Electronic Supplementary Material (ESI) for Dalton Transactions.

Formation of the Spirocyclic, Si-Centered Cage Cations $[ClP(NSiMe_3)_2Si(NSiMe_3)_2P_5]^+$ and $[P_5(NSiMe_3)_2Si(NSiMe_3)_2P_5]^{2+}$

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Supporting Information

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This PDF file includes:

1. Materials and Methods

General Remarks.

All manipulations were performed in a Glovebox MB Unilab produced by MBraun or using standard Schlenk techniques[S1] under an atmosphere of purified Argon (purchased from Westfalen AG). Dry, oxygen-free solvents (drying reagent in brackets; [CaH_2]: CH_2Cl_2, C_6H_5F and 1,2-$C_6H_4F_2$; [sodium / benzophenone]: Et_2O, THF, toluene, C_6H_6 [sodium]: pentane and n-hexane) were employed. Deuterated benzene (C_6D_6) was purchased from Sigma-Aldrich and distilled from sodium prior to use. Anhydrous deuterated dichloromethane (CD_2Cl_2) was purchased from Sigma-Aldrich. All distilled and deuterated solvents were stored either over molecular sieves (4 Å; CH_2Cl_2, C_6H_5F, 1,2-$C_6H_4F_2$) or potassium mirror (Et_2O, toluene, C_6H_6, pentane, n-hexane). Reagents such as $GaCl_3$, PCl_3, Me_3SiCl, $SiCl_4$, and $LiN(SiMe_3)_2$ were purchased from either Sigma-Aldrich or STREM Chemicals. All phosphanes, organic liquids and $SiCl_4$ unless purchased in redistilled quality were distilled prior to use. $GaCl_3$ was sublimed prior to use. Elemental white phosphorus (P_4) was donated by Thermphos International B.V.. P_4 was stored in water and dried with Me_3SiCl and recrystallized from CS_2 prior to use. Compounds **5**,[S2] and **8**[S3] were prepared according to literature known procedures. All glassware was oven-dried at 160 °C prior to use. NMR spectra were measured on either a Bruker ADVANCE III spectrometer (^1H (400.03 MHz), ^{13}C (100.59 MHz), ^{15}N (40.54 MHz), ^{31}P (161.94 MHz), ^{29}Si (79.49 MHz)) or a Bruker ADVANCE II spectrometer (^1H (200.13 MHz), ^{31}P (81.01 MHz)) at 26 °C unless indicated otherwise. All ^{13}C NMR spectra were exclusively recorded with composite pulse decoupling. Assignments of the carbon atoms in the ^{13}C spectra were performed via indirect deduction from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts were referenced to $\delta_{TMS} = 0.00$ ppm (^1H, ^{13}C) and $\delta_{H3PO4}(85\%) = 0.00$ ppm (^{31}P, externally). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. Absolute values are reported except for coupling constants derived by means of line shape iteration (vide infra). Assignments of individual resonances were done using 2D techniques (HMBC, HSQC, HH-COSY, PP-COSY) when necessary. Yields of products in solution were determined by integration of all resonances observed in the corresponding ^{31}P NMR spectra. For compounds which give rise to a higher order spin system in the $^{31}P\{^1H\}$ NMR spectrum, the resolution enhanced $^{31}P\{^1H\}$ NMR spectrum was transferred to the software gNMR, version 5.0, by Cherwell Scientific.[S4] The full line shape iteration procedure of gNMR was applied to obtain the best match of the fitted to the experimental spectrum. $^1J(^{31}P^{31}P)$ coupling constants were set to negative values[S5] and all other signs of the coupling constants were obtained accordingly. The designation of the spin systems were performed by convention. The spin system is considered to be higher order and consecutive letters are assigned if $\Delta\delta(P_iP_{ii})/^nJ(P_iP_{ii}) < 10$. For $\Delta\delta(P_iP_{ii})/^nJ(P_iP_{ii}) > 10$, the spin system is considered to be pseudo first order and the assigned letters are separated. Melting points were recorded on an electrothermal melting point apparatus (Barnstead Electrothermal IA9100) in sealed capillaries under Argon atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperatures using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd:YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was used for recording IR spectra. Alternatively, IR spectra were measured on a Bruker Vector 22 using KBr pellets. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder. UV/vis spectra were recorded on a Varian Cary 50 Conc UV/visible spectrophotometer. Mass spectra where recorded on a Thermo Scientific Orbitrap LTQ XL at the Organisch Chemisches Institut, University of Münster, Germany. Parent cations were separated and fragmented using appropriate potentials in order to obtain exact masses of the fragment-cations. Elemental analyses were performed on a Vario EL III CHNS elemental analyzer at the IAAC, University of Münster, Germany.

X-ray Diffraction Studies.

Single crystals were coated with Paratone-N oil, mounted using a glass fiber pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected either on a Bruker Quazar diffractometer equipped with a microfocus sealed tube MoK$_\alpha$ source ($\lambda = 0.71073$ Å) with a Montel mirror at 153(2) K and a scan width of 0.3°. Data reduction was done using the Bruker SMART[S6] software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). Structure solutions were found with the SHELXS-97 package using the direct method and were refined with SHELXL-97[S7] against F^2 using first isotropic and anisotropic thermal parameters for all non-hydrogen atoms. A SiMe$_3$-group of **7** is disordered over two positions with a s.o.f. (site occupancy factor) of 50 : 50. The molecular structure of **13**[Ga$_2$Cl$_7$]$_2$ features two **13**[Ga$_2$Cl$_7$]$_2$ molecules in the asymmetric unit and two Ga$_2$Cl$_7$ anions are disordered over two positions with a s.o.f.s of 52 : 48 and 88 : 12, respectively. Hydrogen atoms were generated with idealized geometries and isotropically refined using a riding model. Further details are given in tables S1 and S2 (pages S6 and S7).

S2. Spectroscopic Data

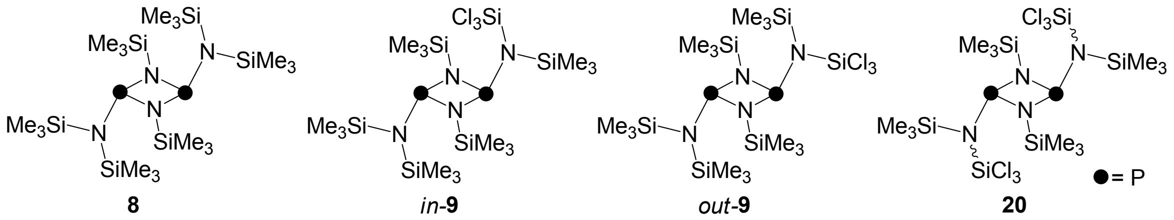

Figure S1. Observed side products **8**, *in*-**9**, *out*-**9** and **20** in the reaction of **5** with $SiCl_4$.

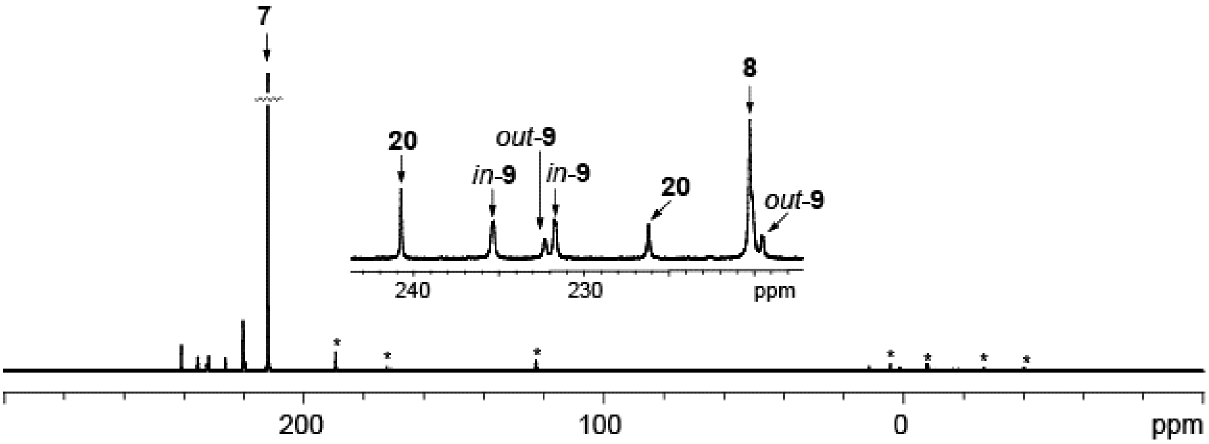

Figure S2. $^{31}P\{^1H\}$ NMR spectrum of the residue obtained in the reaction of **5** with $SiCl_4$ (C_6D_6-capillary, C_6H_5F, rt); unidentified side products are marked with asterisks.

Note: Compound **8** ($\delta(P) = 220.9$ ppm) represents the head to tail dimer of iminophosphane **5** (~ 16%)[S2] and the two AX spin systems are consistent with *trans*-conformers of unsymmetrically-substituted diphosphadiazane derivatives. The minor species (~ 5%) is identified as *out*-**9** ($\delta(P_A) = 219.5$ ppm, $\delta(P_X) = 232.3$ ppm, $^2J(P_AP_X) = 12.0$ Hz) [The designators *in*- and *out*- in **9** describe the arrangement of the $SiCl_3$ moiety pointing above and below the four-membered $[NP]_2$-ring (*in*-) or away from it (*out*-)] which is formed upon reaction of dimer **8** with one equivalent $SiCl_4$ accompanied by Me_3SiCl elimination. The second AX spin system (~ 8%) is assigned to *in*-**9** ($\delta(P_A) = 231.7$ ppm, $\delta(P_X) = 235.4$ ppm, $^2J(P_AP_X) = 14.5$ Hz). Interconversion of *in*-**9** to *out*-**9** is not observed due to the high barrier of rotation reported for exocyclic P–N bonds in amino-substituted diphosphadiazanes (**8**: $\Delta G > 27$ kcal/mol).[S3] The formation of *in*-**9** is supported by the ^1H NMR spectra. Both $SiMe_3$-groups pointing away from the four-membered $[NP]_2$-ring reveal a close proximity to the lone pairs of electrons of the adjacent P atoms. Thus, relatively large, through space $^4J(PH)$ coupling constants are observed ($\delta(H) = 0.42$ ppm, $^4J(PH) = 3.4$ Hz; $\delta(H) = 0.30$ ppm, $^4J(PH) = 3.7$ Hz).[S3] On basis of the obtained results and by comparison of the observed resonances the two remaining singlets in the low field part of the $^{31}P\{^1H\}$ NMR spectrum are tentatively assigned to conformers of **20** ($\delta(P) = 240.7$ ppm, $\delta(P) = 220.3$ ppm).

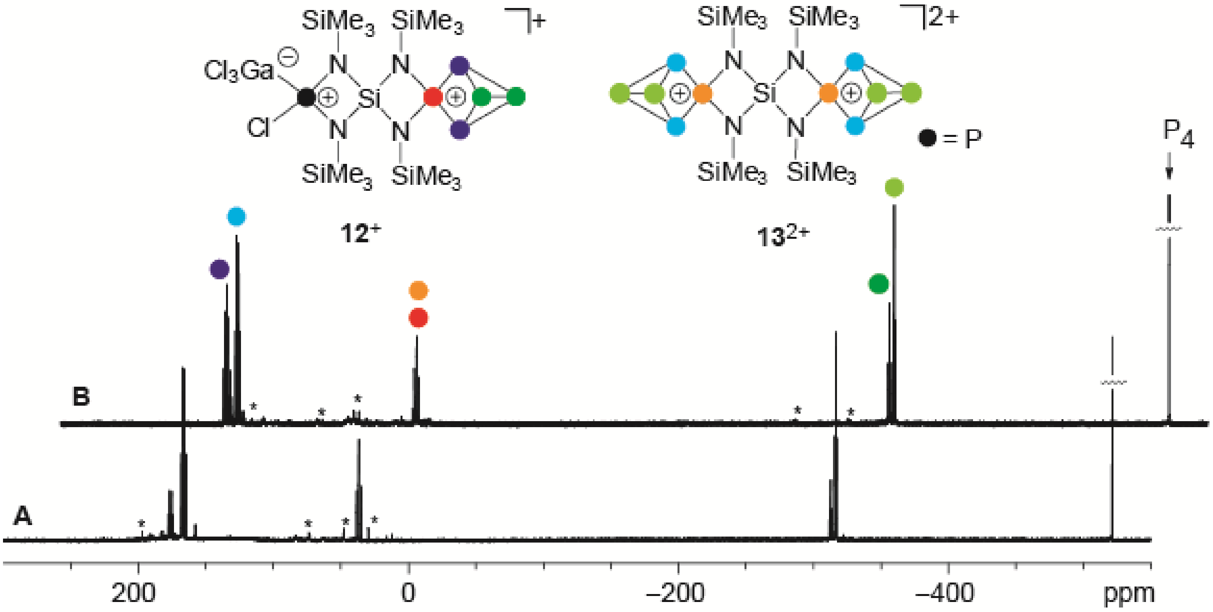

Figure S3. $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures of **7**, P_4 and $GaCl_3$ in **A**: a 1 : 1 : 2 and **B**: a 1 : 2 : 4 stoichiometry (both: C_6H_5F, C_6D_6-capillary, rt); small amounts of unidentified side products are marked with asterisks.

3. Crystallographic Details for compounds 7 and 13$[Ga_2Cl_7]_2$

Table S1. Crystallographic Data of **7** and **13**$[Ga_2Cl_7]_2$

	7	**13**$[Ga_2Cl_7]_2$
Formula	$C_{12}H_{36}Cl_2N_4P_2Si_5$	$C_{12}H_{36}Cl_{14}Ga_4N_4P_{10}Si_5$
MG [g mol^{-1}]	509.74	1461.78
Colour	colourless, block	colourless, block
Crystal System	monoclinic	triclinic
Space group	$P2_1$	P-1
a [Å]	10.4180(3)	9.9999(1)
b [Å]	10.3333(3)	23.7473(3)
c [Å]	12.9878(4)	26.3333(3)
α [°]	90	63.844(1)
β [°]	90.739(1)	79.463(1)
γ [°]	90	86.969(1)
V [Å^3]	1398.05(7)	5515.6(1)
Z	2	4
T [K]	153(2)	153(1)
Crystal size [mm]	0.14x0.14x0.08	0.50x0.43x0.33
ρ_c [mg m^{-3}]	1.211	1.760
F(000)	540	2872
$\lambda_{MoK\alpha}$, Å	0.71073	0.71073
θ_{min} [°]	1.57	0.88
θ_{max} [°]	28.70	27.88
Index range	$-14 \le h \le 14$	$-13 \le h \le 13$
	$-13 \le k \le 13$	$-31 \le k \le 31$
	$-17 \le l \le 17$	$-34 \le l \le 34$
μ [mm^{-1}]	0.567	3.030
Absorption correction	multi-scan	multi-scan
Reflection collected	15164	68756
Reflection unique	7108	26252
R_{int}	0.0141	0.0298
Reflection obs. [F > 2σ(F)]	6879	19583
Residual density [e Å^{-3}]	0.412 - –0.143	2.046 - –1.815
Parameters	264	999
GooF	1.072	1.057
R_1 [I > 2σ(I)] [a]	0.0267	0.0468
wR_2 (all data) [b]	0.0687	0.1208
CCDC	1060461	1060463

[a] $R_1 = \sum \| F_0 | - | F_c \| / \sum | F_0 |$. [b] $wR_2 = \left[\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0)^2] \right]^{1/2}$, where

$w = \left[\sigma^2 (F_0^2) \right]^{-1}, P = \left(\max(F_0^2, 0) + 2 * F_c^2 \right) / 3$

Table S2. Crystallographic Data of **13**[Ga_2Cl_7][$GaCl_4$] and **19**[$GaCl_4$]•C_6H_5F

	13[Ga_2Cl_7][$GaCl_4$]	**19**[$GaCl_4$]•C_6H_5F
Formula	$C_{12}H_{36}Cl_{11}Ga_3N_4P_{10}Si_5$	$C_{18}H_{41}Cl_5FGaN_4P_6Si_5$
MG [g mol^{-1}]	1285.71	905.79
Colour	colourless, block	colourless, irregular
Crystal System	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	13.7339(9)	9.7057(1)
b [Å]	25.044(1)	18.107(3)
c [Å]	14.6026(7)	23.856(1)
α [°]	90	90
β [°]	92.797(1)	93.677(1)
γ [°]	90	90
V [$Å^3$]	5016.6(4)	4183.9(1)
Z	4	4
T [K]	153(2)	153(2)
Crystal size [mm]	0.21x0.18x0.12	0.19x0.08x0.05
ρ_c [mg m^{-3}]	1.702	1.438
F(000)	2544	1848
$\lambda_{MoK\alpha}$, Å	0.71073	1.54178
θ_{min} [°]	1.48	3.07
θ_{max} [°]	27.88	68.24
Index range	$-18 \le h \le 17$	$-10 \le h \le 10$
	$-32 \le k \le 32$	$-21 \le k \le 21$
	$-19 \le l \le 19$	$-23 \le l \le 28$
μ [mm^{-1}]	2.643	7.587
Absorption correction	multi-scan	multi-scan
Reflection collected	50683	24341
Reflection unique	11964	7461
R_{int}	0.0229	0.0391
Reflection obs. [F > 2σ(F)]	10240	6461
Residual density [e $Å^{-3}$]	1.431 - –1.001	1.259 - –0.633
Parameters	418	373
GooF	1.044	1.058
R_1 [I > 2σ(I)] [a]	0.0306	0.0481
wR_2 (all data) [b]	0.0811	0.1440
CCDC	1060462	1060464

[a] $R_1 = \sum \| F_0 | - | F_c \| / \sum |F_0|$. [b] $wR_2 = \left[\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0)^2] \right]^{1/2}$, where $w = \left[\sigma^2 (F_0^2) \right]^{-1}, P = \left(\max(F_0^2, 0) + 2 * F_c^2 \right) / 3$

4. References

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