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Dimeric (Tris(*tert*-butyl)silyl)phosphanyl (Tris(*tert*-butyl)silyl)phosphanediyl Gallane: A Molecule with a Ga–P–Ga Heteroallyl System

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The metathesis reaction of potassium (tris(*tert*-butyl)silyl)phosphanide with $GaCl_3$ in a molar ratio of 1:1 leads to the formation of $[Cl_2GaP(H)Si^tBu_3]_2$ (**1**) as a mixture of cis and trans isomers with very large ^1J(P,H) and ^2J(P,P) coupling constants. The molecular structure of **1** shows a Ga_2P_2 cycle with nearly planar coordinated phosphorus atoms under neglection of the hydrogen atoms and Ga–P distances of 239 pm. The reaction of $GaCl_3$ with 3 equiv of potassium (tris(*tert*-butyl)silyl)phosphanide as well as the reaction of **1** with 2 equiv of $KP(H)Si^tBu_3$ yields $[^tBu_3SiP(H)Ga(\mu\text{-}PSi^tBu_3)]_2$ **(2)**. The central moiety comprises a four-membered Ga_2P_2 cycle with one planar P atom and extremely short Ga–P bonds of approximately 226 pm, the other being in a pyramidal environment with an angle sum of 298.4°. The structure of **2** can be described as a GaPGa heteroallyl system which is bonded to a phosphanidyl substituent. This idea and its dependency on the steric demand of the trialkylsilyl groups are investigated by DFT calculations on different isomers of **2**.

Introduction

Phosphinogallanes gained interest as synthons for the synthesis of gallium phosphide, GaP, a material with zinc blende structure.[1] The adduct of $GaCl_3$ and $P(SiMe_3)_3$ formed in high yield in hydrocarbon solvents with a Ga−P bond length of 238 pm.[2] This complex eliminated chlorotrimethylsilane and gave dimeric $Cl_2Ga-P(SiMe_3)_2$ with a central four-membered Ga_2P_2 cycle with an average Ga−P distance of 238 pm.[3] In this molecule the Ga−P−Si angles varied between 111.0 and 116.6°. Thermal decomposition yielded GaP, characterized by X-ray diffraction.[2,4] Further procedures for preparing molecules with Ga_2P_2 cycles applied the metalation reaction; thus, the bisalkylated derivatives $[R_2GaP(SiMe_3)_2]_2$ were available for a wide variety of alkyl substituents such as Me,[5,6] Et,[7] $CH_2{}^tBu$,[8] and CH_2SiMe_3.[9] The partial substitution of the trimethylsilyl groups by hydrogen leads to less steric strain and an enlargement of the ring size to a Ga_3P_3.[10] Due to valuable applications the group 13/15 organometallic compounds are still of enormous interest.[11]

Cycles having bonds between the heavier elements of the boron and nitrogen groups with coordination numbers of 3 are far less common. In acyclic phosphanides of three-coordinate gallanes with GaP, PGaP, and GaPGa fragments the Ga−P bond lengths vary between 219 and 236 pm, depending on the double bond character.[12] A cyclic arylgallium (triphenylsilyl)phosphanediide with a planar Ga_2P_2 moiety showed a pyramidically coordinated phosphorus atom with large Ga−P distances of 234 pm and an angle sum at the P atom of 325.5°.[13]

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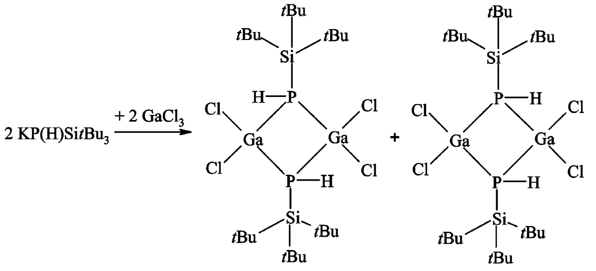
Another reason for the interest in gallium phosphorus compounds is the unusual bonding situation. A double bond can be discussed as a consequence of back-bonding of the pnictogen lone pair into a p-orbital of the boron group element.[12,14] However, an efficient π-bond requires planar geometries at both atoms, and only a few examples of Ga derivatives of the heavier pnictogens with planar coordination spheres at the pnictogen atom are known.[12] Petrie and Power[15] 10 years ago published a digallylphosphane with an almost planar phosphorus atom and Ga−P distances of 226 pm and a Ga−P−Ga angle of 136°. Just recently, a Ga−As multiple bond system with a bond length of 231 pm was reported by von Hänisch.[16] Sterical protection of this reactive structural element was achived by using triisopropylsilyl groups as well as the $(thf)_3Li$ fragment. Herein, we describe a GaPGa heteroallylic system which bonds to a phosphanidyl substituent.

Synthesis and Discussion

Synthesis. The metathesis reaction of potassium (tris(*tert*-butyl)silyl)phosphanide[17] with gallium trichloride in toluene yields dichloro((tris(*tert*-butyl)silyl)phosphino)gallane (**1**) according to eq 1. The two possible isomers with trans and cis configuration of the PH groups of the cycle are formed in a ratio of 3:1.

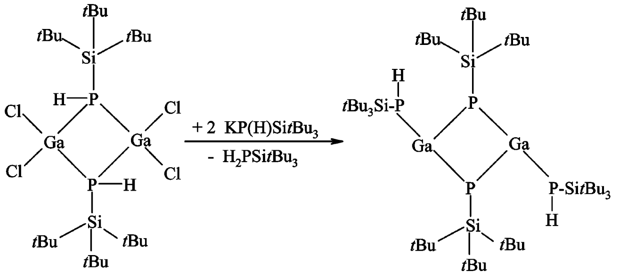


1 *trans* **1** *cis*

(1)

Colorless dimeric **1** shows remarkable ^{31}P NMR data as described earlier for an analogous In_2P_2 cycle.[18] The trans isomer of **1** is discussed in detail; the values of the cis isomer are given in brackets. The resonance at $\delta = -159.1$ (-138.0) shows an AA′XX′ pattern; however, the signals have a half-height width of 73.5 Hz (74 Hz), partly a consequence of the quadrupole momentum of the gallium atoms ($I = 3/2$), a temperature dependency is not detectable. Special attention has to be drawn to the $^1J(P,H)$ coupling constant of 277 Hz (277 Hz). Usually, these coupling constants show values of approximately 200 Hz, which are even smaller with alkali metal counterions.[17] In $H_2PSi^tBu_3$ a chemical shift of $\delta = -264.3$ and a $^1J(P,H)$ value of 185.6 Hz are observed.[17,19] The $^2J(P,P)$ coupling constant shows an extremely large value of 237 Hz (252 Hz), which lies in the region of $^1J(P,P)$ couplings.[20] In four-membered M_2P_2 cycles of the alkaline earth metals $^2J(P,P)$ coupling constants up to 135 Hz for $(Me_3Si)_2N{-}Ca(DME){-}PHSi^iPr_3$ were detected.[21] M_4P_4 heterocubane structures also show smaller $^2J(P,P)$ values. In the series $Ba_nSn_{4-n}(PSi^tBu_3)_4$ the corresponding coupling constants vary between 26 Hz ($n = 1$)[22] and 34 Hz ($n = 2$) and finally 14 Hz ($n = 3$).[23,24] To understand and interpret these results, an X-ray structure determination was performed.

To achive more steric strain on the Ga_2P_2 cycle, compound **1** is reacted with excess of potassium (tris(*tert*-butyl)silyl)phosphanide according to eq 2 to give $[^tBu_3SiP(H)Ga(\mu\text{-}PSi^tBu_3)]_2$ **(2),** which can also be prepared directly by the reaction of $GaCl_3$ with potassium (tris(*tert*-butyl)silyl)phosphanide in a molar ratio of 1:3.



1 **2**

(2)

The ^{31}P NMR spectrum shows a doublet of triplets at $\delta = -223$ for the terminal phosphanide groups with a coupling constant of $^1J(P,H) = 190$ Hz at room temperature. At +60 °C a broad singulet can be detected at $\delta = -85$ for the bridging phosphanide ligands. At low temperatures the doublet of triplets collapses into a doublet with two broad resonances, while two singulets at $\delta = -40$ and -99 are detected for the bridging phosphanide groups. The question regarding this molecule concerns the bonding situation within the four-membered cycle with the two chemically different phosphorus atoms. Due to the low coordination number of 3 and the Lewis acidity at the gallium atom, a Ga−P double bond can be discussed. Therefore, an X-ray structure determination and DFT calculations were performed.

Molecular Structures. A perspective representation of dimeric **1** is given in Figure 1. Atoms generated by crystallographic inversion symmetry ($-x + 1, -y, -z$) are marked with apostrophes. The central fragment comprises the planar four-membered Ga_2P_2 cycle. Even though $[Cl_2GaP(SiMe_3)_2]_2$

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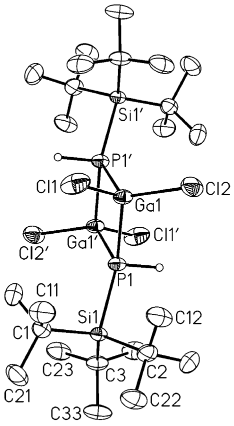


Figure 1. Molecular structure of $[Cl_2GaP(H)Si^tBu_3]_2$ **(1)**. The ellipsoids represent a probability of 40%. The H atoms are neglected for clarity reasons with the exception of the P-bonded ones. The symmetry-generated atoms are marked with apostrophes. Selected bond lengths (pm) and angles (deg): Ga1−Cl1 216.0(1), Ga1−Cl2 216.5(1), Ga1−P1 238.3(1), Ga1−P1′ 239.4(1), P1−Si1 231.4(2), P1−H1 137(2), Si1−C1 191.5(5), Si1−C2 192.5(4), Si1−C3 192.2(4); Cl1−Ga1−Cl2 111.07(6), P1−Ga1−P1′ 90.05(4), P1−Ga1−Cl1 117.42(5), P1−Ga1−Cl2 109.47(5), P1′−Ga1−Cl1 110.09(5), P1′−Ga1−Cl2 117.55(5), Ga1−P1−Ga1′ 89.95(4), Ga1−P1−Si1 130.14(5), Ga1′−P1−Si1 130.40(5), Ga1−P1−H1 96(2), Ga1′−P1−H1 99(2), Si1−P1−H1 103(2).

Table 1. Comparison of Selected Structural Parameters of $[Cl_2GaP(H)Si(^tBu)_3]_2$ (**1**) and $[Cl_2GaP(SiMe_3)_2]_2$ (Mean Values of Bond Lengths (pm) and Angles (deg)

	$[Cl_2GaP(SiMe_3)_2]_2$	**1**
Ga−Cl	217.5	216.3
Ga−P	237.9	238.8
P−Si	228.7	231.4
P−H		137
Cl−Ga−Cl	107.1	111.1
P−Ga−P	93.6	90.1
Ga−P−Ga	86.4	90.0
Ga−P−Si	112.7/115.9	130.1
Ga−P−Si	111.0/116.6	130.4

Table 2. Crystallographic Parameters and Details of Data Collection and Refinement Procedures of **1** and **2**

param	**1**·toluene	**2**
empirical formula	$C_{31}H_{64}Cl_4Ga_2P_2Si_2$	$C_{48}H_{110}Ga_2P_4Si_4$
fw	836.18	1063.07
temp *T* (K)	200(2)	200(2)
space group[31]	*C*2/*c*	$P\bar{1}$
a (pm)	1597.21(2)	1419.93(8)
b (pm)	1483.45(2)	2006.4(1)
c (pm)	1809.19(3)	2249.0(2)
α (deg)	90	99.357(7)
β (deg)	96.7464(6)	93.082(7)
γ (deg)	90	99.600(7)
V (nm^3)	4.2568(1)	6.2121(7)
Z	4	4
ρ_{calcd} (g·cm^3)	1.305	1.137
λ (Å)	0.710 73	0.710 73
μ (cm^{-1})	1.668	1.075
collcd reflcns	27 881	36 003
indep reflcns	2958	18 375
obsd reflcns ($I > 2\sigma(I)$)	2487	12 336
abs corr	numerical	numerical
max/min transm	0.898/0.720	0.808/0.688
$wR_2{}^a$ (on F^2)	0.1474	0.1385
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0446	0.0524
s^b on F^2	1.141	0.894
CCDC no.[37]	CCDC-217325	CCDC-199291

[a] Definitions of the *R* indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

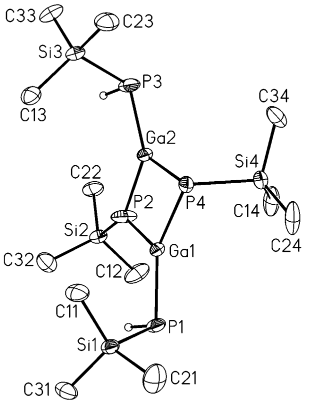
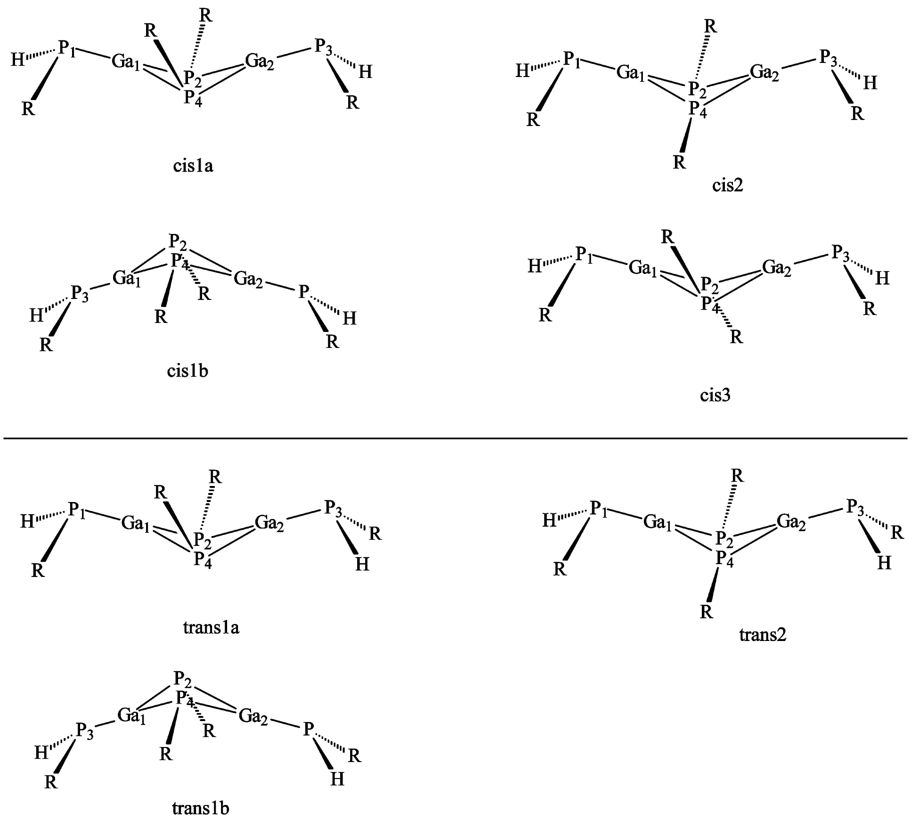


Figure 2. Molecular structure of $[^tBu_3SiP(H)\text{-}GaPSi^tBu_3]_2$ **(2)**. The ellipsoids represent a probability of 40%, and the methyl group are omitted for clarity reasons. The P-bonded hydrogen atoms are shown with arbitrary radii. Selected bond lengths (pm) and angles (deg): Ga1−P1 230.8(1), Ga1−P2 226.4(2), Ga1−P4 233.8(2), Ga2−P2 225.2(2), Ga2−P3 230.5(2), Ga2−P4 233.4(1), P1−Si1 229.5(2), P2−Si2 224.6(2), P3−Si3 228.7(2), P4−Si4 229.9(2), P1−H1 122(5), P3−H3 134(5); P1−Ga1−P2 126.39(6), P1−Ga1−P4 136.23(5), P2−Ga1−P4 97.72(5), P2−Ga2−P3 130.11(6), P2−Ga2−P4 97.72(5), P3−Ga2−P4 132.12(6), Ga1−P1−Si1 112.38(6), Ga1−P1−H1 87(2), Si1−P1−H1 100(2), Ga1−P2−Ga2 84.08(5), Ga1−P2−Si2 136.25(8), Ga2−P2−Si2 138.65(8), Ga2−P3−Si3 110.85(7), Ga2−P3−H3 98(2), Si3−P3−H3 95(2), Ga1−P4−Ga2 80.68(5), Ga1−P4−Si4 108.57(6), Ga2−P4−Si4 109.15(7).

contains a similar central moiety, these structures show significant differences as summarized in Table 1.

In **1** the Ga−Cl bonds are shorter and the Cl−Ga−Cl angle is strongly widened. Furthermore, the Ga−P−Si bond angles of 130° are extremely large and, hence, the Ga_2PSi fragment is flattened, even more than in the above-mentioned $[RGaPSiPh_3]_2$[13] with a triply coordinated phosphorus atom. These kinds of distortions have never been observed earlier for phosphinogallanes regardless of the substituents at the gallium atom and are a consequence of the extreme sterical demand of the tris(*tert*-butyl)silyl substituent. The molecular structure of $[^tBu_3SiP(H)GaPSi^tBu_3]_2$ **(2)** and the numbering scheme are given in Figure 2. The gallium atoms Ga1 and Ga2 show the low coordination number of 3 and are in a planar environment. The metal centers are bridged by two phosphanediide ligands, and terminally bonded phosphanide substituents complete the coordination spheres of the gallium atoms.

Special attention has to be drawn to the bridging phosphorus atoms. Whereas the atom P2 is coordinated planarity, the other bridging pnictogen atom shows an angle sum of 298.4° and is in a pyramidal environment. This observation could suggest a bonding situation as symbolized in Figure 4. The four-membered cycle contains the Ga1−P2−Ga2 fragment with short Ga−P bond lengths of approximately 226 pm, whereas the other endocyclic distances to P4 display values of more than 233 pm. Furthermore, the P2−Si2 bond length is small compared to the other P−Si distances in this molecule, a consequence of the electrostatic attraction between the anionic phosphorus and the partly positive silicon atom. In the monoanionic terminal phosphanide substitutents we found P1−Si1 and P3−Si3 values of 229 pm. Even though the phosphorus atom P4 is in a bridging position



cis1a

cis2

cis1b

cis3

trans1a

trans2

trans1b

Figure 3. Molecular models and numbering of atoms of all isomers of **2**.

Table 3. Selected Calculated Structural Data for All Calculated Species (B3LYP) (Distances in Å, Angles in deg)

R		Ga_1-P_2 ring	Ga_1-P_4 ring	$\Delta(Ga-P)$ ring	Ga_1-P_1 term	P_2-P_4	Ga−Ga	$Ga_1-P_2-Ga_2$	$P_2-Ga_1-P_4$	$P_2-Ga_1-P_1$	Ga_1-P_1-H	$P_2-Ga_1-P_4-Ga_2$	$P_1-Ga_1-P_2-P_4$	ΔE (kcal/mol)
H	cis/trans1a	2.390	2.390	0.000	2.368	3.572	2.910	75.0	96.7	131.3	94.0	30.3	171.6	0.0
	cis/trans1b	2.390	2.390	0.000	2.369	3.568	2.920	75.3	96.6	131.7	93.8	−30.1	176.1	0.3
	cis/trans2	2.379	2.419	0.040	2.368	3.667	2.956	76.8	99.7	130.3	94.2	22.8	168.2	2.0
SiH_3	cis1a	2.380	2.380	0.000	2.360	3.580	2.967	77.1	97.5	130.9	94.8	24.4	175.1	0.0
	cis1b	2.385	2.376	−0.009	2.361	3.561	2.989	77.6	96.8	129.7	94.8	−24.6	171.1	0.8
	cis2	2.372	2.389	0.017	2.361	3.647	3.051	80.0	100.0	129.8	94.7	6.2	171.3	1.5
	trans1a	2.379	2.381	0.002	2.360	3.578	2.966	77.1	97.5	130.9	94.8	24.7	174.9	0.0
	trans1b	2.380	2.381	0.001	2.361	3.559	2.988	77.7	96.8	129.9	94.9	−24.9	171.0	0.8
	trans2	2.374	2.387	0.013	2.361	3.647	3.055	79.6	100.1	130.0	95.2	3.5	173.6	1.4
$SiMe_3$	cis1a	2.368	2.378	0.010	2.359	3.578	2.972	77.8	97.8	132.1	94.9	22.8	177.8	0.0
	cis1b	2.374	2.356	−0.018	2.360	3.469	3.011	78.7	94.3	129.3	94.6	−27.2	166.8	4.2
	cis2	2.358	2.390	0.032	2.360	3.633	3.027	79.8	99.9	126.4	94.5	10.5	164.1	2.9
	trans1a	2.371	2.375	0.004	2.359	3.578	2.971	77.5	97.9	131.9	94.7	22.9	178.1	0.0
	trans1b	2.369	2.368	−0.001	2.364	3.499	3.021	79.3	95.3	129.2	94.7	−24.7	164.1	4.1
	trans2	2.369	2.382	0.013	2.358	3.642	3.040	79.8	100.1	125.6	95.0	2.9	164.4	1.8
$Si(CMe_3)_3$, expt		2.264	2.338	0.074	2.308	3.454	3.024	84.1	97.7	130.1	98.4	3.9	177.5	

between the metal centers, the P−Si bond is elongated and has a large value of 230 pm. All of these observations could give rise to prefer the description of a phosphanidyl, which is coordinated to an allylic $[RGa{=}P(R')GaR]^+$ moiety. To test this model, DFT calculations were performed to verify this bonding situation.

Theoretical Investigations. To obtain insight into the structure and bonding of **2**, several model species of the type $[RP(H)GPR]_2$ (R = H, SiH_3, $SiMe_3$) and their isomers (Figure 3) have been studied by DFT (B3LYP) calculations and population analysis (NBO).[24−28] These results are summarized in Tables 3 and 4. All investigated isomers are very close in energy (ΔE < 5 kcal/mol) and are easily converted

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Table 4. Calculated Partial Charges (NPA Analysis), Hybridization, Occupancies (Occc), and Donor−Acceptor Interactions of the Cis2 Species (Figure 3)

R	H	$P_{1/3}$	P_2	P_4	Ga
H	0.020	−0.297	−0.658	−0.624	+0.859
SiH_3	0.030	−0.487	−0.879	−0.851	+0.953
$SiMe_3$	0.023	−0.559	−0.948	−0.918	+0.955

	$\sigma(P_2{-}Ga)$	$LP(P_2)$	occ p-LP(Ga)/e	LP(P2/4) → p-LP(Ga) (kcal/mol)	LP(P1) → p-LP(Ga) (kcal/mol)
H	$0.84\ sp^{6.58} + 0.54\ sp^{2.08}$	$sp^{0.75}$	0.184	5.2/1	4.5
SiH_3	$0.85\ sp^{6.13} + 0.52\ sp^{2.09}$	$sp^{0.83}$	0.201	7.0/5.3	6.0
$SiMe_3$	$0.86\ sp^{5.90} + 0.51\ sp^{2.07}$	$sp^{1.00}$	0.232	8.09/5.8	7.0

into each other. Hence lattice effects may be responsible for the fact that not the global isomer (cis1 structure) but an intermediate cis1/cis2 structure was experimentally observed. The X-ray study of **2** displayed another interesting structural feature: there are three significantly different P−Ga distances (see Table 3 and Figures 2 and 3), a fairly short $d(P_1{-}Ga) = 225$, a larger $d(P_2{-}Ga) = 233$, and a medium $d(P_{3/4}{-}Ga) = 230$ pm. All P−Ga distances are slightly shorter than the sum of the covalent radii (cf. $r_{cov}(P) + r_{cov}(Ga) = 236$ pm). Inspection of the theoretically obtained structural data revealed (i) that the d(Ga1−P2/4) bond lengths decrease for all isomers of **2** the larger R (which correlates with an increasing negative charge at the P atom) and (ii) that the different bond lengths within the GaPGaP ring arise due to symmetry *and* steric effects. The Ga−P1 bond lengths show a changing pattern with only very small deviations. As expected, the Ga1−P2−Ga2 angles increases the larger the R substituent. All species show a slightly bent four-membered ring (dihedral angles between 164 and 177°). Also, the atoms P2−Ga1−P2−P4 (and P3−Ga2−P2−P4, respectively) form a plane; however, the deviation from planarity is smallest for the cis2 and trans2 isomers, which is nicely in agreement with the experimentally observed data.

The intriguing structural feature of **2** can be rationalized by a qualitative VB consideration. Canonical Lewis structures of types **A**−**E** (Figure 4) are easily anticipated. Because natural atomic populations of the d-type AOs on P or Ga atoms are so small, expanded valence-shell VB structures would be expected to make very minor contributions to the ground-state resonance scheme; hence, we have not considered expanded valence shell Lewis structures (e.g. population of d-type atomic orbitals is less than 0.01 electrons).

In all investigated species, the Ga−P bonds are highly polarized with roughly 70% of the P−Ga σ bond localized on the P atom. The polarization increases along $R = SiMe_3 > SiH_3 > H$ displaying a fairly large charge transfer the larger the R group (Table 4). Somewhat smaller is the polarization of the P−Si bonds (60% on the P atom) whereas the P−H bond represents an almost covalent bond.

The calculated NAO partial charges of all investigated species ($Q_{P1} \cong -0.5$, $Q_{P4} \cong -1$, $Q_{Ga1} \cong +1$e, Table 4) support the conclusion that resonance structure **A** should be the most important one.[25] This structure suggests very polar Ga−P bonds. Nevertheless, both Ga atoms in structure **A** possess an electron sextet as well as an empty p-orbital which is oriented vertically to the Ga_2P_2 plane.[24] Thus, the electronic situation in **A** should be similar to the boron trihalides.[26] These compounds are stabilized by intramolecular donor−acceptor interactions which lead to B−X double bonds. To investigate if **2** is also stabilized by partial Ga−P double bonds NBO analyses of **2** and the related cis2 isomers were performed.[27,28] During this procedure either structure **A** (for all model compounds) or **B** (for **2**) possessing a π-bond between P2 and Ga2 was found to be the energetically favored Lewis formula. Since this π-bond in **2** is localized with 90% at the P atom, this NBO is better described as a lone pair on P which is slightly delocalized in a π-bond manner over the adjacent Ga atoms. Hence, structure **A** seems to be also the primary structure for **2**. The investigation of the intramolecular donor−acceptor interactions revealed that all lone pairs of the P atoms in all investigated species are somewhat delocalized into the empty p-type AO of the Ga atoms being responsible for some kind of "π-character" along the P−Ga bond axis. This donor−acceptor interaction increases the larger R and the smaller the Ga−P distances (Table 4). In accordance with this, the occupation of the empty p-LP(Ga) of the Ga atoms [0.18 (H), 0.20 (SiH_3), and 0.23 e ($SiMe_3$)] and the energy gain due to this LP(P) → p-LP(Ga) interaction [$\Sigma LP(P_{2/4}) \rightarrow p\ LP(Ga_{1/2})$: 10 (H), 14 ($SiH_3$), 16 ($SiMe_3$) kcal/mol, Table 4] also increases.

For **2** this delocalization of the P lone pair is found mainly along the Ga1−P2 and Ga2−P2 bonds (26 kcal/mol) but not along the Ga1−P4−Ga2 unit corresponding to resonance between structures **A** ↔ **B** ↔ **C**. Despite the fact that both formulas **B** and **C** possess a positive formal charge at P2 and a negative formal charge at one Ga atom, the strong polarization at the Ga−P σ-bond and the π-bond leads to a negative partial charge at the P atom and a positive partial charge at the Ga atom. Since this "π-character" is relatively small and the Ga−P bonds are fairly ionic, structure **A** represents the primary Lewis formula followed by structures **B** and **C** according to the NBO analysis. This is also in accordance with the obtained structural data: The shortest bond with the strongest double bond character was observed for P2−Ga1 and P2−Ga2. The longest bond was observed for P4−Ga1 and P4−Ga2, respectively, without noteworthy π-bonding contribution and average lengths of P3/4−Ga1/2 230 pm. The contribution of the mesomeric forms **D** and **E** are small; however, they clearly explain why the exocyclic Ga−P bonds are even shorter than the Ga1/2−P4 bonds.

Summary

The heteroallylic $[RGa{=}PR'GaR]^+$ moiety with a GaPGa system which is bonded to a (tris(*tert*-butyl)silyl)phosphanidyl substituent is a novel structural element in the chemistry of cyclic gallylphosphanides. The X-ray structural parameters clearly show two short Ga−P bonds with small amounts of π-character and two long endocyclic Ga−P bonds. DFT calculations verify that this bonding situation is strongly a consequence of the demanding tris(*tert*-butyl)silyl groups and symmetry decrease. Smaller trialkylsilyl

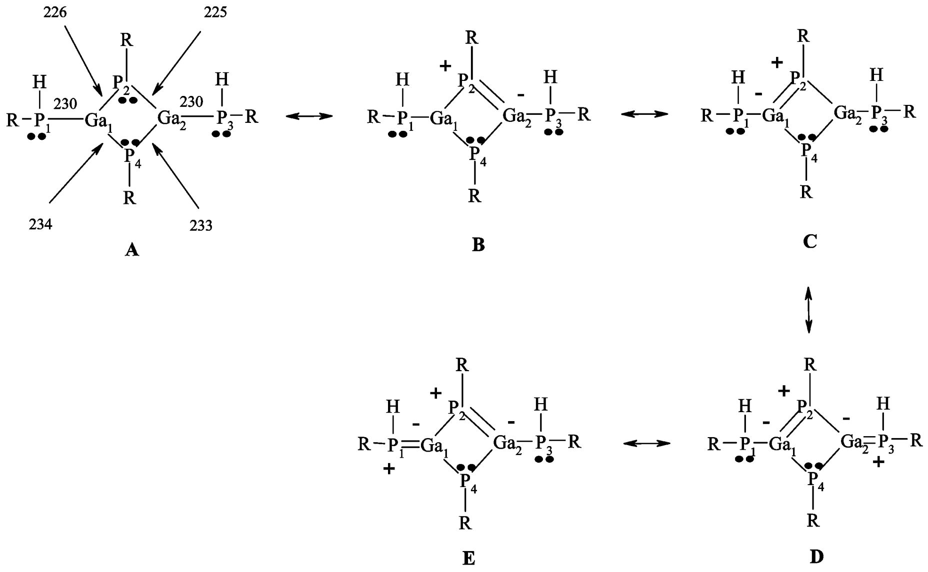

Figure 4. Valence bond illustration of **2**. The numbers represent bond lengths in pm (R = $\mathrm{Si}^t\mathrm{Bu}_3$).

substituents lead to a partial balancing out of these bond length differences.

Experimental Section

General Procedures. All experiments and manipulations were carried out under an atmosphere of argon. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. Starting $\mathrm{KP(H)Si}^t\mathrm{Bu}_3$[17] was prepared according to a literature procedure.

Bis[dichloro(*μ*-(tris(*tert*-butyl)silyl)phosphino)gallane] (1). Potassium (tris(*tert*-butyl)silyl)phosphanide (1.65 g, 4.65 mmol) was dissolved in 20 mL of toluene and added to a suspension of 0.82 g of $\mathrm{GaCl_3}$ (4.65 mmol) in 1.9 mL of toluene at −78 °C. During the warming to room temperature the reaction mixture turned yellow. After the mixture was stirring for 1 day at room temperature, a yellow solution and a colorless precipitate formed. The solid material was removed and the volume reduced to a few milliliters. Within 1 day 0.86 g of colorless crystals (1.16 mmol, 25%) of **1** precipitated. Mp: 251 °C (dec). ^{31}P NMR: $\delta = -159.14$ (m, $\Delta_{1/2} = 73.5$ Hz, $^1J(\mathrm{P,H}) = 277.7$ Hz, $^2J(\mathrm{P,P}) = 237.5$ Hz, $^3J(\mathrm{P,H}) = -12.0$ Hz, $^4J(\mathrm{H,H}) = 0$ Hz). ^{1}H NMR: $\delta = 1.11$ (s, $\mathrm{CH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: $\delta = 30.9$ (s, $\mathrm{CH_3}$), 22.9 (d, C, $^2J(\mathrm{P,C}) = 5.3$ Hz). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR: $\delta = 39.9$ ($|^1J(\mathrm{P,Si}) + {}^3J(\mathrm{P,Si})| = 29.0$ Hz). IR (cm^{-1}): $\nu = 2302$ (PH). Anal. Calcd for $\mathrm{C_{12}H_{28}Cl_2GaPSi}$ (M_r = 744.048): C, 43.71; H, 7.81. Found: C, 43.62; H. 7.61.

Bis[(tris(*tert*-butyl)silyl)phosphanyl(*μ*-(tris(*tert*-butyl)silyl)phosphanediyl)gallane] (2). Gallium trichoride (1.09 g, 6.19 mmol) was dissolved in 20 mL of toluene, and 5.02 g of $\mathrm{KP(H)Si}^t\mathrm{Bu}_3$ (18.57 mmol) was added. The solution turned orange immediately, and a precipitate formed. All solid materials were removed by decanting, and the volume of the mother liquor was reduced to a few milliliters. At room temperature 2.14 g of orange prisms of **2** (4.02 mmol, 65%) precipitated. Mp: 315 °C (dec). ^{31}P NMR (+60 °C): $\delta = -222.9$ (dt, PHSi, $^1J(\mathrm{P,H}) = 190.1$ Hz, $^2J(\mathrm{P,P}) = 16.0$ Hz), −67.3 (br, PSi). ^{31}P NMR (room temperature): $\delta = -223.71$ (PHSi, $^1J(\mathrm{P,H}) = 190.2$ Hz, $^2J(\mathrm{P,P}) = 17.1$ Hz). ^{31}P NMR (−60 °C): $\delta = -224.6$ (PHSi, $^1J(\mathrm{P,H}) = 195.2$ Hz), −40 (broad, PSi), −99 (broad, PSi). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR: $\delta = 35.3$ (PHSi, $^1J(\mathrm{P,Si}) = 60.6$ Hz), 35.8 (PSi, $^1J(\mathrm{P,Si}) = 54.4$ Hz). ^{1}H NMR: $\delta = 1.33$ (s, $\mathrm{CH_3}$, $\mathrm{P(H)Si}^t\mathrm{Bu}_3$), 1.35 (s, $\mathrm{CH_3}$, $\mathrm{PSi}^t\mathrm{Bu}_3$), PH signal not detectable. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: $\delta = 32.0$ ($\mathrm{CH_3}$ of $\mathrm{PSi}^t\mathrm{Bu}_3$), 31.6 ($\mathrm{CH_3}$ of $\mathrm{P(H)Si}^t\mathrm{Bu}_3$), 24.4 (C of $\mathrm{PSi}^t\mathrm{Bu}_3$, $^2J(\mathrm{P,C}) = 6.5$ Hz), 23.0 (C of $\mathrm{P(H)Si}^t\mathrm{Bu}_3$, $^2J(\mathrm{P,C}) = 6.1$ Hz). IR (cm^{-1}): $\nu = 2302$ (PH). Anal. Calcd for $\mathrm{C_{24}H_{55}GaP_2Si_2}$ (M_r = 531.515): C, 54.23; H, 10.43. Found: C, 53.78; H, 10.55.

Structure Determinations. Data were collected on a STOE-IPDS diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 71.073$ pm) using oil-coated[29,30] rapidly cooled single crystals. Crystallographic parameters, details of data collection, and refinement procedures are summarized in Table 2.

All structures were solved by direct methods with the program SIR97[32] and refined with the software package SHELXL-97.[33] Neutral scattering factors were taken from Cromer and Mann[34] and for the hydrogen atoms from Stewart et al.[35] The non-hydrogen atoms were refined anisotropically. The H atoms were considered with a riding model under restriction of ideal symmetry at the corresponding atoms; however, the P-bonded hydrogen atoms were refined isotropically.

Computational Methods. Our goal was to compare the structures and energies of different Ga−P isomers of the type [RP(H)−

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(30) NBO analysis: The perturbation energy of second order was calculated according to the equation $\Delta_{\varphi\varphi^*}E^{(2)} = -2((\langle\varphi|h^F\varphi^*\rangle)^2/\epsilon_{\varphi^*} - \epsilon_{\varphi})$, with h^F as Fock operator.

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$GaPR]_2$ (R = H, SiH_3, $SiMe_3$); 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 for several isomers of **2** were calculated by using the hybrid density functional theory (B3LYP) with the program package Gaussian 98.[25] We ran two sets of computations: (i) For all elements a standard 6-31G(d,p) basis set was used. (ii) A 6-31G(d,p) standard basis set was applied for all atoms, except for gallium, for which multielectron-adjusted quasirelativistic effective core potentials (ECP28MWB) with the electronic configuration for Ga of $[Ar]d^{10}$ were used. Both the pseudopotential and the corresponding basis set (which was slightly changed: introduction of d functions with the coefficient = 0.207) were those of the Stuttgart group.[36]

Comparison of these data sets shows differences in bond lengths no larger than 0.01−0.02 Å. The bond angles in all these molecules are rather constant and relatively independent of the basis sets. Finally, to save CPU time and to obtain a consistent set of data, we decided to use a pseudopotential for gallium and a 6-31G(d,p) basis for all other atoms.

NBO analyses[27] were carried out to investigate the bonding in all molecules at the HF level utilizing the optimized B3LYP geometry. The computed geometrical parameters for all molecules are collected in Table 3, and selected results of the NBO analyses are in Table 4. The computed frequencies, relative energies, and absolute energies are given as Supporting Information.

NBO population analysis for **2** was carried out with the structure fixed at that determined from X-ray analysis of **2** to investigate the bonding and hybridization in this experimentally observed species (single point at HF level).

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Complete data with structure factors are also available free of charge from the Cambridge Crystallographic Data Centre.[37] Further data for the NBO analyses, etc., are available free of charge via the authors.

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(39) Crystallographic data can be obtained free of charge on application to the Cambridge Crystallographic Data Centre {12 Union Road, Cambridge, CB2 1EZ, U.K. [fax (internat.) + 44(0)1223/336033; E-mail deposit@ccdc.cam.ac.uk]}.