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Communications

Temperature-dependant Electron Shuffle in Molecular Group 13/15 Intermetallic Complexes

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*Dedicated to Prof. Dr. R. Zellner on the occasion of his 70th birthday*

*Abstract: Mono-valent RAl (R = HC[C(Me)N(2,6-i-Pr$_2$C$_6$H$_3$)]$_2$) reacts with E$_2$Et$_4$ (E = Sb, Bi) with insertion into the weak E-E bond and subsequent formation of RAl(EEt$_2$)$_2$ (E = Sb **1**; Bi **2**). The analogous reaction of RGa with E$_2$Et$_4$ yields a temperature-dependant equilibrium between RGa(EEt$_2$)$_2$ (E = Sb **3**; Bi **4**) and the starting reagents. RIn does not interact with Sb$_2$Et$_4$ under various reaction conditions, but formation of RIn(BiEt$_2$)$_2$ (**5**) was observed in the reaction with Bi$_2$Et$_4$ at low temperature.*

Since the discovery of the first mono-valent group 13 diyl Cp*Al more than 20 years ago,[1] compounds of the general type R'M [M = Al, Ga; R' = Cp*, diketiminates, ...] have emerged from laboratory curiosities to versatile compounds in inorganic and organic syntheses.[2] The powerful reducing activity of *β*-diketiminate aluminum and gallium complexes make them very unique and they were used for the activation of small molecules such as azides, diimines, O$_2$, S$_8$, P$_4$, acetylene and others.[3] Reduction reactions of RGa with main metal compounds such as SnCl$_2$[4] and Bi(OR")$_3$[5] yielded novel gallyl-supported tin clusters [Sn$_7${Ga(Cl)(R)}$_2$] and [Sn$_{17}${Ga(Cl)(R)}$_4$] and galla-dibismuthenes [RGa(OR")Bi]$_2$ (R" = C$_6$F$_5$, SO$_2$CF$_3$). These reactions straightforwardly proceeded with oxidation of the group 13 metal and subsequent metal-metal bond formation. Mono-valent group 13 complexes RM were also found to serve as unique ligands in transition metal chemistry due to the presence of a metal-centered electron lone pair.[6] Metal olefin, carbonyl and isonitrile complexes were found to react with MR' with substitution of the carbonyl group and formation of intermetallic cluster complexes as was reported by Fischer et al.[7]

Despite these significant findings, there still remains interest in understanding the bonding situation in intermetallic compounds containing only weak metal-metal interactions and how the electrons interact in these complexes. Due to our general interest in weak metal-metal bonding,[8] in particular in group 13-Bi compounds,[9] we became interested in reactions of mono-valent group 13 compounds RM (M = Al,[10] Ga,[11] In[12]; (R = HC[C(Me)N(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_2$) with low-valent group 15 complexes of the general type Et$_2$E-EEt$_2$ containing the heaviest group 15 elements, Sb and Bi.[13] We herein report on the formation of a temperature-dependant

equilibrium between metal-metal bonded species RM(EEt$_2$)$_2$ and the starting reagents RM and E$_2$Et$_4$.

Equimolar reactions of RAl with E$_2$Et$_4$ (E = Sb, Bi) in toluene occurred with insertion of RAl into the E-E bond and formation of RAl(EEt$_2$)$_2$ (E = Sb **1**; Bi **2**) in moderate yields. **1** and **2** are air and moisture sensitive and soluble in common organic solvents. **1** is stable in solution whereas **2** slowly decomposes with formation of BiEt$_3$ and elemental Bi. ^{1}H and ^{13}C NMR spectra of freshly prepared **1** and **2** show characteristic resonances of the organic substituents, i.e. the ^{1}H NMR spectrum of **1** in C$_6$D$_6$ exhibits single resonances for the *γ*-H and two methyl groups of the C$_3$N$_2$Al ring at 4.94 and 1.52 ppm, respectively. The diastereotopic methyl protons of the isopropyl substituents appear as two doublets at 1.14 and 1.51 ppm and the methine proton as septet at 3.61 ppm. A triplet and a multiplet at 1.40 and 1.73 ppm confirm the presence of the ethyl groups. The ^{13}C{^{1}H} NMR spectrum of **1** shows 12 signals as was expected including the characteristic resonances due to the *γ*-CH (100.40 ppm), the remaining two C$_3$N$_2$Al ring carbons (172.42 ppm), the methine (29.61 ppm) and the methyl carbon atoms of isopropyl groups (26.73, 25.94 ppm) as well as the methyl (17.33 ppm) and methylene carbon atoms (-3.33 ppm) of the ethyl groups. ^{1}H and ^{13}C NMR spectra of **1** and **2** indicate the C$_{2v}$ symmetric structure related to the *β*–diketiminate ligands.
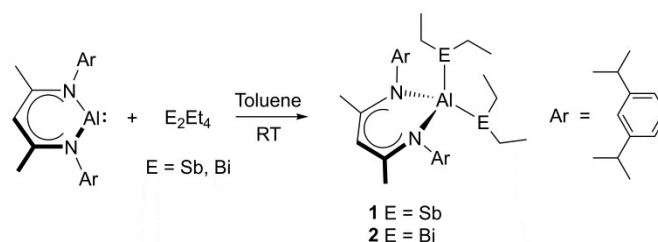
Scheme 1. Synthesis of **1** and **2**.

The reactions of equimolar amounts of RGa with E$_2$Et$_4$ differ significantly from those of RAl. Yellow crystals of RGa(SbEt$_2$)$_2$ (**3**) were isolated from a reaction with Sb$_2$Et$_4$ in hexane at -30 ºC. The ^{1}H NMR spectrum of isolated crystals shows resonances due to **3** as well as traces of RGa, which could not be excluded by repeated re-crystallization. Elemental analysis (C, H, N) of **3**, however, confirms its analytically pure nature. The temperature sensitivity of M-E σ-bonded compounds is well known, i.e. [Me$_2$GaBi(SiMe$_3$)$_2$]$_3$ decomposes in non-coordinating solvents with formation of Me$_3$Ga, Bi$_2$(SiMe$_3$)$_4$ and elemental Ga, whereas in coordination solvents the formation of (Me$_3$Si)$_3$Bi, Me$_3$Ga and an insoluble metallic precipitate was observed.[9d] We therefore investigated the thermal stability of **3** in C$_6$D$_6$ by temperature-variable ^{1}H NMR spectroscopy.

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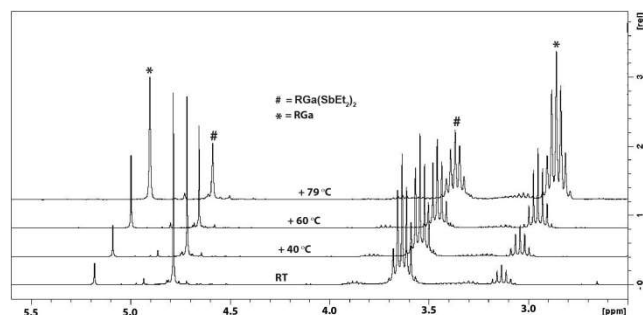   E-mail: stephan.schulz@uni-due.de

Figure 1. Temperature-dependant ^{1}H NMR study of isolated crystals of **3**; the relative intensity of the signals of **3** (#) and RGa (*) are clearly temperature-dependant and fully reversible.

3 starts to dissociate at 40 °C into RGa and Sb$_2$Et$_4$ and the dissociation gradually increased at 60 °C and 80 °C (Figure 1). Cooling the reaction solution back to 25 °C resulted in an increase of the resonances due to **3** and a decrease of the resonances due to RGa and Sb$_2$Et$_4$, respectively, demonstrating that **3** shows a very unique chemical equilibrium with RGa and Et$_4$Sb$_2$ (scheme 2). The position of this equilibrium depends on the reaction temperature, indicating comparable metal-metal bond strengths of the Ga-Sb and the Sb-Sb bonds. The decreasing concentration of **3** with increasing temperature is therefore most likely entropy driven.

Comparable results were observed for the reaction of RGa with Bi$_2$Et$_4$. Isolation of analytically pure RGa(BiEt$_2$)$_2$ (**4**) from the 1:1 mixture of RGa and Bi$_2$Et$_4$ (Figure S9) was even more difficult since under diluted conditions spontaneous crystallization of RGa occurred. However, pure **4** was isolated in good amount by changing the molar ratio of RGa and Bi$_2$Et$_4$ into 1:2. Under these conditions, the molar ratio of **4** to RGa increases up to 5:1 (Figure S10). The ^{1}H NMR spectrum of isolated crystals of **4** again shows a 1:1 molar ratio of **4** and RGa, clearly proving the formation of an equilibrium. Analytical data of **3** and **4** show their pure nature in solid state. **3** and **4** are stable at ambient temperature, but their stability in solution is significantly reduced due to the formation of E$_2$Et$_4$, which are only fairly stable in solution. ^{1}H and ^{13}C NMR spectra of **3** and **4** are similar to those of **1** and **2**. Even though the extent of shifts of the resonances in the ^{1}H NMR compared to the free ligands RM differs, they all show a similar pattern, i.e. the γ-H and the methyl protons of β–diketiminate ligand are shifted to higher field whereas the isopropyl groups of the phenyl rings are shifted to lower field.
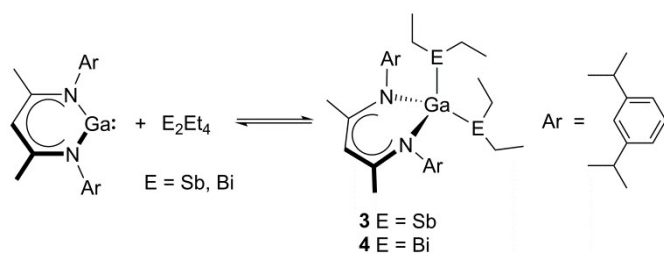
As the basicity considerably decreases from Al^I to Ga^I and In^I, it is reasonable to assume even weaker bonding interactions between RIn and E$_2$Et$_4$. In fact, RIn did not react with Sb$_2$Et$_4$, whereas its reaction with Bi$_2$Et$_4$ at ambient temperature gave traces (9 %) of a new set of resonances which point to the formation of RIn(BiEt$_2$)$_2$ (**5**). Based on the integration of the starting compound RIn and the product **5** in the ^{1}H NMR spectra, the concentration of **5** increases with increasing the concentration of Bi$_2$Et$_4$ from one to four molar ratio (26 %) as well as by cooling the 1:1 reaction mixture to –60 °C (19 %), also indicating the presence of a chemical equilibrium as was observed for **3** and **4**. Unfortunately, isolation of **5** from the mixtures was not possible since at low temperatures, RIn crystallizes much faster than **5**, whereas decomposition of Bi$_2$Et$_4$ occurred at ambient temperature. It should be noted that no such reversible equilibrium phenomenon was observed for **1** at 80 °C (Figure S3). A temperature-dependent NMR experiment was not carried out for **2** due to its temperature sensitivity.

Reversible activation reactions of p-block element compounds are rare and almost limited to the activation of small molecules such as H$_2$ and CO$_2$ by frustrated Lewis pairs (FLP).[14] Nikonov et al. reported on the reversible reaction of RAl and RAlH$_2$, yielding the dialane R(H)Al-Al(H)R.[15] In addition, alkynes reversibly react with Lappert's stannylene [(Me$_3$Si)$_2$CH]$_2$Sn and with a digallane,[16,17] whereas the reversible, temperature controlled binding and release of C$_2$H$_4$ was observed in reactions with a distannyne and with Si(II) complexes.[18,19] Power et al. reported on the reversible, photoinduced activation of P$_4$ by reaction with a Ge(II) compound.[20] In contrast, the formation of a fully reversible equilibrium between a low-valent main group metal complex and the corresponding intermetallic complex is without precedence.

Single crystals of **1** – **4** suitable for X-ray diffraction analysis were grown from saturated *n*-hexane solutions. **1** – **4** crystallize in the monoclinic space groups *P*2$_1$/*c* (**1** – **3**) and *P*2$_1$/*n* (**4**).[21] Since the conformation in **1** - **4** is roughly the same, only the solid state structure of **4** is presented in Figure 2. Crystal data and the details of the structure determinations are summarized in the SI file.
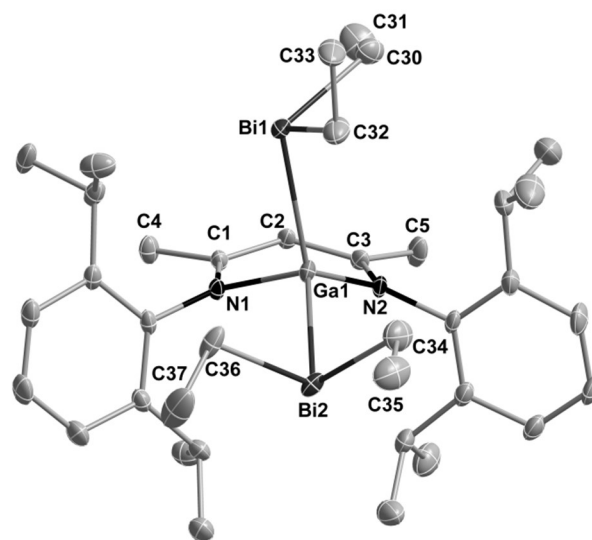
Figure 2. Molecular structure of RGa(BiEt$_2$)$_2$ **4**. H-atoms and second orientation of the disordered BiEt$_2$-group have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level. M-E bond lengths are 2.6586(7), 2.7169 (7) Å (**1**); 2.7318(16), 2.804(2) Å (**2**); 2.6246(3), 2.6743(5) Å (**3**); 2.6961(6), 2.7303(10) Å (**4**).

Scheme 2. Chemical equilibrium of **3** and **4** with RGa and E$_2$Et$_4$.

The group 13 metal atoms in **1** - **4** each adopt a distorted tetrahedral geometry, whereas the group 15 metal atoms show pyramidal coordination spheres. In contrast to the planar C_3N_2M rings in the starting reagents RM, the metal atom M in the C_3N_2M heterocycles in **1** – **4** is out of plane (deviation from best plane of the ligand backbone 0.781(2) Å **1**, 0.801(6) Å **2**, 0.850(3) Å **3**, 0.862(5) Å **4**). The bite angles of the chelating organic ligand R are 97.39(8)° (**1**), 97.16(18)° (**2**), 94.86(8)° (**3**) and 94.27(15)° (**4**), respectively. The two independent Al-N distances in **1** and **2** differ only slightly (1.9172(19), 1.9291(19) Å **1**; 1.916(4) Å, 1.932(4) Å **2**), whereas the Al-E bond lengths vary significantly (2.6586(7), 2.7169 (7) Å **1**; 2.7318(16), 2.804(2) Å **2**), probably due to the disorder of one EEt$_2$ group. The Ga-N bond lengths in **3** (1.990(2), 2.0059(19) Å) and **4** (1.991(4), 2.013(4) Å) are elongated compared to the Al-N bond lengths in **1** and **2**, whereas the Ga-E bond lengths (2.6246(3), 2.6743(5) Å **3**; 2.6961(6), 2.7303(10) Å **4**) are comparable.

The M-N bond distances in **1** – **4** are significantly shorter than those observed in the starting reagents RM,[10,11] which results from the change of the formal oxidation states of the group 13 metal atoms from +I to +III. The M-E bonds are also shorter compared to those observed in the acid-base adducts such as t-Bu$_3$AlSbR$_3$ (R = Et 2.845(1) Å, i-Pr 2.9267(4) Å), R$_3$AlSbt-Bu$_3$ (R = Me 2.834(1) Å; Et 2.873(1) Å),[22] Et$_3$AlSb(SiMe$_3$)$_3$ (2.841(1) Å),[23] t-Bu$_3$GaSbR$_3$ (R = Et, 2.8479(5) Å; i-Pr, 2.9618(2) Å),[24] t-Bu$_3$MBii-Pr$_3$ (M = Al, 3.088(1) Å;[25] Ga, 3.135(1) Å),[9b] (Et$_4$Bi$_2$)(Mt-Bu$_3$)$_2$ (M = Al, 3.084(1); Ga, 3.099(2), 3.114(2) Å),[9c] Et$_3$MBi(SiMe$_3$)$_3$ (M = Al 2.921(2) Å,[25] Ga 2.966(1) Å[9b]), but comparable to the sum of the respective covalent radii.[26] Moreover, they agree with those observed in M-E σ-bonded compounds [R$_2$MER'$_2$]$_2$ and (dmap)M(R$_2$)ER'$_2$ (M = Al, Ga; E = Sb, Bi; R = alkyl, R' = alkyl, SiMe$_3$; dmap = 4-dimethylamino pyridine).[27,28] The distances between the two group 15 elements in **1** – **4** are too far to be considered for any possible bonding interactions. The E-M-E angles of the major component of the disorder are 117.33(3)° (**1**), 118.42(12)° (**2**), 119.155(17) (**3**) and 119.89(7) (**4**), however due to the disorder they are only of limited reliability.

In summary, monovalent RAl reacts straightforward with Et$_4$E$_2$ (E = Sb, Bi) with insertion into the metal-metal bond and formation of RAl(EEt$_2$)$_2$, whereas the insertion reaction of RGa into Et$_4$E$_2$ is fully reversible and temperature dependant. In contrast, RIn only reacted with Bi$_2$Et$_4$ at ambient temperature with formation of RIn(BiEt$_2$)$_2$ (**5**) in very low yield. **1** - **5** represent rare examples of metal organic complexes of heavy group 15 elements (Sb, Bi), in which the group 13/15 molar ratio is 1:2.[29]

Experimental Section

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General Procedures. All manipulations were performed in Ar atmosphere using standard Schlenk and glove-box techniques. Toluene and hexane were dried using mBraun Solvent Purification System. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. Starting reagents RM (R = HC[C(Me)N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$; M = Al, Ga and In)[10-12] and E$_2$Et$_4$ (E = Sb, Bi)[30] were prepared by literature methods. ^{1}H (300 MHz) and ^{13}C{^{1}H} (75.5 MHz) NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer and referenced to internal C$_6$D$_5$H (^{1}H: δ = 7.15; ^{13}C: δ = 128.62)[31] and IR spectra in a glovebox using an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Microanalyses were performed at the elemental analysis laboratory of University of Duisburg-Essen.

Synthesis of RAl(SbEt$_2$)$_2$ (1). A solution of RAl (60 mg, 0.135 mmol) and Sb$_2$Et$_4$ (48.6 mg, 0.135 mmol) in 2 mL of toluene was stirred at ambient temperature for 1h. The solvents were removed at reduced pressure, yielding a yellow-orange residue, which was dissolved in 2 mL of n-hexane and stored at -

30 °C for 1 day to afford analytically pure orange crystals of **1**. Yield: 60 mg (0.112 mmol, 55 %). Anal. Calcd. for C$_{37}$H$_{61}$AlSb$_2$N$_2$: C, 55.25; H, 7.64; N, 3.48. Found: C, 55.5; H, 7.75; N, 3.54%. IR (neat): ν 2959 (m), 2916 (m), 2853 (m), 1512 (m), 1433 (w), 1369 (s), 1310 (m), 1251 (m), 1167 (m), 1097 (m), 1013 (s), 933 (m), 864 (m), 794 (s), 752 (m), 683 (w), 635 (w), 528 (w), 486 (w), 443 (w), 401 (m) cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.14 (s, 6 H, C$_6$H$_3$(^{i}Pr)$_2$), 4.94 (s, 1 H, γ-CH-), 3.61 (sept, 4 H, -CH(CH$_3$)$_2$), 1.73 (m, 8 H, -CH_2CH$_3$), 1.52 (s, 6 H, ArNCCH_3), 1.50 (d, 12 H, -CH(CH_3)$_2$), 1.40 (t, 12 H, -CH$_2$CH_3), 1.14 (d, 12 H, J = 6.6 Hz, -CH(CH_3)$_2$). ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ 172.42 (ArNCCH$_3$), 145.12 (C$_6$H$_3$), 141.69 (C$_6$H$_3$), 127.98 (C$_6$H$_3$), 125.52 (C$_6$H$_3$), 100.40 (γ-CH-), 29.61 (-CH(CH$_3$)$_2$), 26.73 (-CH(CH$_3$)$_2$), 25.94 (-CH(CH$_3$)$_2$), 24.44 (ArNCCH$_3$), 17.33 (BiCH$_2$CH$_3$), 1.76 (BiCH$_2$CH$_3$), -3.33 (BiCH$_2$CH$_3$).

Synthesis of RAl(BiEt$_2$)$_2$ (2). **2** was synthesized by a procedure similar to that of **1** using RAl (87.5 mg, 0.197 mmol) and Bi$_2$Et$_4$ (105.1 mg, 0.197 mmol). Yield: 110 mg (0.112 mmol, 57 %). Anal. Calcd. for C$_{37}$H$_{61}$AlBi$_2$N$_2$: C, 45.40; H, 6.28; N, 2.86. Found: C, 45.90; H, 6.32; N, 2.76%. IR (neat): ν 2970 (m), 2926 (m), 2849 (m), 1519 (m), 1431 (w), 1365 (s), 1310 (m), 1255 (w), 1173 (w), 1129 (m), 1013 (m), 936 (m), 859 (m), 793 (m), 755 (m), 634 (w), 524 (w), 436 (m), 397 (m) cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.13 (s, 6 H, C$_6$H$_3$(^{i}Pr)$_2$), 4.95 (s, 1 H, γ-CH-), 3.52 (sept, 4 H, -CH(CH$_3$)$_2$), 2.37 (m, 8 H, -CH_2CH$_3$), 1.99 (t, 12 H, -CH$_2$CH_3), 1.54 (s, 6 H, ArNCCH_3), 1.48 (d, 12 H, J = 6.9 Hz, -CH(CH_3)$_2$), 1.16 (d, 12 H, -CH(CH_3)$_2$). ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ 172.82 (ArNCCH$_3$), 145.15 (C$_6$H$_3$), 141.89 (C$_6$H$_3$), 127.96 (C$_6$H$_3$), 125.49 (C$_6$H$_3$), 100.84 (γ-CH-), 30.33 (-CH(CH$_3$)$_2$), 26.97 (-CH(CH$_3$)$_2$), 26.05 (-CH(CH$_3$)$_2$), 24.50 (ArNCCH$_3$), 18.35 (BiCH$_2$CH$_3$), -9.17 (BiCH$_2$CH$_3$).

Synthesis of RGa(SbEt$_2$)$_2$ (3). This was synthesized by a procedure similar to that of **1** using RGa (90 mg, 0.185 mmol) and Sb$_2$Et$_4$ (66.4 mg, 0.185 mmol). Yield: 87 mg (0.114 mmol, 62 %). Anal. Calcd. for C$_{37}$H$_{61}$GaSb$_2$N$_2$: C, 52.46; H, 7.26; N, 3.31. Found: C, 52.7; H, 7.28; N, 3.35%. IR (neat): ν 2964 (m), 2922 (m), 2858 (m), 1550 (m), 1512 (m), 1433 (m), 1374 (s), 1310 (m), 1257 (w), 1167 (m), 1108 (w), 1013 (m), 938 (m), 853 (w), 794 (m), 752 (m), 683 (w), 619 (w), 523 (w), 486 (w), 433 (w) cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.14 (m, 6 H, C$_6$H$_3$(^{i}Pr)$_2$), 4.78 (s, 1 H, γ-CH-), 3.64 (sept, 4 H, -CH(CH$_3$)$_2$), 1.72 (m, 8 H, -CH_2CH$_3$), 1.56 (s, 6 H, ArNCCH_3), 1.50 (d, 12 H, -CH(CH_3)$_2$), 1.32 (t, 12 H, -CH$_2$CH_3), 1.18 (d, 12 H, J = 6.6 Hz, -CH(CH_3)$_2$). ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ 169.92 (ArNCCH$_3$), 144.97 (C$_6$H$_3$), 143.29 (C$_6$H$_3$), 127.48 (C$_6$H$_3$), 125.32 (C$_6$H$_3$), 98.80 (γ-CH-), 29.34 (-CH(CH$_3$)$_2$), 26.65 (-CH(CH$_3$)$_2$), 25.99 (-CH(CH$_3$)$_2$), 24.39 (ArNCCH$_3$), 16.57 (SbCH$_2$CH$_3$), -1.27 (SbCH$_2$CH$_3$).

Synthesis of RGa(BiEt$_2$)$_2$ (4). **Method 1**: A solution of RGa (228 mg, 0.468 mmol) in toluene (10 mL) was added dropwise to a solution of Bi$_2$Et$_4$ (250 mg, 0.468 mmol) in toluene (10 mL) and stirred for 1h at ambient temperature. The solvent was removed under reduced pressure and the resulting residue dissolved in 3 mL of n-hexane. Yellow crystals of RGa and red crystals of **4** were formed upon storage at ambient temperature after 2-3 days. Dissolution of the red crystals (**4**) in hexane and storage at ambient temperature again yielded a 1:1:1 mixture of RGa, Bi$_2$Et$_4$ and **4** (figure S9). Yield: 203 mg (0.199 mmol, 42 %). **Method 2**: A mixture of RGa (114 mg, 0.234 mmol) and Bi$_2$Et$_4$ (250 mg, 0.468 mmol) was stirred at ambient temperature in 2 mL of n-hexane for 30 min. The reaction mixture was kept at -30 °C for 24h, yielding red crystals of analytically pure **4**. Yield: 153 mg (0.150 mmol, 64 %). Anal. Calcd. for C$_{37}$H$_{61}$GaBi$_2$N$_2$: C, 43.50; H, 6.02; N, 2.74. Found: C, 43.50; H, 6.03; N, 2.73%. IR (neat): ν 2964 (m), 2916 (m), 2853 (m), 1545 (w), 1512 (m), 1427 (w), 1375 (m), 1311 (w), 1258 (m), 1173 (w), 1131 (w), 1098 (m), 1014 (m), 934 (w), 849 (w), 790 (s), 753 (w), 663 (w), 519 (w), 439 (w), 397 (w) cm^{-1}. The ^{1}H and ^{13}C NMR spectra showed the mixture of **4** and RGa. Only the resonances of **4** in the ^{1}H NMR spectrum could be assigned. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.14 (m, 6 H, C$_6$H$_3$(^{i}Pr)$_2$), 4.79 (s, 1H, γ-CH-), 3.57 (sept, 4 H, -CH(CH$_3$)$_2$), 2.39 (m, 8 H, -CH_2CH$_3$), 1.94 (t, 12 H, -CH$_2$CH_3), 1.58 (s, 6 H, ArNCCH_3), 1.48 (d, 12 H, -CH(CH_3)$_2$), 1.20 (d, 12 H, J = 6.9 Hz, -CH(CH_3)$_2$).

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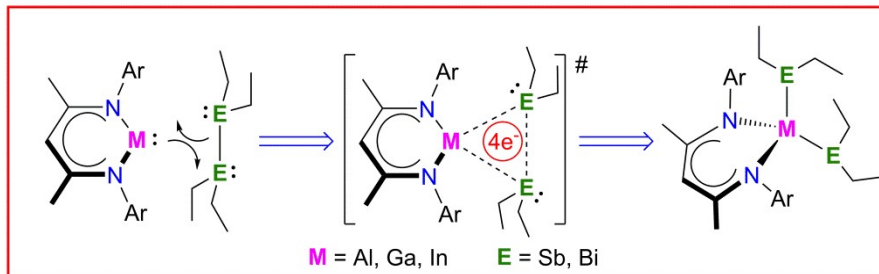
Entry for the Table of Contents (Please choose one layout)

Layout 2:

M = Al, Ga, In   E = Sb, Bi

Reactions of monovalent RAl with E_2Et_4 (E = Sb, Bi) proceed with E-E bond cleavage and formation of $RAl(EEt_2)_2$, whereas RGa forms a reversible chemical equilibrium with E_2Et_4 and $RGa(EEt_2)_2$. RIn does not react with Sb_2Et_4, but also forms a reversible equilibrium with Bi_2Et_4 at low temperatures.