Inorganic Chemistry

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Lewis Acid Assisted Methyl/Chlorine Exchange in Silylated Hydrazinochlorophosphanes

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Supporting Information

ABSTRACT: Differently substituted hydrazinophosphanes of the type $(Me_3Si)_2N-N(SiMe_3)-PR^1R^2$ (R^1 = Cl with R^2 = Me, C_6F_5 and R^1 = Me, R^2 = C_6H_5) have been studied in the reaction with Lewis acids such as ECl_3 (E = Al, Ga). For $(Me_3Si)_2N-N(SiMe_3)-P(Cl)(Me)$ and $(Me_3Si)_2N-N(SiMe_3)-P(Me)(C_6H_5)$, only adduct formation was found while a chlorine/methyl exchange reaction was observed for $(Me_3Si)_2N-N(SiMe_3)-P(Cl)R$ (R = C_6H_5 and C_6F_5) leading to the formation of $(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Me)R$, which crystallize as ECl_3 adducts. The free hydrazinophosphanes can be obtained by removal of the Lewis acid with the help of a strong base such as 4-(dimethylamino)pyridine (DMAP).

INTRODUCTION

The low-coordination number chemistry of the group 15 elements (N, P) has been extensively developed in the past thanks to the use of bulky groups and is now well-established.[1−4] It has been possible to characterize these reactive species due to their kinetic and thermodynamic stabilization by appropriate substitution.

Only recently reactions of the silylated hydrazinophosphane $(Me_3Si)_2N-N(SiMe_3)-PCl_2$ (**1a**) (Scheme 1)[5] and the analogous hydrazinoarsane $(Me_3Si)_2N-N(SiMe_3)-AsCl_2$[6] with $GaCl_3$ as the Lewis acid were investigated. Triggered by the action of $GaCl_3$ (Scheme 1) $(Me_3Si)_2N-N(SiMe_3)-PCl_2$ (**1a**) was transformed into a five-membered PN heterocycle (compound **2** in Scheme 1).[7−9] This new reaction has been classified as a formal $GaCl_3$-assisted [3 + 2] cycloaddition,[10] which only occurs when Me_3Si-Cl elimination releases the hidden 1,3 dipole molecule and the dipolarophile, respectively. Moreover, at the end of the reaction sequence the formed heterocycle, the neutral triazadiphosphol RN_3P_2 (R = $(Me_3Si)_2N$), is stabilized as $GaCl_3$ mono- or diadduct.[7] Interestingly, $(Me_3Si)_2N-N(SiMe_3)-PCl_2$ (**1a**) represents an ambivalent species which can react as dipolarophile and/or as 1,3 dipole. In any case, a Lewis acid such as ECl_3 (E = Ga, Al) or BR_3 (R = C_6F_5) is necessary for (i) decreasing of the activation barrier for the Me_3Si-Cl elimination[5] and (ii) for stabilizing the "naked" azaphosphole by adduct formation.[7−9]

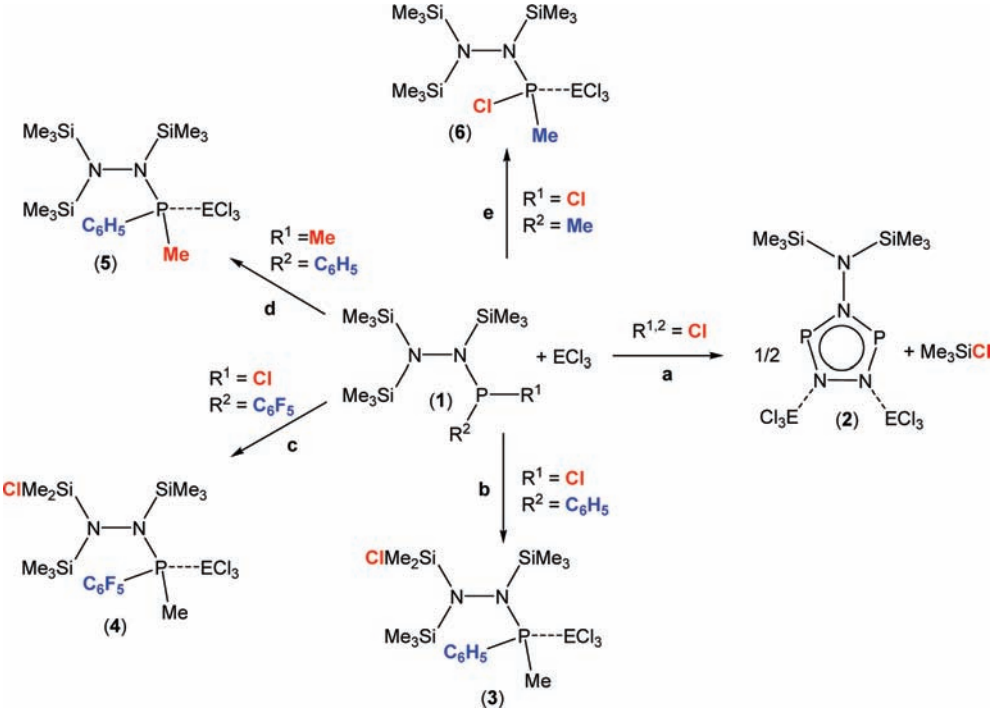
Lately, the concept of a $GaCl_3$-assisted [3 + 2] cycloaddition has been proven in a series of other reactions, involving even other heteroelements such as arsenic.[6,11] For instance the reaction of the kinetically stabilized iminophosphane Mes*—N═P—Cl, (Mes* = 2,4,6-tri-*tert*-butylphenyl), a good dipolarophile, with $(Me_3Si)_2N-N(SiMe_3)-PCl_2$ (**1a**), a "disguised" 1,3-dipole, yielded also a triazadiphosphole (RN_3P_2, R = Mes*).[9] The first tetrazaphosphole[8] 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 arsenic analog led to the first tetrazarsole.[11] 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 (−30−25 °C), whereas classical triazole-forming reactions require elevated temperatures.

In contrast to $(Me_3Si)_2N-N(SiMe_3)-PCl_2$ (**1a**), the reaction of the analogous hydrazinoarsane $(Me_3Si)_2N-N(SiMe_3)-AsCl_2$ with $GaCl_3$ gave no binary arsenic−nitrogen heterocycle.[6] In this reaction, both chlorine atoms attached to the arsenic atom were exchanged by a methyl group from one of the trimethylsilyl groups at the terminal nitrogen (Scheme 2), and finally, a $GaCl_3$ adduct was formed. The Lewis acid $GaCl_3$ is easily removed by addition of a stronger base such as 4-(dimethylamino)pyridine (DMAP).

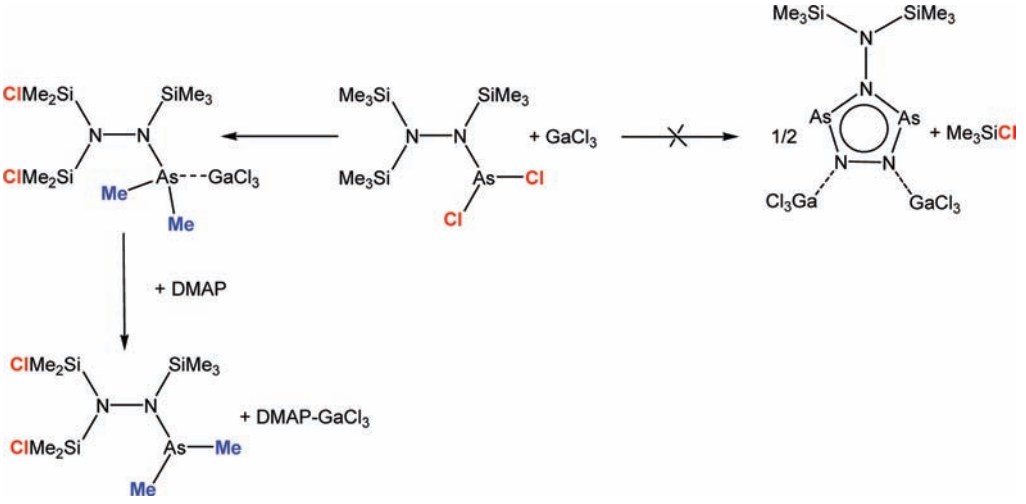
The different reaction channels observed for $(Me_3Si)_2N-N(SiMe_3)-PCl_2$ (**1a**) and $(Me_3Si)_2N-N(SiMe_3)-AsCl_2$ when $GaCl_3$ is added prompted us to have a closer look into the reaction mechanism. For this reason differently substituted hydrazinophosphanes of the type $(Me_3Si)_2N-N(SiMe_3)-PR^1R^2$ (R^1 = Cl with R^2 = Me, C_6H_5, C_6F_5 and R^1 = Me, R^2 = C_6H_5) have been studied in the reaction with Lewis acids such as ECl_3 (E=Al, Ga). Here we report on similar methyl/chlorine exchange reactions, observed for the first time in substituted hydrazinophosphanes, when treated with $GaCl_3$ or $AlCl_3$.

Received: January 3, 2011
Published: February 22, 2011

Scheme 1. Reaction Channels for Substituted $(Me_3Si)_2N-N(SiMe_3)-PR^1R^2$ (1a−e) upon Adding ECl_3 (E = Al, Ga)



Scheme 2. Methyl/Chlorine Exchange Reaction in the Silylated Hydrazinoarsane



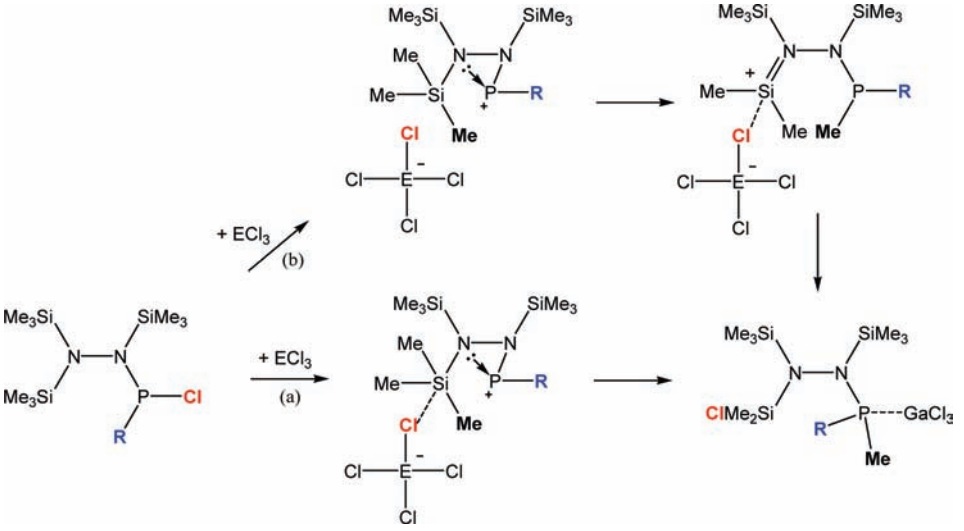
RESULTS AND DISCUSSION

General Remarks. Different hydrazinophosphanes, $(Me_3Si)_2N-N(SiMe_3)-PR^1R^2$ (**1**) (Scheme 1) have been studied in the reaction with Lewis acids of the type ECl_3 (E = Al, Ga). The substitution pattern R^1/R^2 was changed from Cl/Cl (**1a**), Cl/Me (**1e**), Cl/aryl (aryl = C_6H_6 (**1b**), and C_6F_5 (**1c**)) to Me/Ph (**1d**). While all chlorophosphanes should be capable of forming a $[(Me_3Si)_2N-N(SiMe_3)-PR^2]^+$ ion (besides the formation of ECl_4^-) upon addition of the Lewis acid, only for the chlorine/aryl-substituted species a chlorine/methyl exchange reaction was observed, also when the electron withdrawing C_6F_5 group was used (Scheme 1). In the case of the hydrazino(chloro)methylphosphane (**1e**), only adduct formation was found. Obviously, aryl substitution is needed to stabilize the transition state for a chlorine/methyl exchange which can be assumed to be a hydrazinophosphenium ion as displayed in Scheme 3.

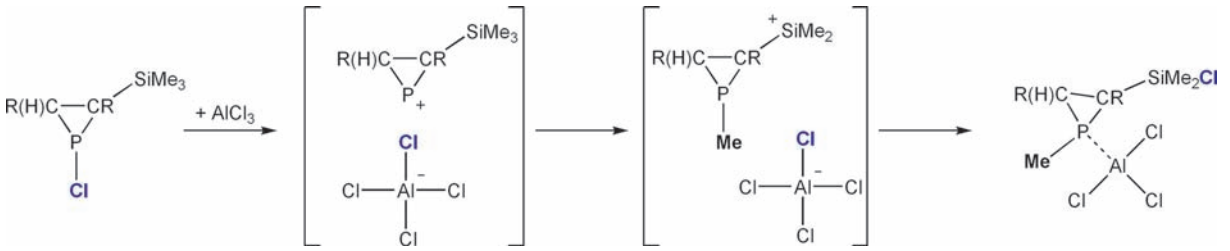
Reactions with Si−C bond cleavage catalyzed by the action of Lewis acids are known.[12] For example a methyl migration from silicon to gallium was found in the reaction of $GaCl_3$ and $SiMe_4$ for which an intermediate with bridging Cl and Me between Si and Ga was assumed, finally leading to the formation of Me_3SiCl

dx.doi.org/10.1021/ic200005q |*Inorg. Chem.* 2011, 50, 2691–2702

Scheme 3. Possible Reaction Mechanism for the Chlorine/Methyl Exchange Reaction in Aryl-Substituted Chlorohydrazinophosphanes (E = Al, Ga; (a) Concerted and (b) Stepwise Reaction)



Scheme 4. 1-Chlorophosphirane Reacting with $AlCl_3$ to Give a Phosphirane−$AlCl_3$ Complex Displaying a Chloro/Methyl Exchange[13]



and $(MeGaCl_2)_2$. Niecke et al. already described a similar methyl/chlorine exchange reaction in chlorophosphiranes as displayed in Scheme 4.[13] With these three-membered chlorophosphiranes in mind we believe that formation of a cyclic cation, $[(Me_3Si)_2N{-}N(SiMe_3){-}PR]^+$ (R = aryl), as the reactive intermediate represents the key species for the observed chlorine/methyl exchange reaction. The cationic intermediate is best stabilized by aryls but not by the methyl group, which explains the different reaction channels. A three-membered cation was also discussed for the Me_3SiCl elimination in the reaction sequence which finally led to the formation of the triazadiphosphole **2** (Scheme 1).[14] Presumably, the reaction occurs either in a concerted manner or stepwise (Scheme 3, compare reaction pathway **a** and **b**).

In the intramolecular Me/Cl exchange reactions as displayed in Scheme 1, the Lewis acid ECl_3 mediates the substitution and forms an ECl_3 adduct at the end of the exchange reaction. Reaction of **3a** and **4** with a Lewis base e.g. 4-(dimethylamino)pyridine (DMAP) yields the free hydrazinophosphanes, so that ECl_3 can be considered a catalyst.

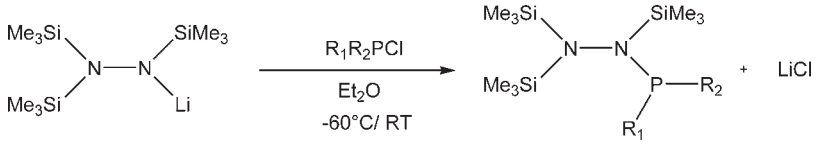
Another similar reaction was reported by Carmalt et al.: The reaction of $GaCl_3$ with $(Me_3Si)_3N$ yielded, among other products, dimeric $(MeGaCl_2)_2$.[15] In that case, the product $(MeGaCl_2)_2$ is the result of monochloride substitution and transfer of a methyl ligand from the silyl group of the amine to the Ga center. A methyl/chlorine exchange is also assumed in the formation of the $GaCl_3$ diadduct of the six-membered oxadisilathiadiazine heterocycle $O(SiMe_2)(NSN)(SiMe_2)$ as hydrolysis product of the reaction of bis(trimethylsilyl)sulfur diimide and $GaCl_3$.[16] However, in these examples of methyl/chlorine exchange reactions, $GaCl_3$ is part of an *inter*molecular exchange reaction, whereas in conversions of $(Me_3Si)_2N{-}N(SiMe_3){-}P(Cl)R$ (R = C_6H_5 (**1b**), C_6F_5 (**1c**)), the Lewis acid $GaCl_3$ works only as a catalyst in an *intra*molecular Me/Cl exchange reaction.

Synthesis of Substituted Hydrazinophosphanes. The salt elimination reaction of chlorophosphanes, $R^1R^2P{-}Cl$, with bis-[lithium-tris(trimethylsilyl)hydrazide], $\{Li[N(SiMe_3){-}N(SiMe_3)_2]\}_2$, in diethyl ether at low temperatures (−60 to −40 °C) represents a fast and clean reaction (reaction time 1 h, yield >90% row product) resulting in the formation of LiCl and the hydrazinophosphanes, $(Me_3Si)_2N{-}N(SiMe_3){-}PR^1R^2$ (R^1 = Cl with R^2 = C_6H_5 (**1b**); R^1 = Me and R^2 = C_6H_5 (**1d**); $R^{1,2}$ = Cl (**1a**); Scheme 5). Furthermore $(Me_3Si)_2N{-}N(SiMe_3){-}P(C_6F_5)Cl$ (**1c**) can easily be prepared when a solution of $(Me_3Si)_2N{-}N(SiMe_3){-}PCl_2$ (**1a**) in CH_2Cl_2 is treated with a solution of pentafluorophenylsilver, AgC_6F_5, in CH_2Cl_2 at ambient temperature (Scheme 6).

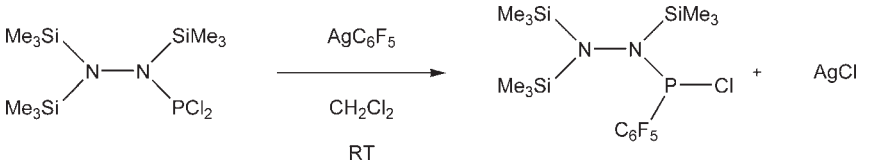
It should be noted that the attempted synthesis of *N,N′,N′*-tris(trimethylsilyl) hydrazino-chloro(2,4,6-tri-*tert*- butylphenyl)-phosphane, $(Me_3Si)_2N{-}N(SiMe_3){-}P(Mes^*)Cl$ (Mes^* = 2,4,6-tri-*tert*-butylphenyl), according to Scheme 5 led to a reaction

dx.doi.org/10.1021/ic200005q |*Inorg. Chem.* 2011, 50, 2691–2702

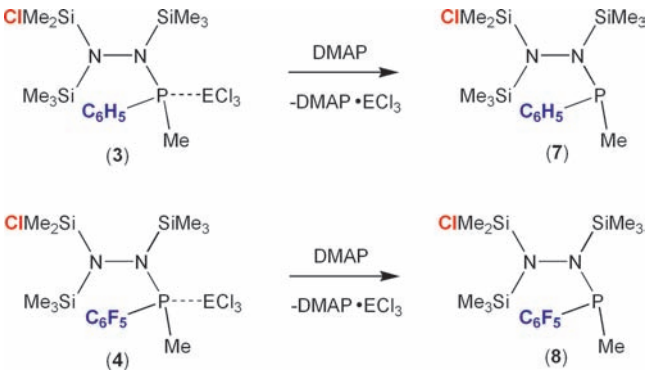
Scheme 5. Synthesis of Hydrazinophosphanes (R^1 = Cl with R^2 = C_6H_5 (1b); R^1 = Me and R^2 = C_6H_5 (1d); R^1 = Cl and R^2 = Me (1e); $R^{1,2}$ = Cl (1a))



Scheme 6. Synthesis of *N*,*N*′,*N*′-Tris (trimethylsilyl) hydrazine- (pentafluorophenyl) chlorophosphane $(Me_3Si)_2N—N(SiMe_3)—P(C_6F_5)Cl$ (1c)



Scheme 7. Synthesis of Free *N*′-(Dimethylchlorosilyl)-*N*, *N*′-bis(trimethylsilyl)hydrazino(methyl)(aryl)phosphanes 7 and 8



mixture from which besides the starting material 2,4,6-tri-*tert*-butylphenyl-dichlorophosphane, Mes*—PCl_2, bis(2,4,6-tri-*tert*-butylphenyl)diphosphene, Mes*—P═P—Mes*, and *N*,*N*-bis-(trimethylsilyl) amino-(2,4,6-tri-*tert*-butylphenyl) phosphazene, $(Me_3Si)_2N—N═P—Mes^*$, could be identified. In a second experiment, we treated $(Me_3Si)_2N—N(SiMe_3)—PCl_2$ (**1a**) with LiMes*, but again a mixture of Mes*—P═P—Mes* and $(Me_3Si)_2N—N═P—Mes^*$ was obtained.

All hydrazinophosphanes, $(Me_3Si)_2N—N(SiMe_3)—PR^1R^2$ (R^1 = Cl with R^2 = C_6H_5 (**1b**); R^1 = Cl with R^2 = C_6F_5 (**1c**); R^1 = Me and R^2 = C_6H_5 (**1d**); $R^{1,2}$ = Cl (**1a**)) are thermally stable up to over 140 °C and are volatile above 60 °C in vacuum. Hence, they are easily purified by sublimation at 60−120 °C and 10^{-3} mbar (separation from traces of LiCl) resulting in colorless ceraceous solids. All species are air and moisture sensitive but under argon stable over a long period as a solid and in common organic solvents (e.g., Et_2O, CH_2Cl_2, *n*-hexane, etc.). The very good solubility in almost all common organic solvents makes all compounds good precursors for further synthesis.

Synthesis of Hydrazinophosphane Adducts. The treatment of all methyl substituted hydrazinophosphanes with a Lewis acid such as $GaCl_3$ or $AlCl_3$ led to adduct formation (Scheme 1, compounds **5** and **6**) in a straightforward high-yield reaction, while the chloro/aryl substituted compounds displayed a chlorine/methyl exchange followed by adduct formation yielding finally *N*′-(dimethylchlorosilyl)-*N*,*N*′-bis(trimethylsilyl)hydrazino(methyl)(aryl)phosphanes as ECl_3 adducts (Scheme 1, compounds **3a**, **3b**, and **4**). Addition of a stronger base such as DMAP afforded the free *N*′-(dimethylchlorosilyl)-*N*,*N*′-bis(trimethylsilyl)hydrazino(methyl)(aryl)phosphanes (**7** aryl = C_6H_5, **8** aryl = C_6F_5) as colorless materials. All species are air and moisture sensitive. While adducts **3a** and **3b** were isolated as colorless crystals, adduct **4** is a colorless viscous oil. Removal of the $GaCl_3$ in both adducts by means of DMAP led to the solid materials **7** and **8**, respectively (Scheme 7).

Spectroscopic Characterization. All compounds have been characterized by elemental analysis, vibrational, mass, and NMR spectroscopy (nuclei: ^1H, ^{13}C, ^{19}F, ^{29}Si, ^{31}P).

As previously shown for a series of silylated hydrazinophosphanes $(Me_3Si)_2N—N(SiMe_3)—PR^1R^2$ (R^1 = R^2 = Cl (**1a**); R^1 = R^2 = Ph; R^1 = Cl, R^2 = Ph (**1b**))[5] there are two possible isomers: a *cis*- and a *trans*-isomer (Scheme 8 top, isomer A and B).[6] The rotation around the P−N bond is sterically hindered leading to constitution isomers which can be regarded as diasteromers.[5,14] Both isomers can form adducts upon addition of a Lewis acid ECl_3, so that also for the adducts two isomers can be expected. A more complicated situation is found for adducts **3** and **4** as well as the adduct-free compounds **7** and **8**. Due to the introduction of one $ClMe_2Si$ group at only one of the terminal nitrogen atoms of the hydrazino group, the whole hydrazino moiety becomes chiral (Scheme 8 bottom). Hence, in addition to both isomers A1 and B1, two further isomers A2 and B2 must be considered. Since the phosphorus atom also represents an asymmetric center two pairs of diastereomers (A1, A2, B1, and B2) can be observed. Furthermore, for each diastereomer its mirror image (enantiomer) exists (A1′, A2′, B1′, and B2′), leading to an overall number of eight possible isomers (Scheme 9). By means of NMR techniques, only the diastereomers can be distinguished, when measured in achiral solvents.

The NMR spectra of investigated compounds showed that the tris(trimethylsilyl)-substituted hydrazinophosphanes **1b**−**1e** and

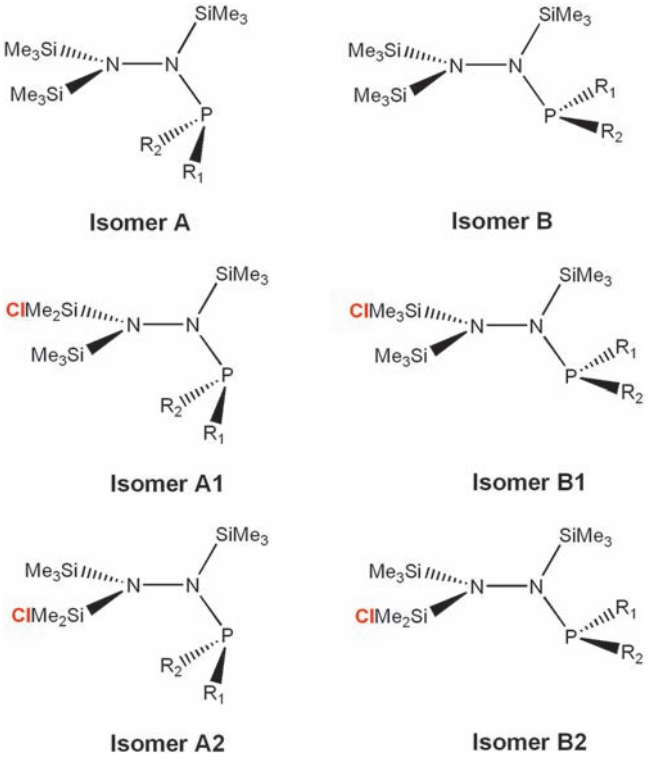
dx.doi.org/10.1021/ic200005q |*Inorg. Chem.* 2011, 50, 2691–2702

Table 1. $^{31}P\{^{1}H\}$ NMR Shifts (25 °C, CD_2Cl_2, 121.49 MHz)

species	^{31}P NMR shift
$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(C_6F_5)Me$ (**8**)	31.3 (A1)
	32.7 (A2)
$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(C_6H_5)Me$ (**7**)	41.0 (A1)
	41.8 (A2)
$(Me_3Si)_2N-N(SiMe_3)-P(Me)Ph$ (**1d**)	42.9
$(Me_3Si)_2N-N(SiMe_3)-PPh_2$	61.4[a]
$(Me_3Si)_2N-N(SiMe_3)-P(C_6F_5)Cl$ (**1c**)	105.7
$(Me_3Si)_2N-N(SiMe_3)-P(Cl)Ph$ (**1b**)	145.2
$(Me_3Si)_2N-N(SiMe_3)-P(Cl)Me$ (**1e**)	159.5
$(Me_3Si)_2N-N(SiMe_3)-PCl_2$ (**1a**)	166.6[a]
$(Me_3Si)_2N-N(SiMe_3)-P(Me)Ph\cdot GaCl_3$ (**5**)	33.7 (br)
$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Ph)Me\cdot GaCl_3$ (**3a**)	34.0 (br) (A1)
$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Ph)Me\cdot AlCl_3$ (**3b**)	27.5 (br)
$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(C_6F_5)Me\cdot GaCl_3$ (**4**)	43.6 (br)
	44.6 (br)
$(Me_3Si)_2N-N(SiMe_3)-P(Cl)Me\cdot GaCl_3$ (**6**)	98.0 (br)

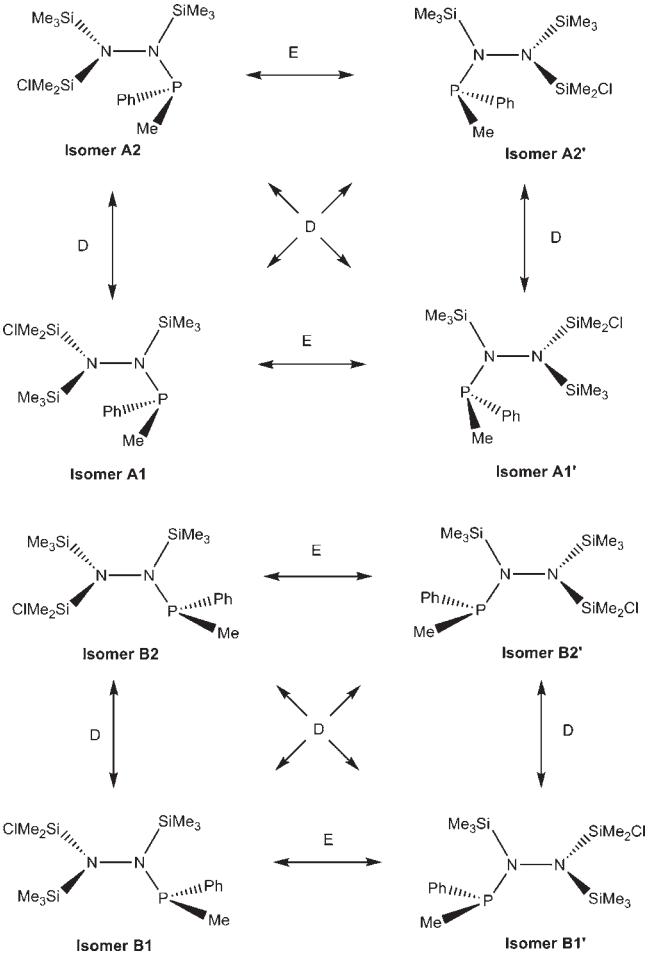
[a] Reference 5.

Scheme 8. Diastereomers of Hydrazinophosphanes



the adducts **5** and **6** exist in solution as one species which was confirmed as being the *cis*-isomers (isomers A). For the (dimethylchlorosilyl)bis(trimethylsilyl)-substituted compounds **3a**, **3b**, **4**, **7**, and **8**, signals of two isomers appeared which were assigned to isomers A1 and A2. The assignment was done on the basis of the ^{1}H NMR spectra. For example, in the ^{1}H NMR spectrum (as also in spectra of the other nuclei) of **7**, having the dimethylchlorosilyl moiety at the terminal N atom, two sets of

Scheme 9. Diastereomers (D) and Enantiomers (E) of Hydrazinophosphanes 7 with Two Chiral Centers[a]



[a] (top) *cis*-Isomers A1 and A2 with the according enantiomers A1′ and A2′, (bottom) *trans*-isomers B1 and B2 with the according enantiomers B1′ and B2′.

signals are observed in a ratio of 62%: 38%. A closer look at the region of the SiMe signals shows, that two signals are significantly shifted compared to the other signals. In fact, one $SiMe_3$ signal of the minor species (δ ^{1}H = −0.06) and one signal of the two nonequivalent (diastereotopic) Me groups of the $SiMe_2Cl$ moiety for the major species (δ ^{1}H = −0.11) are high-field shifted. These findings can only be explained by the anisotropy effect of the phenyl group which must be arranged nearly to the corresponding Me groups (on the same side of the N−N−P plane) confirming here the *cis* arrangement of the P moiety. Therefore, the major species (62%) can be defined as the isomer A1, whereas the minor species proves to be the isomer A2. The same item can be considered for compound **8** and also for the adducts **3a** and **3b**.

In the case of the tris(trimethylsilyl)-substituted compounds, the high-field shift of one Me signal proves again the cis arrangement of the P moiety (isomer A). The fact that for **1e** and **6** no high-field shift of any $SiMe_3$ signal was observed is understandable due to the absence of the phenyl group and supports the discussion above.

Also, ^{31}P NMR spectroscopy is a powerful tool to study the methyl/chlorine exchange reaction, isomers, and the dynamics in solution. The ^{31}P NMR data are summarized in Table 1.

dx.doi.org/10.1021/ic200005q |*Inorg. Chem.* 2011, 50, 2691–2702

Table 2. Crystallographic Details of 1c, 3a, and 3b

	1c	3a	3b
chem formula	$C_{15}H_{27}ClF_5N_2PSi_3$	$C_{15}H_{32}Cl_4GaN_2PSi_3$	$C_{15}H_{32}AlCl_4N_2PSi_3$
form wght [g mol^{-1}]	481.08	567.19	524.45
color	colorless	colorless	colorless
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a [Å]	15.509(3)	9.7090(19)	9.7093(4)
b [Å]	12.823(3)	15.819(3)	15.8340(5)
c [Å]	11.945(2)	18.523(5)	17.5820(6)
β [deg]	99.81(3)	110.96(3)	100.026(2)
V [Å^3]	2340.7(8)	2656.6(10)	2661.73(17)
Z	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.365	1.418	1.309
μ [mm^{-1}]	0.428	1.639	0.678
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
measured reflections	24985	44518	41783
independent reflections	6751	7710	8468
reflections with $I > 2\sigma(I)$	5772	6890	6622
R_{int}	0.0335	0.0180	0.0292
$F(000)$	1000	1168	1096
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0351	0.0330	0.0360
wR_2 (F^2)	0.1076	0.0995	0.1025
GooF	1.077	1.059	1.052
parameters	253	244	251
CCDC no.	811885	811886	811887

Table 3. Crystallographic Details of 5, 6, and 8

	5	6	8
chem formula	$C_{16}H_{35}Cl_3GaN_2PSi_3$	$C_{10}H_{30}Cl_4GaN_2PSi_3$	$C_{15}H_{27}ClF_5N_2PSi_3$
form wght [g mol^{-1}]	546.77	505.12	481.08
color	colorless	colorless	colorless
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$	$P2_1/c$
a [Å]	9.8091(3)	8.5157(2)	16.6656(8)
b [Å]	15.7487(5)	12.6961(4)	9.3800(4)
c [Å]	17.4956(6)	11.0010(3)	15.2884(8)
β [deg]	99.759(2)	99.6790(10)	99.467(2)
V [Å^3]	2663.62(15)	1172.46(6)	2357.4(2)
Z	4	2	4
$\rho_{calc.}$ [g cm^{-3}]	1.363	1.431	1.355
μ [mm^{-1}]	1.535	1.847	0.425
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
measured reflections	47351	17472	25693
independent reflections	9630	6068	4628
reflections with $I > 2\sigma(I)$	7860	5820	3312
R_{int}	0.0260	0.0216	0.0422
$F(000)$	1136	520	1000
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0299	0.0177	0.1030
wR_2 (F^2)	0.0820	0.0464	0.2632
GooF	1.069	1.014	1.068
parameters	245	201	471
CCDC no.	811888	811889	811890

As shown in Table 1, the δ ^{31}P values of the NNP species are in the range expected on the basis of numerous data from the literature.[3,17] Successive replacement of chlorine at phosphorus by a methyl or phenyl group leads to increased ^{31}P nuclear shielding (e.g., **1a** → **1e** $\Delta\delta$ ^{31}P = −7.1, **1a** → **1b** $\Delta\delta$ ^{31}P = −21.4, **1a** → **1c** $\Delta\delta$ ^{31}P = −60.9).[18] As already described for the ^{1}H NMR spectra, it can be assumed that all considered free hydrazinophosphanes adopt the cis configuration in solution. Hence, also only a single ^{31}P NMR resonance is observed for all considered species except from the products of the Me/Cl exchange reaction (**7** and **8**) for which two resonances for the diastereomers A1 and A2 (Schemes 8 and 9, Table 1) are observed. According to the ^{1}H and ^{31}P NMR signal intensities, an A1:A2 ratio of 62:38 is observed for species **7** and 60:40 for **8**, respectively. Substitution of a C_6H_5 by a C_6F_5 moiety decreases the chemical shift from ca. 41/42 (**7**) to 31/33 ppm (**8**) (Table 1). Except ^{1}H and ^{31}P NMR, also the ^{13}C, ^{19}F, and ^{29}Si NMR spectra support the existence of two diasteromers; however, the substituent effects on the chemical shifts are less pronounced (e.g., ^{29}Si A1 isomer: 12.5, 13.6, or 14.1, and 19.3 ppm for **7** vs 14.0, 17.2, and 18.5 ppm for **8**). According to our NMR study, all adduct-free hydrazinophosphanes are stable for several days in solution. However, upon addition of a Lewis acid such as $GaCl_3$, the spectra change rapidly leading to decomposition and complex reaction mixtures, respectively. Therefore, it was difficult to obtain usable spectra of some hydrazinophosphane adducts (e.g., **4** and **6**). For example, according to the ^{31}P NMR spectra, measured immediately after dissolving hydrazinophosphane $GaCl_3$ adducts **3a**, **4**, **5**, and **6** in CH_2Cl_2, broad resonances (adducts) and traces of sharp resonances (adduct-free hydrazinophosphanes) were observed as well as resonances of decomposition products.

X-ray Crystallography. The structures of $GaCl_3$ adducts **3a**, **5**, and **6**, $AlCl_3$ adduct **3b** and the free hydrazinophosphanes $(Me_3Si)_2N-N(SiMe_3)-P(Cl)(C_6F_5)$ (**1c**) and $(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Me)(C_6F_5)$ (**8**) have been determined. Tables 2 and 3 present the X-ray crystallographic data. ORTEP representations of the molecular structure along with selected structural data are shown in Figures 1−4.

For compounds of the type $(Me_3Si)_2N-N(SiMe_3)-PR^1R^2$, two diastereomers with respect to the position of the PR^1R^2 group can be discussed as displayed in Scheme 8. While addition of a Lewis acid always leads to the formation of a structure derived from isomer A due to decreased steric repulsion (Figure 1 and 2), for the free uncoordinated compounds (e.g., in $(Me_3Si)_2N-N(SiMe_3)-PCl_2$ (**1a**), $(Me_3Si)_2N-N(SiMe_3)-P(Cl)(C_6H_5)$ (**1b**))[5,19] often a configuration according to isomer B, which is energetically preferred according to quantum chemical calculations, is found.[14] However, in $(Me_3Si)_2N-N(SiMe_3)-P(Cl)(C_6F_5)$ (**1c**) and $(Me_3Si)_2N-N(SiMe_3)-P(Me)(C_6F_5)$ (**8**), respectively, a structure of type A is observed. Interestingly, in the structure of the $AlCl_3$ adduct of $(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Cl)(C_6H_5)$ (**3b**) (Figure 1 left), the position of the chlorine atom is disordered, corresponding to a superposition of both possible diasteromers (A1 and A2) of Scheme 7. The chlorine atom can either be attached to the Si2 or Si3 atom. Free refinement of the chlorine occupancy displayed a 0.826(2):0.174(2) ratio between both isomers. A similar but even more complicated disorder is found for $(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Me)(C_6F_5)$ (**8**) (Figures 4 and S1 in the

dx.doi.org/10.1021/ic200005q |Inorg. Chem. 2011, 50, 2691–2702

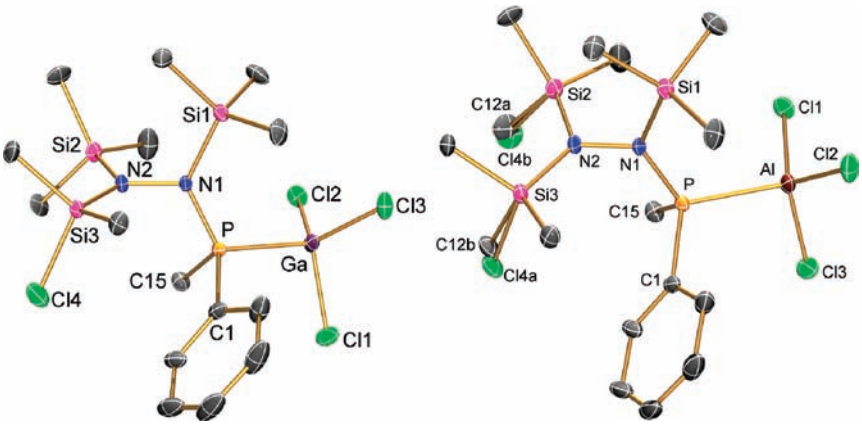


Figure 1. ORTEP drawing of $GaCl_3$ or $AlCl_3$ adducts **3a** and **3b**. Thermal ellipsoids with 30% probability at 173 K (hydrogen atoms omitted). Selected bond lengths are in angstroms, and angles in degrees. $GaCl_3$ adduct: P−N1 1.679(2), P−C15 1.805(2), P−C1 1.809(2), P−Ga 2.3892(7), Si1−N1 1.805(2), Si3−N2 1.757(2), N1−N2 1.466(2); N1−P−C15 109.21(9), N1−P−C1 112.81(8), C15−P−C1 104.6(1), N1−N2−Si3 118.6(1), N1−N2−Si2 118.0(1), Si3−N2−Si2 123.23(9), N2−N1−P 116.0(1), N2−N1−Si1 117.6(1), P−N1−Si1 126.27(9). $AlCl_3$ adduct: P−N1 1.686(1), P−C15 1.810(2), P−C1 1.814(2), P−Al 2.4303(6), Si1−N1 1.799(1), Si2−Cl4B 1.95(1), Si2−C12A 1.87(1), Si3−C12B 1.91(2), Si3−Cl4A 2.077(8), N1−N2 1.472(2); N1−P−C15 108.44(7), N1−P−C1 111.92(6), C15−P−C1 103.72(8), N2−N1−P 116.60(8), N2−N1−Si1 117.51(8), P−N1−Si1 125.78(7), N1−N2−Si3 118.55(9), N1−N2−Si2 117.88(9).

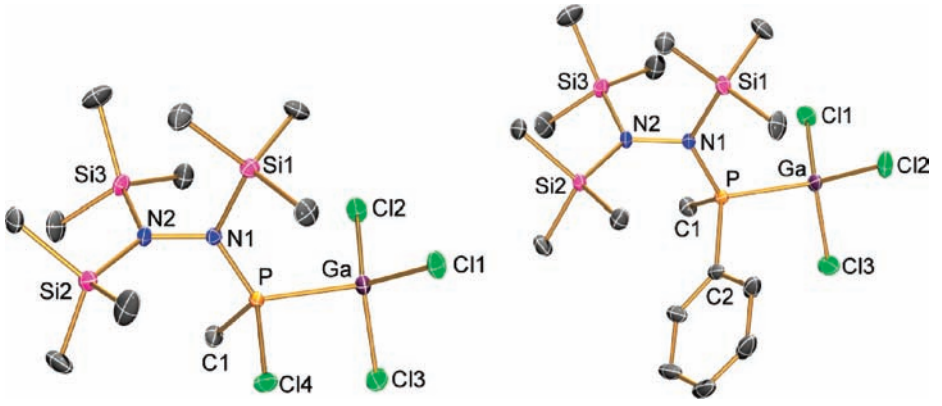


Figure 2. ORTEP drawing of $GaCl_3$ adducts **5** and **6** with thermal ellipsoids with 30% probability at 173 K (hydrogen atoms omitted). Selected bond lengths are in angstroms, and angles in degrees. **5**: Ga−P 2.4201(3), P−N1 1.647(1), P−C1 1.793(2), P−Cl4 2.0470(5), N1−N2 1.463(2), Si1−N1 1.811(1), N2−Si2 1.774(1), Si3−N2 1.771(1); N1−N2−Si2 119.59(9), Si3−N2−Si2 124.07(7), N1−P−C1 110.01(7), N1−P−Cl4 110.83(5), C1−P−Cl4 101.73(6), N2−N1−P 117.61(8), N2−N1−Si1 119.54(8), P−N1−Si1 122.60(6), N1−N2−Si3 115.88(9). **6**: Ga−P 2.3876(3), P−N1 1.674(1), P−C1 1.804(1), P−C2 1.810(1), N1−N2 1.470(1), N1−Si1 1.796(1), N2−Si3 1.774(1), N2−Si2 1.775(1); N1−P−C1 109.75(6), N1−P−C2 113.01(6), C1−P−C2 104.40(7), N2−N1−P 115.20(8), N2−N1−Si1 118.56(7), P−N1−Si1 126.16(6), N1−N2−Si3 117.58(7), N1−N2−Si2 118.83(7), Si3−N2−Si2 122.93(6).

Supporting Information). Here, the asymmetric unit consists of a superposition of the two possible diasteromers (A1, A2) due to a positional disorder of the chlorine position (ratio Cl1a:Cl2a, 0.293(10):0.207(10); ratio Cl1b:Cl2b, 0.319(10):0.181(10)). In addition the whole molecule lies on a pseudo mirror plane, leading to a disorder of the whole molecule (1:1 ratio). Hence, all possible diastereomeres (A1, A2 and A1′, A2′) of Scheme 9 are found in the asymmetric unit.

All hydrazinophosphane species adopt a staggered configuration, in which the two planes formed around the two trigonal planar nitrogen atoms (P—N1—N2—Si3 and N1—N2—Si2—Si3) are almost perpendicular to each other. This perpendicular configuration is stable. No rotation about the N—N axis is observed according to NMR studies. The almost trigonal-planar environment around both nitrogen atoms can be attributed to hyperconjugative effects caused by delocalization of the nitrogen lone pair into the σ^* Si—C bonds.[5,14] The phosphorus atom sits always in a pyramidal environment with bond angles between 100° and 105°. In contrast to the P—C bond lengths (between 1.79 and 1.85 Å), the experimentally determined P—N bond lengths of 1.64 - 1.69 Å are considerably shorter than expected for a typical P—N single bond (cf. $\Sigma r_{cov.}$ = 1.80 (1.76) Å).[20,21] Such short P—N distances (average 1.67 Å) had been previously found in a series of amino/iminophosphanes (R_2N—P═N—R′)[3a] and also in *cyclo*diphosph(V)azenes (P—N: 1.66−1.68 Å).[22] The σ bond system along the P—N1—N2 unit is highly polarized between P1 and N2 and almost ideally covalent between the adjacent N1—N2 single bond with a bond distance of 1.46−1.47 Å (cf. $\sum r_{cov}$ = 1.4 Å). The P—Cl distances are rather long with 2.047 Å in **2** and 2.105 Å in $(Me_3Si)_2N$—$N(SiMe_3)$—$P(Cl)(C_6F_5)$ and compare well with 2.043(3) Å in PCl_3. The slightly increased P—Cl distance in $(Me_3Si)_2N$—$N(SiMe_3)$—$P(Cl)(C_6F_5)$ can also be explained by hyperconjugation as already discussed for $(Me_3Si)_2N$—$N(SiMe_3)$—PCl_2 and $(Me_3Si)_2N$—$N(SiMe_3)$—$P(Cl)(C_6H_5)$.[5,23,24] Due to steric repulsion, the N—N—P angles in the adduct species between

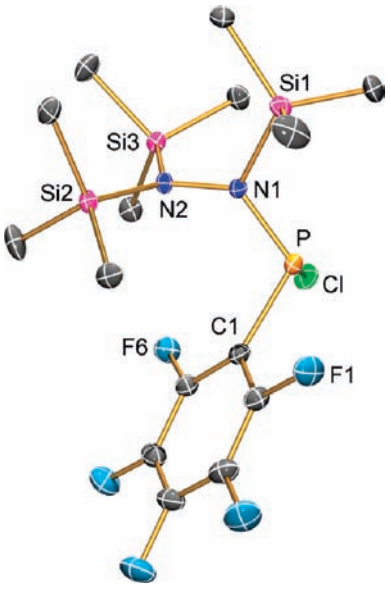


Figure 3. ORTEP drawing of $(Me_3Si)_2N-N(SiMe_3)-P(Cl)(C_6F_5)$ (**1c**) with thermal ellipsoids with 30% probability at 173 K (hydrogen atoms omitted). Selected bond lengths are in angstroms, and angles in degrees: P−N1 1.671(1), P−C1 1.853(2), P−Cl 2.1050(6), Si1−N1 1.808(1), Si2−N2 1.769(1), Si3−N2 1.776(1), N1−N2 1.461(1); N1−P−C1 107.1(6), N1−P−Cl 107.80(4), C1−P−Cl 97.07(5), N2−N1−P 125.46(8), N2−N1−Si1 121.46(8).

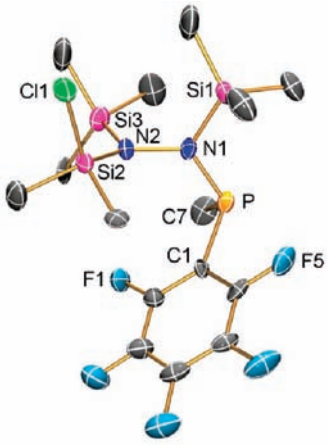


Figure 4. ORTEP drawing of the major part of the disordered molecule **8** with thermal ellipsoids with 30% probability at 173 K (hydrogen atoms omitted). Selected bond lengths are in Å, and angles in degrees: P1−N1 1.689(9), P1−C1 1.897(9), P1−C7 1.97(7), N1−N2 1.49(1), N1−Si1 1.762(9), N2−Si2 1.74(1), N2−Si3 1.78(1), Si2−Cl1 2.026(8); N1−P1−C1 108.0(5), N1−P1−C7 108(3), C1−P1−C7 105(2), N2−N1−P1 121.0(7), N2−N1−Si1 120.8(7), P1−N1−Si1 118.1(5), N1−N2−Si2 119.6(8), N1−N2−Si3 115.5(7), Si2−N2−Si3 122.8(6), N1−Si1−C9 109.5(8).

116° and 118° are slightly larger compared with that found in adduct-free $(Me_3Si)_2N—N(SiMe_3)—P(Ph)Cl$ (110.5(2)°) (isomer B type structure).[5] On the contrary, an even larger N—N—P angle with 125.4° is found for free $(Me_3Si)_2N—N(SiMe_3)—P(Cl)(C_6F_5)$, which adopts an isomer A type structure. Here sterical strain between the C_6F_5 and the $N(SiMe_3)_2$ moieties causes the larger N—N—P angle.

The bond between ECl_3 (E = Al, Ga) and the phosphorus of the hydrazinophosphane can be considered as a donor−acceptor bond.[7,25] The Ga···P distance of 2.38−2.42 Å is very comparable with that in $(t\text{-Bu})_2(Cl)P\cdots GaCl_3$ (2.40(1) Å)[26] and slightly longer than in the sterically less hindered $Me_3P\cdots GaCl_3$ (2.353(2) Å).[27] The Al···P distance amounts to 2.4303(6), in accord with that found in $(Me_3Si)_3P\cdots AlCl_3$ (2.392(4) Å,[28] cf. $\sum r_{cov}$ = 2.40 Å).[20b]

CONCLUSION

Several hydrazinophosphanes of the type $(Me_3Si)_2N-N(SiMe_3)-P(Cl)R$ (R = Me, C_6H_5, C_6F_5) and $(Me_3Si)_2N-N(SiMe_3)-P(Me)(C_6H_5)$ have been studied in the reaction with $GaCl_3$ and $AlCl_3$ as Lewis acids. A chlorine/methyl exchange reaction was observed for $(Me_3Si)_2N-N(SiMe_3)-P(Cl)R$ (R = C_6H_5 and C_6F_5) leading to the formation of $(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Me)R$, after removal of the Lewis acid by means of a strong base such as DMAP. In the case of $(Me_3Si)_2N-N(SiMe_3)-P(Cl)(Me)$ and $(Me_3Si)_2N-N(SiMe_3)-P(Me)(C_6H_5)$, only adduct formation was found. Obviously, aryl substitution is needed to stabilize the transition state for a chlorine/methyl exchange which can be assumed to be a hydrazinophosphenium ion. The chlorine/methyl exchange can be utilized to generate selectively a $(Me_3ClSi)(Me_3Si)N-N(SiMe_3)$ group.

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,[29] dried over P_4O_{10}, and freshly distilled prior to use. Diethylether and THF were dried over Na/benzophenone and freshly distilled prior to use, *n*-hexane and *n*-pentane were dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. $AlCl_3$ (99.999%, Acros), $GaCl_3$ (99.999%, Sigma-Aldrich), *N*,*N*-dimethylaminopyridine DMAP (99%, Aldrich), and *n*-BuLi (2.5 M, Acros) were used as received. PCl_3 (99%, Acros), methyldichlorophosphane $MePCl_2$ (98%, Merck), and phenyldichlorophosphane $PhPCl_2$ (97%, Alfa Aesar) were freshly distilled prior to use. Methylphenylchlorophosphane PhMePCl[30] was prepared according to a literature procedure and freshly destilled prior to use. Pentafluorophenylsilver AgC_6F_5,[31] Lithium-*N*,*N*′,*N*′-tris(trimethlysilyl)hydrazide $Li[(Me_3Si)_2N-N(SiMe_3)]$,[32] *N*,*N*′,*N*′-tris(trimethylsilyl)hydrazinodichlorophosphane $(Me_3Si)_2N-N(SiMe_3)PCl_2$ (**1a**),[33] and 2,4,6-tri-*tert*-butylphenyldichlorophosphane Mes*PCl_2[34] have been reported previously and were prepared according to literature procedures. *N*,*N*′,*N*′-tris(trimethylsilyl)hydrazinochlorophenylphosphane $(Me_3Si)_2N-N(SiMe_3)-PPhCl$ (**1b**)[5] has been reported previously and was prepared according to a modified procedure.

NMR. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^{29}Si INEPT, $^{19}F\{^1H\}$, and ^1H NMR spectra were recorded on Bruker spectrometers AVANCE 300 and AVANCE 500, respectively. The ^1H and ^{13}C chemical shifts were referenced to solvent signals (C_6D_6: δ ^1H = 7.15, δ ^{13}C = 128.0. CD_2Cl_2: δ ^1H = 5.31, δ ^{13}C = 54.0). The ^1H 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 $CFCl_3$, TMS, and H_3PO_4 (85%), respectively. CD_2Cl_2 was dried over P_4O_{10}, and C_6D_6 was dried over Na/benzophenone.

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

Raman. A Bruker VERTEX 70 FT-IR with 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 C/H/N/S-Mikroanalysator TruSpec-932 from Leco were used.

Melting Points. These are uncorrected (EZ-Melt, Stanford Research Systems). A heating rate of 20 °C min^{-1} (clearing points are reported) was used.

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.

$(SiMe_3)_2N-N(SiMe_3)-P(Cl)Ph$ (1b). To a solution of $PhPCl_2$ (0.895 g, 5.00 mmol) in 10 mL Et_2O at −40 °C, a solution of $Li[(Me_3Si)_2N-N(SiMe_3)]$ (1.273 g, 5.00 mmol) in 25 mL Et_2O was added dropwise under stirring over a period of 10 min. The mixture was stirred for 2 h at −40 °C and was then warmed to room temperature and stirred for 10 min. The solvent was removed in vacuo, and the colorless residue was extracted with 20 mL *n*-hexane and filtered, resulting in a yellowish solution. Removal of solvent in vacuo resulted in a colorless solid. Sublimation at 65 °C for 12 h in vacuo yields 1.435 g (3.67 mmol 73%) of **1b** as a colorless crystalline solid. All analytical data are identical to the literature. Additional data. ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.01 (s, 9H, $Si(CH_3)_3$), 0.23 (s, 9H, $Si(CH_3)_3$), 0.32 (d, 9H, $J(^{31}P-^1H)$ = 0.8 Hz, $Si(CH_3)_3$), 7.44 (m, 3H, *m*-Ph, *p*-Ph), 7.95 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.1 (d, $J(^{31}P-^{13}C)$ = 2.3 Hz, $Si(CH_3)_3$), 3.2 (br, $J(^{31}P-^{13}C)$ = 0.9 Hz, $Si(CH_3)_3$), 3.5 (d, $J(^{31}P-^{13}C$ = 3.7 Hz, $Si(CH_3)_3$), 128.5 (d, $^3J(^{31}P-^{13}C)$ = 6.9 Hz, *m*-Ph), 131.0 (m, *p*-Ph), 133.0 (d, $^2J(^{31}P-^{13}C)$ = 27.0 Hz, *o*-Ph), 138.6 (d, $^1J(^{31}P-^{13}C)$ = 38.4 Hz, *i*-Ph). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 10.2, 11.0, 19.0. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 145.2. IR (ATR, 32 scans) 3076 (w), 3047 (w), 3020 (w), 2952 (m), 2901 (m), 1477 (m), 1462 (w), 1432 (m), 1402 (m), 1357 (w), 1330 (w), 1309 (m), 1266 (m), 1248 (s), 1182 (m), 1157 (m), 1086 (m), 1072 (m), 1020 (m), 1003 (w), 992 (w), 937 (s), 914 (s), 863 (w), 831 (m), 814 (m), 768 (m), 745 (s), 698 (m), 687 (m), 662 (m), 645 (w), 621 (m), 590 (s).

$(Me_3Si)_2N-N(SiMe_3)-P(C_6F_5)Cl$ (1c). To a solution of $(Me_3Si)_2N-N(SiMe_3)-PCl_2$ (0.689 g, 2.00 mmol) in 5 mL CH_2Cl_2, a solution of AgC_6F_5 (0.577 g, 2.10 mmol) in 20 mL CH_2Cl_2 was added dropwise under stirring over a period of 20 min at room temperature. The yellow suspension was stirred 20 min at room temperature. Removal of solvent in vacuo resulted in a yellowish solid which was extracted with 10 mL *n*-hexane. The yellow suspension was filtered, and the solvent was removed in vacuo, resulting in a yellow oil. Sublimation at 95 °C for 20 h in vacuo yields 0.285 g (0.59 mmol, 22%) of **1c** as a colorless ceraceous solid. Mp 91 °C. Anal calc % (found) for $C_{15}H_{27}ClF_5N_2PSi_3$ (481.06): C 37.45 (37.16), H 5.66, (5.40), N 5.82 (5.72). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.08 (s, 9H, $Si(CH_3)_3$), 0.288 (d, 9H, $J(^{31}P-^1H)$ = 0.5 Hz, $Si(CH_3)_3$), 0.295 (d, 9H, $J(^{31}P-^1H)$ = 1.0 Hz, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.0 (d, $J(^{31}P-^{13}C)$ = 6.5 Hz, $Si(CH_3)_3$), 3.1 (d, $J(^{31}P-^{13}C)$ = 0.8 Hz, $Si(CH_3)_3$), 3.3 (m, $Si(CH_3)_3$), 115.0 (m, *i*-C_6F_5), 138.0 (m, $^1J(^{19}F-^{13}C)$ = 255 Hz), 147.7 (m, $^1J(^{19}F-^{13}C)$ = 255 Hz), (*o*-C_6F_5, *m*-C_6F_5), 144.0 (m, $^1J(^{19}F-^{13}C)$ = 152 Hz, *p*-C_6F_5). $^{19}F\{^1H\}$ NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −126.1 (m, 2F), −149.4 (tt, 1F, $^3J(^{19}F-^{19}F)$ = 20.5 Hz, $^4J(^{19}F-^{19}F)$ = 5.0 Hz), −161.3 (m, 2F). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 10.5, 12.1, 21.1. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 105.7 (t, $^3J(^{31}P-^{19}F)$ = 64.0 Hz). IR (ATR, 32 scans): 2960 (m), 2904 (m), 1636 (m), 1515 (s), 1469 (s), 1407 (m), 1379 (m), 1284 (m), 1265 (w), 1249 (s), 1142 (m), 1084 (s), 1049 (w), 1026 (w), 1003 (w), 978 (s), 902 (m), 882 (m), 831 (w), 818 (w), 780 (m), 768 (w), 754 (m), 727 (m), 678 (m), 659 (m), 646 (w), 629 (m), 608 (m), 584 (m), 571 (m). Raman (200 mW, 1049 scans, 25 °C, cm^{-1}): 2963 (5), 2909 (10), 2794 (1), 2755 (1), 1638 (2), 1520 (1), 1413 (2), 1379 (1), 1312 (1), 1286 (1), 1269 (1), 1249 (1), 1139 (1), 1089 (1), 1048 (1), 976 (1), 885 (1), 826 (1), 784 (1), 746 (1), 683 (2), 649 (5), 631 (1), 586 (2), 522 (1), 506 (2), 468 (2), 444 (2), 419 (3), 392 (1), 338 (1), 230 (3), 205 (2), 184 (2). MS (CI^+, isobutane): 247 $[M - PCl(C_6F_5)]^+$, 445 $[M - Cl]^+$, 481 $[M - H]^+$.

$(Me_3Si)_2N-N(SiMe_3)-P(Me)Ph$ (1d). To a solution of PhPMeCl (0.753 g, 4.75 mmol) in 5 mL Et_2O, a solution of $Li[(Me_3Si)_2N-N(SiMe_3)]$ (1.209 g, 4.75 mmol) in 20 mL Et_2O was added dropwise under stirring over a period of 10 min at −60 °C. The resulting yellowish solution was stirred for 10 min at −60 °C and was then warmed to room temperature, resulting in a yellowish suspension which was stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with 10 mL *n*-hexane and filtered. Removal of solvent and drying in vacuo resulted in a yellowish ceraceous solid. Sublimation at 65 °C over a period of 24 h yields 1.42 g (3.83 mmol, 81%) **1d** as colorless ceraceous solid. Mp 68 °C. Anal calc % (found) for $C_{16}H_{35}N_2PSi_3$ (370.69): C 51.84 (51.53), H 9.52 (10.07), N 7.56 (7.71). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.00 (s, 9H, $Si(CH_3)_3$), 0.22 (d, 9H, $J(^{31}P-^1H)$ = 0.8 Hz, $Si(CH_3)_3$), 0.29 (s, 9H, $Si(CH_3)_3$), 1.60 (d, 3H, $^2J(^{31}P-^1H)$ = 7.6 Hz, CH_3), 7.34−7.42 (m, 3H, *m*-Ph, *p*-Ph), 7.70 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.4 (d, $J(^{31}P-^{13}C)$ = 1.4 Hz, $Si(CH_3)_3$), 3.7 (d, $J(^{31}P-^{13}C)$ = 5.5 Hz, $Si(CH_3)_3$), 3.8 (d, $J(^{31}P-^{13}C)$ = 1.0 Hz, $Si(CH_3)_3$), 14.9 (d, $^1J(^{31}P-^{13}C)$ = 19.2 Hz, CH_3), 128.3 (d, $^3J(^{31}P-^{13}C)$ = 6.6 Hz, *m*-Ph), 129.6 (s, *p*-Ph), 133.8 (d, $^2J(^{31}P-^{13}C)$ = 22.4 Hz, *o*-Ph), 141.5 (d, $^1J(^{31}P-^{13}C)$ = 20.4 Hz, *i*-Ph). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 8.9, 8.9, 12.4. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 42.9. IR (ATR, 32 scans): 3073 (w), 3055 (w), 2952 (m), 2900 (m), 1486 (w), 1473 (w), 1434 (m), 1415 (m), 1323 (w), 1306 (w), 1246 (s), 1179 (w), 1157 (w), 1099 (m), 1070 (w), 1024 (m), 897 (s), 828 (s), 770 (s), 742 (s), 698 (s), 670 (s), 639 (m), 618 (m), 603 (m), 582 (m), 531 (w). Raman (400 mW, 1000 scans, 25 °C, cm^{-1}): 3058 (3), 2957 (5), 2903 (10), 1587 (2), 1572 (1), 1412 (1), 1263 (1), 1247 (1), 1180 (1), 1157 (1), 1099 (1), 1028 (2), 1002 (4), 917 (1), 901 (1), 844 (1), 742 (1), 674 (2), 640 (3), 619 (1), 510 (1), 493 (1), 433 (1), 403 (2), 319 (1), 296 (1), 236 (2), 204 (1). MS (CI^+, isobutane): 73 $[SiMe_3]^+$, 174 $[Me_3Si-NN-SiMe_3]$, 210 $[M - (PhMeP)]^+$, 355 $[M - Me]^+$, 371 $[M + H]^+$.

$(Me_3Si)_2N-N(SiMe_3)-P(Cl)Me$ (1e). To a solution of $MePCl_2$ (0.368 g, 3.15 mmol) in 10 mL Et_2O at −60 °C, a solution of $(Me_3Si)_2N-N(SiMe_3)Li$ (0.764 g, 3.00 mmol) in 10 mL Et_2O was added dropwise under stirring over a period of 10 min. The resulting suspension was stirred for 10 min at −60 °C and was then warmed to room temperature. After stirring for 2 h at this temperature, the solvent was removed in vacuo and 10 mL *n*-hexane was added. Filtration and removal of solvent in vacuo yielded 0.585 g (1.77 mmol, 60%) of **1e** as a colorless solid. Mp 137 °C (dec). Anal calc % (found) for $C_{10}H_{30}ClN_2PSi_3$ (329.04): C 36.50 (34.37), H 9.19 (8.90), N 8.51 (8.74). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.23 (s, 9H, $Si(CH_3)_3$), 0.25 (s, 9H, $Si(CH_3)_3$), 0.34 (s, 9H, $Si(CH_3)_3$), 1.86 (d, 3H, $^2J(^{31}P-^1H)$ = 14.0 Hz, CH_3). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 2.82 (d, $^3J(^{31}P-^{13}C)$ = 4.8 Hz, $Si(CH_3)_3$), 2.93 (s, $Si(CH_3)_3$), 3.04 (d, $^4J(^{31}P-^{13}C)$ = 2.8 Hz, $Si(CH_3)_3$), 22.8 (d, $^1J(^{31}P-^{13}C)$ = 33.0 Hz, CH_3). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 10.2, 10.2, 17.4. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 159.5. IR (ATR, 32 scans): 2954 (m), 2900 (m), 1410 (m), 1248 (s), 1046 (w), 1026 (w), 956 (m), 916 (s), 901 (s), 872 (s), 829 (s), 815 (s), 768 (s), 754 (s), 675 (s), 664 (w), 641 (m), 619 (m), 607 (m), 586 (m). Raman (500 mW, 800 scans, 25 °C, cm^{-1}): 2957 (5), 2903 (10), 1412 (2), 1263 (1), 1249 (1), 1047 (1), 875 (1), 840 (1), 771 (1), 752 (1), 696 (2), 682 (2), 663 (2), 641 (5), 518 (1), 505 (1), 481 (1), 436 (2), 415 (2), 377 (2), 356 (1), 327 (1), 290 (1), 234 (2), 189 (2), 140 (1), 109 (1). MS (FAB^+, NBA): 293 $[M - Cl]^+$, 313 $[M - Me]^+$, 327 $[M - H]^+$.

$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Ph)Me\cdot GaCl_3$ (3a). To a solution of $(Me_3Si)_2N-N(SiMe_3)-P(Ph)Cl$ (0.782 g, 2.00 mmol) in 10 mL CH_2Cl_2 at −70 °C, a solution of $GaCl_3$ (0.370 g, 2.10 mmol) in 5 mL CH_2Cl_2 was added dropwise under stirring over a period of 10 min. The red solution was warmed to room temperature and stirred for 12 h.

The resulting colorless solution was concentrated to incipient crystallization in vacuo and stored at −25 °C for a period of 12 h, resulting in the deposition of colorless crystals. After removal of supernatant by syringe, the crystals were washed with 1 mL *n*-hexane and dried in vacuo which yields 0.675 g (1.19 mmol, 60%) of **3a** as a colorless crystalline solid. Mp 177 °C. Anal calc % (found) for $C_{15}H_{32}Cl_4GaN_2PSi_3$ (567.19): C 31.76 (30.66), H 5.69 (5.70), N 4.94 (4.53). NMR: (ratio A1:A2 = 62:38). (A1) ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = −0.06 (s, 3H, $SiCl(CH_3)_2$), 0.43 (s, 9H, $Si(CH_3)_3$), 0.51 (s, 3H, $SiCl(CH_3)_2$), 0.53 (s, 9H, $Si(CH_3)_3$), 2.35 (d, 3H, $^2J(^{31}P-^1H)$ = 7.6 Hz, CH_3), 7.52−7.69 (m, 3H, *m*-Ph, *p*-Ph), 7.95 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.4 (s, $Si(CH_3)_3$), 3.4 (s, $SiCl(CH_3)_2$), 3.5 (s, $Si(CH_3)_3$), 6.1 (s, $SiCl(CH_3)_2$), 8.3 (d, $^1J(^{31}P-^{13}C)$ = 45.0 Hz, CH_3), 129.5 (d, $^3J(^{31}P-^{13}C)$ = 11.0 Hz, *m*-Ph), 131.0 (d, $^1J(^{31}P-^{13}C)$ = 13.5 Hz, *i*-Ph), 133.9 (s, *p*-Ph), 134.3 (d, $^2J(^{31}P-^{13}C)$ = 11.9 Hz, *o*-Ph). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 17.2, 22.5, 24.6 (or 24.2). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 34.0 (br). (A2) ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.06 (s, 9H, $Si(CH_3)_3$), 0.53 (s, 9H, $Si(CH_3)_3$), 0.76 (s, 3H, $SiCl(CH_3)_2$), 0.79 (s, 3H, $SiCl(CH_3)_2$), 2.30 (d, 3H, $^2J(^{31}P-^1H)$ = 7.6 Hz, CH_3), 7.52−7.69 (m, 3H, *m*-Ph, *p*-Ph), 7.83 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.2 (s, $Si(CH_3)_3$), 3.7 (s, $Si(CH_3)_3$), 5.7 (s, $SiCl(CH_3)_2$), 6.4 (s, $SiCl(CH_3)_2$), 9.6 (d, $^1J(^{31}P-^{13}C)$ = 43.0 Hz, CH_3), 129.6 (d, $^3J(^{31}P-^{13}C)$ = 11.0 Hz, *m*-Ph), 131.0 (d, $^1J(^{31}P-^{13}C)$ = 13.5 Hz, *i*-Ph), 134.0 (d, $^2J(^{31}P-^{13}C)$ = 11.5 Hz, *o*-Ph), 134.0 (s, *p*-Ph). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 16.2, 24.2 (or 24.6), 25.1. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 34.0 (br). IR (ATR, 32 scans): 3086 (w), 3061 (w), 2958 (m), 2920 (w), 2902 (w), 1588 (m), 1575 (w), 1486 (m), 1462 (w), 1439 (m), 1411 (m), 1335 (w), 1317 (m), 1298 (m), 1284 (w), 1256 (s), 1163 (m), 1120 (m), 1104 (m), 1019 (m), 1002 (w), 974 (m), 915 (w), 894 (m), 879 (m), 827 (m), 808 (m), 795 (w), 745 (s), 689 (s), 653 (s), 638 (w), 604 (m), 592 (m). Raman (200 mW, 400 scans, 25 °C, cm^{-1}): 3068 (3), 2995 (4), 29863 (4), 2909 (10), 2845 (1), 2814 (1), 2789 (1), 1589 (3), 1414 (1), 1321 (1), 1190 (1), 1165 (1), 1105 (1), 1029 (2), 1001 (3), 922 (1), 843 (1), 736 (1), 692 (2), 655 (2), 638 (1), 617 (1), 595 (1), 556 (1), 530 (1), 502 (1), 477 (1), 448 (1), 416 (1), 383 (1), 343 (5), 238 (1), 196 (1), 177 (1), 156 (1), 136 (2). MS (CI^+, isobutane): 355 $[M - Cl - GaCl_3]^+$, 391 $[M - GaCl_3 + H]^+$.

$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Ph)Me\cdot AlCl_3$ (3b). To a suspension of $AlCl_3$ (0.051 g, 3.785 mmol) in 5 mL CH_2Cl_2 at −30 °C a solution of $(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Ph)Me$ (0.160 g, 0.361 mmol) in 2 mL CH_2Cl_2 was added under stirring. After 30 min stirring at −30 °C, the colorless suspension was warmed to room temperature and stirred for 1 h. The resulting colorless solution was then concentrated to incipient crystallization in vacuo and stored at room temperature for 1 h, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying in vacuo yielded 0.136 g (0.259 mmol, 72%) of **3b** as colorless crystals. Mp 104 °C (dec). Anal calc % (found) for $C_{15}H_{32}AlCl_4N_2PSi3$ (524.45): C 34.35 (34.34), H 6.15 (6.36), N 5.34 (5.53). NMR: (ratio A1:A2 = 65:35). (A1) ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = −0.08 (s, 3H, $SiCl(CH_3)_2$), 0.43 (s, 9H, $Si(CH_3)_3$), 0.47 (s, 3H, $SiCl(CH_3)_2$), 0.53 (s, 9H, $Si(CH_3)_3$), 2.25 (d, 3H, $^2J(^{31}P-^1H)$ = 5.8 Hz, CH_3), 7.93 (m, 2H, *o*-Ph), 7.52−7.58 (m, 2H, *m*-Ph), 7.59−7.63 (m, 1H, *p*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.4 (s, $Si(CH_3)_3$), 3.4 (s, $SiCl(CH_3)_2$), 3.7 (s, $Si(CH_3)_3$), 6.1 (s, $SiCl(CH_3)_2$), 8.3 (d, $^1J(^{31}P-^{13}C)$ = 40.3 Hz, CH_3), 129.3 (d, $^3J(^{31}P-^{13}C)$ = 10.5 Hz, *m*-Ph), 130.9 (d, $^1J(^{31}P-^{13}C)$ = 13.5 Hz) or 131.1 (d, $^1J(^{31}P-^{13}C)$ = 12.8 Hz) (*i*-Ph), 133.3 (s, *p*-Ph), 134.2 (d, $^2J(^{31}P-^{13}C)$ = 12.5 Hz, *o*-Ph). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 27.5 (br). (A2) ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.02 (s, 9H, $Si(CH_3)_3$), 0.54 (s, 9H, $Si(CH_3)_3$), 0.73 (s, 3H, $SiCl(CH_3)_2$), 0.78 (s, 3H, $SiCl(CH_3)_2$), 2.19 (d, 3H, $^2J(^{31}P-^1H)$ = 5.5 Hz, CH_3), 7.82 (m, 2H, *o*-Ph), 7.52−7.58 (m, 2H, *m*-Ph), 7.59−7.63 (m, 1H, *p*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.1 (s, $Si(CH_3)_3$), 3.9 (s, $Si(CH_3)_3$), 5.7 (s, $SiCl(CH_3)_2$), 6.5 (s, $SiCl(CH_3)_2$), 9.6 (d, $^1J(^{31}P-^{13}C)$ = 37.5 Hz, CH_3), 129.4 (d, $^3J(^{31}P-^{13}C)$ = 10.5 Hz, *m*-Ph), 130.9 (d, $^1J(^{31}P-^{13}C)$ = 13.5 Hz) or 131.1 (d, $^1J(^{31}P-^{13}C)$ = 12.8 Hz) (*i*-Ph), 133.3 (s, *p*-Ph), 134.0 (d, $^2J(^{31}P-^{13}C)$ = 12.0 Hz, *o*-Ph). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 27.5 (br). IR (ATR, 32 scans): 3059 (w), 2957 (m), 2920 (w), 2903 (w), 1589 (m), 1486 (w), 1439 (m), 1410 (m), 1316 (w), 1300 (m), 1257 (s), 1162 (w), 1120 (m), 1102 (w), 1042 (m), 1004 (w), 974 (m), 939 (w), 898 (m), 878 (m), 830 (s), 807 (s), 744 (s), 689 (s), 650 (m), 637 (m), 606 (w), 591 (m). Raman (700 mW, 1500 scans, 25 °C, cm^{-1}): 3176 (1), 3149 (1), 3070 (3), 3019 (2), 2995 (3), 2963 (4), 2908 (10), 1590 (3), 1576 (1), 1413 (2), 1271 (1), 1191 (1), 1164 (1), 1104 (1), 1029 (2), 1001 (3), 948 (1), 916 (1), 880 (1), 849 (1), 795 (1), 757 (1), 733 (1), 693 (3), 656 (1), 638 (3), 618 (1), 517 (1), 507 (1), 478 (1), 455 (1), 421 (2), 400 (1), 379 (1), 346 (3), 308 (1), 250 (2), 211 (1), 181 (1), 158 (1), 129 (1), 110 (1). MS (FAB^+, NBA): 210 $[M - AlCl_3 - N(SiMe_3)SiMe_3Cl]^+$, 355 $[M - AlCl_3 - Cl]^+$, 391 $[M - AlCl_3 + H]^+$.

$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(C_6F_5)Me\cdot GaCl_3$ (4). To a solution of $(Me_3Si)_2N-N(SiMe_3)-P(C_6F_5)Cl$ (0.285 g, 0.592 mmol) in 4 mL CH_2Cl_2 a solution of $GaCl_3$ (0.110 g, 0.622 mmol) in 3 mL CH_2Cl_2 was added dropwise under stirring over a period of 10 min at −70 °C. The red solution was stirred for 10 min at this temperature and was then warmed to room temperature. Stirring for 12 h at this temperature resulted in a yellowish solution. Removal of solvent in vacuo yielded 0.320 g (0.87 mmol, 82%) of **4** as a colorless viscous oil. Mp 3 °C (144 °C dec). Anal calc % (found) for $C_{15}H_{27}Cl_4F_5GaN_2PSi_3$ (657.15): C 27.42 (26.87), H 4.14 (4.22), N 4.26 (4.04). NMR: (ratio A1:A2 = 60:40). $^{31}P\{^1H\}$ NMR (25 °C, CH_2Cl_2/C_6D_6, 121.5 MHz): δ = 43.6 (br), 44.6 (br). IR (ATR, 32 scans): 2959 (m), 2920 (m), 1646 (m), 1591 (w), 1520 (s), 1490 (s), 1398 (m), 1307 (m), 1259 (s), 1153 (w), 1107 (s), 1089 (w), 1028 (m), 971 (m), 950 (w), 898 (m), 880 (w), 834 (s), 807 (m), 754 (m), 725 (w), 684 (m), 647 (m), 631 (w), 584 (m). Raman (400 mW, 1000 scans, 25 °C, cm^{-1}): 2994 (3), 2965 (4), 2909 (10), 2814 (1), 1646 (2), 1591 (1), 1523 (1), 1483 (1), 1416 (2), 1307 (1), 1272 (1), 1232 (1), 1085 (1), 1029 (1), 979 (1), 946 (1), 902 (1), 875 (1), 844 (1), 797 (1), 752 (1), 734 (1), 685 (2), 639 (3), 588 (2), 512 (2), 446 (2), 421 (2), 394 (2), 358 (2), 345 (3), 288 (1), 246 (1), 204 (1), 180 (1), 151 (1), 135 (1), 115 (1).

$(Me_3Si)_2N-N(SiMe_3)-P(Me)Ph\cdot GaCl_3$ (5). To a solution of $(Me_3Si)_2N-N(SiMe_3)-P(Me)Ph$ (0.371 g, 1.00 mmol) in 5 mL CH_2Cl_2 at −60 °C a solution of $GaCl_3$ (0.185 g, 1.05 mmol) in 5 mL CH_2Cl_2 was added dropwise under stirring over a period of ten minutes. The colorless solution was warmed to room temperature and stirred for three hours. The solution was then concentrated to incipient crystallization in vacuo and stored at room temperature for one hour, resulting in the deposition of colorless crystals. Removal of supernatant and drying in vacuo yield 0.39 g (0.71 mmol, 71%) of **5** as a colorless crystalline solid. Mp 190 °C. Anal calc % (found) for $C_{16}H_{35}Cl_3GaN_2P$-Si_3 (546.77): C 35.15 (34.47), H 6.45, (6.54), N 5.12 (5.23). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = −0.04 (s, 9H, $Si(CH_3)_3$), 0.34 (s, 9H, $Si(CH_3)_3$), 0.49 (s, 9H, $Si(CH_3)_3$), 2.21 (d, 3H, $^2J(^{31}P-^1H)$ = 7.0 Hz, CH_3), 7.51−7.65 (m, 3H, *m*-Ph, *p*-Ph), 7.79 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.23 (s, $Si(CH_3)_3$), 3.63 (s, $Si(CH_3)_3$), 3.72 (s, $Si(CH_3)_3$), 8.8 (d, $^2J(^{31}P-^{13}C)$ = 43.0 Hz, CH_3), 129.4 (d, $^2J(^{31}P-^{13}C)$ = 11.8 Hz, *m*-Ph), 133.5 (br d, *p*-Ph), 133.8 (d, $^2J(^{31}P-^{13}C)$ = 11.8 Hz, *o*-Ph), *i*-Ph not displayed. ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 13.0, 13.8, 22.6. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 33.7 (br). IR (ATR, 32 scans): 2956 (m), 2900 (m), 1588 (m), 1574 (w), 1485 (m), 1439 (m), 1410 (m), 1317 (w), 1298 (w), 1282 (w), 1253 (s), 1164 (m), 1120 (m), 1103 (m), 1014 (w), 1004 (w), 994 (w), 976 (m), 920 (s), 878 (s), 826 (s), 771 (s), 749 (s), 691 (s), 667 (s), 643 (m), 623 (m), 600 (m), 585 (m). Raman (200 mW, 1049 scans, 25 °C, cm^{-1}): 3177 (1), 3149 (1), 3071 (4), 3061 (3),

3023 (2), 2995 (3), 2961 (5), 2928 (5), 2907 (10), 1589 (3), 1576 (1), 1411 (1), 1272 (1), 1252 (1), 1190 (1), 1164 (1), 1145 (1), 1 104 (1), 1029 (2), 1001 (2), 924 (1), 880 (1), 854 (1), 751 (1), 736 (1), 692 (1), 667 (1), 643 (3), 617 (1), 506 (1), 448 (1), 420 (1), 400 (1), 380 (1), 356 (3), 342 (1), 270 (1), 232 (1), 197 (1), 152 (1), 137 (1), 111 (1), 99 (1), 83 (2). MS (FAB$^+$, NBA): 210 [M − $GaCl_3$ − $N(SiMe_3)(SiMe_2Cl)$]$^+$, 247 [$N(SiMe_3)N(SiMe_3)_2$]$^+$, 355 [M − Me]$^+$, 371 [M − $GaCl_3$ + H]$^+$.

$(Me_3Si)_2N-N(SiMe_3)-P(Cl)Me\cdot GaCl_3$ (6). To a solution of $(Me_3Si)_2N-N(SiMe_3)-P(Cl)Me$ (0.443 g, 1.35 mmol) in 5 mL CH_2Cl_2 at −60 °C a solution of $GaCl_3$ (0.250 g, 1.418 mmol) in 5 mL CH_2Cl_2 was added dropwise under stirring over a period of 10 min. The colorless solution was stirred for 10 min at −60 °C and was then warmed to room temperature. The yellowish solution was then concentrated to incipient crystallization in vacuo and stored at room temperature for one hour, resulting in the deposition of colorless crystals. Removal of supernatant by syringe and drying in vacuo yielded 0.49 g (0.97 mmol, 72%) of **6** as a colorless crystalline solid. Mp 92 °C (dec). Anal calc % (found) for $C_{10}H_{30}Cl_4GaN_2PSi_3$ (505.12): C 23.78 (23.60), H 5.99, (5.99), N 5.55 (5.81). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.28 (s, 9H, $Si(CH_3)_3$), 0.37 (s, 9H, $Si(CH_3)_3$), 0.54 (s, 9H, $Si(CH_3)_3$), 2.38 (br s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 98.0 (br). IR (ATR, 32 scans): 2957 (m), 2904 (w), 1444 (w), 1406 (m), 1297 (w), 1284 (m), 1256 (s), 1162 (w), 1108 (w), 1015 (m), 1000 (w), 923 (m), 890 (s), 826 (s), 769 (w), 758 (m), 679 (w), 667 (m), 654 (w), 645 (w), 621 (m), 606 (m). Raman (200 mW, 1049 scans, 25 °C, cm^{-1}): 2964 (4), 2906 (10), 1413 (1), 1273 (1), 1254 (1), 1035 (1), 930 (1), 849 (1), 734 (1), 685 (1), 644 (4), 609 (1), 497 (1), 434 (1), 393 (2), 343 (5), 252 (1), 200 (1), 131 (1), 116 (1), 104 (1), 91 (1).

$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(C_6H_5)Me$ (7). To a solution of $(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(Ph)Me\cdot GaCl_3$ (**3a**) (1.718 g, 3.04 mmol) in 10 mL CH_2Cl_2, a solution of *N*,*N*-dimethylaminopyridine (0.389 g, 3.187 mmol) in 5 mL CH_2Cl_2 was added dropwise under stirring over a period of 10 min at 0 °C. The colorless suspension was stirred for 10 min at 0 °C and was then warmed to room temperature. After stirring for ten minutes, the solvent was removed in vacuo, resulting in a colorless residue. After addition of 10 mL *n*-hexane and stirring for 10 min in the supersonic bath, the suspension was filtered, resulting in a colorless solution. Removal of solvent and drying in vacuo resulted in a colorless solid. Sublimation at 65 °C for 2 h in vacuo yielded 0.787 g (2.02 mmol, 66%) of **7** as a colorless ceraceous solid. Mp 164 °C. Anal calc % (found) for $C_{15}H_{32}ClN_2PSi_3$ (391.11): C 46.06 (45.17), H 8.25 (7.99), N 7.16 (7.28). NMR: (ratio A1:A2 = 62:38). (A1) ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = −0.11 (s, 3H, $SiCl(CH_3)_2$), 0.26 (d, 9H, $J(^{31}P-^1H)$ = 0.8 Hz, $Si(CH_3)_3$), 0.35 (s, 9H, $Si(CH_3)_3$), 0.36 (s, 3H, $SiCl(CH_3)_2$), 1.55 (d, 3H, $^2J(^{31}P-^1H)$ = 7.5 Hz, CH_3), 7.35−7.40 (m, 3H, *m*-Ph, *p*-Ph), 7.67 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.3 (d, $J(^{31}P-^{13}C)$ = 1.8 Hz, $Si(CH_3)_3$), 3.4 (d, $J(^{31}P-^{13}C)$ = 2.2 Hz, $Si(CH_3)_3$), 4.4 (d, $^4J(^{31}P-^{13}C)$ = 1.8 Hz, $SiCl(CH_3)_2$), 5.5 (s, $SiCl(CH_3)_2$), 14.6 (d, $^1J(^{31}P-^{13}C)$ = 17.9 Hz, CH_3), 128.5 (d, $^3J(^{31}P-^{13}C)$ = 7.5 Hz, *m*-Ph), 130.2 (s, *p*-Ph), 134.2 (d, $^2J(^{31}P-^{13}C)$ = 23.8 Hz, *o*-Ph), 140.2 (d, $^1J(^{31}P-^{13}C)$ = 17.4 Hz, *i*-Ph). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 12.5, 13.6 (or 14.1), 19.3. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 41.0. (A2) ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = −0.06 (s, 9H, $Si(CH_3)_3$), 0.23 (d, 9H, $J(^{31}P-^1H)$ = 0.8 Hz, $Si(CH_3)_3$), 0.61 (s, 3H, $SiCl(CH_3)_2$), 0.63 (s, 3H, $SiCl(CH_3)_2$), 1.62 (d, 3H, $^2J(^{31}P-^1H)$ = 7.5 Hz, CH_3), 7.35−7.40 (m, 3H, *m*-Ph, *p*-Ph), 7.74 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 2.9 (d, $J(^{31}P-^{13}C)$ = 1.5 Hz, $Si(CH_3)_3$), 3.3 (d, $J(^{31}P-^{13}C)$ = 1.0 Hz, $Si(CH_3)_3$), 5.2 (s, $SiCl(CH_3)_2$), 6.4 (d, $^4J(^{31}P-^{13}C)$ = 1.0 Hz, $SiCl(CH_3)_2$), 14.9 (d, $^1J(^{31}P-^{13}C)$ = 17.9 Hz, CH_3), 128.4 (d, $^3J(^{31}P-^{13}C)$ = 7.5 Hz, *m*-Ph), 130.0 (s, *p*-Ph), 134.3 (d, $^2J(^{31}P-^{13}C)$ = 23.4 Hz, *o*-Ph), 140.1 (d, $^1J(^{31}P-^{13}C)$ = 17.0 Hz, *i*-Ph). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 11.7, 14.1 (or 13.6), 19.6. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 41.8. IR (ATR, 32 scans): 3072 (w), 3055 (w), 2957 (m), 2903 (m), 2366 (w), 2355 (w), 2336 (w), 1434 (m), 1414 (m), 1308 (m), 1247 (s), 1180 (w), 1158 (m), 1099 (m), 1070 (w), 1022 (m), 1002 (w), 985 (w), 923 (s), 896 (s), 854 (m), 829 (m), 808 (m), 790 (m), 744 (s), 698 (m), 679 (m), 652 (s), 633 (m), 618 (m), 607 (s), 589 (m), 556 (w). Raman (200 mW, 400 scans, 25 °C, cm^{-1}): 3057 (3), 2962 (5), 2906 (10), 1586 (2), 1572 (1), 1503 (1), 1411 (1), 1317 (1), 1290 (1), 1250 (1), 1180 (1), 1098 (1), 1027 (1), 1002 (2), 936 (1), 899 (1), 873 (1), 792 (1), 749 (1), 703 (1), 679 (1), 651 (1), 633 (1), 496 (1), 468 (1), 433 (1), 396 (1), 318 (1), 137 (1). MS (CI$^+$, isobutane): 355 [M − Cl]$^+$, 391 [M + H]$^+$.

$(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(C_6F_5)Me$ (8). To a solution of $(Me_2ClSi)(Me_3Si)N-N(SiMe_3)-P(C_6F_5)Me\cdot GaCl_3$ (**4**) (0.600 g, 0.913 mmol) in 10 mL CH_2Cl_2, a solution of *N*,*N*-dimethylaminopyridine (0.117 g, 0.959 mmol) in 5 mL CH_2Cl_2 was added dropwise under stirring over a period of 10 min at 0 °C. The resulting yellowish solution was stirred for 10 min at 0 °C and was then warmed to room temperature. After stirring for 1 h at this temperature, the solvent was removed in vacuo and a yellowish solid was obtained. Extraction with 8 mL *n*-hexane, filtration, and removal of solvent in vacuo resulted in a yellowish oil which slowly solidifies upon standing. Sublimation at 60 °C for 3 h yields 74 mg (0.15 mmol, 16%) of **8** as a colorless crystalline solid. Mp 52 °C. Anal calc % (found) for $C_{15}H_{27}ClF_5N_2PSi_3$ (481.06): C 37.45 (37.43), H 5.66 (4.75), N 5.82 (5.63). NMR: (ratio A1:A2 = 60:40). (A1) ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.04 (s, 3H, $SiCl(CH_3)_2$), 0.32 (s, 9H, $Si(CH_3)_3$), 0.33 (d, 9H, $J(^{31}P-^1H)$ = 1.1 Hz, $Si(CH_3)_3$), 0.44 (s, 3H, $SiCl(CH_3)_2$), 1.75 (dt, 3H, $^2J(^{31}P-^1H)$ = 9.4 Hz, $J(^{19}F-^1H)$ = 1.6 Hz, CH_3). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 3.00 (s, $Si(CH_3)_3$), 3.21 (s, $Si(CH_3)_3$), 4.49 (d, $^4J(^{31}P-^{13}C)$ = 1.8 Hz), $SiCl(CH_3)_2$), 5.83 (s, $SiCl(CH_3)_2$), 12.2−14.5 (m, CH_3). $^{19}F\{^1H\}$ NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −161.6 (m, 2F), −151.1 (tt, 1F, $^3J(^{19}F-^{19}F)$ = 20.4 Hz, $^4J(^{19}F-^{19}F)$ = 4.0 Hz), −127.4 (m, 2F). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 14.0, 17.2, 18.5. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 31.3 (t, $^3J(^{31}P-^{19}F)$ = 44.0 Hz). (A2) ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 0.03 (s, 9H, $Si(CH_3)_3$), 0.31 (d, 9H, $J(^{31}P-^1H)$ = 1.1 Hz, $Si(CH_3)_3$), 0.57 (s, 3H, $SiCl(CH_3)_2$), 0.62 (s, 3H, $SiCl(CH_3)_2$), 1.79 (dt, 3H, $^2J(^{31}P-^1H)$ = 9.7 Hz, $J(^{19}F-^1H)$ = 1.6 Hz, CH_3). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 2.9−3.1 (m, $Si(CH_3)_3$), 5.53 (s, $SiCl(CH_3)_2$), 5.88 (s, $SiCl(CH_3)_2$), 12.2−14.5 (m, CH_3). $^{19}F\{^1H\}$ NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −162.0 (m, 2F), −151.4 (tt, 1F, $^3J(^{19}F-^{19}F)$ = 20.4 Hz, $^4J(^{19}F-^{19}F)$ = 4.0 Hz), −127.4 (m, 2F). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ = 12.2, 17.2, 20.4. $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 32.7 (t, $^3J(^{31}P-^{19}F)$ = 44.0 Hz). IR (ATR, 32 scans): 2958 (m), 2903 (m), 2141 (m), 1940 (w), 1640 (m), 1514 (s), 1463 (s), 1417 (m), 1376 (m), 1284 (m), 1251 (s), 1137 (w), 1083 (s), 1020 (m), 974 (s), 918 (m), 901 (s), 861 (m), 831 (m), 808 (w), 792 (w), 754 (m), 729 (m), 710 (w), 681 (m), 655 (m), 633 (m), 605 (m), 588 (m), 534 (m). Raman (400 mW, 1000 scans, 25 °C, cm^{-1}): 3479 (1), 2969 (5), 2910 (10), 1640 (2), 1514 (1), 1498 (1), 1416 (2), 1376 (1), 1316 (1), 1283 (1), 1250 (1), 1180 (1), 1137 (1), 1082 (1), 1022 (1), 979 (1), 907 (1), 868 (1), 823 (1), 794 (1), 754 (1), 685 (2), 656 (1), 636 (3), 586 (2), 559 (1), 503 (2), 446 (2), 410 (3), 397 (2), 379 (1), 339 (1), 308 (1), 231 (1), 208 (1), 138 (1), 111 (1). MS (CI$^+$, isobutane): 445 [M − Cl]$^+$, 481 [M + H]$^+$.

■ ASSOCIATED CONTENT

Supporting Information. Experimental information, structure elucidation, synthesis of compounds, references, and a crystallographic information file. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

We are indepted to R. Kuzora and Dr. C. Hubrich (Univ. Rostock). Generous support by the University of Rostock is gratefully acknowledged. We would like to thank the Deutsche Forschungsgemeinschaft (SCHU 1170/4-1) for financial support.

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