Comprehensive study on reactions of group 13 diyls with tetraorganodipentelanes

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Dedicated to Prof. Peter Jutzi on the occasion of his 80th birthday.

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Abstract. L^1Ga $\{L^1 = HC[C(Me)N(2,6-iPr_2C_6H_3)]_2\}$ reversibly reacts with E_2Ph_4 ($E = Sb, Bi$) in a temperature-dependent equilibrium reaction with insertion into the E-E bond and formation of $L^1Ga(EPh_2)_2$ ($E = Sb$ **1**, Bi **2**). Analogous findings were observed in the reactions of L^2Ga $\{L^2 = (C_6H_{11})_2NC[N(2,6-iPr_2C_6H_3)]_2\}$ with E_2R_4 ($R = Ph, Et$), yielding $L^2Ga(EPh_2)_2$ ($E = Sb$ **3**, Bi **4**) and $L^2Ga(EEt_2)_2$ ($E = Sb$ **5**, Bi **6**). **1 - 3** and **5** were isolated by fractional crystallization at low temperature, whereas **4** and **6** could not be isolated in their pure form even at low temperature. In contrast, reactions of $[Cp^*Al]_4$ ($Cp^* = C_5Me_5$) with Sb_2R_4 ($R = Ph, Et$) and Bi_2Et_4 did not proceed with insertion into the E-E bonds but with formation of $(Cp^*Al)_3E_2$ ($E = Sb$, **7**; Bi , **8**), whereas the reaction with Bi_2Ph_4 yielded metallic bismuth. **8** was also formed in the reaction of $[Cp^*Al]_4$ and $BiEt_3$ at ambient temperature, whereas the analogous reaction of $[Cp^*Al]_4$ with $SbEt_3$ did not yield **7** even under drastic reaction conditions (120 °C, 3 days). In contrast, Cp^*Ga and Sb_2R_4 ($R = Ph, Et$) were found to react only at elevated temperature (120 °C) with formation of antimony metal.

Introduction

The synthesis and reactivity of monovalent group 13 diyls of the general type RM ($M = Al, Ga$), in which the metal centers adopt the oxidation state +I, has been investigated since the landmarking synthesis of $[Cp^*Al]_4$ ($Cp^* = C_5Me_5$) in 1991. $[Cp^*Al]_4$ was initially prepared by Schnöckel et al. by metathesis reaction of a metastable $AlCl$ solution with Cp^*_2Mg , whereas Roesky et al. reported on a more convenient method by reduction reaction of Cp^*AlCl_2 with potassium.[1] Since then, several alanediylys RAl and gallanediyls RGa have been synthesized by metathesis reaction or by reduction reaction of trivalent species RMX_2 ($M = Al, Ga, X = \text{halide}$), in particular compounds containing sterically demanding terphenyl ligands[2] and N,N'-chelating ligands such as diimines, guanidates, diiminophosphinates, and β -diketiminates,[3] respectively. Monovalent group 13 diyls typically adopt monomeric (RM) or oligomeric ($[RM]_x$) structures with metal-metal bonds in solution and in the solid state, depending on the steric demand and coordination properties of the organic substituent. Aside from their interesting structures, group 13 diyls received increasing interest due to their fascinating properties in reactions with organic compounds and in coordination chemistry. L^1M ($M = Al, Ga; L^1 = HC[C(Me)N(2,6-iPr_2C_6H_3)]_2$) containing the sterically demanding N,N'-chelating β -diketimate ligand L^1 showed very promising properties in the activation of small molecules including P_4 , O_2 , S_8 , azobenzene and azides,[4] respectively, as was also observed for Cp^*M ($M = Al, Ga$).[5] In addition, L^1M was also found to activate a variety of main group element $H-X$ ($X = H, B, C, Si, N, P, O$),[6] C-F and C-O σ -bonds,[7] while L^1Ga was found to readily insert into several main group metal-X bonds of heavy group 13 (Ga, In), 14 (Ge, Sn, Pb) 15 (Bi) and 16 elements (Te), respectively.[8] This reactivity results from the presence of a metal centered electron lone pair, resulting in nucleophilic properties (Lewis basic), and due to the presence of a formally vacant π -orbital, rendering the molecules electrophilic (Lewis acidic). Quantum chemical calculations revealed that the electronic structure of L^1Al and L^1Ga slightly differs with respect to their singlet-triplet energy gap (Al : 34.3–45.7 kcal/mol; Ga : 51.7–55.5 kcal/mol) and HOMO-LUMO separation (Al : 75.76 kcal/mol; Ga 96.24 kcal/mol)[9] and as a consequence, the reactivity of alanediyyl L^1Al and gallanediyl L^1Ga was also found to slightly differ. While L^1Al shows very promising applications in bond activation reactions as mentioned before, L^1Ga also showed very promising properties as stabilizing terminal ligand in main group metal[10] and transition metal chemistry.[11] This was also observed for Cp^* -substituted alane- and gallanediyls Cp^*M ($M = Al, Ga$), which are strong σ -donors and serve as powerful two-electron ligands in transition metal complexes[12] and in Lewis acid-base reactions, i.e. in reactions with earth

alkaline metal complexes Cp^*_2M ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$)[13] and group 13 trialkyls $t\text{-Bu}_3\text{M}$ ($\text{M} = \text{Al}, \text{Ga}$).[14]

Our general interest in group 13/15 chemistry prompted us to investigate reactions of L^1M ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) with group 15 compounds such as distibines and dibismuthines E_2Et_4 , which occurred with insertion into the E-E bonds[15] as was previously observed in reactions of L^1Al with diphosphines.[16] In addition, reactions of L^1Ga with BiEt_3 [17] and EX_3 ($\text{E} = \text{As}, \text{Sb}, \text{Bi}; \text{X} = \text{NR}_2, \text{halide}$)[18] proceeded with insertion into Bi-C bonds and E-X bonds, respectively. In addition, L^1Ga was found react with $[\text{Cp}^*\text{Sb}]_4$ with elimination of decamethylfulvalen (Cp^*_2) and subsequent formation of $[(\text{L}^1\text{Ga})_2(\mu, \eta^{2:2}\text{-Sb}_4)]$,[19] whereas stable stibanyl- and bismuthinyl radicals $[\text{L}^1(\text{X})\text{Ga}]\text{E}^\cdot$ ($\text{E} = \text{Sb}, \text{Bi}; \text{X} = \text{Cl}, \text{I}$) were formed in reactions with Cp^*EX_2 . [20]

To investigate the role of the organic ligand of group 13 diyls on the outcome of these reactions, we systematically reacted $\text{L}^{1,2}\text{Ga}$ $\{\text{L}^2 = (\text{C}_6\text{H}_{11})_2\text{NC}[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]_2\}$, Cp^*Ga and $[\text{Cp}^*\text{Al}]_4$ with dipnictines E_2R_4 ($\text{E} = \text{Sb}, \text{Bi}; \text{R} = \text{Ph}, \text{Et}$).

Experimental Section

General Procedures. Argon gas was purified by passing the gas through pre-heated Cu_2O pellets and molecular sieves columns. Reactions were carried out using standard Schlenk and glove-box techniques. Toluene and *n*-hexane were dried using a mBraun Solvent Purification System, degassed and stored in Schlenk flasks under argon atmosphere. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. L^1Ga ($\text{L}^1 = \text{HC}[\text{C}(\text{Me})\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]_2$),[4e], L^2Ga ($\text{L}^2 = (\text{C}_6\text{H}_{11})_2\text{NC}[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]_2$),[21] Cp^*M ($\text{M} = \text{Al}, \text{Ga}$)[22] and E_2R_4 ($\text{E} = \text{Sb}, \text{Bi}; \text{R} = \text{Et}, \text{Ph}$)[23] were prepared according to literature methods. ^1H (300 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (75.5 MHz) NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer and referenced to internal $\text{C}_6\text{D}_5\text{H}$ (^1H : $\delta = 7.15$; ^{13}C : $\delta = 128.62$).[24] **1 - 6** form temperature-dependent equilibria with the starting reagents in solution state as was shown by ^1H and ^{13}C NMR spectroscopy. The spectra are rather complex due to the presence of resonances of the starting reagents, but tentative assignments of the resonances are given. IR spectra were recorded in a glovebox under argon atmosphere using an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Microanalyses were performed at the Elemental Analysis Laboratory of the University of Duisburg-Essen. Melting points were determined in sealed glass capillaries and are not corrected.

Synthesis of $\text{L}^1\text{Ga}(\text{SbPh}_2)_2$ (1). A solution of L^1Ga (53 mg, 0.109 mmol) and Sb_2Ph_4 (60 mg, 0.109 mmol) in 2 mL of toluene was stirred at ambient temperature for 1 h. The solvents were

removed at reduced pressure, yielding a yellow residue, which was dissolved in 1 mL of *n*-hexane and stored at room temperature. Analytically pure yellow crystals of **1** were obtained after storage for one day. Yield: 85 mg (0.082 mmol, 75 %). M.p. 168 °C (dec.). Anal. Calcd. for C₅₃H₆₁N₂GaSb₂: C, 61.25; H, 5.92; N, 2.70. Found: C, 61.17; H, 5.88; N, 2.74%. ¹H NMR (C₆D₆, 8 °C, 300 MHz): δ 7.83-6.81 (m, 26 H, C₆H₃(*i*-Pr)₂, Sb(C₆H₅)₂, 4.96 (s, 1 H, γ-CH), 3.87 (br sept, 2 H, CH(CH₃)₂), 3.49 (br sept, 2 H, CH(CH₃)₂), 1.63 (br d, 6 H, CH(CH₃)₂), 1.60 (s, 6 H, CCH₃), 1.13 (br d, 6 H, CH(CH₃)₂), 0.80 (br d, 6 H, CH(CH₃)₂), 0.76 (br d, 6 H, CH(CH₃)₂). ¹³C NMR (C₆D₆, 25 °C, 75.5 MHz): δ 170.3 (CCH₃), 146.3, 143.4, 142.6, 139.5, 138.4, 138.1, 135.5, 132.0, 129.3, 128.7, 127.5, 127.0, 126.0, 124.7 (C₆H₃(*i*-Pr)₂, C₆H₅), 99.0 (γ-CH), 35.0 (CH(CH₃)₂), 29.7 (br, CH(CH₃)₂), 28.6 (br, CH(CH₃)₂), 25.9 (br, CH(CH₃)₂), 25.5 (br, CH(CH₃)₂), 25.2 (br, CH(CH₃)₂), 24.3 (CCH₃). IR: ν 3051, 2959, 2922, 2861, 1511, 1468, 1431, 1382, 1315, 1254, 1162, 1094, 1016, 930, 850, 801, 721, 691, 629, 525, 445, 396 cm⁻¹.

Synthesis of L¹Ga(BiPh₂)₂ (2). **2** was synthesized by a similar procedure to that of **1** using L¹Ga (100 mg, 0.205 mmol) and Bi₂Ph₄ (149 mg, 0.205 mmol). Yield: 167 mg (0.138 mmol, 67 %). M.p. 117 °C (dec.). Anal. Calcd. for C₅₃H₆₁N₂GaBi₂: C, 52.45; H, 5.07; N, 2.31. Found: C, 53.1; H, 5.11; N, 2.24%. ¹H NMR (toluene-*d*₈, -20 °C, 300 MHz): δ 8.18-6.87 (m, 26 H, C₆H₃(*i*Pr)₂, Bi(C₆H₅)₂), 4.90 (s, 1 H, γ-CH), 3.76 (br sept, 2 H, CH(CH₃)₂), 3.30 (br sept, 2 H, CH(CH₃)₂), 1.59 (s, 6 H, CCH₃), 1.54 (br d, 6 H, CH(CH₃)₂), 1.10 (br d, 6 H, CH(CH₃)₂), 0.76 (br d, 6 H, CH(CH₃)₂), 0.68 (br d, 6 H, CH(CH₃)₂). ¹³C NMR (C₆D₆, 25 °C, 75.5 MHz): δ 170.4 (CCH₃), 142.7, 130.2, 128.9, 128.4, 127.5, 126.5, (C₆H₃(*i*-Pr)₂, C₆H₅), 99.2 (γ-CH), 35.0 (CH(CH₃)₂), 29.7 (br, CH(CH₃)₂), 27.2 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 25.3 (br, CH(CH₃)₂), 24.3 (CH(CH₃)₂), 20.9 (CCH₃). IR: ν 3051, 2965, 2922, 2861, 1566, 1511, 1468, 1425, 1376, 1309, 1254, 1162, 1094, 1057, 1014, 934, 855, 794, 714, 695, 622, 524, 438 cm⁻¹.

Synthesis of L²Ga(SbPh₂)₂ (3). **3** was synthesized by a similar procedure to that of **1** using L²Ga (28 mg, 0.046 mmol) and Sb₂Ph₄ (25 mg, 0.046 mmol). Analytically pure **3** was obtained as pale-yellow crystals from saturated *n*-hexane solution after storage at 8 °C for one day. Yield: 30 mg (0.026 mmol, 56 %). M.p. 151-153 °C. Anal. Calcd. for C₆₁H₇₆N₃GaSb₂: C, 62.91; H, 6.58; N, 3.61. Found: C, 62.77; H, 6.64; N, 3.64%. ¹H NMR (toluene-*d*₈, 25 °C, 300 MHz): δ 7.27-6.84 (m, 16 H, C₆H₃(*i*-Pr)₂, Sb(C₆H₅)₂), 3.99 (sept, ³J_{HH} = 6.6 Hz, 4 H, CH(CH₃)₂), 3.66 (m, 2 H, NCH), 1.50-1.41 (m, 12 H, Cy-CH₂), 1.45 (d, ³J_{HH} = 6.9 Hz, 12 H, CH(CH₃)₂), 1.25 (d, ³J_{HH} = 6.6 Hz, 12 H, CH(CH₃)₂), 0.97-0.81 (m, 8 H, Cy-CH₂). ¹³C NMR

(toluene-*d*₈, 25 °C, 75.5 MHz): δ 162.2 (CN₃), 144.6, 141.1, 139.2, 134.7, 128.6, 127.0, 125.7, 124.7, 124.0, 123.4 (C₆H₃(*i*-Pr)₂, C₆H₅), 59.0 (NCH), 34.8 (Cy-CH₂), 28.9 (CH(CH₃)₂), 28.0 (CH(CH₃)₂), 27.1 (Cy-CH₂), 25.6 (Cy-CH₂), 24.3 (CH(CH₃)₂). IR: ν 3056, 2950, 2919, 2850, 1573, 1454, 1423, 1367, 1324, 1280, 1249, 1193, 1156, 1093, 1056, 1018, 956, 894, 856, 825, 794, 763, 726, 688, 508, 445, 389 cm⁻¹.

Synthesis of L²Ga(SbEt₂)₂ (5). A 1:2 molar mixture of L²Ga (50 mg, 0.082 mmol) and Sb₂Et₄ (59 mg, 36 μ L, 0.163 mmol) was suspended in *n*-hexane (1.5 mL) and heated to 70 °C for 10 minutes, yielding a light-yellow solution. The solution was cooled to ambient temperature and stored at 0 °C. Pale yellow crystals of **5** were formed after two weeks, which were isolated by filtration and dried in vacuo. Yield: 43 mg (0.044 mmol, 54 %). M.p. 143-145 °C. Anal. Calcd. for C₄₅H₇₆N₃GaSb₂: C, 55.59; H, 7.88; N, 4.32. Found: C, 55.80; H, 8.04; N, 4.46%. ¹H NMR (toluene-*d*₈, 25 °C, 300 MHz): δ 7.10-7.02 (m, 6 H, C₆H₃(*i*-Pr)₂), 3.90 (sept, ³J_{HH} = 6.6 Hz, 4 H, CH(CH₃)₂), 3.50 (m, 2 H, NCH), 2.02-1.77 (m, 12 H, Cy-CH₂, SbCH₂CH₃), 1.43-1.36 (m, 36 H, CH(CH₃)₂, SbCH₂CH₃), 0.97-0.62 (m, 16 H, Cy-CH₂). ¹³C NMR (toluene-*d*₈, 25 °C, 75.5 MHz): δ 160.9 (CN₃), 144.7, 141.1, 125.4, 124.2 (C₆H₃(*i*-Pr)₂), 58.8 (NCH), 34.7 (Cy-CH₂), 28.6 (CH(CH₃)₂), 28.4 (CH(CH₃)₂), 27.0 (Cy-CH₂), 25.7 (Cy-CH₂), 23.9 (CH(CH₃)₂), 16.4 (SbCH₂CH₃), -0.1 (SbCH₂CH₃). IR: ν 2963, 2932, 2857, 1454, 1423, 1374, 1324, 1249, 1174, 1093, 1018, 950, 863, 800, 763, 744, 713, 688, 657, 508, 489, 396 cm⁻¹.

L²Ga(BiPh₂)₂ (4) and L²Ga(BiEt₂)₂ (6). **4** and **6** could not be isolated in their pure form from the reaction equilibrium. Upon cooling solutions of **4** and **6** in *n*-hexane to -30 °C, L²Ga and Bi₂Ph₄ start to crystallize and therefore shifted the equilibrium to the side of the starting reagents. ¹H NMR spectra of the reaction equilibria as well as temperature-dependent *in situ* NMR studies are given in the supporting information file (Figs. S18 – S21).

Synthesis of (Cp*Al)₃Sb₂ (7). In a J-Young NMR tube, a suspension of [Cp*Al]₄ (50 mg, 0.077 mmol) and Sb₂R₄ (R = Et: 22 mg, 13.4 μ L, 0.062 mmol; R = Ph: 34 mg, 0.062 mmol) in toluene-*d*₈ (0.5 mL) was heated to 80 °C and the reaction progress was monitored *via* ¹H NMR spectroscopy. A complete consumption of all starting reagents was observed after 1 day. The resulting solution was cooled to ambient temperature. Orange crystals of **7** were formed upon storage at 0 °C for one week, which were filtered and washed with 2 mL of *n*-hexane. The yields in both reactions varied from 64-70 % and a maximum of 32 mg of **7** was obtained from the reaction with Sb₂Et₄. ¹H NMR (C₆D₆, 300 MHz): δ 2.08 (s, 45 H, C₅(CH₃)₅). ¹³C NMR (C₆D₆, 75.5 MHz): δ 116.1 (C₅Me₅), 12.0 (C₅Me₅).

Synthesis of (Cp*Al)₃Bi₂ (8). *Method A:* In a J-Young NMR tube, a suspension of [Cp*Al]₄ (50 mg, 0.077 mmol) and Bi₂Et₄ (33 mg, 13.2 μ L, 0.062 mmol) in toluene-*d*₈ (0.5 mL) was stirred at ambient temperature and the reaction was periodically monitored *via* ¹H NMR spectroscopy. The reaction occurred slowly, finally yielding **8** in very small amount within 3 days. During this period, a complete disproportionation of Bi₂Et₄ into BiEt₃ was observed. Further heating of this solution to 120 °C yielded considerable amounts of **8** after three days. The solution was filtered, and the metallic precipitate was washed with 2 mL of toluene. The combined filtrate was concentrated under reduced pressure and kept at -30 °C for one day to give red microcrystals.

Method B: A suspension of [Cp*Al]₄ (199 mg, 0.308 mmol) and BiEt₃ (121 mg, 67 μ L, 0.409 mmol) in toluene (10 mL) was heated to 120 °C for 4 days. The reaction mixture was filtered to remove traces of Bi metal, concentrated to 2 mL and kept at -30 °C for one day to give red microcrystals. Yield: 63 mg (0.069 mmol, 34 %). M.p. 226 °C (dec.). Anal. Calcd. for C₃₀H₄₅Al₃Bi₂: C, 39.83; H, 5.01. Found: C, 39.40; H, 4.98%. ¹H NMR (C₆D₆, 300 MHz): δ 2.06 (s, 45 H, C₅(CH₃)₅). ¹³C NMR (C₆D₆, 75.5 MHz): δ 116.5 (C₅Me₅), 13.4 (C₅Me₅). IR (neat): ν 2904, 2849, 1425, 1370, 800, 591, 432 cm⁻¹.

Results and discussion

Equimolar amounts of L¹Ga and E₂Ph₄ (E = Sb, Bi) react with insertion of L¹Ga into the E-E bond and formation of L¹Ga(EPh₂)₂ (E = Sb **1**; Bi **2**). **1** and **2** form reversible, temperature-dependent reaction equilibria with the starting reagents as was previously observed for the analogous Et-substituted derivatives L¹Ga(EEt₂)₂.^[15] The same is observed when isolated samples of **1** and **2** are dissolved in non-polar solvents as was shown by ¹H NMR spectroscopy (Figure 1). The equilibria (starting reagents vs. reaction products) resulting from the reaction of equimolar amounts of L¹Ga and E₂Ph₄ in toluene-*d*₈ at room temperature are 1:11 (**1**) and 1:2 (**2**) (Table S1). Upon cooling, the resonances due to **1** and **2** increase and the equilibrium is completely shifted to **1** at -20 °C, whereas **2** shows a maximum intensity at -80 °C with a molar ratio of 1:3 (L¹Ga vs. **2**). ¹H NMR spectra of isolated crystals of **1** and **2** show broad resonances at room temperature, but the signals became sharper and well resolved at lower temperatures. For instances, the ¹H NMR spectra of **1** in C₆D₆ at 8 °C and **2** in toluene-*d*₈ at -20 °C exhibit single resonances for the γ -H (**1**, 4.96; **2**, 4.90 ppm) and two methyl groups (**1**, 1.60; **2**, 1.59 ppm) of the C₃N₂Ga ring. The methyl protons of the isopropyl substituents appear as four doublets (**1**, 0.76, 0.80, 1.13, 1.63; **2**, 0.68, 0.76, 1.10, 1.54 ppm) and the methine proton as two septets (**1**, 3.49, 3.87; **2**, 3.30, 3.76 ppm). The aryl protons show several multiplets between 6.80 and 8.22 ppm, including those of the -EPh₂ groups. The

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** at room temperature shows sharp single resonances for the γ -CH (99.0 ppm), two $\text{C}_3\text{N}_2\text{Ga}$ ring carbon atoms (170.3 ppm) and the C_3N_2 methyl groups (24.3 ppm) and broad resonances for the methine (35.0, 29.7 ppm) and methyl carbon atoms of the isopropyl groups (28.6, 27.2, 25.9, 25.5, 25.2 ppm), whereas the ^{13}C NMR spectrum of **2** is complicated due to presence of a mixture of L^1Ga , Bi_2Ph_4 and **2**.

Scheme 1. Synthesis of **1** – **6** by insertion reaction of $\text{L}^{1,2}\text{Ga}$ with E_2R_4 (E = Sb, Bi; R = Et, Ph).

Figure 1. Variable temperature $^1\text{H}\{^{13}\text{C}\}$ NMR spectra of **1** (a) and **2** (b). Only γ -CH and $-\text{CH}(\text{CH}_3)_2$ signals are shown.

In order to investigate the role of the organic substituent of the gallanediyl on the formation and the nature of the equilibrium in solution, the guanidinate-substituted gallanediyl L^2Ga ($\text{L}^2 = (\text{C}_6\text{H}_{11})_2\text{N}-\text{C}[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]_2$)[21] was chosen. The Ga(I) center within the four-membered metallacycle of L^2Ga is sterically less shielded by the N-substituents than in the five-membered metallacycles $[\text{Ga}\{\text{N}(\text{R})\text{CH}_2\}_2]^-$ (R = *t*-Bu, 2,6-*i*Pr₂C₆H₃)[25] and the six-membered metallacycle of L^1Ga . This is indicated by the smaller endocyclic N-Ga-N bond

angles, which steadily increase with increasing ring size (L^2Ga , $63.77(7)^\circ$;^[21] $[Ga\{N(R)CH\}_2]^-$: $R = t\text{-Bu}$, $81.8(3)^\circ$; $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$, $83.02(11)^\circ$;^[25] L^1Ga , $87.53(5)^\circ$ [4e]). Therefore, the Ga(I) center in L^2Ga is expected to interact differently with dipentelanes E_2R_4 than L^1Ga .

In situ 1H NMR spectra of the reaction of equimolar amounts of L^2Ga with E_2R_4 ($E = Sb, Bi$; $R = Ph, Et$) in toluene- d_8 show the formation of the expected insertion compounds, $L^2Ga(ER_2)_2$ (Ph : Sb **3**, Bi **4**; Et : Sb **5**, Bi **6**), which form equilibria with the starting reagents. Comparing the relative ratios of the $-CHMe_2$ resonances addressed to $L^{1,2}Ga$ and $L^{1,2}Ga(ER_2)_2$ ($E = Sb, Bi$), it becomes clear that the concentration of **3** – **6** in the equilibrium at ambient temperature are significantly lower than those observed for **1**, **2** as well as previously reported for $L^1Ga(Et_2)_2$ (Table S1).^[15] However, pure **3** and **5** were isolated from saturated solutions in *n*-hexane upon storage at $8^\circ C$. Crystals of **5** was obtained from a solution of L^2Ga and Sb_2Et_4 in a molar ratio of 1:2, which was applied to shift the equilibrium toward the formation of **5**. The 1H NMR spectra of isolated samples of **3** and **5** show characteristic septets for the $-CHMe_2$ groups at 3.99 and 3.90 ppm, while resonances of the cyclohexyl and $-CHMe_2$ groups form overlapping multiplets. The $^{13}C\{^1H\}$ NMR spectra of **3** and **5** show distinct singlets for the CN_3 (162.2 ppm, **3**; 160.9 ppm, **5**) and cyclohexyl-HCN carbon atoms (59.0 ppm, **3**; 58.8 ppm, **5**). A tentative assignment of the resonances as well as overlaid spectra of **3** and **5** along with starting reagents is given in the experimental section.

All attempts to isolate pure $L^2Ga(BiR_2)_2$ (Ph , **4**; Et , **6**) from the reaction mixtures through fractional crystallization failed. L^2Ga and Bi_2Ph_4 started to crystallize from solutions in *n*-hexane and toluene upon cooling below $-30^\circ C$. We therefore performed variable temperature (VT) 1H -NMR studies with 1:1 molar mixtures of L^2Ga and Bi_2R_4 ($R = Ph$ **4**, Et **6**). While the molar ratios of L^2Ga to **4** / **6** in toluene- d_8 at ambient temperature are 6:1 and 2.6:1, respectively, the relative concentration of **6** in the reaction mixtures was found to increase upon cooling and the highest molar ratios of L^2Ga to **6** of 1:1.6 was observed at $-20^\circ C$. The equilibrium ratio remains constant below $-20^\circ C$ for **6** and no considerable variation is seen at lower temperatures for $L^2Ga(BiPh_2)_2$ **4**.

To further support the above interpretations, the reductive elimination of $L^{1,2}Ga$ and E_2Ph_4 from **1** – **3** were studied by 1H NMR spectroscopy (Equation 1). Equilibrium constants (K_{eq}) were determined by measuring the concentration of **1** – **3**, $L^{1,2}Ga$ and E_2Ph_4 in the temperature range between 293 and 353 K (Table S2) and the thermodynamic parameters (ΔH , ΔS and ΔG) were extracted from van't Hoff plots (Table 1, Figure 2, Figures S28 and S29). At lower

temperatures **3** has larger K_{eq} than those of **1** and **2** suggesting a favorable reductive elimination of $L^{1,2}Ga$ and Sb_2Ph_4 from **3**. Furthermore, the dissociation enthalpy (ΔH) are smaller for **3** than those of **1** and **2**. ΔG values suggest that reductive eliminations of $L^{1,2}Ga$ and E_2Ph_4 from **1** – **3** are endergonic processes.

Equation 1: Reductive elimination of $L^{1,2}Ga$ and E_2Ph_4 from $L^{1,2}Ga(EPh_2)_2$.

Compounds	$\Delta H(kJmol^{-1})$	$\Delta S(JK^{-1}mol^{-1})$	$\Delta G(kJmol^{-1})$
1	75.9	189.9	19.2
2	66.2	181.8	12
3	55.5	150.9	10.5

Table 1: ΔH , ΔS and ΔG values (298 K) from van't Hoff plots of the equilibrium reactions of **1** – **3**. Uncertainties associated with the proton signal integrations and temperature variations during the $^1H\{^{13}C\}$ NMR measurements are not shown.

Figure 2: van't Hoff plot of the equilibrium reaction of **1** with L¹Ga and Sb₂Ph₄.

Single crystals of **1**, **2** and **5** suitable for X-ray diffraction analyses were grown within one day from saturated solutions of **1**, **2** and **5** in *n*-hexane upon storage at ambient temperature (**1**, **2**) and at 8 °C (**5**), respectively.[26] **1** and **2** crystallize in the triclinic space group *P*-1. **2** includes a highly disordered *n*-hexane solvent molecule, whose electron density was excluded from the refinement by SQUEEZE (see SI).

Figure 3. Solid state structure of $L^1Ga(SbPh_2)_2$ (**1**). H-atoms have been omitted for clarity and thermal ellipsoids are shown with 50% probability level. Selected bond lengths [Å] and angles [°]: Sb1-Ga1 2.8458(13), Sb2-Ga1 2.6469(11), Ga1-N1 1.993(6), Ga1-N2 2.030(6), N1-Ga1-N2 94.3(2), N1-Ga1-Sb2 109.53(19), N2-Ga1-Sb2 108.56(17), N1 Ga1 Sb1 107.9(2), N2 Ga1 Sb1 96.32(18), Sb2 Ga1 Sb1 132.71(4).

Figure 4. Solid state structure of $L^1Ga(BiPh_2)_2$ (**2**). H-atoms have been omitted for clarity and thermal ellipsoids are shown with 50% probability level. Selected bond lengths [Å] and angles [°]: Ga1-Bi1 2.7310(5), Ga1-Bi2 2.8036(5), Ga1-N2 1.9955(14), Ga1-N1 2.0312(14), N2-Ga1-N1 94.06(6), N2-Ga1-Bi1 108.93(4), N1-Ga1-Bi1 107.50(4), N2-Ga1-Bi2 107.36(4), N1-Ga1-Bi2 95.86(4), Bi1-Ga1-Bi2 134.756(10).

Figure 5. Solid state structure of $L^2Ga(SbEt_2)_2$ (**5**). Hydrogen and disordered atoms have been omitted for clarity and thermal ellipsoids are shown with 50% probability level. Selected bond lengths [Å] and angles [°]: Sb1-Ga1 2.6420(9), Sb2-Ga1 2.6534(8), Ga1-N2 2.006(5), Ga1-N1 2.030(5), N2-Ga1-N1 65.7(2), N2-Ga1-Sb1 113.00(15), N1-Ga1-Sb1 105.11(15), N2-Ga1-Sb2 114.67(15), N1-Ga1-Sb2 116.05(15), Sb1-Ga1-Sb2 126.21(3).

The structures of **1** and **2** are comparable to those observed for the Et-substituted derivatives $L^1Ga(EtEt_2)_2$.^[15] The Ga atom in the C_3N_2Ga heterocycles in **1** and **2** is out of plane (deviation from best plane of the ligand backbone 0.885(9) Å **1**, 0.9074(17) Å **2**), whereas **5** has an almost planar four membered NCNGa ring (rms deviation from best plane 0.0158 Å). The Ga atoms in **1**, **2** and **5** each adopt a distorted tetrahedral coordination geometry, whereas the Sb and Bi metal atoms show pyramidal coordination spheres. The bite angles of the

chelating β -diketiminate ligand L^1 in **1** ($94.3(2)^\circ$) and **2** ($94.06(6)^\circ$) are considerable larger compared to that of guanidinate ligand L^2 in **5** ($65.7(2)^\circ$). The two independent Ga-N distances in **1**, **2** and **5** are virtually identical ($1.993(6)$, $2.030(6)$ Å **1**; $1.9955(14)$ Å, $2.0312(14)$ Å **2**; $2.006(5)$, $2.030(5)$ Å **5**), whereas the two Ga-Sb bond lengths in **1** vary significantly ($2.6469(11)$, $2.8458(13)$, Å **1**) and in **2** and **5** vary slightly ($2.7310(5)$, $2.8036(5)$ Å **2**; $2.6420(9)$, $2.6534(8)$ Å **5**). The Ga-E bonds in **1** and **2** are elongated compared to those observed in $L^1Ga(EEt_2)_2$ ($2.6246(3)$, $2.6743(5)$ Å Sb; $2.6961(6)$, $2.7303(10)$ Å Bi),[15] but comparable to the sum of the respective covalent radii (Ga 1.24 Å; Sb 1.40 Å; Bi 1.51 Å)[27] and to those reported for monomeric compounds $(dmap)Ga(R_2)ER'_2$ (E = Sb, Bi; R = alkyl, R' = alkyl, SiMe₃; dmap = 4-dimethylamino pyridine)[28] as well as for four- and six-membered heterocyclic compounds $[R_2GaE(SiMe_3)_2]_x$ (E = Sb, 2.65-2.76 Å, E = Bi, 2.74-2.78 Å).[28] In contrast, Lewis acid-base adducts $R_3Ga-ER'_3$ such as $t\text{-Bu}_3GaSbR_3$ (R = Et, $2.8479(5)$ Å; $i\text{-Pr}$, $2.9618(2)$ Å),[28] $t\text{-Bu}_3GaBi\text{-}i\text{-Pr}_3$ ($3.135(1)$ Å),[29]) $(Et_4Bi_2)(Ga\text{-}t\text{-Bu}_3)_2$ ($3.099(2)$, $3.114(2)$ Å),[30] and $Et_3GaBi(SiMe_3)_3$ ($2.966(1)$ Å)[29] show significantly elongated Ga-E bond lengths. The E-Ga-E angles of $132.71(4)^\circ$ (**1**), $134.76(10)^\circ$ (**2**) and $126.21(3)^\circ$ (**5**) are significantly larger than those observed in $LGa(EEt_2)_2$ (Sb, $119.155(17)^\circ$; Bi, $119.89(7)^\circ$).[15]

Reactivity Studies with Cp^*M (M = Al, Ga)

To further investigate the specific influence of the organic ligand of the group 13-diyl, we became interested in the analogous reactions of Cp^* -substituted alanediyil $[Cp^*Al]_4$ and gallanediyil Cp^*Ga . The reactivity of $[Cp^*Al]_4$ and Cp^*Ga toward E_2R_4 (E = Sb, Bi; R = Et, Ph) significantly differs from that observed for $L^{1,2}M$ (M = Al, Ga).[15] $[Cp^*Al]_4$ was found to slowly react with Sb_2R_4 (R = Et, Ph) at room temperature with formation of $(Cp^*Al)_3Sb_2$ (**7**) within three days. The reaction is faster at elevated temperatures and $(Cp^*Al)_3Sb_2$ **7** is quantitatively formed at 80°C within one day. The reaction mechanism of 1: 4 molar amounts of $[Cp^*Al]_4$ and Sb_2R_4 was studied by *in situ* ^1H NMR studies. According to these studies, the formation of $Cp^*Al(SbR_2)_2$ as reaction intermediate via insertion of Cp^*Al into the Sb-Sb bond can be excluded. **7** and the analogous arsenic derivative $(Cp^*Al)_3As_2$ were previously obtained in reactions of $[Cp^*Al]_4$ with cyclotetraarsine and -stibine $(t\text{-BuE})_4$ (E = As, Sb). The reaction of $[Cp^*Al]_4$ and $(t\text{-BuSb})_4$ was reported to proceed with formation of $t\text{-Bu}_3Sb$. [31] A similar germeryl-bridged $[(C_6F_5)_2Ge]_3Bi_2$ was prepared from the reaction of $(C_6F_5)_2GeH_2$ with Et_3Bi , which proceeded with the elimination of ethane.[32] The reaction of $[Cp^*Al]_4$ with Bi_2Et_4 in toluene also required high reaction temperatures ($> 80^\circ\text{C}$) and resulted in the formation of $(Cp^*Al)_3Bi_2$ (**8**) in low yield. *In situ* ^1H NMR spectroscopy proved that the formation of **8** occurred after disproportionation of Bi_2Et_4 into Bi metal and

BiEt₃, which started at 55 °C, followed by the reaction of [Cp*Al]₄ with BiEt₃, which occurred with Bi-C bond activation and subsequent formation of **8**. **8** was also obtained in moderate yield in an independent study in the reaction of BiEt₃ with [Cp*Al]₄ in toluene at 120 °C. In contrast, the reactions of Cp*Ga and [Cp*Al]₄ with Bi₂Ph₄ proceeded already at ambient temperature with formation of metallic bismuth. Although Cp*Ga did not react with Sb₂R₄ (R = Et, Ph) and Bi₂Et₄ at room temperature, it reacted under drastic conditions (120 °C, 3 days) with formation of metallic antimony and bismuth, respectively, as was proven by elemental dispersive X-ray analysis (EDX).

Scheme 2. Reactions of Cp*Ga and [Cp*Al]₄ with E₂R₄ (E = Sb, Bi; R = Et, Ph) and formation of (Cp*Al)₃M₂ (E = Sb **7**, Bi **8**).

7 and **8** are air and moisture sensitive and moderately soluble in benzene, toluene and fluorobenzene. The ¹H NMR spectra of **7** and **8** in benzene-*d*₆ are almost identical and show a sharp singlet at 2.06 ppm (**7**) and 2.08 ppm (**8**) for the Cp* ring, whereas the ¹³C NMR spectra consist of two singlets (12.0 ppm, 116.1 ppm, **7**; 13.4 ppm, 116.5 ppm, **8**) for the methyl and cyclopentadienyl carbon atoms. The molecular structure of **8** was further determined by single-crystal X-ray diffraction analysis. The structure of **7** could not be solved but the unit cell dimensions obtainable suggest it is isostructural.

Single crystals of **8** suitable for X-ray diffraction analysis were grown from saturated benzene solutions at room temperature. **8** crystallize in the hexagonal crystal system. Problems with disorder made the choice of the space group ambiguous. The best model was found with space group *P*6₃.

Figure 6. Solid state structure of $(\text{Cp}^*\text{Al})_3\text{Bi}_2$ (**8**). H-atoms and disordered Cp^*Al units have been omitted for clarity and thermal ellipsoids (C isotropic) are shown with 50% probability level. Parts depicted in pale colors are generated via 3-fold rotational symmetry.

The Cp^*Al unit is disordered over two positions by pseudo two-fold symmetry and the major component comprises about 70%. Owing to this disorder, the structural parameters of **8** are of only limited reliability or insignificant for the vast use of re- and constraints. The molecular structure of **8** shows an Al_3Bi_2 framework adopting a trigonal-bipyramidal structure. The two apical Bi atoms are bridged by three Cp^*Al moieties and the Al atoms adopt equatorial positions (Figure 6). The Bi and Al atoms adopt distorted pyramidal and tetrahedral coordination geometries, respectively. The Bi-Al bond lengths range from 2.692(13) to 2.867(13) Å, which is close to the sum of the covalent single bond radii (Al, 1.26 Å; Bi, 1.51 Å).[27] Furthermore, the Al-Bi-Al ($63.3(4)^\circ$ - $68.0(4)^\circ$) and Bi-Al-Bi ($102.50(12)^\circ$, $102.5(3)^\circ$)

bond angles differ significantly from the ideal values of a regular trigonal-bipyramidal structure (90° and 109.5°). The Cp^* ligand in **8** likely adopts a η^5 coordination mode.

Quantum chemical calculations. To investigate the electronic nature and bonding situation of $(\text{Cp}^*\text{Al})_3\text{Bi}_2$ **8** and to compare this with analogous compounds containing the lighter group 15 elements, DFT calculations on $(\text{Cp}^*\text{Al})_3\text{E}_2$ ($\text{E} = \text{P}, \text{P}', \text{As}, \text{As}', \text{Sb}, \text{Sb}', \text{Bi}, \text{Bi}'$) were performed. All quantum chemical calculations were employed with the ORCA quantum chemistry package (version 4.0).[33] Ground-state geometry optimizations were calculated with the composite approach PBEh-3c,[34] utilizing the geometrical counterpoise correction (gCP)[35], the atom-pairwise dispersion correction with Becke-Johnson damping scheme (D3BJ)[36]. The RIJK approximation was employed to accelerate the calculations in conjunction with the appropriate auxiliary basis sets (def2-SVP/JK).[37] Additionally, effective core potentials (ECP) were employed for the Sb and Bi atoms.[38,39] Natural bond orbital analysis was performed using the NBO 6.0 program.[40]

The calculated bond lengths (Al-Bi Å) and angles (Al-Bi-Al $^\circ$, Bi-Al-Bi $^\circ$) of **Bi'** agree very well with the experimental values of **8** and deviate only by 0.8% (bond lengths) and 1.5% (bond angles), respectively. The DFT calculations on **P'** - **Bi'** reveal covalent bonds between Al and the pnictogen atoms with Mayer bond orders (MBOs) of 0.81 - 0.85. Based on NBO analysis, the Al-E bonding orbitals show constant p-character of 59% on the Al atom and an increasing p-character of 82% (P), 84% (As), 87% (Sb) and 90% (Bi) on the pnictogen. As a result, s-character of the electron lone-pair of the group 15 element E steadily increases with increasing atomic number of the pnictogen from 47% (P), 54% (As), 63% (Sb) to finally 72% (Bi).

The atomic charges and Al-E bond polarities steadily decrease from **P'** (Al: 1.3 *e*, P: -1.0 *e*, pol.: 26%-74%), **As'** (Al: 1.2 *e*, As: -0.9 *e*, pol.: 29%-71%), **Sb'** (Al: 1.0 *e*, Sb: -0.6 *e*, pol.: 35%-65%) to **Bi'** (Al: 1.2 *e*, As: -0.9 *e*, pol.: 29%-71%) due to the decreasing difference in electronegativity between Al and the respective pnictogen atom.

Figure 7. HOMO and LUMO of **XP** and **XB**.

In the case of **P'**, **As'** and **Sb'**, the HOMO is a representation of the p-orbitals on the pnictogen, facing the Al₃-plane with small contributions from the Cp* ligands π -systems (Figure 7). In **Bi'**, the order of orbitals is switched, so that a different set of p-orbitals represents the HOMO, facing one Cp* ligand, with a stronger contribution from the Cp* ligands π -systems. The LUMO is expanded over the whole molecule in all cases.

Conclusions.

In summary, gallanediyls containing β -diketiminate (L¹) and guanidinate (L²) ligands reversibly react with E₂R₄ (E = Sb, Bi; R = Ph, Et) with insertion into the E-E bond and formation of L^{1,2}Ga(ER₂)₂. The position of the reaction equilibrium is significantly affected by the organic substituents (L^{1,2}, Et, Ph), the E-E bond strengths as well as the molar ratio of the starting reagents. In contrast, [Cp*Al]₄ reacts with Sb₂R₄ (R = Ph, Et) and Bi₂Et₄ with formation of (Cp*Al)₃E₂ (E = Sb, **7**; Bi, **8**). Analogous reactions of Cp*Ga and E₂R₄ only yielded metallic antimony and bismuth.

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The following files are available free of charge.

Supporting Information (PDF) including ¹H, ¹³C NMR and IR spectra of **1** - **8** as well as crystallographic details and quantum chemical calculations.

CCDC-1846071 (**1**), -1843322 (**2**), -1843323 (**5**), and -1843324 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[26] **1**: [C₅₆H₆₄GaN₂Sb₂], *M* = 1078.33, yellow crystal, (0.150 × 0.120 × 0.015 mm); triclinic, space group *P*-1; *a* = 11.5155(8) Å, *b* = 12.6896(8) Å, *c* = 19.0438(11) Å; α = 79.327(5)°, β = 80.734(5)°, γ = 67.987(5)°, *V* = 2522.5(3) Å³; *Z* = 2; μ = 1.630 mm⁻¹; ρ_{calc} = 1.420 g·cm⁻³; 18888 reflections (θ_{max} = 25.000°), 8783 unique (*R*_{int} = 0.0713); 539

parameters; largest max./min in the final difference Fourier synthesis $2.263 \text{ e} \cdot \text{\AA}^{-3} / -1.138 \text{ e} \cdot \text{\AA}^{-3}$; max./min. transmission 0.947/0.808; $R_1 = 0.0838$ ($I > 2\sigma(I)$), $wR_2 = 0.1461$ (all data).

2: $[\text{C}_{59}\text{H}_{75}\text{Bi}_2\text{GaN}_2]$, $M = 1299.89$, colorless crystal, $(0.159 \times 0.133 \times 0.119 \text{ mm})$; triclinic, space group $P\bar{1}$; $a = 11.421(2) \text{ \AA}$, $b = 12.599(2) \text{ \AA}$, $c = 18.841(3) \text{ \AA}$; $\alpha = 80.002(8)^\circ$, $\beta = 81.030(9)^\circ$, $\gamma = 68.224(7)^\circ$, $V = 2466.9(7) \text{ \AA}^3$; $Z = 2$; $\mu = 7.699 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.750 \text{ g} \cdot \text{cm}^{-3}$; 99724 reflections ($\theta_{\text{max}} = 33.571^\circ$), 18970 unique ($R_{\text{int}} = 0.0336$); 533 parameters; largest max./min in the final difference Fourier synthesis $1.251 \text{ e} \cdot \text{\AA}^{-3} / -1.159 \text{ e} \cdot \text{\AA}^{-3}$; max./min. transmission 0.75/0.51; $R_1 = 0.0197$ ($I > 2\sigma(I)$), $wR_2 = 0.0440$ (all data).

5: $[\text{C}_{45}\text{H}_{76}\text{GaN}_3\text{Sb}_2]$, $M = 972.30$, pale yellow crystal, $(0.230 \times 0.170 \times 0.092 \text{ mm})$; triclinic, space group $P\bar{1}$; $a = 9.8989(12) \text{ \AA}$, $b = 11.6851(13) \text{ \AA}$, $c = 20.310(2) \text{ \AA}$; $\alpha = 85.025(6)^\circ$, $\beta = 85.115(6)^\circ$, $\gamma = 75.497(6)^\circ$, $V = 2260.9(5) \text{ \AA}^3$; $Z = 2$; $\mu = 1.810 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.428 \text{ g} \cdot \text{cm}^{-3}$; 105882 reflections ($\theta_{\text{max}} = 33.251^\circ$), 16357 unique ($R_{\text{int}} = 0.0746$); 482 parameters; largest max./min in the final difference Fourier synthesis $2.951 \text{ e} \cdot \text{\AA}^{-3} / -3.505 \text{ e} \cdot \text{\AA}^{-3}$; max./min. transmission 0.75/0.51; $R_1 = 0.0814$ ($I > 2\sigma(I)$), $wR_2 = 0.1958$ (all data).

8: $[\text{C}_{30}\text{H}_{45}\text{Al}_3\text{Bi}_2]$, $M = 904.56$, dark red crystal, $(0.430 \times 0.380 \times 0.350 \text{ mm})$; hexagonal, space group $P6_3$; $a = 11.1596(8) \text{ \AA}$, $b = 11.1596(8) \text{ \AA}$, $c = 14.7597(11) \text{ \AA}$; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 1591.9(3) \text{ \AA}^3$; $Z = 2$; $\mu = 11.139 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.887 \text{ g} \cdot \text{cm}^{-3}$; 10555 reflexes ($\theta_{\text{max}} = 25.242^\circ$), 3704 unique ($R_{\text{int}} = 0.0805$); 84 parameters; Flack-Parameter $x = 0.57(4)$; largest max./min in the final difference Fourier synthesis $3.467 \text{ e} \cdot \text{\AA}^{-3} / -2.184 \text{ e} \cdot \text{\AA}^{-3}$; max./min. transmission 0.0392/0.1045; $R_1 = 0.0459$ ($I > 2\sigma(I)$), $wR_2 = 0.1328$ (all data).

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TOC entry

Gallanediyls $L^{1/2}\text{Ga}$ react with dipentelanes R_4E_2 in a temperature-dependent equilibrium reaction with insertion into the E-E bond and formation of $L^{1/2}\text{Ga}(\text{ER}_2)_2$, whereas analogous reactions of $[\text{Cp}^*\text{Al}]_4$ yields $(\text{Cp}^*\text{Al})_3\text{E}_2$.

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