

Synthesis and characterization of 1,3-bis[2,4,6-tri(*tert*-butyl)phenyl]-2,4-bis[tri(*tert*-butyl)silyl]-1,3- diinda-2,4-diphosphetane, a dimeric phosphanylidene indane with three-coordinate indium and phosphorus atoms

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Abstract

The metathesis reaction of potassium tri(*tert*-butyl)silylphosphanide with bis[2,4,6-tri(*tert*-butyl)phenyl]indium bromide gives (2,4,6-*t*Bu₃C₆H₂)₂In–P(H)Si*t*Bu₃ (**1a**), the subsequent elimination of tri(*tert*-butyl)benzene yields [(2,4,6-*t*Bu₃C₆H₂)In–PSi*t*Bu₃]₂ (**2a**) which can be regarded as a dimeric phosphanylidene indane. The X-ray structure confirms the dimeric nature of this 1,3-diinda-2,4-diphosphetane with three-coordinate indium and phosphorus atoms and short In–P bond lengths of 250 pm. The analogous reaction with the gallium derivative and the smaller potassium triisopropylsilylphosphanide leads to the formation of monomeric (2,4,6-*t*Bu₃C₆H₂)₂Ga–P(H)Si*t*Pr₃ (**1b**) with three-coordinate gallium and phosphorus atoms.

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1. Introduction

Phosphanylgallanes and phosphanylindanes of the type R₂E–PR'₂ oligomerize and form cyclic compounds whereas oligomeric phosphanylideneindanes RE = PR' give cubane or hexagonal prismatic structures [1,2], depending on the bulkiness of the substituents R and R'. The expectation that small phosphanylgallanes and indanes are valuable precursors for the synthesis of GaP and InP induced an intense research with respect to these semiconductors [3]. Monomeric phosphanylgallanes such as (*t*Bu)₂GaP(*t*Bu)SiPh₃ [4] or (2,4,6-Me₃C₆H₂)₂GaP(*t*Bu)₂ [5] contain phosphorus atoms in

a pyramidal environment. The monomeric digallylphosphane MesP{Ga(Trip)₂}₂ · Et₂O [6] (Trip = 2,4,6-*i*Pr₃C₆H₂) contains a planar three-coordinate phosphorus center. In [*t*Bu₃SiP(H)–Ga(μ-PSi*t*Bu₃)]₂ a Ga–P–Ga heteroallylic system with one planarily coordinated P atom (Ga–P 225.8 pm) is realized, the other bridging phosphorus atom (Ga–P 233.6 pm) is in a pyramidal environment [7]. Only very few dimeric phosphanylindanes with In₂P₂ cycles such as [(allyl)₂InP*t*Bu₂]₂ [8], [Et₂InP(SiMe₃)₂]₂ [1], and [Ph₂InP(SiMe₃)₂]₂ [9] with four-coordinate indium and phosphorus atoms have been synthesized. As of yet no dimeric phosphanylideneindane with three-coordinate indium atoms is known. Also a monomeric phosphanylideneindane of the type RIn = PR' remains unknown. This fact can be understood as a consequence of the high standard enthalpies for the oligomerization process according to equation

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$\text{HIn} = \text{PH} \rightarrow 1/2[\text{HInPH}]_2$ with a value of -150 kJ mol^{-1} [10].

$(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2)_2\text{InBr}$ reacts at low temperatures with $\text{KP(H)Si}t\text{Bu}_3$ in heptane. The metathesis step yields $(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2)_2\text{In-P(H)Si}t\text{Bu}_3$ (**1a**) and the subsequent intramolecular metalation step eliminates 1,3,5-tri(*tert*-butyl)benzene and $(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2)\text{In} = \text{PSi}t\text{Bu}_3$ is formed which dimerizes immediately to the 1,3-diinda-2,4-diphosphetane $[(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2)\text{InPSi}t\text{Bu}_3]_2$ (**2a**). In order to verify the intermediate we changed the group 13 metal and varied the bulkiness of the trialkylsilyl group. The metathesis reaction of $(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2)_2\text{GaCl}$ with $\text{KP(H)Si}t\text{Pr}_3$ yielded a mixture of monomeric $(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2)_2\text{Ga-P(H)Si}t\text{Pr}_3$ (**1b**) (see Fig. 1) and traces of dimeric $[(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2)\text{GaPSi}t\text{Pr}_3]_2$ (**2b**) (Eq. (1)) which results from an elimination of $2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_3$. In **1b** [11] the dihedral angle between the gallium-bound $2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$ ligand and the H atom at the phosphorus (H–P–Ga–Cl) lies at 20° . This fact suggests an intramolecular synelimination of $1,3,5\text{-}t\text{Bu}_3\text{C}_6\text{H}_3$ to give the corresponding phosphanylidene gallane and indane (**A**), respectively, which dimerizes immediately. Also the bulkier tri(*tert*-butyl)silyl ligand leads to the formation of monomeric $(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2)_2\text{GaP(H)Si}t\text{Bu}_3$ (**1c**) and dimeric $[(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2)\text{GaP-Si}t\text{Bu}_3]_2$ (**2c**). The NMR data are summarized in Table 1.

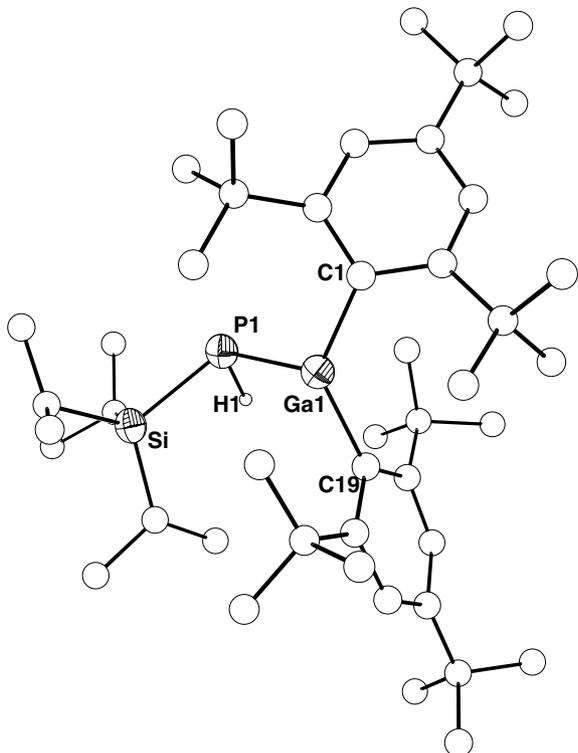
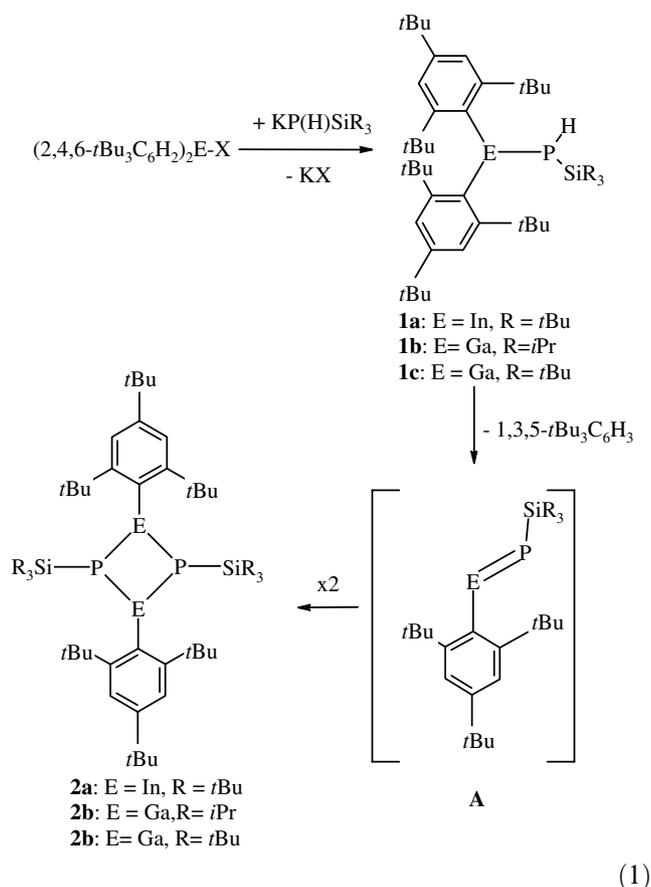


Fig. 1. Molecular structure of **1b**. The ellipsoids represent a probability of 25%. The H atoms are neglected for clarity reasons. Selected bond lengths (pm): Ga1–P1 235.3(3), P1–Si1 221.9(5), Ga1–C1 198(1), Ga1–C19 203(1); angles ($^\circ$): C1A–Ga1–C19 128.6(5), C1A–Ga1–P1 113.6(3), C19–Ga1–P1 113.6(4), Ga1–P1–Si1 120.8(2).

Elimination of tri(*tert*-butyl)benzene and formation of the 1,3-digalla- and 1,3-diinda-2,4-diphosphetanes leads to a low-field shift of the ^{31}P resonance of approximately 60 ppm.



The molecular structure of **2a** is represented in Fig. 2. Very small In–P bond lengths of 250 pm are found within the In_2P_2 cycle with three-coordinate In and P atoms. The angle sum at In1 is 360° . Due to sterical reasons the $2,4,6\text{-tri}(t\text{-butyl})\text{phenyl}$ ligands show a perpendicular arrangement to the In_2P_2 ring. The phosphorus atom P1 shows a trigonal pyramidal environment with an angle sum of 342° . Relevant structural parameters are compared with those of related compounds (Table 2). The Ga–P and In–P bond lengths depend on the coordination number and the charge of the group 13 and 15 elements. In order to overcome the large dimerization energy of phosphanylidene indanes and gallanes sterically more demanding ligands have to be chosen at the group 13 element and phosphorus atom.

2. Experimental

2.1. General remarks

All reactions were performed in an argon atmosphere. The solvents were thoroughly dried and distilled

Table 1
Selected NMR data for **1** and **2** (C₆D₆)

	1a	1b	1c	2a	2b	2c
$\delta(^{31}\text{P})$	–238.9	–214.81	–227.6	–187.0	–147.0	–165.9
$^1J(\text{P,H})/\text{Hz}$	196	200	205	–	–	–

prior to use. KP(H)Si*t*Bu₃ [15] was prepared according to the literature procedure.

Synthesis of 2a. (2,4,6-*t*Bu₃C₆H₂)₂InBr (0.27 g, 1.0 mmol) was dissolved in 20 mL of heptane and added to a suspension of freshly prepared potassium tri(*tert*-butyl)silylphosphanide (0.27 g, 1.0 mmol) in 15 mL of heptane at –78 °C. The reaction mixture was slowly warmed to room temperature whereby a colorless solid precipitated. This solid material was removed and the volume of the solution reduced to a few milliliters. At 30 °C colorless crystals of [(2,4,6-*t*Bu₃C₆H₂)InP*t*Bu₃]₂ (0.37 mmol, 37%) precipitated. M.p. 248 °C. ¹H NMR (C₆D₆): δ 7.62 (aromatic H), 1.80 (*o-t*Bu), 1.39

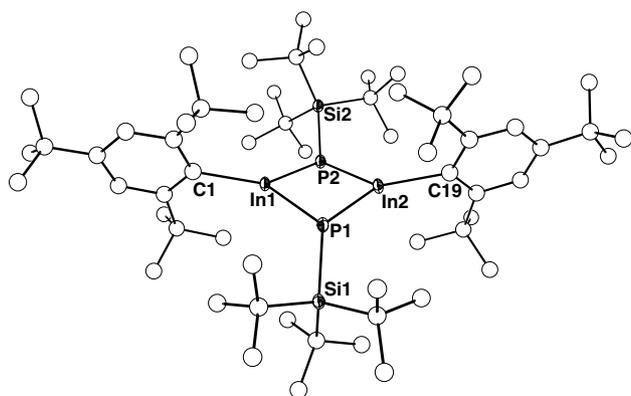


Fig. 2. Molecular structure of **2a**. The ellipsoids represent a probability of 25%. The H atoms are neglected for clarity reasons and carbon atoms drawn with arbitrary radii. Selected bond lengths (pm): In1–P1 251.5(2), In1–P2 250.3(2), In2–P1 249.3(2), In2–P2 250.9(2), P1–Si1 225.5(3), P2–Si2 226.9(3), In1–C1 219.7(6), In2–C19 219.5(6); angles (°): P1–In1–P2 92.2(6), P1–In1–C1 131.5(2), P2–In1–C1 136.0(2), P1–In2–P2 92.6(6), P2–In2–C19 134.0(2), P1–In2–C19 132.77(17), In2–P2–Si2 129.4(9), In1–P2–In2 86.5(6), In1–P2–Si2 126.0(9), In1–P1–Si1 125.4(9), In2–P1–Si1 130.0(9).

Table 2
Comparison of selected structural parameters of selected phosphanylindanes and phosphanylindanes (E = Ga, In; average values of bond lengths (pm) and angles (°))

	E–P	P–Si	E–C	EPE	PEP	Lit.
Ph ₃ GaP(SiMe ₃) ₃	254.0	228.2	200	–	–	[12]
[Me ₂ GaP(SiMe ₃) ₂] ₂	244.8	225.4	198.3	91.8	88.2	[13]
1b	235.3	221.9	201	–	–	
(<i>t</i> Bu) ₂ GaP(<i>t</i> Bu)SiPh ₃	229.5	225.9	201	–	–	[4]
(2,4,6-Me ₃ C ₆ H ₂) ₂ GaP(<i>t</i> Bu) ₂	232.1	–	198.3	–	–	[5]
MesP{Ga(Trip) ₂ } ₂ · Et ₂ O	225.7	–	198.2	136.2	–	[6]
(Me ₃ CCH ₂) ₃ InP(SiMe ₃) ₃	288.0	227.1	221	–	–	[14]
[Ph ₂ InP(SiMe ₃) ₂] ₂	261.2	226.2	–	92.97	87.03	[9]
2a	250.5	226.2	219.6	86.59	92.41	

(*p-t*Bu), 1.09 (Si*t*Bu). ¹³C NMR (C₆D₆): δ 156.3, 150.4, 123.5, 119.7, 35.1, 33.7, 32.6, 31.4, 30.7, 30.6. ²⁹Si{¹H} NMR (C₆D₆): 28.7. ³¹P NMR (C₆D₆): δ –187.0. IR [cm^{–1}]: ν 2963 s, 2905 w, 2862 w, 1596 w, 1478 w, 1391 w, 1363 w, 1262 vs, 1095 vs, 1021 vs, 898 w, 804 vs. MS–EI⁺ [*m/z*]: 1181 (M⁺), 1124 (M⁺ – *t*Bu).

2.2. X-ray structure determination of 2a

Data was collected on a STOE IPDS diffractometer with graphite Mo K α radiation ($\lambda = 0.71073$ Å). Crystallographic details are summarized in Table 3. The structure was solved and refined with the programs SIR97 [16], SHELXL-93 and SHELXL-97 [17]. Neutral scattering factors were taken from Cromer and Mann [18] and for the hydrogen atoms from Stewart et al. [19].

Table 3
Crystallographic data of **2a** as well as details of the structure solution and refinement procedures^a

Compound	2a
Formula	In ₂ C ₆₀ H ₁₁₂ P ₂ Si ₂
FW (g mol ^{–1})	1181.29
<i>T</i> (K)	200
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.9067(4)
<i>b</i> (Å)	15.6528(4)
<i>c</i> (Å)	17.3559(5)
α (°)	68.386(1)
β (°)	84.244(1)
γ (°)	67.035(2)
<i>V</i> (nm ³)	3229.8(2)
<i>Z</i>	2
<i>d</i> _{calcd} (g cm ^{–3})	1.215
μ (mm ^{–1})	0.833
<i>F</i> (0 0 0)	1256
Scan range (°)	6.2 < 2θ < 50.0
Measured data	35,468
Unique data (<i>R</i> _{int})	11,210 (0.096)
Absorption correction	None
Parameters	595
Restraints	0
<i>wR</i> ₂ ^a (all data, on <i>F</i> ²)	0.1205
<i>R</i> ₁ ^a (all data)	0.1144
Data with <i>I</i> > 2 σ (<i>I</i>)	7165
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0621
Goof <i>s</i> ^b on <i>F</i> ²	1.02
Residual density (e nm ^{–3})	1.61/–0.79

^a Definition of the *R* values: $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (0.0385P)^2$, where $P = (F_o^2 + 2F_c^2)/3$.

^b $s = \{ \sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p) \}^{1/2}$.

Supporting information available

Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-269322 for **2a**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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