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An Unusual Reaction: a $GaCl_3$-Assisted Methyl/Chlorine Exchange in Silylated Hydrazinodichloroarsane

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N,N′,N′-[Tris(trimethylsilyl)]hydrazino(dichloro)arsane, $(Me_3Si)_2N–N(SiMe_3)–AsCl_2$ (**1**), has been transformed into the corresponding *N*-trimethylsilyl-*N′,N′*-bis-(dimethylchlorosilyl)hydrazinodimethylarsane in a two-step synthesis: (i) Addition of $GaCl_3$ to **1** results in the formation of the corresponding hydrazinodimethylarsane $GaCl_3$ adduct (**2**). (ii) Reaction of **2** with 4-(dimethylamino)pyridine (DMAP) yielded the adduct-free hydrazinodimethylarsane (**3**). The intriguing methyl/chlorine exchange with $GaCl_3$ as transfer/exchange reagent represents a new synthetic route to the hitherto unknown *N*-trimethylsilyl-*N′,N′*-bis-(dimethylchlorosilyl)hydrazinodimethylarsane in contrast to the same reaction of the phosphorus analogue that results in the formation of triazadiphospholes. The new exchange reaction was unambiguously proven by NMR and X-ray studies (**1**: monoclinic, $P2_1/c$, $a = 9.5002(19)$ Å, $b = 13.840(3)$ Å, $c = 17.226(5)$ Å, $\beta = 120.12(2)°$; $V = 1959.1(8)$ Å^3, $Z = 4$; **2**: orthorhombic, *Pbca*; $a = 11.7766(2)$ Å, $b = 13.9927(2)$ Å, $c = 28.3298(4)$ Å; $V = 4668.37(12)$ Å^3, $Z = 4$; **3**: monoclinic, $P2_1/c$, $a = 12.015(2)$ Å, $b = 12.466(3)$ Å, $c = 13.031(3)$ Å, $\beta = 98.20(3)°$; $V = 1931.8(7)$ Å^3, $Z = 4$). Structural comparisons of the hydrazinoarsanes with their $GaCl_3$ adducts provide interesting similarities and differences. Computations at the B3LYP level reveal that the exchange process is –34 kcal/mol exergonic.

Introduction

$GaCl_3$-assisted elimination reactions followed by [3+2] cycloadditions[1] have been established in chemistry only recently.[2−4] This new reaction type was first applied in phosphorus/nitrogen chemistry to the reaction of silylated hydrazino(dichloro)phosphane, $(Me_3Si)_2N{-}N(SiMe_3){-}PCl_2$, with $GaCl_3$ resulting in the formation of the novel neutral triazadiphosphole, RN_3P_2 ($R = (Me_3Si)_2N$) stabilized as $GaCl_3$ adduct (Scheme 1).[2] Since this reaction only occurs when $GaCl_3$ is added to a solution of $(Me_3Si)_2N{-}N(SiMe_3){-}PCl_2$ in common organic solvents (e.g., CH_2Cl_2, benzene, etc.), this new reaction type was coined a $GaCl_3$-assisted [3+2] cycloaddition. Interestingly, $(Me_3Si)_2N{-}N(SiMe_3){-}PCl_2$ represents an ambivalent species which can react as dipolarophile and/or 1,3-dipole as displayed in Scheme 1. In any case, $GaCl_3$ is needed to release the “disguised” dipolarophile and 1,3-dipole, respectively, by triggering the $Me_3Si{-}Cl$ elimination. Hence, $GaCl_3$ is responsible for two important things: (i) decreasing of the activation barrier to $Me_3Si{-}Cl$ elimination[5] and (ii) stabilization of the “naked” azaphosphole by adduct formation.[2−4]

Shortly thereafter, the concept of a $GaCl_3$-assisted [3+2] cycloaddition was proven first in the reaction of kinetically stabilized iminophosphane, $Mes^*{-}N{=}P{-}Cl$, ($Mes^* = 2,4,6$-

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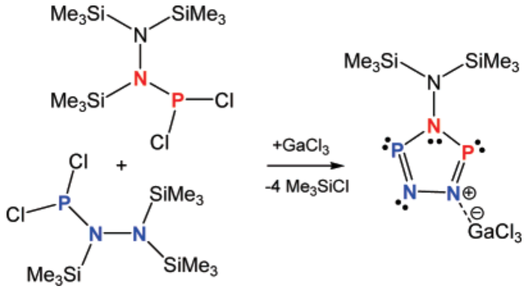
Scheme 1. $GaCl_3$-Assisted [3+2] Cycloaddition with the Ambivalent Hydrazino(dichloro)phosphane, $(Me_3Si)_2N{-}N(SiMe_3){-}PCl_2$, Which Can React as Dipolarophile and/or 1,3-Dipole, Leading to Triazadiphospholes

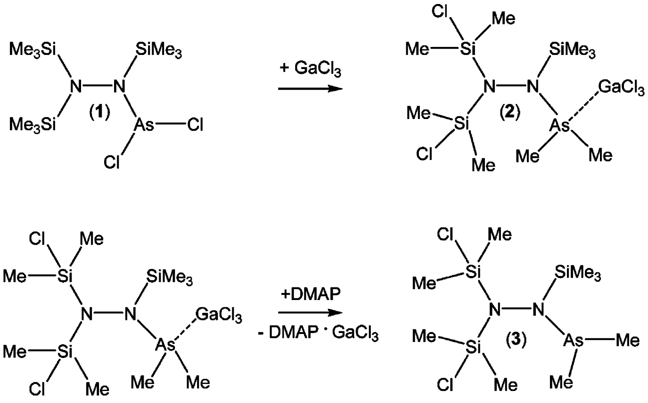


tri-*tert*-butylphenyl), a good dipolarophile, with the "disguised" 1,3-dipole $(Me_3Si)_2N{-}N(SiMe_3){-}PCl_2$ leading to the formation of another triazadiphosphole[4] (RN_3P_2, R = Mes*), and second the first tetrazaphosphole,[6] $R'N_4P$ (R = Mes*) was obtained when Mes*−N=P−Cl is reacted with $Me_3Si{-}N_3$ in the presence of $GaCl_3$.

All studied $GaCl_3$-assisted [3+2] cycloadditions represent fast, high-yielding (>95%), and clean reactions and can be carried out even at low temperatures (−30−25 °C) whereas, for example, triazole-forming cycloaddition may require elevated temperatures.[1]

In contrast to the well-established PN chemistry with low-coordinated phosphorus(III),[7−9] the chemistry of compounds containing low-coordinated arsenic(III) has been studied less widely.[10] Hence, it seemed promising to apply the $GaCl_3$-assisted [3+2] cycloaddition to arsenic, especially since binary azarsoles of the type RN_xAs_y (R = bulky group, x, y = 1−4 with $x + y = 5$) are completely unknown. Herein we report on the synthesis and reaction of $(Me_3Si)_2N{-}N(SiMe_3){-}AsCl_2$ (**1**) with $GaCl_3$ resulting in an intriguing methyl/chlorine exchange. Moreover, the structure, bonding, and charge transfer of hydrazinoarsane adducts and the free arsanes are discussed on the basis of experimental (X-ray elucidation) and theoretical data (DFT calculations).

Scheme 2. $GaCl_3$-Assisted Methyl/Chlorine Exchange in Hydrazino(dichloro)arsane, $(Me_3Si)_2N{-}N(SiMe_3){-}AsCl_2$



Results and Discussion

Treatment of N,N',N'-[tris(trimethylsilyl)]hydrazino(dichloro)phosphane, $(Me_3Si)_2N{-}N(SiMe_3){-}PCl_2$, with gallium trichloride, yielded the kinetically stabilized 4-bis(trimethylsilyl)amino-1,2,4,3,5-triazadiphosphole (Scheme 1). Therefore, we adopted this method to synthesize the analogous arsenic compound. However, the reaction of **1** with $GaCl_3$ resulted in the unexpected formation of a silylated hydrazino(dimethyl)arsane gallium trichloride adduct (**2**), as shown in Scheme 2.

The formation of the intriguing hydrazino(dimethyl)arsane $GaCl_3$ adduct was unequivocally proven by 2D NMR (^1H vs ^{13}C), X-ray, and MS studies. Furthermore, the methyl/chlorine exchange was confirmed by the removal of the Lewis acid (Scheme 2) with the help of a stronger base such as DMAP, 4-(dimethylamino)pyridine, yielding the free hydrazino(dimethyl)arsane (**3**) which also has been fully characterized (NMR, X-ray, MS). Both reactions (Scheme 2) can be reproduced with moderate yields (ca. 53−54%).

To the best of our knowledge, $GaCl_3$-assisted methyl/chlorine exchange reactions between silicon and arsenic or even other elements have not been reported yet. Si−C cleavage in reactions with $GaCl_3$ is known,[11] e.g., a methyl migration from silicon to gallium was previously 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 Me_3SiCl and $(MeGaCl_2)_2$. In contrast to this reaction, $GaCl_3$ works only as a catalyst in the intramolecular Cl/Me exchange reaction of **1**.

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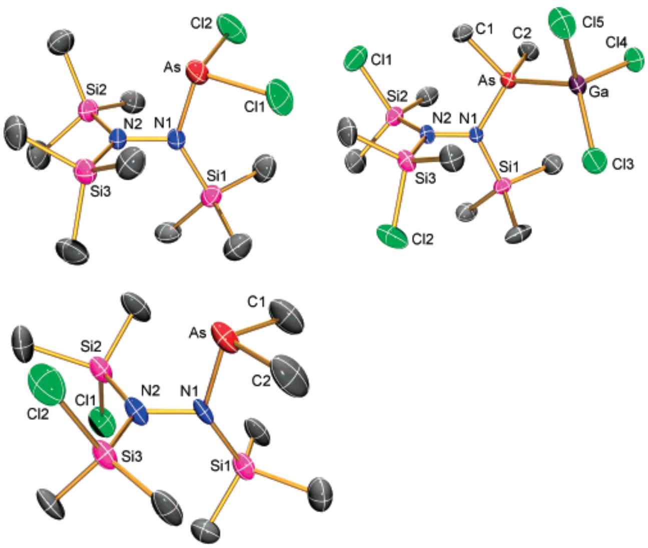

Figure 1. ORTEP drawing of the molecular structure of one independent molecule of **1**, **2**, and **3** in the crystal. Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted for clarity).

Another similar reaction was published by Carmalt et al. in the reaction of $GaCl_3$ with $(Me_3Si)_3N$, yielding, among other things, dimeric $(MeGaCl_2)_2$.[12] 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. Hence, $GaCl_3$ is again part of the exchange reaction, whereas in the reaction between **1** and $GaCl_3$ (Scheme 2), the $GaCl_3$ works only as transfer reagent.

Synthesis. **1** was isolated in a high-yield two-step synthetic procedure:[13] (i) lithiation of tris(trimethylsilyl)hydrazine with *n*-BuLi at 20 °C and (ii) addition of $AsCl_3$ at low temperature (−40 °C). The facile synthesis of **2** from **1** simply by adding 1 equiv of $GaCl_3$ was carried out in CH_2Cl_2 at −15 °C, yielding an orange solution. Within 3 h this reaction mixture was slowly warmed up to ambient temperature, and after removal of the solvent, a red oil was isolated. After extraction and recrystallization from *n*-pentane at 5 °C, pure colorless crystals of **2** suitable for X-ray studies were isolated. With a view to preparing the free hydrazino(dimethyl)arsane, the acid/base reaction of **2** was carried out with DMAP as base. Accordingly, a solution of **2** in CH_2Cl_2 was reacted with 1 equiv of DMAP at 0 °C. A colorless precipitate of DMAP·$GaCl_3$ was observed immediately. After removal of CH_2Cl_2, the residue was extracted with *n*-pentane. Recrystallization at −35 °C from CF_3Cl yielded colorless crystals of **3**. Analytical and spectroscopic data for **3** were consistent with the formation of the Lewis acid free hydrazino(dimethyl)arsane.

Compound **1**, **2**, and **3** are thermally stable up to over 100 °C. **1** and **3** are volatile at this temperature in a vacuum. Hence, both crude products (of **1** and **3**) are easily purified by sublimation (**1**, 60 °C; **3**, 20 °C; 10−3 mbar). Since recrystallization of **1** and **3** from organic solvents leads only to colorless, very ceraceous solids (often amorphous), it is extremely difficult to obtain crystals suitable for X-ray studies. We finally succeeded after slow evaporation of CF_3Cl from a saturated solution of **1** and **3**, respectively.

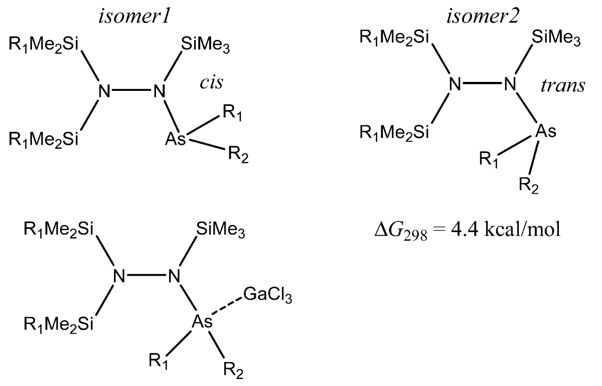

Figure 2. Isomers of hydrazinoarsanes ($R_{1,2}$ = Me, Cl).

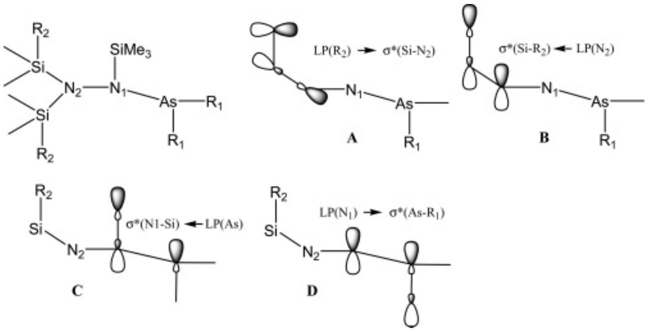

Figure 3. Intramolecular donor−acceptor interaction (hyperconjugation) according to NBO analysis displaying the delocalization of lone pairs in hydrazinoarsanes ($R_{1,2}$ = C, Cl; R_2 = Cl in A).

All three species are extremely air and moisture sensitive, but under argon, they are stable over a long period in both solid and common organic solvents (e.g., benzene, CH_2Cl_2, ether, etc.). The very good solubility in almost all common organic solvents makes all three arsanes good precursors for further synthesis. It should be noted that both **1** and **2** are odorless while **3** is a very malodorous substance.

Structure and Bonding. Crystallographic data of **1**, **2**, and **3** have been summarized in Table 1. The perspective view of **1**, **2**, and **3** is depicted in Figure 1, selected structural data are given in Table 2. According to our computations two different isomers that are close in energy (ΔG_{298} = 4.4 kcal/mol) are possible, a cis and a trans isomer (Figure 2). Interestingly, while the adduct **2** adopts the trans configuration, the $GaCl_3$-free compounds **1** and **3** display the energetically favored cis configuration (Figures 1 and 2, see also next section). Obviously, upon adduct formation, steric repulsion forces the hydrazinoarsane into cis configuration. Furthermore, the X-ray experiment of **2** revealed an unusual eclipsed configuration along the As···Ga donor−acceptor bond. This eclipsed configuration represents a transition state at the level of theory applied with a small activation barrier to rotation of ΔG_{298} = 2.6 kcal/mol, as shown by DFT computations (see next section). Thus, a very flat potential energy surface for the intramolecular rotation about the

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Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
formula	$C_9H_{27}Cl_2N_2AsSi_3$	$C_9H_{27}Cl_5GaN_2AsSi_3$	$C_9H_{27}AsCl_2N_2Si_3$
fw	393.42	569.49	393.42
color	colorless	colorless	colorless
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
a, Å	9.5002(19)	11.7766(2)	12.015(2)
b, Å	13.840(3)	13.9927(2)	12.466(3)
c, Å	17.226(5)	28.3298(4)	13.031(3)
α, deg	90.00	90.00	90.00
β, deg	120.12(2)	90.00	98.20(3)
γ, deg	90.00	90.00	90.00
V, Å^3	1959.1(8)	4668.4(1)	1931.8(7)
Z	4	8	4
$\rho_{calcd.}$, g cm^{-3}	1.334	1.620	1.353
μ, mm^{-1}	2.178	3.307	2.208
$\lambda_{\text{Mo Ka}}$ [Å]	0.71073	0.71073	0.71073
T, K	200(2)	200(2)	200(2)
reflns collected^a	21 967	28 431	11 456
independent reflns	4489	5341	2050
obsd. reflns	3541	4064	1935
R_{int}	0.0622	0.074	0.0644
F(000)	816	2288	816
R1^b	0.0457	0.0365	0.0744
wR2^c	0.0948	0.0948	0.1907
GOF	1.102	1.03	1.163
no. params/ restraints	163	190	163
CCDC No.	642027	642028	642029

[a] $I > 2\sigma(I)$. [b] Final R [$I > 2\sigma(I)$]. [c] R indices (all data).

As···Ga bond can be assumed and only small lattice effects are necessary to favor the observed eclipsed arrangement.

As expected for silylated hydrazine compounds,[5] all three species revealed similar structural features with respect to the hydrazine moiety: (i) all species have a distorted trigonal-planar geometry (sum of angles ca. 360°) around the two nitrogen atoms and both trigonal planes are almost perpendicular to each other (Table 2, ∠Si3−N2−N1−As = 85−97°) and (ii) all silyl groups adopt a staggered configuration.

Hence, as displayed by NBO analysis,[14] the one lone pair on both nitrogen atoms is localized in a pure p-type atomic orbital. Both lone pairs are also perpendicular to each other.[15] As a consequence, the p-type lone pair at the N1 atom (notation: p-LP) is slightly further delocalized resulting in intramolecular interactions (noncovalent effects). As indicated by an investigation of the noncovalent effects,[14] there are two significant interactions of the N1 lone pair (p-LP) with the two unoccupied, localized antibonding σ*(As−R$_1$) orbitals (Figure 3D, Table 3). The fairly diffuse lone pair localized at the As atom possesses a large amount of s character (**1**, 82%; **3**, 67%)[16,17] and interacts only weakly with the unoccupied σ*(N−Si) bond orbital (Figure 3C). Both intramolecular donor−acceptor interactions (R$_1$ = Cl in **1** and R$_1$ = C in **2**, **3**; Figure 3C and D; Table 3) account for the rather short As−N1 distance (with the strongest interaction in **1**) by introducing a small amount of π interaction (Figure 3C and D). In agreement with the order of the donor−acceptor interactions (**1** > **2** ≅ **3**), the smallest As−N bond length is found in **1** with 1.804(2) Å followed by 1.851(2) Å in **2** and 1.856(6) Å in **3** (cf. $\sum r_{cov}$ = 1.91 Å).[18] Similar structural features with short As−N distances (1.82−1.88 Å)[19] have already been observed in a series of amino/iminoarsanes[13a,20,21] and cyclo-triarsa-1,3,5-triazanes (cf. 1.707(2) Å in the iminoarsane RAs═NR, R = 2,4,6-tris(trifluoromethyl)phenyl).[22]

The arsenic atom of the hydrazinoarsanes sits in a pyramidal environment with bond angles between 93° and 104°. As expected upon adduct formation, the N−N−As angle increases from 104.9(2)° (in **1** and **3**) to 115.6(2)° (in **2**) due to an enlarged steric repulsion introduced by the bulky $GaCl_3$ fragment. Besides, the As···N2 distance increases from 2.606(2) Å in **1** and 2.667(6) Å in **3** to 2.811(2) Å in **2** when the adduct is formed. Actually, these As···N2 distances are fairly short ($\sum r_{vdW}$ = 3.54 Å), indicating strong intramolecular van der Waals interactions.

As expected, the two $Me_2(Cl)Si$ groups of the amino moiety in **2** and **3** adopt a staggered position with the Cl atoms in a trans configuration and parallel to the lone pair localized at the amino nitrogen atom. Hence, delocalization of lone pair electron density along the Cl−Si−N unit according to Figure 2A and B is observed. Upon adduct formation, a significant decrease of the Si−Cl bond distance is found (**2**, 2.072(1) and 2.069(1) Å; **3**, 2.122(3) and 2.205(3) Å).

Adducts such as **2** are typical charge-transfer complexes, and the bond between the $GaCl_3$ and the hydrazinoarsane can be regarded as a donor−acceptor bond[2] (d(Ga−As) = 2.4897(5) Å; cf. 2.470−2.581 Å in $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$).[23] According to NBO analysis, the charge transfer is about 0.37e in **2** (cf. 0.17e in the $(Me_3Si)_2N(SiMe_3)−NAsCl_2\cdot GaCl_3$ adduct). The σ-bond system in all considered hydrazinoarsanes along the As−N1−N2 unit is highly polarized between As and N1 and is almost ideally covalent between the adjacent N1−N2 single bonds with bond distances of 1.463(3)−1.493(8) Å (Table 2). The calculated natural atomic population (NAO)[14] net charges in the adduct **2** are Q_{As} = +1.27e on arsenic, Q_{N1} = −1.03e on the adjacent nitrogen and Q_{N2} = −1.17e on the second nitrogen atom (a summary of all partial charges can be found in Table S1 of the Supporting Information).

Chlorine/Methyl Exchange. To gain further insight into the intriguing $GaCl_3$-assisted chlorine/methyl exchange, DFT

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Table 2. Comparison of Selected Bond Distances (Å), Selected Bond Angles (deg), and Sums of Angles at Selected Centers

	1	**2**	**3**
N1−N2	1.473(3)	1.463(3)	1.493(8)
N1−As	1.804(2)	1.851(2)	1.856(6)
N2···As	2.606(2)	2.811(2)	2.667(6)
As−$R_{1,2}$[a]	2.2033(10)/2.2333(12)	1.924(3)/1.936(3)	1.874(9)/2.014(10)
As−Ga	−	2.4897(5)	−
Si−Cl	−	2.072(1), 2.069(1)	2.122(3), 2.205(3)
N2−N1−As	104.93(16)	115.6(2)	105.0(4)
As−N1−Si1	132.51(13)	122.5(1)	133.4(3)
N2−N1−Si1	122.26(17)	121.0(2)	120.8(4)
R1−As−R2	94.74(4)	103.0(2)	93.2(5)
Cl−Ga−Cl	−	110.4−112.5	−
∑N1	359.7	359.1	359.2
∑N2	360.0	359.5	359.9
Si2−N2−N1−As	91.14(18)	90.9(4)	91.8(4)

[a] R = Cl in **1** and C in **2** and **3**.

Table 3. Intramolecular Donor−Acceptor Interactions[a]

	Figure 3A	Figure 3B	Figure 3C	Figure 3D
1 (cis)	−	5.6/2.4	4.4	14.4/4.2
2 (trans)	8.8/7.8	10.4/8.6	−	6.2/1.0
3 (cis)	8.5/8.0	10.2/10.2	2.9	4.9/1.9

[a] The second-order perturbation energies are given in kcal/mol.[34]

computations have been carried out. Experimentally, we know that the reaction of the phosphorus analogue results in the formation of triazadiphosphole adducts with almost 100% yield (Scheme 1),[2−4] while the heavier arsenic species prefers the formation of a $GaCl_3$ adduct which is accompanied by a Cl/CH_3 exchange (Scheme 2, yield 53%). Interestingly, the Cl/CH_3 exchange represents an exergonic process for both hydrazinodichloropnictogens according to eq 1 (E = P, As). However, the exchange reaction of the phosphorus analogue is energetically preferred by 11.4 kcal/mol ($\Delta_{eq1}G_{298} = -45.4$ (P), -34.0 kcal/mol (As)). Also, comparison of both formal adducts reveals an exergonic process according to eq 2 ($\Delta_{eq2}G_{298} = -25.8$ (P); -15.2 kcal/mol (As)). Without $GaCl_3$, neither the cyclization nor the Cl/Me exchange reaction can be observed, although at least the latter one is still exergonic for both species ($\Delta_{eq3}G_{298} = -22.4$ (P); -20.3 kcal/mol (As)):

$$(Me_3Si)_2N{-}(Me_3Si)N{-}ECl_2 + GaCl_3 \rightarrow (Me_2(Cl)_2Si)N{-}(Me_3Si)N{-}E(Me)_2{\cdot}GaCl_3 \tag{1}$$

$$(Me_3Si)_2N{-}(Me_3Si)N{-}ECl_2{\cdot}GaCl_3 \rightarrow (Me_2(Cl)Si)_2N{-}(Me_3Si)N{-}E(Me)_2{\cdot}GaCl_3 \tag{2}$$

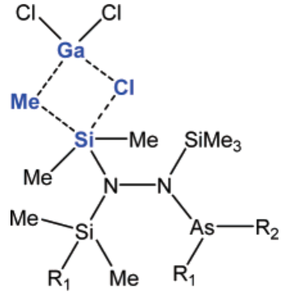
$$(Me_3Si)_2N{-}(Me_3Si)N{-}ECl_2 \rightarrow (Me_2(Cl)Si)_2N{-}(Me_3Si)N{-}E(Me)_2 \tag{3}$$

$$2(Me_3Si)_2N{-}(Me_3Si)N{-}ECl_2 \rightarrow (Me_3Si)_2N{-}(N_3E_2)_{ring} + 4Me_3SiCl \tag{4}$$

$$2(Me_3Si)_2N{-}(Me_3Si)N{-}ECl_2 + GaCl_3 \rightarrow (Me_3Si)_2N{-}(N_3E_2)_{ring}{\cdot}GaCl_3 + 4Me_3SiCl \tag{5}$$

In the case of the hydrazinodichlorophosphane, a 1,2-elimination of $Me_3Si{-}Cl$ is assumed as an initial step finally leading to the triazadiphosphole in an exergonic reaction (Scheme 1). The formation of the analogue triazadiarsole was not observed although also exergonic ($\Delta_{eq4}G_{298} = -71.6$ (P); -64.8 kcal/mol (As); $\Delta_{eq5}G_{298} = -79.7$ (P); -86.8 kcal/mol (As)).

Scheme 3. Suggested Transition State for the Me/Cl Exchange



Because of the electronegativity difference between Si and C, the Me groups in $SiMe_3$ are partially negatively charged. The delocalization of the p-type lone pair of the adjacent N into the σ^*(Si−C) bonds (Figure 3B) enhances the negative charge, especially on the C atoms perpendicular to the lone pair. This interaction weakens the Si−C bond. The Si−C bond cleavage/Si−Cl bond formation possibly occurs via an intermediate with bridging Me and Cl between Si and Ga as shown in Scheme 3. Such a direct concerted Me/Cl exchange via a four-membered transition state has already been assumed by Schmidbaur and Findeiss[11a] in the reaction of $GaCl_3$ with $SiMe_4$ yielding Me_3SiCl and $MeGaCl_2$. A similar situation can be discussed for the second exchange process between $MeGaCl_2$ and the $RAsCl_2$ moiety (R = hydrazine group).[24] Nevertheless, $GaCl_3$ is always involved in four Me/Cl exchange reactions. In the exchange $GaCl_3$ acts *only* as Cl/Me transfer reagent until the exchange reactions are finished and the $GaCl_3$ adduct **2** is formed. (It should be

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(24) So far we can not rule out the following other mechanisms: (i) intermolecular steps (two molecules of **1** can be involved) along the reaction path and (ii) ionic species may be involved in the reaction, e.g., a chlorine abstraction induced by the Lewis acid $GaCl_3$ resulting in a $GaCl_4$ salt seem to be possible.

noted that reaction mixture of $GaCl_3$ and $GaMe_3$ display rapid Me/Cl exchange, as shown by ^{71}Ga NMR studies.)[25]

Of course, the phosphorus analogue of **1** shows similar structural and electronic features, so that $GaCl_3$ should also be capable of attacking the $SiMe_3$ groups in $(Me_3Si)_2N-N(SiMe_3)-PCl_2$, which, however, was not experimentally observed. So far we have no explanation for the different reaction pathways (Schemes 1 and 2), but we do stress that both reactions can easily be reproduced in high yields. The potential energy surfaces of $(Me_3Si)_2N-N(SiMe_3)-ECl_2 + GaCl_3$ (E = P, As) are currently under investigation.

Conclusion

In contrast to the $GaCl_3$-assisted formal [3+2] cycloaddition of hydrazino(dichloro)phosphane, for the arsenic analogue, a new reaction pathway was observed resulting in an intriguing methyl/chlorine exchange with $GaCl_3$ as the transfer reagent. This new exchange reaction was unambiguously proven by NMR and X-ray studies. Computations at the B3LYP level of theory indicate an exergonic exchange reaction for both the phosphorus and arsenic analogues which, however, was only observed in the latter case. The thermodynamic stabilization of these chlorinated systems appears in the important antiperiplanar interactions between nitrogen/chlorine lone pairs and adjacent σ^* acceptor orbitals. In future studies, we will investigate if this methyl/chlorine exchange reaction triggered by addition of $GaCl_3$ can be generalized and applied to similar element organic species.

Experimental Section

Caution: *Due the high toxicity of organoarsenic compounds, proper safety precautions are necessary.*

General Information. All manipulations were carried out under oxygen- and moisture-free conditions using standard Schlenk or drybox techniques. Diethyl ether and *n*-pentane were distilled under argon from sodium benzophenone immediately before use. Dichloromethane was dried over P_4O_{10} and freshly distilled prior to use. Bis[lithium-tris(trimethylsilyl)hydrazide] was prepared according to the procedure given in the literature.[26,27] Arsenic trichloride was purchased from Merck; DMAP and gallium trichloride from Aldrich Chemical Co, and CF_3Cl from Dupont. All chemical were dried and purified prior to use.

^{1}H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were obtained on a JEOL EX 400 NMR spectrometer (400.2, 100.6, and 79.5 MHz respectively) or on a BRUKER ARX 300 NMR spectrometer (75.5 MHz ^{13}C) and were referenced either to protic impurities in the deuterated solvent (^{1}H) or externally to $SiMe_4$ ($^{13}C\{^1H\}$,$^{29}Si\{^1H\}$). A Perkin-Elmer Spectrum One FT-IR spectrometer with a DuraSampl*IR*II Diamond ATR sensor from SensIR Technologies was used to obtain the IR spectra. A Perkin-Elmer Spectrum 2000 NIR FT equipped with a Nd:YAG laser (1064 nm) was used to obtain Raman spectra. An Analysator Elementar Vario EL was used for elemental analysis (CHN). A Jeol MStation JMS 700 was used for mass spectra. Melting points are uncorrected (Büchi B540).

X-ray Structure Determination. X-ray quality crystals of **1** and **2** were selected at −50 °C in Galden HT230 oil and mounted on a glass fiber in a low-temperature N_2 stream. A suitable crystal of compound **2** was selected in silicon oil at room temperature. All samples were cooled to 200(2) K during measurement. Data for compounds **1** and **3** were collected on a Oxford Xcalibur3 CCD diffractometer; data for compound **2** was collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ nm). The structures were solved by direct methods (SHELXS-97 (**1** and **3**); SIR-97 (**2**))[28,29] and refined by full-matrix least-squares procedures (SHELXL-97). Semiempirical absorption corrections were applied for **1** and **3** using the ABSPACK[30] program, and a numerical absorption correction for **2** using XRed.[31] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the refinement at calculated positions using a riding model.

***N*,*N*′,*N*′-[Tris(trimethylsilyl)]hydrazino(dichloro)arsane (1).**[13] Two methods have been applied. (i) To a solution of $AsCl_3$ (3.988 g, 22.0 mmol) in diethyl ether (25 mL) at −40 °C was added a solution of lithium-*N*,*N*′,*N*′-[tris(trimethylsilyl)]hydrazide, $LiN(SiMe_3)N(SiMe_3)_2$, (5.090 g, 20.0 mmol) in diethyl ether (100 mL) slowly over 20 min. The slurry was stirred at 20 °C for 12 h, and precipitation of LiCl was observed. The solvent was removed at 20 °C, and the residue was extracted over a frit (F4) with *n*-pentane (20 mL). The solvent was removed under vacuum, yielding a white ceraceous solid of **1**. Yield: 5.90 g (86%). (ii) To a solution of *N*,*N*′,*N*′ tris(trimethylsilyl) hydrazine, $(Me_3Si)_2N-N(SiMe_3)H$ (2.466 g, 10.0 mmol) in diethyl ether (40 mL) at 20 °C was added a solution of *n*-BuLi (6.25 mL, 1,6 M solution, 10 mmol) in diethyl ether over a period of 10 min. After being stirred for 1 h at 20 °C, the volume of the reaction mixture was increased to 60 mL and slowly added to a solution of $AsCl_3$ (1.994 g, 11.0 mmol) in diethyl ether (25 mL) at −40 °C. The slurry was stirred at 20 °C for 12 h. The solvent was removed, and the residue was extracted over a frit (F4) with *n*-pentane (40 mL). The solvent was removed under vacuum, yielding a white ceraceous solid of **1**. Yield: 3.28 g (83%). **1** was sealed in glass tubes and stored at −20 °C. **1** was purified by sublimation (10^{-3} mbar, 60 °C) prior to use. mp: 92 °C (sublimation). FT-IR (cm^{-1}): 2955 vs, 2901 m, 1442 w, 1405 w, 1250 vs, 1025 m, 911 s, 867 s, 828 vs, 814 vs, 766 m, 753 m, 681 w, 651 m, 634 w, 619 w. Raman (200 mW, 25 °C, cm^{-1}): 2960 (44), 2903 (100), 1411 (15), 1269 (3), 1253 (4), 1027 (4), 878 (9), 837 (7), 752 (8), 685 (20), 654 (43), 637 (44), 563 (6), 396 (28), 382 (35), 357 (94), 322 (58), 230 (27), 185 (32), 135 (9). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 0.24 (s, 18 H, $((CH_3)_3Si)_2N$), 0.39 (s, 9 H, $((CH_3)_3Si)_2N$). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 2.31 (s, $((CH_3)_3Si)_2N$), 2.39 (s, $((CH_3)_3Si)_2N$). ^{29}Si NMR (CD_2Cl_2, 25 °C): δ 14.1 (s, $(Si(CH_3)_3)_2N$), 21.1 (s, $Si(CH_3)_3$). $C_9H_{27}N_2AsCl_{32}$ (393.41): calcd N 7.12, C 27.48, H 6.92, Cl 18.02; found N 6.99, C 27.49, H 7.06, Cl 17.84. Crystals suitable for single-crystal X-ray studies were obtained by cooling a saturated solution of **1** in CF_3Cl slowly to −35 °C.

***N*-Trimethylsilyl-*N*′,*N*′-bis-(dimethylchlorosilyl)hydrazinodimethylarsane $GaCl_3$ adduct (2).** A solution of $GaCl_3$ (0.194

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g, 1.1 mmol) in dichloromethane (20 mL) was added slowly to a solution of **1** (0.393 g, 1.0 mmol) in dichloromethane (20 mL) at −15 °C. Within 3 h the orange solution was warmed up to ambient temperature, with constant stirring. Removal of the solvent in vacuo deposited a red oil, which was extracted with *n*-pentane (10 mL). After separation of the two phases, the *n*-pentane was removed in vacuo, yielding colorless crystals. Yield: 0.30 g (53%); mp: 70 °C (dec). FT-IR (cm^{-1}): 2961 s, 2930 m, 2906 m, 1583 w, 1505 w, 1405 m, 1256 vs, 1042 m, 922 s, 886 m, 826 vs, 802 vs, 759 m, 685 w, 667 m, 640 w. Raman (200 mW, 25 °C, cm^{-1}): 3025 (12), 3001 (25), 2971 (40), 2932 (74), 2908 (91), 1411 (16), 1265 (5), 1043 (20), 889 (7), 812 (13), 760 (10), 689 (25), 642 (36), 623 (49), 592 (76), 501 (8), 479 (22), 399 (40), 383 (100), 351 (80), 287 (23), 234 (46), 192 (49), 140 (23). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 0.42 (s, 9 H, $(CH_3)_3Si$), 0.71 (s, 6 H, $(CH_3)_2ClSi$), 0.72 (s, 6 H, $(CH_3)_2Si$), 1.94 (s, 6H, $(CH_3)_2As$). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 2.34 (s, $Si(CH_3)_3$), 4.52 (s, $(CH_3)_2ClSi$), 4.61 (s, $(CH_3)_2ClSi$), 12.8 (s, $(CH_3)_2As$). ^{29}Si NMR (CD_2Cl_2, 25 °C): δ 14.8 (s, $SiCl(CH_3)_2$), 23.5 (s, $Si(CH_3)_3$). MS (EI, 70 eV, >5%, 25 °C); *m*/*z* (%): 392 (60) $[M]^+$, 377 (89) $[M - Me]^+$, 357 (65) $[M - Cl]^+$, 287 (59) $[M - AsMe_2]^+$. $C_9H_{27}N_2Cl_5AsGaSi_3$ (569.49): calcd C 18.98, H 4.78, N 4.92, Cl 31.24; found C 18.51, H 4.79, N 4.92, Cl 31.09. Crystals suitable for single-crystal X-ray studies were obtained by cooling a saturated solution of **2** in *n*-pentane slowly to 5 °C.

***N*-Trimethylsilyl-*N′*,*N′*-bis-(dimethylchlorosilyl)hydrazinodimethylarsane (3).** A solution of DMAP (0.134 g, 1.1 mmol) in dichloromethane (5 mL) was added to a solution of **2** (0.569 g, 1.0 mmol) in dichloromethane (30 mL) at 0 °C over 10 min. After being stirred for 10 min at ambient temperature, the solvent was removed in vacuo. The residue was extracted with *n*-pentane (20 mL) over a frit (F4). Removal of the *n*-pentane yielded a white, very ceraceous solid of **3**. Yield: 0.21 g (54%); mp: 142 ° (dec). FT-IR (cm^{-1}): 2961 vs, 2911 s, 2722 m, 2603 w, 1565 w, 1503 w, 1410 m, 1252 vs, 1123 w, 1098 w, 1033 m, 951 s, 871 s, 825 s, 801 vs, 747 m, 665 m, 632 w. Raman (200 mW, 25 °C, cm^{-1}): 2966 (39), 2911 (100), 2800 (5), 1416 (17), 1248 (6), 1033 (3), 804 (5), 776 (6), 751 (5), 684 (20), 633 (30), 564 (60), 478 (10), 402 (15), 386 (47), 314 (8), 239 (38), 191 (36). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 0.22 (s, 9 H, $(CH_3)_3Si$), 0.63 (s, 12 H, $((CH_3)_2ClSi)_2N$), 1.29 (s, 6H, $(CH_3)_2As$). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 3.19 (s, $Si(CH_3)_3$), 4.31 (s, $(CH_3)_2ClSi$), 4.74 (s, $(CH_3)_2ClSi$), 15.4 (s, $(CH_3)_2As$). ^{29}Si NMR (CD_2Cl_2, 25 °C): δ 14.3 (s, $SiCl(CH_3)_2$), 20.4 (s, $Si(CH_3)_3$); *m*/*z* (%): 392 (49) $[M]^+$, 377 (100) $[M - Me]^+$, 357 (49) $[M - Cl]^+$, 287 (60) $[M - AsMe_2]^+$, 93.1 (10) $[ClMe_2Si]^+$, 73.1 (26) $[Me_3Si]^+$. $C_9H_{27}N_2Cl_5AsGaSi_3$ (393.41): calcd C 27.48, H 6.92, N 7.12, Cl 18.02; found C 27.71, H 6.94, N 6.93, Cl 17.62. Crystals suitable for single-crystal X-ray studies were obtained by cooling a saturated solution of **3** in CF_3Cl slowly to −35 °C.

Computational Details. Our goal was to compare the structures and energetics of different $GaCl_3$ adducts and isomers of hyradrazinophosphanes and arsanes. Therefore, it was important to carry out the calculations in such a way that the results could be compared reliably with each other. The structural and vibrational data of all considered species and adducts were calculated by using the hybrid density functional theory (B3LYP) with the program package Gaussian 98.[32] A 6-31G(d,p) standard basis set was applied for all atoms, except for gallium and arsenic, for which multielectron adjusted quasirelativistic effective core potentials (ECP28MWB) of the Stuttgart group with the following electronic configuration: $[Ar]d^{10}$ were used.[33] For Ga and As, a (5s5p1d)/[3s3p1d] valence basis set (311,311,1) was utilized (d-functions with the coefficient = 0.207000 (Ga); 0.401524 (As)). All stationary points were characterized as minima by a frequency analysis. Frequency data can be obtained from the authors.

NBO[14] and MO analyses were carried out to investigate the bonding in all molecules at the B3LYP level utilizing the optimized B3LYP geometry.

The computed geometrical parameters and selected results of the NBO analyses for all investigated species are collected in the Supporting Information. Relative and absolute energies are listed in Table S2, NPA charges in Table S1.

It should be emphasized that the computation was carried out for a single, isolated (gas-phase) molecule. There may well be significant differences among gas-phase, solution, and solid-state data.

Acknowledgment. We are indebted to Prof. T. M. Klapötke for access to his X-ray diffractometer, Prof. A. Kornath for the use of a low-temperature mounting device, and Prof. K. Karagiosoff for helpful discussions of NMR data. This work has been supported by the Deutsche Forschungsgemeinschaft (SCHU 1170/4-1).

Supporting Information Available: Relative and absolute energies, NBO data, and theoretically optimized structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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