

NMR spectroscopy and crystal structure of $[\text{Me}_2\text{GaP}(\text{H})\text{Si}t\text{Bu}_3]_2$ and theoretical investigations of the model compounds $[\text{R}'_2\text{GaP}(\text{H})\text{R}'']_2$

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Dedicated to Professor Hubert Schmidbaur.

Abstract

The dimeric phosphanylgallanes $[\text{R}'_2\text{GaP}(\text{H})\text{Si}t\text{Bu}_3]_2$ with $\text{R}' = \text{Me}, \text{Cl}$ [Inorg. Chem. 43 (2004) 3756] were synthesized by metathesis reactions. The obtained compounds were characterized by NMR spectroscopy and single crystal X-ray crystallography. In order to compare the structures and to compare the relative energies of isomers, theoretical investigations were performed on the phosphanylgallane model compounds of the type $[\text{R}'_2\text{GaP}(\text{H})\text{R}'']_2$ by using the hybrid density functional theory (B3LYP). Different 1,3- and 2,4-substituted dimeric phosphanylgallanes with $\text{R}' = \text{Cl}, \text{Me}, \text{Et}$ and $\text{R}'' = \text{H}, \text{SiH}_3$ and SiMe_3 as well as their monomers were calculated and could be correlated to the *cis-trans* isomerization equilibrium constants which were accessible by integration of suitable ^{31}P NMR signals.

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1. Introduction

Four-membered rings with group 13 and 15 elements have been studied intensely over the last years due to their application in the field of semiconductor research and production. Phosphinoalanes, -gallanes, and -indanes have been synthesized in order to obtain single-source precursors for AlP [2], GaP [3,4], and InP [5], for example by thermolysis reactions. Theoretical studies by means of the density functional theory supported the understanding of the properties of these compounds. Group 13/15 clusters and cages such as $(\text{GaP})_n$ have

been investigated and their properties correlated to their size [6]. Starting from $[\text{H}_2\text{E}^{\text{III}}\text{E}^{\text{V}}\text{H}_2]_2$ with E^{III} being an element of the boron group (triele) and E^{V} being a pnictogen (pentele) [7], calculations have been performed and their results were compared to the molecular structures obtained by single crystal X-ray crystallography. Due to computational limits, sterical factors had to be neglected and small substituents were considered for theoretical investigations. However, demanding groups stabilize these molecules and make them synthetically accessible. The intramolecular steric strain defines the size of the $(\text{E}^{\text{III}}\text{P})_n$ cycles in compounds such as $(\text{R}'_2\text{E}^{\text{III}}\text{-PR}'')_n$ and of the cages in compounds such as $(\text{R}'\text{E}^{\text{III}}\text{PR}'')_n$ with R' being an alkyl or halide group. The elimination of ClSiMe_3 from the complexes of the type $\text{ClR}'_2\text{E}^{\text{III}}\text{-P}(\text{SiMe}_3)_3$ yielded the dimers

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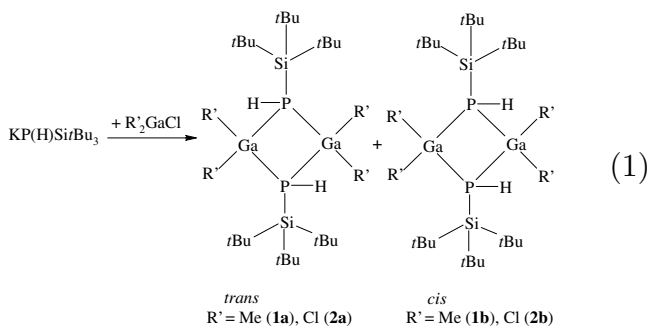
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$[\text{R}'_2\text{E}^{\text{III}}\text{P}(\text{SiMe}_3)_2]_2$ with E^{III} as aluminum [8], gallium [9], and indium [10]. The steric strain determines not only the degree of oligomerization but also the bonding parameters as can be shown for example for the phosphanyl gallanes. In the adduct of GaCl_3 and $\text{P}(\text{SiMe}_3)_3$, the Ga–P bond length was 238 pm [9]. Elimination of chlorotrimethylsilane gave dimeric $\text{Cl}_2\text{Ga–P}(\text{SiMe}_3)_2$ with a central four-membered Ga_2P_2 cycle with average Ga–P distances of 238 pm [9]; in this molecule the Ga–P–Si angles varied between 111.0° and 116.6° . Thermal decomposition reactions yielded GaP as characterized by X-ray diffraction [3,4,11,12]. Also Lewis base stabilized phosphinoalane $\text{dmap–AlMe}_2\text{P}(\text{SiMe}_3)_2$ with GaMe_3 yields the heterocycle $[\text{Me}_2\text{GaP}(\text{SiMe}_3)_2]_2$ after rearrangement reactions [13]. Otherwise cycles can be cleaved with dmap and monomeric coordinated gallanes like $[(\text{dmap})\text{Me}_2\text{Ga–P}(\text{SiMe}_3)]$ can be stabilized [13]. Further procedures to prepare molecules with Ga_2P_2 cycles applied the metallation reactions, thus the bisalkylated derivatives $[\text{R}'_2\text{Ga–P}(\text{SiMe}_3)_2]_2$ were available for a wide variety of alkyl substituents such as Me [15,16], Et [17], Bu [12], CH_2tBu [18], and CH_2SiMe_3 [19].

2. Discussion

2.1. Synthesis

Ga_2P_2 cycles with the sterical demanding tri(*tert*-butyl)silyl ligand at the phosphorus atom can be prepared by reacting potassium tri(*tert*-butyl)silylphosphanide with chlorodimethylgallane in DME, which yields dimeric dimethyl tri(*tert*-butyl)silylphosphinogallane (**1**) (1,1,3,3-tetramethyl-2,4-bis[tri(*tert*-butyl)silyl]-1,3-digalla-2,4-diphosphetane) according to Eq. (1). However, the two possible isomers with a *trans* and *cis* configuration of the PH groups form in a ratio of 7:1. Reacting GaEt_3 with $\text{H}_2\text{PSiMe}_2\text{R}$ ($\text{R} = \text{CMe}_2i\text{Pr}$), von Haenisch also observed *cis* and *trans* isomers for $(\text{Et}_2\text{GaPH–SiMe}_2\text{R})_2$ [20]. The reaction of GaCl_3 with $\text{KP}(\text{H})\text{Si}t\text{Bu}_3$ leads to the previously described $[\text{Cl}_2\text{GaP}(\text{H})\text{Si}t\text{Bu}_3]_2$ (**2**) (1,1,3,3-tetrachloro-2,4-bis[tri(*tert*-butyl)silyl]-1,3-digalla-2,4-diphosphetane) [1].



The *cis* isomer of dimeric **1** is discussed in detail, whereas the values of the *trans* isomer are given in

Table 1

Comparison of selected NMR parameters of $[\text{Me}_2\text{GaP}(\text{H})\text{Si}t\text{Bu}_3]_2$ (**1**) and $[\text{Cl}_2\text{GaP}(\text{H})\text{Si}t\text{Bu}_3]_2$ (**2**)

	<i>trans</i> - 1a	<i>cis</i> - 1b	<i>trans</i> - 2a	<i>cis</i> - 2b
^{31}P NMR				
$\delta(^{31}\text{P})$	–214.5	–205.4	–159.1	–138.0
$^1J(\text{P,H})$	254.7	249.2	277.7	277
$^2J(\text{P,P})$	229	270.0	236.9	252
$^3J(\text{P,H})$	–3.5	0.4	–12.0	<0.4

brackets. Colorless **1** shows remarkable NMR data listed in Table 1. The chemical ^{31}P NMR shift lies at $\delta = -205.4(-214.5)$ with an AA'XX' pattern which allows the evaluation of the coupling constants between the phosphorus and hydrogen atoms. Furthermore, the $^3J(\text{P,H})$ coupling of the gallium-bonded methyl groups to the phosphorus atom is accessible. Special attention has to be addressed to the $^1J(\text{P,H})$ coupling constant of 249 Hz (255 Hz). Typically, $^1J(\text{P,H})$ coupling constants show values of approximately 200 Hz which can even be smaller with electropositive counterions $\{^1J(\text{P,H})$ of $\text{MP}(\text{H})\text{Si}t\text{Bu}_3$: M = Li, 165.9 Hz; Na, 163.5 Hz; K, 140.0 Hz; Rb, 141.7 Hz; Cs, 141.3 Hz [21]}. In $\text{H}_2\text{PSi}t\text{Bu}_3$, values of $\delta = -264.3$ for the chemical shift and of $^1J(\text{P,H}) = 185.6$ Hz were observed [22].

The endocyclic $^2J(\text{P,P})$ coupling constant shows an extremely large value of 270 Hz (229 Hz), which lies in the region of $^1J(\text{P,P})$ couplings (P_2H_4 : $^1J(\text{P,H}) = 186.5$ Hz; $^1J(\text{P,P}) = 227.4$ Hz [23]). In four-membered M_2P_2 cycles of the alkaline earth metals, $^2J(\text{P,P})$ coupling constants up to 135 Hz for $(\text{Me}_3\text{Si})_2\text{N–Ca}(\text{DME})\text{–PHSi}t\text{Pr}_3$ were detected [24]. M_4P_4 heterocubane structures also show smaller $^2J(\text{P,P})$ values; in the series of $\text{Ba}_n\text{Sn}_{4-n}(\text{PSi}t\text{Bu}_3)_4$ the corresponding coupling constants vary from 26 Hz ($n = 1$) to 34 Hz ($n = 2$) and finally to 14 Hz ($n = 3$).

2.2. Molecular structures

A perspective representation of **1b** is given in Fig. 1. The central fragment of *cis* $[\text{Me}_2\text{GaP}(\text{H})\text{Si}t\text{Bu}_3]_2$ is the four-membered Ga_2P_2 cycle, which shows a butterfly geometry whereas centrosymmetric *trans* $[\text{Cl}_2\text{GaP}(\text{H})\text{Si}t\text{Bu}_3]_2$ contains a planar Ga_2P_2 cycle. The structural parameters of $[\text{R}'_2\text{GaP}(\text{H})\text{Si}t\text{Bu}_3]_2$ ($\text{R}' = \text{Me}$ (**1b**), Cl (**2a**) [1]), $[\text{Et}_2\text{GaP}(\text{SiMe}_3)_2]_2$ [17] and $[\text{Me}_2\text{GaP}(\text{H})\text{SiMe}_3]_2$ (*cis*, calculated) are summarized in Table 2.

2.3. Computational details

Our goal was to compare the structures and energetic differences of different 1,3- and 2,4-substituted dimeric phosphanyl gallanes $[\text{R}'_2\text{GaP}(\text{H})\text{R}'']_2$ ($\text{R}' = \text{Cl}, \text{Me}, \text{Et}$; $\text{R}'' = \text{H}, \text{SiH}_3$ and SiMe_3) as well as their monomers. In order to obtain reliable data, the structural and vibrational data of all monomeric and dimeric species were calculated by using the hybrid density functional theory

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