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Alkali metal salts of ditopic carbanionic carbenes as reagents

for the synthesis of novel complexes of group 12 and 14 metals

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Abstract. Reaction of the lithiated N-heterocyclic carbene $[:C[N(2,6\text{-}^iPr_2C_6H_3)]_2(CH)CLi]_n$ (**LiIPr**) with KO^{t}Bu in diethylether (Et$_2$O) afforded the novel organo-potassium compound $[:C[N(2,6\text{-}^iPr_2C_6H_3)]_2(CH)CK(THF)_2]$ (**KIPr·2THF**). Both **LiIPr** and **KIPr** can be interpreted as ditopic carbanionic carbenes (or alkali metal salts of anionic "dicarbenes") and are interesting precursors for the synthesis of novel metal complexes bearing carbanionic carbenes as ligands. Reaction of **KIPr** with $M[N(SiMe_3)_2]_2$ (M = Zn, Sn) afforded salts of the anionic three coordinate complexes $[M\{C(CH)[N(2,6\text{-}^iPr_2C_6H_3)]_2C:\}\{N(SiMe_3)_2\}_2]^-$ (M = Zn (**1**) and Sn (**2**)). Contrasting reactivity was observed for the other group 14 bis-amide compounds $M[N(SiMe_3)_2]_2$ (M = Ge, Pb), which initially appear to yield analogous 1:1 complexes (M = Ge (**3**) and Pb (**4**)), however over time give rise to compounds bearing two ditopic carbanionic carbenes $([M\{C(CH)[N(2,6\text{-}^iPr_2C_6H_3)]_2C:\}_2\{N(SiMe_3)_2\}]^-$; Ge (**5**) and Pb (**6**)) and the tris-amide anions $([M\{N(SiMe_3)_3\}]^-)$, presumably via a Schlenk-type equilibrium. Compounds **5** and **6** can be directly synthesized by reacting $M[N(SiMe_3)_2]_2$ (M = Ge, Pb) with two equivalents of **KIPr**, respectively.

Introduction

Ditopic carbanionic carbenes, also referred to as anionic "dicarbenes", are accessible by direct deprotonation,[1] chemical reduction,[2] or metal-mediated C−H activation of N-heterocyclic carbenes (NHCs) with unsaturated backbones (either as free ligands or in metal complexes).[3] Such

transformations afford formally anionic NHC ligands capable of bridging metal centres via the C4 and C5, or C2 and C4, positions (Scheme 1, Types A and B, respectively). The resulting carbanionic carbenes can be represented using a variety of resonance structures, some of which suggest significant carbenic character at the metallated positions (hence such species also being described as "dicarbenes"). These transformations at the ligand backbone are amongst the many possible reactions available to NHC ligands. A variety of related C−H, C−C and C−N bond activation reactions at the nitrogen atom functionalities have also previously been reported for transition metal/NHC complexes.[4–6] However despite the growing number of examples documenting their chemical reactivity, over the last twenty years NHCs have proven to be pivotal supporting ligands for a variety of catalytically active metal complexes.[7]

TYPE A
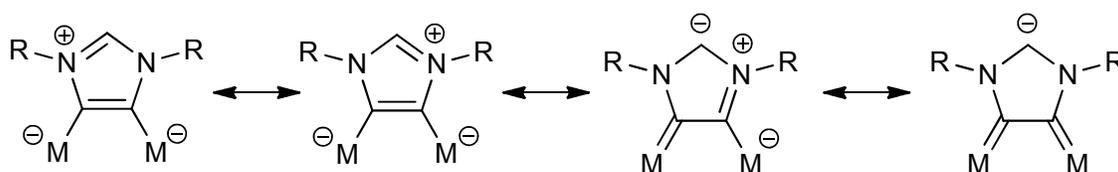
TYPE B
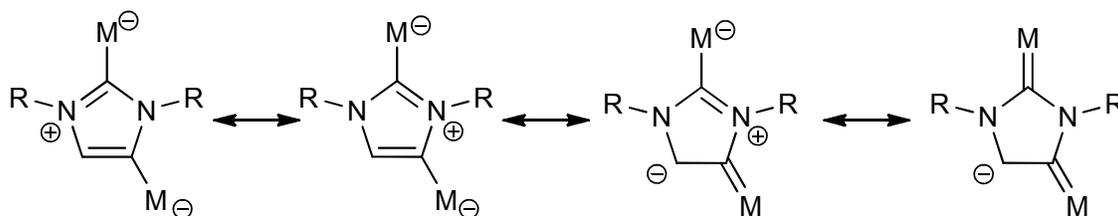
Scheme 1. Bimetallic ditopic carbanionic carbenes (anionic "dicarbenes") derived from the deprotonation, reduction, or activation of alkenic C−H bonds in unsaturated imidazolylidene N-heterocyclic carbene complexes.

Ditopic carbanionic carbenes are capable of bridging two metal centres via different carbon atoms of the NHC ring and as such are reminiscent of neutral 1,2,4-triazole-3,5-diylidenes.[8] Both types of backbone-activated imidazol-2-ylidenes involve a metal bonded to the carbanionic C4 position

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(which has significant vinylic character). This bonding mode is closely related to that observed for transition metal complexes of "abnormally-bonded" carbenes, first reported by Crabtree and co-workers.[9] Such "abnormal" carbenes are also termed mesoionic because they cannot be represented by a Lewis structure without invoking two opposing charges on the ligand.

Robinson's recent report describing the isolation of the lithiated N-heterocyclic carbene [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)CLi]$_n$ (**LiIPr**),[1a] prompted us to address whether the carbanionic carbene moiety can be stabilized as a free anion, *i.e.* [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C]$^-$. With this objective in mind we synthesized the organo-potassium compound [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)CK(THF)$_2$] (**KIPr·2THF**) by reaction of LiIPr with KO^{t}Bu. Attempts to sequester the potassium cation with 2,2,2-crypt resulted in the decomposition of the sequestering agent and the generation of the protonated carbene 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr), consistent with the high Brønsted basicity of the proposed [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C]$^-$ carbanion. **KIPr** was also used as a reagent for the synthesis of novel complexes of group 12 and group 14 post-transition metals by reaction with M[N(SiMe$_3$)$_2$]$_2$ (M = Zn, Ge, Sn, Pb). These reactions afforded the anionic three coordinate complexes [M{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}{N(SiMe$_3$)$_2$}$_2$]$^-$ (M = Zn (**1**), Sn (**2**), Ge(**3**) and Pb (**4**)). However, spectroscopic studies revealed that while **1** and **2** are stable in solution indefinitely, compounds **3** and **4** readily decompose, presumably via Schlenk-type equilibria, to [M{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}$_2${N(SiMe$_3$)$_2$}]$^-$ (M = Ge (**5**) and Pb (**6**)) and the tris-amide compounds [M{N(SiMe$_3$)$_2$}$_3$]$^-$.

Results and discussion

*Synthesis of [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)CK] (**KIPr**)*

The lithiated N-heterocyclic carbene [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)CLi]$_n$ (**LiIPr**) was prepared according to the method reported by Robinson and co-workers.[1a] This compound was synthesized as

part of an on-going project aimed at accessing novel metal complexes bearing ditopic carbanionic carbenes by reactions with metal bis(bistrimethylsilyl)amides. However, in our experience, the reactivity of **LiIPr** is often complicated by the generation of Li[N(SiMe$_3$)$_2$] and subsequent deprotonation of trimethylsilyl substituents. We therefore sought to generate an alternative carbanionic carbene by replacement of the lithium with a different alkali metal.

Reaction of LiIPr with KO^{t}Bu in diethylether at −78 °C followed by slow warming of the reaction mixture to room temperature afforded an orange solution from which [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)CK] (**KIPr**) could ultimately be isolated. The high solubility of the LiO^{t}Bu side product allows for the isolation of a lithium-free salt (as evidenced by the absence of a resonance in the ^{7}Li NMR spectrum). The ^{1}H and ^{13}C{^{1}H} NMR spectra are consistent with a asymmetric alkenic backbone. This is evident by the observation of two methine resonances (3.04 and 3.28 ppm) and a single alkenic proton (6.07 ppm) in a 2:2:1 ratio, respectively, in the ^{1}H NMR spectrum. Four doublet resonances were also observed for the diasterotopic methyl substituents alongside the requisite number of aromatic protons. Similarly the ^{13}C{^{1}H} spectrum reveals resonances arising from the carbenic carbon, the carbanionic site, and the protonated alkenic centre at 215.1, 176.3 and 126.8 ppm, respectively. It is interesting to note that upon addition of 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]-hexacosane) to a solution of **KIPr** the ^{1}H NMR spectrum shows the formation of the protonated carbene (IPr) and resonances consistent with the degradation of the sequesting agent. This implies that the carbanionic moiety present in **KIPr** is unstable as a "free" species and rapidly deprotonates 2,2,2-crypt. Thus it seems unlikely that [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C]$^-$ may be isolated without an accompanying metal interaction.

KIPr·2THF could be crystallized by slow diffusion of hexane into a saturated THF solution of **KIPr**. **KIPr**·2THF crystallizes in the space group $P2_12_12_1$ and reveals one-dimensional zig-zag chains

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along the crystallographic *b* axis in which ditopic carbanionic carbenes [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C]$^-$ are bridged by potassium cations (see Figure 1; Table 1 contains selected experimental data for all of the structures reported herein). The potassium cations interact with the "conventional" carbenic site of one dicarbene (K1−C1: 2.905(2) Å) and the carbanionic (or "abnormal") site of an adjacent dicarbene (K1−C3': 2.812(2) Å). As expected, the latter contact is shorter due to a greater electrostatic interaction between a formally anionic carbon centre and K$^+$ (sum of radii 2.71−2.76 Å).[10] Unsurprisingly, there are no significant differences between the anionic [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C]$^-$ moiety present in **KIPr·2THF** and Robsinson's **LiIPr·THF** system.[1a]
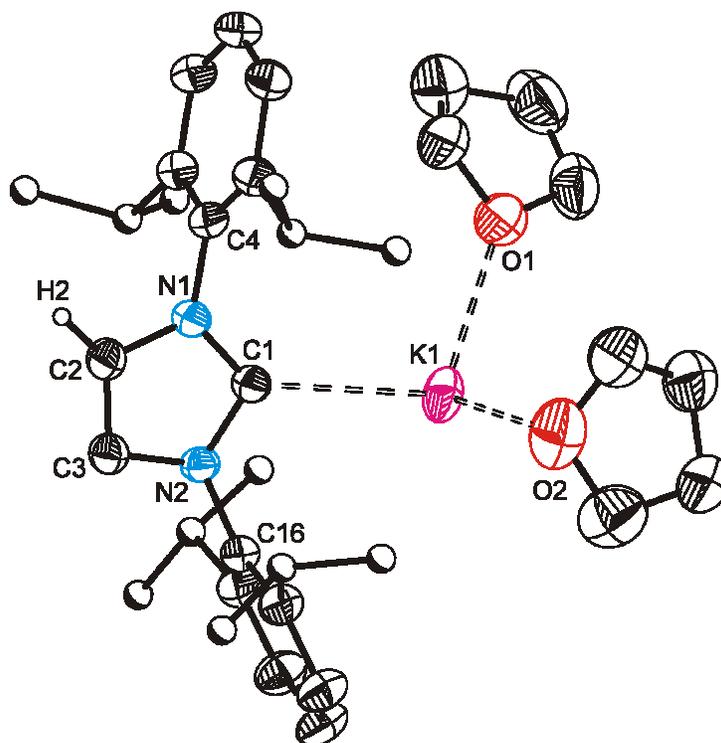

Figure 1. Molecular structure of **KIPr·2THF** (anisotropic displacement ellipsoids pictured at 50% probability level). All hydrogen atoms (with the exception of H2) have been omitted for clarity. Atoms of ^{i}Pr groups are pictured as spheres of arbitrary radius. Selected inter-atomic distances (Å): C1−N1: 1.352(3); C1−N2: 1.376(3); N1−C2: 1.412(3); N2−C3: 1.429(3); C2−C3: 1.362(3); N1−C4: 1.431(3); N2−C16: 1.434(3); C2−H2: 0.95(3); K1−C1: 2.905(2); K1−C3': 2.812(2). Symmetry operation ': −x, 0.5+y, 0.5−z.

*Synthesis of 1:1 adducts between **KIPr** and M[N(SiMe₃)₂]₂ (M = Zn, Sn)*

KIPr has proven to be a useful reagent for the synthesis of novel organometallic complexes bearing ditopic carbanionic carbenes. The possibility of sequestering the cation using 2,2,2-crypt or 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) allows for the carbenic site of the ligand to remain available for further coordination.

Reactions of **KIPr** with $M[N(SiMe_3)_2]_2$ (M = Zn and Sn) in 1:1 stoichiometric ratio affords the three-coordinate anionic complexes $[M\{C(CH)[N(2,6\text{-}^iPr_2C_6H_3)]_2C:\}\{N(SiMe_3)_2\}_2]^-$ (M = Zn (**1**), Sn (**2**); see Scheme 2). The ^1H NMR spectra for the crude reaction mixtures are consistent with complexes bearing a single "abnormally" bonded N-heterocyclic carbene which has no proton associated with the carbenic (C2) position. A table comparing NMR data for all reported compounds is provided in the ESI. The most diagnostic resonances in the ^1H NMR spectra are those arising from the alkenic and the diisopropylphenyl methine protons which occur in a 1:2:2 ratio (observed, respectively, at 6.92, 3.23 and 3.03 ppm for **1** and 7.01, 3.26 and 3.06 ppm for **2**). Compounds **1** and **2** are stable in solution indefinitely as adducts with no apparent change to their NMR spectra.
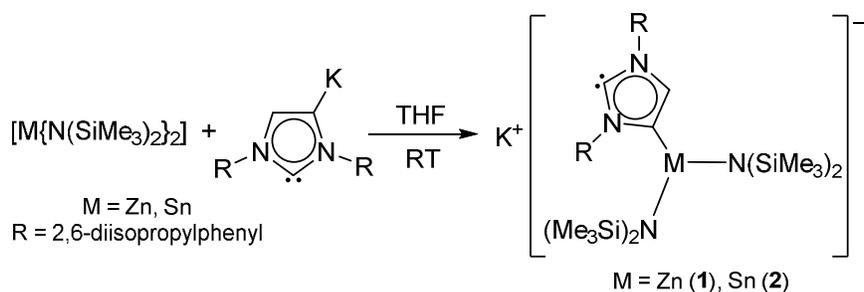
Scheme 2. Synthesis of **1** and **2** by reaction of $[M\{N(SiMe_3)_2\}_2]$ with **KIPr**.

Further confirmation of the formation of the three-coordinate $[M\{C(CH)[N(2,6\text{-}^iPr_2C_6H_3)]_2C:\}\{N(SiMe_3)_2\}_2]^-$ complexes was obtained by means of negative ion-mode electrospray mass-spectrometry which revealed the molecular ions at *m/z* values of 773.9 and 826.2 for **1** and **2**, respectively.

Crystals of **1** and **2** could be grown by addition of one equivalent of a cation sequestering agent to the aforementioned reaction mixtures and slow diffusion of hexane into saturated THF solutions of the products. This method afforded the salts [K(2,2,2-crypt)][**1**]·THF and [K(18-crown-6)(THF)$_2$][**2**]·0.5THF (see Figures 2 and 3, respectively). As expected, the zinc (II) complex was found to display a trigonal planar coordination geometry ($\Sigma_{bond\ angles}$ = 360.0°), while the analogous tin (II) compound is trigonal pyramidal on account of its sterogenic lone-pair ($\Sigma_{bond\ angles}$ = 300.1°). The metal-carbanionic carbene distances are 2.008(1) and 2.277(3) Å for **1** and **2** (Δd = 0.27 Å), respectively, which is consistent with the greater covalent radius of tin relative to zinc (Δr_{cov} = 0.17 − 0.32 Å).[10] A similar effect is observed for the M−N distances to the amide ligands which are, on average, 0.25 Å longer for **2**. It is interesting to note, therefore, that bond metric data vary as expected due to differences in covalent radii and that there is no obvious structural effect resulting from the increased steric clash that would be expected for a trigonal pyramidal structure relative to a trigonal planar system.

Anionic trigonal planar zinc (II) complexes analogous to **1** have previously been reported and show comparable bond metrics. For example, the [Zn{N(SiMe$_3$)}$_3$]$^-$ anionic moiety previously reported by the groups of Dehnicke and Mulvey have Zn−N bond distances that range between 1.963(2) and 1.981 (2) Å and are comparable to those observed for **1** (2.000(1) and 1.949(1)).[11] A closely related complex bearing two ditopic carbanionic carbenes, [{:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)C}$_2$Zn(mes)]$^-$, was also recently reported by our research group and shows a good agreement with the Zn−C$_{carbene}$ bond distance observed in **1** (2.023(2) and 2.009(2) Å compared to 2.008(1)Å in **1**).[2c] By contrast, a search of the Cambridge Structural Database reveals a dearth of three coordinate tin (II) bis-amide complexes of the type [Sn{N(SiMe$_3$)}$_2$L] or [Sn{N(SiMe$_3$)}$_2$R]$^-$.[12] Closely related trigonal pyramidal tin (II) compounds are known.[13] To our knowledge there are no reported examples of tin

(II) complexes bearing carbanionic dicarbene ligands, however complexes bearing neutral carbenes

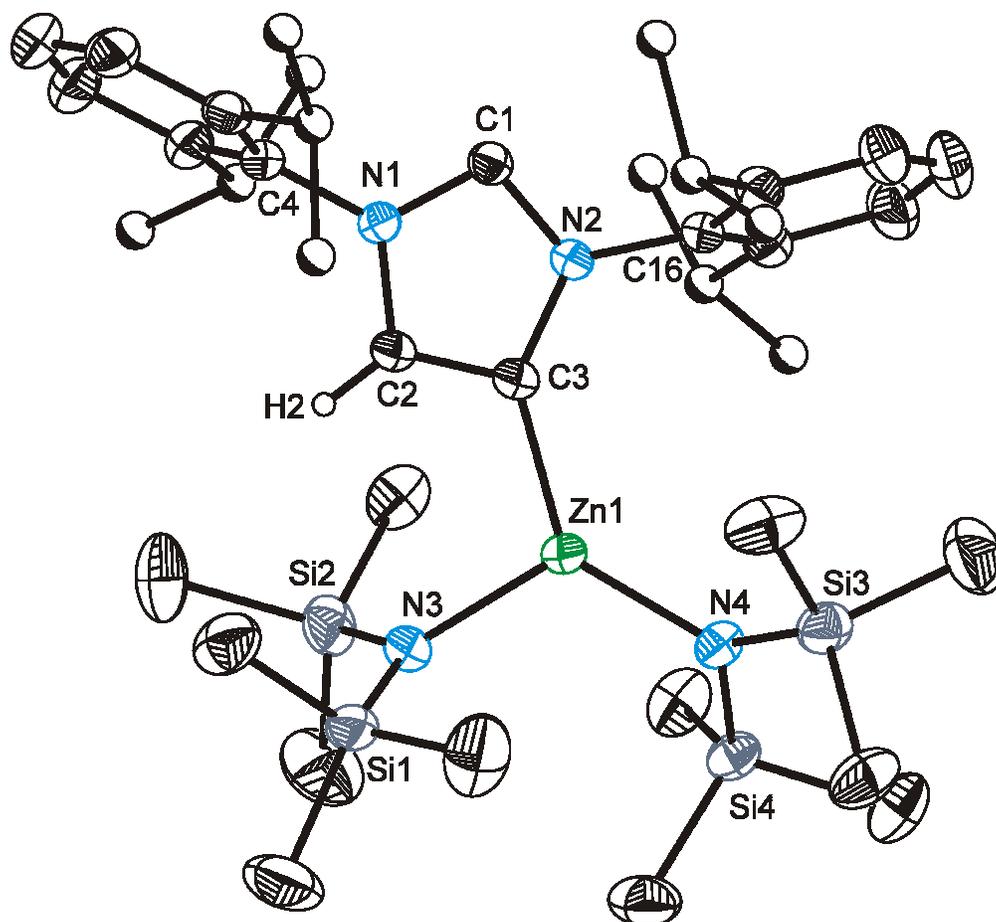have previously been reported by our research group and others.[14]

Figure 2. Molecular structure of the anionic moiety in [K(2,2,2-crypt)][**1**]·THF (anisotropic

displacement ellipsoids pictured at 50% probability level). All hydrogen atoms (with the exception of

H2) have been omitted for clarity. Atoms of ^{i}Pr groups are pictured as spheres of arbitrary radius.

Selected inter-atomic distances (Å) and angles (°): Zn1−C3: 2.008(1); Zn1−N3: 2.000(1); Zn1−N4:

1.949(1); C1−N1: 1.357(2); C1−N2: 1.371(2); N1−C2: 1.400(2); N2−C3: 1.427(2); C2−C3:

1.358(2); N1−C4: 1.439(2); N2−C16: 1.442(2); C2−H2: 0.95(2); N3−Si1: 1.698(1); N3−Si2:

1.699(1); N4−Si3: 1.701(1); N4−Si4: 1.708(1); C3−Zn1−N3: 107.60(6); C3−Zn1−N4: 135.52(6);
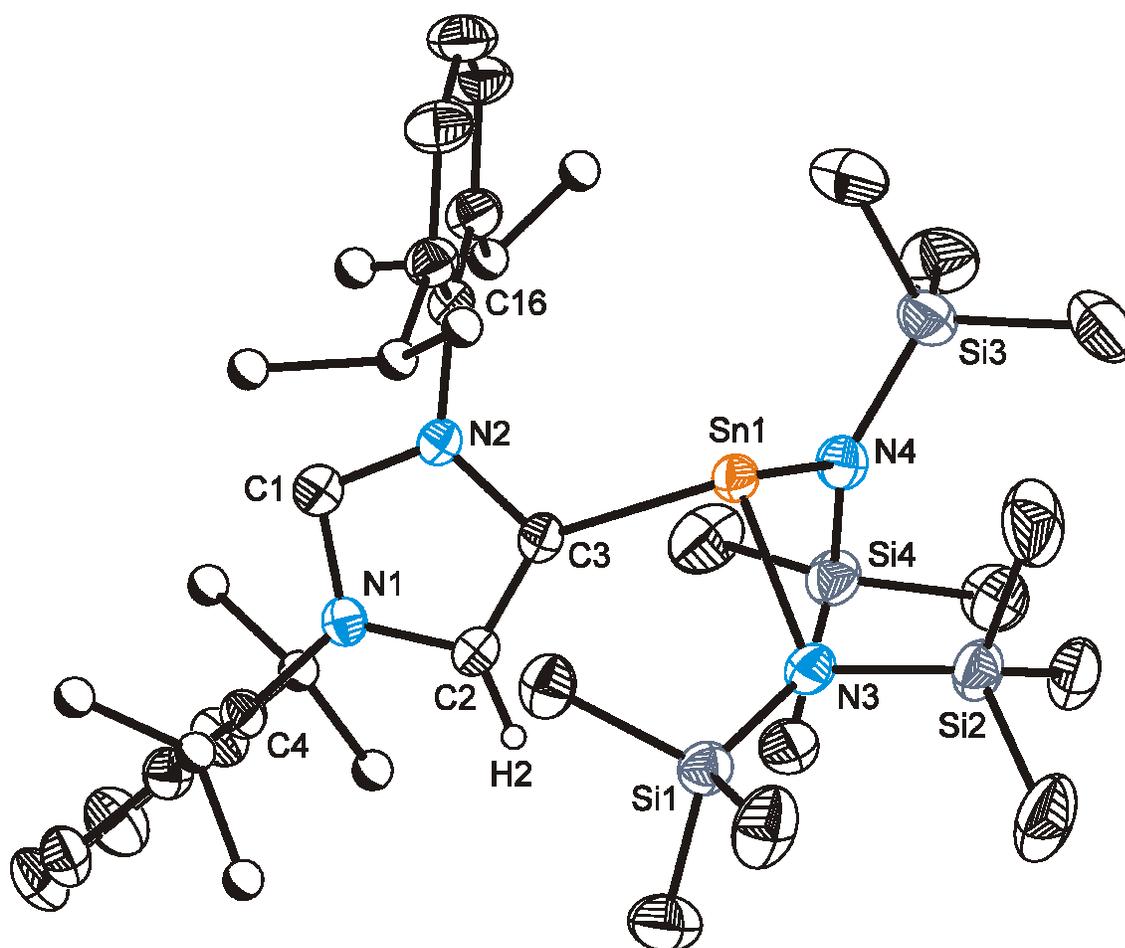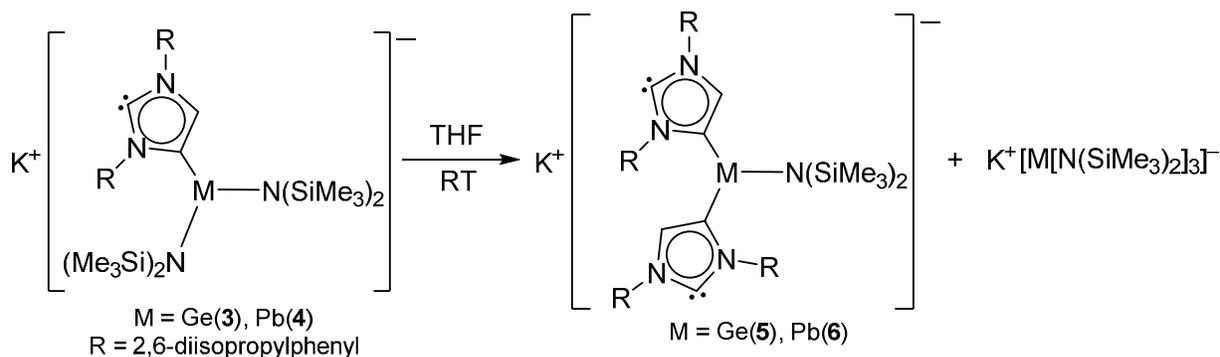
N3−Zn1−N4: 116.87(5).

Figure 3. Molecular structure of the anionic moiety in [K(18-crown-6)(THF)₂][**2**]·0.5THF (anisotropic displacement ellipsoids pictured at 50% probability level). All hydrogen atoms (with the exception of H2) have been omitted for clarity. Atoms of ^{i}Pr groups are pictured as spheres of arbitrary radius. Selected inter-atomic distances (Å) and angles (°): Sn1−C3: 2.277(3); Sn1−N3: 2.249(2); Sn1−N4: 2.198(2); C1−N1: 1.362(3); C1−N2: 1.368(3); N1−C2: 1.395(3); N2−C3: 1.422(3); C2−C3: 1.363(4); N1−C4: 1.439(3); N2−C16: 1.448(3); N3−Si1: 1.710(3); N3−Si2: 1.720(2); N4−Si3: 1.715(3); N4−Si4: 1.724(3); C3−Sn1−N3: 102.76(9); C3−Sn1−N4: 94.61(9); N3−Sn1−N4: 102.77(9).

*Attempted synthesis of 1:1 adducts between **KIPr** and M[N(SiMe$_3$)$_2$]$_2$ (M = Ge, Pb)*

A similar methodology to that employed for the synthesis of **1** and **2** was also used to synthesize the analogous germanium and lead compounds. Reaction of **KIPr** with one equivalent of M[N(SiMe$_3$)$_2$]$_2$ (M = Ge, Pb) in THF reveals the formation of [M{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}{N(SiMe$_3$)$_2$}$_2$]$^-$ (M = Ge (**3**), Pb (**4**)) by ^{1}H NMR spectroscopy. The NMR spectra are very similar to those of **1** and **2** and display an asymmetrically coordinated ditopic carbene. There are two methine resonances and a single alkenic proton which integrate in a 2:2:1 ratio. These were observed at for 3.08, 3.48 and 6.83 ppm for **3** and 3.06, 3.19 and 7.00 ppm for **4** (a full comparison of the ^{1}H NMR spectra for these compounds is provided in the ESI). The spectra are consistent with the formation of a 1:1 adduct containing a three-coordinate group 14 metal centre bearing two amides and a ditopic carbanionic carbene. However, when these solutions were left to stand for several hours, the NMR spectra increased in complexity.

Attempts to crystallize samples of **3** and **4** were unsuccessful, largely because in solution these species decompose over time, presumably via a Schlenk-like equilibrium to afford the bis-ditopic carbene complexes [M{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}$_2${N(SiMe$_3$)$_2$}]$^-$ (M = Ge (**5**), Pb (**6**)) and the corresponding metal tris-amide complexes [M{N(SiMe$_3$)$_2$}$_3$]$^-$ (as pictured in Scheme 3). In the case of the lead compound (**4**), this process is accompanied by extensive metallic decomposition, presumably a result of the instability of the tris-amide compound.

Scheme 3. Synthesis of **5** and **6** by decomposition of **3** and **4**.

Due to the relative instability of **3** and **4** in solution, no structural data could be recorded for compositionally pure samples. However compound **3** was found to co-crytallize alongside **5** in [K(18-crown-6)(THF)$_2$]$_2$[**3**][**5**]·THF (see Figure 4).
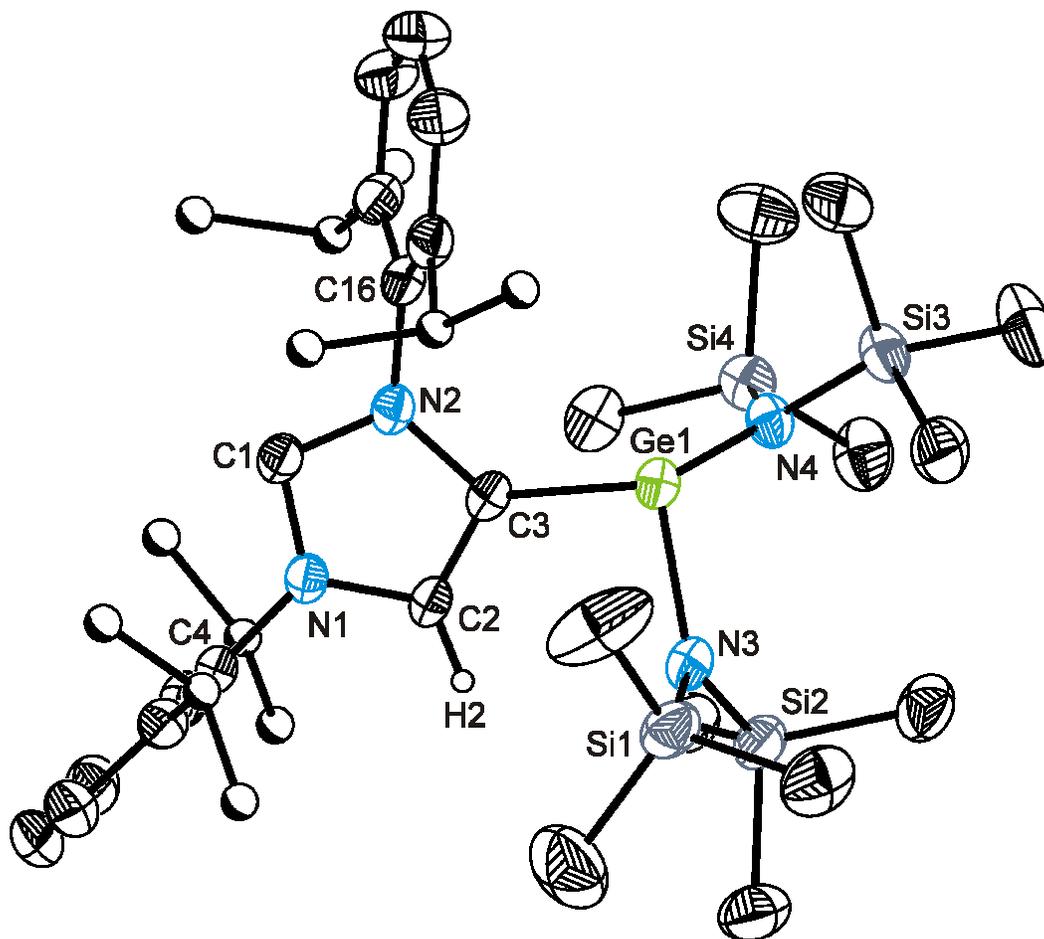
Figure 4. Molecular structure of **3**, one of the anionic moieties present in [K(18-crown-6)(THF)$_2$]$_2$[**3**][**5**]·THF (anisotropic displacement ellipsoids pictured at 50% probability level). All hydrogen atoms (with the exception of H2) have been omitted for clarity. Atoms of ^{i}Pr groups are pictured as spheres of arbitrary radius. Selected inter-atomic distances (Å) and angles (°): Ge1−C3: 2.059(2); Ge1−N3: 2.021(2); Ge1−N4: 1.984(2); C1−N1: 1.360(3); C1−N2: 1.371(3); N1−C2: 1.401(3); N2−C3: 1.431(3); C2−C3: 1.345(3); N1−C4: 1.430(3); N2−C16: 1.445(3); N3−Si1: 1.721(2); N3−Si2: 1.710(2); N4−Si3: 1.729(2); N4−Si4: 1.717(2); C3−Ge1−N3: 94.74(9); C3−Ge1−N4: 107.27(9); N3−Ge1−N4: 102.62(9).

Compound **3** exhibits a trigonal pyramidal germanium (II) centre coordinated by two amides and a carbanionic carbene via the backbone (C4/C5) position. The sum of the bond angles about the group 14 element centre for **3** is similar to that recorded for **2** ($\Sigma_{bond\ angles}$ = 304.6° *c.f.* $\Sigma_{bond\ angles}$ = 300.1° for **2**). The metal-carbanionic carbene distance is 2.059(2) Å for **3**, which is 0.22 Å shorter than the Sn−C distance in **2** and entirely consistent with the smaller covalent radius of germanium relative to tin (Δr = 0.19 Å).[10] A similar effect is observed for the Ge−N distances to the amide which are 2.021(2) and 1.984(2) Å and also 0.23 Å shorter than the equivalent distances in **2**.

A targeted synthesis of compounds **5** and **6** could be achieved by employing two equivalents of **KIPr** for every one equivalent of the M[N(SiMe$_3$)$_2$]$_2$ reagents. The ^{1}H NMR spectra of the crude reaction mixtures reveal the formation of K[N(SiMe$_3$)$_2$] as a side-product in addition to some complex resonances arising from the products. Judging by the number and intensity of the NMR resonances, compound **5** and **6** contain two equivalent ditopic carbenes with restricted rotation of the N−Dipp and M−N(SiMe$_3$)$_2$ bonds. This is not unsurprising considering the enormous degree of steric congestion around the metal centres. The ^{1}H NMR spectrum of **5** reveals four methine septet resonances (3.06, 3.04, 2.99 and 2.87 ppm) and eight doublets arising from the methyl substitutents (1.25, 1.16, 1.11, 1.08, 1.00, 0.95 and 0.87; two of which overlap). There is only a single alkenic proton resonance arising from the carbenes at 6.93 ppm which integrates as two protons. The data from the ^{13}C NMR spectra are consistent with this analysis and reveal inequivalent *ortho-* and *meta-* resonances for aromatic carbons belonging to the same Dipp group (twelve resonances in total arising from the aromatic carbon nuclei). Similarly two silicon resonances in the ^{29}Si NMR spectrum and two Si(CH$_3$)$_3$ environments in the ^{1}H spectrum confirm the reduced rotation around the metal−amide bond. The NMR data for **6** are similar to those recorded for **5** and are provided in the experimental section.
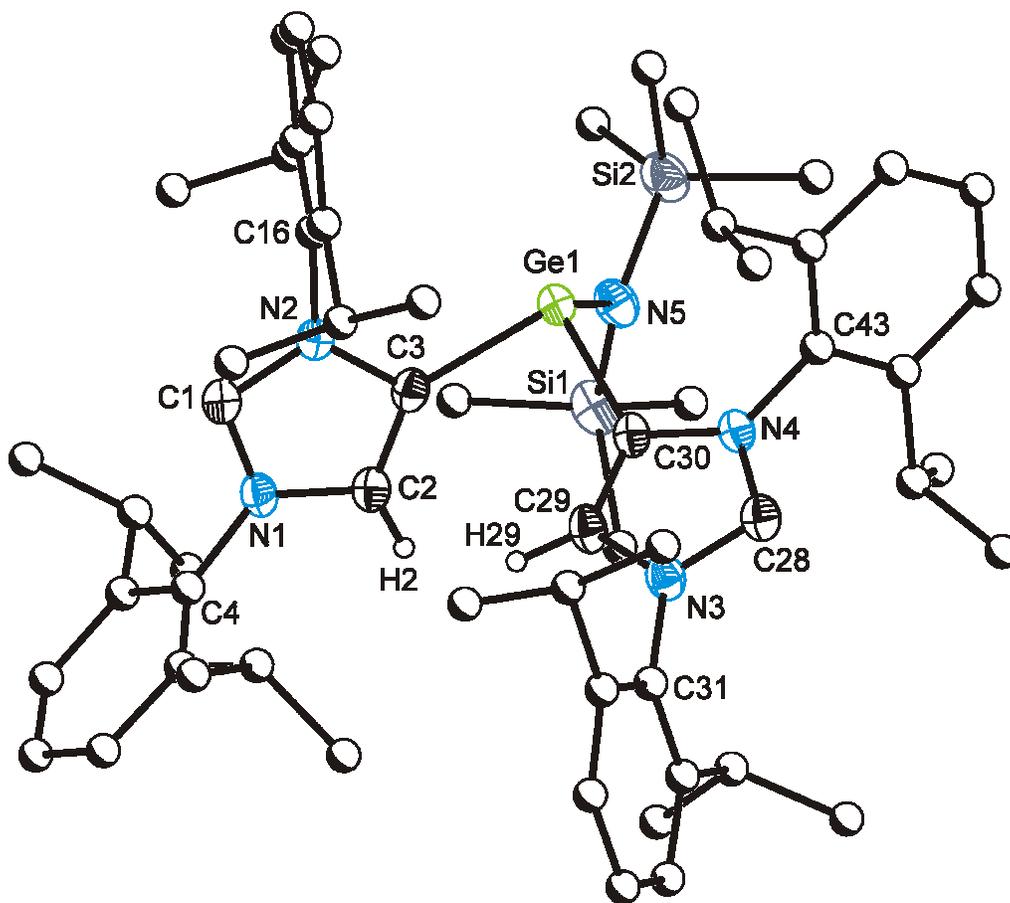
Figure 5. Molecular structure of the anionic moiety present in [K(18-crown-6)(THF)$_2$][**5**]·THF (anisotropic displacement ellipsoids pictured at 50% probability level). All hydrogen atoms (with the exception of H2) have been omitted for clarity. Atoms of Dipp and amide methyl groups are pictured as spheres of arbitrary radius for clarity. Selected inter-atomic distances (Å) and angles (°): Ge1−C3: 2.067(2); Ge1−C30: 2.038(2); Ge1−N5: 1.993(2); C1−N1: 1.362(3); C1−N2: 1.366(3); N1−C2: 1.396(2); N2−C3: 1.420(2); C2−C3: 1.360(3); N1−C4: 1.437(2); N2−C16: 1.448(3); C28−N3: 1.366(2); C28−N4: 1.374(3); N3−C29: 1.396(2); N4−C30: 1.417(2); C29−C30: 1.363(3); N3−C31: 1.438(3); N4−C43: 1.438(2); N5−Si1: 1.718(2); N5−Si2: 1.726(2); C3−Ge1−C30: 92.13(7); C3−Ge1−N5: 103.33(7); C30−Ge1−N5: 104.67(7).
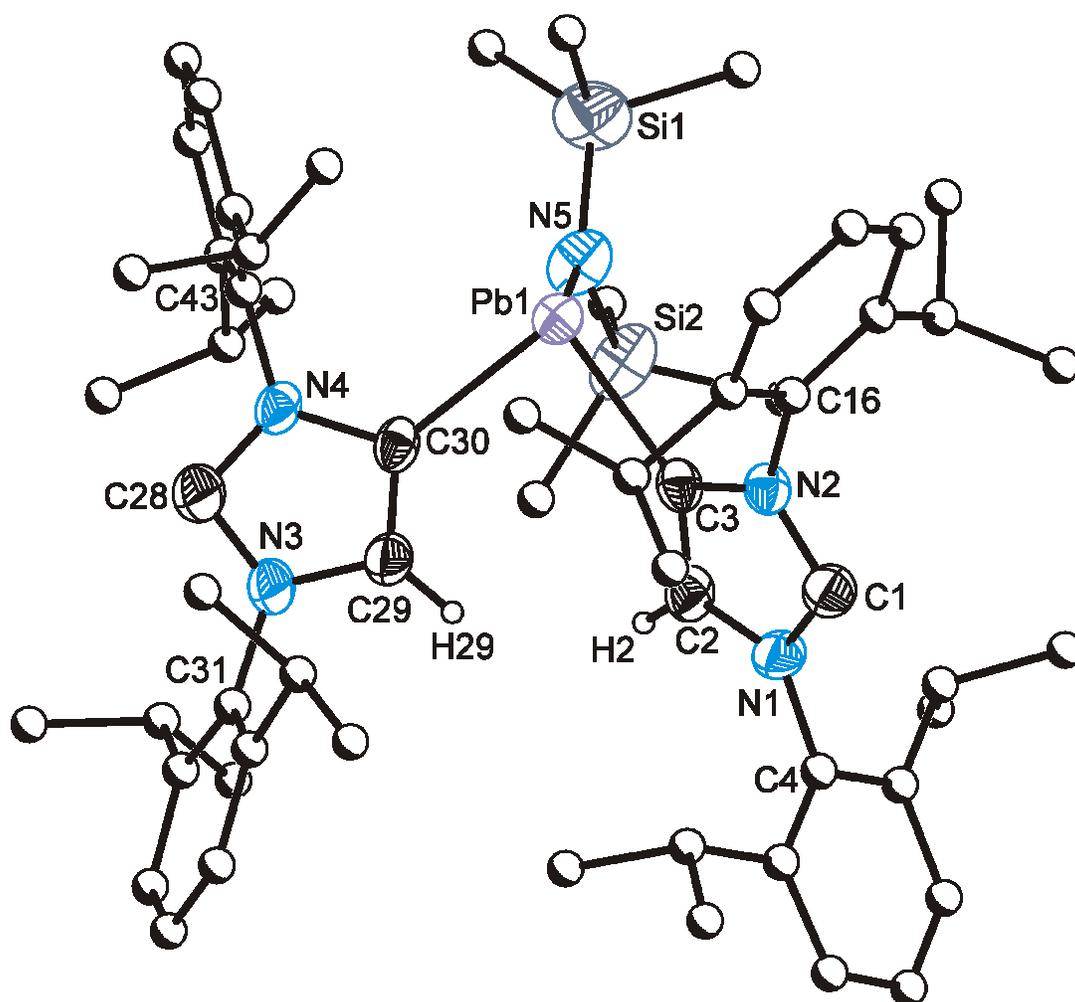
Figure 6. Molecular structure of one of the two anionic moieties present in the asymmetric unit of [K(18-crown-6)(THF)$_2$][**6**]·THF (anisotropic displacement ellipsoids pictured at 50% probability level). All hydrogen atoms (with the exception of H2) have been omitted for clarity. Atoms of Dipp and amide methyl groups are pictured as spheres of arbitrary radius for clarity. Selected inter-atomic distances (Å) and angles (°): Pb1−C3: 2.362(5); Pb1−C30: 2.339(5); Pb1−N5: 2.333(4); C1−N1: 1.368(6); C1−N2: 1.368(6); N1−C2: 1.397(6); N2−C3: 1.422(6); C2−C3: 1.362(6); N1−C4: 1.440(6); N2−C16: 1.440(5); C28−N3: 1.361(7); C28−N4: 1.367(6); N3−C29: 1.390(6); N4−C30: 1.419(6); C29−C30: 1.341(7); N3−C31: 1.467(7); N4−C43: 1.437(6); N5−Si1: 1.699(5); N5−Si2: 1.712(5); C3−Pb1−C30: 88.10(15); C3−Pb1−N5: 100.81(15); C30−Pb1−N5: 101.94(16).

Single crystal X-ray diffraction data for compounds **5** and **6** reveal trigonal pyramidal coordination environments around the group 14 elements and confirm the presence of two ditopic carbenes per metal centre. The geometries of **5** and **6** are comparable and display a great degree of steric congestion due to adjacent Dipp substituents (this is in line with previously discussed NMR data). The sum of the ligand−metal−ligand bond angles for **5** and **6** are similar to the other previously trigonal pyramidal structures discussed earlier (*vide supra*; $\Sigma_{\text{bond angles}}$ = 300.1° and 290.9 for **5** and **6**, respectively). Similarly, the M−C bond distances are also very similar to what we observed earlier. M−C bond distances in **5** are very closely-related to those observed for **3** (2.067(2) and 2.038(2) Å, *c.f.* 2.059(2)Å for **3**). The Pb−C distances for **6** are 2.362(5) and 2.339(5) Å (typically 0.29 Å longer than the analogous distances observed for **5** and in line with reported Δr_{cov} values of 0.23 and 0.26 Å).

Conclusions

We have shown that a novel alkali metal compound of a ditopic carbanionic carbene (**KIPr**) can be used as a synthon for the generation of novel polar organometallic species of the group 12 and group 14 elements. This chemistry bodes well for the development of novel species where a strongly polar covalent bond exists between a metal and an "abnormally-bonded" carbene which can still bind at the C2 carbenic site. On-going studies aimed at exploiting the unquenched carbenic nature of the ligands in such complexes for the activation of small molecules and supramolecular chemistry are currently underway.

Table 1. Selected X-ray data collection and refinement parameters for **KIPr**, [K(2,2,2-crypt)][**1**]·THF, [K(18-crown-6)(THF)$_2$][**2**]·0.5THF, [K(18-crown-6)(THF)$_2$]$_2$[**3**][**5**]·THF, [K(18-crown-6)(THF)$_2$][**5**]·THF and [K(18-crown-6)(THF)$_2$][**6**]·THF.

	KIPr	[K(2,2,2-crypt)][**1**]·THF	[K(18-crown-6)(THF)$_2$][**2**] ·0.5THF	[K(18-crown-6)(THF)$_2$]$_2$[**3**][**5**]·THF	[K(18-crown-6)(THF)$_2$][**5**]·THF	[K(18-crown-6)(THF)$_2$][**6**]·THF
Formula	C$_{35}$H$_{51}$KN$_2$O$_2$	C$_{61}$H$_{115}$KN$_6$O$_7$Si$_4$Zn	C$_{61}$H$_{115}$KN$_4$O$_{8.5}$Si$_4$Sn	C$_{143}$H$_{247}$Ge$_2$K$_2$N$_9$O$_{17}$Si$_6$	C$_{84}$H$_{136}$GeKN$_5$O$_9$Si$_2$	C$_{84}$H$_{136}$KN$_5$O$_9$PbSi$_2$
Fw [g mol^{-1}]	570.88	1261.42	1310.72	2756.42	1527.85	1662.45
crystal system	orthorhombic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	P2$_1$2$_1$2$_1$	P2$_1$/n	P2$_1$/c	P−1	P−1	P2$_1$/c
a (Å)	10.8804(1)	19.8505(1)	10.5971(1)	20.3166(2)	13.2441(1)	22.8186(1)
b (Å)	14.4926(1)	19.5586(1)	34.5475(2)	20.3325(2)	17.9105(2)	26.9545(2)
c (Å)	21.7725(2)	20.5305(1)	20.9338(1)	21.3303(2)	20.1807(2)	29.4392(2)
α (°)				104.6430(10)	78.741(1)	
β (°)		113.518(1)	104.365(1)	100.5850(10)	71.387(1)	90.504(1)
γ (°)				102.5840(10)	89.273(1)	
V (Å^3)	3433.20(5)	7308.82(8)	7424.32(9)	8049.90(14)	4443.00(7)	18106.3(2)
Z	4	4	4	2	2	8
radiation, λ (Å)			Mo Kα, 0.71073			
T (K)			150			
ρ$_{calc}$ (g cm^{-3})	1.104	1.146	1.173	1.137	1.142	1.220
μ (mm^{-1})	0.185	0.507	0.513	0.528	0.472	1.989
reflections collected	75520	32762	32574	60361	35110	73916
independent reflections	7781	16634	16832	36417	20161	40687
parameters	365	779	860	1666	964	1881
R(int)	0.0510	0.0174	0.0343	0.0327	0.0241	0.0448
R1/wR2,[a] I ≥ 2σI (%)	5.48/14.75	3.52/8.56	4.61/11.60	5.36/12.24	4.71/11.48	5.82/11.77
R1/wR2,[a] all data (%)	6.49/15.64	4.73/9.39	6.98/12.75	8.88/14.29	6.42/12.66	10.23/1367
GOF	1.035	1.039	1.021	1.016	1.020	1.038

[a] R1 = [Σ||F$_o$| − |F$_c$||]/Σ|F$_o$|; wR2 = {[Σw[(F$_o$)^2 − (F$_c$)^2]^2]/[Σw(F$_o$^{2})^2]}$^{1/2}$; w = [σ^2(F$_o$)^2 + (AP)^2 + BP]$^{-1}$, where P = [(F$_o$)^2 + 2(F$_c$)^2]/3 and the A and B values are 0.0946 and 0.94 for **KIPr**, 0.0424 and 3.35 for [K(2,2,2-crypt)][**1**]·THF, 0.0634 and 6.00 for [K(18-crown-6)(THF)$_2$][**2**]·0.5THF, 0.0578 and 6.55 for [K(18-crown-6)(THF)$_2$]$_2$[**3**][**5**]·THF, 0.0580 and 2.77 for [K(18-crown-6)(THF)$_2$][**5**]·THF, and 0.0469 and 43.44 for [K(18-crown-6)(THF)$_2$][**6**]·THF.

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Experimental

Experimental Section

General synthetic methods: All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at < 0.1 ppm H_2O and < 0.1 ppm O_2). $M[N(SiMe_3)_2]_2$ (M = Zn, Ge, Sn, Pb)), 1,3-bis(diisopropylphenyl)-imidazol-2-ylidene (IPr) and **LiIPr** were prepared according to previously reported literature procedures.[15,16,1a] 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]-hexacosane; VWR, 99%) and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane; 99%, Alfa Aesar) were used as received after careful drying under vacuum. Hexane (hex; HPLC grade, Sigma-Aldrich) and diethylether (Et_2O; pesticide residue grade, Fisher) were purified using an MBraun SPS-800 solvent system. Tetrahydrofuran (THF; HPLC grade, Sigma-Aldrich) was distilled over a sodium metal/benzophenone mixture. d_8-THF (99.5 %, Fluorochem) was dried over CaH_2 and vacuum distilled. All dry solvents were stored under argon in gas-tight ampoules. Additionally hexane, Et_2O and THF were stored over activated 3 Å molecular sieves.

*Synthesis of [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)CK] (**KIPr**).* [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)CLi]$_n$ (2.873 g, 7.29 mmol) and KO^{t}Bu (0.818 g, 7.29 mmol) were weighed into a Schlenk tube and cooled to −78 °C. Diethyl ether (50 mL) was added slowly under argon on a Schlenk line. The solution was allowed to stir for 30 minutes before being warmed to room temperature and stirred for a further 60 minutes resulting in an orange solution. The solution was filtered and concentrated to 5 mL, to which THF (40 mL) was added while stirring to give a white precipitate and an orange solution (containing LiO^{t}Bu). The mixture was cooled to −78 °C and filtered to yield a fine white powder. The solid was then washed with a further 20 mL of THF followed by 40 mL of hexane. The fine powder was dried under vacuum for 3 hours to afford 1.740 g (56% yield) of [:C[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$(CH)CK] (**KIPr**).

Anal. Calcd. for $KC_{27}H_{35}N_2$ (426.68): C 76.01%, H 8.27%, N 6.56%. Found: C 74.15%, H 8.17%, N 6.30%. Samples were found to reproducibly give low carbon values. The product could be crystallized by slow diffusion of hexane into a saturated THF solution to yield [:C[N(2,6-$^iPr_2C_6H_3$)]$_2$(CH)CK(THF)$_2$] as colourless crystals which were dried under an argon flow for 1 hour after decantation of the solvent. Anal. Calcd. for $KC_{35}H_{51}N_2O_2$ (570.89): C 73.64%, H 9.00%, N 4.91%. Found: C 72.94%, H 8.46%, N 5.48%. ESI-MS, negative-ion mode (THF): *m/z* 389.0 (100%) [:C{N(2,6-$^iPr_2C_6H_3$)CHC:}]⁻, 815.1 (10%) {[:C{N(2,6-$^iPr_2C_6H_3$)CHC:}]$_2$K}⁻. ^{1}H NMR (500.30 MHz, d_8-THF, 298K): δ (ppm) 7.13 (m, 1H; *para*-Dipp), 7.09 (m, 2H; *meta*-Dipp), 7.05 (s, 3H; *meta*- and *para*-Dipp), 6.07 (s, 1H; NCC*H*N), 3.28 (sept, $^3J_{H–H}$ = 7.0 Hz, 2H; C_6H_3\{C*H*(CH$_3$)\}$_2$), 3.04 (sept, $^3J_{H–H}$ = 7.0 Hz, 2H; C_6H_3\{C*H*(CH$_3$)\}$_2$), 1.12 (d, $^3J_{H–H}$ = 7.0 Hz, 6H; C_6H_3\{CH(C*H$_3$*)\}$_2$), 1.10 (d, $^3J_{H–H}$ = 7.0 Hz, 6H; C_6H_3\{CH(C*H$_3$*)\}$_2$), 1.08 (d, $^3J_{H–H}$ = 7.0 Hz, 12H; C_6H_3\{CH(C*H$_3$*)\}$_2$). ^{13}C\{^{1}H\} NMR (125.80 MHz, d_8-THF, 298K): δ (ppm) 215.1 (*C*N$_2$), 176.3 (NC*C*HN), 149.5 (*ipso*-Dipp), 147.2 (*ortho*-Dipp), 146.8 (*ortho*-Dipp), 143.8 (*ipso*-Dipp), 126.8 (NC*C*HN), 126.5 (*para*-Dipp), 125.7 (*para*-Dipp), 123.0 (*meta*-Dipp), 122.7 (*meta*-Dipp), 28.7 (C_6H_3\{*C*H(CH$_3$)\}$_2$), 28.6 (C_6H_3\{*C*H(CH$_3$)\}$_2$), 25.5 (C_6H_3\{CH(*C*H$_3$)\}$_2$, obscured by d_8-THF resonance, observable in ^{13}C DEPT 135 experiment), 25.4 (C_6H_3\{CH(*C*H$_3$)\}$_2$), 24.5 (C_6H_3\{CH(*C*H$_3$)\}$_2$), 24.0 (C_6H_3\{CH(*C*H$_3$)\}$_2$). No resonance observed in ^{7}Li NMR spectrum.

Synthesis of [K(2,2,2-crypt)][Zn{C(CH)[N(2,6-$^iPr_2C_6H_3$)]$_2$C:}{N(SiMe$_3$)$_2$}$_2$] ([K(2,2,2-crypt)][1]). **KIPr** (21 mg, 0.049 mmol) was weighed out in a glass vial in a glovebox and d_8-THF (500 μl) was added to form a slurry. Zn[N(SiMe$_3$)$_2$]$_2$ (20 μL, 0.049 mmol) was added via a microsyringe and the mixture stirred until a clear solution remained. 2,2,2-crypt (19 mg, 0.049 mmol) was added to the solution and stirred until the solid dissolved. The solution was then transferred to an NMR tube and characterized. Slow diffusion of hexane into a saturated solution of the reaction product afforded colourless crystals of [K(2,2,2-crypt)][**1**]·THF suitable for single crystal X-ray diffraction (44 mg,

76% crystalline yield). Anal. Calcd. for $C_{57}H_{107}KN_6O_6Si_4Zn$ (1189.35): C 57.59%, H 9.07%, N

7.07%. Found: C 57.60%, 8.55%, N 6.70%. ESI-MS, negative-ion mode (THF): *m/z* 773.9 (100%)

$[Zn\{C(CH)[N(2,6\text{-}^iPr_2C_6H_3)]_2C:\}\{N(SiMe_3)_2\}_2]^-$, 544.6 (85%) $[Zn\{N(SiMe_3)_2\}_3]^-$. ^1H NMR (499.94

MHz, d_8-THF, 298K): δ (ppm) 7.21 (m, 1H; *para*-Dipp), 7.13 (m, 2H; *meta*-Dipp), 7.11 (s, 3H;

meta- and *para*-Dipp), 6.92 (s, 1H; NCC*H*N), 3.54 (s, 12H; 2,2,2-crypt), 3.50 (t, $^3J_{H–H}$ = 4.6 Hz, 12H;

2,2,2-crypt), 3.23 (sept, $^3J_{H–H}$ = 7.0 Hz, 2H; $C_6H_3\{C\mathit{H}(CH_3)\}_2$), 3.03 (sept, $^3J_{H–H}$ = 7.0 Hz, 2H;

$C_6H_3\{C\mathit{H}(CH_3)\}_2$), 2.51 (t, $^3J_{H–H}$ = 4.6 Hz, 12H; 2,2,2-crypt), 1.28 (d, $^3J_{H–H}$ = 7.0 Hz, 6H;

$C_6H_3\{CH(C\mathit{H}_3)\}_2$), 1.16 (d, $^3J_{H–H}$ = 7.0 Hz, 6H, $C_6H_3\{CH(C\mathit{H}_3)\}_2$), 1.10 (d, $^3J_{H–H}$ = 7.0 Hz, 12H;

$C_6H_3\{CH(C\mathit{H}_3)\}_2$), −0.08 (s, satellites $^2J_{H–Si}$ = 6.4 Hz, 36H; $N\{Si(C\mathit{H}_3)_3\}_2$). $^{13}C\{^1H\}$ NMR (125.82

MHz, d_8-THF, 298K): δ (ppm) 219.9 (CN_2), 152.6 (NCCHN), 147.5 (*ortho*-Dipp), 146.6 (*ortho*-

Dipp), 145.4 (NCCHN), 142.0 (*ipso*-Dipp), 133.2 (*ipso*-Dipp), 127.8 (*para*-Dipp), 126.9 (*para*-

Dipp), 123.4 (*meta*-Dipp), 123.3 (*meta*-Dipp), 71.5 (2,2,2-crypt), 68.6 (2,2,2-crypt), 54.9 (2,2,2-

crypt), 29.1 ($C_6H_3\{\mathit{C}H(CH_3)\}_2$), 28.7 ($C_6H_3\{\mathit{C}H(CH_3)\}_2$), 27.1 ($C_6H_3\{CH(\mathit{C}H_3)\}_2$), 25.2

($C_6H_3\{CH(\mathit{C}H_3)\}_2$), 24.7 ($C_6H_3\{CH(\mathit{C}H_3)\}_2$), 23.5 ($C_6H_3\{CH(\mathit{C}H_3)\}_2$), 7.1 ($N\{Si(\mathit{C}H_3)_3\}_2$).

$^{29}Si\{^1H\}$ NMR (99.31 MHz, d_8-THF, 298K): δ (ppm) −9.7 (s).

[K(18-crown-6)][Sn{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}{N(SiMe$_3$)$_2$}$_2$] ([K(18-crown-6)][2]). As described

above using Sn[N(SiMe$_3$)$_2$]$_2$ (67 mg, 0.152 mmol), **KIPr** (65 mg, 0.152 mmol) and 18-crown-6 (40

mg, 0.152 mmol) in THF (5 mL). The solution was filtered into an ampoule. Slow diffusion of

hexane into the THF solution afforded colourless crystals of [K(18-crown-6)(THF)$_2$][**2**]·0.5THF

suitable for single crystal X-ray diffraction (165 mg, 96% crystalline yield). Anal. Calcd. for

$C_{59}H_{111}KN_4O_8Si_2Sn$ (1218.52): C 58.17%, H 9.18%, N 4.60%. Found C 56.25%, H 8.74%, N 4.34%.

ESI-MS, negative-ion mode (THF): *m/z* 826.2 (100%) $[Sn\{C(CH)[N(2,6\text{-}$

$^iPr_2C_6H_3)]_2C:\}\{N(SiMe_3)_2\}_2]^-$. ^1H NMR (499.94 MHz, d_8-THF, 298K): δ (ppm) 7.21 (m, 1H; *para*-

Dipp), 7.14 (overlapping multiplets, 3H; *meta*- and *para*-Dipp), 7.10 (m, 2H; *meta*-Dipp), 7.01 (s,

1H; NCC*H*N), 3.58 (s, 24H; 18-crown-6), 3.26 (sept, $^3J_{H–H}$ = 7.0 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 3.06

(sept, $^3J_{H–H}$ = 7.0 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 1.30 (d, $^3J_{H–H}$ = 7.0 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.17

(d, $^3J_{H–H}$ = 7.0 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.10 (d, $^3J_{H–H}$ = 7.0 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.09 (d,

$^3J_{H–H}$ = 7.0 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 0.04 (s, satellites $^2J_{H–Si}$ = 6.3 Hz, 36H; N{Si(C*H$_3$*)$_3$}$_2$).

^{13}C{^{1}H} NMR (125.80 MHz, d_8-THF, 298K): δ (ppm) 218.7 (*C*N$_2$), 163.2 (NC*C*HN), 147.5 (*ortho*-

Dipp), 147.1 (*ortho*-Dipp), 143.7 (*ipso*-Dipp), 141.7 (*ipso*-Dipp), 130.4 (*para*-Dipp), 127.8 (*para*-

Dipp), 127.3 (NC*C*HN), 123.4 (*meta*-Dipp), 123.2 (*meta*-Dipp), 71.3 (18-crown-6), 29.5

(C$_6$H$_3${*C*H(CH$_3$)}$_2$), 28.6 (C$_6$H$_3${*C*H(CH$_3$)}$_2$), 27.3 (C$_6$H$_3${CH(*C*H$_3$)}$_2$), 25.5 (C$_6$H$_3${CH(*C*H$_3$)}$_2$),

24.8 (C$_6$H$_3${CH(*C*H$_3$)}$_2$), 23.3 (C$_6$H$_3${CH(*C*H$_3$)}$_2$), 7.6 (s, satellites $^3J_{C–Sn}$ = 24.1 Hz, $^1J_{C–Si}$ = 53.2 Hz

N{Si(*C*H$_3$)$_3$}$_2$). ^{29}Si{^{1}H} NMR (99.32 MHz, d_8-THF, 298K): δ (ppm) –6.1 (s). ^{119}Sn {^{1}H} NMR

(186.43 MHz, d_8-THF, 298K): δ (ppm) 10.9 (s).

[K(18-crown-6)][Ge{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}}{N(SiMe$_3$)$_2$}$_2$] ([K(18-crown-6)][3]). As detailed

above using Ge[N(SiMe$_3$)$_2$]$_2$ (34 mg, 0.086 mmol), **KIPr** (37 mg, 0.086 mmol) and 18-crown-6 (23

mg, 0.084 mmol) in THF (5 mL). The ^{1}H NMR spectrum of the crude reaction mixture collected

immediately after the dissolution of the reagents is consistent with the formation of **3** (*vide infra*),

however over time these resonances decrease in intensity and new resonances appear in the

spectrum. Filtration of the reaction mixture afforded a colourless solution. Slow diffusion of hexane

into this solution afforded colourless crystals which were identified as [K(18-crown-

6)(THF)$_2$][Ge{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}{N(SiMe$_3$)$_2$}$_2$][Ge{C(CH)[N(2,6-

^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}$_2${N(SiMe$_3$)$_2$}]·THF by single crystal X-ray diffraction. ESI-MS, negative-ion mode

(THF): *m/z* 544.3 (100%) [Ge{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}{N(SiMe$_3$)}]⁻ + [Ge{N(SiMe$_3$)$_2$}$_3$]⁻,

771.6 (40%) [Ge{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}{N(SiMe$_3$)$_2$}$_2$]⁻, 1008.9 (15%) [Ge{C(CH)[N(2,6-

^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}$_2${N(SiMe$_3$)$_2$}$_2$]⁻. ^{1}H NMR (500.30 MHz, d_8-THF, 289K): δ (ppm) 7.20 (t, 1H; *para*-

Dipp), 7.14 (d, 2H; *meta*-Dipp), 7.11 (s, 3H; *meta*- and *para*-Dipp), 6.83 (s, 1H; NCC*H*N), 3.53 (s,

24H; 18-crown-6), 3.48 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H; $C_6H_3\{CH(CH_3)\}_2$), 3.08 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H; $C_6H_3\{CH(CH_3)\}_2$), 1.32 (d, $^3J_{H-H}$ = 7.0 Hz, 6H; $C_6H_3\{CH(CH_3)\}_2$), 1.16 (d, $^3J_{H-H}$ = 7.0 Hz, 6H; $C_6H_3\{CH(CH_3)\}_2$), 1.12 (d, $^3J_{H-H}$ = 7.0 Hz, 6H; $C_6H_3\{CH(CH_3)\}_2$), 1.06 (d, $^3J_{H-H}$ = 7.0 Hz, 6H; $C_6H_3\{CH(CH_3)\}_2$), 0.03 (s, satellites $^2J_{H-Si}$ = 5.6 Hz, 36H; $N\{Si(CH_3)_3\}_2$). $^{13}C\{^1H\}$ NMR (125.80 MHz, d_8-THF, 298K): δ (ppm) 219.7 (CN_2), 157.1 (NCCHN), 147.5 (*ortho*-Dipp), 147.1 (*ortho*-Dipp), 142.9 (*ipso*-Dipp), 142.0 (*ipso*-Dipp), 128.3 (*para*-Dipp), 127.8 (*para*-Dipp), 127.0 (NCCHN), 123.3 (*meta*-Dipp), 123.2 (*meta*-Dipp), 71.2 (18-crown-6), 29.9 ($C_6H_3\{CH(CH_3)\}_2$), 28.7 ($C_6H_3\{CH(CH_3)\}_2$), 27.8 ($C_6H_3\{CH(CH_3)\}_2$), 25.5 ($C_6H_3\{CH(CH_3)\}_2$, obscured by THF resonance), 24.6 ($C_6H_3\{CH(CH_3)\}_2$), 22.8 ($C_6H_3\{CH(CH_3)\}_2$), 7.5 ($N\{Si(CH_3)_3\}_2$). $^{29}Si\{^1H\}$ NMR (99.32 MHz, d_8-THF, 298K): δ (ppm) −5.6.

[K(18-crown-6)][Pb{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}{N(SiMe$_3$)$_2$}$_2$] *([K(2,2,2-crypt)][4])*. As detailed above using Pb[N(SiMe$_3$)$_2$]$_2$ (31 mg, 0.059 mmol), KIPr (25 mg, 0.059 mmol) and 18-crown-6 (16 mg, 0.059 mmol) in in d_8-THF (500 μL). The pale yellow solution was then transferred to an air-tight NMR tube and characterised by multielement NMR spectroscopy. ^1H NMR (500.30 MHz, d_8-THF, 298K): δ (ppm) 7.05–7.22 (m, 6H; *meta*- and *para*-Dipp), 7.00 (s, 1H; NCCHN), 3.55 (s, 24H; 18-crown-6), 3.19 (sept, $^3J_{H-H}$ = 7.0 Hz, 2H; $C_6H_3\{CH(CH_3)\}_2$), 3.06 (sept, $^3J_{H-H}$ = 7.0 Hz, 2H; $C_6H_3\{CH(CH_3)\}_2$), 1.29 (d, $^3J_{H-H}$ = 7.0 Hz, 6H; $C_6H_3\{CH(CH_3)\}_2$), 1.16 (d, $^3J_{H-H}$ = 7.0 Hz, 6H; $C_6H_3\{CH(CH_3)\}_2$), 1.10 (d, $^3J_{H-H}$ = 7.0 Hz, 12H; $C_6H_3\{CH(CH_3)\}_2$), 0.12 (satellites $^2J_{H-Si}$ = 6.6 Hz, 36H, $N\{Si(CH_3)_3\}_2$). $^{13}C\{^1H\}$ NMR (125.80 MHz, d_8-THF, 298K): δ (ppm) 216.1 (CN_2), 147.6 (*ortho*-Dipp), 147.2 (*ortho*-Dipp), 143.4 (NCCHN), 135.4 (NCCHN), 127.9 (*para*-Dipp), 127.6 (*para*-Dipp), 123.4 (*meta*-Dipp), 123.3 (*meta*-Dipp), 71.3 (18-crown-6), 29.1 ($C_6H_3\{CH(CH_3)\}_2$), 28.6 ($C_6H_3\{CH(CH_3)\}_2$), 26.9 ($C_6H_3\{CH(CH_3)\}_2$), 25.6 ($C_6H_3\{CH(CH_3)\}_2$), 24.8 ($C_6H_3\{CH(CH_3)\}_2$), 24.1 ($C_6H_3\{CH(CH_3)\}_2$), 7.8 ($N\{Si(CH_3)_3\}_2$). $^{29}Si\{^1H\}$ NMR (99.32 MHz, d_8-THF, 298K): δ (ppm) −9.7 (s).

[K(18-crown-6)][Ge{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}$_2${N(SiMe$_3$)$_2$}]   *([K(18-crown-6)][5]).*

Ge[N(SiMe$_3$)$_2$]$_2$ (43 mg, 0.109 mmol) was added to a glass vial in a glovebox and dissolved in THF

(5 mL). **KIPr** (93 mg, 0.219 mmol) was added to the mixture and stirred until a clear solution was

obtained. 18-crown-6 (58 mg, 0.219 mmol) was added to the solution and stirred until the solid

dissolved. The solution was filtered into a crystallisation ampoule and layered with hexane to afford

colourless crystals of [K(18-crown-6)(THF)$_2$][**5**]·THF suitable for single crystal X-ray diffraction

(125 mg, 77% crystalline yield). Anal. Calcd. for C$_{72}$H$_{112}$GeKN$_5$O$_6$Si$_2$ (1311.60): C 65.93%, H

8.61%, N 5.34%. Found: C 63.11%, H 8.26%, N 5.02%. ESI-MS, negative-ion mode (THF): m/z

1002.0 (100%) [Ge{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}$_2${N(SiMe$_3$)$_2$}]$^-$. ^{1}H NMR (499.94 MHz, d_8-THF,

298K): δ (ppm) 7.19 (t, 2H; *para*-Dipp), 7.01–7.12 (m, 10H; *meta*- and *para*-Dipp), 6.93 (s, 2H;

NCC*H*N), 3.48 (s, 24H; 18-crown-6), 3.06 (sept, $^3J_{H–H}$ = 6.8 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 3.04 (sept,

$^3J_{H–H}$ = 6.8 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 2.99 (sept, $^3J_{H–H}$ = 6.8 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 2.87

(sept, $^3J_{H–H}$ = 6.8 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 1.25 (d, $^3J_{H–H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.16

(d, $^3J_{H–H}$ = 6.8 Hz, 12H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.11 (d, $^3J_{H–H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.08 (d,

$^3J_{H–H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.00 (d, $^3J_{H–H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 0.95 (d, $^3J_{H–}$

$_H$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 0.87 (d, $^3J_{H–H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 0.03 (s, satellites

$^2J_{H–Si}$ = 6.0 Hz, 18H; N{Si(C*H$_3$*)$_3$}$_2$), –0.44 (s, satellites $^2J_{H–Si}$ = 6.0 Hz, 18H; N{Si(C*H$_3$*)$_3$}$_2$), –0.21

(present in crude reaction mixture, 18H, s, $^2J_{H–Si}$ = 6.1 Hz, KN{Si(C*H$_3$*)$_3$}$_2$). ^{13}C{^{1}H} NMR (125.82

MHz, d_8-THF, 298K): δ (ppm) 214.6 (*C*N$_2$), 154.1, 147.7, 147.5, 147.1, 147.0, 143.2, 140.9, 128.4,

128.1, 127.8, 123.9, 123.6, 123.5, 123.1, 71.2 (18-crown-6), 29.5 (C$_6$H$_3${*C*H(CH$_3$)}$_2$), 29.0

(C$_6$H$_3${*C*H(CH$_3$)}$_2$), 28.6 (C$_6$H$_3${*C*H(CH$_3$)}$_2$, two overlapping resonances), 26.7 (C$_6$H$_3${CH(*C*H$_3$)}$_2$),

26.2 (C$_6$H$_3${CH(*C*H$_3$)}$_2$), 25.6 (C$_6$H$_3${CH(*C*H$_3$)}$_2$, two overlapping resonances, obscured by THF

resonance, observable in ^{13}C DEPT 135 experiment), 25.0 (C$_6$H$_3${CH(*C*H$_3$)}$_2$, obscured by THF

resonance, observable in ^{13}C DEPT 135 experiment), 24.9 (C$_6$H$_3${CH(*C*H$_3$)}$_2$), 24.2

(C$_6$H$_3${CH(*C*H$_3$)}$_2$), 22.6 (C$_6$H$_3${CH(*C*H$_3$)}$_2$), 7.2 (N{Si(*C*H$_3$)$_3$}$_2$), 7.1 (N{Si(*C*H$_3$)$_3$}$_2$), 6.9

(KN{Si(CH_3)$_3$}$_2$, observable in crude reaction mixture). ^{13}C{^{1}H} DEPT 135 NMR (125.82 MHz, d_8-THF): δ (ppm) 128.4, 128.1, 127.8, 123.9, 123.6, 123.5, 123.1, 71.2 (18-crown-6), 29.5, 29.0, 28.6 (two overlapping resonances), 26.7, 26.2, 25.6 (two overlapping resonances), 25.0, 24.9, 24.2, 22.6, 7.2, 7.1. ^{29}Si{^{1}H} NMR (99.32 MHz, d_8-THF, 298K): δ (ppm) –2.6 (s), –3.5 (s), –25.1 (present in crude reaction mixture, s, KN{Si(CH_3)$_3$}$_2$).

[K(18-crown-6)][Pb{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}$_2${N(SiMe$_3$)$_2$}] ([K(18-crown-6)][6]).

Pb[N(SiMe$_3$)$_2$]$_2$ (37 mg, 0.077 mmol) was added to a glass vial in a glovebox and dissolved in THF (5 mL). **KIPr** (60 mg, 0.140 mmol) and 18-crown-6 (37 mg, 0.140 mmol) were added to the yellow solution and stirred until a clear solution was obtained. Filtration of the reaction mixture followed by slow diffusion of hexane into the solution afforded colourless crystals of [K(18-crown-6)(THF)$_2$][**6**]·THF suitable for single crystal X-ray diffraction. (88 mg, 79% crystalline yield). Anal. Calcd. for C$_{72}$H$_{112}$KN$_5$O$_6$PbSi$_2$ (1445.90): C 59.81%, H 7.81%, N 4.84%. Found: C 59.90%, H 7.59%, N 4.70%. ESI-MS, negative-ion mode (THF): *m/z* 1136.6 (100%) [Pb{C(CH)[N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}$_2${N(SiMe$_3$)$_2$}]$^-$. ^{1}H NMR (500.30 MHz, d_8-THF, 298K): δ (ppm) 7.04–7.19 (m, 12H; *meta-* and *para*-Dipp), 6.96 (s, 2H; NCC*H*N), 3.48 (s, 24H, 18-crown-6), 3.04 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 2.98 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 2.93 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 2.89 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H; C$_6$H$_3${C*H*(CH$_3$)}$_2$), 1.25 (d, $^3J_{H-H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.13 (d, $^3J_{H-H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.12 (d, $^3J_{H-H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.09 (d, $^3J_{H-H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.07 (d, $^3J_{H-H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.02 (d, $^3J_{H-H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 1.00 (d, $^3J_{H-H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), 0.86 (d, $^3J_{H-H}$ = 6.8 Hz, 6H; C$_6$H$_3${CH(C*H$_3$*)}$_2$), –0.23 (s, 36H; N{Si(C*H$_3$*)$_3$}$_2$. ^{13}C{^{1}H} NMR (100.62 MHz, d_8-THF, 298K): δ (ppm) 217.1 (*C*N$_2$), 191.8 (N*C*CHN), 147.8, 147.7, 147.1, 146.9, 144.1, 142.0, 134.2 (NCC*H*N), 127.8, 127.4, 123.5, 123.4, 123.1, 122.7, 71.3 (18-crown-6), 29.1, 28.9, 28.8, 28.6, 26.4, 26.3, 25.5 (obscured by THF resonance), 25.4, 25.1 (obscured

by THF resonance), 24.9, 24.2, 23.1, 7.5 (N{Si(CH_3)$_3$}$_2$). ^{13}C{^{1}H} DEPT 135 NMR (125.82 MHz,

d_8-THF, 298K): δ (ppm) 134.2, 127.8, 127.4, 123.5, 123.4, 123.1, 122.7, 71.3 (18-crown-6), 29.1

(C_6H_3{CH(CH_3)}$_2$), 28.9 (C_6H_3{CH(CH_3)}$_2$), 28.8 (C_6H_3{CH(CH_3)}$_2$), 28.6 (C_6H_3{CH(CH_3)}$_2$),

26.4   (C_6H_3{CH(CH_3)}$_2$),   26.3   (C_6H_3{CH(CH_3)}$_2$),   25.5   (C_6H_3{CH(CH_3)}$_2$),   25.4

(C_6H_3{CH(CH_3)}$_2$), 25.1 (C_6H_3{CH(CH_3)}$_2$), 24.9 (C_6H_3{CH(CH_3)}$_2$), 24.2 (C_6H_3{CH(CH_3)}$_2$),

23.1 (C_6H_3{CH(CH_3)}$_2$), 7.5 (N{Si(CH_3)$_3$}$_2$). ^{29}Si{^{1}H} NMR (99.32 MHz, d_8-THF, 298K): δ (ppm)

–6.1 (s).

Characterization Techniques

Single crystal X-ray diffraction data were collected using an Enraf-Nonius kappa-CCD

diffractometer equipped with a 95 mm CCD area detector. Crystals were selected under Paratone-N

oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2

cooling device.[17] Data were collected at 150 K using graphite monochromated Mo K$_\alpha$ radiation (λ =

0.71073 Å). Equivalent reflections were merged and the diffraction patterns processed with the

DENZO and SCALEPACK programs.[18] Structures were subsequently solved using direct methods or

using the charge flipping algorithm as implemented in the program SUPERFLIP,[19] and refined on F^2

using the SHELXL 97-2 package.[20]

NMR samples were prepared inside an inert atmosphere glovebox in NMR tubes equipped with a

gas-tight valve. ^{1}H and ^{13}C NMR spectra were acquired at 500.30 and 125.8 MHz, respectively on a

Bruker AVII or AVIII NMR spectrometer. ^{1}H and ^{13}C spectra are reported relative to TMS and were

referenced to the most downfield residual solvent resonance (d_8-THF: δ$_H$ 3.58 ppm, δ$_C$ 67.57 ppm).

Elemental analyses were performed by Elemental Microanalysis Ltd., Devon. 5–10 mg samples were

sent in sealed, evacuated Pyrex ampoules.

Electronic Supplementary Information. CCDC 994655−994660 contain the supplementary crystallographic data for this paper (www.ccdc.cam.ac.uk/data_request/cif). NMR and ESI-MS spectra are also available.

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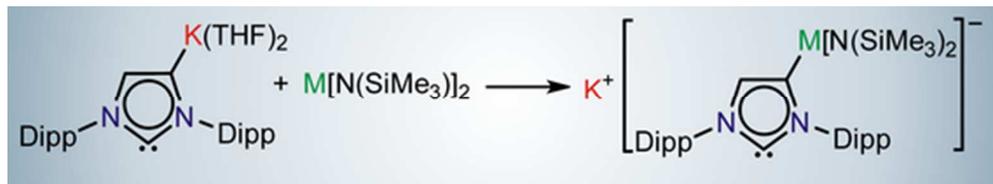
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