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Article

Complexes of an Anionic Gallium(I) *N*-Heterocyclic Carbene Analogue with Group 14 Element(II) Fragments: Synthetic, Structural and Theoretical Studies

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The reactions of the anionic gallium(I) *N*-heterocyclic carbene (NHC) analogue, [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}], Ar = $C_6H_3Pr^i{}_2$-2,6, with the heavier group 14 alkene analogues, $R_2E{=}ER_2$, E = Ge or Sn, R = –CH(SiMe$_3$)$_2$, have been carried out. In 2:1 stoichiometries, these lead to the ionic [K(tmeda)][R$_2$EGa{[N(Ar)C(H)]$_2$}] complexes which exhibit long E–Ga bonds. The nature of these bonds has been probed by DFT calculations, and the complexes have been compared to neutral NHC adducts of group 14 dialkyls. The 4:1 reaction of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] with $R_2Sn{=}SnR_2$ leads to the digallyl stannate complex, [K(tmeda)][RSn[Ga{[N(Ar)C(H)]$_2$}]$_2$], presumably via elimination of KR. In contrast, the reaction of the gallium heterocycle with PbR$_2$ affords the digallane(4), [Ga{[N(Ar)C(H)]$_2$}]$_2$, via an oxidative coupling reaction. For sake of comparison, the reactions of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] with $Ar'_2E{=}EAr'_2$, E = Ge, Sn or Pb, Ar′ = $C_6H_2Pr^i{}_3$-2,4,6, were carried out and led to either no reaction (E = Ge), the formation of [K(tmeda)][Ar′$_2$SnGa{[N(Ar)C(H)]$_2$}] (E = Sn), or the gallium(III) heterocycle, [Ar′Ga{[N(Ar)C(H)]$_2$}] (E = Pb). Salt elimination reactions between [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] and the guanidinato group 14 complexes [(Giso)ECl], E = Ge or Sn, Giso = [$Pr^i{}_2$NC{N(Ar)}$_2$]$^-$, gave the neutral [(Giso)EGa{[N(Ar)C(H)]$_2$}] complexes. All complexes have been characterized by NMR spectroscopy and X-ray crystallographic studies.

Introduction

The coordination chemistry of compounds containing a group 13 center in the +1 oxidation state is a rapidly emerging area. In this field, singlet metal diyls, :MR, M = Al−In, R = alkyl, aryl, etc., have been most studied as ligands for p- and d-block metal fragments.[1] More recently, the neutral six-membered heterocycles of Roesky[2] and Power,[3] [:M{[N(Ar)C(Me)]$_2$CH}], M = Al or Ga, Ar = $C_6H_3Pr^i{}_2$-2,6, have been enlisted by several groups for this cause.[4] Our group has been interested in studying the coordination chemistry of the anionic five-membered heterocyclic complex, [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}], **1**,[5] which is a valence isoelectronic analogue of the *N*-heterocyclic carbene (NHC) class of ligand. This has proven to be very fruitful, and complexes with a range of s-, p-, and d-block metal fragments have been reported.[6] Throughout this work a number of similarities with NHCs have been exhibited by **1**, including the ability of the heterocycle to stabilize thermally labile or low oxidation state metal fragments.

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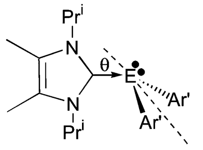
Chart 1



2 (Ar' = $C_6H_2Pr^i_3$-2,4,6)
E = Sn (θ = 68.6°, $Sn-C_{(carbene)}$ = 2.379(5) Å)
E = Pb (θ = 70.5°, $Pb-C_{(carbene)}$ = 2.540(5) Å)

Perhaps most success has come from the p-block coordination chemistry of **1**, which is known to form complexes with group 13, 15, 16, and 17 centers.[6] In contrast, attempts to form complexes of **1** with group 14 fragments have not been so rewarding, although some progress has been made. In this respect, theoretical studies on models of **1** have suggested that the heterocycle should be considered as a diamido complex of a Ga^+ center because of the electronegativity differences between Ga and N.[7] As a result, it is possible that this center could act as a nucleophile through its largely sp-hybridized singlet lone pair or as an electrophile by accepting donor electron density into its effectively empty gallium p-orbital, orthogonal to the heterocycle plane. In practice, although the strongly nucleophilic properties of **1** have been amply demonstrated, we have yet to coordinate even very strong group 14 nucleophiles such as NHCs to the Ga center of **1**. It is of interest, however, that the reaction of **1** with one imidazolium cation, $[HC\{N(Mes)C(H)\}_2]Cl$, IMesHCl, Mes = $C_6H_2Me_3$-2,4,6, has resulted in the oxidative insertion of its gallium center into a C−H bond of the cation and the formation of the NHC−gallium hydride heterocycle complex, $[HGa\{[N(Ar)C(H)]_2\}(IMes)]$.[8]

To further investigate the analogies between **1** and NHCs and to potentially prepare group 14 complexes of the heterocycle, we explored its reaction with heavier alkene analogues, $R_2E{=}ER_2$, E = Ge, Sn or Pb, and related compounds here. This work is directly related to earlier studies by Weidenbruch et al. who looked at the reactions of an NHC, $:C\{N(Pr^i)C(Me)\}_2$, with $Ar'_2E{=}EAr'_2$, Ar′ = $C_6H_2Pr^i_3$-2,4,6, E = Sn[9] or Pb.[10] In solutions, the distannene and diplumbene reaction precursors exist in equilibrium with their monomeric stannylene and plumbylene forms, $:EAr'_2$ (cf. carbenes, $:CR_2$), which form weakly coordinated complexes, **2** (Chart 1), with the NHC. The weakness of these interactions was shown by the fact that the complexes exhibit no $E-C_{(carbene)}$ double-bond character, have very long $E-C_{(carbene)}$ interactions, and possess relatively obtuse fold angles (*θ*) between the donor and acceptor fragments. It is of note that similar structural features have been reported for NHC complexes of GeI_2[11] and $SnCl_2$[12] and benzannulated NHC complexes of benzannulated N-heterocyclic silylenes, germylenes, stannylenes, and plumbylenes.[13] The results of the reactions between **1** and $R_2E{=}ER_2$, R = $-CH(SiMe_3)_2$, or Ar′; E = Ge, Sn or Pb (N.B: $Pb\{CH(SiMe_3)_2\}_2$ monomeric in the solid state) are compared to the work of Weidenbruch and are reported herein. For the sake of comparison, the outcomes of the salt elimination reactions of **1** with the monomeric guanidinato element chlorides, [(Giso)ECl], E = Ge, or Sn, Giso = $[Pr^i_2NC\{N(Ar)\}_2]^-$, are also described.

Experimental Section

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high purity argon. Diethyl ether, hexane, and toluene were distilled over Na/K alloy. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker DXP400 spectrometer operating at 400.13 and 100 MHz, respectively, or a JEOL Eclipse 300 spectrometer operating at 300.52 and 75.57 MHz, respectively, and were referenced to the resonances of the solvent used. $^{29}Si\{^1H\}$ NMR spectra were recorded on a JEOL Eclipse 300 spectrometer operating at 59.7 MHz and were referenced to $SiMe_4$. $^{119}Sn\{^1H\}$ NMR spectra were recorded on a Bruker AMX 500 spectrometer operating at 186.4 MHz and were referenced to $SnMe_4$. EI mass spectra and accurate mass EI mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were obtained from Medac Ltd. Where reproducible microanalyses could not be obtained because of the solvent of crystallization or the highly air-sensitive nature of the compound, the NMR spectra of the samples suggested purities of >95%. $[K(tmeda)][:Ga\{[N(Ar)C(H)]_2\}]$,[5] $[Ge\{CH(SiMe_3)_2\}_2]_2$,[14] $[Sn\{CH(SiMe_3)_2\}_2]_2$,[14] $[Sn(Ar')_2]_3$,[15] and $[Pb(Ar')_2]_2$[16] were synthesized by literature procedures. [(Giso)GeCl] and [(Giso)SnCl] were synthesized by unpublished procedures which involved the 1:1 reaction of [Li(Giso)][17] with either $GeCl_2$(dioxane) or $SnCl_2$ in diethyl ether. All other reagents were used as received.

The geometries of the model anions $[\{(Me_3Si)_2C(H)\}_2EGa\{[N(Ph)C(H)]_2\}]^-$, E = Ge or Sn, were optimized using the Gaussian 98 package,[18] employing the methods recommended by Boehme and Frenking.[19] That is the BP86 density functional method[20] with a 6-31G* basis set on C, N, and H[21] and Stuttgart−Dresden ECP/basis sets for Si, Ga, and Sn,[22] augmented by a d-type polarization function with an exponent of 0.207 on Ga, 0.183 on Sn and 0.246 on Ge.[23] Atomic charges, orbital populations, and bonding analyses were obtained from the NBO scheme[24] of the optimized structure. To comply with the maximum basis functions allowed by the NBO program, 6-31G basis sets were applied to the C and H atoms outside the gallium heterocycle and those not directly bound to the group 14 centers.

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Preparation of $[K(tmeda)][Ge\{CH(SiMe_3)_2\}_2Ga\{[N(Ar)C(H)]_2\}]$ (3). A solution of $[K(tmeda)][:Ga\{[N(Ar)C(H)]_2\}]$ (0.31 g, 0.51 mmol) in diethyl ether (20 cm^3) was added over 5 min to a solution of $[Ge\{CH(SiMe_3)_2\}_2]_2$ (0.20 g, 0.26 mmol) in diethyl ether (20 cm^3) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 24 h. Volatiles were removed in vacuo, and the residue was extracted with hexane (40 cm^3). Concentration to ca. 20 cm^3 and storage at −30 °C overnight yielded yellow crystals of **3** (0.28 g, 56%). mp: 110−112 °C (dec). ^1H NMR (400 MHz, C_6D_6): δ 0.16 (s, 18H, $Si(CH_3)_3$), 0.18 (s, 2H, $CH(SiMe_3)_2$) 0.22 (s, 18H, $Si(CH_3)_3$), 1.29 (d, $^3J_{HH} = 6.75$ Hz, 12H, $(CH_3)_2CH$), 1.32 (d, $^3J_{HH} = 6.75$ Hz, 12H, $(CH_3)_2CH$), 1.68 (s, 4H, NCH_2), 1.70 (s, 12 H, $(CH_3)_2N$), 3.84 (sept., $^3J_{HH} =$ 6.75 Hz, 4H, $CHMe_2$), 6.27 (s, 2H, $CH{=}CH$), 6.88 (t, $^3J_{HH} = 7.55$ Hz, 2H, *p*-ArH), 7.03 (d, $3J_{HH} = 7.55$ Hz, 4H, *m*-ArH). $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6): δ 3.1 ($CH(SiMe_3)_2$), 3.8 ($Si(CH_3)_3$), 4.5 ($Si(CH_3)_3$), 23.4 ($CH(CH_3)_2$), 26.6 ($CH(CH_3)_2$), 28.5 ($CHMe_2$), 45.5 ($N(CH_3)_2$), 57.0 ($N(CH_2)$), 121.9 (*C*N), 123.1 (*m*-Ar*C*), 123.7 (*p*-Ar*C*), 146.8 (*o*-Ar*C*), 150.3 (*ipso*-Ar*C*). $^{29}Si\{^1H\}$ NMR (59.7 MHz, C_6D_6): δ −0.95, −0.20 (*Si*Me$_3$). IR (Nujol): ν 1583 (s), 1564 (s), 1250 (s), 1101 (s), 1014 (s), 844 (s) cm^{-1}. (MS/EI) *m*/*z*: 446 $[Ga\{[N(Ar)C(H)]_2\}H^+$, 100%], 377 $[\{N(Ar)C(H)\}_2H^+$, 46%].

Preparation of $[K(tmeda)][Sn\{CH(SiMe_3)_2\}_2Ga\{[N(Ar)C(H)]_2\}]$ (4). A solution of $[K(tmeda)][:Ga\{[N(Ar)C(H)]_2\}]$ (0.27 g, 0.45 mmol) in diethyl ether (60 cm^3) was added over 1 h to a solution of $[Sn\{CH(SiMe_3)_2\}_2]_2$ (0.19 g, 0.23 mmol) in diethyl ether (40 cm^3) at −50 °C. The reaction mixture was stirred for 2 h, warmed to room temperature, and stirred for 24 h. Volatiles were removed in vacuo, and the residue was extracted with hexane (40 cm^3). Concentration to ca. 20 cm^3 and storage at −30 °C overnight yielded large red crystals of **4** (0.16 g, 35%). mp: 130−132 °C (dec). ^1H NMR (400 MHz, C_6D_6): δ 0.17 (s, 2H, $CH(SiMe_3)_2$), 0.20 (s, 18H, $Si(CH_3)_3$), 0.28 (s, 18H, $Si(CH_3)_3$), 1.29 (d, $^3J_{HH} =$ 6.77 Hz, 12H, $(CH_3)_2CH$), 1.32 (d, $^3J_{HH} = 6.77$ Hz 12H, $(CH_3)_2CH$), 1.67 (s, 4H, NCH_2), 1.72 (s, 12H, $(CH_3)_2N$), 3.87 (sept, $^3J_{HH}$ $= 6.77$ Hz, 4H, $CHMe_2$), 6.30 (s, 2H, $CH{=}CH$), 6.88 (t, $^3J_{HH} =$ 7.61 Hz, 2H, *p*-ArH), 7.04 (d, $^3J_{HH} = 7.61$ Hz, 4H, *m*-ArH). $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6): δ 3.8 ($CH(SiMe_3)_2$), 4.4 ($Si(CH_3)_3$), 4.7 ($Si(CH_3)_3$), 24.2 ($CH(CH_3)_2$), 26.4 ($CH(CH_3)_2$), 28.5 ($CHMe_2$), 45.2 ($N(CH_3)_2$), 56.7 ($N(CH_2)$), 122.2 (*C*N), 123.0 (*m*-Ar*C*), 123.8 (*p*-Ar*C*), 146.9 (*o*-Ar*C*), 150.2 (*ipso*-Ar*C*). $^{29}Si\{^1H\}$ NMR (59.7 MHz, C_6D_6): δ −0.04, 0.31 (*Si*Me$_3$). $^{119}Sn\{^1H\}$ NMR (186.4 MHz, C_6D_6): δ −97.9 (pw 233 Hz at 1/2 peak height). IR (Nujol): ν 1588 (s), 1565 (m), 1248 (s), 1113 (s), 1020 (s) cm^{-1}. (MS/EI) *m*/*z*: 446 $[Ga\{[N(Ar)C(H)]_2\}H^+$, 67%], 377 $[\{N(Ar)C(H)\}_2H^+$, 100%]. Anal. Calcd for $C_{46}H_{90}N_4Si_4KGaSn$: C, 53.17; H, 8.73; N, 5.39%. Found: C, 52.42; H, 8.60; N, 5.38%.

Preparation of $[K(tmeda)][Sn\{CH(SiMe_3)_2\}[Ga\{[N(Ar)C(H)]_2\}]_2]$ (5). A solution of $[K(tmeda)][:Ga\{[N(Ar)C(H)]_2\}]$ (0.56 g, 0.92 mmol) in diethyl ether (20 cm^3) was added over 5 min to a solution of $[Sn\{CH(SiMe_3)_2\}_2]_2$ (0.20 g, 0.23 mmol) in diethyl ether (20 cm^3) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. Volatiles were removed in vacuo, and the residue was extracted with hexane (40 cm^3). Concentration to ca. 15 cm^3 and storage at −30 °C overnight yielded orange crystals of **5**. (0.10 g, 16%). mp: 188−190 °C (dec). ^1H NMR (400 MHz, C_6D_6): δ 0.28 (s, 1H, $CH(SiMe_3)_2$), 0.35 (s, 18H, $Si(CH_3)_3$), 1.40 (br overlapping m, 48H, $(CH_3)_2CH$), 1.87 (s, 12H, $(CH_3)_2N$), 1.96 (s, 4H, NCH_2), 3.84 (br overlapping m, 8H, $CHMe_2$), 6.35 (br s, 4H, $CH{=}CH$), 7.11−7.15 (m, 12H, ArH). $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6): δ 1.2 ($CH(SiMe_3)_2$), 3.3 ($Si(CH_3)_3$), 23.9, 24.9, 26.0, 26.3 ($CH(CH_3)_2$), 28.1, 28.2 ($CHMe_2$), 45.3 ($N(CH_3)_2$), 57.0 ($N(CH_2)$), 123.0 (br, *C*N), 123.7 (br, *m*-Ar*C*), 124.4 (br, *p*-Ar*C*), 146.4 (br, *o*-Ar*C*), 152.6 (br, *ipso*-Ar*C*). $^{29}Si\{^1H\}$ NMR (59.7 MHz, C_6D_6): δ 0.30 (*Si*Me$_3$). IR (Nujol): ν 1652 (m), 1625 (m), 1594 (m), 1249 (s), 1106 (s), 1021 (s) cm^{-1}. (MS/EI) *m*/*z*: 446 $[Ga\{[N(Ar)C(H)]_2\}H^+$, 18%], 377 $[\{N(Ar)C(H)\}_2H^+$, 41%].

Preparation of $[K(tmeda)][Sn(Ar')_2Ga\{[N(Ar)C(H)]_2\}]$ (7). A solution of $[Sn(Ar')_2]_3$ (0.40 g, 0.25 mmol) in diethyl ether (60 cm^3) at −55 °C was irradiated at 256 nm for 3 h, yielding a red solution. This was cooled to −78 °C, and a solution of $[K(tmeda)][:Ga\{[N(Ar)C(H)]_2\}]$ (0.46 g, 0.76 mmol) in diethyl ether (30 cm^3) was added over 10 min. The reaction mixture was allowed to warm to room temperature over 12 h; then the volatiles were removed in vacuo, and the residue was extracted with hexane (120 cm^3). Concentration to ca. 80 cm^3 and storage at −30 °C overnight yielded orange crystals of **7**. (0.79 g, 92%). mp: 141−145 °C (dec). ^1H NMR (400 MHz, C_6D_6): δ 0.75 (d, $^3J_{HH} = 6.87$ Hz, 12H, p-$CH(CH_3)_2\{Ar'\}$), 0.91 (v tr, $^3J_{HH} = 6.80$ Hz, 24H, o-$CH(CH_3)_2\{Ar'\}$), 0.99 (d, $^3J_{HH} = 6.80$ Hz, 12H, $CH(CH_3)_2\{Ar\}$), 1.08 (d, $^3J_{HH} =$ 6.80 Hz, 12H, $CH(CH_3)_2\{Ar\}$), 1.45 (s, 12H, $N(CH_3)_2$), 1.50 (s, 4 H, NCH_2), 2.53 (sept., $^3J_{HH} = 6.87$ Hz, 2 H, p-$CHMe_2\{Ar'\}$), 3.46, 3.59 (2× sept, $^3J_{HH} = 6.80$ Hz, 2 × 4H, $CHMe_2\{Ar'$ and $Ar\}$), 6.09 (s, 2 H, $CH{=}CH$), 6.65 (t, $^3J_{HH} = 7.41$ Hz, 2H, p-$ArH\{Ar\}$), 6.76 (s, 4H, m-$ArH\{Ar'\}$), 6.78 (d, $^3J_{HH} = 7.41$ Hz, 4H, m-$ArH\{Ar\}$). $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6): δ 24.0, 24.4, 24.8, 25.1, 25.7 ($CH(CH_3)_2$), 28.5, 34.5, 39.6 ($CH(CH_3)_2$), 45.0 ($N(CH_3)_2$), 56.8 (NCH_2), 120.3 (*C*N), 122.5, 122.9, 123.9, 146.3, 146.9, 150.2, 153.9, 155.0 (Ar*C*). $^{119}Sn\{^1H\}$ NMR (186.4 MHz, C_6D_6): δ −306.7 (p.w. 251 Hz at 1/2 peak height). IR (Nujol): ν 1842 (m), 1666 (m), 1594 (s), 1556 (s), 1260 (s), 1099 (s) cm^{-1}. (MS/EI) *m*/*z*: 1126 [M^+, 3%], 648 $[Ar'Ga\{[N(Ar)C(H)]_2\}^+$, 100%], 446 $[Ga\{[N(Ar)C(H)]_2\}H^+$, 13%], 377 $[\{N(Ar)C(H)\}_2H^+$, 14%].

Preparation of $[Ar'Ga\{[N(Ar)C(H)]_2\}]$ (8). A solution of $[K(tmeda)][:Ga\{[N(Ar)C(H)]_2\}]$ (0.28 g, 0.46 mmol) in diethyl ether (30 cm^3) was added over 10 min to a solution of $[Pb(Ar')_2]_2$ (0.28 g, 0.23 mmol) in diethyl ether (20 cm^3) at −78 °C. The reaction mixture was warmed to room temperature over 2 h, during which time a lead mirror formed on the side of the vessel. Volatiles were then removed in vacuo, and the residue was extracted with hexane (40 cm^3). Concentration to ca. 5 cm^3 and storage at −30 °C

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overnight yielded yellow crystals of **8**. (0.04 g, 13%). mp: 112−114 °C. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 0.77 (d, $^3J_{\mathrm{HH}} = 6.67$ Hz, 12H, *o*-CH(C*H*$_3$)$_2${Ar′}), 0.80 (d, $^3J_{\mathrm{HH}} = 6.90$ Hz, 6H, *p*-CH(C*H*$_3$)$_2${Ar′}), 0.87 (d, $^3J_{\mathrm{HH}} = 6.80$ Hz, 12H, CH(C*H*$_3$)$_2${Ar}), 0.98 (d, $^3J_{\mathrm{HH}} = 6.80$ Hz, 12H, CH(C*H*$_3$)$_2${Ar}), 2.36 (sept, $^3J_{\mathrm{HH}} = 6.90$ Hz, 1H, *p*-C*H*(Me)$_2${Ar′}), 2.48 (sept, $^3J_{\mathrm{HH}} = 6.67$ Hz, 2H, *o*-C*H*(Me)$_2${Ar′}), 3.45 (sept, $^3J_{\mathrm{HH}} = 6.80$ Hz, 4H, C*H*(Me)$_2${Ar}), 6.14 (s, 2H, C*H*═C*H*), 6.58 (s, 2H, *m*-Ar*H*{Ar′}), 6.71−6.89 (m, 6H, Ar*H*{Ar}). ^{13}C{^{1}H} NMR (75.6 MHz, $\mathrm{C_6D_6}$): δ 23.7, 23.9, 24.6, 25.7 (CH(*C*H$_3$)$_2$), 28.5, 34.4, 40.9 (*C*H(CH$_3$)$_2$), 120.2 (*C*N), 121.42, 123.8, 125.3, 133.3, 144.5, 144.7, 151.9, 155.3 (Ar*C*). IR (Nujol): ν 1659 (m), 1593 (s), 1557 (m), 1260 (s), 1203 (s), 1118 (s), 1101 (s), 1058 (s), 934 (s) cm^{-1}. (MS/EI) *m*/*z*: 648 [M$^+$, 80%], 446 [Ga{[N(Ar)C(H)]$_2$}H$^+$, 5%], 377 [{N(Ar)C(H)}$_2$H$^+$, 83%]. Accurate MS (EI) calcd for $\mathrm{C_{41}H_{59}N_2{}^{69}Ga}$: 648.3929. Found: 648.3926. Anal. Calcd for $\mathrm{C_{41}H_{59}N_2Ga}$: C, 75.80; H, 9.15; N, 4.31%. Found: C, 74.97; H, 9.20; N, 4.40%.

Preparation of [(Giso)GeGa{[N(Ar)C(H)]$_2$}] (9). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.25 g, 0.41 mmol) in toluene (20 cm^3) was added over 5 min to a solution of [(Giso)GeCl] (0.24 g, 0.41 mmol) in toluene (10 cm^3) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. Volatiles were removed in vacuo, and the residue was extracted with hexane (20 cm^3). Concentration to ca. 5 cm^3 and storage at −30 °C overnight yielded light red crystals of **9** (0.26 g, 64%). mp: 149−152 °C (dec). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 0.77 (d, $^3J_{\mathrm{HH}} = 6.98$ Hz, 12H, (C*H*$_3$)$_2$CHN), 1.10 (2× coincidental d, $^3J_{\mathrm{HH}} = 6.71$ Hz, 12H, (C*H*$_3$)$_2$CH, Ge ring), 1.21 (d, $^3J_{\mathrm{HH}} = 6.89$ Hz, 12H, (C*H*$_3$)$_2$CH, Ga ring), 1.28 (d, $^3J_{\mathrm{HH}} = 6.81$ Hz, 6H, (C*H*$_3$)$_2$CH, Ge ring), 1.34 (d, $^3J_{\mathrm{HH}} = 6.81$ Hz, 6H, (C*H*$_3$)$_2$CH, Ge ring), 1.40 (d, $^3J_{\mathrm{HH}} = 6.89$ Hz, 12H, (C*H*$_3$)$_2$CH, Ga ring), 3.57 (sept, $^3J_{\mathrm{HH}} = 6.71$ Hz, 2H, C*H*Me$_2$, Ge ring), 3.68 (sept, $^3J_{\mathrm{HH}} = 6.81$ Hz, 2H, C*H*Me$_2$, Ge ring), 3.74 (sept, $^3J_{\mathrm{HH}} = 6.89$ Hz, 4H, C*H*Me$_2$, Ga ring), 3.87 (sept, $^3J_{\mathrm{HH}} = 6.98$ Hz, 2H, NC*H*Me$_2$), 6.40 (s, 2H, C*H*N) 7.03−7.29 (m, 12H, Ar*H*). ^{13}C{^{1}H} NMR (100.6 MHz, $\mathrm{C_6D_6}$): δ 22.9 (CH(*C*H$_3$)$_2$, Ge ring), 23.0 (CH(*C*H$_3$)$_2$, Ge ring), 23.2 (NCH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$, Ga ring), 25.6 (CH(*C*H$_3$)$_2$, Ga ring), 26.1 (CH(*C*H$_3$)$_2$, Ge ring), 27.8 (CH(*C*H$_3$)$_2$, Ge ring), 28.2 (*C*HMe$_2$, Ga ring), 28.4 (*C*HMe$_2$, Ge ring), 28.7 (*C*HMe$_2$, Ge ring), 49.0 (N*C*HMe$_2$), 122.5 (*C*N), 122.9, 124.1, 124.1, 124.8, 126.6, 138.5, 144.8, 145.3, 145.8, 147.5 (Ar*C*), 154.9 (*C*N$_3$). IR (Nujol): ν 1612 (w), 1586 (w), 1408 (s), 1256 (s), 1211 (w), 1120 (s), 1055 (m), 937 (w) cm^{-1}. (MS/EI) *m*/*z*: 981 [M$^+$, 5%], 377 [{N(Ar)C(H)}$_2$H$^+$, 8%]. Accurate MS (EI) calcd for $\mathrm{C_{57}H_{84}N_5GaGe}$: 981.5189. Found: 981.5182. Anal. Calcd for $\mathrm{C_{57}H_{84}N_5GaGe}$: C, 69.74; H, 8.62; N, 7.13%. Found: C, 69.61; H, 8.76; N, 7.32%.

Preparation of [(Giso)SnGa{[N(Ar)C(H)]$_2$}] (10). A solution of [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}] (0.29 g, 0.48 mmol) in toluene (20 cm^3) was added over 5 min to a solution of [(Giso)SnCl] (0.30 g, 0.48 mmol) in toluene (10 cm^3) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. Volatiles were removed in vacuo, and the residue was extracted with hexane (20 cm^3). Concentration to ca. 5 cm^3 and storage at −30 °C overnight yielded deep red crystals of **10** (0.26 g, 52%). mp: 205−206 °C. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 0.81 (d, $^3J_{\mathrm{HH}} = 6.91$ Hz, 12H, (C*H*$_3$)$_2$CHN), 1.12 (2× coincidental d, $^3J_{\mathrm{HH}} = 6.75$ Hz, 12H, (C*H*$_3$)$_2$CH, Sn ring), 1.23 (d, $^3J_{\mathrm{HH}} = 6.92$ Hz, 12H, (C*H*$_3$)$_2$CH, Ga ring), 1.30 (d, $^3J_{\mathrm{HH}} = 6.75$ Hz, 6H, (C*H*$_3$)$_2$CH, Sn ring), 1.37 (d, $^3J_{\mathrm{HH}} = 6.75$ Hz, 6H, (C*H*$_3$)$_2$CH, Sn ring), 1.40 (d, $^3J_{\mathrm{HH}} = 6.92$ Hz, 12H, (C*H*$_3$)$_2$CH, Ga ring), 3.61 (sept, $^3J_{\mathrm{HH}} = 6.75$ Hz, 2H, C*H*Me$_2$, Sn ring), 3.76 (overlapping m, 6H, C*H*Me$_2$, Ga (4H) and Sn (2H) rings), 3.92 (sept, $^3J_{\mathrm{HH}} = 6.91$ Hz, 2H, NC*H*Me$_2$), 6.51 (s, 2H, C*H*N) 7.10−7.28 (m, 12H, Ar*H*). ^{13}C{^{1}H} NMR (100.6 MHz, $\mathrm{C_6D_6}$): δ 22.9 (CH(*C*H$_3$)$_2$, Sn ring), 23.2 (CH(*C*H$_3$)$_2$, Sn ring), 23.4 (NCH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$, Ga ring), 25.6 (CH(*C*H$_3$)$_2$, Ga ring), 26.0 (CH(*C*H$_3$)$_2$, Sn ring), 27.6 (CH(*C*H$_3$)$_2$, Sn ring), 28.1 (*C*HMe$_2$, Ga ring), 28.5 (*C*HMe$_2$, Sn ring), 28.6 (*C*HMe$_2$, Sn ring), 49.1 (N*C*HMe$_2$), 122.9 (*C*N), 123.1, 123.9, 124.1, 125.0, 125.8, 139.9, 143.9, 145.2, 145.4, 147.0 (Ar*C*), 159.8 (*C*N$_3$). ^{119}Sn{^{1}H} NMR (186.4 MHz, $\mathrm{C_6D_6}$): δ 454.8 (pw 420 Hz at 1/2 peak height). IR (Nujol): ν 1613 (m), 1584 (m), 1256 (s), 1212 (m), 1116 (s), 1056 (m), 934 (w) cm^{-1}. (MS/EI) *m*/*z*: 1027 [M$^+$, 15%], 377 [{N(Ar)C(H)}$_2$H$^+$, 7%]. Accurate MS (EI) calcd for $\mathrm{C_{57}H_{84}N_5GaSn}$: 1027.4999. Found: 1027.5002. Anal. Calcd for $\mathrm{C_{57}H_{84}N_5GaSn}$: C, 66.62; H, 8.24; N, 6.81%. Found: C, 66.20; H, 8.30; N, 6.90%.

X-ray Crystallography. Crystals of **3**−**5** and **7**−**10** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 150 K, and the structures were solved by direct methods and refined on F^2 by full-matrix least-squares (SHELX97)[25] using all unique data. All non-hydrogen atoms are anisotropic (except the carbon atoms of the hexane of crystallization in the structure of **5**) with H atoms included in calculated positions (riding model). The X-ray data collected for **7** were weak. This led to the high *r* factors for this structure. Despite this, the molecular connectivity displayed by this structure is unambiguous. Crystal data and the details of the data collections and refinement are given in Table 1.

Results and Discussion

Reactions with Heavier Group 14 Alkene Analogues and PbR$_2$. The 2:1 reactions of **1** with Lappert's heavy alkene analogues, R$_2$E═ER$_2$, E = Ge or Sn, R = CH(SiMe$_3$)$_2$, or the plumbylene, R$_2$Pb, were carried out in diethyl ether at −78 °C with subsequent slow warming to room temperature. When E = Ge or Sn, the anionic complexes **3** and **4** were formed in moderate to good yields (Scheme 1). These complexes are closely related to **2** and likely result from coordination of the gallium heterocycle to the :ER$_2$ fragments which are known to be in equilibrium with R$_2$E═ER$_2$ in solution.[14] In contrast, the reaction with the plumbylene proceeded with deposition of lead metal and the formation of the known digallane(4), [Ga{[N(Ar)C(H)]$_2$}]$_2$.[26] The latter outcome presumably results from the relatively strongly reducing nature of the Ga(I) center of **1**. In attempts to form 2:1 complexes of the gallium heterocycle with :ER$_2$ fragments, **3** and **4** were reacted with a further equivalent of **1**. No reaction occurred with **3**, but surprisingly, that with **4** afforded the digallyl stannate complex **5** in a low isolated yield. No other products could be identified in the reaction mixture. It seems reasonable that the reaction that gave **5** proceeds via a dianionic intermediate, **6**, which then eliminates "KCH(SiMe$_3$)$_2$". It is noteworthy that we have previously observed the elimination of potassium alkyls in 2:1 reactions of **1** with metal dialkyls.[6g] Seemingly, **3** remains unreactive toward **1** because of the smaller radius and lower Lewis acidity of its Ge center relative to the Sn center of **4**.

To test the generality of these reactions and to draw closer comparisons with Weidenbruch's work, **1** was reacted with

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Table 1. Summary of Crystallographic Data for Compounds **3**−**5** and **7**−**10**

	3	**4**	**5**·(hexane)	**7**	**8**	**9**	**10**
empirical formula	$C_{46}H_{90}GaGeKN_4Si_4$	$C_{46}H_{90}GaKN_4Si_4Sn$	$C_{71}H_{121}Ga_2KN_6Si_2Sn$	$C_{62}H_{98}GaKN_4Sn$	$C_{41}H_{59}GaN_2$	$C_{57}H_{84}GaGeN_5$	$C_{57}H_{84}GaN_5Sn$
fw	992.99	1039.09	1412.15	1126.95	649.62	981.60	1027.70
cryst syst	orthorhombic	orthorhombic	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$Pca2_1$	$Pbca$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	21.370(4)	20.846(4)	14.4970(19)	12.574(3)	13.088(3)	17.899(4)	10.068(2)
b (Å)	14.035(3)	19.909(4)	16.782(2)	20.341(4)	16.091(3)	18.398(4)	20.314(4)
c (Å)	38.065(8)	28.145(6)	17.605(3)	25.091(5)	20.166(4)	17.119(3)	26.952(5)
α (deg)	90	90	77.940(10)	93.00(3)	109.23(3)	90	90
β (deg)	90	90	76.270(10)	91.05(3)	105.13(3)	90.16(3)	91.27(3)
γ (deg)	90	90	71.460(10)	99.22(3)	91.58(3)	90	90
vol (Å^3)	11417(4)	11681(4)	3903.1(9)	6324(2)	3840.8(13)	5637(2)	5511.1(19)
Z	8	8	2	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.155	1.182	1.202	1.184	1.123	1.157	1.239
μ (mm^{-1})	1.187	1.073	1.127	0.924	0.744	1.049	0.981
F(000)	4256	4400	1496	2392	1400	2096	2168
cryst size (mm)	0.25 × 0.25 × 0.15	0.30 × 0.25 × 0.20	0.25 × 0.25 × 0.20	0.23 × 0.20 × 0.17	0.30 × 0.30 × 0.20	0.50 × 0.50 × 0.40	0.25 × 0.15 × 0.15
θ range (deg)	1.74−26.37	2.92−27.55	2.93−26.48	4.10−25.20	2.97−26.03	3.18 to 27.00	2.94 to 26.00
reflns collected	100 746	103 668	55 245	40 379	49 660	41 622	19 123
R_{int}	0.0784	0.0792	0.0911	0.0418	0.0944	0.0526	0.0426
data/restraints/params	22 380/73/1165	13 392/18/538	15 862/6/746	22 107/24/1292	14 935/0/832	12 279/0/597	10 778/24/597
GOF on F^2	1.026	1.021	1.041	1.165	1.032	1.023	1.017
R1 indices [$I > 2\sigma(I)$][a]	0.0474	0.0368	0.0462	0.1366	0.0474	0.0356	0.0444
wR2 indices (all data)[a]	0.1038	0.0814	0.1142	0.3337	0.1127	0.0804	0.0958
largest peak and hole (e A^{-3})	0.714 and −0.426	0.810 and −0.758	1.216 and −0.829	2.704 (near Sn1) and −2.007 (near Ga1)	0.507 and −0.615	0.322 and −0.307	0.973 and −0.685

[a] $R1(F) = \{\Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. $wR2(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o{}^2|^2\}^{1/2}$ where w is the weight given each reflection.

$Ar'_2E{=}EAr'_2$, E = Ge, Sn (generated in situ), or Pb. In contrast to the formation of **3**, no reaction was observed with $Ar'_2Ge{=}GeAr'_2$. This is perhaps not surprising as the Ge=Ge bond in $Ar'_2Ge{=}GeAr'_2$ is significantly shorter and stronger than that in $\{(Me_3Si)_2C(H)\}_2Ge{=}Ge\{C(H)(SiMe_3)_2\}_2$. Accordingly, the latter largely dissociates into monomeric germylene fragments in solution,[14] whereas the former can behave as the dimeric digermene in solution,[27] although partial dissociation into germylene fragments is also likely for this compound. Similar to the formation of **4**, the reaction of **1** with an in situ generated solution of $Ar'_2Sn{=}SnAr'_2$ (which is known to be in equilibrium with the corresponding stannylene in solution) afforded the anionic complex, **7**, in an almost quantitative yield (Scheme 1). As opposed to the formation of **5**, when **7** was treated with a second equivalent of **1**, no reaction occurred. This might be the result of a reduced steric accessibility of the Ga heterocycle to the Sn center of **7** relative to that in **4**. When **1** was reacted with $Ar'_2Pb{=}PbAr'_2$, lead metal deposition was observed, as in its reaction with $Pb\{CH(SiMe_3)_2\}_2$. In this case, however, the only other identifiable product was the gallium heterocycle, **8**, which probably forms via the lead analogue of **7** which is most likely unstable at room temperature. Indeed, the neutral NHC adduct, **2** (E = Pb), is unstable in solution above −70 °C and decomposes to 1,3,5-triisopropylbenzene.[10] It is of note that a closely related gallium heterocycle,

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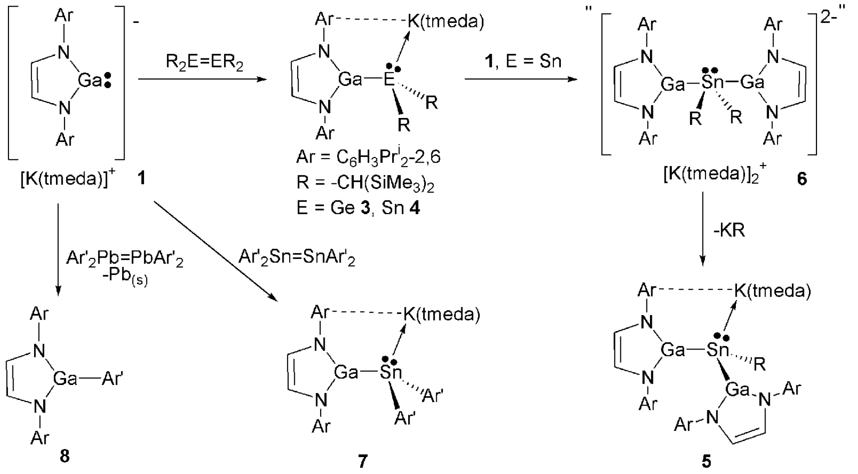
Scheme 1



$[(Me_3Si)_3CGa\{[N(Pr^i)C(H)]_2\}]$, has been recently reported to result from the reaction of the diazabutadiene, $\{N(Pr^i)C(H)\}_2$, with the tetrameric gallium diyl, $[\{GaC(SiMe_3)_3\}_4]$.[28] Attempts to intentionally prepare **8** via the reaction of **1** with Ar′Br were not successful and led to the formation of the known paramagnetic gallium(II) dimer $[BrGa\{[N(Ar)C(H)]_2^{\bullet}\}]_2$.[29]

The spectroscopic data for the anionic 1:1 and 2:1 complexes, **3**−**5** and **7**, suggest that the gallium heterocycle(s) remains coordinated to the germylene or stannylene fragments in solution. The ^1H and $^{13}C\{^1H\}$ NMR spectra are, however, more symmetrical than would be expected if the solid-state structures (vide infra) of the complexes were retained in solution. It is likely that the aryl-coordinated [K(tmeda)] cation of each complex either migrates rapidly (on the NMR time scale) between the aryl groups of the anions or the complexes are in equilibria between the contact ion pairs and ion separate salts. Such equilibria may be facilitated by the arene solvent (C_6D_6) used for the NMR experiments. All attempts to shed light on any fluxional processes occurring in solution (D_8-toluene) by variable-temperature NMR studies were thwarted by the poor solubility of the complexes at low temperatures. An examination of the ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra of **3** and **4** revealed these complexes to possess two sets of chemically inequivalent $SiMe_3$ groups in solution, as might be expected. The $^{119}Sn\{^1H\}$ NMR spectra of **4** and **7** each displayed broad singlet resonances at considerably higher fields (−97.9 and −306.7 ppm, respectively) than have reported for the related neutral complex, **2** (E = Sn, 710 ppm).[9] This is not surprising considering the anionic nature of these complexes which can be compared to trialkyl stannate anions (e.g., $LiSnMe_3$; $^{119}Sn\{^1H\}$ NMR −189.2 ppm).[30] No signal was observed in the $^{119}Sn\{^1H\}$ NMR spectrum of **5**. This is likely the result of the significant quadrupolar broadening of that signal by the two gallium centers coordinated to tin in that complex. Finally, the NMR spectra of the gallium heterocycle, **8**, are consistent with its solid-state structure and warrant no further comment.

X-ray crystallographic analyses of complexes **3**−**5**, **7**, and **8** were carried out. The molecular structures of **4**, **5**, and **8** are depicted in Figures 1−3. The crystal structure of **7** is of poor quality because of weak data but shows the complex to be structurally similar to **4**. As a result, a discussion of its molecular structure is only included in the Supporting Information, although some comparisons with the structures of **3**−**5** will be made here. Compounds **3** and **4** also have similar structures and therefore only the molecular structure of **4** is shown in Figure 1. The complexes are monomeric contact ion pairs in which the Ge or Sn centers are coordinated by two alkyl ligands and one gallium heterocycle. As in previously reported complexes of the gallium heterocycle,[6] its Ga−N distances and N−Ga−N angle are shorter and more obtuse, respectively, than those in the free heterocycle. The potassium centers of **3** and **4** are chelated by a molecule of tmeda, have an η^6-interaction with one of the aryl substituents of the gallium heterocycle, and are coordinated by the lone pair of the Ge or Sn center, respectively. The Ge−K and Sn−K bond lengths in these complexes (cf. 3.495(4) Å in **7**) lie in the normal ranges for such interactions.[31] In contrast, the Ge−Ga bond in **3** is very long and outside the known range (2.407−2.494 Å).[31] Although there have been no previously structurally characterized Sn−Ga bonds in molecular compounds, that in **4** (cf. 2.6660(18) Å in **7**) lies outside the sum of the covalent radii for the two elements (2.65 Å)[32] and therefore may be considered weak. This is, of course, very similar to the weak NHC−E interactions in **2**, and as in those compounds, the fold angles, θ, between the E−Ga vector and the C−E−C least-squares planes are obtuse at 70.5 (**3**) and 70.9° (**4**). Interestingly, this angle is considerably more acute in **7**

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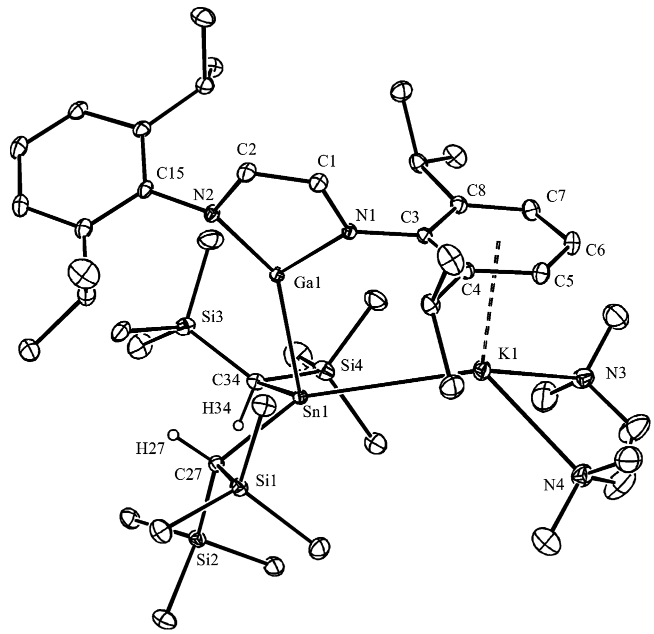

Figure 1. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[K(tmeda)][Sn\{CH(SiMe_3)_2\}_2Ga\{[N(Ar)C(H)]_2\}]$ (**4**); hydrogen atoms (except H(27) and H(34)) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−C(34) = 2.268(2), Sn(1)−C(27) = 2.280(2), Sn(1)−Ga(1) = 2.7186(6), Sn(1)−K(1) = 3.6407(9), Ga(1)−N(2) = 1.909(2), Ga(1)−N(1) = 1.9294(19), K(1)−N(4) = 2.820(3), K(1)−N(3) = 2.833(3), N(1)−C(1) = 1.397(3), N(2)−C(2) = 1.397(3), C(1)−C(2) = 1.343(3), K(1)−centroid (C(3)−C(8)) = 2.939(3), C(34)−Sn(1)−C(27) = 99.81(9), C(34)−Sn(1)−Ga(1) = 104.23(7), C(27)−Sn(1)−Ga(1) = 100.10(6), C(34)−Sn(1)−K(1) = 123.34(7), C(27)−Sn(1)−K(1) = 133.40(6), Ga(1)−Sn(1)−K(1) = 86.571(13), N(2)−Ga(1)−N(1) = 85.79(8), N(2)−Ga(1)−Sn(1) = 147.95(6), N(1)−Ga(1)−Sn(1) = 120.10(6). Selected bond lengths (Å) and angles (deg) for $[K(tmeda)][Ge\{CH(SiMe_3)_2\}_2Ga\{[N(Ar)C(H)]_2\}]$ (**3**): Ge(1)−C(27) = 2.085(4), Ge(1)−C(34) = 2.091(4), Ge(1)−Ga(1) = 2.5396(8), Ge(1)−K(1) = 3.4418(12), Ga(1)−N(2) = 1.911(4), Ga(1)−N(1) = 1.925(4), K(1)−N(3) = 2.783(4), K(1)−N(4) = 2.959(4), N(1)−C(1) = 1.398(6), N(2)−C(2) = 1.404(6), C(1)−C(2) = 1.324(6), K(1)−centroid (C(3)−C(8)) = 2.931(3), C(27)−Ge(1)−C(34) = 105.81(18), C(27)−Ge(1)−Ga(1) = 106.13(12), C(34)−Ge(1)−Ga(1) = 97.15(14), C(27)−Ge(1)−K(1) = 106.21(12), C(34)−Ge(1)−K(1) = 143.45(14), Ga(1)−Ge(1)−K(1) = 90.47(2), N(2)−Ga(1)−N(1) = 85.59(15), N(2)−Ga(1)−Ge(1) = 148.55(11), N(1)−Ga(1)−Ge(1) = 123.60(11).

(62.3°) but closer to the value for **2** (E = Sn) which incorporates the same stannylene fragment as **7**. The length of the E−Ga bonds and the magnitude of the fold angles, θ, for **3** and **4** suggest that the lone pair of the gallium heterocycle donates into the empty p-orbital of the germylene or stannylene fragments and that there is little "rehybridization" of the Ge or Sn centers upon coordination. Further evidence for this comes from the KEC_2 fragment which is not distorted far from planar as judged by the angle between the K−E vector and the EC_2 least-squares plane (**3**, 26.1°; **4**, 16.2°). It is interesting that this angle is significantly more acute in **4** which means that the coordination environment of the tin center directly opposite the gallium heterocycle is exposed. This could allow a second gallium heterocycle to attack the metal, as proposed for the mechanism of formation of the digallyl stannate, **5**.

The molecular structure of **5** is depicted in Figure 2. It is a monomeric contact ion pair with a tin center that possesses a distorted tetrahedral geometry. As in the previously described complexes, the potassium center is chelated by a molecule of tmeda, has an η^6-arene interaction, and is coordinated by the tin lone pair. Both the Sn−K and Sn−Ga distances are significantly shorter than those in **4** and the intraheterocyclic geometries are similar to those in previously reported complexes. The crystal structure of the monomeric, neutral gallium heterocycle, **8**, (Figure 3) contains two crystallographically independent molecules in the asymmetric unit which show no significant geometrical differences. As a result, geometric parameters for only one molecule are included in the caption of Figure 3. The gallium heterocycle is effectively planar and forms an angle of 52.3° with the Ar′ plane. The Ga−N bond lengths and N−Ga−N angle are similar to those in $[(Me_3Si)_3CGa\{[N(Pr^i)C(H)]_2\}]$[28] but shorter and more obtuse, respectively, than is normal for metal complexes of the gallium heterocycle.

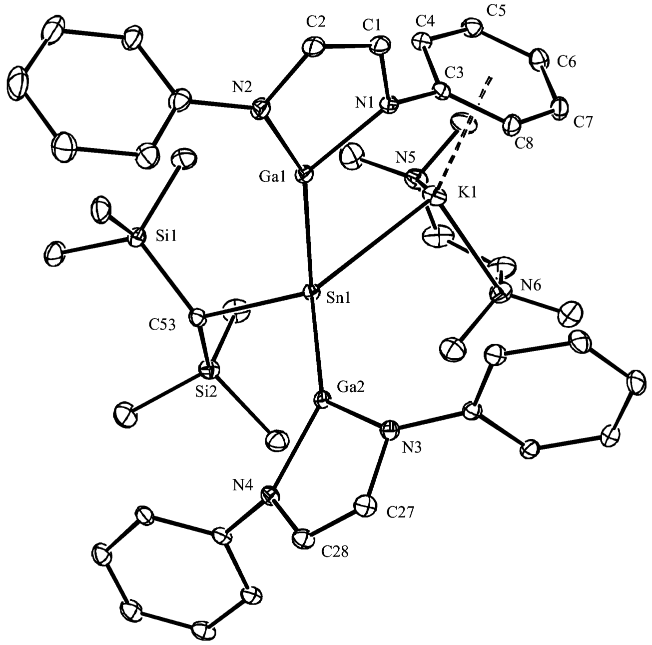

Figure 2. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[K(tmeda)][Sn\{CH(SiMe_3)_2\}[Ga\{[N(Ar)C(H)]_2\}]_2]$ (**5**); isopropyl groups and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg °): Sn(1)−C(53) = 2.259(3), Sn(1)−Ga(2) = 2.6361(5), Sn(1)−Ga(1) = 2.6610(6), Sn(1)−K(1) = 3.5082(10), Ga(1)−N(2) = 1.895(3), Ga(1)−N(1) = 1.916(3), Ga(2)−N(3) = 1.901(3), Ga(2)−N(4) = 1.902(3), K(1)−N(5) = 2.769(3), K(1)−N(6) = 2.784(3), N(1)−C(1) = 1.399(4), N(2)−C(2) = 1.402(4), N(3)−C(27) = 1.401(4), N(4)−C(28) = 1.400(4), C(1)−C(2) = 1.332(5), C(27)−C(28) = 1.336(5), K(1)−centroid (C(3)−C(8)) = 2.866(3), C(53)−Sn(1)−Ga(2) = 98.11(8), C(53)−Sn(1)−Ga(1) = 108.57(9), Ga(2)−Sn(1)−Ga(1) = 96.009(16), C(53)−Sn(1)−K(1) = 123.22(8), Ga(2)−Sn(1)−K(1) = 134.39(2), Ga(1)−Sn(1)−K(1) = 88.767(19), N(2)−Ga(1)−N(1) = 86.73(12), N(2)−Ga(1)−Sn(1) = 155.80(9), N(1)−Ga(1)−Sn(1) = 117.35(8), N(3)−Ga(2)−N(4) = 87.51(11), N(3)−Ga(2)−Sn(1) = 138.80(8), N(4)−Ga(2)−Sn(1) = 133.38(8).

To shed light on the nature of the weak Ga−E bonds in **3** and **4**, DFT calculations were carried out on the model anions, $[\{(Me_3Si)_2C(H)\}_2EGa\{[N(Ph)C(H)]_2\}]^-$, E = Ge or Sn. These complexes converged with similar geometries to those of **3** and **4**, although the bonds about the heavier group 14 and gallium centers were overestimated by 3−5%, as has been previously seen for DFT studies on metal complexes of the $[Ga\{[N(Ph)C(H)]_2\}]^-$ heterocycle.[6] In addition, the angles between the planes of the phenyl substituents and the plane of the gallium heterocycle are significantly more acute than in the experimental complexes. This is, no doubt, a result

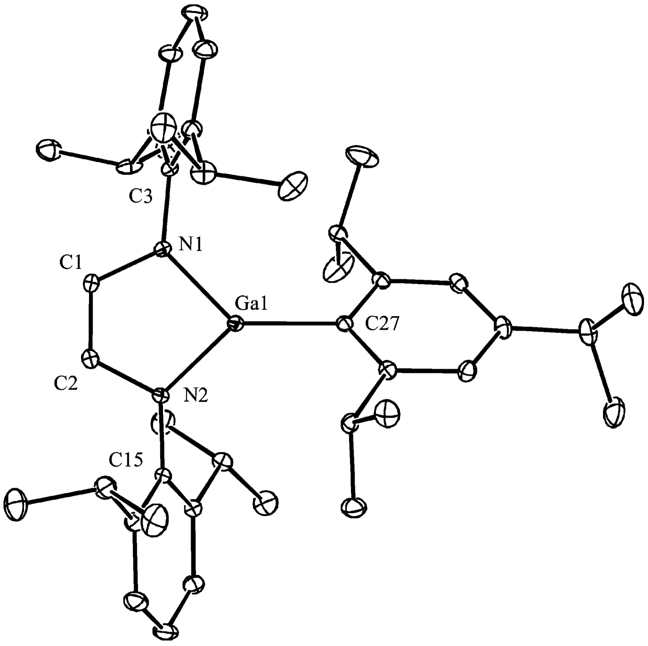

Figure 3. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[\mathrm{Ar'Ga\{[N(Ar)C(H)]_2\}}]$ (**8**); hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)−N(1) = 1.846(2), Ga(1)−N(2) = 1.848(2), Ga(1)−C(27) = 1.936(3), N(1)−C(1) = 1.400(3), N(2)−C(2) = 1.406(3), C(1)−C(2) = 1.343(4), N(1)−Ga(1)−N(2) = 89.65(10), N(1)−Ga(1)−C(27) = 134.58(10), N(2)−Ga(1)−C(27) = 135.77(10), C(1)−N(1)−Ga(1) = 108.76(17), C(2)−N(2)−Ga(1) = 108.15(17).

of the lack of phenyl substitution in the model anions. Despite this and the fact that coordination to countercations has not been taken into account in the model systems, the angles about the E centers of the theoretical anions are close to those for **3** and **4**. Most importantly, the fold angles, θ, (E = Ge (72.4°), Sn (74.8°)) are in good agreement with the experimental complexes.

An NBO analysis of the Ga−E bonds (Wiberg bond indices for E = Ge and Sn are 0.998 and 0.952, respectively) in $[\{(\mathrm{Me_3Si})_2\mathrm{C(H)}\}_2\mathrm{EGa\{[N(Ph)C(H)]_2\}}]^-$ revealed that the orbital contributions from the E centers are of very high p-character (for E = Ge, s = 4.4% and p = 95.4% and for E = Sn, s = 4.7% and p = 95.1%), while the orbital contributions from the donating Ga centers have s- to sp-character (for E = Ge, s = 77.6% and p 22.3% and for E = Sn, s = 64.4% and p = 35.5%). This is consistent with the apparently weak E−Ga bonds and the minimal "rehybridization" of the E centers upon heterocycle coordination. As might be expected, the lone pairs at the E centers of the anions have significant s-character (E = Ge (78.6%), Sn (80.9%)). The orbitals that have the greatest contribution to the E−Ga bonds and the E lone pairs are the HOMO−3 and HOMO−1, respectively, which differ in energy by 32.3 and 31.4 kcal/mol for **9** and **10,** respectively. Illustrations of these orbitals for the germanium system are depicted in Figure 4. The HOMO and HOMO−2 are largely ligand-based orbitals.

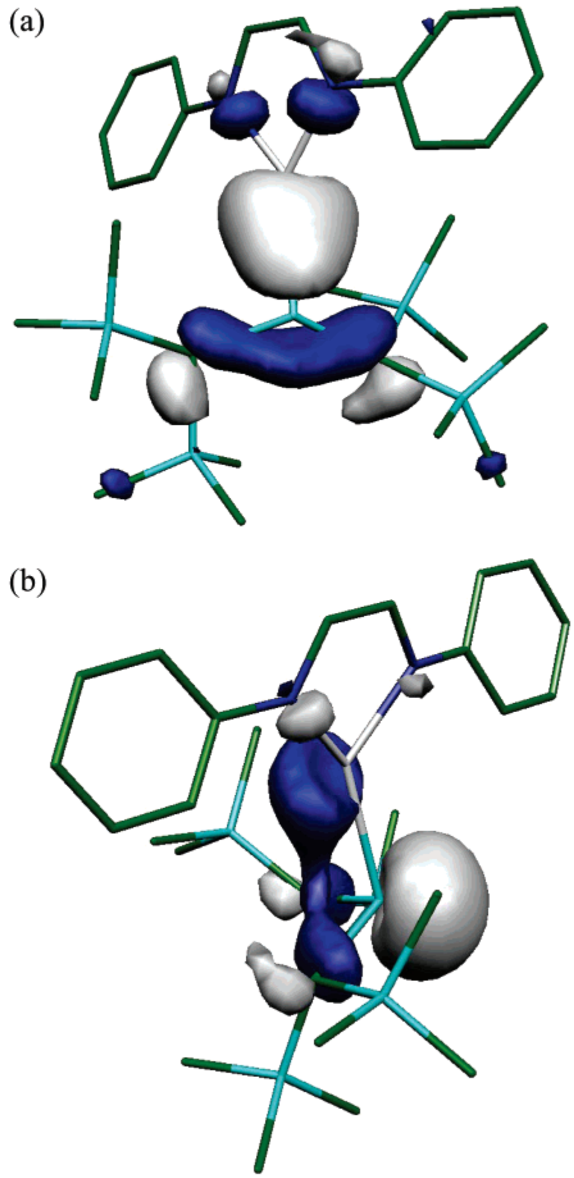

Figure 4. Representations of (a) the HOMO−3 and (b) the HOMO−1 of the model anionic system $[\{(\mathrm{Me_3Si})_2\mathrm{C(H)}\}_2\mathrm{GeGa\{[N(Ph)C(H)]_2\}}]^-$.

Reactions with Guanidinato Group 14 Element(II) Chlorides. Complexes **3** and **4** can be considered as weakly bound "adducts" of an anionic gallium(I) heterocycle with germylene or stannylene fragments. It was thought logical to attempt the preparation of germanium(II) and tin(II) complexes of the heterocycle that contain more normal covalent bonds for the purpose of comparison. Obviously, this should be achievable by salt elimination reactions between **1** and compounds of the type REX, E = Ge or Sn, X = halide. However, all previous attempts to use **1** in metathesis reactions with metal halide complexes have been unsuccessful, leading to paramagnetic gallium(II) dimers, $[\mathrm{XGa\{[N(Ar)C(H)]_2^{\bullet}\}}]_2$,[29] presumably via insertion of the Ga(I) center into the M−X bond of the precursor, followed by decomposition. Recently, we have discovered that if the metal halide precursor incorporates a bulky neutral or anionic chelating ligand, then the formation of $[\mathrm{XGa\{[N(Ar)C(H)]_2^{\bullet}\}}]_2$ can be circumvented. We have developed synthetic routes to monomeric germanium(II) and tin(II) halide complexes (e.g., [(Giso)ECl] E = Ge or Sn)[33] stabilized by

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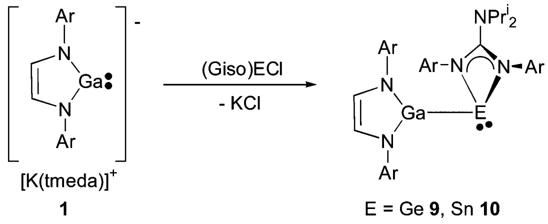
(33) Jones, C.; Junk, P. C.; Stasch, A. unpublished results.

Scheme 2



very bulky guanidinate ligands and saw these as ideal starting materials for this study.

The 1:1 reactions of **1** with [(Giso)ECl], E = Ge or Sn, in toluene led to good yields of the monomeric germanium or tin−gallyl complexes, **9** and **10** (Scheme 2). Both compounds were found to be unreactive toward excess **1**. The ^{1}H and ^{13}C{^{1}H} NMR spectra of both complexes are similar and consistent with the retention of their solid state structures in solution. The presence of only two methyl doublet resonances for the isopropyl groups of the gallium heterocycle in the spectra of both compounds suggests that the rotation of that heterocycle about the E−Ga bond is not restricted. This has been noted previously for complexes of the heterocycle.[6] Despite this, resonances for four chemically inequivalent sets of methyl groups from the group 14 heterocycle aryl substituents were necessarily observed in the spectra of the complexes. The ^{119}Sn{^{1}H} NMR spectra of **10** exhibits a broad singlet (454.8 ppm) in the normal region for neutral complexes, containing a 3-coordinate tin(II) center (cf. **2**; E = Sn, δ 710 ppm).[9]

Compounds **9** and **10** have similar structures, and so only the molecular structure for **9** (Figure 5) is included here. Relevant geometric parameters for **10** are included in the caption of Figure 5. Both compounds are monomeric and contain heavily distorted pyramidal germanium or tin centers. Although the Ge−Ga bond of **9** is significantly shorter than that of **3**, it still lies outside the otherwise known range for such bonds.[31] Similarly, the Sn−Ga distance for **10** is less than that for **4** (but longer than that for **7**) but can still be considered long. The reason for these long interactions must be partly the steric crowding between the bulky gallium and group 14 heterocycles. Another manifestation of this is that the gallium−group 14 element bonds are significantly “skewed” with the E−Ga−{C(32)−C(33) bond midpoint} angles being markedly distorted from the ideal 180° (**9**, 153.5°; **10**, 157.9°). In all other aspects, the geometries of the effectively planar gallium heterocycles in both compounds are almost symmetrical and unremarkable. Although the four-membered Ge and Sn heterocycles are strained, their guanidinate ligands appear to be largely delocalized, and their E−N bond lengths lie well within the reported ranges.[31] The angles between the two heterocycles are 74.9° in **9** and 76.7° in **10**.

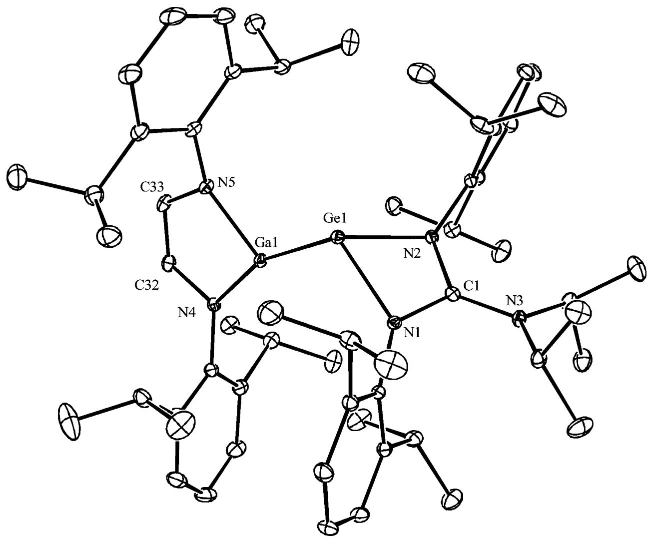


Figure 5. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [(Giso)GeGa{[N(Ar)C(H)]$_2$}] (**9**); the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) = 1.9971(15), Ge(1)−N(2) = 2.0148(16), Ge(1)−Ga(1) = 2.5157(7), Ga(1)−N(4) = 1.8825(16), Ga(1)−N(5) = 1.8898(16), N(1)−C(1) = 1.353(2), N(2)−C(1) = 1.346(2), N(3)−C(1) = 1.369(2), N(4)−C(32) = 1.396(2), N(5)−C(33) = 1.389(3), C(32)−C(33) = 1.344(3), N(1)−Ge(1)−N(2) = 65.03(6), N(1)−Ge(1)−Ga(1) = 108.98(5), N(2)−Ge(1)−Ga(1) = 105.07(4), N(4)−Ga(1)−N(5) = 87.10(7), N(4)−Ga(1)−Ge(1) = 161.38(5), N(5)−Ga(1)−Ge(1) = 110.50(5), C(1)−N(1)−Ge(1) = 93.53(11), C(1)−N(2)−Ge(1) = 92.95(11), N(2)−C(1)−N(1) = 106.08(16). Selected bond lengths (Å) and angles (deg) for [(Giso)SnGa{[N(Ar)C(H)]$_2$}] (**10**): Sn(1)−N(1) = 2.188(3), Sn(1)−N(2) = 2.215(3), Sn(1)−Ga(1) = 2.6888(6), Ga(1)−N(4) = 1.882(3), Ga(1)−N(5) = 1.890(3), N(1)−C(1) = 1.365(4), N(2)−C(1) = 1.345(4), N(3)−C(1) = 1.371(4), N(4)−C(32) = 1.401(4), N(5)−C(33) = 1.388(5), C(32)−C(33) = 1.349(5), N(1)−Sn(1)−N(2) = 60.18(10), N(1)−Sn(1)−Ga(1) = 104.39(8), N(2)−Sn(1)−Ga(1) = 99.70(7), N(4)−Ga(1)−N(5) = 87.56(13), N(4)−Ga(1)−Sn(1) = 157.14(9), N(5)−Ga(1)−Sn(1) = 114.63(10), C(1)−N(1)−Sn(1) = 95.3(2), C(1)−N(2)−Sn(1) = 94.7(2), N(2)−C(1)−N(1) = 109.1(3).

Conclusions

In summary, the reactions of an anionic gallium(I) heterocyclic complex, [K(tmeda)][:Ga{[N(Ar)C(H)]$_2$}], with a variety of heavier group 14 element(II) precursors have been carried out. In the case of the reactions with R$_2$E=ER$_2$, E = Ge or Sn, the ionic [K(tmeda)][R$_2$EGa{[N(Ar)C(H)]$_2$}] complexes, which exhibit long E−Ga bonds, are formed. The tin complex exhibits the first structurally characterized example of such a bond in a molecular compound. The nature of the E−Ga bonds has been probed by DFT calculations, and the complexes have been shown to be closely related to neutral NHC adducts of group 14 dialkyls. It is of interest that the tin complex reacts with a further equivalent of the gallium heterocycle (to give [K(tmeda)][RSn[Ga{[N(Ar)C(H)]$_2$}]$_2$]), whereas its germanium counterpart is unreactive. Moreover, the complexes, Ar′$_2$E=EAr′$_2$, E = Ge, Sn, or Pb, were found to be, in general, less reactive than R$_2$E=ER$_2$ toward the gallium heterocycle. The study has also highlighted the utility of the anionic gallium(I) heterocycle in potassium halide elimination reactions for the first time. Its reaction with bulky monomeric guanidinato group 14 halide complexes has given neutral complexes, [(Giso)EGa{[N(Ar)C(H)]$_2$}], E = Ge or Sn, with covalent E−Ga bonds that are shorter than the E−Ga interactions seen in the aforementioned anionic complexes. Despite this, these bonds are still long, presumably because of considerable steric crowding within the complexes.

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Supporting Information Available: Crystallographic data as CIF files for **3**−**5** and **7**−**10**, details of the molecular structure of **7**, and Cartesian coordinate files and details of the NBO analyses of the model anions, $[\{(Me_3Si)_2C(H)\}_2EGa\{[N(Ph)C(H)]_2\}]^-$, E = Ge or Sn. This material is available free of charge via the Internet at http://pubs.acs.org.

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