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Alkyl Abstraction from a Trialkylyttrium Complex $[YR_3(thf)_2]$ ($R = CH_2SiMe_3$) Using a Group-13 Element Lewis Acid ER_3 (E = B, Al, Ga, In) – Structural Characterisation of the Ion Pair $[YR_2(thf)_4]^+[GaR_4]^-$ and of ER_3 (E = B, Al, Ga)

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The alkyl abstraction reaction of $[YR_3(thf)_2]$ ($R = CH_2SiMe_3$) with group-13 trialkyl complexes $[(ER_3)_n]$ (E = B, Ga, In: n = 1; E = Al: n = 2) forming cationic yttrium species $[YR_2(thf)_4]^+[ER_4]^-$ (E = Al, Ga, In) shows a strong dependence on the Lewis acidic metal centre E and on the solvent basicity. Whilst the boron compound does not react with $[YR_3(thf)_2]$, the heavier homologues form the ion pairs $[YR_2(thf)_4]^+[ER_4]^-$ (E = Al, Ga, In) which dissociate to give the neutral compounds in apolar solvents such as benzene. Single-crystal structure analysis of the gallate $[YR_2(thf)_4]^+[GaR_4]^-$ shows the presence of an ion pair with *cis*-arranged alkyl ligands in the octahedral yttrium cation and a tetrahedral gallate anion. Group-13 trialkyl compounds $[(ER_3)_n]$ (E = B, Al, Ga), all liquids at room temperature, and $[Li(12\text{-crown-}4)_2]^+[AlR_4]^-$ were characterised by single-crystal X-ray diffraction and NMR spectroscopy.

Introduction

There has recently been an increasing interest in cationic alkyl complexes of rare-earth metals, due to their enhanced electrophilicity and application in homogeneous catalysis, most prominently in α-olefin polymerisation catalysis.[1] One way to generate and isolate the cationic species is to irreversibly react neutral trialkyl complexes $[LnR_3(L)_n]$ with a weak Brønsted acid such as $[NEt_3H][BPh_4]$ or a strong Lewis acid such as $[Ph_3C][B(C_6F_5)_4]$. Another way is an alkyl abstraction with neutral Lewis acids, in particular group-13 organometallic compounds such as $[B(C_6X_5)_3]$ (X = H, F). The resulting ion pairs are either charge-separated or consist of contact ion pairs, such as $[ScMe_2(Me_3\text{-}TACN)(\mu\text{-}Me)B(C_6F_5)_3]$, (TACN = 1,4,7-triazacyclononane) prepared from $[ScMe_3(Me_3\text{-}TACN)]$ and $[B(C_6F_5)_3]$ in thf.[2] In the context of studying homogeneous ethylene polymerisation catalysis by $[Y(CH_2SiMe_3)_3(thf)_2]/[PhNMe_2H][B(C_6F_5)_4]/[AlR_3]$ we isolated a charge-separated ion pair $[Y(CH_2SiMe_3)_2(thf)_4]^+[Al(CH_2SiMe_3)_4]^-$ (**1a**) from the reaction of $[Y(CH_2SiMe_3)_3(thf)_2]$ and $[Al(CH_2SiMe_3)_3(thf)]$ that underwent further protonolysis to afford the dication $[Y(CH_2SiMe_3)(thf)_5]^+[B(C_6F_5)_4]^-{}_2$.[3,4] We report here a solvent dependent reversible equilibrium between ionic **1a** and its neutral precursors $[Y(CH_2SiMe_3)_3(thf)_2]$ and $[Al(CH_2SiMe_3)_3(thf)]$ and an extension of this alkyl abstraction reaction to the use of homologous group-13 trialkyl compounds $[\{E(CH_2SiMe_3)_3\}_n]$ (E = B, **3**, n = 1; E = Al, **4**, n = 2; E = Ga, **5**, n = 1; E = In, **6**, n = 1). In addition, we present the crystal structures of the group-13 trialkyl complexes **3**–**5**.[5]

Results and Discussion

Cationic Yttrium Complexes

Encouraged by the facile formation of **1a** by reaction of the trialkyl compound $[Y(CH_2SiMe_3)_3(thf)_2]$ with a stoichiometric amount of the trialkylaluminium **4** in thf,[3,4] attempts were made to synthesise yttrium cationic complexes bearing the analogous borate, gallate and indate anions, $[B(CH_2SiMe_3)_4]^-$, $[Ga(CH_2SiMe_3)_4]^-$, and $[In(CH_2SiMe_3)_4]^-$ respectively. It was found, however, that whilst the reaction proceeds at ambient temperature for the gallium and indium species **5** and **6** in thf, no reaction was observed with the borane **3** in [D$_8$]thf or [D$_5$]bromobenzene at elevated temperatures up to 60 °C. The lack of reactivity of **3** is not only due to insufficient Lewis acidity of the boron atom in **3**, as $[B(CH_2SiMe_3)_4]^-$ is a known species with a variety of cations,[6] but it appears that the neutral boron compound is not sufficiently electrophilic to abstract an alkyl group from the yttrium centre. A possible explanation is the formation of a very stable adduct with thf, as is the case in the alkyl abstraction from $[Y(CH_2SiMe_3)_3(thf)_2]$

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using [$B(C_6F_5)_3$], where heating of the reaction mixture was necessary for the abstraction to proceed.[4] The low reactivity of **3** towards Lewis bases compared to the remaining group-13 species is also illustrated in its negligible water sensitivity, whereas **4**–**6** all react with water.[5] The formation of alkyl gallates and indates [$Y(CH_2SiMe_3)_2(thf)_4$]$^+$-[$E(CH_2SiMe_3)_4$]$^-$ (E = Ga, **1b**; In, **1c**) as charge-separated ion pairs in thf solutions (vide infra) represents the first cationic rare-earth metal alkyl complexes with these anions (Table 1). Previously only neutral complexes with bridging alkyl groups bound to gallium were reported.[7]

Table 1. Selected bond lengths [Å] and bond angles [°] for **1b**[a] and **7c**.

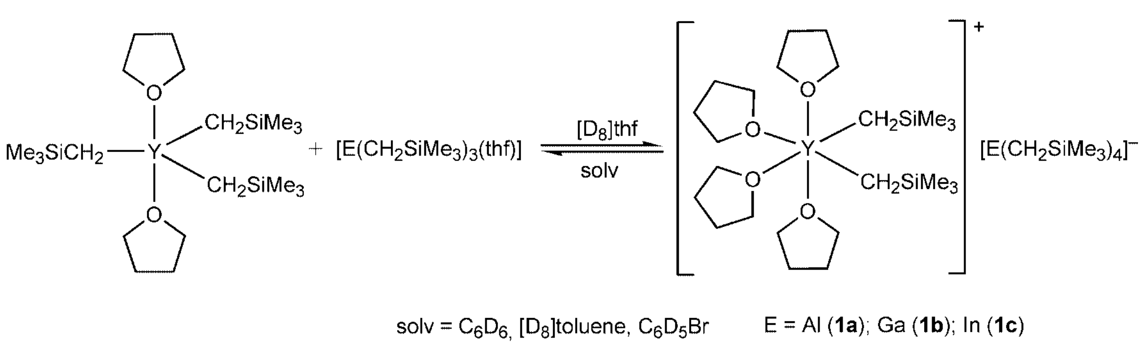
[$Y(CH_2SiMe_3)_2(thf)_4$]$^+$ [$Ga(CH_2SiMe_3)_4$]$^-$ (**1b**)		[$Li(12\text{-crown-}4)_2$]$^+$ [$Al(CH_2SiMe_3)_4$]$^-$ (**7c**)	
Y2–C41	2.400(3)		
Y2–C45	2.368(3)		
Y2–O5	2.479(2)		
Y2–O6	2.3349(19)		
Y2–O7	2.3243(19)		
Y2–O8	2.424(2)		
C41–Y2–C45	102.94(11)		
Ga1–C25	2.038(3)	Al–C17	2.0300(13)
Ga1–C29	2.040(3)	Al–C18	2.0247(14)
Ga1–C33	2.057(3)	Al–C19	2.0278(14)
Ga1–C37	2.031(3)	Al–C20	2.0311(14)
C33–Ga1–C37	108.06(11)	C17–Al–C18	114.80(6)
C37–Ga1–C25	107.98(13)	C17–Al–C19	106.43(6)
C37–Ga1–C29	109.59(11)	C17–Al–C20	107.58(6)

[a] For **1b** only one of the two crystallographically independent ion pairs chosen.

Based on the results from X-ray crystallographic and NMR spectroscopic analysis in [D_8]thf, complex **1a** was described previously as a charge-separated ion pair.[3,4] When measured in less donating solvents, such as [D_6]benzene, [D_8]toluene and [D_5]bromobenzene, the previously isolated complex **1a** dissociates to form [$Y(CH_2SiMe_3)_3(thf)_2$] and [$Al(CH_2SiMe_3)_3(thf)$] (Scheme 1). The NMR spectra are exact superpositions of the spectra of the corresponding neutral species.[8] A notable feature for the $AlCH_2$ signal in the ^1H NMR spectra ([D_8]thf) is that the signal in [$Al(CH_2SiMe_3)_3(thf)$] is a singlet, whilst the corresponding resonance in the anion [$Al(CH_2SiMe_3)_4$]$^-$ is a distorted sextet due to coupling to quadrupolar aluminium ($I = 5/2$) that collapses to a singlet in the $^1H\{^{27}Al\}$ decoupled spectrum (Figure 1). Correspondingly, the ^{27}Al NMR shows a nonet at $\delta = 150.9$ ppm with $^2J_{Al,H} = 9.0$ Hz. The same NMR spectroscopic features are found for the lithium salts containing the anion [$Al(CH_2SiMe_3)_4$]$^-$ (vide infra), confirming the ion separation in thf solution.

Addition of one equivalent of 12-crown-4 to a [D_6]benzene solution of **1a** results in complete ionisation of the neutral species to form the previously reported ion pair [$Y(CH_2SiMe_3)_2(12\text{-crown-}4)(thf)$]$^+$[$Al(CH_2SiMe_3)_4$]$^-$ (**2a**).[4] Similarly, upon addition of [D_8]thf to the [D_6]benzene solution of the neutral compounds, dissociation occurs, depending on the solvent mixture and temperature. An investigation of **1a** in a range of [D_6]benzene/[D_8]thf mixtures (composition range 40–60 mol-% of [D_8]thf) and at different temperatures was therefore conducted. However, even inside this reduced range, an exact quantification of equilibrium constants $K = c([Y(CH_2SiMe_3)_2(thf)_4][Al(CH_2SiMe_3)_4])/c([Y(CH_2SiMe_3)_3(thf)_2])\cdot c([Al(CH_2SiMe_3)_3(thf)])$ for the equilibrium depicted in Scheme 1 remained difficult due to peak overlapping in the ^1H NMR spectra. An increase in the amount of [D_8]thf leads to an increase in the dissociation constant K. Using a 60:40 mixture [D_8]thf/[D_6]benzene, variable-temperature NMR measurements were conducted at 25 °C, 35 °C, and 45 °C. Using the van't Hoff equation $d(\ln K)/dT = \Delta_r H°/RT^2$, the standard enthalpy change for the ionisation $\Delta_r H°$ is estimated as about $-70\ \text{kJ mol}^{-1}$ at 308 K. The exchange equilibrium is slow on the NMR timescale, as coupling patterns of the neutral and cationic yttrium species are observed.

Similarly to the aluminate **1a**, both gallate **1b** and indate **1c** form charge-separated complexes in thf solutions. The signals in their NMR spectra belonging to the [$Y(CH_2SiMe_3)_2(thf)_4$]$^+$ cation are identical to those reported for the aluminate **1a** and similar to those of compounds containing other anions (Table 2), indicating that the anions are only weakly coordinating in the [D_8]thf solutions.[9] Probably due to the quadrupolar nature of Ga ($I = 3/2$) and In ($I = 9/2$), the ^1H NMR signals assigned to the ECH_2 (E = Ga, In) protons are very broad (Figure 2). The corresponding signal for the indate **1c** in the ^{13}C NMR spectrum is not detected, as was previously noted for the ^{13}C signals of BCH_2 in similar complexes containing the [$B(C_6X_5)_3(CH_2SiMe_3)$]$^-$ (X = H, F) anions.[4]



Scheme 1.

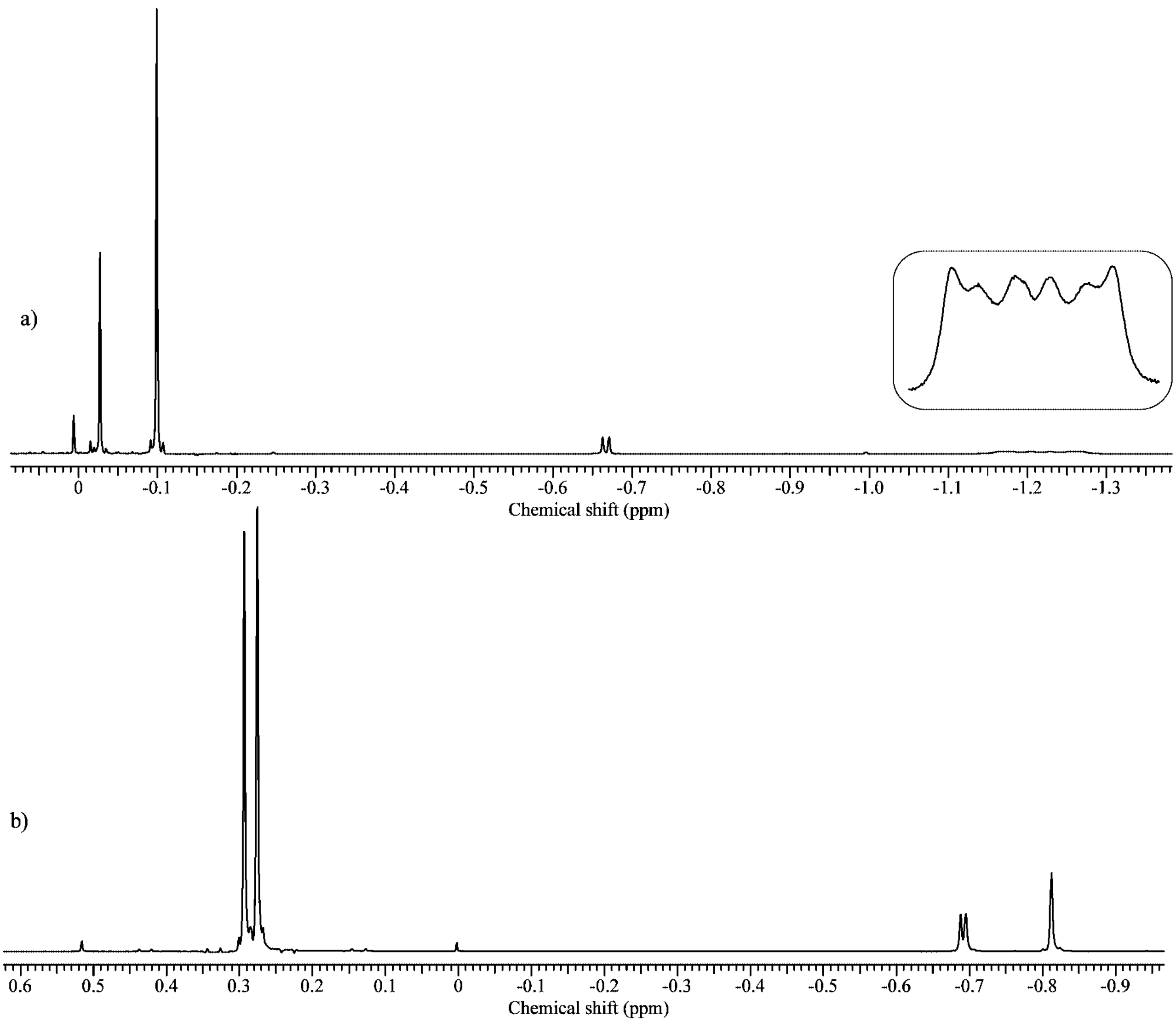


Figure 1. ^{1}H NMR spectra at 25 °C of $[Y(CH_2SiMe_3)_2(thf)_4]^+[Al(CH_2SiMe_3)_4]^-$ (**1a**) in a) [D$_8$]thf and b) in C_6D_6.

Table 2. ^{1}H NMR spectroscopic data (25 °C, [D$_8$]thf) for $[Y(CH_2SiMe_3)_2(thf)_4]^+[A]^-$.

Anion [A]	δ_H of YCH_2 (ppm)	$^2J_{Y,H}$ (Hz)	Ref.
$[Ga(CH_2SiMe_3)_4]$	–0.68	3.0	this work
$[In(CH_2SiMe_3)_4]$	–0.68	3.3	this work
$[Al(CH_2SiMe_3)_4]$	–0.68	3.2	this work
$[B(C_6F_5)_4]$	–0.69	3.2	[4]
$[BPh_4]$	–0.77	3.3	[4]
$[B(C_6F_5)_3(CH_2SiMe_3)]$	–0.70	2.9	[4]
$[BPh_3(CH_2SiMe_3)]$	–0.80	3.2	[4]

When NMR spectra of **1b** and **1c** are measured in [D$_6$]benzene, [D$_8$]toluene, and [D$_5$]bromobenzene, it is found that on the NMR timescale all CH_2 protons and all $SiMe_3$ protons are equivalent in these solvents. The peaks in the ^{1}H NMR spectra appear broad, and lack any coupling pattern to yttrium. It is therefore postulated that the molecules are fluxional and exchange alkyl groups intermolecularly (due to the lack of coupling) fast on the NMR timescale. Spectra of **1b** in [D$_8$]thf and [D$_6$]benzene are shown in Figure 2. This situation is similar to that found in compounds of the type $MR_2{\cdot}ZnR_2$ (M = Sr or Ba; R = CH_2SiMe_3).[10] NMR spectroscopic analysis of these compounds showed that all alkyl groups are chemically and magnetically equivalent on the NMR timescale and an equilibrium between neutral alkyl complexes, "ate" complexes, contact ion pairs and solvent separated ions was proposed in the literature.[10–12]

A further example for solvent dependence of the structures and for intra-/intermolecular exchange was reported for $[La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}BPh_4]$, where the tetraphenylborate anion is coordinating to the lanthanum centre in aromatic solvents. In constrast to the case of **1b** and **1c**, irreversible charge separation is achieved by solvation to give $[La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}(thf)_3][BPh_4]$ in thf.[13]

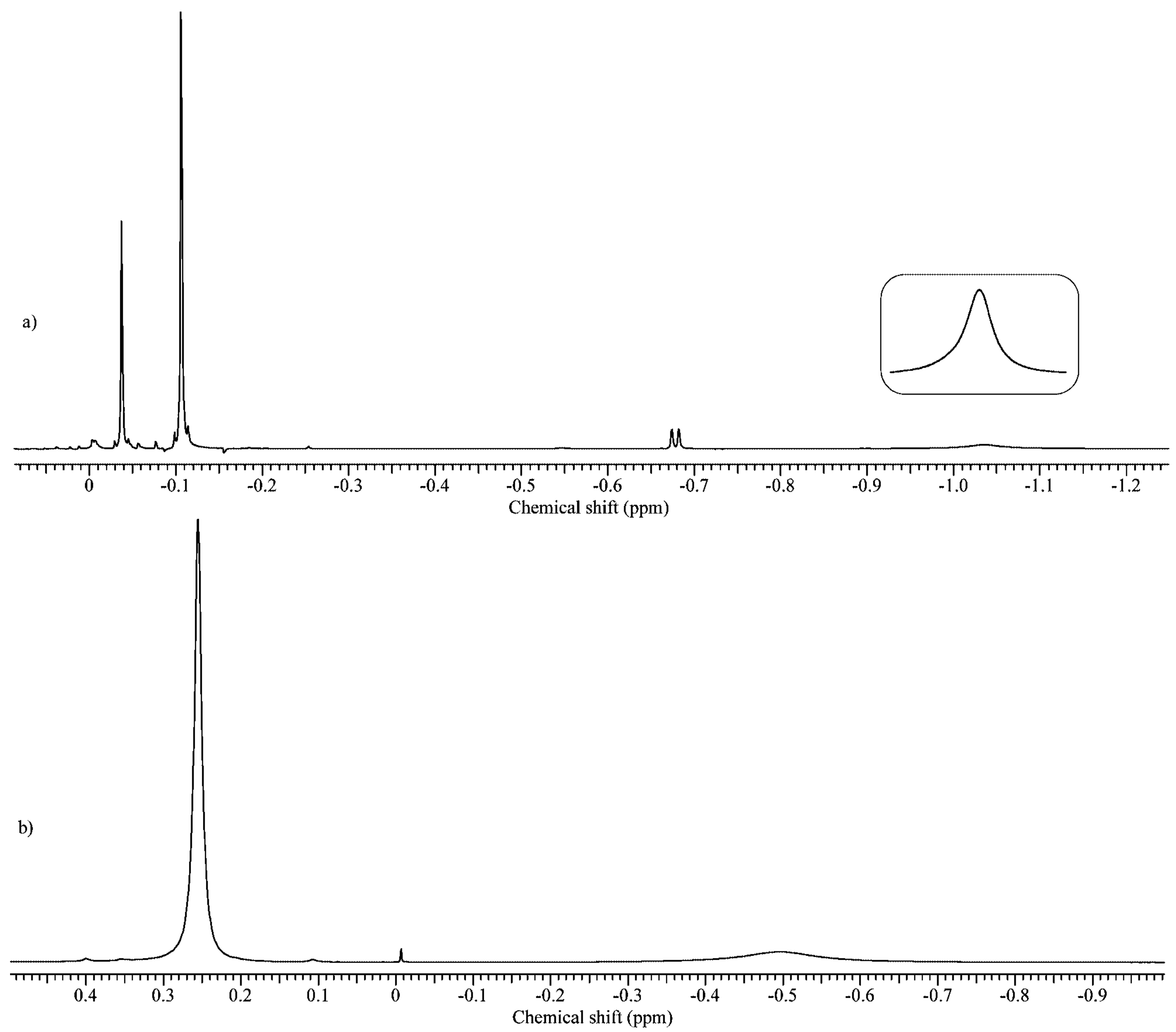


Figure 2. ^1H NMR spectra at 25 °C of $[Y(CH_2SiMe_3)_2(thf)_4][Ga(CH_2SiMe_3)_4]$ (**1b**) in a) [D$_8$]thf and b) in C_6D_6.

Upon addition of one equivalent of 12-crown-4 to [D$_6$]-benzene solutions of **1b** and **1c** the molecules separate into the charge-separated ion pairs $[Y(CH_2SiMe_3)_2(12\text{-crown-}4)(thf)]^+[E(CH_2SiMe_3)_4]^-$ (E = Ga, **2b**; In, **2c**), as was observed for **1a**. The peaks arising from the cationic yttrium species are similar in all three cases, implying only weakly coordinating anions.

Single crystals of the gallate **1b** suitable for X-ray analysis were grown by slowly cooling a thf/pentane solution to –30 °C. The unit cell contains two sets of independent ion pairs, each expressing slightly distorted tetrahedral geometry around the gallium atom and distorted octahedral geometry around the yttrium centre (Figure 3). Whilst the cationic fragments express a similar octahedral geometry with *cis*-arranged alkyl groups to that observed in $[Y(CH_2SiMe_3)_2(thf)_4]^+[Al(CH_2SiMe_3)_4]^-$ (**1a**),[3] the anionic fragments are slightly more distorted from perfect tetrahedral geometry than their aluminate counterparts, with C–Ga–C angles ranging from 107.98(13)° to 111.02(11)°, compared to C–Al–C bond angles only ranging from 108.9(2)° to 109.8(3)° (vide infra).

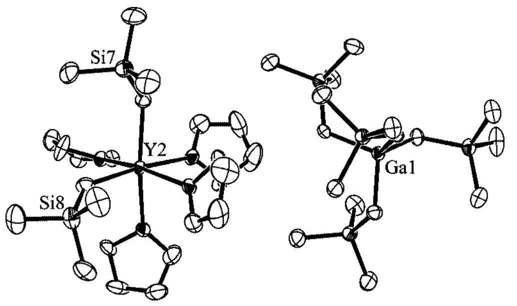


Figure 3. ORTEP representation of one ion pair of $[Y(CH_2SiMe_3)_2(thf)_4]^+[Ga(CH_2SiMe_3)_4]^-$ (**1b**). Displacement ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity.

The Y–C bond lengths range from 2.375(3) Å to 2.400(3) Å and thus lie within the range of distances reported in the literature for cationic and neutral (trimethylsilymethyl)yttrium complexes as are the Y–O distances [2.324(2) Å to 2.478(2) Å].[4] The Ga–C distances found in the two anions range from 2.031(3) Å to 2.058(3) Å (mean 2.042 Å) and are very similar to those found for the sterically less demanding benzyl ligand in $[Mg_3Br_{2.4}Cl_{1.6}(OEt_2)_6][Ga(CH_2Ph)_4]_2\cdot 0.5$ toluene (2.039 Å mean),[14] the terminal trimethylsilylmethyl ligand in $[Li(dioxane)_{1.5}][Ga(CH_2SiMe_3)_4]$ (2.025 Å mean),[15] and the bulky fluorenyl ligand in $[Li(DME)_3][Ga(C_{13}H_9)_4]$ (2.062 Å mean).[16] Compared to the parent molecule **5** the bonds have increased in length by about 5%.

Structure of Tris(trimethylsilylmethyl) Group-13 Metal Complexes

To compare the Lewis acidity of the group-13 complexes we have carried out structural comparison of the (trimethylsilylmethyl)boron, -aluminium and -gallium compounds **3**–**5**. As expected, only the aluminium compound turned out to be dinuclear (Table 3).

Table 3. Selected bond lengths [Å] and bond angles [°] for **3**, **4** and **5**.

	$[B(CH_2SiMe_3)_3]$	$[\{Al(CH_2SiMe_3)_3\}_2]$	$[Ga(CH_2SiMe_3)_3]$
M–M	–	2.8328(13)	–
M–C1	1.567(3)	2.031(2)	1.954(4)
M–C2	1.563(3)	1.958(2)	1.971(3)
M–C3	1.573(3)	1.958(2)	1.952(4)
M–C1′	–	2.336(2)	–
C1–Si1	1.871(2)	1.909(2)	1.852(4)
C2–Si2	1.8820(19)	1.854(2)	1.855(4)
C3–Si3	1.874(2)	1.858(2)	1.852(4)
C1–M–C2	119.01(17)	116.46(10)	118.61(16)
C2–M–C3	121.12(17)	115.35(9)	121.82(16)
C3–M–C1	119.82(18)	111.53(9)	119.56(15)
M–C1–M′	–	80.55(7)	–
M–C1–Si1	117.13(13)	109.10(10)	116.60(19)
M–C2–Si2	114.27(14)	130.21(12)	114.82(19)
M–C3–Si3	119.73(15)	124.75(11)	118.24(19)
M–C1′–Si1′	–	167.57(12)	–

Tris(trimethylsilylmethyl)boron

As expected, the crystal structure of tris(trimethylsilylmethyl)boron (**3**), Figure 4, revealed discrete molecules, structurally similar to BEt_3 with respect to the arrangement of the ligands around the central atom.[17] The three B–C–Si angles [117.04° on average, ranging from 114.27(14)° to 119.73(15)°] deviate from the ideal tetrahedral angle 109.47° at the carbon, which was already observed in other tris(alkyl) boron compounds (cf. BEt_3: B–C–C average: 118.9°,[17] or $BtBu_3$: B–C–C 120.6(2)°[18]). In these compounds, hyperconjugation was invoked to justify these abnormally large values. In **3** however, it is more likely that the important steric bulk of the trimethylsilyl groups dictates their orientation, rather than hyperconjugation. Indeed, the B–C–Si angles of the two groups pointing towards each other [B–C1–Si1 117.13(13)° and B–C3–Si3 119.73(15)°] are found to be larger than the corresponding angle in the third alkyl group [B–C2–Si2 114.27(14)°].

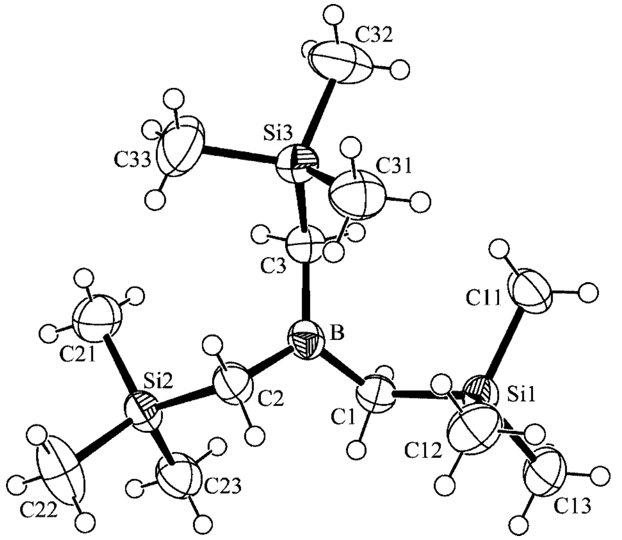


Figure 4. ORTEP representation of the molecular structure of $[B(CH_2SiMe_3)_3]$ (**3**). Displacement ellipsoids of non-H atoms drawn at the 50% probability level.

The B–C bond lengths [1.568 Å mean, ranging from 1.563(3) Å to 1.573(3) Å] do not present any particular deviation from the values typically observed in homoleptic boron compounds. The same was observed for the C–B–C angles, the planar geometry around the boron centre being almost perfect (Σ_{C-B-C} = 359.95°).

Tris(trimethylsilylmethyl)aluminium

As many other homoleptic (e.g. $[(AlMe_3)_2]$,[19] $[(AlPh_3)_2]$,[20] $[\{Al(cyclo\text{-}Pr)_3\}_2]$,[21] $[\{Al(C_6H_4\text{-}2\text{-}Me)_3\}_2]$[22]) and mixed-alkyl (e.g. $[\{AlMe_2(\mu\text{-}Ph)\}_2]$,[23] $[\{AliBu_2(\mu\text{-}C{=}CtBu)\}_2]$[24]) aluminium species, $[\{Al(CH_2SiMe_3)_3\}_2]$ (**4**), Figure 5, was found to adopt a dimeric structure. The molecule shows crystallographic inversion symmetry and exhibits in addition two non-equivalent C–Al bonds for each bridging carbon in the solid state. Only few organoaluminium compounds have so far been reported to exhibit such unsymmetrical bridges (e.g. $[\{AlPh_2(\mu\text{-}C{\equiv}CPh)\}_2]$,[25] or $[\{AlMe_2(\mu\text{-}C{\equiv}CMe)\}_2]$[26]). Until now, to the best of our knowledge, no homoleptic dimeric trialkylaluminium compound featuring non-equivalent bridges has been reported. Thus **4** appears to be the first example for this coordination mode in the solid state. These findings are in agreement with a previous report that **4** is only partially dimerised in benzene solution based on cryoscopic measurements.[27]

Due to steric bulk of the CH_2SiMe_3 groups, the Al–Al distance observed in $[\{Al(CH_2SiMe_3)_3\}_2]$ of 2.8328(13) Å is amongst the longest reported. As a consequence, the Al–C1–Al′ bridge angle of 80.55(7)° is also slightly larger than usually observed (Table 4). Only heteroleptic aluminium de-

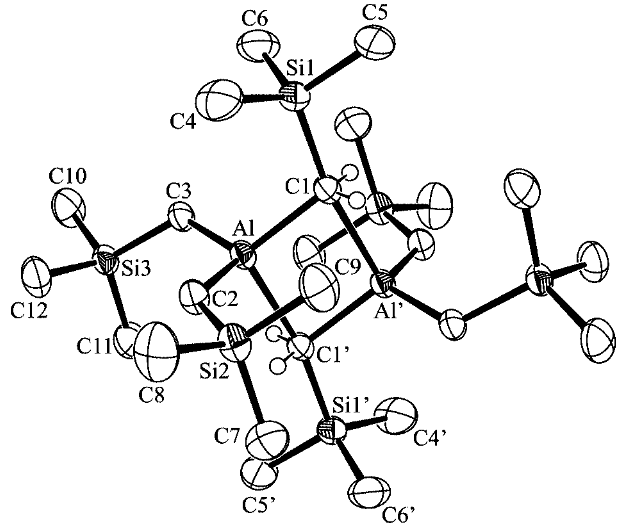


Figure 5. ORTEP representation of the molecular structure of $[\{Al(CH_2SiMe_3)_3\}_2]$ (**4**). Displacement ellipsoids of non-H atoms drawn at the 50% probability level; only hydrogen atoms bonded to bridging carbons shown.

rivatives bearing rigid bridging groups like $[\{AlPh_2(\mu\text{-}C{\equiv}CPh)\}_2]$ (Al–C_b–Al 91.73°)[25] or $[\{AlMe_2(\mu\text{-}C{\equiv}CMe)\}_2]$ [Al–C_b–Al 92.0(1)°],[26] or bulky bridging groups, like $[\{Al(C_6H_4\text{-}2\text{-}Me)_3\}_2]$ [Al–C_b–Al 81.9(1)°],[22] display larger bridge angles.

Table 4. Al–Al bond lengths [Å] and Al–C_b–Al angles [°] for dimeric organoaluminium compounds.

Compound	Al–Al [Å]	Al–C_b–Al [°]	Ref.
$[\{Al(CH_2SiMe_3)_3\}_2]$	2.8328(13)	80.55(7)	this work
$[(AlMe_3)_2]$	2.700(10)	78.0(3)	[19]
$[\{AlMe_2(\mu\text{-}Ph)\}_2]$	2.690(4)	77.8(2)	[23]
$[(AlPh_3)_2]$	2.702(2)	76.5(2)	[20]
$[\{Al(C_6H_4\text{-}2\text{-}Me)_3\}_2]$	2.817(2)	81.9(1)	[22]
$[\{Al(cyclo\text{-}Pr)_3\}_2]$[a]	2.618(3)/2.607(3)	78.2(3)/77.9(2)	[21]

[a] First value determined at 22 °C, second at –67 °C.

In **4** the $SiMe_3$ fragment of the bridging ligands is oriented away from the second aluminium centre [Al–C_b–Si1 109.10(10)° and Al′–C_b–Si1 167.57(12)°]. The two protons and the trimethylsilyl group bonded to the bridging carbons are in a staggered conformation with the silicon being located 0.2539(8) Å outside of the plane defined by Al, C_b, Al′ and $C_b{}'$. The sum of the C–Al–C angles around the aluminium ($\Sigma_{C\text{–}Al\text{–}C}$ = 343.34°) represents a non-negligible deviation from planarity, with the aluminium situated 0.4748 Å above the C1–C2–C3 plane. The bonds to the terminal alkyl groups [Al–C2 and Al–C3 1.958(2) Å] were found to be in the typical range for this type of compound. The Al–C bond of the bridging ligand [Al–C1 2.031(2) Å] shows considerable elongation; the second bridging contact [Al–C1′ 2.336(2) Å] is the longest ever reported in such a dimer. $[(AlPh_3)_2]$ is the only other known compound with bridging contacts of that magnitude [Al–C_b 2.180(5) and Al–$C_b{}'$ 2.184(5) Å].[20]

Tris(trimethylsilylmethyl)gallium

$[Ga(CH_2SiMe_3)_3]$ (**5**), Figure 6, crystallises with four equivalent monomeric molecules per unit cell. Unlike in $[GaEt_3]$,[28] in which the three ethyl groups adopt a propeller-like configuration (in only three of the four independent molecules of the unit cell however), the CH_2SiMe_3 groups in **5** adopt a structure resembling that of **3**. Two alkyl groups occupy the same side of the molecule, and display enlarged Ga–C–Si angles [116.60(19)° and 118.24(19)°] whilst the third one lies on the opposite side and is more bent towards the gallium centre [Ga–C2–Si2 114.82(19)°]. With an average value of 116.55°, the Ga–C–Si angles express the same deviation from the expected value as does the boron homologue (117.04° mean). In **5** hyperconjugation again has smaller influence on the molecular geometry than the steric requirements of the ligands. The Ga–C bond lengths [1.959 Å mean, ranging from 1.952(4) Å to 1.971(3) Å] fall within the range of already reported values, as well as the C–Si bonds. The three groups define a perfectly planar skeleton around the gallium ($\Sigma_{C\text{–}Ga\text{–}C}$ = 359.99°).

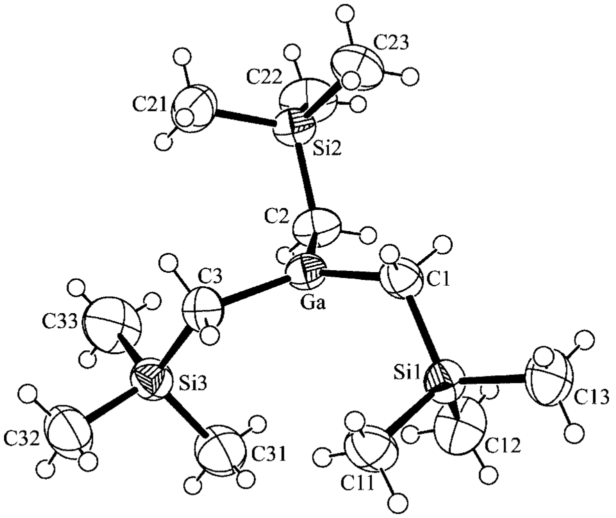


Figure 6. ORTEP representation of the molecular structure of $[Ga(CH_2SiMe_3)_3]$ (**5**). Displacement ellipsoids drawn at the 50% probability level.

That $[Ga(CH_2SiMe_3)_3]$ is monomeric is of no great surprise, since other structurally characterised trialkylgallium compounds which do not contain ligand-based electron pairs tend to be monomeric. $[GaEt_3]$ exhibits short intermolecular contacts in the solid-state structure, and $[GaMe_3]$ shows a tetrameric arrangement of the molecules in the lattice, the interactions in both compounds being however very weak.[28] Dimeric gallium compounds require electron-donating bridging ligands, such as $[\{GaMe_2(\mu\text{-}C{\equiv}CMe)\}_2]$,[29] $[\{Ga(CH{=}CH_2)_3\}_2]$,[30] $[\{GaMe_2(\mu\text{-}C{\equiv}CPh)\}_2]$,[31] $[\{Ga(CH_2Ph)_2Br\}_2]$ or $[\{Ga(CH_2Ph)_2(NH\textit{t}Bu)\}_2]$.[32] The solid-state structure of a TMEDA adduct of $[Ga(CH_2SiMe_3)_3]$, $[\{Ga(CH_2SiMe_3)_3\}_2]\cdot Me_2NCH_2CH_2NMe_2$[33] shows slightly elongated Ga–C bonds (by 1.6% on average) compared to the parent molecule [$Ga(CH_2SiMe_3)_3$], but no significant influence of the TMEDA coordination could be seen in the length of the C–Si bonds.

Lithium Tetrakis(trimethylsilylmethyl)aluminates

To compare with the structure of the ion pair [$Y(CH_2SiMe_3)_2(thf)_4$]$^+$[$Al(CH_2SiMe_3)_4$]$^-$ (**1a**), solvent separated lithium derivatives of the [$Al(CH_2SiMe_3)_4$]$^-$ anion were prepared.[3] Upon addition of two equivalents of TMEDA or 12-crown-4 to [Li]$^+$[$Al(CH_2SiMe_3)_4$]$^-$ (**7a**),[34] obtained by reaction of [$\{Al(CH_2SiMe_3)_3\}_2$] with $LiCH_2SiMe_3$, the corresponding adducts [$Li(TMEDA)_2$]$^+$[$Al(CH_2SiMe_3)_4$]$^-$ (**7b**) and [Li(12-crown-4)$_2$]$^+$[$Al(CH_2SiMe_3)_4$]$^-$ (**7c**) were isolated. Crystals of **7c** were obtained from cooling a saturated thf solution. The geometry around the aluminium centre is further shifted towards a regular tetrahedral arrangement compared to that in the neutral parent [$\{Al(CH_2SiMe_3)_3\}_2$] (Figure 7). Thus, the three C–Al–C angles of the alkyl groups composing the "base" of the tetrahedron display very close values [106.43(6)°, 107.32(6)° and 107.58(6)°] whilst the fourth alkyl group (involving C18) forms together with the three other ligands angles of 110.02(6)°, 110.35(6)° and 114.80(6)°. All four Al–C bonds are almost equal (2.028 Å on average).

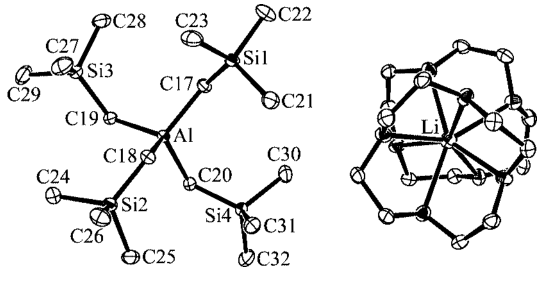


Figure 7. ORTEP representation of the molecular structure of [Li(12-crown-4)$_2$]$^+$[$Al(CH_2SiMe_3)_4$]$^-$ (**7c**). Displacement ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity.

The anionic part of [$Y(CH_2SiMe_3)_2(thf)_4$]$^+$[$Al(CH_2SiMe_3)_4$]$^-$ (**1a**)[3] displays a geometry much closer to a regular tetrahedral arrangement. The three alkyl groups defining the base of the structure show C–Al–C angles of 109.7(2)°, 109.7(2)° and 109.8(3)°. Angles of 109.19° in average (σ = 0.2°) are measured between the fourth group and each of the three others. The aluminate anion in complex **1a** seems to be less influenced by the presence of the counter cation, and therefore adopts a perfectly tetrahedral geometry. Similar Al–C bond lengths and Al–C–Si angles were measured in **1a** (2.033 Å mean, cf. 2.029 Å in **7c**; 122.20° mean, cf. 124.17° in **7c**).

Conclusions

The Lewis acid induced alkyl transfer reaction of the prototypical rare earth metal alkyl complex [$Y(CH_2SiMe_3)_3(thf)_2$] with group-13 metal compounds [$\{E(CH_2SiMe_3)_3\}_n$] proceeds to give an ion pair [$Y(CH_2SiMe_3)_2(thf)_4$]$^+$-[$E(CH_2SiMe_3)_4$]$^-$ for E = Al, Ga and In in thf solution. In the presence of aromatic hydrocarbons, however, recombination to form the neutral precursors [$Y(CH_2SiMe_3)_3(thf)_2$] and [$E(CH_2SiMe_3)_3(thf)$] occurs. The small boron compound [$B(CH_2SiMe_3)_3$] failed to react with [$Y(CH_2SiMe_3)_3(thf)_2$] for kinetic reasons as well as for reduced Lewis acidity. The present results may be relevant to the reversible chain transfer reaction between rare earth metal alkyl catalyst and cocatalyst such as aluminium and zinc alkyl during olefin polymerisation.[1,3,4,35]

Experimental Section

General: All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Thf and pentane were distilled from sodium benzophenone ketyl and sodium benzophenone ketyl triglyme, respectively. Deuterated thf and benzene were dried with sodium, distilled and degassed prior to use; deuterated dichloromethane was dried with CaH_2, then distilled and degassed. Anhydrous $AlBr_3$, $GaCl_3$, $InCl_3$, YCl_3, and $BF_3{\cdot}OEt_2$ (STREM) were used as received. $LiCH_2SiMe_3$[36] and [$Y(CH_2SiMe_3)_3(thf)_2$][37] were prepared according to literature procedure. All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded at room temperature on a Bruker DRX 400 spectrometer (^{1}H 400.1 MHz, ^{13}C 100.6 MHz) or on a Varian Unity 500 spectrometer (^{1}H 499.6 MHz, ^{13}C 125.6 MHz, ^{11}B 160.3 MHz, ^{7}Li 194.2 MHz, ^{27}Al 130.2 MHz) unless otherwise stated. All chemical shifts are given in ppm. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to $SiMe_4$. ^{11}B NMR spectra were referenced externally to a saturated solution of $NaBH_4$ in D_2O. ^{7}Li NMR spectra were referenced externally to a 1 mol L^{-1} solution of LiCl in D_2O. ^{27}Al NMR spectra were referenced externally to a 1.5 mol L^{-1} solution of $Al(NO_3)_3$ in D_2O.

[$Y(CH_2SiMe_3)_2(thf)_4$][$Al(CH_2SiMe_3)_4$] (1a): The compound was prepared according to the literature procedure.[3,4] ^{1}H NMR (200 MHz; [D$_8$]thf): δ = –1.22 (sextet, $AlCH_2$, $^2J_{Al,H}$ = 9.0 Hz, 8 H), –0.68 (d, $^2J_{Y,H}$ = 3.2 Hz, 4 H, YCH_2), –0.11 [s, 36 H, $AlCH_2Si(CH_3)_3$], 0.03 [s, 18 H, $YCH_2Si(CH_3)_3$], 1.77 (16 H, β-CH_2, thf), 3.62 (16 H, α-CH_2, thf) ppm. ^{27}Al NMR (130 MHz; [D$_8$]thf): δ = 150.9 (nonet, $^2J_{Al,H}$ = 9.0 Hz) ppm. ^{1}H NMR (400 MHz; C_6D_6): δ = –0.81 (s, 6 H, $AlCH_2$), –0.69 (d, $^2J_{Y,H}$ = 2.8 Hz, 6 H, YCH_2), 0.28 [s, 27 H, $AlCH_2Si(CH_3)_3$], 0.29 [s, 27 H, $YCH_2Si(CH_3)_3$], 1.27 (16 H, β-CH_2, thf), 3.72 (16 H, α-CH_2, thf) ppm. ^{13}C{^{1}H} NMR (100 MHz; C_6D_6): δ = –0.67 ($AlCH_2$), 3.30 [$AlCH_2Si(CH_3)_3$], 4.58 [$YCH_2Si(CH_3)_3$], 25.14 (β-CH_2, thf), 33.70 (d, $^1J_{Y,C}$ = 35.5 Hz, YCH_2), 69.99 (α-CH_2, thf) ppm.

[$Y(CH_2SiMe_3)_2(thf)_4$][$Ga(CH_2SiMe_3)_4$] (1b): To a solution of [$Y(CH_2SiMe_3)_3(thf)_2$] (974 mg, 1.969 mmol) in thf (5 mL), [$Ga(CH_2SiMe_3)_3$] (653 mg, 1.969 mmol) in thf (5 mL) was added dropwise whilst stirring. Upon complete addition, the reaction mixture was stirred for further 10 min and all volatiles were subsequently removed under reduced pressure to yield a colourless solid, which was washed with pentane and dried under vacuum to yield **1b** as a colourless solid (1650 mg, 86%). Single crystals suitable for X-ray diffraction analysis could be obtained by slow cooling of a saturated thf/pentane solution of **1b**. ^{1}H NMR (400 MHz; [D$_8$]thf): δ = –1.04 (br. s, 8 H, $GaCH_2$), –0.68 (d, $^2J_{Y,H}$ = 3.0 Hz, 4 H, YCH_2), –0.11 [s, 36 H, $GaCH_2Si(CH_3)_3$], –0.04 [s, 18 H, YCH_2-

$\mathrm{Si(C}H_3)_3]$, 1.77 (16 H, β-$\mathrm{CH_2}$, thf), 3.62 (16 H, α-$\mathrm{CH_2}$, thf) ppm. ^{13}C NMR (100 MHz; [D$_8$]thf): δ = 2.67 ($\mathrm{GaCH_2}$), 4.02 [$\mathrm{GaCH_2Si(}C\mathrm{H_3)_3}$], 4.07 [$\mathrm{YCH_2Si(}C\mathrm{H_3)_3}$], 26.31 (β-$\mathrm{CH_2}$, thf), 37.47 (d, $^{1}J_{\mathrm{Y,C}}$ = 41.6 Hz, $\mathrm{YCH_2}$), 68.21 (α-$\mathrm{CH_2}$, thf) ppm. ^{1}H NMR (400 MHz; $\mathrm{C_6D_6}$): δ = –0.49 (br. s, 12 H, $\mathrm{GaCH_2}$ and $\mathrm{YCH_2}$), 0.26 [br. s, 54 H, $\mathrm{YCH_2Si(C}H_3)_3$ and $\mathrm{GaCH_2Si(C}H_3)_3$], 1.31 (16 H, β-$\mathrm{CH_2}$, thf), 3.70 (16 H, α-$\mathrm{CH_2}$, thf) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz; $\mathrm{C_6D_6}$): δ = 3.64 [br., $\mathrm{GaCH_2Si(}C\mathrm{H_3)_3}$ and $\mathrm{YCH_2Si(}C\mathrm{H_3)_3}$], 25.24 (β-$\mathrm{CH_2}$, thf), 33.82 (v br, $\mathrm{GaCH_2}$ and $\mathrm{YCH_2}$), 69.56 (α-$\mathrm{CH_2}$, thf) ppm. $\mathrm{C_{40}H_{98}GaO_4Si_6Y}$ (970.36): calcd. C 49.51, H 10.17; found C 48.61, H 10.43%.

[$\mathrm{Y(CH_2SiMe_3)_2(thf)_4}$][$\mathrm{In(CH_2SiMe_3)_4}$] (1c): To a solution of [$\mathrm{Y(CH_2SiMe_3)_3(thf)_2}$] (487 mg, 0.984 mmol) in thf (5 mL), [$\mathrm{In(CH_2SiMe_3)_3}$] (371 mg, 0.984 mmol) in thf (5 mL) was added dropwise whilst stirring. Upon complete addition, the reaction mixture was stirred for a further 10 min and volatiles were subsequently removed under reduced pressure to yield an oily solid, which was washed with pentane and dried under vacuum to yield **1c** as a colourless solid (823 mg, 82.4%). ^{1}H NMR (400 MHz; [D$_8$]thf): δ = –1.07 (br. s, 8 H, $\mathrm{InCH_2}$), –0.68 (d, $^{2}J_{\mathrm{Y,H}}$ = 3.3 Hz, 4 H, $\mathrm{YCH_2}$), –0.10 [s, 36 H, $\mathrm{InCH_2Si(C}H_3)_3$], –0.04 [s, 18 H, $\mathrm{YCH_2Si(C}H_3)_3$], 1.77 (16 H, β-$\mathrm{CH_2}$, thf), 3.62 (16 H, α-$\mathrm{CH_2}$, thf) ppm. ^{13}C NMR (100 MHz; [D$_8$]thf): δ = 4.02 [$\mathrm{InCH_2Si(}C\mathrm{H_3)_3}$], 4.06 [$\mathrm{YCH_2Si(}C\mathrm{H_3)_3}$], 26.31 (β-$\mathrm{CH_2}$, thf), 37.47 (d, $^{1}J_{\mathrm{Y,C}}$ = 42.5 Hz, $\mathrm{YCH_2}$), 68.20 (β-$\mathrm{CH_2}$, thf), the signal for the $\mathrm{InCH_2}$ carbons was not detected ppm. ^{1}H NMR (400 MHz; $\mathrm{C_6D_6}$): δ = –0.48 (br. s, 12 H, $\mathrm{InC}H_2$ and $\mathrm{YC}H_2$), 0.28 [br. s, 54 H, $\mathrm{InCH_2Si(C}H_3)_3$ and $\mathrm{YCH_2Si(C}H_3)_3$], 1.34 (16 H, β-$\mathrm{CH_2}$, thf) 3.65 (16 H, α-$\mathrm{CH_2}$, thf) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz; $\mathrm{C_6D_6}$): δ = 3.79 [br., $\mathrm{InCH_2Si(}C\mathrm{H_3)_3}$ and $\mathrm{YCH_2Si(}C\mathrm{H_3)_3}$], 25.38 (β-$\mathrm{CH_2}$, thf), 69.12 (β-$\mathrm{CH_2}$, thf) ppm. the signals for the $\mathrm{InCH_2}$/$\mathrm{YCH_2}$ carbons were not detected. $\mathrm{C_{40}H_{98}InO_4Si_6Y}$ (1015.45): calcd. C 47.31, H 9.72; found C 46.28, H 9.94%.

NMR-Tube Synthesis of [$\mathrm{Y(CH_2SiMe_3)_2(12\text{-}crown\text{-}4)(thf)}$][$\mathrm{Al(CH_2SiMe_3)_4}$] (2a): To a solution of [$\mathrm{Y(CH_2SiMe_3)_2(thf)_4}$][$\mathrm{Al(CH_2SiMe_3)_4}$] (20 mg, 21.6 µmol) in $\mathrm{C_6D_6}$, neat 12-crown-4 (3.5 µL, 21.6 µmol) was added and the reaction mixture was shaken. ^{1}H NMR (400 MHz; $\mathrm{C_6D_6}$): δ = –0.68 (d, $^{2}J_{\mathrm{Y,H}}$ = 3.0 Hz, 4 H, $\mathrm{YCH_2}$), –0.62 (br. s, 8 H, $\mathrm{AlCH_2}$), 0.23 [s, 18 H, $\mathrm{YCH_2Si(C}H_3)_3$], 0.50 [s, 36 H, $\mathrm{AlCH_2Si(C}H_3)_3$], 1.42 (16 H, β-$\mathrm{CH_2}$, thf), 3.36 (br. s, 16 H, $\mathrm{CH_2}$, 12-crown-4), 3.58 (16 H, α-$\mathrm{CH_2}$, thf) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz; $\mathrm{C_6D_6}$): δ = 3.30 ($\mathrm{AlCH_2}$), 4.30 [$\mathrm{YCH_2Si(}C\mathrm{H_3)_3}$], 4.83 [$\mathrm{AlCH_2Si(}C\mathrm{H_3)_3}$], 25.68 (β-$\mathrm{CH_2}$, thf), 36.73 (d, $^{1}J_{\mathrm{Y,C}}$ = 40.7 Hz, $\mathrm{YCH_2}$), 68.00 (br., $\mathrm{CH_2}$, 12-crown-4), 68.37 (α-$\mathrm{CH_2}$, thf) ppm.

[$\mathrm{Y(CH_2SiMe_3)_2(12\text{-}crown\text{-}4)(thf)}$][$\mathrm{Ga(CH_2SiMe_3)_4}$] (2b): To a solution of [$\mathrm{Y(CH_2SiMe_3)_3(thf)_2}$] (200 mg, 0.38 mmol) in thf (2 mL) were successively added [$\mathrm{Ga(CH_2SiMe_3)_3}$] (131 mg, 0.38 mmol) in thf (1 mL) and neat 12-crown-4 (70 mg, 0.38 mmol). The resulting clear solution was stirred for five minutes, after which the volatiles were removed under vacuum. Washing with pentane (2 × 10 mL) and drying afforded **2b** as a white powder (315 mg, 89%). ^{1}H NMR (400 MHz; $\mathrm{C_6D_6}$): δ = –0.68 (d, $^{2}J_{\mathrm{Y,H}}$ = 3.1 Hz, 4 H, $\mathrm{YCH_2}$), –0.43 (s, 8 H, $\mathrm{GaCH_2}$), 0.22 [s, 18 H, $\mathrm{YCH_2Si(C}H_3)_3$], 0.49 [s, 36 H, $\mathrm{GaCH_2Si(C}H_3)_3$], 1.44 (4 H, β-$\mathrm{CH_2}$, thf), 3.17 and 3.43 (2 × 8 H, m, $\mathrm{CH_2}$, 12-crown-4), 3.59 (4 H, α-$\mathrm{CH_2}$, thf) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz; $\mathrm{C_6D_6}$): δ = 2.5–3.8 (br. m, $\mathrm{GaCH_2}$), 4.32 [$\mathrm{YCH_2Si(}C\mathrm{H_3)_3}$], 4.65 [$\mathrm{GaCH_2Si(}C\mathrm{H_3)_3}$], 25.64 (β-$\mathrm{CH_2}$, thf), 36.85 (d, $^{1}J_{\mathrm{Y,C}}$ = 41.6 Hz, $\mathrm{YCH_2}$), 67.58 (12-crown-4), 68.61 (α-$\mathrm{CH_2}$, thf) ppm. $\mathrm{C_{36}H_{90}GaO_5Si_6Y}$ (930.25): calcd. C 46.48, H 9.75; found C 45.83, H 9.43%.

[$\mathrm{Y(CH_2SiMe_3)_2(12\text{-}crown\text{-}4)(thf)}$][$\mathrm{In(CH_2SiMe_3)_4}$] (2c): Following the procedure described for **2b**, [$\mathrm{Y(CH_2SiMe_3)_3(thf)_2}$] (200 mg, 0.38 mmol) in thf (2 mL) was treated with [$\mathrm{In(CH_2SiMe_3)_3}$] (131 mg, 0.38 mmol) in thf (1 mL) and neat 12-crown-4 (70 mg, 0.38 mmol). Identical work-up afforded **2c** as a white powder (333 mg, 90%). ^{1}H NMR (400 MHz; $\mathrm{C_6D_6}$): δ = –0.68 (d, $^{2}J_{\mathrm{Y,H}}$ = 3.2 Hz, 4 H, $\mathrm{YCH_2}$), –0.47 (br. s, 8 H, $\mathrm{InCH_2}$), 0.22 [s, 18 H, $\mathrm{YCH_2Si(C}H_3)_3$], 0.48 [s, 36 H, $\mathrm{InCH_2Si(C}H_3)_3$], 1.44 (4 H, β-$\mathrm{CH_2}$, thf), 3.17 and 3.41 (m, 2 × 8 H, $\mathrm{CH_2}$, 12-crown-4), 3.59 (4 H, α-$\mathrm{CH_2}$, thf) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz; $\mathrm{C_6D_6}$): δ = 4.30 [$\mathrm{YCH_2Si(}C\mathrm{H_3)_3}$], 4.60 [$\mathrm{InCH_2Si(}C\mathrm{H_3)_3}$], 25.66 (β-$\mathrm{CH_2}$, thf), 36.79 (d, $^{1}J_{\mathrm{Y,C}}$ = 41.6 Hz, $\mathrm{YCH_2}$), 67.57 (12-crown-4), 68.53 (α-$\mathrm{CH_2}$, thf) ppm. the signal for the $\mathrm{InCH_2}$ carbons was not detected. $\mathrm{C_{36}H_{90}InO_5Si_6Y}$ (975.35): calcd. C 44.33, H 9.30; found C 43.78, H 9.15%.

[$\mathrm{B(CH_2SiMe_3)_3}$] (3): This compound was synthesised according to the procedure described in the literature[5a] and isolated as a colourless liquid (9745 mg, 74.5%), m.p. –32 °C. ^{1}H NMR (500 MHz; $\mathrm{C_6D_6}$): δ = 0.12 [s, 27 H, $\mathrm{Si(CH_3)_3}$], 0.93 (s, 6 H, $\mathrm{BCH_2}$) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (125 MHz, $\mathrm{C_6D_6}$): δ = 0.02 [$\mathrm{Si(CH_3)_3}$], 23.80 ($\mathrm{BCH_2}$) ppm. ^{11}B NMR (160 MHz, $\mathrm{C_6D_6}$): δ = 78.8 ppm.

[$\mathrm{\{Al(CH_2SiMe_3)_3\}_2}$] (4): The product was synthesised according to the procedure described in literature[5b] and isolated as a colourless liquid (6490 mg, 75.0%), m.p. –18 °C. ^{1}H NMR (500 MHz; $\mathrm{C_6D_6}$): δ = –0.54 (s, 6 H, $\mathrm{AlCH_2}$), 0.00 [s, 27 H, $\mathrm{Si(CH_3)_3}$] ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (125 MHz; $\mathrm{C_6D_6}$): δ = 0.27 [$\mathrm{Si(CH_3)_3}$], 2.65 ($\mathrm{AlCH_2}$) ppm. ^{27}Al NMR (130 MHz; $\mathrm{C_6D_6}$): δ = 290.3 ppm.

[$\mathrm{Ga(CH_2SiMe_3)_3}$] (5): The product was synthesised according to the published procedure[5c] and isolated as a colourless liquid (2575 mg, 65.2%), m.p. –42 °C. ^{1}H NMR (400 MHz. $\mathrm{CD_2Cl_2}$): δ = 0.06 [s, 27 H, $\mathrm{Si(CH_3)_3}$], 0.08 (s, 6 H, $\mathrm{GaCH_2}$) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz. $\mathrm{CD_2Cl_2}$): δ = 2.4 [$\mathrm{Si(CH_3)_3}$], 12.5 ($\mathrm{GaCH_2}$) ppm.

[$\mathrm{In(CH_2SiMe_3)_3}$] (6): The product was synthesised according to the published procedure[5d] and isolated as a colourless liquid (4701 mg, 55.2%), m.p. –45 °C. ^{1}H NMR (400 MHz. $\mathrm{CD_2Cl_2}$): δ = –0.06 (s, 6 H, $\mathrm{InCH_2}$), 0.03 [s, 27 H, $\mathrm{Si(CH_3)_3}$] ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz. $\mathrm{CD_2Cl_2}$): δ = 2.47 [$\mathrm{Si(CH_3)_3}$], 10.79 ($\mathrm{InCH_2}$) ppm.

[Li][$\mathrm{Al(CH_2SiMe_3)_4}$] (7a): The procedure described in the literature[34] for the synthesis of **4** was slightly modified: In the glovebox, $\mathrm{Al(CH_2SiMe_3)_3}$ (289 mg, 1 mmol) was dissolved in pentane (3 mL); $\mathrm{Li(CH_2SiMe_3)}$ (94 mg, 1 mmol) in pentane (3 mL) was added dropwise at room temperature. A colourless precipitate formed immediately and the suspension was stirred for 1 h. Filtration, washing with pentane (2 × 5 mL) and drying in vacuo afforded **4** (328 mg, 86%) as a colourless powder. ^{1}H NMR (500 MHz; [D$_8$]thf): δ = –1.22 (br. m, 8 H, $\mathrm{AlCH_2}$), –0.11 [s, 36 H, $\mathrm{Si(CH_3)_3}$] ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz; [D$_8$]thf): δ = 1.51 (sextet, $^{1}J_{\mathrm{Al,C}}$ = 60 Hz, $\mathrm{CH_2}$), 3.78 [s, $\mathrm{Si(CH_3)_3}$] ppm. ^{27}Al NMR (130 MHz; [D$_8$]thf): δ = 150.1 (nonet, $^{2}J_{\mathrm{Al,H}}$ = 9.0 Hz) ppm. ^{7}Li NMR (194 MHz, [D$_8$]thf): δ = –0.54 ppm.

[$\mathrm{Li(tmeda)_2}$][$\mathrm{Al(CH_2SiMe_3)_4}$] (7b): In the glovebox, neat tmeda (191 mg, 1.65 mmol) was added at once to a solution of **4** (315 mg, 0.82 mmol) in thf (3 mL), and the resulting clear solution stirred overnight. After all volatiles were removed in vacuo, the residue was washed three times with 5 mL of pentane, and dried in vacuo. The product was isolated as a colourless powder (255 mg, 51%). ^{1}H NMR (500 MHz, [D$_8$]thf): δ = –1.22 (br. m, 8 H, $\mathrm{AlCH_2}$), –0.10 [s, 36 H, $\mathrm{Si(CH_3)_3}$], 2.15 [s, 24 H, $(\mathrm{C}H_3)_2\mathrm{N}$], 2.31 (s, 8 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (125 MHz, [D$_8$]thf): δ = 2.00 (sextet, $^{1}J_{\mathrm{Al,C}}$ = 60 Hz, $\mathrm{AlCH_2}$), 4.23 [s, $\mathrm{Si(CH_3)_3}$], 46.2 [$(C\mathrm{H_3)_2N}$], 58.9 ($\mathrm{N}C\mathrm{H_2}C\mathrm{H_2N}$) ppm. ^{27}Al NMR (130 MHz, [D$_8$]thf): δ = 150.2 (nonet, $^{2}J_{\mathrm{Al,H}}$ = 9.0 Hz) ppm. ^{7}Li NMR (194 MHz, [D$_8$]thf): δ = –0.53 ppm. $\mathrm{C_{28}H_{76}AlLiN_4Si_4}$ (615.20): calcd. C 54.67, H 12.45, N 9.11; found C 55.00, H 12.94, N 9.78%.

Table 5. Crystallographic and data collection parameters for compounds **1b**, **3**, **4**, **5**, and **7c**.

Compound	**1b**	**3**	**4**	**5**	**7c**
Empirical formula	$C_{40}H_{98}GaO_4Si_6Y$	$C_{12}H_{33}BSi_3$	$C_{24}H_{66}Al_2Si_6$	$C_{12}H_{33}GaSi_3$	$C_{32}H_{76}AlLiO_8Si_4$
M_r	970.35	272.46	577.27	331.37	735.21
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$
a [Å]	21.548(3)	6.5339(11)	10.009(2)	6.5482(5)	10.4405(10)
b [Å]	15.689(3)	16.378(3)	10.4113(16)	16.9374(17)	21.327(2)
c [Å]	34.434(5)	18.764(3)	11.3479(18)	18.838(3)	20.566(2)
α [°]			108.780(13)		
β [°]	102.661(5)	105.097(13)	103.538(16)	101.271(10)	104.481(2)
γ [°]			111.771(15)		
V [Å^3]	11358(3)	1938.7(6)	952.0(3)	2049.0(4)	4433.8(7)
Z	8	4	1	4	4
D_{calc} [g cm^{-3}]	1.135	0.933	1.007	1.074	1.101
T [K]	133(2)	223(2)	248(2)	223(2)	115(2)
μ(Mo-K_α) [mm^{-1}]	1.649	0.226	0.277	1.501	0.194
F(000)	4192	608	320	712	1616
θ Range [°]	1.80–27.05	2.25–28.22	3.11–28.09	2.20–28.01	2.17–29.67
Number of reflections collected	138759	13002	9202	11146	62561
Number of reflections observed [$I>2\sigma(I)$]	12522	3097	3830	3640	8661
Number of independent reflections (R_{int})	24727 (0.1409)	4721 (0.0840)	4601 (0.0318)	4697 (0.0541)	12168 (0.0880)
Data/restraints/parameters	24727/18/973	4721/0/154	4601/0/162	4697/0/154	12168/0/415
Goodness-of-fit on F^2	0.831	1.008	1.011	1.071	0.938
R_1, wR_2 [$I>2\sigma(I)$]	0.0404, 0.0709	0.0520, 0.1110	0.0471, 0.1119	0.0484, 0.1179	0.0412, 0.0930
R_1, wR_2 (all data)	0.1105, 0.0802	0.0930, 0.1209	0.0615, 0.1182	0.0684, 0.1351	0.0591, 0.0974
Largest difference in peak and hole [e Å^{-3}]	0.628 and –0.573	0.372 and –0.172	0.434 and –0.308	0.616 and –1.191	0.564 and –0.453

[Li(12-crown-4)$_2$][Al(CH$_2$SiMe$_3$)$_4$] (7c): Following the same protocol as for **7b**, this compound was obtained by addition of two equivalents of neat 12-crown-4 (290 mg, 1.65 mmol) to a solution of **4** (315 mg, 0.82 mmol) in thf (3 mL). After work-up, the product was isolated as a colourless powder (320 mg, 53%). A saturated thf solution was cooled down to –40 °C to afford crystals suitable for X-ray diffraction. ^{1}H NMR (500 MHz, [D$_8$]thf): δ = –1.22 (br. m, 8 H, AlCH$_2$), –0.10 [s, 36 H, Si(CH$_3$)$_3$], 3.68 (s, 32 H, 12-crown-4) ppm. ^{13}C{^{1}H} NMR (125 MHz, [D$_8$]thf): δ = 2.00 (sextet, $^1J_{Al,C}$ = 60 Hz, AlCH$_2$), 4.23 [s, Si(CH$_3$)$_3$], 70.2 (12-crown-4) ppm. ^{27}Al NMR (130 MHz, [D$_8$]thf): δ = 150.2 (nonet, $^2J_{Al,H}$ = 9.0 Hz) ppm. ^{7}Li NMR (194 MHz, [D$_8$]thf): δ = –0.21 ppm. $C_{32}H_{76}AlLiO_8Si_4$ (735.22): calcd. C 52.28, H 10.42; found C 52.54, H 10.44%.

X-ray Diffraction: Data collections were performed with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Single crystals of **3**, **4**, and **5** were directly grown on a NONIUS CAD4 diffractometer. Capillaries containing ca. 2 µL of **3**, **4**, and **5** were exposed in appropriate geometry (χ = 90°) to a cold stream of N$_2$; the samples completely solidified. The temperature of the gas stream was gradually increased to the melting point, retaining only a small fraction of solid in the tip of the capillary. Slow cooling resulted in a crystalline sample. The procedure was repeated until single crystals of satisfactory quality were obtained; their diffraction pattern was directly registered on the CAD4 diffractometer. The structures of **3** and **5** are closely related and probably isomorphous. Intensity data for **1b** and **7c** were collected on a Bruker CCD D8 goniometer equipped with a SMART APEX CCD detector. Data were processed using SAINT and SADABS to yield the reflection data file.[38] Subsequent calculations were carried out using the SHELXS and SHELXL programs.[39] Analytical scattering factors for neutral atoms were used throughout the analysis.[40] The hydrogen atoms attached to the bridging carbon atom in **4** were freely refined; all other H atoms were included at calculated positions. Crystal data, parameters of data collection and convergence results for the diffraction experiments are compiled in Table 5.

CCDC-621523 (for **1b**), -620839 (for **3**), -620838 (for **4**), -620840 (for **5**), -620841 (for **7c**) 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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