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Cyclic Arsenic−Nitrogen Cations

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A series of different *cyclo*-diarsa-diazenium salts bearing several bulky groups such as supermesityl (Mes* = 2,4,6-$t\mathrm{Bu}_3\mathrm{C}_6\mathrm{H}_2$) and *m*-terphenyl (2,6-Mes_2-$\mathrm{C}_6\mathrm{H}_3$, Mes = 2,4,6-$\mathrm{Me}_3\mathrm{C}_6\mathrm{H}_2$) and anions such as triflate (OTf = $\mathrm{SO}_3\mathrm{CF}_3$ = trifluoromethylsulfonate) and tetrachloridogallate (GaCl_4^-) were synthesized and fully characterized. The novel 1-chloro-*cyclo*-1,3-diarsa-2,4-diazenium cation represents the first example of a binary cyclic As(III)/N four-membered heterocyclic cation, with a di- and tricoordinated As atom and a delocalized π bond along the $\mathrm{NAs}^{(+)}\mathrm{N}$ unit. The addition of excess $\mathrm{Me}_3\mathrm{SiN}_3$ yields the fully characterized cationic arsenic azide, 1-azido-*cyclo*-1,3-diarsa-2,4-diazenium-μ-azido-hexachlorido-digallate. The $\mathrm{Cl}^-/\mathrm{N}_3^-$ exchange is triggered by the action of the Lewis acid GaCl_3. Depending on the $\mathrm{Me}_3\mathrm{SiN}_3$ stoichiometry, different μ-azido-hexachlorido-digallate salts with either 1-chloro- or 1-azido-*cyclo*-1,3-diarsa-2,4-diazenium cations or even a mixture of both are observed. Moreover, it was of special interest to study the distances between the cationic arsenic center and the anion in *cyclo*-diarsa-diazenium salts. A correlation between the color of the salt and the anion/cation distance, ranging between 2 and 8 Å in *cyclo*-diarsa-diazenium salts of the type $[\mathrm{R}_2\mathrm{N}_2\mathrm{As}_2\mathrm{Y}]^+\mathrm{X}^-$ depending on the bulky group R (R = Mes*, Ter), the substituent Y (Y = Cl, N_3, OTf), and the anion X^- (X = OTf, GaCl_4, $\mathrm{Cl}_3\mathrm{Ga}{-}\mathrm{N}_3{-}\mathrm{GaCl}_3$), was established.

Introduction

Cyclodipnictadiazanes $(\mathrm{RENR}')_2$ are known for all pnictogens E from phosphorus to bismuth[1−4] and represent potential starting materials for, for example, cations, ring-opening oligomerization, and polymerization.

As first discovered by Olah and Oswald for alkyl derivatives, cyclodiarsadiazanes are readily prepared by the addition of excess primary amine to AsCl_3.[5] Burfurd et al. have recently developed a high-yield ring expansion reaction for cyclodiphosphadiazanes to give cyclotriphosphatriazanes by means of Lewis acids such as GaCl_3.[6] Later, this process was extrapolated to the analogous arsenic derivatives providing high-yield preparations of trimers $(\mathrm{RNAsCl})_3$ starting from the dimer $(\mathrm{RNAsCl})_2$ (R = 2,6-dimethylphenyl (Dmp) and 2,6-diisopropylphenyl (Dipp)).[7]

In recent years (besides the ring expansion reaction), Lewis-acid-assisted reactions such as [3+2] cyclizations or methyl/halogen exchange with nitrogen−pnictogen compounds have attracted considerable interest. With the help of such reactions, it was possible to generate a series of low-coordinated P(III)/N and As(III)/N heterocycles and cationic PN species bearing reactive multiple EN bonds (E = P, As).[6−16]

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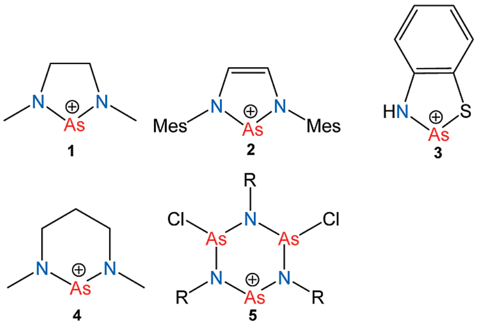
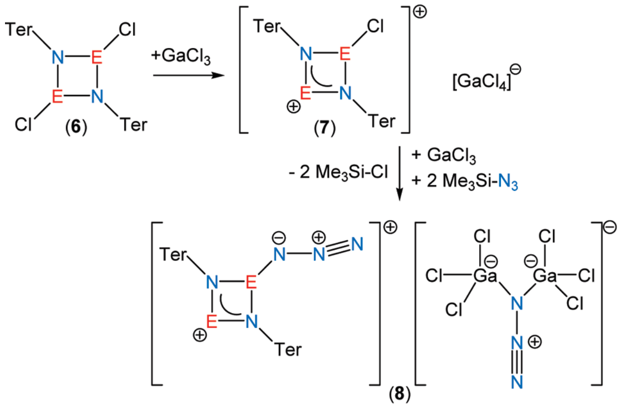
Scheme 1. Known Cyclic As−N Cations (**5**: R = Dipp)[7,17−20]



Scheme 2. Synthesis of *cyclo*-1,3-Dipnicta-2,4-diazenium Cations (E = P, As; Ter = 2,6-Mes$_2$-C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$)



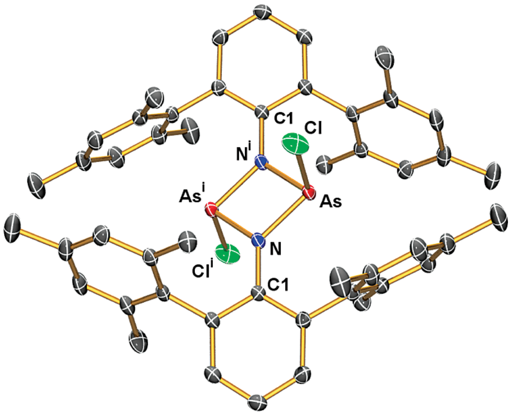
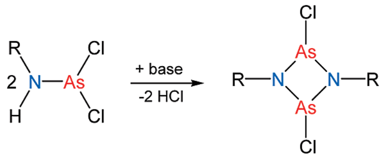


Figure 1. ORTEP drawing of the molecular structure of **6a** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: As−N^i 1.862(1), As−N 1.871(1), As−Cl 2.2605(7), As−As^i 2.874(1), N−C1 1.409(2); N^i−As−N 79.30(6), N^i−As−Cl 98.99(5), N−As−Cl 98.39(5), As^i−N−As 100.70(6), N^i−As−N−As^i 0.0.

Scheme 3. Synthesis of 1,3-Dichloro-*cyclo*-1,3-diarsa-2,4-diazanes (**6**: R = Ter; **9**: R = Mes*)



An interesting aspect of the chemistry of the heavier group 15 elements, in terms of both structure and reactivity, which continues to receive significant attention, is the area of cationic compounds with low coordination numbers.[21] Especially in the case of arsenic, only a few cyclic As−N cations with a dicoordinated cyclic As center are known (Scheme 1).

Recently, the synthesis and full characterization of a 1-chloro-*cyclo*-1,3-diphospha-2,4-diazenium salt was reported.[22] A chlorine−azide exchange in the 1-chloro-*cyclo*-1,3-diphospha-2,4-diazenium salt led to the isolation of the first cationic phosphorous azide, a 1-azido-*cyclo*-1,3-diphospha-2,4-diazenium cation. With the knowledge that it is possible to prepare salts with a *cyclo*-1,3-diphospha-2,4-diazenium cation bearing a covalently bound azide, it was our idea to prepare the heavier arsenic analog (Scheme 2). To achieve this goal, two problems had to be solved: (i) the synthesis of a hitherto unknown cyclic binary As/N cation (**7**) with a dicoordinated As center and (ii) a chloride−azide exchange in this cation. Reactive azido compounds with four-membered cationic, binary As/N rings are particularly challenging to synthesize. The introduction of bulky groups such as *m*-terphenyl (Ter = 2,6-Mes$_2$-C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$)[23] and delocalization have been found to be the keys to stabilizing heavy element double bonds in low coordinated reactive species.[10,11]

We report here (i) the first structural characterization of a 1-chloro-*cyclo*-1,3-diarsa-2,4-diazenium cation (**7**, E = As, Scheme 2) as well as (ii) the formation and full characterization of the intriguing 1-azido-*cyclo*-1,3-diarsa-2,4-diazenium-μ-azido-hexachlorido-digallate (**8**) and different mixed salts of **7** and **8** depending on the stoichiometry of Me$_3$SiN$_3$ added (Scheme 2).

Moreover, we report on the synthesis of a series of different *cyclo*-diarsa-diazenium salts bearing several bulky groups such as supermesityl (Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$) and *m*-terphenyl and anions such as triflate (OTf = SO$_3$CF$_3$ = trifluoromethylsulfonate) and tetrachloridogallate (GaCl$_4^-$). In this context, it is of special interest to study the distances between the cationic arsenic center and the anion. According to the

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Table 1. Selected bond lengths and angles along with reported data of **5**, and **9**

compound	**9** from ref 24	**6**	**10**[a]	**11**	**7**	**12**	**8**	**5** from ref 7
crystal color	colorless	yellow	yellow	orange	black	black	black	yellow
λ^{exp}(nm)[b]	[c]		418(429)[d]	578(418)[d]	554	566	559	
d_{long}(As−X^1)[e]	2.235(4)	2.2605(7)	1.964(1)	2.2242(9)	7.030(3)	6.875(1)	6.266(2)	2.708(1)
d_{short}(As−X^2)[f]	2.235(4)	2.2605(7)	1.964(1)	2.159(2)	2.182(5)	2.178(7)	1.938(2)	2.207(1) 2.209(1)
d_{short}(As−N)	1.840(8)	1.862(1)	1.842(1)	1.819(2) 1.830(2)	1.799(2)[g] 1.827(2)	1.793(2) 1.825(2)	1.799(3) 1.812(2)	1.786(2)[g] 1.793(2)
d_{long}(As−N)	1.855(7)	1.871(1)	1.844(1)	1.886(2) 1.886(2)	1.928(2)[g] 1.901(2)	1.914(2) 1.911(2)	1.915(3) 1.901(3)	1.881(2)[g] 1.864(2)
$\Delta(d_{long} - d_{short})$	0.015	0.008	0.002	0.067 0.056	0.128 0.074	0.121 0.086	0.116 0.089	0.095 0.071
<(N−As−N)[h]	80.4(3)	79.30(6)	81.55(6)	77.83(8)	81.8(1)	81.93(8)	82.1(1)	103.8(1)
<(N−As−N)[i]	80.4(3)	79.30(6)	81.55(6)	77.83(8)	76.6(1)	76.65(8)	76.8(1)	99.1(1) 98.4(1)

[a] $P2_1/c$ structure, data of the $P2_1/n$ structure can be found in the Supporting Information. [b] UV−vis experiments in diluted CH_2Cl_2 solutions. [c] It has been shown that **9** monomerizes in CH_2Cl_2 solution with a deep red color.[14] [d] Values in parentheses were determined in toluene (non-polar solvent). [e] X^1 = Cl for **5**, **6**, **7**, **11**, **12**; X^1 = OTf for **10**; X^1 = N$_3$ = **8**. [f] X^2 = OTf for **10** and **11**; Cl for **5**, **6**, and **7**. [g] for **5**, **7**, **8**, and **12**: d_{short} = As$_{di\text{-}coordinated}$−N, d_{long} = As$_{tri\text{-}coordinated}$−N. [h] Corresponds to <(N−As$_{di\text{-}coordinated}$−N) in the cationic species. [i] Corresponds to <(N−As$_{tri\text{-}coordinated}$−N) in the cationic species.

little published data, these distances vary between 2.0 and 2.7 Å. Here, we want to establish a clear correlation between the color of the cation and the closest anion/cation distance in *cyclo*-diarsa-diazenium salts of the type $[R_2N_2As_2Y]^+X^-$ depending on the bulky group R (R = Mes*, Ter), the substituent Y (Y = Cl, N$_3$, OTf), and the anion X$^-$ (X = OTf, GaCl$_4$, Cl$_3$Ga−N$_3$−GaCl$_3$).

Results and Discussion

Synthesis of *cyclo*-1,3-Diarsa-2,4-diazanes and *cyclo*-1,3-Diarsa-2,4-diazenium Cations. Reactions of bases such as triethylamine or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and aminodichloroarsanes of the type [RN(H)−AsCl$_2$] (R=Mes* and Ter) readily provide access to 1,3-dichloro-2,4-bis-(2,4,6-tri-*tert*-butylphenyl)-*cyclo*-1,3-diarsa-2,4-diazane ([Mes*−N−AsCl]$_2$; **9**) and bis[2,4-bis(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazane ([Ter−N−AsCl]$_2$; **6**), respectively (Scheme 3).[14] Compound **6** crystallizes dependent on the solvent, either without any solvent (from CH$_2$Cl$_2$, Figure 1, Tables 1 and 2) or with tetrahydrofurane (THF) or toluene (Schemes S1−S3 and Tables S1, S4−6 in the Supporting Information).

Investigation of the equilibrium[14] between cyclic diarsadiazane [Mes*−N−AsCl]$_2$ and its monomer, the iminoarsane, by means of temperature-dependent ^{1}H NMR techniques revealed the presence of such an equilibrium as already proposed by Burford et al.[20] The white crystalline dimer [Mes*−N−AsCl]$_2$ is readily dissolved in CH$_2$Cl$_2$, but the colorless solution from the beginning becomes red, the color of the monomeric species, Mes*N=As−Cl. It was of interest to study the effect of the bulky group on both the synthetic routes and the dimer/monomer equilibrium. Hence, instead of the supermesityl group (Mes*), the *m*-terphenyl group was also used for kinetic stabilization of the iminoarsane (R−N=As−Cl), displaying an astonishingly stable dimer [TerNAsCl]$_2$ in solution and in the solid phase, which has already been observed for the analogous phosphorous compound.[22] In contrast to [Mes*−N−AsCl]$_2$, the *m*-terphenyl-substituted analog does not monomerize in solution, as shown by ^{1}H NMR techniques. No monomeric Ter−N=As−Cl could be detected.

Table 2. Crystallographic Details of **6**, **10**, and **11**

	6a[a]	**10a**[b]	**11**
chem. formula	$C_{48}H_{50}As_2Cl_2N_2$	$C_{38}H_{58}As_2F_6N_2O_6S_2$	$C_{49}H_{50}As_2ClF_3N_2O_3S$
fw [g mol^{-1}]	875.64	966.82	989.26
color	yellow	yellow	orange
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	8.6360(17)	11.289(2)	13.742(3)
b [Å]	10.658(2)	16.454(3)	14.494(3)
c [Å]	11.458(2)	16.409(5)	23.784(5)
α [deg]	79.40(3)	90.00	90.00
β [deg]	86.56(3)	133.431(17)	91.51(3)
γ [deg]	82.36(3)	90.00	90.00
V [Å^3]	1026.7(3)	2213.4(11)	4735.6(16)
Z	1	2	4
ρ_{calcd} [g cm^{-3}]	1.416	1.451	1.388
μ [mm^{-1}]	1.794	1.673	1.566
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
measured reflns	29442	41726	68264
independent reflns	7529	7989	13675
reflns with $I > 2\sigma(I)$	6134	7006	9900
R_{int}	0.0304	0.0295	0.0448
F(000)	452	1000	2032
R_1 ($R[F^2 > 2\sigma(F^2)]$)	0.0331	0.0265	0.0462
wR_2 (F^2)	0.0734	0.0602	0.1182
GoF	1.038	1.041	1.055
params	250	263	562

[a] Two further structures of **6** have been determined (**6a**: solvent free, **6b**: with toluene, **6c** with Thf, see Supporting Information). [b] A second data set (**10b**) was measured and can be found in the Supporting Information.

Burford et al. assumed that, depending on the steric strain in derivatives of [RENR′]$_2$ (E = P, As; R = Cl, R′ = organic group), the dimer can be destabilized with respect to the monomer.[6,7,9] The addition of Lewis acids such as GaCl$_3$ or AlCl$_3$ resulted in ring-opening oligomerization, with 1-halo-2,4-di(aryl)-*cyclo*-1,3-dipnicta-2,4-diazenium cations discussed as intermediates.[6,7] The only arsenic/nitrogen cation which could be isolated in such a ring-opening oligomerization represents the trimer **5** (Scheme 1).[7]

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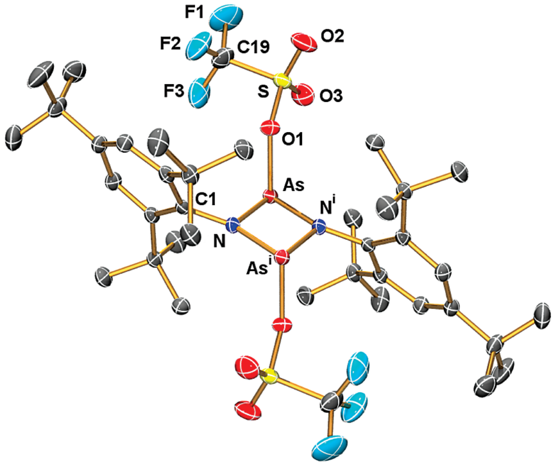
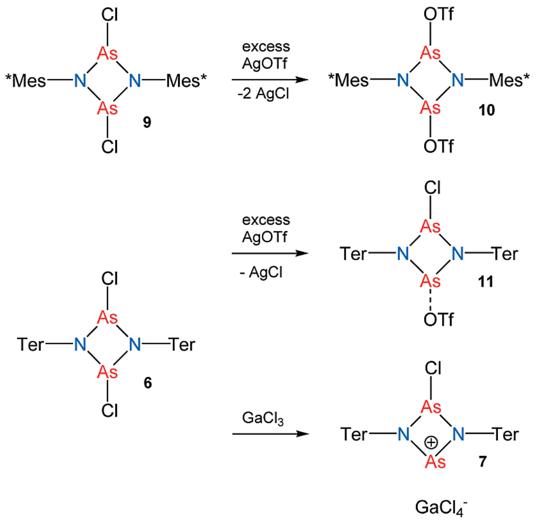


Figure 2. ORTEP drawing of the molecular structure of **10** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: As−N 1.842(1), As−N^i 1.844(1), As−O1 1.964(1), As−As^i 2.7918(5), N−C1 1.452(2), N−As^i 1.844(1); N−As−N^i 81.55(6), N−As−O1 93.35(6), N^i−As−O1 99.75(5), C1−N−As^i 140.1(1), As−N−As^i 98.45(6).

Scheme 4. Reaction of 1,3-Dichloro-*cyclo*-1,3-diarsa-2,4-diazanes (R = Ter, Mes*) with AgOTf and $GaCl_3$



The first observation of a monochlorodiphosphadiazenium cation ($R_2N_2P_2Cl^+$, R = *t*Bu) was reported by Cowley et al. in the reaction of the corresponding *cyclo*-diphosphadiazane with $AlCl_3$, independent of reaction stoichiometry, as displayed by a detailed ^{31}P NMR study.[25] Recently, the isolation and full characterization of the 1-azido- and 1-chloridodiphosphadiazenium cations was achieved by the introduction of the sterically demanding *m*-terphenyl group. Thus, it seemed interesting to study chloride abstraction in $[Mes^*-N-AsCl]_2$ and $[Ter-N-AsCl]_2$ by means of silver triflate, AgOTf, and gallium trichloride, $GaCl_3$, in detail.

In a high-yield reaction, $[Mes^*-N-AsCl]_2$ (**9**) is transformed into the yellow crystalline 1,3-bis-(trifluoromethylsulfonato)-2,4-bis-(2,4,6-tri-*tert*-butylphenyl)-*cyclo*-1,3-diarsa-2,4-diazane (**10**) by the addition of 2 equiv of AgOTf (Figure 2, Scheme 4). On the contrary, the same reaction between ($[Ter-N-AsCl]_2$) (**6**) and 2 equiv of AgOTf led only to the formation of the singly substituted 1-chloro-3-trifluoromethylsulfonato-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazane (**11**; Figure 3). Triflate-substituted *cyclo*-1,3-diarsa-2,4-diazanes (**10** and **11**) are astonishingly thermally stable (**10**, 174°; **11**, 252 °C decomposition) and moisture-sensitive but stable under an argon atmosphere over a long period as a solid and in polar solvents at ambient temperature. Both compounds are easily prepared in bulk and are infinitely stable when stored in a sealed tube. Interestingly, both compounds dissolve in nonpolar solvents (e.g. toluene) with a yellow color, while in a polar solvent such as CH_2Cl_2, compound **11** dissolves red−violet in contrast to compound **10**, which still exhibits a yellow color (see below).

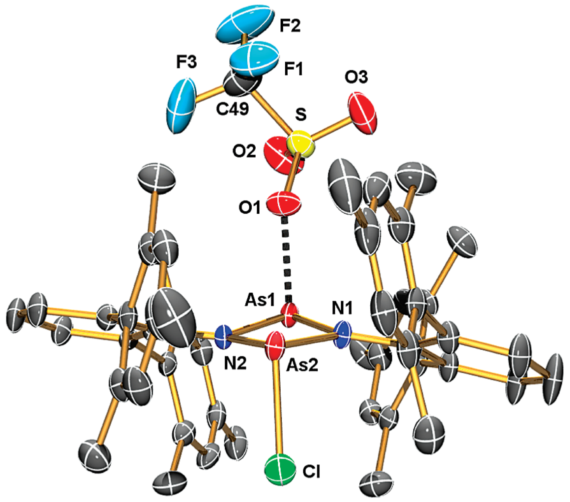


Figure 3. ORTEP drawing of the molecular structure of **11** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: As1−N1 1.819(2), As1−N2 1.830(2), As1−O1 2.159(2), As1−As2 2.8453(7), As2−N1 1.886(2), As2−N2 1.886(2), As2−Cl 2.2242(9), N1−As1−N2 80.98(9), N1−As1−O1 93.56(9), N2−As1−O1 92.46(9), N1−As2−N2 77.83 (8), N1−As2−Cl 96.68(7), N2−As2−Cl 98.98(7), As1−N1−As2 100.34(9), As1−N2−As2 99.93(8), N2−As1−As2−N1 168.8(1).

A "true" salt with separated anions and cations represents the 1-chloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl) phenyl]-*cyclo*-1,3-diarsa-2,4-diazenium tetrachloridogallate (**7**), which was isolated in the reaction of **6** with $GaCl_3$ (Scheme 4, Figure 4, see below). Crystals of *cyclo*-1,3-diarsa-2,4-diazenium salt **7** are black and moisture-sensitive but stable under an argon atmosphere over a long period as a solid and in CH_2Cl_2 at ambient temperature. The black appearance vanishes rapidly when traces of H_2O are present. Crystals of **7** dissolve with a deep red−violet color in CH_2Cl_2. Compound **7** can be prepared in bulk and is also infinitely stable when stored in a sealed tube at ambient temperatures.

Cationic Cyclic Arsenic(III) Azides. The reactions of **7** with 1 equiv, 2 equiv, and an excess of Me_3SiN_3 in the presence of one additional equivalent of $GaCl_3$ in CH_2Cl_2 result in facile chloride−azide exchange. However, depending on the stoichiometry, three different products could be isolated (Scheme 5). The first equivalent of Me_3SiN_3 is only used to form a *μ*-azido-hexachlorido-digallate anion ($GaCl_3 + GaCl_4^- + Me_3SiN_3 \rightarrow [Cl_3Ga-N_3-GaCl_3]^- + Me_3SiCl$) within 2 h, while upon the addition

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(25) Cowley, A. H.; Lattman, M.; Wilburn, J.C. *Inorg. Chem.* **1981**, *20*, 2916–2919.

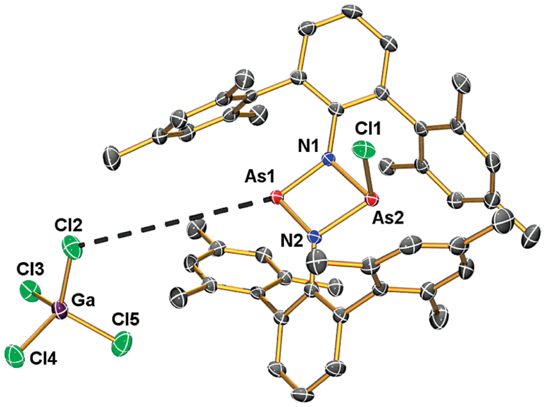

Figure 4. Molecular structure of **7** in the crystal (hydrogen atoms omitted for clarity). As1−Cl2 distance in ångstroms. Selected bond lengths [Å] and angles [deg]: As1−N1 1.799(2), As1−N2 1.828(2), As1−As2 2.872(1), As1···Cl2 7.030(3), As2−N2 1.901(2), As2−N1 1.9270(2), As2−Cl1 2.1820(8), Ga−Cl2 2.1642(9), Ga−Cl3 2.1716(8), Ga−Cl5 2.1785(9), Ga−Cl4 2.1797(8), N1−C1 1.417(3); N1−As1−N2 81.77(8), N2−As2−N1 76.66(8), N2−As2−Cl1 101.22(6), N1−As2−Cl1 91.86(6), As1−N2−As2 100.76(8), C1−N1−As1 132.7(2).

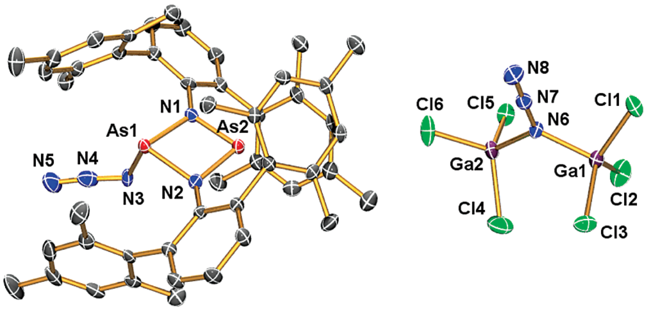

Figure 5. ORTEP drawing of the molecular structure of **8** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): As1−N1 1.799(3), As1−N2 1.812(2), As2−N1 1.901(3), As2−N2 1.915(3), As2−N3 1.938(3), N3−N4 1.216(4), N4−N5 1.131(4), Ga2−N6 1.978(3), Ga2−Cl4 2.140(1), N6−N7 1.252(4), N7−N8 1.126(4), N1−As1−N2 82.1(1), N1−As2−N2 76.8(1), N1−As2−N3 92.2(1), N2−As2−N3 101.0(1), As1−N1−As2 100.7(1), As1−N2−As2 99.7(1), N5−N4−N3 171.5(4), Ga1−N6−Ga2 125.4(1), N8−N7−N6 178.8(3).

of a second equivalent of Me_3SiN_3, only a partial Cl^-/N_3^- exchange occurs in the cation (reaction time 16 h), resulting in mixed crystals with about 3/4 Cl and 1/4 N_3 attached to the As_2N_2 ring. Only when a large excess of Me_3SiN_3 is used and the reaction time is increased (2 days instead of 2 h) is a complete chloride−azide exchange observed and pure **8** formed (Figure 5). Azide formation in the anion and cation can also easily be observed by means of IR spectroscopy (anion: $\nu_{as}(N_3) = 2157$, cation: 2102 cm^{-1}).

Crystals of 1,3-diarsa-2,4-diazenium azide salts are also black and moisture-sensitive but stable under an argon atmosphere over a long period as a solid and in CH_2Cl_2 at ambient temperature. The black appearance vanishes rapidly when traces of H_2O are present. All azide salts are easily prepared in bulk and are infinitely stable when stored in a sealed tube and kept cool at −20 °C in the dark. Albeit salts such as compounds **8**, **12**, and **13** are covalently bound azides, they are neither heat- nor shock-sensitive. Decomposition starts above 142 °C in **8** and 179 °C in **12** (cf. **7**: decomposition $T > 199$ °C).

In the past two decades, neutral, cationic, and anionic binary arsenic(III,V) azide species such as $As(N_3)_3$,[26] $As(N_3)_5$,[27] $[As(N_3)_4]^+$,[28] $[As(N_3)_4]^-$,[29] and $[As(N_3)_6]^-$ [28,29] have been reported and the crystal structures of $As(N_3)_3$[28] and $[As(N_3)_6]^-$ [28,29] determined.[30] In addition, the Lewis-base-stabilized species $As(N_3)_5 \cdot LB$ (LB = pyridine, quinoline, NH_3, N_2H_4, NH_2CN) are known.[31]

The chemistry of azides covalently bound to organoarsenic(III) fragments was opened by Revitt and Sowerby.[32] However, up to now, only two molecular arsenic(III) azides have been structurally characterized: the perfluoroalkyl species bis(trifluoromethyl)arsenic azide, $(CF_3)_2AsN_3$, and trifluoromethylarsenic diazide, $CF_3As(N_3)_2$, which were studied by gas-phase electron diffraction.[33,34] To the best of our knowledge, cyclic cationic arsenic azides are not known yet.

X-Ray Structure Analysis. The solid-state structures of the *cyclo*-diarsa-diazane derivatives **6**, **10**, and **11** are shown in Figures 1−3 and those of the *cyclo*-diarsa-diazenium salts **7** and **8** in Figures 4 and 5. Selected bond lengths and angles are listed in Table 1; crystallographic details are given in Tables 2 and 3. More details are found in the Supporting Information. X-ray-quality crystals of all considered species were selected in Kel-F-oil (Riedel deHaen) or Fomblin YR-1800 (Alfa Aesar) at ambient temperatures. All samples were cooled to either 173(2) K (compounds **6**, **7**, **10**, **11**, and **12**) or 100(2) K (compounds **8** and **13**) during the measurement. It is worth mentioning that compound **10** crystallizes isotypically to the analogous phosphorous and antimony species.[7]

1,3-Diarsa-2,4-diazenium Salts. X-ray elucidation of **7** and crystals from the reaction sequences, as illustrated in Scheme 5 (**8**, **12**, and **13**, see the Supporting Information), revealed novel 1,3-diarsa-2,4-diazenium salts with no significant cation−anion contacts (closest As···Cl contact 7.030(3) Å in **7**, 6.266(2) Å in **8**) and a dicoordinated As(III) atom as part of an As_2N_2 ring, kinetically protected in the pocket formed by the *m*-terphenyl groups (Figure 5). All 1,3-diarsa-2,4-diazenium salts **7**, **8**, **12**, and **13** crystallize isotypically in black blocks in the monoclinic space group $P2_1/c$ with four units per cell. In the case of the azide-containing salts **8**, **12**, and **13**, the cell parameters are almost identical (axes, deviation < 0.2 Å; angles, deviation < 0.4°), which is the reason for the observed

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(26) (a) Klapötke, T. M.; Geissler, P. *J. Chem. Soc. Dalton Trans.* **1995**, 3365–3366. (b) Geissler, P.; Klapötke, T. M.; Kroth, H.-J. *Spectrochim. Acta Part A* **1995**, *51*, 1075–1078. (c) Haiges, R.; Vij, A.; Boatz, J. A.; Schneider, S.; Schroer, T.; Gerken, M.; Christe, K. O. *Chem.−Eur. J.* **2004**, *10*, 508–517.

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(32) Revitt, D. M.; Sowerby, D. B. *J. Chem. Soc., Dalton Trans.* **1972**, *7*, 847–850.

(33) Ang, H. G.; Kwik, W. L.; Lee, Y, W.; Liedle, S.; Oberhammer, H. J. *Mol. Struct.* **1992**, *268*, 389–394.

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Scheme 5. Synthesis of Azido-cyclo-1,3-diarsa-2,4-diazenium salts (Ter = 2,6-Mes$_2$-C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$, X = 3/4Cl, 1/4N$_3$)

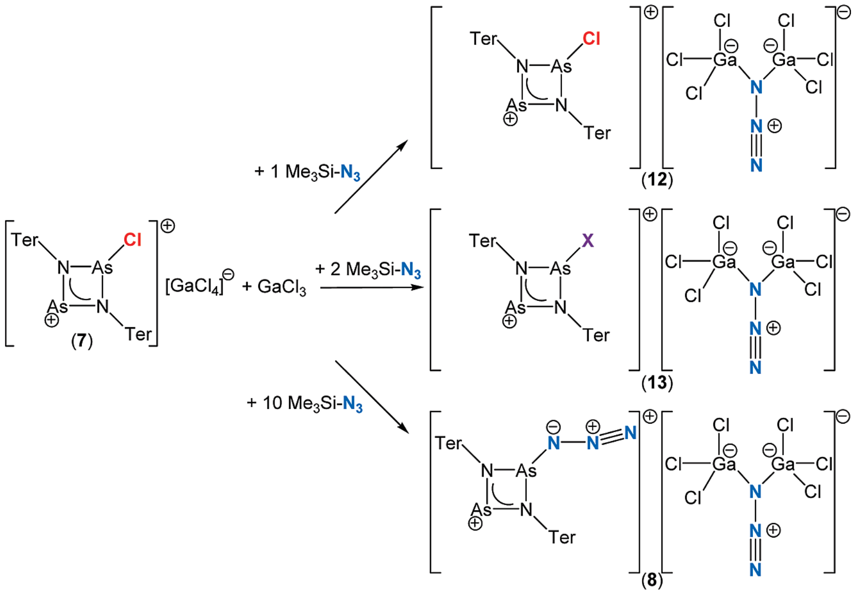

Table 3. Crystallographic Details of Compounds **7** and **8**

	7	8
chem. formula	$C_{48}H_{50}As_2Cl_5GaN_2$	$C_{48}H_{50}As_2Cl_6Ga_2N_8$
fw [g mol^{-1}]	1051.71	1240.94
color	black	black
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a [Å]	14.932(3)	16.018(3)
b [Å]	18.372(4)	15.075(3)
c [Å]	18.318(4)	22.445(3)
α [deg]	90.00	90.00
β [deg]	112.23(3)	103.922(14)
γ [deg]	90.00	90.00
V [Å^3]	4651.6(16)	5260.9(16)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.502	1.567
μ [mm^{-1}]	2.326	2.619
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073
T [K]	173(2)	100(2)
measured reflns	60730	44226
independent reflns	13091	13010
reflns with $I > 2\sigma(I)$	9166	9051
R_{int}	0.0508	0.0497
F(000)	2136	2496
R_1 ($R[F^2 > 2\sigma(F^2)]$)	0.0374	0.0381
wR_2 (F^2)	0.0800	0.0911
GoF	1.026	1.020
params	535	607

formation of mixed crystals in **13** (with 3/4 Cl and 1/4 N$_3$ attached to the As$_2$N$_2$ ring, see the Supporting Information). For all 1,3-diarsa-2,4-diazenium salts, several relatively close contacts between the dicoordinated As center and both terphenyl ligands can be detected. These short contacts amount to 2.76−3.6 Å and are within the sum of the van der Waals radii (d_{vdW}: As···C = 3.7 Å), indicating stabilizing As$_{dicoordinated}$···C$_{terphenyl}$ interactions.

As depicted in Figures 4 and 5, the As$_2$N$_2$ rings are almost planar (deviation from planarity: <N1−As1−N2−As2 = 1.4° in **7**, −6.2° in **8**, and 5.0° in **12**), but slightly distorted with two longer As$_{tricoord.}$−N bond lengths (**7**: 1.927(2)/1.901(2), **8**: 1.915(3)/1.901(3), and **12**: 1.911(2)/1.914(2) Å) and two considerably shorter As$_{dicoord.}$−N distances (**7**, 1.799(2)/1.827(2); **8**, 1.812(3)/1.825(2); and **12**, 1.793(2)/1.825(2) Å; cf. 1.793(2)/1.786(2) Å in trimeric [Dipp$_3$N$_3$As$_3$Cl$_3$]$^+$[GaCl$_4$]$^-$, Dipp = 2,6-diisopropylphenyl).[7] The short As$_{dicoord}$−N distances between 1.79 and 1.83 Å are substantially shorter than the sum of the covalent radii (d_{cov}(N−As) = 1.91 and d_{cov}(N=As) = 1.71 Å),[35] which indicates partial double-bond character for these As−N bonds, while As$_{tricoord.}$−N bond lengths are in the range expected for As−N single bonds. The As$_{dicoord.}$−N distances in **7** (Figure 4) are slightly longer than those in **5** (Scheme 1, Table 1), which can be attributed to a larger steric strain in a four-membered As$_2$N$_2$ ring compared to the six-membered core in **5**, resulting in a stronger repulsion and an elongation of the atomic distances.

So far, little is known about arsenic compounds containing an As−N double bond.[14,24,36] The first fully characterized compound with an As−N double bond (1.714(7) and 1.745(7) Å) was (2,4,6-tri-*tert*-butylphenylamino)(2,4,6-tri-*tert*-butylimino)arsane prepared by Lappert et al. in 1986.[37]

As shown on numerous occasions,[26−33,38] covalently bound azide groups such as in **8** display a trans-bent configuration (regarding the As atom, As−NNN) with a N−N−N bond angle of 171.5(4)°, while the bridging

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(35) Holleman, W. *Lehrbuch der Anorganischen Chemie*, 102. Aufl.; Walter de Gruyter: Berlin, 2007; Anhang IV.

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azide group attached to both $GaCl_3$ moieties is almost linear ($<$N−N−N = 178.8(2)° in **12** and 178.8(2)° in **8**).

General Structural Trends and Crystal Color. In all considered *cyclo*-diarsa-diazane derivatives, **6**, **10**, and **11**, and the *cyclo*-diarsa-diazenium salts, **7**, **8**, **12**, and **13**, as expected, both nitrogen atoms of the As_2N_2 ring are almost trigonal-planar and the tri-coordinated arsenic atom trigonal-pyramidal. The sum of the bond angles at the tri-coordinated arsenic atom ranges between 269 and 277°. Always, an anti configuration is found for the exocyclic substituents of the arsenic centers. The sum of the bond angles at the nitrogen atoms N is always very close to 360°, indicating a planar environment and, hence, a formal sp^2 hybridization. Thus, the molecular structures of **6**, **7**, **10**, and **11** have a square N_2As_2 core and, in the cases of **6** ([Ter−NAs−Cl]$_2$) and **10** ([Mes*−NAs−OTf]$_2$), with crystallographically indistinguishable As−N distances that are in the typical range for derivatives of *cyclo*-1,3-diarsa-2,4-diazanes.[24] However, in contrast to the (pale) yellow crystals of **10**, the crystals of **11** are deep orange. Although in both compounds (**10** and **11**) the As−OTf bonds are highly polar (NBO analysis),[39−42] neither **10** nor **11** can be considered as "true" salts with separated anions and cations in the solid state (see As−X distances in Table 1, X = Cl and O). However, the considerably longer As−O distance in **11** as compared to that in **10** (2.159(2) vs. 1.964(1) Å; cf. d_{cov}(As−O) = 1.95 Å)[35] indicates already the transition to separated ion pairs. Interestingly, **11** displays a red−violet color (578 nm) in a polar solvent such as CH_2Cl_2 and a yellow color (433 nm) in a nonpolar solvent such as toluene, while **10** is yellow in both solvents (427 nm), as studied by means of UV−vis experiments (Table 1). For comparison, the "true" salt **7** dissolves only in the polar solvent CH_2Cl_2 with a red−violet color (554 nm). In the case of **11**, it can be assumed that the red−violet color indicates dissociation in the polar solvent, while the yellow color in nonpolar solvents can be attributed to dissolved molecules of 11 without any significant dissociation of the triflate group.

The main difference between **10** and **11** is the steric demand of the bulky group (Mes* vs *m*-terphenyl). Obviously, the *m*-terphenyl group provides only enough space for one OTf^- anion with a long As−O bond length, so that even with a large excess of AgOTf only monosubstitution occurs, in contrast to the reaction of **9** with an excess of AgOTf, resulting in the doubly substituted species **10** ([Mes*−NAs−OTf]$_2$). In trimeric yellow $[Dipp_3N_3As_3Cl_3]^+[GaCl_4]^-$ (**5**),[7] there is one strong As···Cl contact with a distance of 2.708(1) Å which still seems to be too short to be considered as separated ions, as illustrated by the afore-mentioned notation. As a consequence of the strong interaction, a slightly elongated Ga−Cl distance is found in the $GaCl_4^-$ anion (2.2581(7) compared to 2.14−2.15 Å for the other three Ga−Cl distances). Only increased steric strain as found in **7** (or as in the azides **8**, **12**, and **13**) leads to cation−anion separation (closest contact 7.030(3) Å in **7** as well as in all azide salts) with no elongated Ga−Cl bond; all distances are between 2.16 and 2.18 Å) in the solid state, with no significant cation−anion interactions and a dicoordinated As(III) atom as part of an As_2N_2 ring, embedded in a pocket formed by the *m*-terphenyl groups (Figures 4 and 5). It is interesting to note that, in the case of cation−anion separation, the color of the crystals dramatically changes from yellow to a black appearance (in CH_2Cl_2 solution, red−violet, see UV−vis data in Table 1). Actually, the color seems to be a very good "macroscopic" property to predict if cation−anion separation occurs in solution as well as in the solid state. For instance, the yellow compound **11** dissociates (ion formation) in CH_2Cl_2, exhibiting a red−violet color, but upon crystallization, the color changes back to yellow, which indicates a molecular species, as shown by X-ray analysis. On the contrary, compound **7** also forms ions in CH_2Cl_2 but crystallizes in black crystals, which were shown to be composed of separated ions.

Another interesting structural feature with respect to the question of dicoordination versus tricoordination is the As−N distance within the As_2N_2 core. As depicted in Figures 3 and 5, the As_2N_2 rings of **7** and **11** are also almost planar (deviation from planarity: $<$N1−As1−N2−As2 = 1.3° in **7**, 7.4° in **11**) but distorted with two longer $As_{tri\text{-}coord}$−N bond lengths (**7**, 1.928(2)/1.901(2); **11**, 1.886(2)/1.886(2) Å) and two considerably shorter $As_{di\text{-}coord}$−N distances (**7**, 1.799(2)/1.827(2); **11**, 1.819(2)/1.830(2) Å; cf. 1.793(2)/1.786(2) Å in **5**), again indicating partial double-bond character for these As−N bonds (see above). The difference between both As−N bond lengths increases along **10** < **11** < **7**, in accord with an increasing closest cation−anion contact (Table 1).

Conclusions

In conclusion, we present here the first examples of binary cyclic As(III)/N four-membered heterocyclic cations, with a di- and tricoordinated As atom and a delocalized π bond along the $NAs^{(+)}N$ unit. The addition of an excess of Me_3SiN_3 yields the first fully characterized cyclic cationic arsenic azide. The Cl^-/N_3^- exchange is triggered by the action of the Lewis acid $GaCl_3$. The cation−anion contacts are discussed on the basis of structural and UV−vis data. The larger the distance between the *cyclo*-diarsa-diazenium cation and the anion, the more red-shifted (and deeper) the color in the solid state, while in solution a deep red−violet color is observed. When no significant contacts are detected, the *cyclo*-diarsa-diazenium salt displays a black appearance. Strong cation−anion interactions (short distances) lead to pale yellow crystals and yellow solutions in nonpolar and polar solvents.

Experimental Section

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

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(41) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*; Plenum Press: New York, 1988; p 227.

(42) Weinhold, F.; Landis, C. *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: New York, 2005 and references therein.

Dichloromethane was purified according to a literature procedure,[43] dried over P_4O_{10}, and freshly distilled prior to use. Toluene was dried over Na/K/benzophenone and freshly distilled prior to use. THF and 1,8-diazabicyclo[5.4.0]undec-7-en (98%, Sigma-Aldrich) were dried over Na/benzophenone and freshly distilled prior to use. *n*-Hexane was dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. Trimethylsilylazide (95% Fluka) was distilled prior to use. *N*-[2,4-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)arsane was prepared according to a modified literature procedure.[14] Trimethylsilylchloride (99%, Merck) was freshly distilled prior to use. 2,4,6-Tri-*tert*-butylaniline (99%, Sigma-Aldrich), silver triflate (99%, Fluka), and $GaCl_3$ (99.999%, Sigma-Aldrich) were used as received.

NMR. $^{13}C\{^1H\}$, ^{13}C DEPT, and ^1H NMR spectra were obtained on a Bruker AVANCE 250 or 300 spectrometer and were referenced internally to the deuterated solvent (^{13}C, CD_2Cl_2: $\delta_{reference} = 54$ ppm; toluene-d_8: $\delta_{reference} = 137.5$ ppm) or to protic impurities in the deuterated solvent (^1H, $CDHCl_2$: $\delta_{reference} = 5.31$ ppm; $C_6D_4HCD_3$: $\delta_{reference} = 7.09$ ppm). NMR solvents were dried as depicted above for the undeuterated solvents.

IR. A Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR or a Nicolet 380 FT-IR with Smart Orbit ATR device was used.

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

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

CHN analyses. An Analysator Flash EA 1112 from Thermo Quest was used. Pb_3O_4 was added.

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

DSC. A DSC 823e from Mettler-Toledo was used, with a heating rate of 5 °C/min.

UV−Vis. A Lambda 2 UV/VIS Spectrometer from Perkin Elmer was used.

X-Ray Structure Determination. X-ray-quality crystals of **6**, **6b**, **6c**, **7**, **10a**, **10b**, and **11** were selected in Kel-F-oil (Riedel deHaen). Crystals of **8**, **12**, and **13** were selected in Fomblin YR-1800 (Alfa Aesar) at ambient temperatures. All samples were cooled to 173(2) K (**6**, **6b**, **6c**, **7**, **10a**, **10b**, **11**, and **12**) or 100 (2) K (**8** and **13**) during measurement. The data were collected on a Bruker-Nonius Apex X8 CCD diffractometer (**6**, **6b**, **6c**, **7**, **10a**, 10b, **11**, and **12**) or Bruker Kappa Apex II CCD diffractometer (**8** and **13**) using graphite monochromated Mo Ka radiation ($\lambda = 0.71073$). The structures were solved by direct methods (SHELXS-97)[44] and refined by full-matrix least squares procedures (SHELXL-97).[45] Semiempirical absorption corrections were applied (SADABS).[46] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the refinement at calculated positions using a riding model.

The position of one of the two tetrahydrofurane molecules in **6c** was found to be partially occupied. The occupancy was refined freely (0.896(5)). The other tetrahydrofurane molecule in **6c** was found to be disordered and was split in two parts. The occupancy of each part was refined freely (0.604(11)/0.396(11)). The position of the Cl/azide group in **13** was found to be partially occupied and was split in two parts. The occupancy of each part was refined freely (0.750(4) Cl/0.250(4) N_3).

Synthesis of 1,3-Dichloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazane (6). To a stirred solution of *N*-[2,4-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)arsane (4.743 g, 10.0 mmol) in tetrahydrofurane (50 mL) was added a solution of DBU (1.675 g, 11.0 mmol) in tetrahydrofurane (15 mL) dropwise at −80 °C over a period of 15 min. The resulting yellow suspension was warmed to ambient temperatures over a period of 4 h. The solvent was removed in vacuo, and the yellowish residue was extracted with benzene (40 mL) and filtered (F4), resulting in a champagne-colored solution. Removal of the solvent in vacuo resulted in a yellowish residue, which was recrystallized from dichloromethane (25 mL) at −25 °C over a period of 16 h. Removal of the supernatant by syringe yields 2.285 g (5.22 mmol, 52%) of **6** as a yellowish crystalline solid. Mp: 259 °C (dec.) Anal. Calcd % (found): C, 65.84 (65.79); H, 5.76 (5.73); N, 3.20 (3.20). ^1H NMR (25°C, CD_2Cl_2, 250.13 MHz): δ 1.92 (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 2.44 (s, 6H, CH_3), 6.65 (m, 2H, m-C*H*-Ph), 6.77 (s, 2H, *m*-C*H*-Mes), 6.83 (s, 2H, *m*-C*H*-Mes), 6.91 (m, 1H, p-C*H*-Ph). $^{13}C\{^1H\}$ NMR (25°C, CD_2Cl_2, 75.5 MHz): δ 20.8 (s, CH_3), 21.9 (s, CH_3), 22.0 (s, CH_3), 122.5 (s, aryl-*C*H), 129.3 (s, aryl-*C*H), 129.7 (s, aryl-*C*H), 131.4 (s, aryl-*C*H), 131.5, 135.3, 138.2, 138.9, 138.9, 139.7. IR (ATR, 32 scans): 3063 (w), 3034 (w), 2975 (w), 2915 (m), 2853 (w), 2732 (w), 1610 (w), 1574 (w), 1481 (w), 1449 (m), 1402 (s), 1377 (m), 1225 (s), 1187 (m), 1097 (w), 1080 (m), 1032 (m), 1003 (m), 952 (w), 874 (s), 846 (s), 820 (s), 791 (s), 753 (s), 744 (s), 672 (m), 644 (m), 588 (m), 568 (m), 559 (m), 546 (m), 535 (m). Raman (100 mW, 25 °C, 161 scans, cm^{-1}): 3039 (5), 2982 (3), 2919 (10), 2859 (3), 2734 (2), 1611 (3), 1577 (3), 1477 (1), 1412 (3), 1377 (2), 1302 (3), 1267 (3), 1189 (1), 1160 (1), 1088 (1), 1031 (1), 1005 (1), 947 (1), 740 (1), 689 (1), 565 (2), 518 (1), 460 (1), 424 (2), 380 (1), 314 (3), 274 (1), 233 (1), 177 (2), 145 (2). MS (CI, m/z): 330 $[Ter^*NH_3]^+$, 708 $[M - Cl - Mes - CH_3 + 2H]$, 804 $[M - 2Cl]^+$, 839 $[M - Cl]^+$, 876 $[M + H]^+$.

Synthesis of 1-Chloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazenium Tetrachloridogallate (7). To a stirred solution of 1,3-dichloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazane (0.875g, 1.0 mmol) in toluene (20 mL) was added a solution of $GaCl_3$ (0.194 g, 1.1 mmol) in toluene (5 mL) dropwise at −25 °C over a period of 10 min. The resulting greenish-black suspension was warmed to ambient temperatures over a period of 1 h. The suspension was concentrated to a volume of 0.5 mL in vacuo and was filtered (F4). Drying of the black residue in vacuo yielded 1.003 g (0.95 mmol, 95%) of **2** as a black crystalline solid. Mp: 199 °C (dec.) Anal. Calcd % (found): C, 54.81 (54.62); H, 4.79 (4.71); N, 2.66 (2.47). ^1H NMR (25°C, CD_2Cl_2, 300.13 MHz): δ 1.91 (s, 6H, CH_3), 1.93 (s, 6H, CH_3), 2.42 (s, 6H, CH_3), 7.05 (s, 4H, *m*-C*H*-Mes), 7.08 (m, 2H, *m*-C*H*-Ph), 7.30 (dd, 1H, *p*-C*H*-Ph, $J(^1H-^1H) = 7.0$ Hz, 8.0 Hz). $^{13}C\{^1H\}$ NMR (25°C, CD_2Cl_2, 75.5 MHz): δ 20.9 (s, CH_3), 21.6 (s, *o*-CH_3-Mes), 21.9 (s, *p*-CH_3-Mes), 127.6 (s, aryl-*C*H), 131.0 (s, aryl-*C*H), 131.3, 132.1 (s, aryl-*C*H), 132.3 (s, aryl-*C*H), 134.0, 138.1, 138.5, 138.7, 142.3. IR (ATR, 32 scans): 2973 (w), 2946 (w), 2917 (m), 2854 (w), 2735 (w), 1606 (m), 1465 (w), 1472 (m), 1454 (m), 1444 (m), 1404 (m), 1378 (m), 1323 (w), 1295 (w), 1249 (w), 1215 (s), 1188 (w), 1162 (w), 1125 (w), 1105 (w), 1073 (m), 1028 (m), 1004 (m), 939 (w), 910 (w), 885 (s), 859 (s), 850 (s), 816 (s), 808 (s), 799 (s), 792 (s), 759 (s), 745 (s), 721 (s), 685 (m), 663 (m), 648 (m), 581 (m), 564 (m), 546 (m), 532 (m). Raman (10 mW, 25 °C, 201 scans, cm^{-1}): 3053 (1), 2919 (2), 2851 (1), 1608 (1), 1582 (3), 1479 (1), 1412 (6), 1305 (2), 1255 (10), 1082 (2), 1007 (1), 944 (1), 885 (1), 820 (1), 750 (1), 727 (1), 692 (1), 661 (1), 561 (1), 514 (1), 479 (1), 423 (1), 351 (2), 314 (1), 274 (1), 237 (1). MS (FAB+, Cs, 20 keV, *p*-NBA matrix, M = $Ter_2N_2As_2Cl^+$): 402 $[Ter - NAs]^+$, 805 $[M - Cl + H]^+$, 839 $[M]^+$, 874 $[M + Cl]^+$.

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[43] Fischer, C. B.; Xu, S.; Zipse, H. *Chem.—Eur. J.* **2006**, *12*, 5779–5784.

[44] Sheldrick, G. M.: *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997.

[45] Sheldrick, G. M.: *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

[46] Sheldrick, G. M.: *SADABS*, version 2; University of Göttingen: Göttingen, Germany, 2004.

Synthesis of 1-Azido-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazenium μ-Azido-bis[hexachloridogallium(III)] (8). To a stirred greenish-black solution of 1-chloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazenium tetrachloridogallate (**2**; 1.052g, 1.0 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added a solution of $\mathrm{(CH)_3Si{-}N_3}$ (1.152 g, 10 mmol) in $\mathrm{CH_2Cl_2}$ (5 mL) dropwise at −10 °C over a period of 5 min. $\mathrm{GaCl_3}$ (0.194 g, 1.1 mmol) in $\mathrm{CH_2Cl_2}$ (5 mL) was then added dropwise at −10 °C over a period of 10 min. The resulting greenish-black solution was warmed to ambient temperatures and was stirred for two days. The solvent was removed in vacuo, and the black residue was washed with *n*-hexane (10 mL) and dried in vacuo. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (30 mL) and filtered (F4), resulting in an brownish-black solution. Slow removal of the solvent in vacuo yielded 1.209 g (0.97 mmol, 97%) of **3** as a black crystalline solid. Mp: 142 °C (dec.). Anal. Calcd % (found): C, 46.46 (45.67); H, 4.06 (4.49); N, 9.03 (8.51). ^{1}H NMR (25°C, $\mathrm{CD_2Cl_2}$, 300.13 MHz): δ 1.91 (s, 12H, $\mathrm{C}\mathit{H}_3$), 2.44 (s, 6H, $\mathrm{C}\mathit{H}_3$), 7.04 (m, 2H, *m*-C*H*-Ph), 7.07 (s, 4H, *m*-C*H*-Mes), 7.28 (m, 1H, *p*-C*H*-Ph). ^{13}C{^{1}H} NMR (25°C, $\mathrm{CD_2Cl_2}$, 75.5 MHz): δ 20.9 (s, $\mathit{C}\mathrm{H}_3$), 21.9 (s, $\mathit{C}\mathrm{H}_3$), 127.6 (s, aryl-*C*H), 131.1 (s, aryl-*C*H), 131.4, 132.0 (s, aryl-*C*H), 134.0, 138.3, 138.5, 142.3. IR (ATR, 32 scans): 3052 (w), 2974 (w), 2943 (w), 2919 (m), 2854 (w), 2733 (w), 2155 (s), 2102 (s), 1635 (w), 1606 (m), 1562 (w), 1476 (m), 1455 (m), 1442 (m), 1405 (m), 1378 (m), 1297 (w), 1267 (w), 1218 (s), 1165 (m), 1105 (w), 1074 (m), 1021 (m), 940 (w), 885 (s), 860 (s), 825 (s), 813 (m), 799 (s), 768 (s), 748 (m), 728 (m), 686 (m), 667 (s). MS (FAB+, Cs, 20 keV, *p*-NBA matrix, M = $\mathrm{Ter_2N_2As_2Cl^+}$): 329 $[\mathrm{Ter} - \mathrm{NH_2}]^+$, 330 $[\mathrm{Ter} - \mathrm{NH_3}]^+$, 402 $[\mathrm{Ter} - \mathrm{NAs}]^+$, 805 $[\mathrm{M} - \mathrm{N_3} + \mathrm{H}]^+$, 839 $[\mathrm{M} + \mathrm{Cl} - \mathrm{N_3}]^+$, 956 $[\mathrm{M} + \mathrm{NBA} - \mathrm{N_3} - \mathrm{H}]^+$, 991 $[\mathrm{M} + 2\mathrm{NBA} + \mathrm{Cl} - \mathrm{N_3} + \mathrm{H}]^+$, 1109 $[\mathrm{M} + 2\mathrm{NBA} - \mathrm{N_3} + \mathrm{H}]^+$.

Synthesis of 1,3-Bis-(trifluoromethylsulfonato)-2,4-bis-(2,4,6-tri-*tert*-butylphenyl)-*cyclo*-1,3-diarsa-2,4-diazane (10). To a stirred solution of $\mathrm{Ag(SO_3CF_3)}$ (0.549 g, 2.1 mmol) in toluene (10 mL) was added a solution of 1,3-dichloro-2,4-bis-(2,4,6-tri-*tert*-butylphenyl)-*cyclo*-1,3-diarsa-2,4-diazane (**9**; 0.740g, 1.0 mmol) in toluene (10 mL) dropwise at −60 °C over a period of 15 min under exclusion of light. The resulting orange suspension is warmed to ambient temperatures over a period of 1 h and was then filtered (F4), resulting in an orange solution. Removal of the solvent in vacuo yielded 0.952 g (0.98 mmol, 98%) of **10** as a yellow crystalline solid. Mp: 174 °C (dec.) Anal. Calcd % (found): C, 47.21 (46.78); H, 6.05 (6.12); N, 2.90 (2.72). ^{1}H NMR (25°C, $\mathrm{CD_2Cl_2}$, 250.13 MHz): δ 1.32 (s, 9H, *p*-$\mathrm{C(C}\mathit{H}_3)_3$), 1.56 (s, 18H, *o*-$\mathrm{C(C}\mathit{H}_3)_3$), 7.52 (s, 2H, aryl-C*H*). ^{13}C{^{1}H} NMR (25°C, $\mathrm{CD_2Cl_2}$, 62.9 MHz): δ 31.6 (s, *p*-$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 34.3 (s, *o*-$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 35.6 (s, *p*-$\mathit{C}\mathrm{(CH_3)_3}$), 37.4 (s, *o*-$\mathit{C}\mathrm{(CH_3)_3}$), 120.2 (q, $\mathit{C}\mathrm{F_3}$, $^{1}J(^{13}\mathrm{C}{-}^{19}\mathrm{F})$ = 319 Hz), 124.4 (s, aryl-*C*H), 132.3, 148.4, 151.7. ^{19}F{^{1}H} NMR (25°C, $\mathrm{CD_2Cl_2}$, 235.5 MHz): δ −78.3 (s, $\mathrm{C}\mathit{F}_3$). IR (ATR, 32 scans): 3024 (w), 2958 (m), 2872 (w), 1464 (w), 1423 (w), 1397(w), 1377 (w), 1362 (m), 1292 (m), 1266 (m), 1227 (s), 1205 (s), 1153 (s), 1107 (m), 1020 (s), 926 (m), 879 (m), 856 (m), 820 (m), 783 (m), 757 (m), 734 (m), 658 (m), 633 (s), 593 (m), 574 (m). Raman (75 mW, 25 °C, 200 scans, $\mathrm{cm^{-1}}$): 3058 (2), 2968 (9), 2916 (10), 2790 (2), 2753 (2), 2720 (2), 1596 (4), 1520 (2), 1448 (3), 1414 (2), 1372 (2), 1290 (2), 1240 (4), 1213 (3), 1145 (3), 1113 (2), 1030 (3), 990 (1), 919 (2), 887 (2), 822 (2), 789 (1), 762 (2), 705 (1), 629 (1), 705 (1), 629 (1), 594 (1), 565 (2), 526 (1), 436 (1), 358 (2), 328 (2), 247 (2), 212 (2), 141.5 (2). MS (EI, *m*/*z*, >10 %): 43 (22) $[\mathrm{C_3H_7}]^+$, 57 (43) $[\mathrm{C_4H_9}]^+$, 69 (22) $[\mathrm{CF_3}]^+$, 83 (17), 97 (13), 246 (100) $[\mathrm{Mes^*H}]^+$, 261 (45) $[\mathrm{Mes^*NH_2}]^+$, 329 (12) $[\mathrm{Mes^*NH} + \mathrm{CF_3}]^+$. MS (FAB+, Cs, 20 keV, *p*-NBA matrix): 262 $[\mathrm{Mes^*{-}NH_3}]^+$, 334 $[\mathrm{Mes^*} - \mathrm{NAs}]^+$.

Synthesis of 1-Chloro-3-trifluoromethylsulfonato-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazane (11). To a stirred solution of 1,3-dichloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazane (**6**; 0.875g, 1.0 mmol) in toluene (20 mL) was added a solution of Ag-$\mathrm{(SO_3CF_3)}$ (0.549 g, 1.1 mmol) in toluene (20 mL) dropwise at −70 °C over a period of 10 min under exclusion of light. The resulting orange suspension was warmed to ambient temperatures over a period of 3 h and was then filtered (F4), resulting in an orange solution. Removal of the solvent in vacuo yielded 0.963 g (0.97 mmol, 97%) of **11** as an orange crystalline solid. Mp: 253 °C (dec.) Anal. Calcd % (found): C, 59.49 (59.20); H, 5.09 (5.12); N, 2.83 (3.17). ^{1}H NMR (25°C, toluene-d_8, 250.13 MHz): δ 2.08 (s, 6H, $\mathrm{C}\mathit{H}_3$), 2.19 (s, 6H, $\mathrm{C}\mathit{H}_3$), 2.24 (s, 6H, $\mathrm{C}\mathit{H}_3$), 6.52 (d, 2H, *m*-C*H*-Ph), 6.63 (s, 2H, *m*-C*H*-Mes), 6.72 (dd, 1H, *p*-C*H*-Ph, $J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 6.9 Hz, 7.9 Hz), 6.78 (s, 2H, m-C*H*-Mes). ^{13}C{^{1}H} NMR (25°C, toluene-d$_8$, 62.9 MHz): δ 20.6 (s, $\mathit{C}\mathrm{H}_3$), 21.6 (s, $\mathit{C}\mathrm{H}_3$), 21.8 (s, $\mathit{C}\mathrm{H}_3$), 120.3 (q, $\mathit{C}\mathrm{F_3}$, $^{1}J(^{13}\mathrm{C}{-}^{19}\mathrm{F})$ = 320 Hz), 123.8 (s, aryl-*C*H), 129.6 (s, aryl-*C*H), 130.7 (s, aryl-*C*H), 131.4 (s, aryl-*C*H), 131.0, 134.6, 136.7, 138.6, 139.3. ^{19}F{^{1}H} NMR (25°C, toluene-d_8, 235.5 MHz): δ −77.0 (s, $\mathrm{C}\mathit{F}_3$). IR (ATR, 32 scans): 2974 (w), 2950 (w), 2919 (w), 2859 (w), 1612 (w), 1515 (w), 1446 (w), 1405 (w), 1381 (w), 1337 (w), 1263 (s), 1224 (s), 1174 (s), 1080 (w), 1024 (s), 951 (w), 876 (w), 850 (m), 806 (m), 762 (m), 745 (m), 672 (w), 632 (s), 577 (m), 549 (w). Raman (150 mW, 25 °C, 204 scans, $\mathrm{cm^{-1}}$): 3051 (3), 3013 (3), 2923 (7), 2738 (3), 1611 (5), 1582 (7), 1481 (3), 1419 (7), 1382 (3), 1306 (6), 1262 (10), 1194 (2), 1163 (2). 1034 (2), 1006 (4), 950 (2), 851 (1), 824 (1), 762 (2), 741 (3), 692 (2), 674 (1), 650 (1), 574 (4), 561 (3), 524 (2), 514 (2), 482 (2), 463 (3), 427 (2), 353 (3), 336 (3), 312 (3), 283 (2), 268 (2), 254 (2), 234 (3), 172 (5), 141 (5), 126 (5). MS (FAB+, Cs, 20 keV, *p*-NBA matrix, M = $\mathrm{Ter_2N_2As_2Cl(SO_3CF_3)}$): 330 $[\mathrm{Ter} - \mathrm{NH_3}]^+$, 402 $[\mathrm{Ter} - \mathrm{NAs}]^+$, 805 $[\mathrm{M} - \mathrm{Cl} - \mathrm{SO_3CF_3} + \mathrm{H}]^+$, 839 $[\mathrm{M} - \mathrm{SO_3CF_3}]^+$, 956 $[\mathrm{M} - \mathrm{Cl} + \mathrm{H}]^+$.

Synthesis of 1-Chloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazenium μ-Azido-bis[hexachloridogallium(III)] (12). To a stirred greenish-black solution of 1-chloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazenium tetrachloridogallate (**7**; 1.052g, 1.0 mmol) in $\mathrm{CH_2Cl_2}$ (30 mL) was added a solution of $\mathrm{(CH)_3Si{-}N_3}$ (0.127 g, 1.1 mmol) in $\mathrm{CH_2Cl_2}$ (5 mL) dropwise at −50 °C over a period of 5 min. $\mathrm{GaCl_3}$ (0.194 g, 1.1 mmol) in $\mathrm{CH_2Cl_2}$ (5 mL) was then added dropwise at −50 °C over a period of 10 min. The resulting greenish-black solution was warmed to ambient temperatures over a period of 2 h. The solvent was removed in vacuo, and the black residue was washed with *n*-hexane (5 mL) and dried in vacuo. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (30 mL) and filtered (F4), resulting in a greenish-black solution. Slow removal of the solvent in vacuo yielded 1.213 g (0.98 mmol, 98%) of **12** as a black crystalline solid. Mp: 179 °C (dec.). Anal. Calcd % (found): C, 46.70 (46.49); H, 4.08 (4.01); N, 5.67 (5.24). ^{1}H NMR (25°C, $\mathrm{CD_2Cl_2}$, 250.13 MHz): δ 1.91 (s, 6H, $\mathrm{C}\mathit{H}_3$), 1.92 (s, 6H, $\mathrm{C}\mathit{H}_3$), 2.42 (s, 6H, $\mathrm{C}\mathit{H}_3$), 7.04 (s, 4H, *m*-C*H*-Mes), 7.08 (m, 2H, *m*-C*H*-Ph), 7.30 (m, 1H, *p*-C*H*-Ph). ^{13}C{^{1}H} NMR (25°C, $\mathrm{CD_2Cl_2}$, 62.9 MHz): δ 20.9 (s, $\mathit{C}\mathrm{H}_3$), 21.9 (s, $\mathit{C}\mathrm{H}_3$), 21.9 (s, $\mathit{C}\mathrm{H}_3$-Mes), 127.6 (s, aryl-*C*H), 130.6 (s, aryl-*C*H), 131.1, 132.1 (s, aryl-*C*H), 132.3 (s, aryl-*C*H), 134.0, 136.2, 138.1, 138.5, 138.8, 142.3. IR (ATR, 32 scans): 3053 (w), 2975 (w), 2943 (w), 2918 (m), 2854 (w), 2733 (w), 2157 (s), 1607 (m), 1561 (w), 1474 (m), 1454 (m), 1378 (m), 1323 (w), 1298 (w), 1267 (w), 1255 (w), 1213 (s), 1166 (w), 1125 (w), 1105 (w), 1092 (w), 1074 (m), 1062 (w), 1030 (m), 1012 (w), 1004 (w), 941 (w), 884 (s), 860 (s), 821 (s), 811 (m), 799 (s), 766 (s), 749 (m), 722 (s), 685 (m), 661 (m). MS (FAB+, Cs, 20 keV, *p*-NBA matrix, M = $\mathrm{Ter_2N_2As_2Cl^+}$): 329 $[\mathrm{Ter} - \mathrm{NH_2}]^+$, 402 $[\mathrm{Ter} - \mathrm{NAs}]^+$, 805 $[\mathrm{M} - \mathrm{Cl} + \mathrm{H}]^+$, 839 $[\mathrm{M}]^+$, 956 $[\mathrm{M} + \mathrm{NBA} - \mathrm{Cl} - \mathrm{H}]^+$, 991 $[\mathrm{M} + 2\mathrm{NBA} - \mathrm{Cl} + \mathrm{H}]^+$, 1109 $[\mathrm{M} + 2\mathrm{NBA} - \mathrm{Cl} + \mathrm{H}]^+$.

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Supporting Information Available: Crystallographic data of **6a−c**, **7**, **8**, **9**, **10a−b**, **11**, **12**, and **13** (CIF); experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.