 2F, *o*-CF). ^{29}Si NMR (−70 °C, CD_2Cl_2, 59.6 MHz): δ −217.2 (m, $\mathit{Si}(Si(CH_3)_3)_2Cl$), −11.9 (m, $\mathit{Si}(CH_3)_3$), 6.5 (m, $\mathit{Si}(CH_3)_3$), 9.3 (m, $\mathit{Si}(CH_3)_3$). $^{31}P\{^1H\}$ NMR (−70 °C, CD_2Cl_2, 121.5 MHz): $\delta = -13.2$ (t, $^1J(^{31}P-^{107/109}Ag) \approx 430$ Hz.

Synthesis of Diazaphosphasilole Pentafluorophenylsilver Adduct (5). To a solution of $(Me_3Si)_3Si-N(SiMe_3)PCl_2$ (**1**; 0.253 g, 0.58 mmol) in CH_2Cl_2 (10 mL) at −70 °C was added $AgC_6F_5 \cdot CH_3CN$ (0.193 g, 0.61 mmol). The dark red suspension is warmed to ambient temperature over a period of 8 h. The solvent was removed *in vacuo*, and the red oil was extracted with *n*-hexane (5 mL). The yellow solution was concentrated to incipient crystallization *in vacuo*, resulting in the deposition of colorless crystals. Removal of the supernatant by syringe and drying *in vacuo* yield 0.265 g (0.41 mmol, 71%) of **5** as colorless crystals. Mp: 76 °C (dec.). ^1H NMR (−70 °C, CD_2Cl_2, 300.13 MHz): δ 0.16 (s, 3H, CH_3), 0.22 (s, 18H, $Si(Si(CH_3)_3)_2$), 0.37 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (−70 °C, CD_2Cl_2, 75.5 MHz): δ = −1.2 (m, CH_3), 1.8 (d, $^4J(^{13}C-^{31}P) = 6.1$ Hz, $Si(Si(CH_3)_3)_2)$), 3.8 (s, $Si(CH_3)_3$), 108.6 (m, *i*-C), 114.3 (m, CF), 140.1 (m, CF), 149.1 (m, CF), 208.0 (m, C_q). $^{19}F\{^1H\}$ NMR (−70 °C, CD_2Cl_2, 282.4 MHz): δ −162.5 (m, 2F), −159.6 (t, 1F, $^3J(^{19}F-^{19}F) = 19$ Hz), −107.9 (m, 2F). ^{29}Si NMR (−70 °C, CD_2Cl_2, 59.6 MHz): δ −26.7 (m, $^2J(^{29}Si-^{31}P) = 50$ Hz, $\mathit{Si}(Si(CH_3)_3)_2$), −13.1 (m, $Si(\mathit{Si}(CH_3)_3)_2$), −12.5 (m, $Si(\mathit{Si}(CH_3)_3)_2$), 16.1 (m, $\mathit{Si}(CH_3)_3$). $^{31}P\{^1H\}$ NMR (−70 °C, CD_2Cl_2, 121.5 MHz): δ 177.0.

Synthesis of Diazaphosphasilole Galliumtrichlorid Adduct (6). To a solution of $(Me_3Si)_3SiN(SiMe_3)PCl_2$ (**1**; 2.231 g, 5.12 mmol) in CH_2Cl_2 (10 mL) at ambient temperature wads added acetonitrile (0.210 g, 5.12 mmol). To the colorless solution was added a solution of gallium trichloride (0.899 g, 5.12 mmol) at −40 °C over a period of 15 min. The bright orange solution was warmed to ambient temperature and stirred for 1 h. The solvent was removed *in vacuo*, which resulted in the formation of **6** (4.85 mmol, 95%) as a red solid. Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a saturated CH_2Cl_2 solution to 0 °C. Mp: 103 °C (dec.). Anal. calcd % (found) for $C_{11}H_{30}Cl_4GaN_2PSi_4$ (545.22): C, 24.23 (24.21); H, 5.55 (5.47); N, 5.14 (5.06). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 0.22 (s, 3H, CH_3), 0.38 (d, 18H, $^5J(^1H-^{31}P) = 1.16$ Hz, $Si(Si(CH_3)_3)_2$), 0.46 (d, 9H, $^4J(^1H-^{31}P) = 0.87$ Hz, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ −0.5 (s, CH_3), 0.6 (s, $Si(Si(CH_3)_3)_2$), 1.7 (s, $Si(Si(CH_3)_3)_2$), 3.6 (d, $^3J(^{13}C-^{31}P) = 6.3$ Hz, $Si(CH_3)_3$), 211.1 (d, $^1J(^{13}C-^{31}P) = 50.3$ Hz, C_q). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ −11.6 (m, $^3J(^{29}Si-^{31}P) = 2.1$ Hz, $Si(\mathit{Si}(CH_3)_3)_2$), −9.7 (m, $^3J(^{29}Si-^{31}P) = 2.1$ Hz, $Si(\mathit{Si}(CH_3)_3)_2$), 12.7 (m, $\mathit{Si}(CH_3)_3$), 61.6 (m, $\mathit{Si}(Si(CH_3)_3)_2$). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ 147.4. IR (ATR, 32 scans): 3139 (w), 2954 (m), 2897 (w), 1504 (w), 1485 (m), 1409 (w), 1361 (w), 1249 (s), 1165 (m), 1124 (m), 1049 (w), 1003 (m), 922 (w), 887 (s), 824 (s), 784 (m), 746 (m), 692 (m), 626 (m), 603 (w), 557 (m), 544 (m). Raman (70 mW, 5 scans, 25 °C, cm^{-1}): 2903 (1), 1505 (6), 1432 (2), 1166 (2), 1009 (4), 901 (2), 846 (2), 807 (2), 779 (3), 645 (5), 546 (3), 503 (5), 475 (5), 414 (5), 360 (7), 314 (6), 289 (9), 227 (4), 140 (9), 76 (10). MS (CI^+, isobutane): 297 $[M - GaCl_3 - SiMe_3 + 2H]^+$, 335 $[M - GaCl_3 - Cl + 2H]^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, structure elucidation, synthesis of compounds, and NBO calculations of **6** and **7**. 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.

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