Supporting Information

Sequential Bi-C Bond Activation Reactions of $BiEt_3$ by Insertion Reactions of RE {R = HC[C(Me)N(2,6-*i*-$Pr_2C_6H_3$)]$_2$; E = Al, Ga, In}.

Chelladurai Ganesamoorthy, Dieter Bläser, Christoph Wölper and Stephan Schulz*

Experimental Section

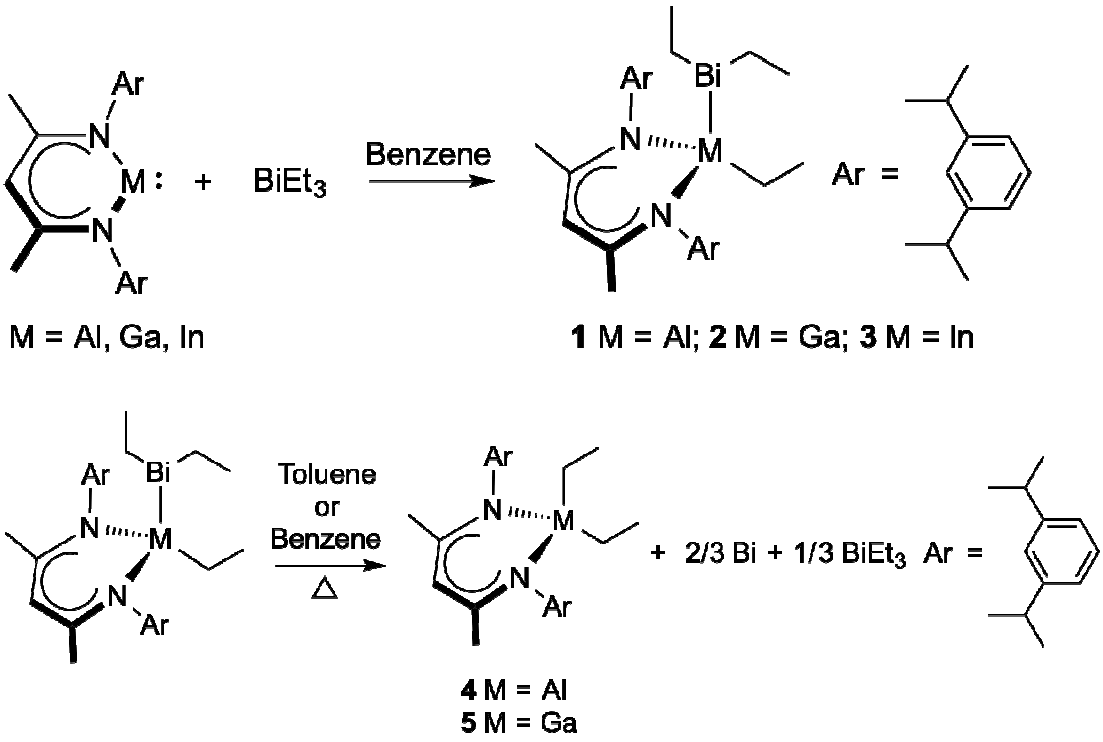
General Procedures. All manipulations were performed in an atmosphere of purified argon using standard Schlenk and glove-box techniques. Toluene and hexane were dried using mBraun Solvent Purification System. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. Anhydrous nature of the solvents were verified by Karl Fischer titration. The compounds RM (R = HC[C(Me)N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$; M = Al, Ga and In)[1] and $BiEt_3$[2] were prepared according to the published procedures. Other chemicals were obtained from commercial sources and purified prior to use.

Instrumentation. The ^{1}H (300 MHz) and ^{13}C{^{1}H} (75.5 MHz) NMR (δ in ppm) spectra were recorded using a Bruker Avance DPX-300 spectrometer and the spectra were referenced to the trace of respective protonated solvent impurities present in the deuterated solvents. Powder X-ray diffraction (XRD) was performed using a Bruker D8 Advance powder diffractometer with Cu $K_{\alpha1}$ radiation (λ 1.540598 Å). The microanalyses were performed at the elemental analysis laboratory of University of Duisburg-Essen. IR spectra were measured in an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The spectrometer was placed in a glovebox so as to perform the FT-IR measurements in inert gas atmosphere. Metal precipitates were analyzed by SEM using a Jeol JSM 6510 equipped with an energy dispersive X-ray spectroscopy (EDX) device (Bruker Quantax 400).

Reference:

1) a) C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, *Angew. Chem.* 2000, **112**, 4444; *Angew. Chem. Int. Ed*. 2000, **39**, 4274; b) N. J. Hardman, B. E. Eichler and P. P. Power, *Chem. Commun.* 2000, 1991; c) M. S. Hill and P. B. Hitchcock, *Chem. Commun.*, 2004, 1818.

2) H. Gilman and J. F. Nelson, *J. Am. Chem. Soc.* 1937, **59**, 935.



Synthesis of RAlEt(BiEt$_2$) (1)

A mixture of RAl (82 mg, 0.184 mmol) and $BiEt_3$ (54.6 mg, 30 μL, 0.184 mmol) in 0.6 mL of C_6D_6 was heated at 75 °C for 5 h. The reaction mixture was periodically monitored using ^{1}H NMR to avoid decomposing **1** into $RAlEt_2$ (**4**) and Bi metal. The solvents were removed under reduced pressure to give a yellow residue, which was redissolved in 1 mL of *n*-hexane and stored at -30 °C for 2 days to afford analytically pure yellow crystals of **1**. Yield: 80 mg (0.108 mmol, 58 %). Anal. Calcd. for $C_{35}H_{56}BiAlN_2$: C, 56.75; H, 7.62; N, 3.78. Found: C, 57.60; H, 7.76; N, 3.79%. IR (neat): ν 2968 (m), 2922 (m), 2859 (m), 1549 (w), 1521 (m), 1435 (m), 1383 (br, s), 1309 (m), 1257 (m), 1172 (m), 1137 (w), 1103 (w), 1017 (m), 989 (m), 932 (m), 863 (m), 800 (m), 755 (m), 715 (w), 640 (w), 577 (m), 520 (w), 411 (s) cm^{-1}. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.13 (m, 6 H, $C_6H_3(^iPr)_2$), 4.79 (s, 1 H, γ-C*H*-), 3.53 (sept, 2 H, -C*H*$(CH_3)_2$), 3.41 (sept, 2 H, -C*H*$(CH_3)_2$), 1.97 & 1.67 (m, 13 H, -AlCH$_2$C*H*$_3$, -BiC*H*$_2$C*H*$_3$), 1.54 (s, 6 H, ArNCC*H*$_3$), 1.52 (d, 6 H, -CH(C*H*$_3$)$_2$), 1.44 (d, 6 H, -CH(C*H*$_3$)$_2$), 1.22 (d, 6 H, -CH(C*H*$_3$)$_2$), 1.06 (d, 6 H, J = 6.6 Hz, -CH(C*H*$_3$)$_2$), 0.37 (q, 2 H, J = 8.1 Hz, -AlC*H*$_2$CH$_3$). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 171.58 (ArN*C*CH$_3$),

145.79 (C_6H_3), 143.81 (C_6H_3), 141.55 (C_6H_3), 127.84 (C_6H_3), 125.46 (C_6H_3), 125.01 (C_6H_3), 98.83 (γ-*C*H-), 30.51 (-*C*H(CH_3)$_2$), 27.77 (-*C*H(CH_3)$_2$), 25.84 (-CH(*C*H_3)$_2$), 25.72 (-CH(*C*H_3)$_2$), 25.45 (-CH(*C*H_3)$_2$), 25.37 (-CH(*C*H_3)$_2$), 24.16 (ArNC*C*H_3), 17.99 (Bi*C*H_2*C*H_3), 12.48 (AlCH_2*C*H_3), -14.83 (Al*C*H_2CH_3).

Synthesis of RGaEt(BiEt$_2$) (2)

A mixture of RGa (300 mg, 0.615 mmol) and $BiEt_3$ (182 mg, 100 µL, 0.614 mmol) in 5 mL of toluene was heated at 80 °C for 24 h. Compound **2** is stable at this temperature even for 2 days. The solvents were removed under reduced pressure to give a yellow residue, which was redissolved in 5 mL of *n*-hexane and stored at -30 °C for 1 day to afford analytically pure yellow crystals of **1**. Yield: 420 mg (0.536 mmol, 87 %). Anal. Calcd. for $C_{35}H_{56}BiGaN_2$: C, 53.65; H, 7.20; N, 3.58. Found: C, 54.20; H, 7.25; N, 3.71%. IR (neat): ν 2966 (m), 2929 (m), 2851 (m), 1549 (m), 1520 (m), 1435 (m), 1393 (s), 1310 (m), 1255 (m), 1171 (m), 1141 (w), 1105 (w), 1015 (w), 937 (w), 853 (m), 788 (s), 757 (m), 661 (w), 619 (w), 511 (m), 439 (m) cm^{-1}. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.13 (m, 6 H, C_6H_3(^{i}Pr)$_2$), 4.66 (s, 1 H, γ-C*H*-), 3.61 (sept, 2 H, -C*H*(CH_3)$_2$), 3.47 (sept, 2 H, -C*H*(CH_3)$_2$), 1.87 & 1.71 (m, 7 H, -GaCH_2C*H*$_3$, -Bi*C*H_2CH_3), 1.58 (s, 6 H, ArNCC*H*$_3$), 1.56 (t, 6 H, -BiCH_2C*H*$_3$), 1.52 (d, 6 H, -CH(C*H*$_3$)$_2$), 1.40 (d, 6 H, -CH(C*H*$_3$)$_2$), 1.23 (d, 6 H, -CH(C*H*$_3$)$_2$), 1.13 (d, 6 H, *J* = 6.9 Hz, -CH(C*H*$_3$)$_2$), 0.83 (q, 2 H, -Ga*C*H_2CH_3). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 169.47 (ArN*C*CH_3), 145.42 (C_6H_3), 143.51 (C_6H_3), 143.16 (C_6H_3), 127.30 (C_6H_3), 125.21 (C_6H_3), 124.82 (C_6H_3), 97.33 (γ-*C*H-), 30.24 (-*C*H(CH_3)$_2$), 27.74 (-*C*H(CH_3)$_2$), 25.78 (-CH(*C*H_3)$_2$), 25.77 (-CH(*C*H_3)$_2$), 25.43 (-CH(*C*H_3)$_2$), 25.34 (-CH(*C*H_3)$_2$), 24.22 (ArNC*C*H_3), 18.38 (BiCH_2*C*H_3), 17.23 (Bi*C*H_2CH_3), 13.29 (GaCH_2*C*H_3), -11.09 (Ga*C*H_2CH_3).

Synthesis of RInEt(BiEt$_2$) (3)

This was synthesized by following the procedure of **1** using RIn (228 mg, 0.429 mmol) and $BiEt_3$ (254 mg, 0.858 mmol). Heating temperature and time duration were 79 ºC and 4 h, respectively. Yield: 0.310 g (0.374 mmol, 87 %). Anal. Calcd. for $C_{35}H_{56}BiInN_2$: C, 50.73; H, 6.81; N, 3.38. Found: C, 50.60; H, 6.79; N, 3.35%. IR (neat): ν 2962 (m), 2917 (m), 2855 (m), 1550 (m), 1510 (m), 1460 (m), 1432 (m), 1381 (br, s), 1314 (s), 1241 (s), 1173 (m), 1128 (br, m), 982 (m), 931 (m), 847 (w),

791 (s), 751 (m), 661 (w), 605 (w), 515 (w), 442 (s) cm^{-1}. ^1H NMR (C_6D_6, 300 MHz): δ 7.11 (m, 6 H, $C_6H_3(^iPr)_2$), 4.66 (s, 1 H, γ-C*H*-), 3.60 (sept, 2 H, -C*H*$(CH_3)_2$), 3.48 (sept, 2 H, -C*H*$(CH_3)_2$), 1.98 (m, 7 H, -InCH_2CH_3, -BiCH_2CH_3), 1.70 (t, 6 H, -BiCH_2CH_3), 1.63 (s, 6 H, ArNCCH_3), 1.47 (d, 6 H, -CH(CH_3)$_2$), 1.33 (d, 6 H, -CH(CH_3)$_2$), 1.26 (d, 6 H, -CH(CH_3)$_2$), 1.18 (d, 6 H, *J* = 6.9 Hz, -CH(CH_3)$_2$), 1.15 (m, 2 H, -InCH_2CH_3). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 169.15 (ArN*C*CH_3), 144.97 (C_6H_3), 144.00 (C_6H_3), 142.90 (C_6H_3), 126.53 (C_6H_3), 124.78 (C_6H_3), 124.61 (C_6H_3), 96.71 (γ-*C*H-), 29.85 (-*C*H$(CH_3)_2$), 28.12 (-*C*H$(CH_3)_2$), 26.30 (-CH(*C*H_3)$_2$), 25.88 (-CH(*C*H_3)$_2$), 25.31 (-CH(*C*H_3)$_2$), 24.88 (-CH(*C*H_3)$_2$), 24.63 (ArNC*C*H_3), 21.02 (BiCH_2*C*H_3), 18.36 (Bi*C*H_2CH_3), 13.95 (InCH_2*C*H_3), -10.64 (In*C*H_2CH_3).

Formation of $RGaEt_2$ (5) from $RGaEt(BiEt_2)$ (2)

Compound **2** (175 mg, 0.223 mmol) in 1 mL of toluene was heated at 120 °C for 15 h. The reaction mixture was filtered and the insoluble gray power was washed with 5 mL of toluene. The combined filtrates were dried under reduced pressure and the resulting white solid was dissolved in minimum amount of *n*-hexane. The solution was kept at -30 °C for 1 day to afford colorless crystals of **5**. Yield: 0.112 g of $RGaEt_2$ (0.205 mmol, 92 %); 0.0214 g of Bi metal. IR (neat): ν 2968 (m), 2919 (m), 2864 (m), 1548 (m), 1516 (m), 1440 (m), 1396 (br, s), 1309 (s), 1255 (m), 1173 (m), 1097 (w), 1010 (m), 934 (m), 858 (w), 798 (s), 754 (m), 640 (m), 542 (m), 499 (m), 444 (m) cm^{-1}. ^1H NMR (C_6D_6, 300 MHz): δ 7.13 (m, 6 H, $C_6H_3(^iPr)_2$), 4.68 (s, 1 H, γ-C*H*-), 3.50 (sept, 4 H, -C*H*$(CH_3)_2$), 1.57 (s, 6 H, ArNCCH_3), 1.36 (d, 12 H, -CH(CH_3)$_2$), 1.23 (t, 6 H, -GaCH_2CH_3), 1.20 (d, 12 H, *J* = 6.9 Hz, -CH(CH_3)$_2$), 0.53 (q, 4 H, *J* = 7.8 Hz, -GaCH_2CH_3). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 169.12 (ArN*C*CH_3), 144.54 (C_6H_3), 142.91 (C_6H_3), 127.11 (C_6H_3), 124.72 (C_6H_3), 97.29 (γ-*C*H-), 28.44 (-*C*H$(CH_3)_2$), 25.58 (-CH(*C*H_3)$_2$), 25.25 (-CH(*C*H_3)$_2$), 23.82 (ArNC*C*H_3), 11.38 (GaCH_2*C*H_3), 4.18 (Ga*C*H_2CH_3).

Single-crystal X-ray analyses. The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated $Mo_{K\alpha}$ radiation, λ = 0.71073 Å) at 100 K. The structures were solved by Direct Methods (SHELXS-97)[1] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-97)[2]. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2) except for **1** where the corrections was done numerically by face-indexing. Hydrogen atoms were refined using a riding model or rigid methyl groups. CCDC 1011108 (**1**),CCDC 1011107 (**2**), CCDC 1011105 (**3**), and CCDC 1011106 (**5**) 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.

	1	**2**	**3**	**5**
Empirical formula	C_{35} H_{56} Al Bi N_2	C_{35} H_{56} Bi Ga N_2	C_{35} H_{56} Bi In N_2	C_{33} H_{51} Ga N_2
M	740.77	783.51	828.61	545.47
Crystal size [mm]	0.28 × 0.24 × 0.21	0.480 × 0.413 × 0.254	0.324 × 0.299 × 0.227	0.460 × 0.430 × 0.380
T [K]	100(1)	100(1)	100(1)	100(1)
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	P -1	P -1	P $2_1/n$	P -1
a [Å]	11.5940(15)	9.0994(6)	8.7410(4)	10.3656(18)
b [Å]	12.2244(16)	12.0444(9)	21.4064(10)	12.119(2)
c [Å]	12.6546(16)	16.5176(12)	19.0397(9)	13.700(2)
α [°]	72.804(6)	74.379(2)	90	71.293(6)
β [°]	88.915(6)	79.774(2)	99.2600(10)	75.982(6)
γ [°]	89.682(6)	85.921(2)	90	73.618(6)
V [Å^3]	1713.1(4)	1715.2(2)	3516.2(3)	1542.0(5)
Z	2	2	4	2

D_{calc} [g · cm^{-1}]	1.436	1.517	1.565	1.175
μ(MoK_α [mm^{-1}])	5.196	5.932	5.677	0.914
Transmissions	0.54/0.38	0.44/0.12	0.50/0.24	0.80/0.69
F(000)	752	788	1648	588
Index ranges	$-16 \le h \le 16$	$-13 \le h \le 13$	$-12 \le h \le 12$	$-15 \le h \le 14$
	$-16 \le k \le 17$	$-17 \le k \le 17$	$-31 \le k \le 31$	$-17 \le k \le 17$
	$-17 \le l \le 17$	$-23 \le l \le 23$	$-28 \le l \le 27$	$-19 \le l \le 19$
θ_{max} [°]	30.086	30.978	31.708	31.426
Reflections collected	48941	55296	127401	34092
Independent reflections	9813	10747	11625	9970
R_{int}	0.0251	0.0508	0.0471	0.0219
Refined parameters	365	365	365	337
R_1 [$I > 2\sigma(I)$][a]	0.0175	0.0278	0.0283	0.0269
wR_2 [all data][a]	0.0437	0.0693	0.0631	0.0751
GooF[b]	1.042	1.046	1.103	1.039
$\Delta\rho_{final}$ (max/min) [e · Å^{-3}]	1.407/-0.592	2.736/-2.248	3.281/-1.236	1.429/-0.292

[a] $R(F) = \Sigma \, ||F_o| - |F_c|| / \Sigma |F_o|$; $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{0,5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ mit $P = [F_o^2 + 2F_c^2]/3$, a and b are constants chosen by the programme; [b] GoF = $[\Sigma\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0,5}$ with n data and p parameters.

[1] G. M. Sheldrick, *Acta Crystallogr.* 1990, **A46**, 467

[2] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) **1997**. (see also: Sheldrick, G. M. Acta Crystallogr. 2008, **A64**, 112)

Table 2. Selected bond distances and bond angles for compound **5**.

5			
Bond distances (Å)		Bond angles (°)	
Ga(1)-C(32)	1.9814(11)	C(32)-Ga(1)-N(2)	110.92(4)
Ga(1)-N(2)	1.9876(9)	C(32)-Ga(1)-N(1)	113.30(4)
Ga(1)-N(1)	1.9979(9)	N(2)-Ga(1)-N(1)	93.75(4)
Ga(1)-C(30)	2.0215(12)	C(32)-Ga(1)-C(30)	117.77(5)
N(1)-C(1)	1.3326(13)	N(2)-Ga(1)-C(30)	110.59(4)
N(1)-C(6)	1.4441(13)	N(1)-Ga(1)-C(30)	107.91(4)
N(2)-C(3)	1.3360(13)	C(1)-N(1)-C(6)	121.17(8)
N(2)-C(18)	1.4365(12)	C(1)-N(1)-Ga(1)	119.93(7)
C(1)-C(2)	1.4104(14)	C(6)-N(1)-Ga(1)	118.71(6)
C(2)-C(3)	1.4010(14)	C(3)-N(2)-C(18)	121.10(8)
		C(3)-N(2)-Ga(1)	120.18(7)
		C(18)-N(2)-Ga(1)	118.67(6)

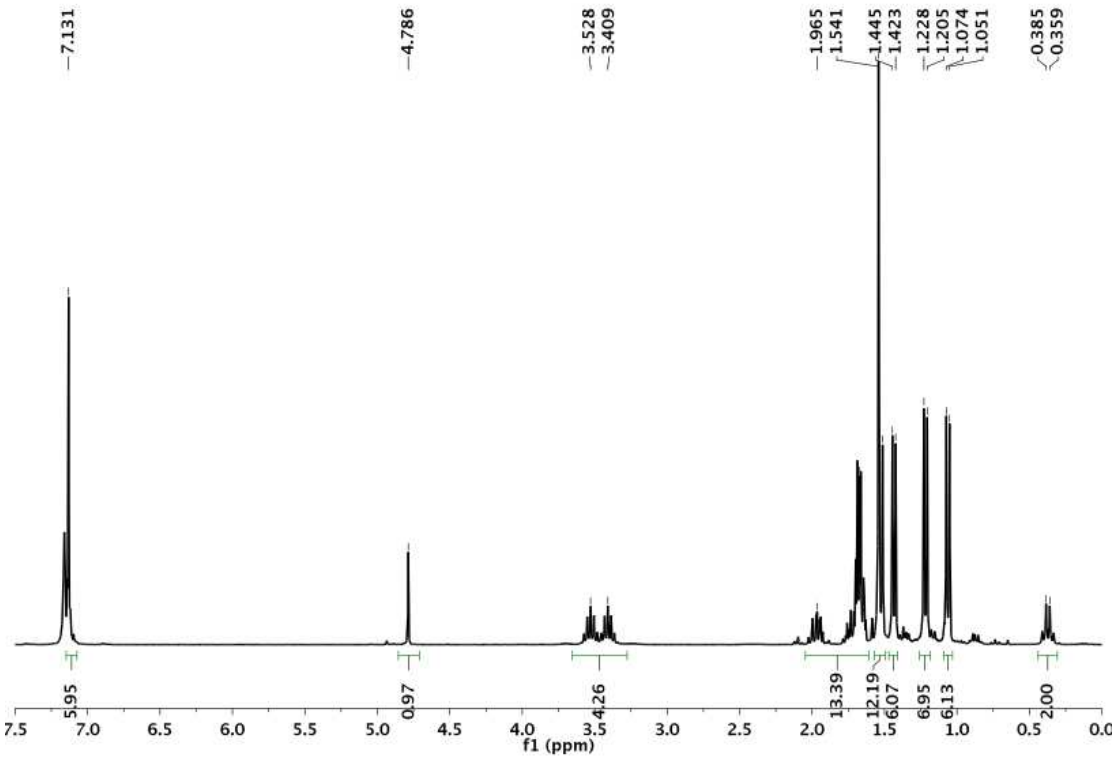


Figure S1. ^{1}H NMR spectrum of RAlEt(BiEt$_2$) (**1**) in C_6D_6.

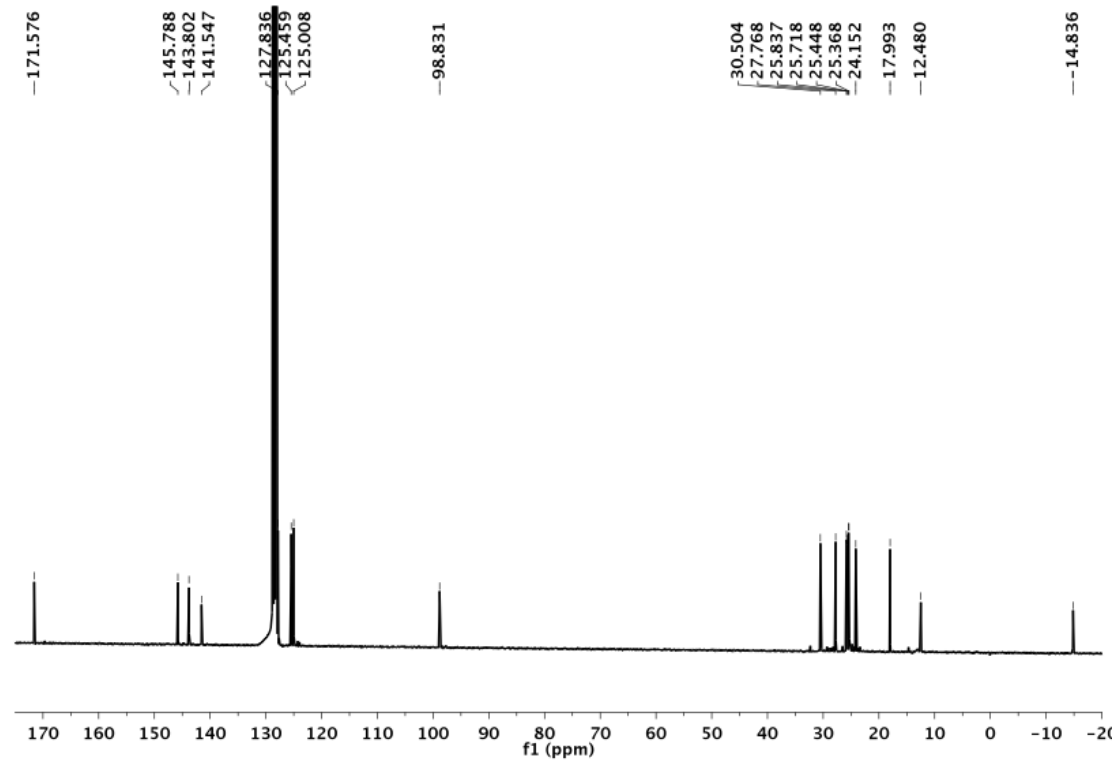


Figure S2. ^{13}C NMR spectrum of RAlEt(BiEt$_2$) (**1**) in C_6D_6.

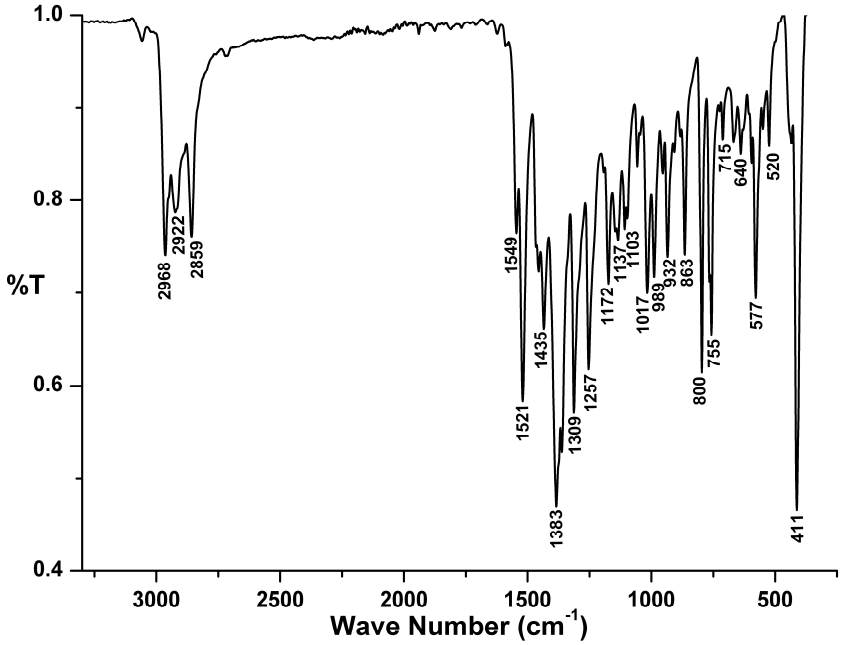


Figure S3. ATR-IR spectrum of $RAlEt(BiEt_2)$ (**1**).

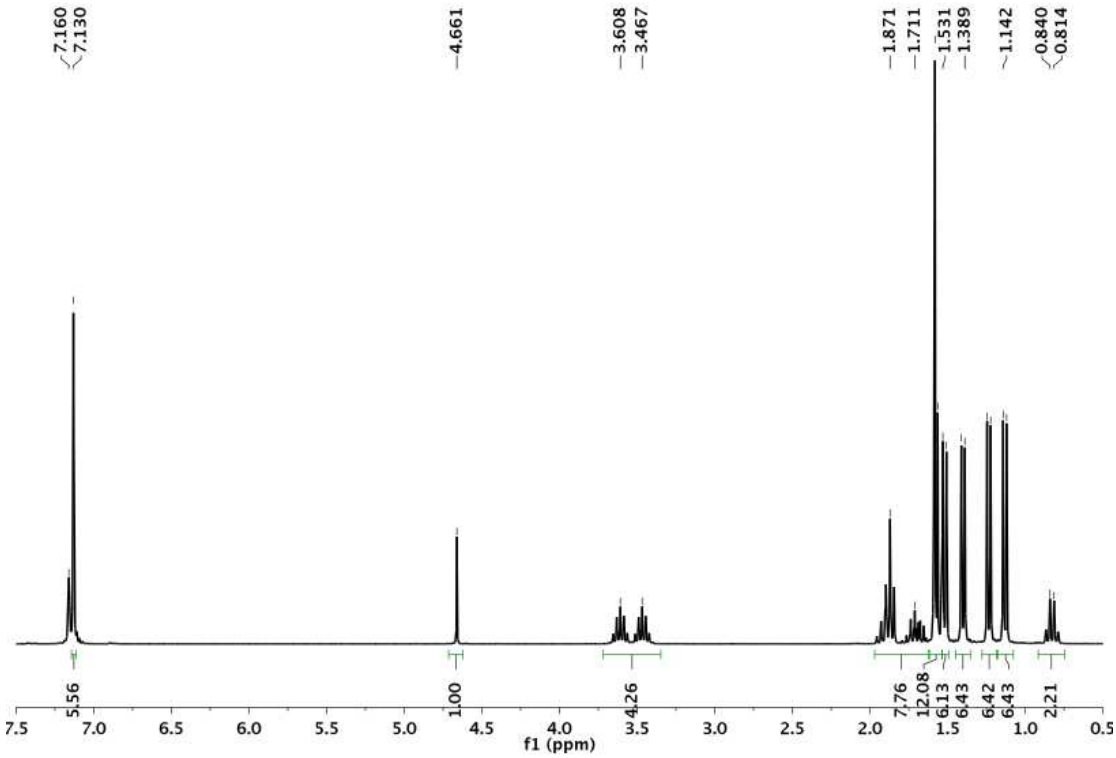


Figure S4. ^1H NMR spectrum of $RGaEt(BiEt_2)$ (**2**) in C_6D_6.

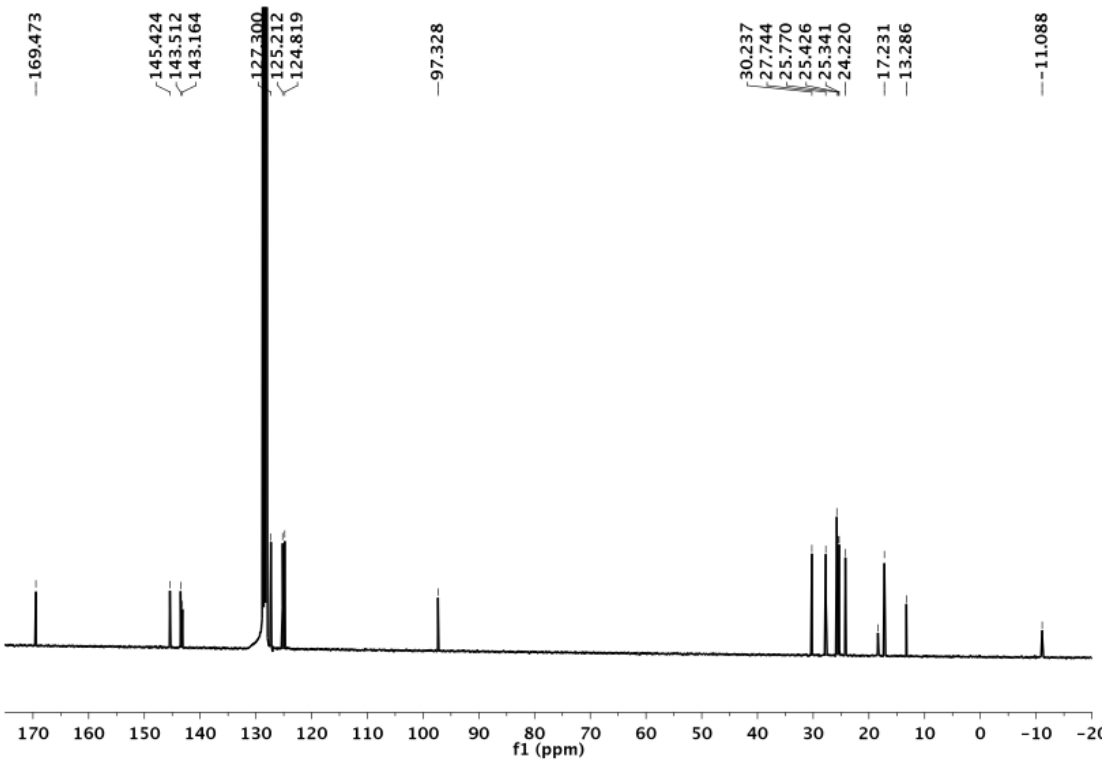


Figure S5. ^{13}C NMR spectrum of RGaEt($BiEt_2$) (**2**) in C_6D_6.

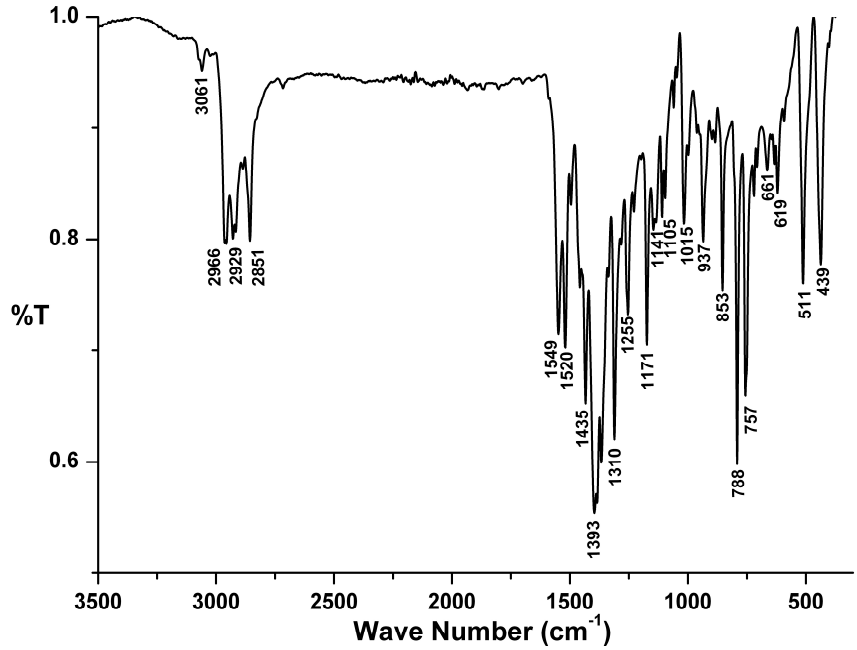


Figure S6. ATR-IR spectrum of RGaEt($BiEt_2$) (**2**).

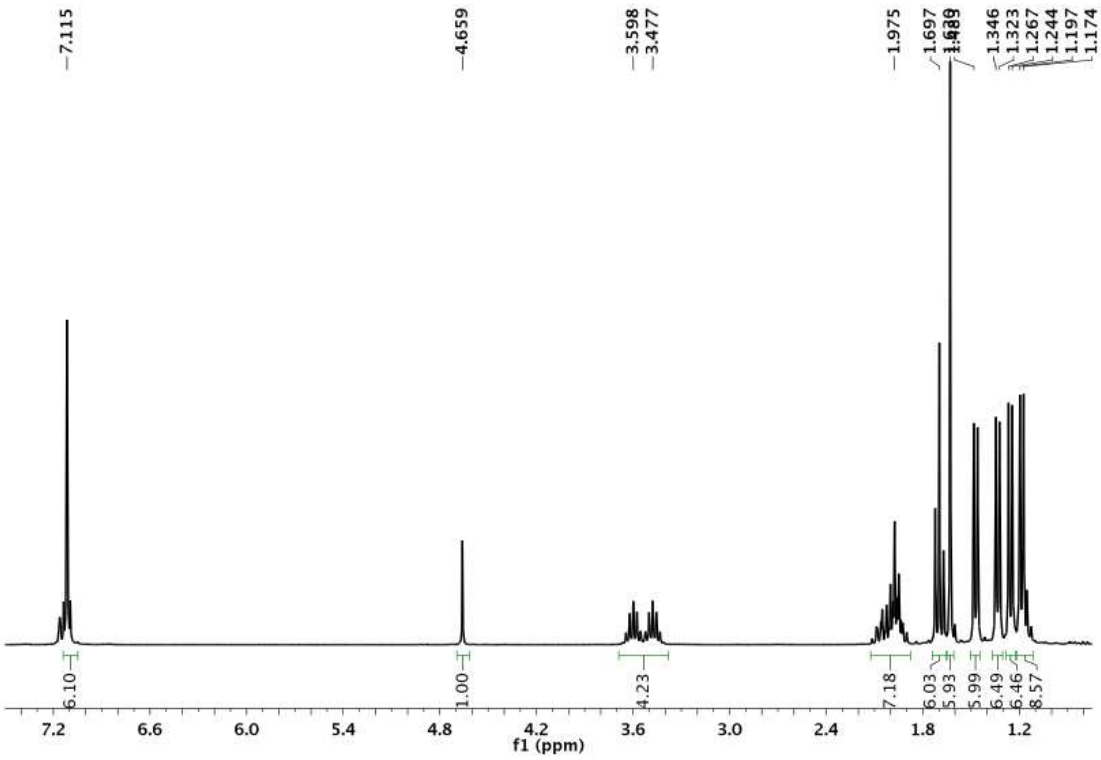


Figure S7. ^{1}H NMR spectrum of RInEt(BiEt$_2$) (**3**) in C_6D_6.

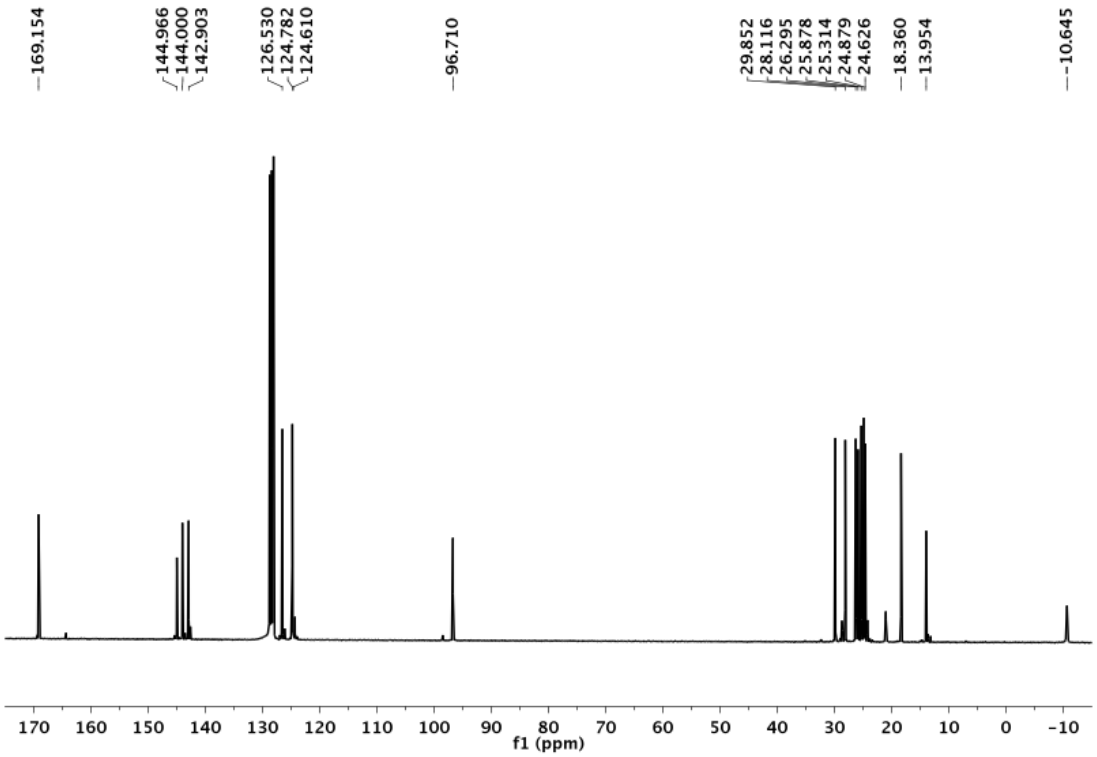


Figure S8. ^{13}C NMR spectrum of RInEt(BiEt$_2$) (**3**) in C_6D_6.

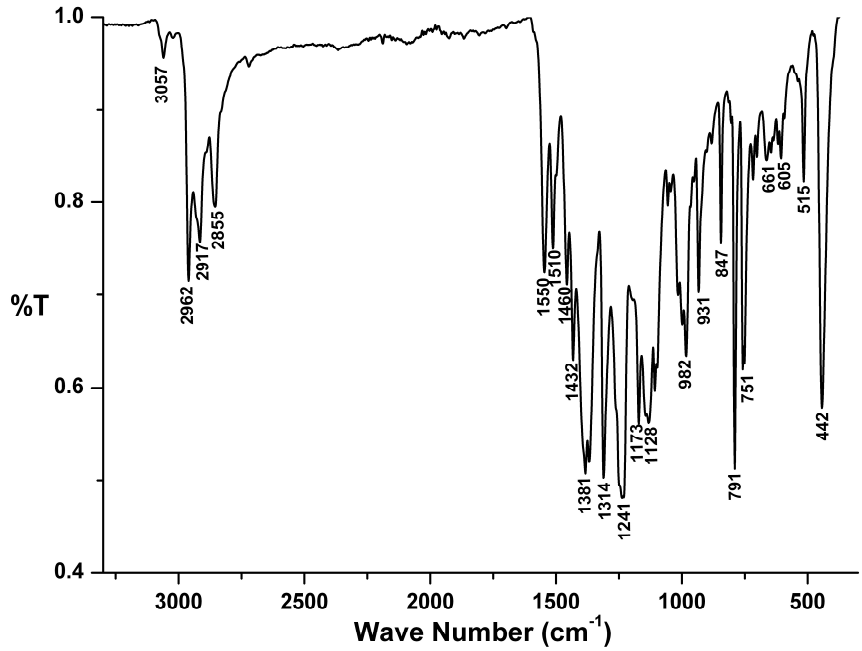


Figure S9. ATR-IR spectrum of $RInEt(BiEt_2)$ (**3**).

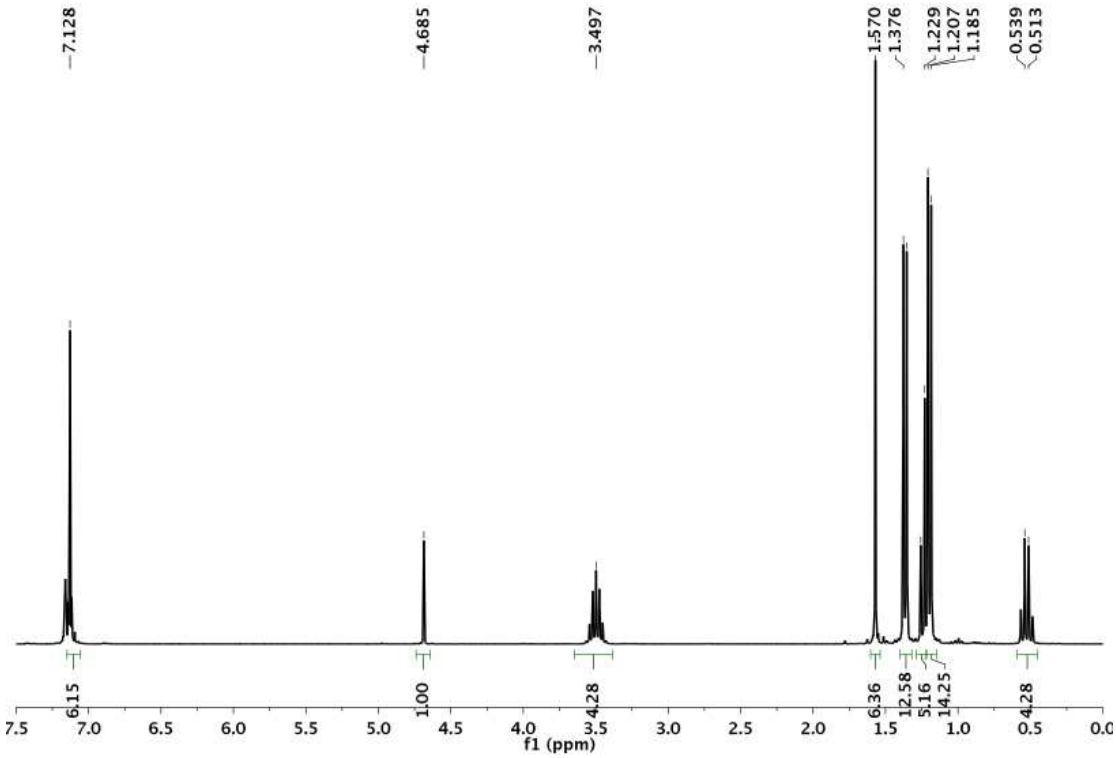


Figure S10. ^1H NMR spectrum of $RGaEt_2$ (**5**) in C_6D_6.

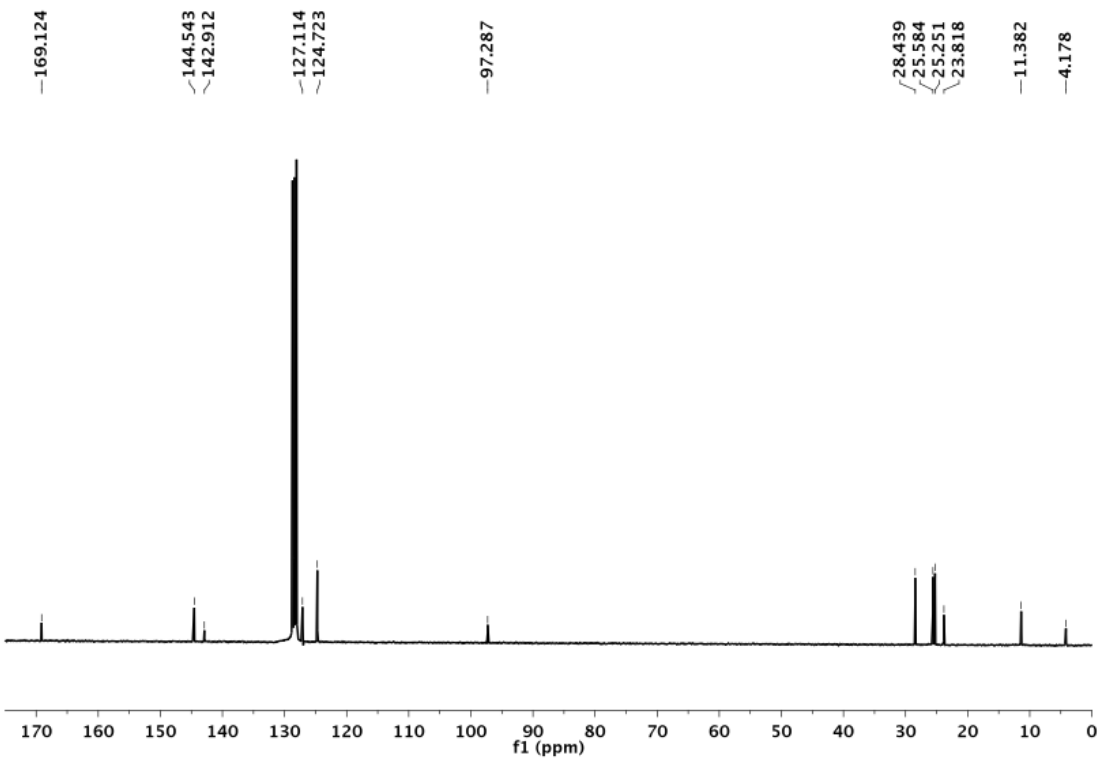


Figure S11. ^{13}C NMR spectrum of $RGaEt_2$ (**5**) in C_6D_6.

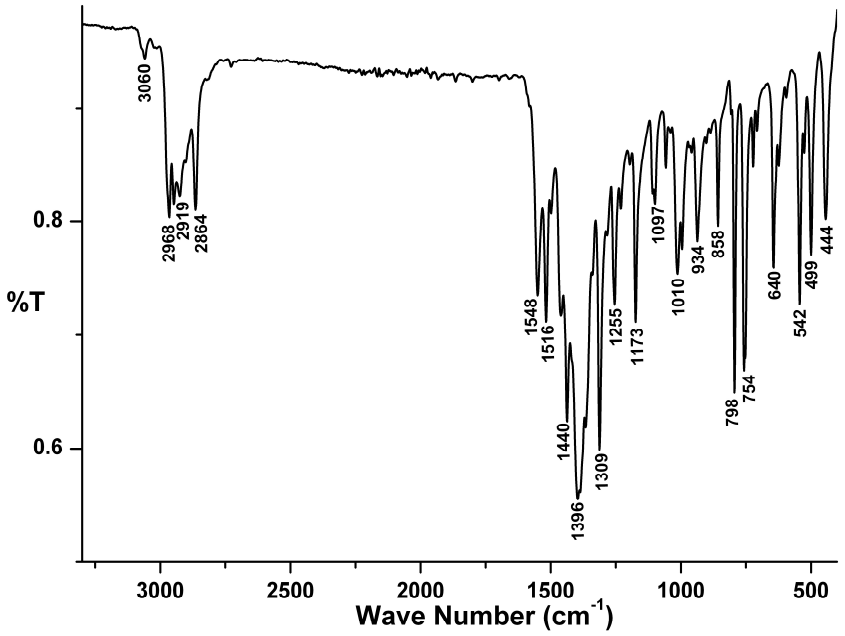


Figure S12. ATR-IR spectrum of $RGaEt_2$ (**5**).

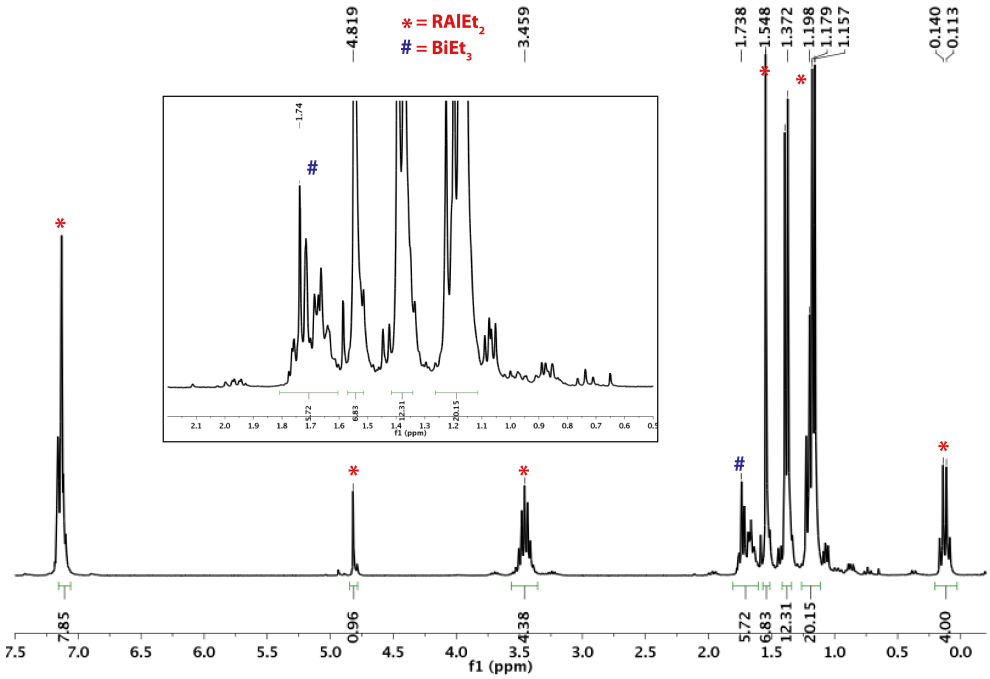


Figure S13. Formation of $RAlEt_2$ (**4**) and $BiEt_3$ from isolated $RAlEt(BiEt_2)$ (**1**). ^1H NMR spectrum of $RAlEt(BiEt_2)$ (**1**) in C_6D_6 after heating at 90 ºC for 5 h.

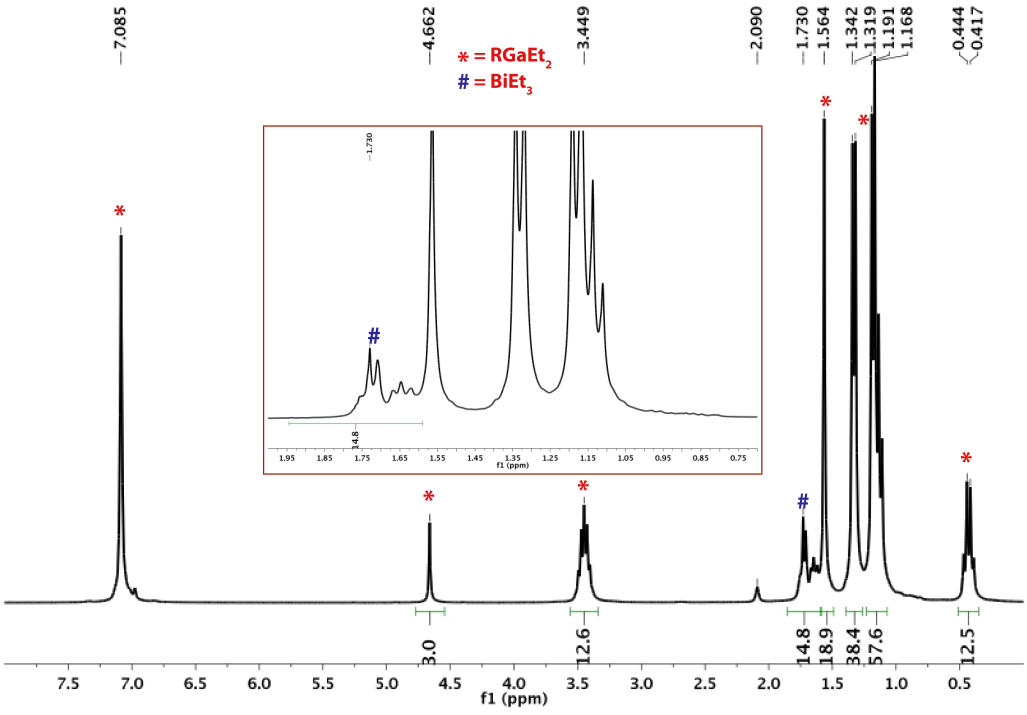


Figure S14. Formation of $RGaEt_2$ (**5**) and $BiEt_3$ from isolated $RGaEt(BiEt_2)$ (**2**). ^1H NMR spectrum of $RGaEt(BiEt_2)$ (**2**) in Toluene-d_8 after heating at 120 ºC for 15 h.

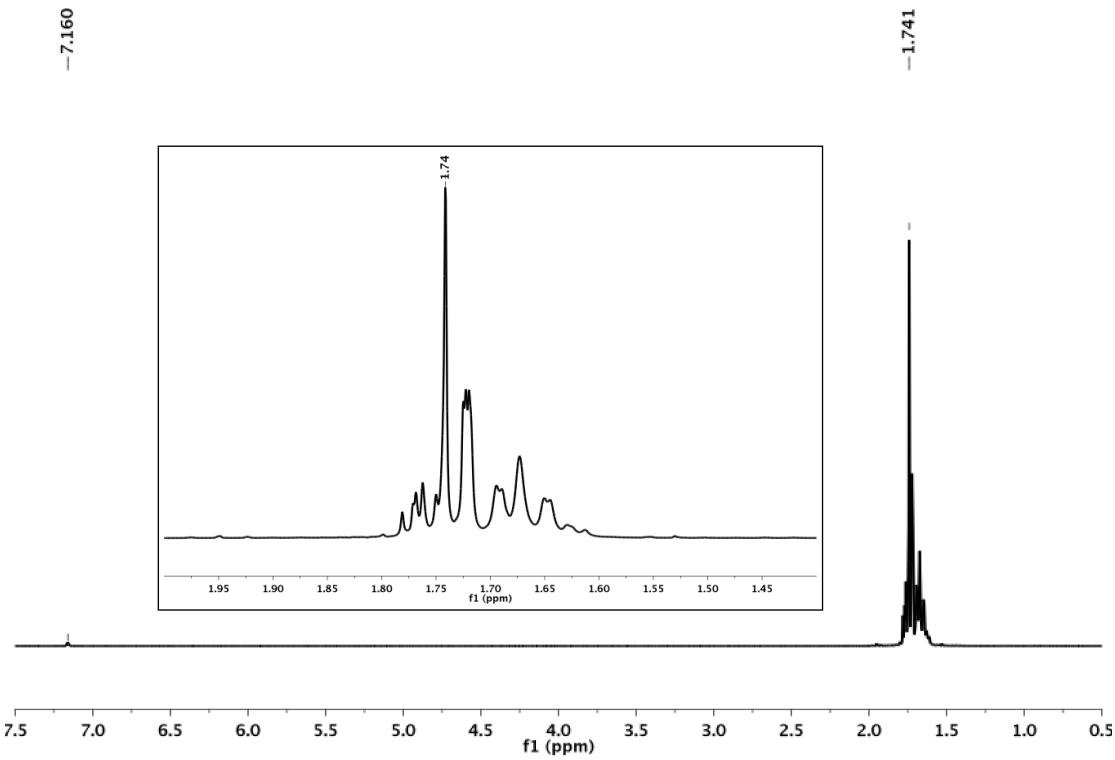


Figure S15. ^{1}H NMR spectrum of $BiEt_3$ in C_6D_6.

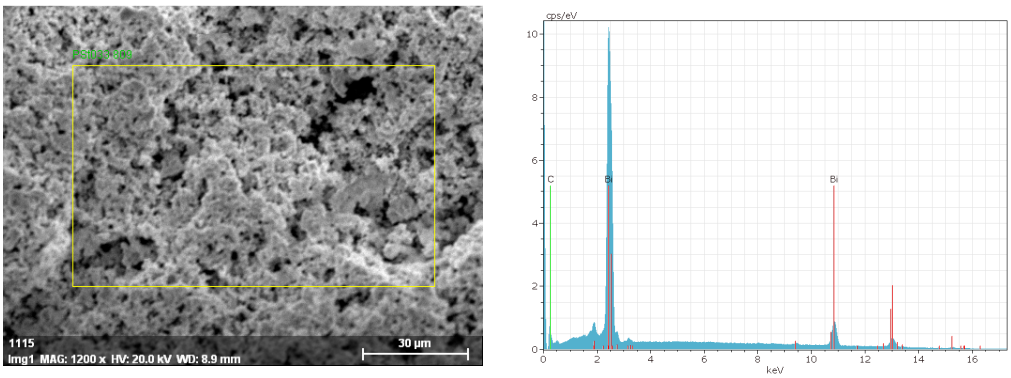


Figure S16. SEM picture and EDX spectrum of the Bi metal formed from compound RGaEt($BiEt_2$) (**2**).

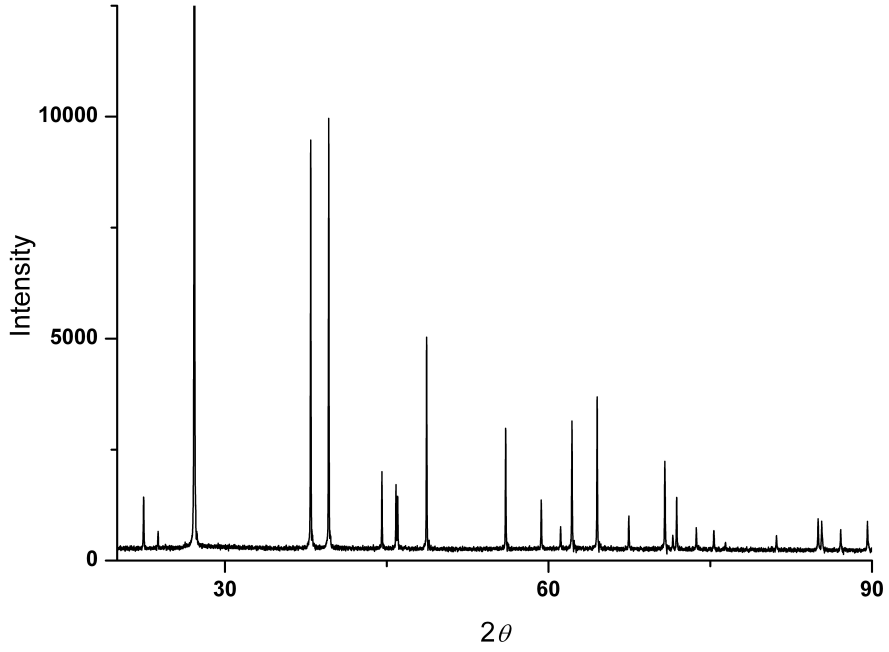


Figure S17. PXRD pattern of the Bi metal obtained from compound RGaEt($BiEt_2$) (**2**).

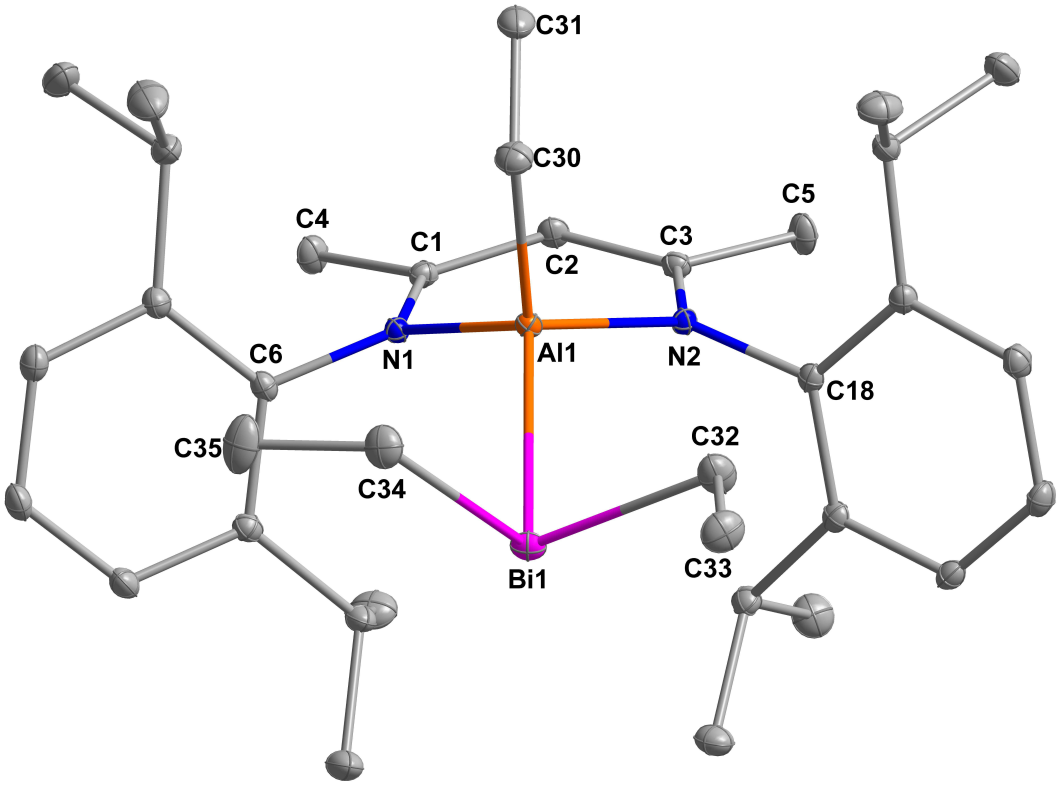


Figure S18. Molecular structure of RAlEt($BiEt_2$) (**1**). H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level.

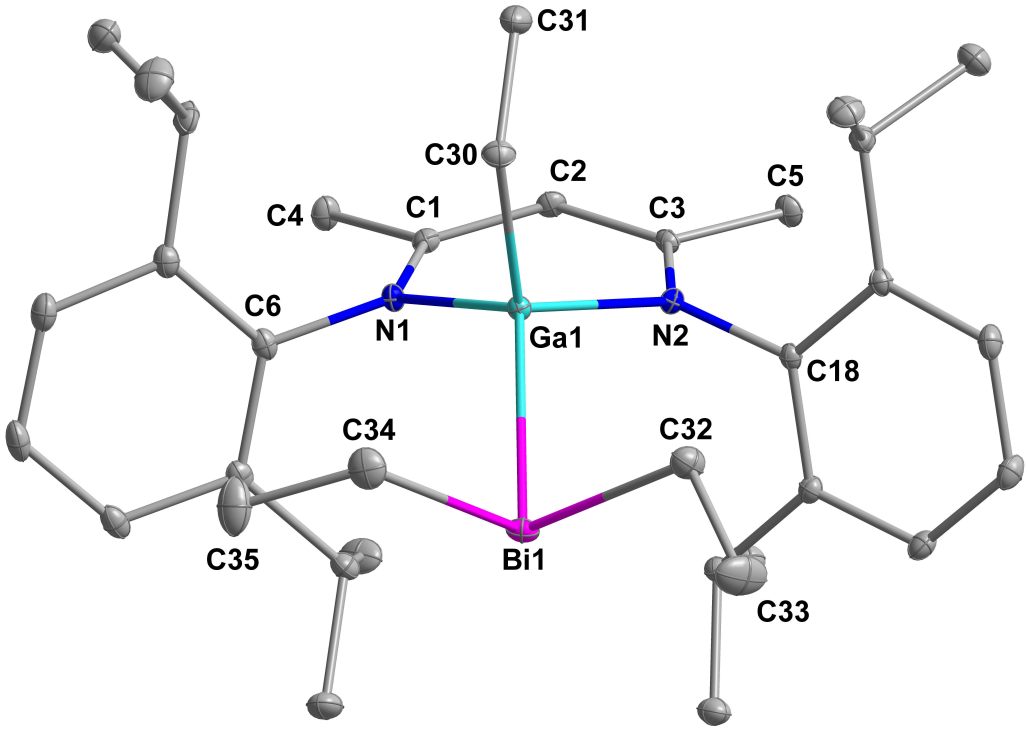


Figure S19. Molecular structure of RGaEt($BiEt_2$) (**2**). H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level.

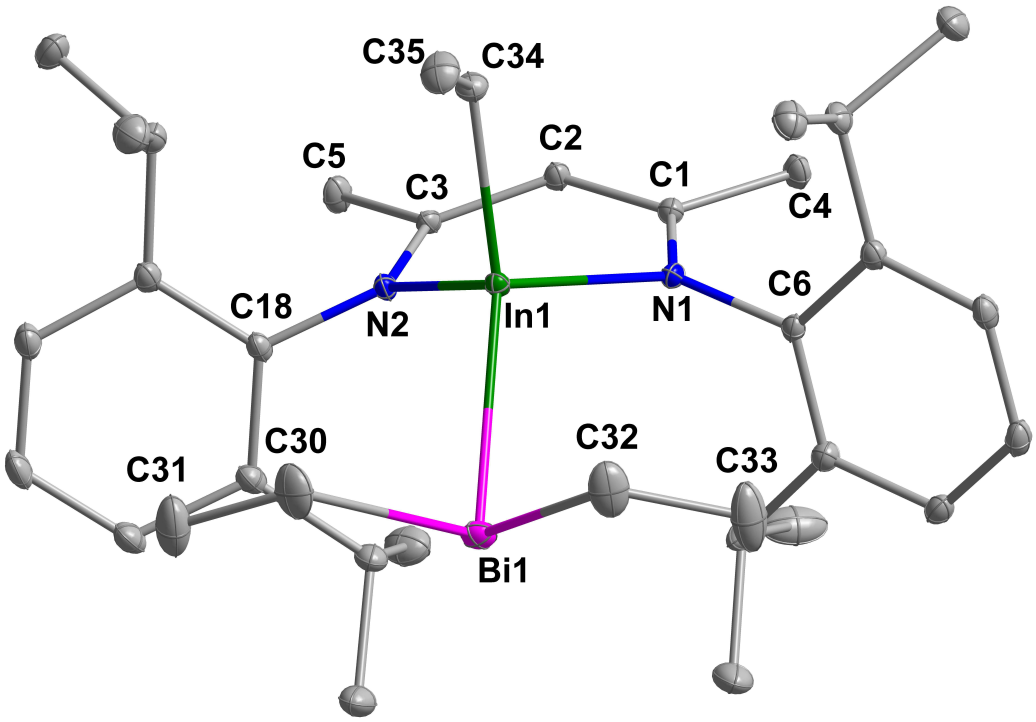


Figure S20. Molecular structure of $RInEt(BiEt_2)$ (**3**). H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level.

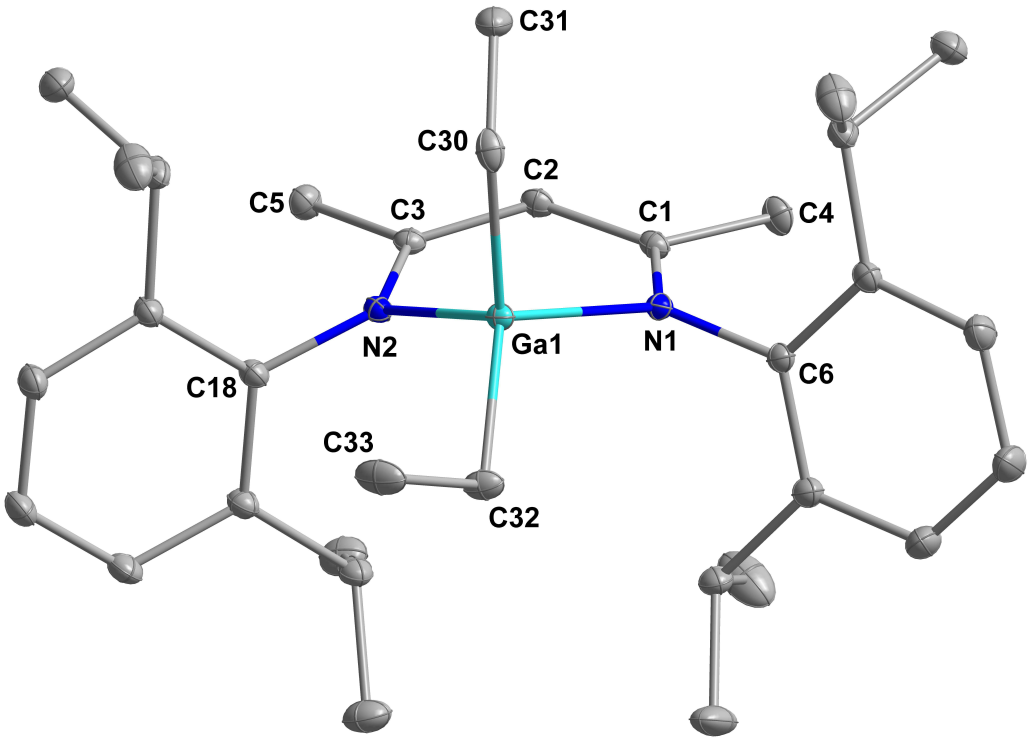


Figure S21. Molecular structure of $RGaEt_2$ (**5**). H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level.