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Introduction

Anions of Group 14 elements of the type $[ER_3]^-$ with alkali metals (M) as counter ions ($[ML_n][ER_3]$, L = additional ligand) have been the subject of various studies for some time. They are typically prepared (for $E \neq C$) by reduction of the corresponding di-element compounds (E_2R_6) or element halides (R_3EX) with an alkali metal. This method is successful for a variety of alkali metal/ E_2R_6 combinations, but other methods have also been employed, *e.g.* the deprotonation of the respective element hydrides, the nucleophilic cleavage of disilanes or the transmetallation of the corresponding mercury element compounds.¹

The aggregation behaviour and the electronic structure of triphenylelement alkali metal compounds (M–EPh₃) in various solvents, as well as in the solid state, have been studied in some detail.^{2–7} The different M–EPh₃ compounds exhibit in

On the structural diversity of [K(18-crown-6)EPh₃] complexes (E = C, Si, Ge, Sn, Pb): synthesis, crystal structures and NOESY NMR study \dagger ‡

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A series of homologous potassium triphenylelement complexes [K(18-crown-6)EPh₃] **6a–e** of group 14 elements (E = C, Si, Ge, Sn, Pb) was synthesised by alkoxide induced heterolytic cleavage of boronelement compounds. The complexes **6a–e** are isolated as storable solids possibly useful as sources of nucleophilic [EPh₃][–] moieties. The solid state structures of **6a–e** were established by X-ray crystal structure determination. Whilst all structures can be described as polymeric chains consisting of alternating [K(18-crown-6)]⁺ and [EPh₃][–] units, the interaction within each chain varies systematically with the coordination properties of E. For Si and Ge, classical E–K coordination along with secondary phenyl–K interactions are characteristic, whilst for Sn and Pb, potassium coordination *via* the phenyl π -system is observed due to inefficient coordination by the free electron pair localised in an 'inert' s-orbital. The carbon derivative is exceptional as the central sp²-hybridised carbon atom gives rise to extensive charge delocalisation and coordination *via* these partially charged π -systems. A ¹H-¹H NOESY NMR spectroscopic study in THF-d₈ suggests appreciable anion/cation interactions for Si to Pb and hence the presence of contact ion pairs.

> solution usually a certain degree of aggregation; hence, they exist as contact ion pairs (CIP) in equilibrium with solventseparated ion pairs (SSIP). This equilibrium depends strongly on the counter ion (M), the polarity of the solvent, the concentration and the temperature. However, the available structural information in the solid state focuses on the lithium compounds $[\text{Li}(\text{L}_n)-\text{EPh}_3]$ (L = donor ligand) and/or the triphenylmethyl derivatives (E = C).^{2–7} In particular, no systematic studies on a homologous series of $[\text{M}(\text{L}_n)-\text{EPh}_3]$ compounds with one alkali metal cation $([\text{M}(\text{L}_n)]^+)$ and all group 14 elements (E) have been conducted.^{7b}

> The use of boron–element (B–E) compounds with E = C is widespread in synthetic chemistry, but also heavier homologues (especially E = Si) have been used *e.g.* as reagents in transition metal catalysed reactions.^{10,11} In 2001 Kawachi *et al.* suggested that the B–Si bond in certain silylboranes is heterolytically cleaved by alkali metal alkoxides and alkyls, respectively, giving the silyl anions (Scheme 1).^{8a} This route, the Lewis base induced B–E cleavage, has recently been applied in a series of transition metal free silyl transfer reactions with different Lewis bases.^{8b–d} In the course of these studies the reaction of certain silylboranes with alkoxides was investigated in some detail.^{8b,e,9} The present work extends the scope of the alkoxide induced B–E bond activation in silylboranes to boron–element compounds of all group 14 elements, as well as to nitrogen substituted boron moieties.

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[†]Dedicated to Prof. Dr Werner Uhl on the occasion of his 60th birthday.

 $[\]ddagger$ Electronic supplementary information (ESI) available: Additional analytical data and the complete set of 1 H- 1 H NOESY NMR spectra of **6a–e**. CCDC 924392–924396 and 893777⁹ (**6b**, structure I). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50523e

Paper



 $\label{eq:Scheme 1} \begin{array}{l} \mbox{Scheme 1} & \mbox{Selected examples of reactions involving the activation of silylboranes by Lewis bases.} \\ \mbox{$^{8a-c,9}$} \end{array}$

Results and discussion

A series of boron-element compounds was synthesised from the dioxaborolane 1 or the diazaborolidine 2 and the corresponding lithium triphenylelement species (Scheme 2). Although boron-element compounds bearing dioxaborolane or diazaborolidine moieties are relatively widespread, only 3b had previously been synthesised and characterised in detail.¹¹⁻¹⁴ As the boron moiety the very common pinacol derived dioxaborolane was chosen for E = C, Si, Ge (3a-c).^{8,11,12} However, for the tin and lead boron compounds (4b,c) a diazaborolidine moiety was used, as the respective dioxaborolane derived compounds are suspected to be of low stability.¹⁴ The silyl diazaborolidine derivative 4a was synthesised for comparison with the dioxaborolane 3b. The synthesis of 3a and 3c from 1 follows a procedure reported for the silicon derivative 3b.¹² The diazaborolidines 4a-4c were successfully synthesised adopting established procedures for related compounds.¹⁵

Whilst the boron–element compounds **3a–c** (E = C, Si, Ge) and **4a–b** (E = Si, Sn) are stable under exclusion of air, **4c** (E = Pb) decomposes readily in solution under inert conditions at room temperature. During this process a black material, presumably elemental lead, is separated.¹⁶ Similar observations have been reported for the related compound ((MeN)₂C₂H₄)B–



Scheme 2 Synthesis of boron-element compounds



Scheme 3 Synthesis of the [K(18-crown-6)EPh₃] complexes 6a-e.

 $PbMe_3$ and the instability of those compounds may account for the fact that only two related boron lead compounds have been reported.^{15*a*,*b*}

Adopting the recently established procedure for the synthesis of **6b** from **3b** and [K(18-crown-6)OtBu] (5), the entire series of homologous [K(18-crown-6)EPh₃] complexes **6a–e** were isolated from **3a–c** and **4a–c** in good to excellent yields (Scheme 3).^{9,17} This extends the scope of the B–E cleavage significantly, on the one side to $E \neq Si$ and on the other side from dioxaborolanes to diazaborolidines. The complexes **6a–e** were obtained as analytically pure, stable (micro-)crystalline solids. No signs of decomposition were observed after storage under inert conditions at –20 °C for several months or at ambient temperature for several days. The complexes **6a–e** were thoroughly characterised by single crystal X-ray diffraction as well as spectroscopically.

Solid-state structures

Single crystal structure determinations were successfully carried out on all homologous complexes **6a–e**. A crystal structure of **6b** (structure I) has been reported earlier but will be discussed here in comparison with other complexes **6a, c, d** and an additional polymorph of **6b** (structure II).⁹

The homologous complexes 6a-e crystallise in a series of closely related structures (Table 1). This series is unique as for the first time a complete set of structures with identical ligands at the potassium atom is obtained. This enables a detailed study of the influence of the nature of E1 on the structures of the complexes 6a-e.

For all structures **6a–e** a similar general structural motive is observed: the $[K(18-C-6)EPh_3]$ moieties form infinite chains, consisting formally of alternating $[K(18-C-6)]^+$ and $[EPh_3]^-$ moieties. However, the interactions and hence the detailed

Compound	6 a ^{<i>a</i>}	6b (structure I) ⁹	6b (structure II)	6c	6d	6e
Chemical formula	C31H39O6K	C30H39O6KSi	C30H39O6KSi	C ₃₀ H ₃₉ O ₆ KGe	C ₃₀ H ₃₉ O ₆ KSn	C30H39O6KPb
Crystallisation conditions	THF/PhMe, rt	$PhMe/C_5H_{12}$, rt	PhMe/C ₅ H ₁₂ , -20 °C	PhMe/C ₅ H ₁₂ , -20 °C	PhMe/C ₅ H ₁₂ , -20 °C	THF/C ₅ H ₁₂ , -20 °C
Formula mass (g mol ⁻¹)	546.72	562.80	562.80	607.30	653.40	741.90
Crystal dimensions (mm ³)	$0.36 \times 0.31 \times 0.28$	$0.41 \times 0.39 \times 0.22$	$0.41 \times 0.31 \times 0.26$	$0.32 \times 0.16 \times 0.13$	$0.47 \times 0.38 \times 0.21$	$0.27 \times 0.24 \times 0.08$
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group (no.)	$P2_{1}(4)$	$P2_{1}/c$ (14)	$Pna2_{1}(33)$	$P2_{1}/c$ (14)	$P2_{1}2_{1}2_{1}$ (19)	$P2_{1}2_{1}2_{1}$ (19)
<i>Z</i> , <i>Z</i> ′	8, 4	4,1	4,1	4,1	4,1	4,1
<i>a</i> (Å)	9.8014(5)	10.0038(4)	18.3527(8)	9.8669(1)	9.6725(2)	9.6839(4)
$b(\dot{A})$	28.769(1)	17.7282(6)	15.2640(8)	17.2748(2)	12.6028(2)	12.5929(4)
$c(\dot{A})$	19.737(1)	17.1680(6)	10.4474(4)	17.9326(2)	24.4563(5)	24.5776(8)
$\alpha(\circ)$	90	90	90	90	90	90
$\beta(\circ)$	90.447(5)	93.224(4)	90	99.857(1)	90	90
γ (°)	90	90	90	90	90	90
Volume (Å ³)	5565.3(5)	3039.9(2)	2926.7(2)	3011.47(6)	2981.2(1)	2997.2(2)
D_{calcd} (Mg m ⁻³)	1.305	1.230	1.277	1.339	1.456	1.644
T(K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Radiation, λ (Å)	MoK _a , 0.71073	MoK _α , 0.71073	MoK _a , 0.71073	CuK _a , 1.54184	MoK _a , 0.71073	MoK _a , 0.71073
$\mu (\mathrm{mm}^{-1})$	0.234	0.253	0.263	2.940	1.036	5.507
Total reflections collected	25 554	66 552	93 602	77 176	73 495	52 235
Total unique reflections	25 554	8687	6396	6263	8585	7157
No. of variables/restraints	1396/1	343/0	343/1	343/0	343/0	343/0
θ range (°)	$2.19 < \theta < 26.00$	$2.30 < \theta < 29.99$	$2.22 < \theta < 27.00$	$3.58 < \theta < 75.91$	$2.26 < \theta < 30.00$	$2.26 < \theta < 28.00$
GooF on F^2	0.869	1.022	1.313	1.036	1.052	1.016
R _{int}	n/a ^a	0.0612	0.0827	0.0304	0.0365	0.0977
$R_1 \left[I > 2\sigma(I) \right]^b$	0.0422	0.0419	0.0873	0.0236	0.0208	0.0380
wR_2 (all data) ^c	0.0781	0.0901	0.1150	0.0642	0.0403	0.0698
Absolute structure parameter	-0.05(3)	n/a	n/a	n/a	-0.021(9)	-0.031(7)
Largest diff. peak/hole $(Å^{-3})$	0.291/-0.550	0.349 / -0.273	0.310/-0.306	0.340/-0.342	0.355/-0.311	1.497/-0.788
CCDC no.	924392	893777	924393	924394	924395	924396

^{*a*} The crystal is a non-merohedral twin; see crystallographic data for details. ^{*b*} $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$. ^{*c*} $wR_2 = (\Sigma[w(F_0^2 - F_c^2)]/\Sigma[F_0^4])^{1/2}$, where $w = 1/[\sigma^2 (F_0^2) + (0.0328P)^2]$ (**6a**), $w = 1/[\sigma^2 (F_0^2) + (0.0307P)^2 + (0.9030P)]$ (**6b**) (structure I)), $w = 1/[\sigma^2 (F_0^2) + (4.4268P)]$ (**6b**) (structure III), $w = 1/[\sigma^2 (F_0^2) + (0.0342P)^2 + (1.2242P)]$ (**6c**), where $P = (F_0^2 + 2F_c^2)/3$, $w = 1/[\sigma^2 (F_0^2) + (0.0144P)^2 + (0.7527P)]$ (**6d**), where $P = (F_0^2 + 2F_c^2)/3$, $w = 1/[\sigma^2 (F_0^2) + (0.0244P)^2]$ (**6c**), where $P = (F_0^2 + 2F_c^2)/3$.

structural motives within these columns are different and depend strongly on the nature of E.

The structures **6a–e** may be categorised into three types: *a*: **6a** (E = C); *b*: **6b** (structure I) (E = Si) and **6c** (E = Ge) and *c*: **6d** (E = Sn) and **6e** (E = Pb). However, the second polymorph of **6b** (structure II) is not fitting well into one of these categories (Tables 1 and 2). The three structure types differ in terms of cell metrics, space group type and other structural parameters. Especially instructive are the intracolumnar angle between the crown ether mean planes (φ (O₆)), the minimum K1–E1 and the intracolumnar K1–K1' distances (Table 2). Generally, the angles (φ (O₆)) included by the individually roughly planar crown ether moieties (Δ _{max}(O₆) \leq 0.363(6) Å) and the K1–K1' distances are specific for a certain structure type (Table 2). These geometrical data are directly correlated to three different coordination modes of the [EPh₃]⁻ anion.

Structure type *a* (6a, E = C). Complex 6a crystallises with four independent [K(18-C-6)CPh₃] moieties in the asymmetric unit (Z = 8, Z' = 4) in a non-centrosymmetric space group of the type P_{2_1} . The individual units of 6a are arranged in two crystallographically independent columns perpendicular to the screw axis and parallel to the *c*-axis, consisting of alternating [K(18-C-6)]⁺ and [CPh₃]⁻ moieties (Fig. 1). The independent columns consist of either the K1/C1 and K1A/C1A or the K1B/C1B and K1C/C1C containing moieties. Both independent

columns exhibit a very similar structure; the one containing K1/C1 and K1A/C1A is discussed exemplarily. The O₆ moiety is roughly planar as indicated by the small maximum deviation of an individual oxygen atom from the mean plane of the oxygen atoms ($\Delta_{max}(O_6)$, Table 2, Fig. 1). A comparably small deviation of the potassium atom from the oxygen atoms mean plane ($\Delta(O_6-K1)$, Table 2) indicates a rather symmetrical axial coordination of K1 by the two π -systems. However, the shorter K–C_{Ph} distance is observed for the phenyl system with the shorter C1–C_{ipso} distance, and hence, for the π -system with the higher negative charge and therefore better donor properties.^{7b,18}

The environment of the central carbon atoms C1 and C1A, respectively, is planar (angular sum ~360°). The bond lengths E1– C_{ipso} are similar and indicative of bond orders between single and double bonds. These data support, together with a bond length within the phenyl rings of 1.34–1.43 Å, an sp² hybridisation of the central carbon atoms and an appreciably delocalised negative charge. However, the individual phenyl groups are, due to steric reasons, not coplanar but in a propeller-like arrangement.⁷ Within a polymeric stack of [K(18-C-6)-EPh₃]_n the [CPh₃]⁻ anions are bridging two potassium atoms (K1, K1A) by coordination *via* the π -systems of two phenyl rings. The differences in the K1/K1A–C_{Ph} distances for the individual atoms C_{Ph} indicate a very unsymmetrical

	6a ^{<i>a</i>}	6b (structure I) ⁹	6b (structure II)	6c	6d	6e
E1=	C1/C1A	Si1	Si1	Ge1	Sn1	Pb1
K1–E1 ^{<i>a</i>} (Å)	4.875(4) (K1, C1) 5.790(4) (K1, C1A) 4.900(4) (K1A, C1A) 5.536(4) (K1A, C1)	3.5404(5)	3.635(1)	3.4252(3)	5.9631(3) 6.4986(3)	6.031(1) 6.521(1)
K1– C_{Ph}^{b} (Å)	3.087(4) (K1, C4) 3.293(4) (K1, C4) 3.120(4) (K1A, C4A) 3.207(4) (K1A, C12)	3.645(2) (C27) 3.663(2) (C28)	3.472(4) (C21) 3.861(4) (C22)	3.290(1) (C16) 3.431(2) (C15)	3.212(2) (C4) 3.438(2) (C3) 3.208(2) (C16) 3.450(2) (C17)	3.207(7) (C4) 3.436(6) (C3) 3.211(7) (C16) 3.485(6) (C17)
E1– C_{ipso} (Å)	1.435(5) (C2) 1.461(5) (C8) 1.465(5) (C14) 1.446(5) (C2A) 1.458(5) (C8A) 1.453(5) (C14A)	1.929(1) (C13) 1.930(1) (C19) 1.929(1) (C25)	1.929(4) (C13) 1.934(4) (C19) 1.941(4) (C25)	2.026(1) (C1) 2.022(1) (C7) 2.026(1) (C13)	2.227(2) (C13) 2.228(2) (C7) 2.245(2) (C1)	2.325(6) (C7) 2.344(6) (C1) 2.331(6) (C13)
C _{ipso} -E1-C _{ipso} (°)	120.4(3) (C2, C14) 122.1(3) (C2, C8) 117.5(3) (C8, C14) 122.7(3) (C2A, C14A) 119.6(3) (C2A, C8A) 117.7(3) (C8A, C14A)	98.85(6) (C13, C25) 99.30(6) (C13, C19) 98.85(6) (C19, C25)	101.7(2) (C13, C25) 102.4(2) (C13, C19) 102.7(2) (C19, C25)	100.23(5) (C7, C13) 101.04(5) (C13, C1) 97.51(5) (C1, C7)	95.14(6) (C7, C13) 96.29(6) (C7, C1) 97.46(5) (C1, C13)	93.3(2) (C7, C13) 96.9(2) (C1, C13) 94.6(2) (C7, C1)
K1–K1 ^{c} (Å)	9.980(1) (K1, K1A) 9.771(1) (K1A K1)	9.107(5)	9.484(1)	9.1449(4)	12.2719(5)	12.334(2)
$\begin{array}{l} \varphi(\mathrm{O}_{6})^{c} \left(^{\circ} \right) \\ \Delta_{\mathrm{max}}(\mathrm{O}_{6})^{d} \left(\overset{\mathrm{A}}{\mathrm{A}} \right) \\ \Delta(\mathrm{O}_{6}\text{-}\mathrm{K1})^{d} \left(\overset{\mathrm{A}}{\mathrm{A}} \right) \end{array}$	24.12(4) 0.363(6) 0.2464(9)	81.75(1) 0.215(1) 0.5045(3)	15.60(5) 0.224(3) 0.4825(7)	81.81(1) 0.3018(9) 0.2286(3)	63.11(2) 0.239(1) 0.1372(3)	63.29(5) 0.204(4) 0.123(1)

^{*a*} The geometrical data within one column are given; the data of the second are comparable (see the main text). ^{*b*} Only selected shortest distances are given. ^{*c*} Angle and distance between two adjacent moieties within one column of $[K(18-c-6)EPh_3]_n$. ^{*d*} Maximum deviation of an oxygen $(\Delta_{max}(O_6))$ or potassium ((O_6)–K1) from the O_6 mean plane.



Fig. 1 Detailed view of a column of **6a** (left) and packing pattern of **6a** (right) with the atom labelling scheme.

coordination by each phenyl π -system and in particular no coordination by the benzylic carbon atoms (C1/C1A).¹⁸ The shortest K–C_{Ph} distances in **6a** are significantly shorter than

the respective distances found in a series of typical K-arene solvates (3.29 Å).¹⁹ This coordination mode is not without precedence among triphenylmethyl potassium complexes. In the monomeric complex ([K(thf)(PMDTA)CPh₃]) a similar, though more symmetric, coordination of the potassium atom is observed. The similarity is illustrated by the comparable K-CPh (3.14-3.25 Å) and C1-Cipso (1.435(5), 1.475(6), 1.460(6) Å) distances.7b On the other side the closely related complex ([K(PMDTA)CPh₃]) exhibits a 'benzylic' coordination of the potassium atom with rather short distances between the potassium atom and the carbon atoms of the 'benzylic' system (2.93–3.21 Å).^{7a} However, secondary interactions to an adjacent phenyl system with distances >4.06 Å are also observed. A coordination mode similar to 6a is observed in the polymeric complex ([K(diglyme)CPh3]). Here, alternating units of $[K(diglyme)]^+$ and $[CPh_3]^-$ moieties form columns with short K–C_{Ph} distances (3.15–3.25 Å).^{7a} In contrast, the crown ether complex [K(18-C-6)C(C₆Cl₅)₃] exhibits a different structural motive: the cation is coordinated by the chlorine atoms.^{7c}

The preference of the potassium cation for the phenyl π -system compared to the 'benzylic' system may be rationalised in terms of hard/soft interactions.^{7b} This affinity of the K⁺ cation to π -systems is well documented and may be competitive with K⁺-dipol interactions.²⁰ However, the energetic difference between coordination to the π -system and the 'benzylic' system, respectively, is small. In conclusion, the motive realised in a particular complex [K(L)CPh₃] depends on subtle changes such as packing or steric effects and especially additional potassium–donor-interactions within the crystal structure (*e.g.* in $[K(18-C-6)C(C_6Cl_5)_3]$ or with additional solvent molecules).⁷ In agreement with this the lighter and harder alkali metals usually show a certain preference for coordination by the 'benzylic' system.⁷

Structure type *b* (6b, 6c, E = Si, Ge). The complexes 6b (structure I) and 6c crystallise with one $[K(18-C-6)EPh_3]$ moiety in the asymmetric unit (Z' = 1) in a space group of the type $P2_1/c$ with similar cell axes and volumes, but different monoclinic angles. Whilst the structures are again best described as $[K(18-C-6)EPh_3]_n$ columns (parallel to the *b*-axis), the mutual orientation of the [K(18-C-6)] moieties within each column is significantly different from structure type *a*. In 6b (structure I) and 6c nearly perpendicular crown ether oxygen mean planes (φ (O₆)) and slightly smaller intercolumnar K–K' distances are observed (Table 2, Fig. 2 and 3).

The difference to structure type a is caused by the fundamentally different coordination mode of the EPh₃ anion in 6b (E = Si) and 6c (E = Ge) compared to 6a (E = C). The atom E may be best described as non- or sp³-hybridised with an appreciable amount of distortion (sum of angles: 297.0° 6b (structure I), 298.8° 6c and 306.8° 6b (structure II)). Thus, the $E(C_{ipso})_3$ moiety is no longer planar, but trigonal-pyramidal with the negative charge essentially localised at E1.³ In agreement with this are the E1-Cipso distances indicative of rather long single bonds (typical bond length: Ge-C(sp³) 1.98 Å, Si- $C(sp^2)$ 1.84 Å).^{21a} These data resemble the values found in structurally characterised, virtually monomeric, lithium [EPh3]⁻ complexes (average Si-Cipso, sum of angles Cipso-Si-Cipso: 1.94 Å, 303.8° ([Li(thf)₃SiPh₃]); 2.01 Å, 294.9° (Li-(Et₂O)₃GePh₃]); 2.02 Å, 298.8° ([Li(tmeda)(thf)GePh₃])).^{5,6}



Fig. 2 Detailed view of a column of **6b** (structure I) (left) and packing pattern of **6b** (structure I) (right) with the atom labelling scheme.



Fig. 3 Detailed view of a column of 6c (left) and packing pattern of 6c (right) with the atom labelling scheme.

The K atoms in **6b** and **6c** are unsymmetrically coordinated by two bridging bidentate $[EPh_3]^-$ moieties. In these structures the coordination by the lone pair located at the atom E1 is – in contrast to **6a** – evident. The distances K1–E1 (Table 2) are considerably shorter than the sum of the van der Waals radii (d_{vdW} : 4.85 Å (K–Si); 4.75 Å (K–Ge)) but slightly longer than the sum of the covalence radii (d_{cov} : 3.23 Å (K–Si); 3.20 Å (K–Ge)), clearly indicating E–K interactions.^{21b}

Short K-C_{Ph} distances on the other side indicate additional interactions of K1 with the phenyl π -systems. The K1-C_{Ph} distances observed are again significantly shorter than the sum of the van der Waals radii (d_{vdW} : 4.45 Å (K–C)).^{21b} However, in the silyl complex 6b (both structures) they are significantly longer than in the germyl complex 6c. In the latter one the K-C_{Ph} distances are only slightly longer than in 6a and in arene solvates (vide supra).¹⁹ The unsymmetrical coordination of the potassium atom is also reflected in the relative position of K1: in 6b (both structures) the potassium atom is placed significantly more out of the crown ether O₆ mean plane towards E1 than in **6c** (Table 2, Δ (O₆-K1)). This may be rationalised by a weaker K-Ge than K-Si interaction and hence a more competitive interaction of K1 with the π -system in 6c. This is also in agreement with the expected more inert character of the free electron pair in the germyl anion.

As mentioned above, a polymorph of **6b** in an orthorhombic space group $Pna2_1$ (Z = 4, Z' = 1) was obtained by crystallisation at a lower temperature (structure II). Whilst the structural parameters of the two structures of **6b** are generally comparable the packing of the individual [K(18-C-6)SiPh₃] entities within a polymeric stack is significantly different. This is indicated especially by the different angles between the O₆ mean planes (φ (O₆)) of the crown ether moieties and intracolumnar K1-K1' distances (Table 2, Fig. 4). But most importantly the



Fig. 4 Detailed view of a column of **6b** (structure II) (left) and packing pattern of **6b** (structure II) (right) with the atom labelling scheme.



Fig. 5 Detail of Si1–K1 coordination in **6b** structure I (left) and II (right). Selected atoms are drawn as spheres with an arbitrary radius. Black: K–(Si1,C13, C14)_{centroid} distance.

interactions between the $[K(18-C-6)]^+$ and the $[SiPh_3]^-$ moieties are different. In structure II as compared to structure I, a longer Si1-K1 distance is observed. Moreover, in structure II much shorter K-C13 and K-C14 distances within one [K(18-C-6)EPh₃] moiety are observed (Fig. 5). K1 is situated nearly symmetrically above the Si1/C13/C14 moiety, suggesting coordination by this 'hetero-benzylic' system rather than by the Si1 atom alone (Fig. 5). However, the Si1-C13 distances in both structures are identical and indicative of a C-Si single bond (vide supra). This is also in agreement with spectroscopic data for closely related systems indicating only minor charge delocalisation between the silicon atom and the phenyl substituents.³ The different coordination may rather be explained by the interaction of the potassium cation with both the electron pair/electron density at the silicon atom and the π -system, than with a classical 'benzylic' coordination to a delocalised charged π -system. In addition, packing effects are certainly of importance. However, the effects are obviously very small as small differences in the crystallisation conditions result in the formation of both polymorphs.

Structure type *c* (6d, 6e, E = Sn, Pb). The third structure type is realised in the compounds 6d (E = Sn) and 6e (E = Pb). These compounds crystallise isomorphically in the orthorhombic system in the *P*2₁2₁2₁ space group type with one [K(18-C-6)EPh₃]



Fig. 6 Detailed view of a column of ${\bf 6d}$ (left) and packing pattern of ${\bf 6d}$ (right) with the atom labelling scheme.



Fig. 7 Detailed view of a column of **6e** (left) and packing pattern of **6e** (right) with the atom labelling scheme.

unit in the asymmetric unit (Table 1). The individual columns of $[K(18-C-6)EPh_3]_n$ are situated on the screw axis parallel to the *c*-axis (Fig. 6 and 7).

The crystal structure of **6e** is only the second of an alkali metal triphenylplumbyl complex and the first of a respective potassium complex.^{4b} The stannyl complex **6d** was reported earlier including a room temperature crystal structure.^{4a} In this

work **6d** is fully characterised and its crystal structure was redetermined at 100 K to ensure comparability with **6a–c,e**.

The structure type c is again best described as columns of alternating $[K(18-C-6)]^+$ and $[EPh_3]^-$ units. However, the K1-K1' distance is significantly longer than in the previously described compounds, whilst the angles between the 18-C-6 moieties ($\varphi(O_6)$) are in between the values found for types a and b (Table 2). The deviation of K1 from the O_6 mean plane is the smallest found so far, indicating a symmetrical coordination of K1 by the two [EPh₃]⁻ moieties. The coordination mode of the $[EPh_3]^-$ entities is similar to **6a**: K1 is coordinated *via* the π -system of two phenyl rings (Fig. 6 and 7).¹⁸ This is indicated by the short K1-C_{Ph} distances and the K1-E1 distances (Table 2), significantly longer than the sum of the van der Waals radii (d_{vdW} : 4.92 Å (K–Sn), 4.77 Å (K–Pb)).^{21b} However, in contrast to 6a, no indication of charge delocalisation between E1 and the aromatic system is apparent from the structural parameters. The E1-Cipso distances are on the long side in the range expected for single bonds (Sn-C(sp³) 2.14 Å, Pb-C(sp³) 2.29 Å)^{21a} and the C_{ipso}-E1-C_{ipso} angles are indicative of an essentially non-hybridised E1 atom. Hence, the negative charge is localised at E1 and, in contrast to 6a, not delocalised into the π -system.³ However, due to the inert character of the free electron pair on E1 localised in an s-orbital, E-K coordination is not preferable compared to coordination via the π -system. In contrast to **6a** the π -systems of phenyl rings do not bear a negative (partial) charge and their coordination properties should be comparable to neutral π -systems. In fact the K-C_{Ph} distances observed in 6d and 6e are typically longer than in 6a but comparable to those found in selected arene solvates (vide supra).¹⁹ In contrast to 6d/e the monomeric lithium complexes [Li(PMDTA)SnPh₃] and [Li(PMDTA)PbPh₃] contain unambiguously Li-E bonds.4b,c In conclusion this shows again that the strong K-n-system interactions are competitive with the classical cation-anion interaction.²⁰

Whilst the atom E1 is not coordinated to the cation in the complexes **6a,d**, it is a nucleophilic site. The *in situ* prepared complexes **6a–d** give smoothly the triphenylelement benzyl compounds Ph_3E-CH_2Ph (E = C, Si, Ge, Sn) upon reaction with benzyl bromide as an exemplary electrophile.^{9,22}

NMR spectroscopy

Numerous NMR spectroscopic investigations on the solution state structure of alkali metal triphenylelement compounds have been reported. However, those studies are restricted to the analysis of resonances of the $[EPh_3]^-$ anion and/or to lithium or cesium derivatives due to the unfavourable NMR properties of the other alkali metals.^{2,3,7b} The compounds **6a–e** were characterised by multinuclear NMR spectroscopy (¹H, ¹³C, ²⁹Si, ¹¹⁹Sn). The ¹H NMR spectra for **6b–e** (E = Si to Pb) show a singlet for the crown ether methylene protons and three well resolved multiplets of the phenyl protons (Fig. 8).²² In contrast, the ¹H NMR spectra of **6a** are indicative of the presence of dynamic processes in solution. At ambient temperature three broadened phenyl signals are observed which become three narrow well resolved multiplets in agreement



Fig. 8 1 H- 1 H-NOESY NMR spectrum of **6e** in THF-d₈ at rt. Inset: Trace of the NOESY spectrum at the shift of the OCH₂ signal. * THF signal.

with an AA'MM'Y spin system at $-76 \, {}^{\circ}C.^{7i,22,23}$ However, no comparable effect of the temperature on the line width of the crown ether methylene singlet signal is observed. Hence, the dynamic process may be mainly associated with a dynamic process within a separated $[Ph_3C]^-$ anion.^{7i,22,23} The ¹³C NMR data show the expected signals for the crown ether methylene and the phenyl carbon atoms.⁹ The chemical shifts of the phenyl carbon atoms resemble the data observed for the corresponding crown ether free compounds.^{3c,d} The observed shift differences of 1–4 ppm, generally most pronounced at the *ipso* carbon atoms, may well be attributed to the influence of the presence of the crown ether on the aggregation in solution.

The chemical shift values for the different atoms E in the $[EPH_3]^-$ anion in **6a,b,d** may also be compared with the NMR data reported for related compounds measured under similar conditions (solvent, temperature). For compound **6b** (E = Si) a ²⁹Si NMR shift of $\delta = -7.1$ ppm is observed to be fitting well to a value of $\delta = -7.5$ ppm for the corresponding crown ether free compound.^{3b,9} The differences in the respective chemical shifts observed for **6a** (E = C, $\delta_C = 90.9$ ppm) and **6d** (E = Sn, $\delta_{Sn} = -103.2$ ppm) compared to the crown ether free analogues ($\delta_C = 88.5$ ppm and $\delta_{Sn} = -108.4$ ppm) may again be explained by the influence of the crown ether on the aggregation in solution.^{3b,c,d}

Moreover, assuming that dissociation of the crown ether ligand from the potassium ion is negligible the crown ether signal is well suited as an NMR probe for the cation. Thus, a ¹H-¹H-NOESY NMR spectroscopic study was conducted in order to obtain a first insight into the aggregation/coordination behaviour in THF-d₈ solution. These experiments complement studies on the ion-pairing of KEPh₃ derivatives performed with different methods (¹H/¹³C NMR, Mössbauer, and UV-Vis spectroscopy) under different conditions.^{2,3,4a,7b} However, this represents the first ¹H-¹H-NOESY NMR study on K(18-C-6)EPh₃ compounds.⁴

The ¹H NMR spectra of **6b-e** in THF-d₈ are similar and show well separated multiplets for the three groups of phenyl protons, whilst a singlet is observed for the crown ether signal (Fig. 8, exemplarily for 6e).²² ¹H-¹H-NOESY NMR spectra (1.0 s mixing time, 40–46 μ mol mL⁻¹) are indicative of NOE between the crown ether signal and the phenyl protons. The strongest NOE signal is observed for the ortho-proton, whilst smaller NOE signals are observed for the meta- and para-protons.²² These data suggest for 6b-e the presence of an appreciable amount of contact ion pairs (CIP) in THF solution at ambient temperature. It has to be emphasised that the NOESY NMR data on 6b-e do not allow conclusions on the mode of coordination in solution. However, with all due care, in all solid state structures of 6b-e, distances of the respective hydrogen atoms $(OCH_2 \text{ to the phenyl protons})$ are found below 4 Å and are in agreement with the observation of an NOE.

These findings appear to be in agreement with the literature data: According to ¹³C NMR spectroscopic studies, KSiPh₃ consists in THF at 25 °C largely of contact ion pairs, although the addition of 18-crown-6 (*in situ* formation of **6b**) leads to less aggregation.^{3d} NMR spectroscopic studies on KEPh₃ (E = Si to Pb) in ethereal solvents generally suggest an equilibrium between solvent-separated ion-pairs (SSIP) and contact ion-pairs (CIP).^{3b} ¹¹⁹Sn Mössbauer studies on crystalline **6d** and on KSnPh₃ in frozen THF solution suggest that similar aggregates as in the crystalline material are present to a certain extent in the frozen solution.^{4a}

The ¹H-¹H-NOESY NMR of **6a** in THF-d₈ does not reveal any NOE contacts of the crown ether signal to the phenyl proton signals even at -76 °C. Hence, the NOESY measurement does not support the presence of contact ion pairs but it has to be emphasised that this certainly does not exclude the presence of anion–cation contacts not detectable within the limits of the method. A UV-Vis spectrum of **6a** in THF-d₈ at ambient temperature exhibits strong absorption bands at 438 and 505 nm. This is in agreement with the results from *in situ* prepared **6a** (λ_{max} at 430 (sh) and 495 nm) which are reported to be indicative of the absences of CIP.^{2a,b}

Conclusions

The [K(18-crown-6)O*t*Bu] (5) induced heterolytic B–E bond cleavage of triphenylelement dioxoborlanes and diazaborolidines has proven to be a versatile route to isolable and stable potassium 18-crown-6 triphenylelement complexes (**6a–e**) of all group 14 elements. Whilst these compounds may be of interest as storable, stoichiometric reagents they exhibit an unexpected structural diversity in the solid state. The solid state structures are best described as polymeric chains of alternating [K(18-C-6)]⁺ cations and [EPh₃]⁻ anions. However, the type of interaction between both entities is different and depends strongly on the nature of E. This may be rationalised by a simple approach considering the increasing s–p-separation towards the heavier group 14 elements. In the case of E = C, sp²-hybridisation is energetically feasible and leads to delocalised benzyl-anions. As a result the potassium atom in the [K(18-

C-6)]⁺ cation is coordinated by two phenyl rings of two different $[EPh_3]^-$ moieties. In the case of E = Si, Ge sp²-hybridisation is not realised, resulting in largely localised silvl/ germyl anions and E-K coordination. The solid state structure may best be described as molecular [K(18-C-6)EPh₃] units connected by additional secondary intermolecular π -system-K interactions to form polymeric columns. However, a polymorph of [K(18-C-6)SiPh₃] was obtained showing appreciable intramolecular π -system-K interaction, and thus a more 'benzylic' coordination of the cation. On the other hand for E = Sn and Pb hybridisation is again not feasible, but due to the inert character of the s-electron pair, E-K coordination by this electron pair is also not efficient. This results in a coordination mode similar to the one observed for E = C, and hence, polymeric chains of alternating [K(18-C-6)]⁺ cations and [EPh₃]⁻ anions with nearly symmetrical coordination of the potassium atom by two phenyl π -systems. In conclusion it may be stated that the interplay of π -system potassium interactions and anion (potassium) cation interactions governs the structural chemistry of [K(18-C-6)EPh₃] complexes.

¹H-¹H-NOESY NMR spectroscopic studies on the [K(18-C-6)-EPh₃] complexes revealed that for E = Si to Pb, contact ion pairs (CIP) are, at least partially, present, whilst for E = C no indications of their presence were found.

Experimental

General

pinB-O*i*Pr^{24a} (1), pinB-SiPh₃¹² (3b), [K(18-crown-6)O*t*Bu] (5),¹⁷ $[K(18\text{-crown-6})SiPh_3]$ (6b)⁹ (from 3b), $Ph_6Ge_2^{24b}$ and $Ph_6Pb_2^{24c}$ N, N'-iso-propylethylendiamine^{24d} (((*i*PrN)₂C₂H₄)H₂) were synthesised as reported. $((i PrN)_2(C_2H_4))B-Br(2)$ has been prepared adopting a reported procedure.^{15d} All other reagents were purchased from commercial sources and used as received. All reactions were performed under an atmosphere of nitrogen employing Schlenk or Glovebox techniques in dried (MBraun solvent purification system) and degassed solvents. NMR spectra were recorded on Bruker Avance II 300, Bruker Avance 400 or Bruker DRX 400 spectrometers. The NMR solvents were dried and degassed using standard techniques. ¹H and ¹³C chemical shifts (δ) are given in ppm relative to Me₄Si, using the resonance of the (residual protio-) solvent as an internal reference (C₆D₆: ¹H NMR: 7.16 ppm, ¹³C NMR: 128.06 ppm; THF-d₈: ¹H NMR: 1.72 ppm, ¹³C NMR: 25.31 ppm).^{24e 11}B, ²⁹Si and ¹¹⁹Sn chemical shifts are reported relative to external BF3·Et2O, Me4Si and Me4Sn, respectively. ¹³C, ¹¹B, ²⁹Si and ¹¹⁹Sn NMR spectra were recorded employing (²⁹Si, ¹¹⁹Sn: inverse-gated) composite pulse ¹H decoupling. ¹H-¹H-NOESY NMR measurements were performed at a 400 MHz instrument employing standard techniques (mixing time: 1 s).²⁵ EI mass spectrometry was performed employing a Finnigan MAT 95 XP spectrometer (70 eV). UV-Vis spectra were recorded under inert conditions in a cuvette equipped with a J. Young valve on a Varian Cary 50 Scan spectrophotometer. Melting points were determined using a Büchi 530 apparatus

in flame sealed capillaries under nitrogen and are not corrected. Elemental analyses were performed using an Elementar vario MICRO cube instrument at the Institut für Anorganische und Analytische Chemie of the Technische Universität Carolo-Wilhelmina zu Braunschweig.

 $((iPrN)_2C_2H_4)B-Br$ (2). A solution of NEt₃ (7.5 g, 74 mmol, 2 eq.) in dry n-hexane (160 mL) was cooled to 0 °C and BBr₃ (9.2 g, 37 mmol, 1 eq.) in n-hexane (25 mL) was added slowly. After warming to rt, N,N'-iso-propylethylendiamine (5.4 g, 37 mmol, 1 eq.) in n-hexane (25 mL) was added and the mixture was heated to 80 °C for 3 h. After cooling to rt the mixture was filtered and the volatiles were removed in vacuo. Crude 2 was obtained as a brown oil sufficiently pure for further reactions. Analytically pure 2 was obtained by bulb-tobulb distillation (0.01 mbar, 60-65 °C) as a colourless liquid. Yield: 5.1 g, 22 mmol, (59%). Found: C, 41.2; H, 7.8; N, 11.8. Calc. for C₈H₁₈N₂BBr: C, 41.25; H, 7.8; N, 12.0%. δ_H(300 MHz; C_6D_6) 0.95 (12 H, d, ³J = 6.7 Hz, $CH(CH_3)_2$), 2.92 (4 H, s, CH_2), 3.83 (2 H, sept., ${}^{3}J = 6.7$ Hz, CH(CH₃)₂). $\delta_{\rm C}(75$ MHz; C₆D₆) 21.3 $(CH(CH_3)_2)$, 41.5 (CH_2) , 45.4 $(CH(CH_3)_2)$. $\delta_B(96 \text{ MHz}; C_6D_6)$ 25.7 (1 B, s, $\Delta w_{\frac{1}{2}} = 100$ Hz). m/z (EI⁺) 232 (M⁺, 28), 217 ([M - $[CH_3]^+$, 100).

pinB-CPh₃ (3a). In dry THF (50 mL) Ph₃CH (2.0 g, 8 mmol, 1 eq.) was cooled to 0 °C and nBuLi (5.2 mL (1.6 M in *n*-pentane), 8 mmol, 1 eq.) was slowly added and the deep red mixture was stirred for 2 h at rt. To this mixture neat 1 (2.6 g, 14 mmol) was added and the reaction mixture was stirred for 40 h at rt. After removal of all volatiles in vacuo the residue was extracted with hot *n*-hexane $(2 \times 30 \text{ mL})$ and filtered. After removal of the solvent in vacuo the residue was purified by column chromatography (Ø 3 cm × 18 cm, Merck Silicagel 60, *n*-pentane \rightarrow *n*-pentane-Et₂O 15:1; $r_{\rm f}$ = 0.5 (*n*-hexane-Et₂O 5:1)). After solvent evaporation the raw product was recrystallised from hot *n*-hexane to give an off-white powder. Yield: 0.4 g, 1 mmol, (13%). Mp 148–150 °C (from *n*-hexane). Found: C, 81.2; H, 7.4. Calc. for C₂₅H₂₇O₂B: C, 81.1; H, 7.4. $\delta_{\rm H}(300 \text{ MHz}; C_6D_6)$ 1.04 (12 H, s, (C(CH_3)_2)_2), 7.09–7.15 (3 H, m, CH_{Ar}), 7.21–7.28 (6 H, m, CH_{Ar}), 7.53–7.58 (6 H, m, CH_{Ar}). $\delta_{\rm C}(75 \text{ MHz}; C_6D_6) 24.4 ((C(CH_3)_2)_2), 52.2 (CPh_3), 84.0 ((C-1)_2)_2)$ $(CH_3)_2)_2$, 126.1 (CH_{Ar}), 128.2 (CH_{Ar}, overlapping with solvent signal), 131.2 (CH_{Ar}), 146.5 (*ipso*-C). $\delta_{\rm B}$ (96 MHz; C₆D₆) 33.8 (1 B, s, $\Delta w_{\frac{1}{2}} = 375$ Hz). m/z (EI⁺) 370 (M⁺, 66), 355 ([M - CH₃]⁺, 5), 293 ($[M - C_6H_5]^+$, 6), 270 ($[M - C_6H_{12}O]^+$, 100), 243 ($[CPh_3]^+$, 34), 193 ($[M - C_6H_5 - C_6H_{12}O]^+$, 22), 243 ($[CPh_2]^+$, 57).

pinB–GePh₃ (3c). To granulated lithium (0.10 g, 14 mmol, 2.9 eq.) in dry THF (10 mL), Ph₆Ge₂ (1.50 g, 2.46 mmol, 0.5 eq.) was added and the mixture was stirred for 16 h at rt. The brownish solution was removed from the excess lithium and added to 1 (1.9 g, 10.2 mmol, 2.1 eq.) in *n*-hexane (30 mL). After 16 h at rt the solvent was removed, the residue extracted with hot *n*-hexane (3×20 mL) and the hot extracts were filtered through a pad of celite. After concentration (~15 mL) the product started to crystallise and the solution was decanted, the precipitate washed with cooled *n*-hexane (1×10 mL) and dried *in vacuo* to give the product as an off-white powder. Yield:

0.65 g, 1.5 mmol, (30%). Mp 119–122 °C (from *n*-hexane). Found: C, 66.8; H, 6.4. Calc. for $C_{24}H_{27}O_2BGe:$ C, 66.9; H, 6.3. $\delta_{H}(300 \text{ MHz}; \text{ C}_6\text{D}_6)$ 0.99 (12 H, s, (C(CH_3)_2)_2), 7.10–7.24 (9 H, m, CH_{Ar}), 7.83–7.78 (6 H, m, CH_{Ar}). $\delta_{C}(75 \text{ MHz}; \text{ C}_6\text{D}_6)$ 24.9 ((C-(CH_3)_2)_2), 84.4 ((C(CH_3)_2)_2), 128.5 (CH_{Ar}), 135.6 (CH_{Ar}), 136.0 (CH_{Ar}), 138.2 (*ipso*-C). $\delta_{B}(96 \text{ MHz}; \text{ C}_6\text{D}_6)$ 35.8 (1 B, s, $\Delta w_{\frac{1}{2}} = 335$ Hz). m/z (EI⁺) 448 ([M + O]⁺, 5), 433 ([M + H]⁺, 3), 432 (M⁺, 3), 305 ([GePh_3]⁺, 10), 228 ([GePh_2]⁺, 100).

((*i*PrN)₂C₂H₄)B-SiPh₃ (4a). To granulated lithium (0.27 g, 39 mmol, 6 eq.) in dry THF (20 mL) a solution of Ph₃SiCl (2.20 g, 7.5 mmol, 1.2 eq.) in THF (30 mL) was added at 0 °C. After stirring for 16 h at rt the solution was removed from excess lithium and cooled to -78 °C. To this solution 2 (1.51 g, 6.5 mmol, 1.0 eq.) in n-pentane (30 mL) was added. After stirring at -78 °C for 15 minutes and for 16 h at rt the volatiles were removed in vacuo. The residue was extracted with dry toluene $(3 \times 20 \text{ mL})$ and the extracts filtered over celite. After removal of the solvent the product was obtained as a brown solid. The product was further purified by fractional crystallization from hot n-hexane. Yield: 2.21 g, 5.4 mmol, (83%). Mp 62-65 °C (from n-hexane). Found: C, 73.5; H, 7.95; N, 6.6. Calc. for C₂₆H₃₃N₂BSi: C, 75.7; H, 8.1; N, 6.8. δ_H(300 MHz; C₆D₆) 0.84 (12 H, d, ${}^{3}J$ = 6.7 Hz, CH(CH₃)₂), 3.12 (4 H, s, CH₂), 3.56 (2 H, sept., ${}^{3}J = 6.7$ Hz, $CH(CH_{3})_{2}$), 7.10–7.20 (9 H, m, CH_{Ar}), 7.85–7.81 (6 H, m, CH_{Ar}). $\delta_{\rm C}$ (75 MHz; C₆D₆) 21.0 (CH(CH₃)₂), 42.0 (CH₂), 46.2 (CH(CH₃)₂), 128.2 (CH_{Ar}), 129.1 (CH_{Ar}), 136.7 (CH_{Ar}), 137.9 (*ipso*-C). $\delta_{\rm B}$ (96 MHz; C₆D₆) 31.9 (1 B, s, $\Delta w_{\frac{1}{2}}$ = 390 Hz). $\delta_{Si}(79.5 \text{ MHz}; C_6D_6) - 23.3 (1 \text{ Si, br. s}). m/z (EI^+) 412.25052$ (Calc. for $C_{26}H_{33}N_2BSi$: 412.25061) (M⁺, 14), 397 ([M - CH₃]⁺, 100), 335 ($[M - C_6H_5]^+$, 4), 259 ($[SiPh_3]^+$, 54), 199 ($[SiPh_2]^+$, 15), $181 ([M - Ph_3]^+, 28).$

((*i*PrN)₂C₂H₄)B-SnPh₃ (4b). To granulated lithium (0.13 g, 17 mmol, 4 eq.) in dry THF (20 mL) a solution of Ph₃SnCl (1.66 g, 4.3 mmol, 1.0 eq.) in THF (15 mL) was added at 0 °C and the mixture was stirred for 16 h at rt. The solution was removed from excess lithium and cooled to -78 °C. To this solution, 2 (1.00 g, 4.3 mmol, 1.0 eq.) in n-pentane (15 mL) was added. After stirring at -78 °C for 30 minutes and 16 h at rt the volatiles were removed in vacuo. The residue was extracted with dry toluene $(3 \times 20 \text{ mL})$ and the extracts were filtered over celite. After concentration and addition of n-pentane the product was obtained as a colourless microcrystalline powder. Yield: 1.42 g, 2.8 mmol, (66%). Mp 105-108 °C (from toluene/n-pentane). Found: C, 61.7; H, 6.9; N, 5.9. Calc. for $C_{26}H_{33}N_2BSn: C, 62.1; H, 6.6; N, 5.6. \delta_H(300 \text{ MHz}; C_6D_6) 0.90$ $(12 \text{ H}, \text{ d}, {}^{3}J = 6.7 \text{ Hz}, \text{ CH}(\text{CH}_{3})_{2}), 3.08 (4 \text{ H}, \text{ s}, \text{CH}_{2}), 3.82 (2 \text{ H})$ H, sept., ${}^{3}J = 6.7$ Hz, $CH(CH_{3})_{2}$), 7.13–7.25 (9 H, m, CH_{Ar}), 7.76–7.79 (6 H, m, ${}^{3}J(SnH) = 49$, 35 Hz (satellites), CH_{Ar}). $\delta_{\rm C}(75 \text{ MHz}; C_6D_6)$ 22.2 (CH(CH₃)₂), 42.3 (CH₂), 47.6 (CH $(CH_3)_2$, 128.6 (CH_{Ar}) , 128.8 (CH_{Ar}) , 138.0 $(^2J(SnC) = 36$ Hz (satellites), o-CH_{Ar}), 141.6 (${}^{1}J(SnC) = 389$ Hz (satellites), *ipso*-C_{Ar}). $\delta_{\rm B}(96$ MHz; C₆D₆) 35.5 (1 B, s, ${}^{1}J({\rm SnB}) = 943$ Hz (satellites), $\Delta w_{\frac{1}{2}} = 290$ Hz). $\delta_{\text{Sn}}(149$ MHz; C₆D₆) -168.5 (1 Sn, br. q, ${}^{1}J(SnB) = 943$ Hz). m/z (EI⁺) 504 (M⁺, 29), 489 $([M - CH_3]^+, 68), 427 ([M - Ph]^+, 100), 351 ([SnPh_3]^+, 3), 273$ $([SnPh_2]^+, 8).$

((*i*PrN)₂C₂H₄)B-PbPh₃ (4c). To Ph₆Pb₂ (1.00 g, 1.14 mmol, 1.0 eq.) in dry THF (20 mL), PhLi (0.63 mL (1.8 M in *n*Bu₂O), 1.13 mmol) was added at 0 °C and stirred for 1 h at 0 °C. To the resulting suspension, 2 (0.27 g, 1.2 mmol, 1.1 eq.) in *n*-pentane (5 mL) was added at -70 °C. After stirring the colourless, heterogeneous mixture for 3 h at -70 to -10 °C the solvent was removed in vacuo keeping the temperature below -10 °C. The residue was extracted with dry *n*-pentane (3 \times 20 mL) at -20 °C, the extracts rapidly filtered over celite and the solvents removed *in vacuo* at -10 °C until the beginning of crystallisation. After 2 h at -20 °C the solvent was decanted and the product dried *in vacuo* at -10 °C. The product was obtained as a microcrystalline, off-white powder. The product decomposes at rt in C₆D₆ solution in 1 h significantly.²² Yield: 0.17 g, 0.29 mmol, (25%). Mp 114-116 °C (from toluene/ n-pentane) under decomposition.²² Found: C, 52.7; H, 5.8; N, 4.7. Calc. for C₂₆H₃₃N₂BPb: C, 52.8; H, 5.6; N, 4.7. δ_H(300 MHz; C_6D_6) 0.90 (12 H, d, ³J = 6.6 Hz, CH(CH₃)₂), 3.05 (4 H, s, CH₂), 3.84 (2 H, sept., ${}^{3}J$ = 6.6 Hz, CH(CH₃)₂), 7.09–7.18 (3 H, m, CH_{Ar}), 7.18–7.29 (6 H, m, CH_{Ar}), 7.71–7.96 (6 H, m, ³*J*(PbH) = 61 Hz (satellites), CH_{Ar}). $\delta_{\rm C}$ (75 MHz; C₆D₆) 22.1 (CH(CH₃)₂), 42.4 (CH₂), 47.8 (²*J*(PbC) = 24 Hz (satellites), $CH(CH_3)_2$), 127.9 (CH_{Ar}, overlapping with solvent signal), 129.5 (${}^{3}J$ (PbC) = 56 Hz (satellites), CH_{Ar}), 138.6 (${}^{2}J$ (PbC) = 61 Hz (satellites), o-CH_{Ar}), 151.1 (*ipso*-C_{Ar}). $\delta_{B}(96 \text{ MHz}; C_{6}D_{6})$ 42.8 (1 B, s, ¹*J*(PbB) = 1379 Hz (satellites), $\Delta w_{\frac{1}{2}} = 220$ Hz)). m/z (EI⁺) 515 ([M - Ph]⁺, 16), 439 ([PbPh₃]⁺, 13), 285 ([PbPh]⁺, 65), 154 ([Ph₂]⁺, 100). Attempts to obtain a ²⁰⁷Pb NMR spectrum were unsuccessful due to the instability of 4c at rt.^{15b,c}

[K(18-C-6)CPh₃] (6a). In a nitrogen filled glovebox, 5 (50 mg, 135 µmol, 1 eq.) and 3a (50 mg, 135 µmol, 1 eq.), each dissolved in dry THF (2 mL), were mixed. After 10 minutes the mixture was layered with PhMe (3-4 mL) and the product precipitated at -20 °C (16 h). The supernatant solution was decanted, the residue washed with dry *n*-pentane $(3 \times 3 \text{ mL})$ and dried in vacuo to give a deep red powder. Single crystals suitable for the X-ray diffraction study were obtained by diffusion of PhMe into a solution in THF at rt. Yield: 61 mg, 112 µmol, (84%). Mp >162 °C (from THF/toluene) under decomposition. Found: C, 67.75; H, 7.1. Calc. for C₃₁H₃₉O₆K: C, 68.1; H, 7.2. $\delta_{\rm H}(400 \text{ MHz}; \text{THF-d}_8; -70 \text{ °C}) 3.51 (24 \text{ H, s, OCH}_2), 5.90 (3 \text{ H,}$ vt, ${}^{3}J = 7$ Hz, *p*-CH_{Ar}), 6.46 (6 H, vdd, ${}^{3}J = 8$, 7 Hz, *m*-CH_{Ar}), 7.29 (6 H, vd, ${}^{3}J$ = 8 Hz, o-CH_{Ar}). $\delta_{\rm C}$ (100 MHz; THF-d₈; -70 °C) 71.0 (OCH₂), 90.9 (CPh₃), 113.1 (p-CH_{Ar}), 123.9 (o-CH_{Ar}), 128.1 (m-CH_{Ar}), 149.8 (ipso-C_{Ar}). λ_{max} /nm (THF) 438 (sh) and 505.

[K(18-C-6)SiPh₃] (6b). For preparation from 3b and analytical data, see ref. 9. 6b can also be obtained from 4a following the same procedure (yield: 58%).

[K(18-C-6)GePh₃] (6c). As described for 6a: 5 (70 mg, 186 μmol, 1 eq.), 3c (80 mg, 186 μmol, 1 eq.); yellow crystalline powder. Single crystals suitable for the X-ray diffraction study were obtained by diffusion of *n*-pentane into the reaction mixture in PhMe at -20 °C. Yield: 71 mg, 117 μmol, (63%). Mp 171–174 °C (from PhMe/*n*-pentane). Found: C, 59.7; H, 6.4. Calc. for C₃₀H₃₉O₆KGe: C, 59.3; H, 6.5. $\delta_{\rm H}$ (400 MHz; THF-d₈) 3.51 (24 H, s, OCH₂), 6.73–6.78 (3 H, m, *p*-CH_{Ar}), 6.84–6.89

(6 H, m, *m*-CH_{Ar}), 7.38–7.42 (6 H, m, *o*-CH_{Ar}). $\delta_{\rm C}$ (100 MHz; THF-d₈) 71.1 (OCH₂), 123.1 (*p*-CH_{Ar}), 126.3 (*o*/*m*-CH_{Ar}), 137.5 (*o*/*m*-CH_{Ar}), 166.3 (*ipso*-C_{Ar}).

[K(18-C-6)SnPh₃] (6d). As described for 6a: 5 (30 mg, 80 μmol, 1.0 eq.), 4b (45 mg, 89 μmol, 1.1 eq.); yellow crystalline powder. Single crystals suitable for an X-ray diffraction study were obtained by diffusion of *n*-pentane into the reaction mixture in PhMe at rt. Yield: 48 mg, 73 μmol, (91%). Mp 145–148 °C (from PhMe/*n*-pentane). Found: C, 55.3; H, 6.3. Calc. for C₃₀H₃₉O₆KSn: C, 55.1; H, 6.0. $\delta_{\rm H}$ (400 MHz; THF-d₈) 3.50 (24 H, s, OCH₂), 6.75–6.81 (3 H, m, *p*-CH_{Ar}), 6.90–6.84 (6 H, m, *m*-CH_{Ar}), 7.54–7.49 (6 H, m, *o*-CH_{Ar}). $\delta_{\rm C}$ (100 MHz; THFd₈) 71.1 (OCH₂), 123.7 (*p*-CH_{Ar}), 126.5 (*m*-CH_{Ar}), 139.4 (²*J*(SnC) = 54 Hz (satellites), *o*-CH_{Ar}), 168.3 (*ipso*-C_{Ar}). $\delta_{\rm Sn}$ (79.5 MHz; THF-d₈) –103.2 (1 Sn, s).

[K(18-C-6)PbPh₃] (6e). In a nitrogen filled glovebox, 5 (35 mg, 93 µmol, 1.0 eq.) and 4c (55 mg, 93 µmol, 1 eq.), each dissolved in dry, precooled THF (1 mL, -20 °C), were mixed. After 5 min at -20 °C the mixture was layered with *n*-pentane (3 mL) and the product was crystallised at $-20 \text{ }^{\circ}\text{C}$ (16 h) to give the product as colourless plates suitable for X-ray crystallography. The solution was decanted, the residue washed with dry *n*-pentane $(3 \times 3 \text{ mL})$ and dried *in vacuo*. Yield: 41 mg, 55 µmol, (59%). Mp 152-156 °C (from THF/n-pentane). Found: C, 48.4; H, 5.5. Calc. for C₃₀H₃₉O₆KPb: C, 48.6; H, 5.3. δ_H(400 MHz; THF-d₈) 3.46 (24 H, s, OCH₂), 6.72–6.81 (3 H, m, p-CH_{Ar}), 6.87-6.97 (6 H, m, m-CH_{Ar}), 7.71-7.81 (6 H, m, o-CH_{Ar}). δ_C(100 MHz; THF-d₈) 71.1 (OCH₂), 123.2 (*p*-CH_{Ar}), 127.7 $({}^{3}J(PbC) = 28 \text{ Hz} \text{ (satellites)}, m-CH_{Ar}\text{)}, 140.4 ({}^{2}J(PbC) = 54 \text{ Hz}$ (satellites), m-CH_{Ar}), 191.5 (ipso-C_{Ar}). Attempts to obtain a ²⁰⁷Pb NMR spectrum were unsuccessful.^{3b}

X-ray crystallography[‡]

All crystals were mounted in inert perfluoroether oil on top of a glass fiber using an XTEMP-2 apparatus at approx. -80 °C and rapidly transferred to the cold nitrogen gas stream of the diffractometer.26a-c The data were either collected on an Oxford Diffraction Xcalibur E instrument using monochromated MoKa radiation at 100(2) K or on an Oxford Diffraction Nova A instrument, using mirror-focused CuKa radiation at 100(2) K. The data were integrated and an empirical absorption correction was performed employing CrysAlisPro software.^{26d} All structures were solved by direct methods (6a, 6b (both structures) and **6d**: SIR-92;^{26e} **6c** and **6e**: SHELXS-97^{26f}) and refined anisotropically for all non-hydrogen atoms by fullmatrix least squares on F² using SHELXL-97.^{26f} All hydrogen atoms were refined employing a riding model. During refinement and analysis of the crystallographic data the programs WinGX, PLATON, ORTEP-III and Diamond were used.^{26g-j}

The crystal of **6a** is non-merohedrically twinned by a 180° rotation about the *b*-axis. Both domains were indexed separately and the data were integrated into a dataset containing intensities of both domains; this dataset was used in the refinement (the twin factor refined to 0.3394(5)). The structure was solved with intensity data of one domain only (R_{int} =

0.1392, w $R_2 = 0.1479$). Further crystallographic details are given in the crystallographic data deposited.[‡]

In ORTEP style plots the thermal ellipsoids are drawn at the 50% probability level. In packing diagrams the atoms are drawn as spheres with arbitrary radii. Hydrogen atoms are omitted for clarity. For clarity symmetry equivalent atoms are not distinguished.

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