Dimeric Di(*tert*-butyl)haloalanes and a Monomeric Di(*tert*-butyl)phosphino-di(*tert*-butyl)alane

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The di(*tert*-butyl)aluminum halides, $t\mathrm{Bu_2AlX}$ (X = Br, I) have been prepared in yields ranging from 55 to 64 % from $\mathrm{AlX_3}$ and Li*t*Bu in a 1 : 2 molar ratio in pentane. In the crystal these pyrophoric compounds are dimeric featuring Al–X–Al bridges. The reaction of $\mathrm{AlCl_3}$ with Li*t*Bu in diethyl ether produced a volatile solvate of composition $t\mathrm{Bu_3Al{-}Cl{-}Al}t\mathrm{Bu_2(OEt_2)}$. Reaction of this species with $\mathrm{AlCl_3}$ at 120 °C yielded a separable mixture of $t\mathrm{Bu_2AlCl}$ and $t\mathrm{Bu_2AlCl(OEt_2)}$. $t\mathrm{Bu_2AlCl}$ and $t\mathrm{Bu_2GaCl}$ react with $t\mathrm{Bu_2PLi}$ to produce the monomeric compounds $t\mathrm{Bu_2E{-}P}t\mathrm{Bu_2}$ (E = Al, Ga). The aluminum compound decomposes at 111 °C to give a mixture of the *cis/trans*-isomers of $[t\mathrm{Bu(H)Al{-}P}t\mathrm{Bu_2}]_2$ while at 200 °C only the *trans*-isomer is formed.

Key words: Di(*tert*-butyl)aluminum Halides, Chloro Penta(*tert*-butyl)dialuminum Diethyl Ether, Di(*tert*-butyl)phosphino-di(*tert*-butyl)alane, NMR Spectra, Crystal Structures

Introduction

It is well known that triorganylalanes like $\mathrm{AlMe_3}$ or $\mathrm{AlEt_3}$ are dimeric in hydrocarbon solvents as well as in the gas phase [1, 2]. However, in the presence of sterically demanding organyl groups such as *tert*-butyl [3, 4] or mesityl [5] they stay monomeric in solution and in the solid state. Organylaluminum halides of types $\mathrm{RAlX_2}$ and $\mathrm{R_2AlX}$ are generally dimeric. Dimerization occurs *via* Al–X–Al bonds [1, 2]. The $t\mathrm{Bu_2AlX}$ halides (X = Cl, I) are also dimeric in the solid state [6, 7] as well as in hydrocarbon solutions in contrast to mesitylaluminum halides which are present as monomers according to ^{27}Al NMR data [8]. This has also been demonstrated for bis(tetramethylpiperidino)-aluminum halides [9], which retain their monomeric character also in the solid state.

In contrast to aminoorganylalanes and amino-aluminum halides little information exists on organylphosphinoalanes [1, 2, 10]. As far as we are aware, no monomeric (organylphosphino)diorganylalanes have been reported as yet. They are potential precursors to AlP materials.

Results

Synthesis

A simple and efficient synthesis of di(*tert*-butyl)aluminum halides was described by Uhl and Schnepf [11]. Using this method we obtained the $t\mathrm{Bu_2AlX}$ compounds (X = Br, I) according to Eq. 1 from pentane solutions in moderate yields (55 – 64 %).

Our attempts to synthesize $t\mathrm{Bu_2AlCl}$ analogously in diethyl ether, expecting the formation of $t\mathrm{Bu_2AlCl{\cdot}OEt_2}$, led to a surprising result because the reaction proceeded, irrespective of the ratio of $\mathrm{AlCl_3}$ to Li*t*Bu from 1 : 1.5 to 1 : 2.5, to compound **3**, as depicted in Eq. 2.

$$\mathrm{AlX_3} + 2\,\mathrm{Li}t\mathrm{Bu} \rightarrow t\mathrm{Bu_2AlX} + 2\,\mathrm{LiX} \qquad \mathrm{X} = \mathrm{Br}, \mathbf{1}, \mathrm{X} = \mathrm{I}, \mathbf{2} \tag{1}$$

$$4\,\mathrm{AlCl_3} + 10\mathrm{Li}t\mathrm{Bu} + 2\,\mathrm{OEt_2} \rightarrow \underset{\mathbf{3}}{2\,t\mathrm{Bu_3Al{-}Cl{-}Al}t\mathrm{Bu_2}} \cdot \mathrm{OEt_2} + 10\,\mathrm{LiCl} \tag{2}$$

$$2\,t\mathrm{Bu_3Al{-}Cl{-}Al}t\mathrm{Bu_2} \cdot \mathrm{OEt_2} + \mathrm{AlCl_3} \rightarrow \rightarrow \underset{\mathbf{4}}{3t\mathrm{Bu_2AlCl}} + \underset{\mathbf{5}}{2\,t\mathrm{Bu_2AlCl} \cdot \mathrm{OEt_2}}, \tag{3}$$

Compound **3** can be distilled without decomposition *in vacuo*. It reacted with $\mathrm{AlCl_3}$ at 120 °C within 5 min under formation of $t\mathrm{Bu_2AlCl}$, **4**, and its diethyl etherate **5** (Eq. 3). These two compounds can be separated by fractional crystallization from hexane.

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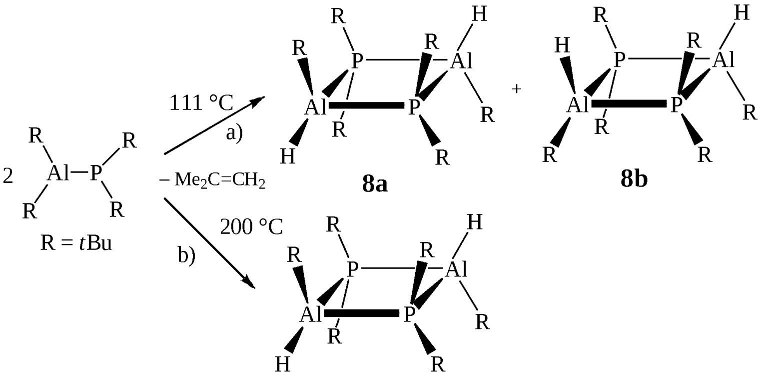
$$t\mathrm{Bu_2ECl} + \mathrm{LiP}t\mathrm{Bu_2} \rightarrow t\mathrm{Bu_2E{-}P}t\mathrm{Bu_2} + \mathrm{LiCl} \qquad \mathbf{6}: \mathrm{E} = \mathrm{Al}, \quad \mathbf{7}: \mathrm{E} = \mathrm{Ga} \tag{4}$$



(5)

Reactions

While $t\mathrm{Bu_3Al}$ [3, 4] is a monomer, in contrast to the di(*tert*-butyl)haloalanes, we expected that subsituents X, which are sterically more demanding than a halogen atom might provide monomeric di(*tert*-butyl)alanes, $t\mathrm{Bu_2AlX}$. To test this assumption we reacted $t\mathrm{Bu_2ECl}$ (E = Al, Ga) with $\mathrm{LiP}t\mathrm{Bu_2}$, as shown in Eq. 4.

Because $t\mathrm{Bu_2AlCl}$ forms readily a diethyl ether adduct [5], we performed the reaction in hexane or pentane solution obtaining **6** in 46 % yield. However, we used an ether solution for the analogous reaction with $t\mathrm{Bu_2GaCl}$, because this compound forms only weak diethyl ether adducts. Compound **7** was isolated in 72 % yield. Cryoscopic molecular weight determinations of **6** and **7** in cyclohexane showed that both compounds are monomeric. They are highly susceptible to hydrolysis, and they react explosively with air.

It is known that $t\mathrm{Bu_2Ga{-}As}t\mathrm{Bu_2}$ decomposes readily with formation of gallium arsenide [12]. Compound **7** decomposed on heating up to 400 °C but no pure product could be isolated. In contrast, the aluminum compound **6** decomposed at 200 °C with dehydroalumination under formation of *all-trans*-hexa-*tert*-butyl-1,3-diphospha-2,4-dialumina-cyclobutane **8a**, as shown in Eq. 5. Heating to temperatures higher than 230 °C led *i. a.* to the formation of metallic aluminum. However, when **6** was heated in toluene (b. p. 111 °C) the NMR spectra showed the presence of **8a**, besides *cis*- hexa-*tert*-butyl-1,3-diphospha-2,4-dialumina-cyclobutane **8b**. This indicates that **8b** is a kinetic reaction product. The two products could not be interconverted into each other in contrast to similar 1,3-diphospha-2,4-dibora-cyclobutanes [13].

NMR Spectra

The ^{27}Al NMR spectrum of compound **3** shows two comparatively sharp signals of equal intensity at δ = 153 and 125 ppm. We attribute the latter to the $\mathrm{Cl}(t\mathrm{Bu_2})\mathrm{AlO}$ unit and the former to the $t\mathrm{Bu_3AlCl}$ unit. This can be compared with the ^{27}Al NMR spectrum for the anion $[t\mathrm{Bu_3Al{-}Br{-}Al}t\mathrm{Bu_3}]^-$ with δ = 154 ppm, $h_{1/2}$ = 3000 Hz [14]. The ^{1}H NMR spectrum shows two sharp signals in a 3 : 2 ratio. The compound also exhibits two sets of ^{13}C NMR resonances for the *t*Bu groups in accord with formula **3**. On the other hand, compound **5** shows a ^{27}Al resonance at δ = 95 ppm for a tetracoordinated Al atom. In contrast, the ^{27}Al NMR signal of **4** in $\mathrm{C_6D_6}$ solution at δ = 161 ppm is rather broad with $h_{1/2}$ = 6000 Hz. This chemical shift lies still in the range for tetracoordinated Al atoms, *i. e.* the compound is present as a dimer. The ^{27}Al NMR signal of $t\mathrm{Bu_2AlBr}$ was observed at δ = 160 ppm, $h_{1/2}$ = 8400 Hz, and that of $t\mathrm{Bu_2AlI}$ at δ = 162 ppm, $h_{1/2}$ = 7900 Hz. Mitzel *et al.* [7] reported for the iodide a chemical shift δ^{27}Al = 149 ppm, $h_{1/2}$ = 6500 Hz. Large line widths are not only typical for tricoordinated Al centers but also for tetracoordinated organylaluminum compounds with low symmetry due to the large quadrupol moment of the Al nucleus [15]. Typical examples are the monomeric 2,2,6,6-tetramethylpiperidino-alanes $\mathrm{tmp_2AlCl}$ (134 ppm, 13 700 Hz), $\mathrm{tmp_2AlBr}$ (130 ppm, 9100 Hz), $\mathrm{tmp_2AlI}$ (130 ppm, 10 000 Hz), [9], and $\mathrm{tmp_2AlMe}$ (173 ppm, 3200 Hz) [16]. The line widths for dimeric $(\mathrm{AlMe_3})_2$ (δ = 153 ppm, $h_{1/2}$ = 850 Hz) or for $(\mathrm{Et_2AlNEt_2})_2$ (δ = 160 ppm, $h_{1/2}$ = 1220 Hz) are significantly smaller [8].

The ^{27}Al chemical shift of compound **6** of δ = 265 ppm shows it to be a monomeric di(*tert*-butyl)-

Table 1. Structural parameters of bis(*tert*-butyl)haloalanes.

Compound	Al–X1	Al–X2	Al–C1	Al–C5		ref.
tBu$_2$AlCl	2.317(4)	2.324(4)	1.982(9)	1.996(6)		[6]
tBu$_2$AlBr	2.463(3)	2.466(3)	1.975(9)	2.01(1)		
tBu$_2$AlI	2.708(1)	2.716(1)	1.987(4)	1.991(3)		
tBu$_2$AlI	2.711(1)	2.717(1)	1.985(2)	1.986(2)		[5]
	X1–Al1–X1A	Al1–X1–Al1A	C1–Al1–C5	C1–Al1–X1	C1–Al1–X1A	
tBu$_2$AlCl	87.2(1)	92.8(1)	123.6(3)	110.3(3)	110.2(3)	[6]
tBu$_2$AlBr	90.07(9)	89.93(9)	122.9(4)	108.6(3)	109.1(3)	
tBu$_2$AlI	93.10(4)	86.90(4)	124.3(2)	108.2(1)	108.5(1)	
tBu$_2$AlI	95.2(7)	95.9(7)	124.2(1)	108.6(1)	108.2(1)	[15]

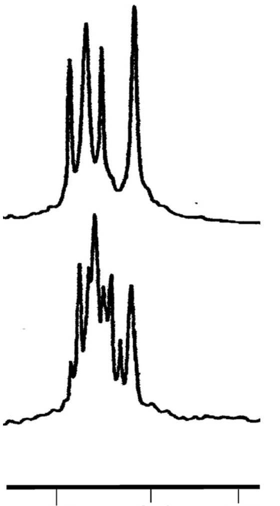


Fig. 1. The ^{1}H NMR spectrum on top was observed for the *trans*-isomer **8a**, the spectrum at the bottom shows a mixture of the *cis*- and *trans*-isomers.

phosphinoalane in solution, the first one of its kind. Its Al atom is similarly shielded as observed for AltBu$_3$ [8]. No ^{79}Ga NMR signals could be observed for the gallium compound **7**. It is well known that ^{79}Ga signals can be even broader than those of ^{27}Al. The monomeric character of both compounds is ascertained by the ^{1}H and ^{13}C NMR spectra. Only the coupling to a single P atom is observed. The PCMe$_3$ group shows doublets with $^3J(^{31}P^1H)$ = 11.8 Hz in the ^{1}H NMR spectrum but singlets in the ^{13}C NMR spectrum while the contrary happens for EtBu$_2$ groups (E = Al, Ga), *i. e.* the ^{13}C signals appear as doublets ($^3J(^{31}P^{13}C)$ = 12.6 Hz, 12.2 Hz for **6** and **7**, respectively). Low temperature ^{1}H NMR spectra of **6** show no rotational barrier for the Al–P bond down to −80 °C.

However, solutions of **6** in THF exhibit a ^{27}Al NMR signal at δ = 151 ppm, *i. e.* the presence of a tetracoordinated Al atom which is due to the formation of tBu$_2$P–AltBu$_2$ · THF. This adduct at 45 °C shows no longer free rotation about the Al–P bond. There are two signals each in the ^{1}H and ^{13}C NMR spectrum for the AltBu$_2$ and PtBu$_2$ groups. In the ^{31}P NMR spectrum two signals at δ = 28.2 and 15.7 ppm are observed in consonance with the presence of rotamers.

The ^{27}Al resonances of compounds **8a/8b** were observed at δ = 144 ppm, *i. e.* the two isomers show the same chemical shifts. However, these two isomers can be distinguished by their ^{31}P NMR spectrum. The ^{31}P resonance for the *trans* isomer **8a** appears at 12.0 ppm, and that of the *cis* isomer **8b** at 3.5 ppm. More information is obtained from the ^{1}HMR spectra (see Fig. 1).

In **8a** the *tert*-butyl groups at the P and Al atoms each are equivalent. They are characterized by a pseudotriplet [$^3J(^{31}P^1H) + {}^5J(^{31}P^1H)$] while the Al$t$Bu groups are represented by a single signal. The intensity ratio of the two resonances is 2 : 1. The presence of Al–H bonds in these isomers is demonstrated by an Al–H stretching band at 1770 cm^{-1}.

X-Ray structure determination

The structure of tBu$_2$AlCl has been determined by Barron *et al.* in 1997 [6]. More recently, Mitzel *et al.* [5] published the structure of tBu$_2$AlI, **2**, in 2005. Its structural data fit very well to those determined for **2** by Krossing in 1997 [15]. Here we report on the missing link tBu$_2$AlBr, **1**. The most relevant structural parameters of the three species are summarized in Table 1.

Fig. 2 shows the molecular structure of dimeric **1** which crystallizes like **2** in the monoclinic space group $P2_1/n$ with Z = 2. A crystallographic center of inversion is located in the Al$_2$Br$_2$ ring. The two Al–Br bonds Al1–Br1 and Al1–Br1A are 2.643(3) and 2.646(3) Å long, *i. e.* they have virtually the same lengths. In contrast, the Al–C distances are slightly different with 1.975(3) and 2.010(9) Å (see Table 1). As can be seen from these data, the four-membered ring of **1** is almost a perfect square as the Br1–Al1–Br2

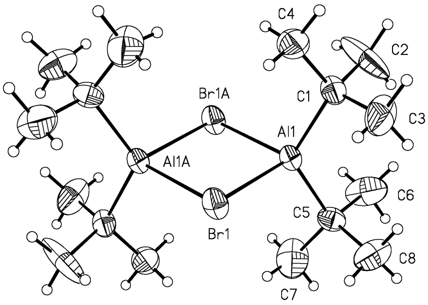


Fig. 2. Molecular structure of $(t\mathrm{Bu_2AlBr})_2$ in the solid state. Displacement ellipsoids are depicted at the 25 % probability level. Relevant bonding parameters are listed in Table 1.

and Al1–Br2–Al1A angles are both 90° within standard deviations. On the other hand, the C1–Al1–C5 bond angle of **1** is quite wide with 122.9(4)°, while the C1–Al1–Br1 and C1–Al1–C5 angles at 108.6(3) and 110.2(3)°, are close to the tetrahedral standard. This demonstrates that amongst the $(t\mathrm{Bu_2AlX})_2$ compounds listed in Table 1 compound **1** is the most symmetrical one. As one moves from $(t\mathrm{Bu_2AlCl})_2$ to $(t\mathrm{Bu_2AlI})_2$ the X–Al–X angles increase, and the Al–X–Al angles decrease. This is the consequence of the increasing Al–X bond lengths. Another typical feature of the structures of **1** and **2** is that Al–X bridging bonds are longer than in $\mathrm{Al_2Br_6}$ [2.399(9) and 2.387(9) Å] and $\mathrm{Al_2I_6}$ [2.66(2), 2.67(2) Å] [17], respectively, while their terminal Al–X bonds are significantly shorter [2.205(9) and 2.20(1) Å for $\mathrm{Al_2Br_6}$, and 1.482(2) and 2.49(2) Å for $\mathrm{Al_2I_6}$]. The longer bonds of solid di-*tert*-butylaluminum halides indicate a weaker bonding situation which is a prerequisite for the dissociation into monomeric units.

Discussion and Conclusion

Like $t\mathrm{Bu_2AlX}$ most other diorganylhaloalanes are dimeric in the solid state even with rather bulky substituents. Typical examples are $[(\mathrm{Ph(Me_3Si)_2C})\mathrm{MeAlCl}]_2$ [18], $(\mathrm{Mes_2AlCl})_2$ [19], $(\mathrm{MeAlCl_2})_2$ [20], $[(\mathrm{Me_3Si})_2\mathrm{CHAlCl_2}]_2$ [21], $\{[(3,5\text{-}i\mathrm{PrC_6H_2})_2 i\mathrm{PrC}]\mathrm{AlBr}\}_2$ [22], $[(\mathrm{F_5C_6})_2\mathrm{AlCl}]_2$ [23], or $[(2,6\text{-}\mathrm{Mes_2Ph})\mathrm{AlCl_2}]_2$ [24]. Amongst the dimeric dialkylaluminum chlorides the Al–Cl bonds of the dimeric dimesitylaluminum chloride are the longest with 2.345 and 2.316 Å. Amongst the dimeric organylaluminum dichlorides the difference in Al–Cl bond lengths is smallest for (2,6-dimesitylphenyl)aluminum dichloride (0.057 and 0.070 Å) [25]. There exists only one other structure for dimeric diorganylaluminum bromides besides $(t\mathrm{Bu_2AlBr})_2$ to be compared in this context, namely $\{[(3,5\text{-}i\mathrm{Pr_2C_6H_3})_2 i\mathrm{PrC}]_2\mathrm{AlBr}\}_2$ [22]. Its Al–Br bonds are slightly longer (2.473 and 2.502 Å), and its Al–Br–Al bond angles are larger than in **1** (92.73, 93.90°). It is interesting to note that the terminal Al–Cl bonds of $(\mathrm{MeAlCl_2})_2$ and $[(\mathrm{Me_3Si})_2\mathrm{CH\text{–}AlCl_2}]_2$ are as short as in gaseous $\mathrm{Al_2Cl_6}$ while the Al–Cl bond lengths in the bridge position are only slightly longer (2.21 and 2.06 Å, respectively) [15]. The present data indicate that steric effects determine the lengths of the Al–X bridge bonds, and, therefore, the stability of the dimer.

In contrast to the chemistry of phosphinoboranes [13, 25], little is known about the chemistry of diorganylphosphino-diorganylalanes [1, 10]. Actually, the review of the structures of organoaluminum compounds by Holloway and Melnik [26] refers only to trimeric $[\mathrm{Me_2Al\text{–}PPh_2}]_3$ [27]. The only other trimeric species is $[\mathrm{I_2Al\text{–}PPh_2}]_3$ [28] although a number of heterocycles containing one or two $\mathrm{R_2Al\text{–}PR_2}$ units are known as parts of ring systems [29 – 32].

However, no mononuclear diorganylphosphino-diorganylalane has been reported as yet. The same is true for diorganylphosphino-diorganylgallanes. The existence of compounds **6** and **7** demonstrates that these kinds of compounds can be prepared provided that the substituents at the Al and P atoms are bulky. The absence of P–Al π bonding is demonstrated by the free rotation about the Al–P bond even at low temperatures. However, hindered rotation is observed for the THF adduct of **6** due to steric overcrowding at the Al atom. The only other monomeric phosphinoalane so far reported is diphenylphosphino-bis(tetramethylpiperidino)alane [29]. As expected, both **6** and **7** are thermally unstable and decompose in a first step by loss of isobutene. In case of compound **6** the four-membered 1,3-diphospha-2,4-dialumina-cyclobutane could be analytically characterized as well by NMR data. We had, however, not the possibility to study the gas phase decomposition of compounds **6** and **7** in order to prepare thin films of AlP or GaP. We are convinced that the di(*tert*-butyl)haloalanes offer many opportunities for the preparation of new materials.

Experimental Section

All experiments were performed in an atmosphere of dry dinitrogen gas using Schlenk techniques. Solvents were dried by use of CaH_2, P_4O_6 or $LiAlH_4$, and distilled in dispensing bottles filled with dry dinitrogen gas. $AlCl_3$ was sublimed prior to use, and $AlBr_3$ as well as AlI_3 were prepared from the elements. Pentane and hexane solutions of Li*t*Bu were supplied by Chemetall GmbH. ^{1}H, ^{13}C and ^{27}Al NMR spectra were recorded with a Jeol GSX 270 instrument.

*Di(tert-butyl)bromoalane (**1**)*

$AlBr_3$ (20.9 g, 78.4 mmol) was suspended in pentane (200 mL) and the suspension cooled to −78 °C. Within 1 h a 1.55 M solution of Li*t*Bu in pentane (101.2 mL, 156.8 mmol) was added while stirring. The mixture was then allowed to attain r. t. over night, and the solid was removed by filtration and then washed with pentane (100 mL). The volume of the combined filtrates was reduced to 1/5 by applying vacuum. After cooling the solution to −78 °C colorless crystals separated on standing over night. These crystals are highly pyrophoric and need to be handled with proper care in an atmosphere of N_2: Yield: 8.75 g (55 %). – NMR (C_6D_6): ^{1}H NMR: δ = 1.10 ppm (s, C*Me*). – ^{13}C NMR: δ = 18.3 (C*Me*$_3$), 29.9 (*C*Me$_3$). – ^{27}Al NMR: δ = 160 ($h_{1/2}$ = 8400 Hz). – $C_8H_{18}AlBr$ (202.97): calcd. Al 13.3, Br 39.4; found Al 13.0, Br 39.6.

*Di(tert-butyl)iodoalane (**2**)*

Prepared in analogy to compound **1**. AlI_3 (3.64 g, 9.4 mmol) was suspended in pentane (60 mL). At −78 °C 6.1 mL of a 1.55 M solution of Li*t*Bu in pentane (9.4 mmol) was added. After stirring over night at ambient temperature the solid was removed by filtration and washed with pentane (30 mL). From the concentrated filtrate crystals of **2** separated on cooling to −78 °C. Yield: 1.50 g (64 %) of colorless pyrophoric crystals. – NMR (C_6D_6): ^{1}H NMR: δ = 1.11 (s, C*Me*$_3$). – ^{13}C NMR: δ = 18.5 (C*Me*$_3$), 30.0 (*C*Me$_3$). – ^{27}Al NMR: δ = 162 ($h_{1/2}$ = 7900 Hz). – $C_8H_{18}AlI$ (249.97): calcd. Al 10.8, I 50.8; found Al 10.1, I 49.3.

*Tris(tert-butyl)aluminum-μ-chloro-bis(tert-butyl)aluminum-diethyl ether (**3**)*

At 0 °C $AlCl_3$ (19 g, 140 mmol) was dissolved in diethyl ether (100 mL). To the stirred solution was dropwise added a 1.4 M solution of Li*t*Bu in pentane (200 mL, 1.4 M, 280 mmol). The resulting suspension was stirred at ambient temperature over night. Insoluble material was then removed by centrifugation. A sticky solid was left after removal of all volatiles from the filtrate under vacuum. Distillation at b. p. 130 °C/4 Torr led to a solid which on crystallization from hexane gave a yield of 21.7 g of **3** (69 %), colorless crystals, m. p. 130 – 134 °C. – ^{1}H NMR: δ = 1.15, 1.24 (C*Me*$_3$, 2 : 3), 3.54, 0.73 (OC*H*$_2$*Me*, ^{3}J (^{1}H^{1}H) = 7.1 Hz; 4 : 6). – ^{13}C NMR: 30.3, 31.6 (C*Me*$_3$), 19.7 (br, *C*Me$_3$), 68.0, 13.2 ppm (O*C*H$_2$*Me*). – ^{27}Al NMR: δ = 153.0, 125.0. – $C_{24}H_{55}OAl_2Cl$ (429.09): calcd. Cl 7.89; found Cl 8.00.

*Di(tert-butyl)chloroalane (**4**) and di(tert-butyl)chloroalane-diethyl ether (**5**)*

A mixture of **3** (4.03 g, 9 mmol) and $AlCl_3$ (0.6 g) was heated to 120 °C for 5 min. Fractional crystallization from hexane (15 mL) yielded *t*Bu$_2$AlCl, **4** (0.7 g, dec.: 126 °C). A third fraction proved to be *t*Bu$_2$AlCl(OEt$_2$), **5** (1.29 g, 57 %) as a paste.

tBu$_2$AlCl, ***4***: ^{1}H NMR: δ = 1.13 – ^{13}C NMR: δ = 29.9 C*Me*$_3$, 18.2 *C*Me$_3$. – ^{27}Al NMR: δ = 161.6 ppm.

tBu$_2$AlCl(OEt$_2$), ***5***: ^{1}H NMR: δ = 1.17 (C*Me*$_3$), 3.58, 0.7 (^{3}J(^{1}H^{1}H) 7.09 Hz). – ^{13}C NMR: δ = 29.9 (C*Me*$_3$), 18.4 (*C*Me$_3$), 67.9, 13.3 (O*C*H$_2$*Me*) – ^{27}Al NMR: δ = 95. – $C_{12}H_{28}OAlCl$ (250.68): calcd. Al 10.76, Cl 14.14; found Al 10.9, Cl 15.2.

*Di(tert-butyl)-di(tert-butyl)phosphanylalan (**6**)*

Li*t*Bu (0.80 g, 5.3 mmol) was suspended in hexane (15 mL) and the stirred suspension cooled to −78 °C. Then a solution of *t*Bu$_2$AlCl (920 mg, 5.2 mmol) in hexane (10 mL) was slowly added. At r. t. the resulting suspension showed a yellow green color. The solid (LiCl, 230 mg) was removed by filtration and the hexane by evaporation in vacuum. The sticky residue yielded a colorless powder of **6** on attempted crystallization from pentane. Yield of **6**: 680 mg (46 %), m. p. 55 – 57 °C. The compound ignites in contact with air. Solutions in Et_2O, C_6H_6 or C_6H_{14} showed a yellow-green color. – Cryoscopic MW in cyclohexane: 231 g/mol, (calcd. 286.4). – ^{1}H NMR (C_6D_6): δ = 1.24 (AlC*Me*$_3$), 1.35 (PC*Me*$_3$, ^{3}J(^{31}P^{1}H) = 11.8 Hz). – ^{13}C NMR: δ = 31.0 (PC*Me*$_3$), 35.4 (AlC*Me*$_3$, ^{3}J(^{31}P^{13}C) = 12.6 Hz). – ^{27}Al NMR: δ = 265.0, v. br. – ^{31}P NMR: δ = 9.5 ppm (^{3}J(^{31}P^{13}C) = 12.6 Hz).

*Di(tert-butyl)-di(tert-butyl)phosphanylgallane (**7**)*

A solution of *t*Bu$_2$GaCl (1.26 g, 5.75 mmol) in diethyl ether (10 mL) was treated at −78 °C with a solution of LiP*t*Bu$_2$ (870 mg, 5.7 mmol) in diethyl ether (10 mL). The color of the resulting suspension changed to yellow-green on warming to ambient temperature. Insoluble LiCl was removed by filtration and the solvent from the filtrate in vacuum. The residue, a yellow oil (1.57 g), solidified within 2 h, m. p. 33 °C. The compound sublimed at 60 °C/10^{-5} Torr to give colorless crystals. – Cryoscopic MW in cyclohexane: 333 g/mol, (calcd. 325.2). – NMR (C_6D_6): ^{1}H NMR: δ = 1.29 (GaC*Me*$_3$), 1.30 (PC*Me*$_3$, ^{3}J(^{31}P^{1}H) = 13.2 Hz). – ^{13}C NMR: δ = 34.6 (GaC*Me*$_3$, ^{3}J(^{31}P^{13}C) = 12.2 Hz), 30.3 (PCMe$_3$). – $C_{16}H_{33}GaP$ (325.17): calcd. C 58.38, H 11.02; found C 57.82, H 10.41.

Table 2. Relevant crystallographic data and data related to structure solution.

Compound	**1**	**2**
Chem. formula	$C_{16}H_{36}Al_2Br_2$	$C_{16}H_{36}Al_2I_2$
Form. wght.	442.22	536.20
Cryst. size, mm^3	$0.2 \times 0.3 \times 0.3$	$0.25 \times 0.25 \times 0.25$
Cryst. system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	8.796(5)	8.644(5)
b, Å	12.120(7)	12.373(7)
c, Å	11.219(4)	11.419(5)
β, deg	109.86(1)	109.16(1)
V, Å^3	1125(1)	1154(1)
Z	2	2
ρ(calc.), mg m^{-3}	1.306	1.543
μ, mm^{-1}	3.674	2.795
F(000), e	456	528
hkl index range	$\pm 11, \pm 14,$ $-15 \rightarrow +9$	$\pm 11, \pm 15,$ $-10 \rightarrow +15$
2θ, deg	58.0	57.4
Temp., K	183	173
Refl. collect.	6353	6380
Refl. unique	1920	2121
Refl. observ. (4 σ)	1215	2018
R_{int}	0.0463	0.0241
No. variables	97	97
Wght. scheme. x/y^{a}	0.0450/6.7058	0.0139/2.1866
GOOF	1.086	1.121
Final R (4σ)	0.0677	0.0232
Final $wR2$ (all data)	0.1480	0.0.547
Larg. res. peak, e Å^{-3}	1.203	0.753

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

*1,2,2,3,4,4-Hexa(tert-butyl)-1,3,2,4-dialuminadisphosphacyclobutane (**8**)*

Half of the product **6** (above) was heated to 200 °C in vacuum. A yellow melt formed, and after a minute the melt became colorless. After 5 min the melt turned grey indicating decomposition. Part of the residue dissolved in diethyl ether, and the insoluble material was removed by filtration. From the filtrate colorless crystals of the *trans*-isomer **8a** separated, m. p. 76 – 78 °C.

The second half of the product **6** (above) was dissolved in toluene (8 mL) and kept for 12 h at reflux. Then the toluene was removed from the solution in vacuum, and the yellow brown, honey-like residue was "crystallized" from pentane. This produced a colorless powder. Yield: 140 mg (55 %) of a mixture of the *cis/trans* isomers, **8a**, **8b**; m. p. 70 – 75 °C. – NMR (C_6D_6): ^{1}H NMR: δ = 1.40 (*trans*, AlC*Me*$_3$), 1.43 (*cis*, AlC*Me*$_3$), 1.45 (*trans*, PC*Me*$_3$, pseudo-t, N = 13.7 Hz), 1.43 – 1.438 (m, *cis/trans*), 4.58 ppm (Al–H). – ^{13}C NMR: δ = 33.1 (*trans*, AlC*Me*$_3$, $^3J(^{31}P^{13}C)$ = 3.7 Hz), 32.2 (PCMe$_3$). – ^{31}P NMR: δ = 12.0 (*trans*), 3.5 (*cis*). – ^{27}Al NMR: 144.0. – $C_{24}H_{56}Al_2P_2$ (460.62): calcd. C 62.58, H 12.25; found C 62.21, H 11.8.

X-Ray structure determinations

A Siemens P4 diffractometer equipped with a low-temperature device and an area detector was used for determining the unit cells and for collecting the data sets of compounds **1** and **2**. The micro chemical laboratory of the Department supplied the elemental analyses.

Crystals of compounds **1** and **2** were covered in a Schlenk tube with dry oxygen-free perfluoroether oil. Several specimens were then transferred onto a glass platelet in the microscope which was cooled by a stream of dinitrogen gas to −30 °C. The selected specimen was placed on the tip of a glass fibre and as quickly as possibly transferred on to the head of the goniometer which was flushed with dinitrogen gas at −80 °C. The unit cell dimensions were calculated from the positions of reflections on 20 frames collected at 5 different orientations using the program SMART [33]. Data collection was performed in the hemisphere mode. A total of 1200 frames were collected at two different χ settings by changing ω by 0.3°. Data were reduced with the program SAINT [33]. SADABS [33] was applied for correcting the data for absorption. The structures were solved and refined by using the program package SHELXTL [33]. Positions of non-hydrogen atoms were refined anisotropically, and the H atoms were added in calculated positions with U_i equals 1.3 times that of the U_{ij} value of the respective carbon atom.

Table 2 contains relevant crystallographic data and data related to data collection and structure solution. CCDC 681783 (**1**) and 681762 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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