Ditrielanes $(R_3Si)_2E{-}E(SiR_3)_2$ and Heterocubanes $(R_3Si)_4E_4Y_4$ (R_3Si = tBu$_3$Si, tBu$_2$PhSi; E = Al, Ga, In, Tl; Y = O, Se)[‡]

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Ditrielanes $R^*_2E{-}ER^*_2$ (R^* = SitBu$_3$; E = Al, In, Tl), $R'_2E{-}ER'_2$ (R' = SitBu$_2$Ph; E = In, Tl) and $R^*_2Ga{-}GaR^*(SiMe_3)$ are prepared in alkanes (i) from ECl_3 (E = Al, In, Tl) and NaR^* via isolable R^*_2ECl (reaction of $GaCl_3$ and NaR^* leads to $R^*_2Ga\dot{-}GaR^*$ instead of $R^*_2Ga{-}GaR^*_2$), (ii) from EBr (E = In, Tl) and NaR^* or NaR' (reaction of AlBr or GaBr and NaR^* leads to $R^*_4Al_4$ or $R^*_8Ga_{18}$ and $R^*_8Ga_{22}$), (iii) from $NaGa_2R^*_3$ and Me_3SiCl. According to X-ray structure analyses, the ditrielanes contain two planar groups R_2EE which are orthogonal to each other (R = R^*; angle REER ca. 90°) or nearly orthogonal (R = R'; angle REER ca. 80°). All compounds are deeply colored. The λ_{max} value of the visible absorption shifts with increasing atomic number of E and with the increasing angle between the R_2EE planes to longer wavelengths (ruby $R^*_4Al_2$, deep-violet $R^*_4In_2$, dark-green $R^*_4Tl_2$; red-violet R'_4In_2, dark-blue R'_4Tl_2). Thermolysis of $R^*_4E_2$ in alkanes at about 100 °C leads to $R^*_3Al_2^{\cdot}/R^*_4Al_3^{\cdot}/R^*_4Al_4$, to $R^*_3Ga_2^{\cdot}/R^*_4Ga_4$, to $(R^*_4In_6)/R^*_8In_{12}$ and to Tl, respectively. R'_4E_2 thermolizes under formation of an In or Tl mirror. The ditrielanes $R^*_4E_2$ are stable against MeOH at normal conditions, but react with HBr under Si–E and E–E bond cleavage with the formation of R^*EBr_2 (e.g. R^*InBr_2) besides R^*H and H_2. Air transforms the ditrielanes into R^*OH or $R'OH$. On the other hand, halogens oxidize $R^*_4E_2$ under formation of R^*_2EHal (e.g. R^*_2AlI), R^*EHal_2 (e.g. R^*InBr_2) or thermolysis products of the dihalides (e.g. $R^*Br/TlBr$). Selenium gives with $R^*_4E_2$ heterocubanes $R^*_4E_4Se_4$ (E = Al, In, Tl). Analogous heterocubanes $R^*_4E_4O_4$ (E = Al, Ga) are synthesized from tetrahedranes $R^*_4E_4$ and oxygen. X-ray structure analyses for $R^*_4In_4Se_4$, $R^*_4Al_4O_4$ – besides the mentioned ditrielanes – are presented.

Introduction

Silyltrielanes $REHal_2$ and R_2EHal with R = R^*= SitBu$_3$ (supersilyl) or R = R' = SitBu$_2$Ph and E = triel = B, Al, Ga, In, Tl, introduced in preceding publications,[1−3] are synthesized with the purpose of dehalogenation to form silylated triel cluster compounds. Indeed, silylditrielanes $R_2E{-}ER_2$ (R = R^*, R'; E = Al, Ga, In, Tl) represent examples with the smallest triel clusters. Its syntheses, characterization, reactions and X-ray structure analyses are presented afterwards together with some heterocubanes $R^*_4E_4Y_4$, which represent reaction products of $R^*_4E_2$ and selenium as well as $R^*_4E_4$ and oxygen (for preliminary communications, relevant to this subject, see refs.[4,5]; for syntheses of some larger silylated triel clusters from R^*EHal_2 and R^*_2EHal see refs.[6−8]).

In fact, except for the compounds dealt with in this publication, only three other examples of *silyl-ditrielanes*, namely $[(Me_3Si)_3Si]_4E_2$ with E = Ga,[9] In,[10] Tl[11] have been published to date. On the other hand, some *organyl-* and *aminyl-ditrielanes* R_4E_2 are known with R = $CH(SiMe_3)_2$/E = Al,[12] Ga,[13] In;[14] R = 2,4,6-iPr$_3C_6H_2$/E = Al,[15] Ga,[16] In;[17] R = 2,4,6-$(CF_3)_3C_6H_2$/E = Ga,[18] In;[18] R = 2,2,6,6-$Me_4NC_5H_6$/E = Ga;[19] and R_2 = −tBuN−MeSi(NtBu)$_2$SiMe−NtBu−/E = Ga,[20] In[20] amongst others (for aminylditrielanes cf. in addition ref.[21]).

Results and Discussion

Syntheses of $R^*_4E_2$ and R'_4E_2 (R^* = SitBu$_3$, R' = SitBu$_2$Ph)

According to Scheme 1, the reactions of NaR^* with *triel(III) compounds* $\mathbf{EX_3}$ (E = Al, Ga, In, Tl; X = Cl, Br) in alkanes at room temperature lead to tetrasupersilylditrielanes $R^*_2E{-}ER^*_2$ [**1**−**4**; due steric and/or electronic reasons, instead of $R^*_4Ga_2$ (**2**) only the radical $R^*_3Ga_2^{\cdot}$ (**2a**) is isolated[5]]. Isolable intermediates are R^*EHal_2 [1,2] and R^*_2EHal.[1,2] As already discussed elsewhere,[5] NaR^* reacts with R^*_2EHal under NaHal elimination to radicals $R^{*\cdot}$ and

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[‡] Compounds of Silicon and Homologues, 150; Supersilyl Compounds of Boron and Homologues, 17. − Part 149 and 16: N. Wiberg, T. Blank, H.-W. Lerner, H. Nöth, T. Habereder, D. Fenske, Z. Naturforsch., Teil B **2001**, *56*, 652−658.

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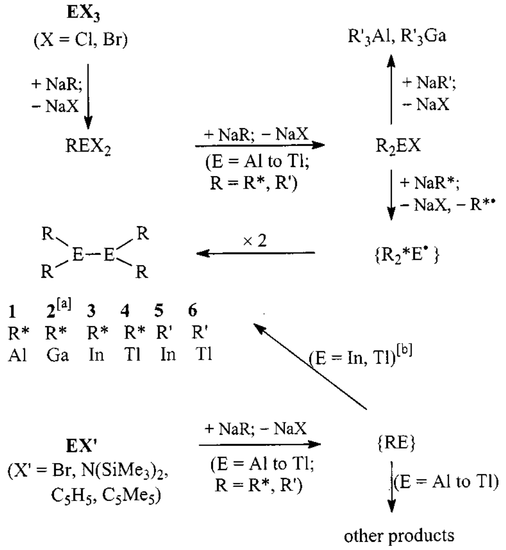
$R^*_2E^{\cdot}$. For steric reasons only the dimerization of the radicals under formation of R^*_2 and $(R^*_2E)_2$ is possible and no recombination of both radicals to form R^*_3E occurs (the cone angle for R* amounts to 130°;[15] even $R^*_2Tl^+$ and NaR* give $R^*_4Tl_2$ and not R^*_3Tl[7]). Obviously, the same is valid for the reaction of the triel(III) compound BX_3 (X = Cl, Br) and NaR*, with the difference that dimerization of the radicals $R^*_2B^{\cdot}$ obtained from R^*BHal_2 [2] and R^*_2BHal[2] is also not possible for steric reasons. Therefore, in the place of $R^*_4B_2$ other products are formed possibly from the anion $R^*_2B^-$, obtained according to the reaction $R^*_2B^{\cdot} + NaR^* \rightarrow NaBR^*_2 + R^{*\cdot}$.[2]



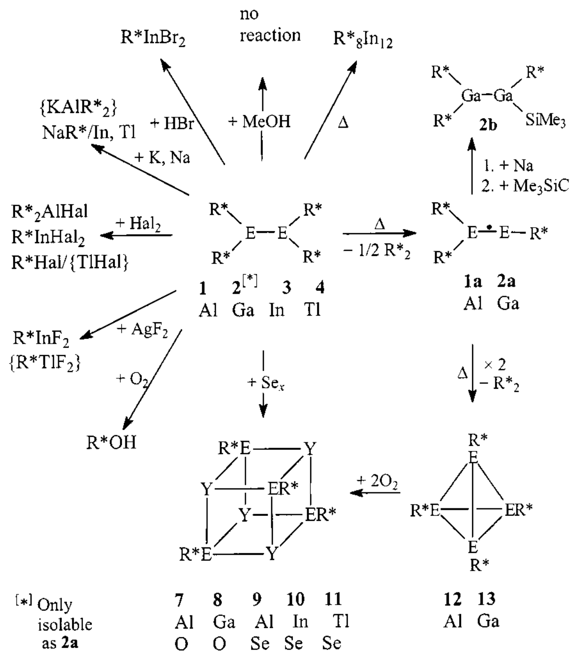
Scheme 1. Syntheses of ditrielanes R_4E_2 with E = Al, Ga, In, Tl and R = R* = Si*t*Bu$_3$ and R = R′ = Si*t*Bu$_2$Ph: [a] instead of $R^*_4Ga_2$ the radical $R^*_3Ga_2^{\cdot}$ (**2a**) is formed (cf. Scheme 2); [b] in the presence of NaR

The reactions of NaR′ instead of NaR* with **EX$_3$** (E = Al, Ga, In; X = Cl, Br) in alkanes (Scheme 1) lead to isolable monotrielanes R'_3E and not to ditrielanes $R'_2E{-}ER'_2$, via $R'EHal_2$ (isolated)[3] and R'_2EHal (not isolated).[3] Certainly, this time the exchange of halogen in R'_2EHal for R′ is possible for steric reasons {the reaction of $GaCl_3$ with $LiSi(SiMe_3)_2$ leads analogously to $[(Me_3Si)_3Si]_3Ga$,[22] whereas $InCl_3$ and $LiSi(SiMe_3)_3$ gives $[(Me_3Si)_3Si]_4In_2$ [10]}.

For the reactions of NaR* or NaR′ with *triel(I) compounds* **EX**, those of InBr or TlBr produce the ditrielanes $R^*_4In_2$, R'_4In_2, or $R^*_4Tl_2$, R'_4Tl_2 (**3**−**6**) besides disilanes R^*_2 and R'_2 as well as indium or thallium, respectively (Scheme 1). In fact, the ditrielane formation is fully unclear to date. Nevertheless, silyltrielylenes RE may probably be the first products of the **EX**/NaR reactions. On the other hand, the action of NaR* on GaBr gives the gallium cluster compounds $R^*_8Ga_{18}$ and $R^*_8Ga_{22}$,[23] the formation of which indicates another possible way of stabilization of gallylene R*Ga. The reaction of AlBr with NaR* leads to $R^*_4Al_4$ (**12**).[24]

The diindanes **3** and **5** are also produced in alkanes from InX [X = $N(SiMe_3)_2$, C_5H_5, C_5Me_5] and NaR* as well as NaR′, and the dithallane **6** forms from $TlN(SiMe_3)_2$ and NaR*. By analogy $[(Me_3Si)_3Si]_4Tl_2$ is prepared from $TlN(SiMe_3)_2$ and $RbSi(SiMe_3)_3$.[11] On the other hand, the reaction of C_5Me_5In with NaR* gives − besides **3** − the octaindane $R^*_6In_8$,[6] whereas the reaction of $TlN(SiMe_3)_2$ with NaR′ leads to an insoluble black substance, not identified to date. Obviously, the indylene R*In or thallylene R′Tl, possibly formed as intermediates in the latter cases, may polymerize with or without elimination of R. In accordance with this, the action of $LiC(SiMe_3)_3$ on InBr leads − possibly by way of $(Me_3Si)_3CIn$ − to $[(Me_3Si)_3C]_4In_4$.[25] In addition, it is worth mentioning that the diindane **3** also forms by reaction of $R^*_6In_8$ (see above) with NaR* in heptane at 25 °C or with Na in benzene at 95 °C.

In concluding this part, we again point to the difficulty of preparing $R^*_4Ga_2$ (**2**), due to its instability against decomposition into $R^*_3Ga_2^{\cdot}$ (**2a**) and $R^{*\cdot}$ (cf. Scheme 2). To date, only one supersilyldigallane, namely $R^*_3Ga_2(SiMe_3)$ (**2b**), has been prepared by reaction of Me_3SiCl with the THF adduct of $NaGa_2R^*_3$, obtained by reduction of **2a** with Na in THF:[5] **2a** + Na and then $Me_3SiCl \rightarrow$ **2b** + NaCl (cf. Scheme 2). Preparation methods for R'_4Al_2 and R'_4Ga_2 are still lacking. Here amongst others, the reactions of *triel(II) compounds* **EX$_2$** like $Ga_2X_4 \cdot 2D$ (D = donor) with NaR′ must be studied, as it is known that the reactions of $Ga_2Br_4 \cdot 2dioxane$ or $In_2Br_4 \cdot 2TMEDA$ with $LiCH(SiMe_3)_2$ lead to $[(Me_3Si)_2CH]_4Ga_2$ or $[(Me_3Si)_2CH]_4In_2$,[13,14] and the reaction of $Ga_2Cl_4 \equiv Ga^+[GaCl_4]^-$ with $LiSi(SiMe_3)_3 \cdot THF$ to $[(Me_3Si)_3Si]_4Ga_2$.[9]



[*] Only isolable as **2a**

Scheme 2. Reactions and thermolyses of ditrielanes $R^*_4E_2$ (E = Al, Ga*), In, Tl; R* = Si*t*Bu$_3$) as well as formation of heterocubanes $R^*_4E_4Y_4$ (E = Al, Ga, In, Tl; Y = O, Se); compounds in brackets are unstable and/or not fully characterized

Table 1. Characterization of ditrielanes R_4E_2 and heterocubanes $R^*_4E_4Y_4$ with R = $SitBu_3$ (R^*), $SitBu_2Ph$ (R'), $SiMe_3$, E = triel and Y = chalcogen

	M.p. [°C][a]	Color	λ_{max} [nm][b]	NMR (C_6D_6): δ($SitBu_3/SitBu_2$)			E–E [Å][d]	Si–E [Å]	E–Y [Å]	Si–E–Si [°]	Y–E–Y/E–Y–E [°]	τ [°][d]
				^1H	^{13}C[c]	$^{29}Si/^{79}Se$						
1: $R^*_4Al_2$	63/dec.	ruby	525	1.36	25.6/35.6	44.7	2.751	2.717	–	128.3	–/–	90.0
2a: $R^*_3Ga_2$	55/dec.	dark-blue		–[e]	–/–[e]	–[e]	2.420	2.50[f]		140.7	–/–	83.5
2b: $R^*_3Ga_2SiMe_3$		red		1.26[g]	25.4/32.4[g]	48.4[g]		–			–/–	
				1.28[g]	25.6/33.9[g]	44.8[g]						
3: $R^*_4In_2$		deep-violet	560	1.35	26.8/34.0	76.8	2.928	2.786[f]	–	130.1	–/–	87.0
4: $R^*_4Tl_2$	56/dec.	dark-green	628	1.32	28.6/33.1	99.5	2.961	2.779[f]	–	130.5[f]	–/–	89.6
5: R'_4In_2		red-violet	530	1.24	23.6/31.9	54.4	2.938	2.737[f]	–	121.4[f]	–/–	79.9
6: R'_4Tl_2	125/dec.	dark-blue	591	1.29	27.0/32.5	103.7	2.881	2.682[f]	–	122.8[f]	–/–	82.2
7: $R^*_4Al_4O_4$		colorless		1.31	24.1/32.2		2.61			–		–
8: $R^*_4Ga_4O_4$	367/dec.	colorless		1.34	24.1/31.9	26.5	2.71	2.49	1.84	–	89.2/90.8	–
9: $R^*_4Al_4Se_4$		light-red		1.34	25.2/32.9	−178		2.42	1.92	–	89.9/90.1	–
10: $R^*_4In_4Se_4$		yellow		1.33	25.5/32.2	44.6/−322	3.55	2.57	2.68	–	96.8/82.9	–
11: $R^*_4Tl_4Se_4$						88.6/−498				–		–

[a] dec. = decomposition. [b] In heptane. [c] First/second shift $CMe_3/C\mathit{Me_3}$. [d] τ = Si–E–E–Si angle; *d* (E–E)/τ for R_4E_2 with R = Dsi = $CH(SiMe_3)_2$, Tip = 2,4,6-$iPr_3C_6H_2$, Pip = 2,2,6,6-$Me_4NC_5H_6$, Mes′ = 2,4,6-$(F_3C)_3C_6H_2$, Hsi = $Si(SiMe_3)_3$, R′′ = 1/2 $-tBuN{-}MeSi(NtBu)_2SiMe{-}NtBu-$. E = Al: Dsi_4Al_2 2.660/8; Tip_4Al_2 2.647/44.8; E = Ga: Dsi_4Ga_2 2.541/4.9, Pip_4Ga_2 2.525/31, Tip_4Ga_2 2.515/43.8, Mes'_4Ga_2 2.479/?, Hsi_4Ga_2 2.599/80; E = In: R''_4In_2 2.768/0, Dsi_4In_2 2.828/6.8, Tip_4In_2 2.775/48, Mes'_4In_2 2.744/86, Hsi_4In_2 2.868/78.6; E = Tl: Hsi_4Tl_2 2.914/78.1.[9–19] [e] Not seen in the NMR spectrum. [f] Mean value. [g] First/second shift R^*_2Ga/R^*Ga; Me_3Si: δ($^1H/^{13}C/^{29}Si$) = 0.173/1.29/19.4.

Characterization of $R^*_4E_2$ and R'_4E_2 (R^* = $SitBu_3$, R' = $SitBu_2Ph$)

Table 1 summarizes the ditrielanes **1–6** prepared by us, together with some characteristic properties. The compounds are remarkable colored and more or less soluble in organic media. They melt with decomposition (see below) and are air-sensitive. In addition, the ditrielanes **1**, **4** and **6** are highly unstable in the presence of light [$R^*_4Al_2$/daylight → *tetrahedro*-$R^*_4Al_4/R^*_2$ (in weeks); $R^*_4Tl_2/R'_4Tl_2$/daylight → $Tl/R^*_2/R'_2$ (in hours)].

The *^1H NMR* and *^{13}C NMR* shifts of the *t*Bu groups of $R^*_4E_2$ and R'_4E_2 appear – according to its peripheral position – in small regions [δ(^1H) = 1.24–1.36; δ(^{13}C) = 31.9–35.6/23.6–28.8]. On the other hand, the *^{29}Si NMR* shifts show E-specific areas at δ ≈ 45–50 for E = Al, Ga, δ ≈ 55–75 for E = In, and δ ≈ 95–105 for E = Tl.

The color of ditrielanes R_4E_2, that is λ_{max} of its *UV/Vis spectra*, depends on the nature of the triel E and on the geometry of the central framework (planar, gauche, orthogonal) which itself is essentially determined by the steric behavior of R. (Certainly, the electronic behavior of R is essential too.) Figure 1 shows the UV/Vis spectra of the ditrielanes R_4E_2 with fixed substituent R = R^* and fixed REER torsion angles τ (90°). Evidently, with increasing atomic number of the triel, λ_{max} of $R^*_4E_2$, shifts to longer wavelengths (525/560/628 nm for **1**/**3**/**4**), corresponding to a bathochromic colorshift from ruby (**1**) to deep-violet (**3**) to dark-green (**4**; accordingly, λ_{max} of **2**, not isolated to date, should have an absorption maximum of about 540 nm). Obviously, according to Table 1, the same is valid for **5** and **6** (τ about 80°; red-violet and dark-blue).

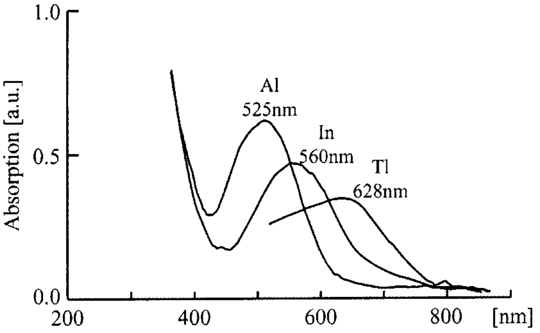


Figure 1. UV/Vis spectra of ditrielanes $R^*_2E{-}ER^*_2$ (E = Al, In, Tl; ε ≈ 50000 for λ_{max})

On the other hand, the color of ditrielanes R_4E_2 with fixed triel E shows a bathochromic shift with increasing REER torsion angle τ. Accordingly, the dialanes $[(Me_3Si)_2CH]_4Al_2$ [12]/$[2,4,6\text{-}iPr_3C_6H_2]_4Al_2$ [15]/$R^*_4Al_2$ with τ = 8/45/90° are colorless/yellow-green/ruby (λ_{max} = 370/420/525 nm), the diindanes $[(Me_3Si)_2CH]_4In_2$ [14]/R'_4In_2/$R^*_4In_2$ with τ = 6/80/90° are orange-red/red-violet/deep-violet (λ_{max} = 380/530/560 nm), or the dithallanes R'_4Tl_2/$R^*_4Tl_2$ with τ = 82/90° are dark-blue/dark-green (λ_{max} = 591/628 nm). [For electronic effects of R cf. yellow $[(Me_3Si)_2CH]_4Ga_2$ (planar)[13] and more electronegatively substituted colorless R''_4Ga_2 (evidently planar as R''_4In_2) with R′′ = 1/2 $-tBuN{-}MeSi(NtBu)_2SiMe{-}NtBu-$.[20]]

Reactions of $R^*_4E_2$ and R'_4E_2 (R^* = $SitBu_3$, R' = $SitBu_2Ph$)

In the following, the behavior of R_4E_2 (R = R^*, R') against acids/bases, redox agents and heat is discussed. The first step of the mentioned reactions may involve addition of a donor or cleavage of the E–E bond as well as cleavage of the Si–E bonds leading to compounds which themselves may give secondary products. Selected reactions that we studied are shown in Scheme 2.

We have never observed − probably for steric reasons − a formation of adducts $R_4E_2{\cdot}D$ of the mentioned ditrielanes **1** and **3−6** with Donors D (e.g. halogenides, ethers). This is unlike other − less overcrowded − ditrielanes which may work as *Lewis acids* [cf. for example the adducts $Dis_4Al_2{\cdot}D$ with Dis = $CH(SiMe_3)_2$ and D = Br^-, H^-, Me^- [26]]. In addition, the ditrielanes **1** and **3** are methanol-stable (certainly, MeOH would act first as a donor against $R^*{}_4E_2$ in the course of methanolyses). Also, our ditrielanes do not work as *Brönsted acids* (e.g. against NaR^*, NaR') unlike Dis_4Al_2 with Dis = $CH(SiMe_3)_2$.[26]

On the other hand, $R^*{}_4In_2$ (**3**) transforms, with excess hydrogen bromide, in benzene at 25 °C into R^*InBr_2 and R^*H (molar ratio 1:1) and also H_2 (Scheme 2). Obviously, **3** behaves here as a *Lewis base* against HBr. The reaction may proceed either by $R^*{}_4In_2 + 4\ HBr \rightarrow R^*{}_2In_2Br_2 + 2\ R^*H + 2\ HBr \rightarrow 2\ R^*InBr_2 + 2\ R^*H + H_2$ (cf. reaction of Dis_4Ga_2 with RCOOH[26]) or − less likely − by $R^*{}_4In_2 + 4\ HBr \rightarrow 2\ R^*{}_2InBr + H_2 + 2\ HBr \rightarrow 2\ R^*InBr_2 + 2\ R^*H + H_2$ (cf. reaction of Dis_4Al_2 with LiOR;[26] certainly, an In−In bond cleavage with HBr would require the ditrielane to be a Lewis base, which is not true for **3** but might be observed for $R^*{}_2In_2Br_2$). In this connection, it is worth mentioning that $R^*{}_4Tl_2$ (**4**) reacts with HBr in a molar ratio of 1:2 (THF, −30 °C) with the formation of R^*H and a red substance. The latter compound may be the dithallane $R^*{}_2Tl_2Br_2$ according to NMR spectroscopy. It slowly decomposes already at −30 °C into R^*Br and a black residue which has not yet been characterized (for some reactions of halosupersilylthallanes cf. ref.[7]). We could synthesize the orange digallane $R^*{}_2Ga_2Cl_2$ by reaction of $R^*GaCl_2{\cdot}THF$ and potassium in heptane, which − according to X-ray structure analysis − exists as a dimer with the As_4S_4 structure (exchange of As/S against Ga/Cl).[27]

Other examples for acid/base reactions of R_4E_2 may be that of $R^*{}_4Tl_2$ (**4**) and $R'{}_4Tl_2$ (**6**) with Ph_3CCl in benzene or cyclohexane at 0 °C which lead exclusively to $R^*{}_2/R'{}_2$ and a colorless residue (TlCl?). Certainly, the course of the mechanism is completely unclear at this time. The acid/base reactions of ditrielanes R_4E_2 (R = R*, R′) with $EHal_3$, which may lead to haloditrielanes $R_nE_2Hal_{4-n}$ (cf. R_nEHal_{3-n} [1,2]), have to be studied.

According to Scheme 2, the ditrielanes $R^*{}_4E_2$ can be both *oxidized* (e.g. with halogens, chalcogenes) and *reduced* (e.g. with alkali metals). The dialane $R^*{}_4Al_2$ (**1**) reacts cleanly in alkanes at 50 °C with iodine or hydrogen − according to Scheme 2 − under formation of the monotrielanes $R^*{}_2AlX$ (X = I, H), as published elsewhere.[5] Obviously, the products are probably formed from the sterically overcrowded dialane as follows: $\mathbf{1} \rightleftarrows 2\ R^*{}_2Al^{\cdot}$; $2\ R^*{}_2Al^{\cdot} + X_2 \rightarrow 2\ R^*{}_2AlX$. Bromine transforms $R^*{}_4In_2$ (**3**) into R^*InBr_2 and R^*Br (Scheme 2). The reaction may proceed either by In−In or by In−Si bond cleavage via $R^*{}_2InBr$ or $R^*{}_2In_2Br_2$. Bromination of $R^*{}_4Tl_2$ (**4**) results − possibly by way of R^*TlBr_2 finally to TlBr ($R^*TlBr_2 \rightarrow R^*Br + TlBr$). Fluorination of $R^*{}_4In_2$ (**3**) with AgF_2 produces − according to Scheme 2 − the dihalide R^*InF_2 ($\mathbf{3} + 4\ AgF_2 \rightarrow 2\ R^*InF_2 + 2\ R^*F + 4\ AgF$). R^*TlF_2 possibly plays the role of an intermediate in the reaction of $R^*{}_4Tl_2$ (**4**) with AgF_2, finally leading to TlF ($R^*TlF_2 \rightarrow R^*F + TlF$).

The main products of the reactions of ditrielanes **1**, **3−6** with air are the silanols tBu_3SiOH (Scheme 2) and $PhtBu_2SiOH$. Selenium transforms $R^*{}_4E_2$ (**1**, **3** and **4**) − according to Scheme 2 − into the heterocubanes $R^*{}_4E_4Se_4$ (**9**, **10**, **11**) and also $R^*{}_2$ (no $R^*{}_2Se$ is formed). This is unlike the reactions of Dis_4E_2 [Dis = $CH(SiMe_3)_2$; E = Al, Ga, In] with transfer agents for chalcogens Y like Me_3NO, Me_2SO, and Et_3PY among others, which lead to compounds $Dis_2E{-}Y{-}EDis_2$.[26] The mechanism for the formation of **9−11** is still unclear. Perhaps, the ditrielanes $R^*{}_4E_2$ react with Se_x − for steric reasons − not to selanes $R^*{}_2E{-}Se{-}ER^*{}_2$ but to diselanes $R^*{}_2E{-}SeSe{-}ER^*{}_2$ which − via $R^*{}_2$ and $R^*E(Se)_2ER^*$ (central four-membered ESeESe ring) − transform into the heterocubanes.

On the other hand, heterocubanes $R^*{}_4E_4O_4$ (**7** and **8**) are produced − according to Scheme 2 − by reaction of the tetrahedranes $R^*{}_4Al_4$ (**12**)[24] and $R^*{}_4Ga_4$ (**13**)[28] with oxygen instead of selenium (cf. Scheme 2). In fact, **12** and **13** are − like other known silyl-substituted tetrahedranes (e.g. $[(Me_3Si)_3Si]_4Ga_4$ [29]) and unlike organyl-substituted tetrahedranes (e.g. $[(Me_3C)_3Si]_4Ga_4$ [30] and $[(Me_3Si)_3C]_4In_4$ [31]) − extremely oxygen-sensitive ($[(Me_3Si)_3C]_4In_4$ may be oxidized with *o*-nitrosotoluene[31]). Certainly, **12** and **13** also react with the oxygen homologues that − as is known − even attack organyl-substituted tetrahedranes like $[(Me_3Si)_3C]_4Ga_4$ [30] and $[(Me_3Si)_3C]_4In_4$ [21]. In this connection the question arises whether the latter reactions can be reversed. In fact, deselenation of **10** should give the tetrahedrane $R^*{}_4In_4$ which has not be prepared to date.[6] For characteristic properties of the mentioned heterocubanes cf. Table 1.

The reactions of ditrielanes with alkali metals have not been studied in detail, thus far. Obviously, potassium transforms the dialane $R^*{}_4Al_2$ (**1**) in pentane at room temperature into an insoluble compound which is also obtained from $R^*{}_2AlHal$ (Hal = Cl, Br) and K and reacts with Ph_3CH under formation of $R^*{}_2AlH$ (for details cf. ref.[2]). On the other hand, $R^*{}_4In_2$ (**3**) or $R^*{}_4Tl_2$ (**4**) give with sodium in benzene or cyclohexane at 40 °C − according to Scheme 2 − supersilylsodium NaR^* and In or Tl along with $R^*{}_2/R^*H$. Radical anions $R_4E_2^{\cdot -}$, which form by reaction of alkali metals with organylditrielanes,[26] are not observed in the case of the ditrielanes **1**, **3** and **4** (certainly, electron intake leads to a planarisation of the ditrielanes,[24] which is sterically impossible for $R^*{}_4E_2$).

Regarding the redox reactions of R_4E_2 (R = R*, R′) so far discussed, there is some reason from mass spectrometric studies (see below) to believe that they start with the formation of radicals $R_2E^{\cdot}$. As stated elsewhere,[5] *thermolysis in solution* leads in the case of $R^*{}_4Al_2$ (**1**), probably by a fast and reversible Al−Al bond dissociation, to radicals $R^*{}_2Al^{\cdot}$ in low equilibrium concentration, but at the same time by a slow and irreversible Si−Al bond dissociation to radicals $R^{*\cdot}$ and $R^*{}_3Al_2^{\cdot}$ (**1a**). The latter are stable at room temperature and transform at 80−100 °C − according to Scheme 2 − possibly via $R^*_2Al_2$ into isolable trialanyl radicals $R^*_4Al_3^{\cdot}$ and *tetrahedro*-tetraalane $R^*_4Al_4$ (**12**),[5] whereas the radicals $R^{*\cdot}$ dimerize under formation of the disilane R^*_2 (the radical $R^*_4Al_3^{\cdot}$ may be formed by addition of $R^*_2Al_2$ and $R^*_2Al^{\cdot}$, and the tetrahedrane **12** by dimerization of $R^*_2Al_2$).[5] On the other hand, $R^*_4Ga_2$ (**2**) very easily thermolizes in solution into $R^{*\cdot}$ and the isolable digallanyl radical $R^*_3Ga_2^{\cdot}$ (**2a**) making the isolation of the digallane **2** unsuccessful to date[5] (the formation of $R^*_2Ga^{\cdot}$, the precursor of **2**, from R^*_2GaHal and NaR^*, only occurs at temperatures where **2** already decomposes into **2a**). The radicals **2a** themselves decompose in alkanes at 100 °C − according to Scheme 2 − possibly via $R^*_2Ga_2$ into the *tetrahedro*-tetragallane $R^*_4Ga_4$ (**13**) along with R^*_2 and R^*H.[28]

According to ESR spectroscopic studies, alkane solutions of $R^*_4In_2$ (**3**) and $R^*_4Tl_2$ (**4**) always contain radicals, the nature of which, however, is unclear. Interestingly, heating of equimolar amounts of **1** and **3** in alkanes at 90 °C do not lead to any cross-over product $R^*_2Al-InR^*_2$, but only to the thermolysis products of **1** (see above), leaving **3** intact. At 100 °C the diindane **3** thermolizes very slowly in alkanes with the formation of the dodecaindane $R^*_8In_{12}$ along with R^*_2 and R^*H (cf. Scheme 2).[6] Thus, an intermediate is formed which may be $R^*_4In_6$ (in fact, it reacts like $R^*_6In_8$ with NaR^* under formation of **3**, see preparation of the diindane). By the way, $R^*_8In_{12}$ also forms by thermolysis of $R^*_6In_8$ in benzene at 100 °C. The dithallane **4** slowly (in hours) decomposes in alkanes at 40 °C into R^*_2 and a dark brown residue (Tl?). The ditrielanes R'_4E_2 (**5**, **6**) are more stable than $R^*_4E_2$ (**3**, **4**) and thermolize in C_6D_6 at 140 °C (**5**) or 106 °C (**6**) under formation of $R'D$ and In or Tl mirrors, respectively.

In high vacuum, the mentioned ditrielanes R_4E_2 ($R = R^*, R'$) are comparably volatile. From the mass spectrum (chemical ionization with NH_3^+) of $R^*_4Al_2$ (**1**), $R^*_4In_2$ (**3**), R'_4In_2 (**5**) and R'_4Tl_2 (**6**) the $M/2^+$ peak is seen instead of an M^+ peak, which is an indication that the ditrielanes vaporize under cleavage of the E−E bonds. Accordingly its *thermolysis* in the *gas phase* takes place under formation of radicals $R_2E^{\cdot}$. In addition, the mass spectra (CI) of **1** (but not of **3**, **5** and **6**) shows peaks for fragments with an intact E−E framework, namely $R^*_2Al_2^+ + H$ and $R^*_2Al_2^+ - tBu$. Obviously, the steric overcrowding of **1** facilitates not only Al−Al, but also Si−Al bond cleavage (in fact, the digallane **2** exists as radical **2a**; see above).

Structures of $R^*_4E_2$, R'_4E_2 and $R^*_4E_4Y_4$ ($R^* = SitBu_3$, $R' = SitBu_2Ph$; Y = O, Se)

The structures of $R^*_4In_2$ (**3**; revisited),[4] $R^*_4Tl_2$ (**4**), R'_4In_2 (**5**), R'_4Tl_2 (**6**), $R^*_4Al_4O_4$ (**7**) and $R^*_4In_4Se_4$ (**10**) are shown in Figures 2−4, together with selected bond lengths and angles. For comparison, bond lengths and angles of $R^*_4Al_2$ (**1**)[5] and $R^*_4Ga_4O_4$ (**8**) [28] are also quoted. In addition, Table 1 presents bond lengths and angles of the ditrielanes and heterocubanes under discussion as well as E−E bond lengths and R−E−E−R torsion angles of other ditrielanes R_4E_2.

According to X-ray structure analyses and Figure 2, in **1**, **3** and **4** the Al, In and Tl atoms are planar coordinated with two Si atoms and one triel atom E, whereby the $EESi_2$ planes are orthogonal or nearly orthogonal to each other (cf. Table 1). Interestingly, in ditrielanes R_4E_2 with sterically less overcrowded silyl substituents the angles between the EER_2 planes decrease with decreasing bulkiness of R and are 79.9° for **5** and 82.2° for **6**, according to Figure 3 and Table 1 {for comparison $[(Me_3Si)_3Si]_4E_2$: 80° (Ga)[9]/78.6° (In)[10]/78.1° (Tl)}.[11] Significant smaller angles between the EER_2 planes show the organylditrielanes Tip_4E_2 and − above all − Dsi_4E_2 [for E = Al/Ga/In in Tip_4E_2 with Tip = 2,4,6-$iPr_3C_6H_2$ 45/44/48° and in Dsi_4E_2 with Dsi = $(Me_3Si)_2CH$ 8/5/7°; cf. Table 1].

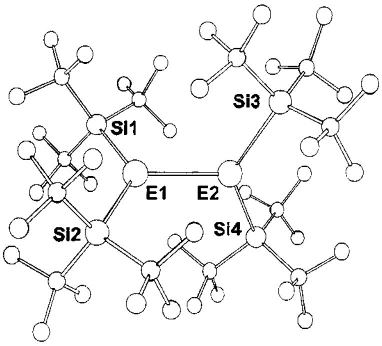


Figure 2. Crystal structures of **1**, **3** and **4** with atom numbering (SCHAKAL; H atoms omitted for clarity); selected distances [Å] and angles [°] with standard deviations: **$R^*_4Al_2$** (local symmetry D_{2d}; E1/E2 = Al1/Al1A; Si1/Si2/Si3/Si4 = Si1/Si1A/Si1B/Si1C; see ref.[5]): Al1−Al1A 2.751(2), Al1−Si1 2.717(5), Si−C (mean value) 1.97; Si1−Al1−Si1A 128.26(5), Si1−Al1−Al1A 115.87(2), C−Si−C (mean value) 109.1; Si−Al−Al−Si 90.0; **$R^*_4In_2$** (local symmetry ca. D_{2d}; E1/E2 = In1/In1A; Si1/Si2/Si3/Si4 = Si1/Si2/Si1A/Si2A): In1−In1A 2.928(3), In1−Si1 2.7835(6), In1−Si2 2.7886(6), Si−C (mean value) 1.96; Si1−In1−Si2 130.13(2), Si1−In1−In1A 115.4(1), Si2−In1−In1A 114.42(1), C−Si−C (mean value) 109.6; Si−In−In−Si 87.0; **$R^*_4Tl_2$** (local symmetry ca. D_{2d}; E1/E2 = Tl1/Tl2): Tl1−Tl2 2.961(1), Tl1−Si1 2.768(3), Tl1−Si2 2.779(4), Tl2−Si3 2.788(3), Tl2−Si4 2.781, Si−C (mean value) 1.95; Si1−Tl1−Si2 130.4(1), Si3−Tl2−Si4 130.5(1), Si1−Tl1−Tl2 114.7(2), Si2−Tl1−Tl2 114.9(2), Si3−Tl2−Tl1 114.4(1), Si4−Tl2−Tl1 115.1(1), C−Si−C (mean value) 110.1; Si−Tl−Tl−Si 89.6

The space-filling properties of the groups R* and R′ lead to unusually long E−E distances in **1** (2.75 Å), **3** (2.93 Å), **5** (2.94 Å), **4** (2.96 Å) and **6** (2.88 Å). Those in $R^*_4E_2$ are longer than those found in any dialane, diindane or dithallane with a covalent E−E bond (cf. Table 1, footnote[d]). As expected, the E−E distances in R_4E_2 increase with increasing bulkiness of R [$CH(SiMe_3)$ (Dsi) < 2,4,6-$iPr_3C_6H_2$ (Tip) < $Si(SiMe_3)_3$ (Hsi) < $SitBu_3$ (R*)], but naturally are also dependent on τ; they amount to 2.65/2.66/2.75 Å for Dsi_4Al_2/Ti_4Al_2/$R^*_4Al_2$; 2.54/2.52/2.60 Å for Dsi_4Ga_2/Tip_4Ga_2/Hsi_4Ga_2; 2.83/2.78/2.87/2.93 Å for Dsi_4In_2/Tip_4In_2/Hsi_4In_2/$R^*_4In_2$; and 2.91/2.96 Å for Hsi_4Tl_2/$R^*_4Tl_2$ (cf. Table 1). Interestingly, the E−E distance decreases on going from R_4Al_2 to analogously substituted R_4Ga_2 by ca. 0.1 Å. This may be due to a decrease of the triel atomic

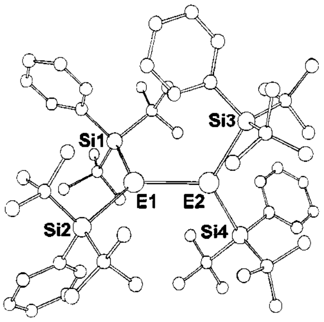


Figure 3. Crystal structures of **5**, **6** with atom numbering (SCHAKAL; H atoms omitted for clarity); selected distances [Å] and angles [°] with standard deviations: **R'_4In_2** (E1/E2 = In1/In2): In1−In2 2.938(1), In1−Si1 2.655(2), In1−Si2 2.795(1), In2−Si3 2.826(2), In2−Si4 2.671(1), Si−C (mean value) 1.96; Si1−In1−Si2 122.74(5), Si3−In2−Si4 120.10(5), Si1−In1−In2 117.73(4), Si2−In1−In2 119.43(4), Si3−In2−In1 113.50(4), Si4−In2−In1 126.39(3), C−Si−C (mean value) 110.4; Si−In−In−Si 79.9; **R'_4Tl_2** (E1/E2 = Tl1/Tl2): Tl1−Tl2 2.881(2), Tl1−Si1 2.674(2), Tl1−Si2 2.685(2), Tl2−Si3 2.685(2), Tl2−Si4 2.687(2), C−Si (mean value) 1.93; Si1−Tl1−Si2 120.69(6), Si3−Tl2−Si4 124.96(6), Si1−Tl1−Tl2 123.37(5), Si2−Tl1−Tl2 115.93(5), Si3−Tl2−Tl1 119.20(5), Si4−Tl2−Tl1 115.76(5), C−Si−C (mean value) 110.5; Si−Tl−Tl−Si 82.19

radius in the direction Al → Ga because of a d-orbital contraction which only effects r_{Ga}, but not r_{Al}. Cf. remarks in ref.[41] It is possible that the atomic radii r_{Al}/r_{Ga} = 1.25/1.26 Å normally used[32] are incorrect and may be exchanged by calculated mean values 1.30/1.24 Å (accordingly r_{In}/r_{Tl} amounts to 1.43/1.53 Å).[10] This means that the steric hindrance increases on going from **1** to **2** with the consequence that **2** is much more unstable with respect to elimination of R* than the dialane. Indeed, **2a** is isolated instead of **2**.

Another consequence of the steric hindrance of the R* or R′ groups to each other in the R_2E and REER parts of the ditrielanes R_4E_2 are unusually long Si−E distances {found in $R^*_4Al_2/R^*_4In_2/R^*_4Tl_2/R'_4In_2/R'_4Tl_2$ 2.72/2.79/2.78/2.74/2.68 Å and in $[(Me_3Si)_3Si]_4E_2$ 2.41 (Ga)[9]/2.66 (In)[10]/2.67 Å (Tl)[11]}. For the same reason the Si−E−Si bond angles are certainly somewhat larger than 120° but much smaller than occurs in the less crowded halogenides R^*_2EHal ($R^*_4Al_2/R^*_4In_2/R^*_4Tl_2/R'_4In_2/R'_4Tl_2$: 128/130/130/121/123°; R^*_2EHal about 150°, see ref.[2]).

The central frameworks of the heterocubanes $R^*_4E_4O_4$ (**7**, **8**[28]), shown in Figure 4, form nearly nondistorted cubes, the corners of which are alternatively occupied by E and O atoms (mean angles AlOAl/OAlO = 90.8/89.2°; GaOGa/OGaO = 90.1/89.9°; cf. also Table 1). Obviously, the oxidation of the tetrahedranes $R^*_4Al_4$ (**12**) or $R^*_4Ga_4$ (**13**) to **7** or **8** which are also described as E_4 tetrahedranes each with a face capped by a chalcogen atom (cf. Scheme 2), leads to an expansion of the Al_4/Ga_4 cores as seen by the E−E distances in **13** (2.57 Å) and **8** (2.71 Å). Indeed, the X-ray structure analysis of **7** refers to crystals that contain **7** and **12** in a molar ratio of 1:2. As is known from crystals containing **8** and **13**, bond lengths and angles lie between those of **8** and **13**. Therefore, the E−E distances in pure **7** are certainly somewhat longer than the 2.61 Å obtained (found for **12** 2.60 Å).

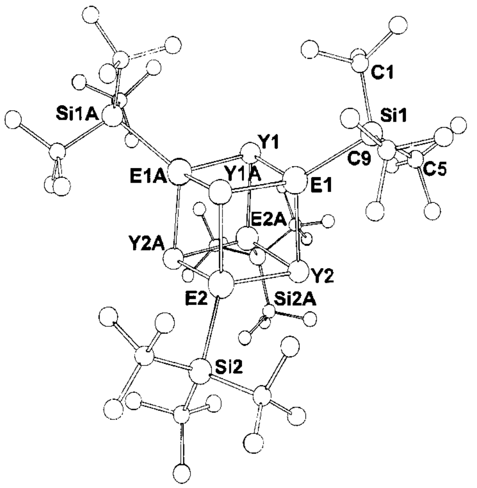


Figure 4. Crystal structures of **7**, **8**, **9** with atom numbering (SCHAKAL; H atoms omitted for clarity); selected distances [Å] and angles [°] with standard deviations [$R^*_4Al_4O_4$ together with $R^*_4Al_4$ (molar ratio 1:2) in the crystal]: **$R^*_4Al_4O_4$** (local symmetry C_2; E =Al, Y = O): Al1−O2 1.826(7), Al1−O1A 1.831(6), Al1−O1 1.838(6), Al1A−O1 1.831(6), Al2−O2A 1.836(6), Al2−O2 1.837(6), Al2−O1A 1.840(6), Al2A−O1 1.840(6), Al2A−O2 1.836(6), Al−Al (mean value) 2.612, Si1−Al1 2.486(1), Si2−Al2 2.486(1), Si−C (mean value) 1.94; Al1A−O1−Al1 90.7(3), Al1A−O1−Al2A 90.7(3), Al1−O1−Al2A 90.4(3), Al1−O2−Al2A 90.9(3), Al1−O2−Al2 91.0(3), Al2A−O2−Al2 90.8(3), O2−Al1−O1A 89.4(3), O2−Al1−O1 89.5(3), O1A−Al1−O1 89.3(3), O2A−Al2−O2 89.2(3), O2A−Al2−O1A 89.1(3), O2−Al2−O1A 88.8(3), Al−Al−Al (mean value) 60.0, Si−Al−Al (mean value) 144.7, Si−Al−O (mean value) 126.0, C−Si−C (mean value) 111.8; **$R^*_4Ga_4O_4$** (local symmetry C_2; E = Ga, Y = O; see ref.[23]): Ga1−O1A 1.923(4), Ga1−O1 1.912(4), Ga1−O2 1.909(4), Ga2−O1A 1.915(3), Ga2−O2 1.902(4), Ga2−O2A 1.928(4), Ga−Ga (mean value) 2.712, Ga1−Si1 2.425(1), Ga2−Si2 2.423(1), Si−C (mean value) 1.93; O2−Ga1−O1 90.2(2), O1−Ga1−O1A 89.7(2), O2−Ga1−O1A 89.96(2), O2−Ga2−O2A 90.1(2), O2−Ga2−O1A 90.2(2), O1A−Ga2−O2A 89.5(1), Ga1A−O1A−Ga2 90.3(2), Ga2−O1A−Ga1 89.7(2), Ga1A−O1A−Ga1 90.3(2), Ga2−O2−Ga1 90.5(2), Ga2−O2−Ga2A 89.9 (2), Ga1−O2−Ga2A 90.0(2), Si−Ga−Ga (mean value) 144.5, Si−Ga−O (mean value) 123.7, C−Si−C (mean value) 112.3; **$R^*_4In_4Se_4$** (local symmetry C_2; E = In, Y = Se): In1−Se1A 2.681(1), In1−Se1 2.682(1), In1−Se2 2.681(1), In2−Se1A 2.680(2), In2−Se2 2.675(1), In2−Se2A 2.677, In−In (mean value) 3.553, In1−Si1 2.577(2) In2−Si2 2.565(3), Si−C (mean value) 1.95; Se2−In1−Se1 96.27(2), Se1−In1−Se1A 95.93(2), Se2−In1−Se1A 97.01(3), Se2−In2−Se2A 97.16(2), Se2−In2−Se1A 97.19(3), Se1A−In2−Se2A 96.97(2), In1A−Se1A−In2 82.76(2), In2−Se1A−In1 82.44(2), In1A−Se1A−In1 83.57(2), In2−Se2−In1 82.54(2), In2−Se2−In2A 82.45(2), In1−Se2−In2A 83.39, In−In−In (mean value) 60.0, Si−In−In (mean value) 144.9, Se−In−Se (mean value) 96.5, In−Se−In (mean value) 82.9, Si−In−Se (mean value) 120.3, C−Si−C (mean value) 112.2

According to Figure 4, the heterocubane $R^*_4In_4Se_4$ (**10**) is analogously structured to **7** or **8**. Certainly, the In_4Se_4 cube deviates somewhat from being regular (mean angles InSeIn/SeInSe = 82.9/96.8°; cf. also Table 1), and the expansion of the In_4 tetrahedrane by going from $R^*_4In_4$ [not synthesized to date; In−In distance must be even shorter than in **3** (2.93 Å)] to **10** (In−In distance 3.55 Å) is very pronounced. Altogether, the heterocubane **10** is analogously structured to the many other heterocubanes $R_4E_4Y_4$ (E = Al, Ga, In; Y = S, Se, Te) which have been prepared to date (e.g. cf. refs.[30,31]).

Experimental Section

General Remarks: All experiments were carried out in flame-dried glass apparatus with standard Schlenk techniques under dry argon or nitrogen. During all manipulations, air and moisture were strictly excluded. The solvents (pentane, heptane, benzene, cyclohexane, toluene, tetrahydrofuran) were distilled from sodium/lead or sodium/benzophenone. Available for use were: H_2, HBr, Cl_2, Br_2, I_2, Se, Ph_3CH, Ph_3CCl, Bu_3SnH, $AlBr_3$, $GaCl_3$, $InBr_3$, InBr, $TlCl_3$, TlBr and AgF_2. The following compounds were synthesized according to literature procedures: NaR*,[33] NaR*·2THF,[33] NaR′,[3] $R*_2AlHal$,[2] C_5H_5In,[34] C_5Me_5In,[35] $TlN(SiMe_3)_2$,[36] C_5H_5Tl,[37] $R*_4Al_4$,[24] and $R*_4Ga_4$.[28] Synthesis of $InN(SiMe_3)_2$ resulted from the addition of $LiN(SiMe_3)_2$ (0.897 g, 5.36 mmol)[40] in 10 mL of THF to InCl (0.806 g, 5.36 mmol) in 20 mL of THF (−78 °C). After warming to 25 °C, the light-yellow solution contained $InN(SiMe_3)_2$ exclusively according to the NMR spectra. Filtration of the insoluble residue (LiCl) and removal of all volatile compounds with an oil-pump vacuum led to colorless $InN(SiMe_3)_2$ in quantitative yield. ^1H NMR (C_6D_6, int. TMS): $\delta = 0.324$. $^{13}C\{^1H\}$ NMR (C_6D_6, int. TMS): $\delta = 5.96$. $^{29}Si\{^1H\}$ NMR (C_6D_6, ext. TMS): $\delta = 2.69$. The products $R*_2$,[33] R*H,[33] R*Hal,[33] R*OH,[38] $R*C_6H_5$,[33] NaR′,[3] R'_2,[39] R′H,[39] R′OH[39] were identified by comparison with authentic samples [tBu$_3$Si in R*OH: $\delta(^1H) = 1.090$; $\delta(^{13}C) = 22.67/29.69$; $\delta(^{29}Si) = 10.30$; tBu$_2$Si in R'_2: $\delta(^1H) = 1.244$, $\delta(^{13}C) = 28.00/33.05$, $\delta(^{29}Si) = 139.5$; tBu$_2$Si in R′H: $\delta(^1H) = 1.063$, $\delta(^{13}C) = 19.1/29.2$, $\delta(^{29}Si) = 13.4$; tBu$_2$Si in R′OH: $\delta(^1H) = 1.073$; $\delta(^{13}C) = 21.5/28.5$; $\delta(^{29}Si) = 1.01$]. For NMR spectra a Jeol GX-270 ($^1H/^{13}C/^{29}Si$: 270.17/67.94/53.67 MHz) and Jeol EX-400 ($^1H/^{13}C/^{29}Si$: 399.78/100.54/79.43 MHz) were used. The ^{29}Si NMR spectra were recorded with the INEPT or DEPT pulse sequence using empirically optimized parameters for the mentioned groups. For mass spectra a Varian CH7 and a MStation JMS 700 of Jeol were used, for UV/Vis spectra a 555-UV/Vis spectrometer from Perkin−Elmer.

Syntheses, Thermolysis and Reactions of $R*_4Al_2$ (1). − (i): $AlBr_3$ (0.537 g, 2.01 mmol) and NaR* (1.35 g, 6.07 mmol) in 60 mL of heptane (−78 °C) gave, after heating at room temperature for 24 h, **1** and $R*_2$ in a molar ratio of 1:1 (according to NMR spectra) along with NaBr. After filtration of the insoluble residue (NaBr) and concentration of the filtrate to 20 mL, tetrasupersilyldialane **1** (0.762 g, 0.896 mmol; 89%) was obtained in 1 week at −23 °C as air-sensitive, methanol-stable, benzene-labile, photo- and thermolabile, ruby crystals which decomposed at 63 °C (the oxidation with *air* leads to R*OH as the only R*-containing compound). **1** also forms from equimolar amounts of $R*_2AlHal$ (Hal = Cl, Br) and NaR* in pentane (see ref.[5]). $C_{48}H_{108}Al_2Si_4$ (851.7): calcd. C 67.34, H 12.73; found C 67.69, H 12.78. NMR: see Table 1. UV/Vis (heptane): $\lambda_{max} = 525$ nm ($\varepsilon \approx 50000$). MS (EI; 70 eV): m/z = 452 (1) $[R*_2Al_2^+]$, 395 (11) $[R*_2Al_2^+ - t\text{Bu}]$, 425 (4) $[R*_2Al^+]$, 368 (8) $[R*_2Al^+ - C_4H_8]$, 226 (13) $[R*Al^+]$. CI (NH_3; 25−50 °C): m/z = 453 (95) $[R*_2Al_2^+ + H]$, 395 (15) $[R*_2Al_2^+ - t\text{Bu}]$, 442 (20) $[R*_2Al^+ + NH_3]$, 425 (40) $[R*_2Al^+]$, 216 (100) $[\text{Si}t\text{Bu}_3^+ + NH_3]$, 199 (5) $[\text{Si}t\text{Bu}_3^+]$. X-ray structure analysis: see Figure 2 and ref.[5] − **(ii):** For thermolysis of **1** see ref.[5] − **(iii):** Irradiation of **1** (0.016 mmol) in C_6D_{12} (0.6 mL) slowly leds (in weeks) to **12**,[24] $R*_2$ and R*H in a molar ratio of ca. 1:1:3. − **(iv):** For reaction of hydrogen and iodine with **1** see ref.[5]; for reaction with oxygen see above; for reaction with selenium see below. − **(v):** In the presence of 0.8 mmol of potassium (K), a red solution of $R*_4Al_2$ (0.042 g, 0.05 mmol) in 10 mL of pentane transforms over 24 h to a gray residue (intermediate colors: violet, green, colorless). The solution then contains $R*_2$ and R*H according to NMR specroscopy. The residue reacts with Ph_3CH to form $R*_2AlH$.[5]

Synthesis, Thermolysis and Reactions of $R*_3Ga_2^{\cdot}$ (2a); Formation of $R*_3Ga_2(SiMe_3)$ (2b). − (i): $GaCl_3$ (0.184 g, 1.045 mmol) and NaR*·2THF (1.35 mmol) in 20 mL of pentane (−30 °C) gave, after warming to room temperature over 24 h, black-blue **2a** (detected by ESR spectroscopy) and $R*_2$ (detected by NMR spectroscopy) along with NaCl. After filtration of the insoluble residue (NaCl), concentration of the filtrate to 7 mL and cooling to −23 °C, superdisilane $R*_2$ formed as colorless crystals and then trisupersilyldigallanyl (**2a**) (0.110 g, 0.15 mmol, 14.4%) over 5 d as oxygen- and moisture-sensitive black-blue crystals, which decomposed at ca. 55 °C. **2a** was also formed from equimolar amounts of $R*_2GaHal$ (Hal = Cl, Br) and NaR* in heptane.[5] For characterization and for thermolysis (formation of **13**) and reduction of **2a** (formation of $NaGa_2R*_3$·3THF) see ref.[5] − **(ii):** Reaction of 0.1 mL of tributylstannane with **2a** in 10 mL of pentane immediately leds to a deep-red solution with − according to NMR spectroscopy (C_6D_6) − an unidentified substance with R* groups [$\delta(^1H) = 1.107, 1.214, 1.322$] along with R*H and $R*_2$. The latter decomposed under decolorization of the C_6D_6 solution. − **(iii):** Reaction of chlorine (0.038 mmol) in 0.1 mL of CCl_4 with **2a** (0.04 mmol) in 10 mL of pentane (−78 °C) immediately led to a deep-red solution which contained − according to NMR spectroscopy (C_6D_6) − unidentified substances with R* groups [$\delta(^1H) = 1.092, 1.205, 1.238, 1.260$; $\delta(^{29}Si) = 6.27, 17.56, 39.91, 51.22$] along with R*H, $R*_2$, R*Cl and $R*_2GaCl$. One compound was identical to the substance found from $R*_4Tl_2$ with Na in C_6D_6 [$\delta(^1H/^{29}Si) = 1.092/6.27$] and obviously contains no Ga and Tl, respectively. The other compounds may be the digallane $R*_3Ga_2Cl$ or products formed from it. − **(iv):** For synthesis of trisupersilyltrimethylsilyldigallane $R*_3Ga_2(SiMe_3)$ (**2b**) from $NaGa_2R*_3$·3THF and Me_3SiCl and for characterization of this digallane see ref.[8]

Syntheses, Thermolysis and Reactions of $R*_4In_2$ (3). − (i): $InCl_3$ (0.778 g, 3.50 mmol) and NaR*·2THF (10.5 mmol) in 40 mL of THF (−78 °C) gave **3** and $R*_2$ in a molar ratio of 1:1 (according to NMR spectra) along with NaCl after warming to room temperature over 5 h. After exchange of THF with 80 mL of toluene, filtration of the insoluble residue (NaCl) and concentration of the filtrate to 20 mL, 0.112 g (1.09 mmol; 63%) of tetrasupersilyldiindane **3** was obtained over some days at −23 °C as air-sensitive, methanol-stable, deep-violet crystals which decomposed at 125 °C (the oxidation with air led to R*OH as the only R*-containing compound). **3** and In (or Na_xIn_y) is also formed from InBr (2.91 mmol) and NaR* (2.91 mmol) in 25 mL of THF (warming from −78 °C to 25 °C[4]) or from C_5H_5In (3.24 mmol) and NaR* (2.50 mmol) in 40 mL of pentane (warming from −78 °C to 25 °C, 12 h), or from $InN(SiMe_3)_2$ (0.49 mmol) and NaR* (0.49 mmol) in 15 mL of pentane (warming from −78 °C to 25 °C, 14 d). $C_{48}H_{108}In_2Si_4$ (1027.4): calcd. C 56.12, H 10.60; found C 55.75, H. 10.53. NMR: see Table 1. UV/Vis (heptane): $\lambda_{max} = 560$ nm ($\varepsilon \approx 50000$). MS (EI; 70 eV): m/z = 513 (19) $[R*_2In^+]$, 457 (3) $[R*_2In^+ - C_4H_8]$, 314 (100) $[R*In^+]$. CI (NH_3; 25−50 °C): m/z = 513 $[R*_2In^+]$. X-ray structure analysis: see Figure 2 and ref.[4] Remarks: Reaction of equimolar amounts of C_5Me_5In and NaR* in pentane (warming from −120 °C to −78 °C/48 h, then to 25 °C) led to **3** and $R*_6In_8$ in a molar ratio of 1:1.[6] $R*_6In_8$ itself thermolized in C_6D_6 at 100 °C/20 d into $R*_8In_{12}$ besides R*D/In and reacted with NaR* in heptane (warming from −78 °C to 25 °C) or with Na in C_6D_6 at 95 °C with the formation of **3** and $R*_2$/In (or Na_xIn_y). − **(ii):** Thermolysis of **3** in alkanes at 100 °C took place via an unidentified intermediate ($R*_4In_6$?) with the formation of $R*_8In_{12}$;[6] the intermediate transformed, in the presence of NaR*·2THF in heptane, into **3** and an unidentified residue (In or Na$_x$In$_y$). Thermolysis of **3** (0.191 mmol) in the presence of **1** (0.101 mmol) in 20 mL of heptane (5 h, 90 °C) led to the thermolysis products of **1**[5]; **3** remained unchanged. − **(iii):** Irradiation of **3** has not been studied thus far. − **(iv):** The reaction of silver difluoride (AgF$_2$) with **3** led to R*InF$_2$, see ref.[1]; for the reaction with oxygen see above; for the reaction with selenium see below. − **(v):** Reaction of sodium (0.9 mmol) and **3** (0.01 mmol) in 0.7 mL of C$_6$D$_6$ led at 40 °C and 3 d to R*$_2$, R*D, R*C$_6$D$_5$ and NaR* in a molar ratio of ca. 1:2:2:7 with a color change from deep-violet to red and formation of a residue (In or Na$_x$In$_y$), according to NMR spectra. − **(vi):** After warming hydrogen bromide (HBr) (0.41 mmol) and **3** (0.071 mmol) in 0.6 mL of C$_6$D$_6$ from −78 °C to room temperature (decolorization, formation of H$_2$), the solution contained R*InBr$_2$ [2] and R*H in a molar ratio of ca. 1:1, according to NMR spectroscopy. − **(vii):** After warming bromine (Br$_2$) (0.07 mmol) and **3** (0.061 mmol) in 4 mL of pentane from −78 °C to room temperature (decolorization), the solution contained R*InBr$_2$ [2] and R*Br in a molar ratio of ca. 1:1 along with a grayish residue, according to NMR spectroscopy.

Syntheses, Thermolysis and Reactions of R*$_4$Tl$_2$ (4). − (i): A solution of TlCl$_3$ (0.584 g, 1.88 mmol) and NaR*·2THF (5.64 mmol) in 30 mL of THF was kept at −78 °C for 20 h and then warmed to room temperature. The dark green solution − over a black residue − then contained an unidentified compound [multiplet at δ(^{29}Si) = 166.2 which points at a substance with two or more Tl atoms]. After filtration of the insoluble residue (NaCl) and concentration of the filtrate to 10 mL, tetrasupersilyldithallane **4** (0.035 g, 0.030 mmol; 24%) was obtained over 14 d at −23 °C as air-sensitive, methanol-stable, deep green crystals which decomposed at 56 °C (the oxidation with air led to R*OH as the only R*-containing compound). The reaction of TlN(SiMe$_3$)$_2$ (0.272 g, 0.746 mmol) and NaR* (0.166 g, 0.746 mmol) in 30 mL of pentane led to NaN(SiMe$_3$)$_2$ [40] and R*$_2$ after 72 h at −90 °C and warming to −30 °C, according to NMR spectroscopy [δ(^{29}Si) = 166.2]. Then, after concentration of the solution to 10 mL, crystals of deep-green **4** were obtained at −23 °C in 14 d. Crystalline **4** and Tl (or Na$_x$Tl$_y$) also formed from TlBr and NaR* in THF (warming from −78 °C to 25 °C)[4] or from C$_5$H$_5$Tl (1.785 mmol) and NaR* (1.785 mmol) in 40 mL of pentane at −80 °C. ^{1}H NMR (C$_6$D$_6$, int. TMS): δ = 1.318 (d, $^4J_{\mathrm{HTl}}$ = 8.4 Hz, 108 H, Si*t*Bu$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, int. TMS): δ = 28.6/33.1 (d/d, $^2J_{\mathrm{CTl}}$/$^3J_{\mathrm{CTl}}$ = 155.8/49.9 Hz, (12 C/36 C, *C*Me$_3$/C*Me*$_3$). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, ext. TMS): δ = 99.5 (two doublets with $^1J_{\mathrm{Si}}{}^{205/203}{}_{\mathrm{Tl}}$ = 1628/1610 Hz; the absence of $^2J_{\mathrm{Si}}{}^{205/203}{}_{\mathrm{Tl}}$ is unclear, 4 Si, Si*t*Bu$_3$). UV/Vis (heptane): $\lambda_{\max}$ = 628 nm ($\varepsilon \approx$ 50000). X-ray structure analysis: see Figure 2. − **(ii):** Thermolysis of **4** in alkanes at 40 °C led to R*$_2$ and a dark-brown residue (Tl?). − **(iii):** Irradiation of **4** in C$_6$D$_{12}$ with daylight led to R*$_2$ and Tl over a few hours. − **(iv):** Reaction of silver difluoride (AgF$_2$) with **4** led to R*F and R*$_2$, see ref.[2]; for the reaction with oxygen see above; for the reaction with selenium see below. − **(v):** By dropwise addition of bromine (Br$_2$) in 10 mL of pentane to **4** (0.1 mmol) in 15 mL of pentane (−78 °C), the solution decolorized with the formation of a residue (TlBr?) and contained only R*Br according to NMR spectroscopy − **(vi):** After warming hydrogen bromide (HBr) (0.358 mmol) and **4** (0.166 mmol) in 0.6 mL of [D$_8$]THF at temperature of liquid nitrogen to −30 °C, the solution changed its color from deep green to red. It then contained a thallium compound which − according to NMR spectroscopy at −30 °C in C$_6$D$_8$O − may have the composition R*BrTl−TlBrR* [δ(^{1}H) = 1.322 (d, $^4J_{\mathrm{HTl}}$ = 8.4 Hz, Si*t*Bu$_3$); δ(^{29}Si) = 98.9 (two d, $^1J_{\mathrm{Si}}{}^{205/203}{}_{\mathrm{Tl}}$ = 1451/1438 Hz, Si*t*Bu$_3$]. The solution decolorized after warming to room temperature and then contained R*Br. At the same time a residue [colorless TlBr, black (R*Tl)$_n$?][7] was formed. The decomposition partly took place at −30 °C. − **(vii):** After warming a mixture of triphenylmethyl chloride (Ph$_3$CCl) (0.083 mmol) and **4** (0.082 mmol) in 0.6 mL of pentane from −196 °C to 25 °C (decolorization; formation of TlCl?), the solution then contained R*$_2$ according to NMR spectroscopy. − **(viii):** Reaction of sodium (Na) (0.9 mmol) and **4** (0.01 mmol) in 0.7 mL of C$_6$D$_6$ led at 40 °C in 1 d, under change of color from deep-green to brown and formation of a residue (Tl or Na$_x$Tl$_y$) to R*$_2$, R*D and NaR* (molar ratio ca. 1:1:1), according to NMR spectroscopy, along with an unidentified substance [δ(^{1}H) = 1.104; δ(^{29}Si) = 6.3].

Syntheses and Thermolysis of R′$_4$In$_2$ (5). − (i): A mixture of InBr (0.207 g, 1.06 mmol) and NaR′ (0.254 g, 1.05 mmol) in 30 mL of pentane/18 mL of THF was kept for 12 h at −78 °C. After warming to 25 °C, the color of the solution changed from yellow to green to deep-violet and it then contained − according to NMR spectroscopy− **5** and R′$_2$ in a molar ratio of 1:1. After filtration of the insoluble residue (NaBr, In) and concentration of the filtrate to 10 mL, tetrakis(di-*tert*-butylphenylsilyl)diindane (**5**) (0.168 g, 0.152 mmol; 85%) was obtained as red-violet, air-sensitive crystals. **5** was also formed from C$_5$Me$_5$In (0.155 g, 0.620 mmol) and NaR′ (0.151 g, 0.622 mmol) in 20 mL of pentane (12 h at −78 °C or 6 h at −120 °C). After warming to 25 °C, the solution exclusively contained − according to NMR spectroscopy − **5** and R′$_2$ in a molar ratio of 1:1. The concentrated filtrate led to crystalline R′$_4$In$_2$ (0.090 g, 0.080 mmol; 75%) at −23 °C. ^{1}H NMR (C$_6$D$_6$, int. TMS): δ = 1.242 (s, 72 H, Si*t*Bu$_2$), 7.840/7.179 (m/m, 8 H/12 H, *m*-/*o*-,*p*-CH of Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$, int. TMS): δ = 23.6/31.9 (s/s, 8 C/24 C, *C*Me$_3$/C*Me*$_3$), 127.8/128.1/128.3/136.9 (s/s/s/s, 8 C/4 C/8 C/4 C, *m*-/*p*-/*o*-/*i*-CH of Ph). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, ext. TMS): δ = 54.4 (s, 4 Si, Si*t*Bu$_2$). UV/Vis (heptane): $\lambda_{\max}$ = 530 nm ($\varepsilon \approx$ 50000). MS (CI: NH$_3$; 25−50 °C): *m*/*z* = 553 [R′$_2$In$^+$]. X-ray structure analysis: see Figure 3. − **(ii):** Thermolysis of 0.127 mmol of **5** in 0.6 mL of C$_6$D$_{12}$ at 140 °C/12 h led to R′D and an In mirror; some **5** remained unchanged. − **(iii):** The oxidation of **5** with air led to R′OH as the only R′-containing compound.

Syntheses, Thermolysis and Reactions of R′$_4$Tl$_2$ (6). − (i): A mixture of TlBr (0.225 g, 0.790 mmol) and NaR′ (0.192 g, 0.790 mmol) in 20 mL of THF was kept for 12 h at −90 °C. After warming to 25 °C, the color of the solution changed from yellow to dark-blue, and it then contained − according to NMR spectroscopy − **6** and R′$_2$ in a molar ratio of 1:1. After filtration of the insoluble residue (NaBr, Tl) and concentration of the filtrate to 5 mL, tetrakis(di-*tert*-butylphenylsilyl)dithallane (**6**) (0.151 g, 0.117 mmol; 94%) was obtained as air-sensitive, photo-labile, black-blue crystals which decomposed at 125 °C. ^{1}H NMR (C$_6$D$_6$, int. TMS): δ = 1.290 (broad, 72 H, Si*t*Bu$_2$), 7.814/7.528 (m/m, 8 H/12 H, *m*-/*o*-/*p*-CH of Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$, int. TMS): δ = 27.0/32.5 (broad/broad, 8 C/24 C, *C*Me$_3$/C*Me*$_3$), 128.6/135.9/137.0/137.7 (s/s/s/s, 8 C/4 C/8 C/4 C, *m*-/*p*-/*o*-/*i*-CH of Ph). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, ext. TMS): δ = 103.7 (2 doublets with $^1J_{\mathrm{Si}}{}^{205/203}{}_{\mathrm{Tl}}$ = 982/973 Hz; the absence of $^1J_{\mathrm{Si}}{}^{205/203}{}_{\mathrm{Tl}}$ is unclear; 4 Si, Si*t*Bu$_2$). UV/Vis (heptane): $\lambda_{\max}$ = 591 nm ($\varepsilon \approx$ 50000). MS (CI; NH$_3$; 25−50 °C): *m*/*z* = 643 (R′$_2$Tl$^+$). X-ray structure analysis: see Figure 3. Remarks: Reaction of equimolar amounts of TlN(SiMe$_3$)$_2$ and NaR′ in alkanes did not lead to **6**, but to a black residue [(R′Tl)$_x$?].[5] − **(ii):** Thermolysis of 0.113 mmol of **6** in 0.6 mL of C$_6$D$_{12}$ at 106 °C/48 h completely led to R′D and a Tl mirror. − **(iii):** Irradiation of **6** in C$_6$D$_{12}$ with daylight led to R′$_2$ and Tl over a few hours. − **(iv):** After warming a mixture of 0.036 mmol of triphenylmethyl chloride (Ph$_3$CCl) and **6** (0.020 mmol) in 0.6 mL of C$_6$D$_{12}$ from −78 °C to 25 °C, it turned from black-blue to colorless within 10 min (formation of TlCl?), and then contained only R'_2, according to NMR spectroscopy. − **(v):** The oxidation of **6** with air led to R′OH as the only R′-containing compound.

Syntheses of $R^*_4E_4Y_4$ (E = triel, Y = O, Se). − (i): Reaction of gray selenium (Se_x) (0.022 g, 0.273 mmol) in 0.8 mL of C_6D_{12} with **1** (0.122 g, 0.144 mmol) led to $R^*_4Al_4Se_4$ (**9**) and R^*_2 and R*H at 60 °C over 12 h. From the reaction mixture at 5 °C **9** was obtained as air- and moisture-sensitive light-red crystals which were not suitable for X-ray analysis but certainly contained molecules structured like **10** (see below). $C_{48}H_{108}Al_4Se_4Si_4$ (1221.5): calcd. C 29.53, H 5.57; found C 29.85, H 5.64. ^1H NMR (C_6D_6, int. TMS): $\delta = 1.337$ (s, 108 H, SitBu$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, int. TMS): $\delta = 25.2/32.9$ (s/s, 12 C/36 C, CMe$_3$/CMe_3). ^{29}Si NMR: Not observed. ^{79}Se NMR (C_6D_6, ext. $SeMe_2$ in C_6D_6): $\delta = -178.4$ (s, 4 Se). − **(ii):** Reaction of gray selenium (Se_x) (0.054 g, 0.681 mmol) in 30 mL of heptane with $R^*_4In_2$ (0.350 g, 0.341 mmol) led at 90 °C in 7 h to $R^*_4In_4Se_4$ (**10**), R^*_2 and R*H. All the volatile compounds were removed in an oil-pump vacuum, the residue was taken up in heptane (30 mL), the precipitate (Se) was then filtered off from the solution and the latter concentrated to 10 mL. From the solution at −23 °C **10** (0.123 g, 0.089 mmol; 46%) was obtained as air- and moisture-sensitive yellow crystals. $C_{48}H_{108}In_4Se_4Si_4$ (1572.9): calcd. C 36.66, H 6.92; found C 36.32, H 6.87. ^1H NMR (C_6D_6, int. TMS): $\delta = 1.328$ (s, 108 H, SitBu$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, int. TMS): $\delta = 25.5/32.2$ (s/s, 12 C/36 C, CMe$_3$/CMe_3). $^{29}Si\{^1H\}$ NMR (C_6D_6, ext. TMS): $\delta = 44.6$ (s, 4 Si, SitBu$_3$). ^{79}Se NMR (C_6D_6, ext $SeMe_2$ in C_6D_6): $\delta = -322.4$ (s, 4 Se). X-ray structure analysis: see Figure 4. − **(iii):** Reaction of gray selenium (Se_x) (0.014 g, 0.178 mmol) in 5 mL of pentane with **4** (0.107 g, 0.090 mmol) led to R^*_2, R*H and a new substance at −30 °C in 8 h [$\delta(^{29}Si) = 88.56$; $\delta(^{79}Se) = -498.3$] which then decomposed at −25 °C in hours. It possibly contained molecules $R^*_4Tl_4Se_4$ (**11**) structured like **9** [$\delta(^{79}Se) = -178.4$] or **10** [$\delta(^{79}Se) = -322.4$]. − **(iv):** From a solution of **12** (0.05 mmol) in 2 mL of heptane in the presence of traces of dry oxygen (O_2) a mixture of **7**/**12** was formed in 2 weeks as air- and moisture-sensitive violet crystals (for **12** see ref.[25]). Further oxidation of **7**/**12** leads to colorless **7**. ^1H NMR (C_6D_6, int. TMS): $\delta = 1.31$ (s, 108 H, SitBu$_3$ of **7**), 1.36 (s, 108 H, SitBu$_3$ of **12**). $^{13}C\{^1H\}$ NMR (C_6D_6, int. TMS): $\delta = 24.1/32.2$ (s/s, 12 C/36 C, CMe$_3$/CMe_3 of **7**), 25.5/32.8 (s/s, 12 C/36 C, CMe$_3$/CMe_3 of **12**). $^{29}Si\{^1H\}$ NMR (C_6D_6, ext. TMS): $\delta = 16.2$ (s, 4 Si, SitBu$_3$ of **12**), not observed (SitBu$_3$ of **7**). X-ray structure analysis: see Figure 4. − **(v):** For synthesis of colorless $R^*_4Ga_4O_4$ (**8**), see ref.[28]; X-ray analysis: see Figure 4.

X-ray Structure Determinations: Siemens P4 with an area detector for $R^*_4Al_2$, $R^*_4Al_4O_4$, $R^*_4Ga_4O_4$, STOE IPDS with an area detector for $R^*_4In_2$, $R^*_4Tl_2$, $R^*_4In_4Se_4$, R'_4In_2, R'_4Tl_2. Crystals were mounted in perfluorpolyether oil. The structures were solved by direct methods [SHELXS-97/SHELXL-97: $R^*_4Al_2$; XS (SHELXS, version 5)/SHELXL-93: $R^*_4Al_4O_4$, $R^*_4Ga_4O_4$; SHELXS/SHELXL-93: $R^*_4In_2$, $R^*_4Tl_2$, $R^*_4In_4Se_4$, R'_4In_2, R'_4Tl_2] and full matrix against F^2. All non-hydrogen atoms were refined anisotropically and H atoms were included in the refinement at calculated positions with a riding model and fixed isotropic U_i values. All tBu groups of **4** were rotationally disordered; this could explain the high R values of the dithallane structure. The structures of the compounds that are shown in Figures 2−4, crystallographic details are summarized in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-163234 ($R^*_4In_2$), -163352 ($R^*_4Tl_2$), -163236 (R'_4In_2), -163353 (R'_4Tl_2), -163233 ($R^*_4Al_4O_4$/$2R^*_4Al_4$), -163235 ($R^*_4In_4Se_4$) (for $R^*_4Al_2$ see ref.[5], for $R^*_4Ga_4O_4$ see ref.[28]). Copies can be obtained free of charge on application

Table 2. Selected parameters of the X-ray structure analyses of the compounds shown in the first line

	$R^*_2Al{-}AlR^*_2$ [5]	$R^*_2In{-}InR^*_2$	$R^*_2Tl{-}TlR^*_2$	$R'_2In{-}InR'_2$	$R'_2Tl{-}TlR'_2$	$R^*_4Al_4O_4$ [a]	$R^*_4Ga_4O_4$ [22]	$R^*_4In_4Se_4$
Formula	$C_{48}H_{108}Al_2Si_4$	$C_{48}H_{108}In_2Si_4$	$C_{48}H_{108}Tl_2Si_4$	$C_{56}H_{92}In_2Si_4$	$C_{56}H_{92}Si_4Tl_2$	$C_{48}H_{108}Al_4Si_4O_4$	$C_{48}H_{108}Ga_4Si_4O_4$	$C_{48}H_{108}In_4Si_4Se_4$
M_r	851.69	1027.37	1206.49	1107.33	1286.46	969.65	1140.65	1572.85
T [K]	173	200	193	193	293	203	173	190
Mo-K_α [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
System	orthorhombic	monoclinic	monoclinic	triclinic	triclinic	monoclinic	trigonal	cubic
Space group	$I\bar{4}$	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$R3\bar{c}$	$Pa\bar{3}$
a [Å]	15.4599(1)	21.2994(9)	20.396(4)	13.108(3)	13.188(4)	23.692(1)	19.807(3)	23.701(4)
b [Å]	15.4599(1)	14.905(1)	15.437(3)	14.394(3)	13.386(5)	12.716(2)	19.807(3)	23.728(8)
c [Å]	13.204	21.539(1)	41.621(8)	19.708(4)	19.815(6)	25.109(2)	61.772(11)	23.747(6)
α [°]	90	90	90	83.52(3)	84.31(4)	90	90	89.94(4)
β [°]	90	103.189(5)	99.97(3)	80.50(3)	80.59(3)	115.901(3)	90	89.85(3)
γ [°]	90	90	90	63.23(3)	63.45	90	120	89.89(3)
V [Å^3]	3155.82(3)	6657.6(7)	12906(45)	3271.2(11)	3085.8(17)	6804.8(10)	20987.3	13355(6)
Z	2	8	8	1	2	4	12	8
ρ [Mg/m^3]	0.896	1.181	1.242	1.124	1.394	0.985	1.172	1.565
μ [mm^{-1}]	0.147	0.797	5.086	0.807	5.325	0.171	1.626	3.643
F(000)	956	2536	4912	1164	1302	2244	7922	6272
2θ [°]	3.72−58.14	5.46−54.04	4.70−54.24	3.88−51.8	5.78−55.92	3.60−55.18	2.72−58.98	4.86−48.24
Ranges	$-19 \le h \le 20$; $-20 \le k \le 20$; $-16 \le l \le 16$	$-27 \le h \le 26$; $-18 \le k \le 19$; $-27 \le l \le 27$	$-21 \le h \le 25$; $-19 \le k \le 11$; $-53 \le l \le 53$	$-12 \le h \le 16$; $-13 \le k \le 16$; $-24 \le l \le 24$	$-16 \le h \le 16$; $-16 \le k \le 17$; $-26 \le l \le 26$	$-29 \le h \le 29$; $-6 \le k \le 15$; $-32 \le l \le 32$	$-25 \le h \le 25$; $-25 \le k \le 25$; $-76 \le l \le 74$	$-24 \le h \le 27$; $-27 \le k \le 27$; $-27 \le l \le 19$
All reflections	9338	6763	25125	13569	18424	13628	39018	41507
Observed (> 4σ)	3403	6763	12448	9606	12799	6841	5157	3531
R_{int}	0.0197	0.00	0.0912	0.0545	0.0539	0.0552	0.0279	0.123
x/y[b]	0.9573/0.9436	0.8548/0.6605	1/1	1/1	1/1	0.1292/18.7670	0.0272/37.5392	1/1
$R1$[c]	0.0461	0.0264	0.1044	0.0498	0.0505	0.0696	0.0284	0.0496
$wR2$[c]	0.1519	0.0780	0.2784	0.1463	0.1154	0.2063	0.0650	0.1226
GOOF	1.304	0.968	0.976	1.063	−	1.082	1.131	0.954
Electron density [eÅ^3]: max./min.	1.513/−0.288	0.429/−0.803	4.588/−3.002	0.804/−0.738	3.172/−2.083	1.317/−0.660	0.340/−0.414	3.172/−2.083

[a] $R^*_4Al_4O_4$ and $R^*_4Al_4$ in mol ratio 1:2. [b] $w^{-1} = \sigma^2F_o^2 + (xP)^2 + yP$ with $P = (F_o^2 + 2\,F_c^2)/3$. [c] $F > 4\sigma(F)$.

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[41] Electrostatic repulsions of the E atoms in organyl- and silylditrielanes R_2E-ER_2 which are stronger for dialanes than for digallanes due to higher similar charges on E in the first case may result in a bond length shortening in direction Al−Al → Ga−Ga (electronegativities: C/Si/Al/Ga = 2.50/1.74/1.47/1.82[32]). On the other hand, the Si−Al/Si−Ga distances in $(tBu_2PhSi)_3E$ (2.59/2.58 Å)[3] or in $R^*{}_2ECl$ (2.53/2.49 Å)[2] shorten in direction Si−Al → Si−Ga, though the electrostatic attractions of Si−E are stronger in the first case. The latter facts confirm the stated decrease of the atomic radius by going from Al (1.30 Å) to Ga (1.24 Å). The bond lengths shortening in direction X−Al → X−Ga (the same non-metal X) may be decreased, or even reversed as a consequence of decreasing electrostatic attractions of X and Al/Ga atoms in direction X−Al → X−Ga (for more electronegative partners X like halogens X−Al bonds are always shorter than X−Ga bonds; e.g. 2.16/2.25 Å in $R^*{}_2Al-Cl$ $R^*{}_2Ga-Cl$[2]).

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