# Syntheses and molecular structure of organo-group 13 metal carbene complexes

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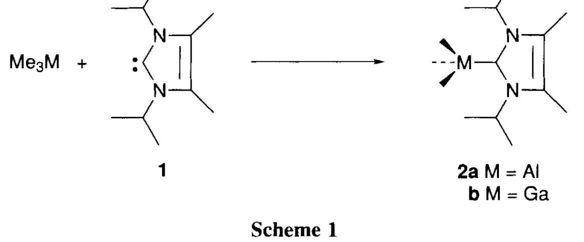
**Trimethylaluminium or trimethylgallium reacts with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene 1 to afford the first organo-group 13 metal carbenes 2 (M = Al 2a, Ga 2b), which are characterized by elemental analyses, IR, $^1$H and $^{13}$C NMR spectroscopy, and single-crystal X-ray diffraction.**

Although recent efforts of this laboratory have focused upon the synthesis and structure of cyclogallanes, cyclic organogallium compounds containing Ga–Ga bonds,[1–3] the Lewis acidity of simple aluminium and gallium alkyls remains of fundamental interest. The propensity of aluminium and gallium alkyls to interact with such Lewis bases as amines, phosphines, arsines and donor solvents, a cornerstone of organometallic chemistry, is well documented.[4] The concept of a carbon-based 'Lewis-base centre' interacting with $R_3M$ (M = Al, Ga) affording a stable Lewis-acid–Lewis-base adduct is intriguing. The carbene carbon atom is a good model of such a Lewis-base centre. Carbenes, highly reactive organic intermediates containing a divalent two-coordinate carbon atom, have attracted considerable attention through the years[5] as they have been shown to participate in a variety of important transformations including insertion, addition and dimerization reactions.[6] This notwithstanding, structural data on carbenes has proven particularly elusive with the first X-ray structural examination, that of 1,3-di-1-adamantylimidazol-2-ylidene, only being reported in 1991.[7] This finding coupled with facile synthetic procedures affording stable carbenes[8] has contributed to a renaissance in this field. Herein, we report the syntheses† and molecular structure of group 13 metal alkyl complexed carbenes **2**, isolated from reaction of trimethylaluminium or trimethylgallium with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene **1** (Scheme 1).

The title compounds, characterized by elemental analyses, IR, $^1$H and $^{13}$C NMR spectroscopy and single-crystal X-ray diffraction,‡ are noteworthy as they represent the first examples, complete with structural characterization, of organoaluminium or -gallium carbene complexes (Fig. 1). Furthermore, this study provides insight into the relative Lewis basicity of imidazolyldiene-based carbenes as a function of group 13 metal alkyl-based Lewis acids.

The literature reveals a paucity of Lewis acid–carbene complexes as only three group 13 Lewis acid–carbene complexes have been reported: a $BH_3$ (**3a**) and a $BF_3$ (**3b**) adduct of 1,3-diethyl-4,5-dimethylimidazol-2-ylidene[9] and an $AlH_3$ adduct of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene **4**.[10]



**Scheme 1**

These air-sensitive compounds are slightly soluble in hexane and readily soluble in benzene, toluene and ethers. The title compounds reside about a mirror plane containing the five-membered carbene ring, the *ipso*-carbon atoms [C(6), C(8), C(9), C(10)], the metal atom and C(1). Among imidazole-based carbenes the N–C–N bond angle is quite consistent with values of 104.3(5)° for **2a**, 104.5(13)° for **2b**, 104.7(1)° for **3a** and 104.1° for **4**. Perhaps the most interesting comparison between **2a** and **4** is found in the Al–$C_{(carbene)}$ distance: that observed in **4** of 2.034(3) Å is considerably shorter than the value of 2.124(6) Å found in **2a** [while the Ga–$C_{(carbene)}$ distance in **2b** is found to be 2.13(2) Å]. The closest related carbene to **1** (which has been characterized by single-crystal X-ray diffraction) is 1,3,4,5-tetramethylimidazol-2-ylidene as Schumann and Kuhn[11] reported samarium- and ytterbium-based complexes with it.

Generally, whenever a four-coordinate aluminium atom has its coordination sphere saturated by a tetrahedral arrangement of carbon atoms the species is one of the simple dimeric aluminium alkyls (or aluminium aryls in the case of triphenylaluminium) possessing the characteristic three-centre–two-electron alkyl (or aryl) bridges. Thus, **2a** is unusual in that while the tetrahedral aluminium atom has its coordination sphere saturated by carbon atoms this complex is monomeric. A particularly intriguing comparison concerns that of the metal–carbon bond distances. While the independent Al–$C_{(methyl)}$ bond distances in **2a** are shown to be 1.940(5) and 2.062(7) Å, the Al–$C_{(carbene)}$ bond distance is considerably longer at 2.124(6) Å. These distances may be placed in further perspective by considering the structure of the $Al_2Me_6$ and $Al_2Ph_6$ dimers. The Al–$C_{(bridge)}$ distance in the trimethylaluminium dimer is found

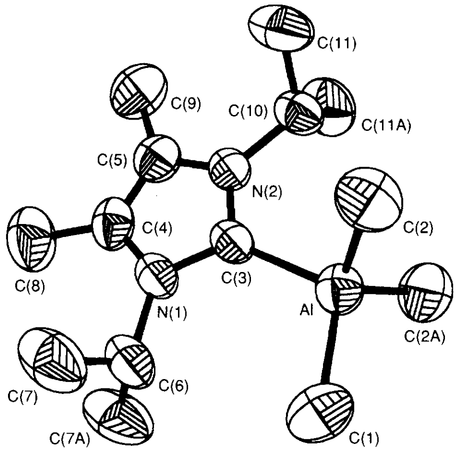


**Fig. 1** Molecular structure of **2a**. Selected bond distances (Å) and angles (°): for **2a**: Al–C(1) 2.062(7); Al–C(2) 1.940(5), Al–C(3) 2.124(6), N(1)–C(3) 1.372(7), N(2)–C(3) 1.404(7); C(2)–Al–C(2a) 110.8(3), C(2)–Al–C(1) 111.0(2), C(2)–Al–C(3) 105.0(2), C(1)–Al–C(3) 113.7(3), N(1)–C(3)–N(2) 104.3(5), N(1)–C(3)–Al 129.9(4), N(2)–C(3)–Al 125.8(4). For **2b**: (the atom numbering scheme for **2b** is the same as that for **2a**). Ga–C(1) 2.08(2), Ga–C(2) 1.95(1), Ga–C(3) 2.13(2), C(2)–Ga(1)–C(2a) 109.5(8), C(2)–Ca–C(1) 110.5(5), C(2)–Ga–C(3) 105.9(8), C(1)–Ga–C(3) 114.2(8), N(1)–C(3)–N(2) 104(1), N(1)–C(3)–Ga 131(1), N(2)–C(3)–Ga(1) 125(1).

to be 2.14(1) Å while the Al–C$_{(terminal)}$ distance is 1.97(1) Å.[12] The corresponding distances for the triphenylaluminium dimer are 2.182 and 1.958 Å for the bridging and terminal Al–C bonds, respectively.[13]

Although structural data on carbenes are becoming more available, such data on group 13 carbenes are still rare. The structure, synthesis and reactivity of these compounds remain under study in this laboratory.

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## Footnotes

† *Syntheses*: **2a**; inside a dry box, $Me_3Al$ (1.0 ml, 10 mmol) was slowly added to a solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene [prepared by the procedure given in ref. 8(*b*)] (1.80 g, 10 mmol) in hexane (30 ml) *via* a syringe. A moderately vigorous, exothermic reaction ensued as evidenced by warming of the reaction vessel. After several hours, **2a** was formed as colourless crystals (yield 90%). Mp 118 °C. Calc. (found) for $C_{14}H_{29}AlN_2$: C, 66.63 (65.49); H, 11.58 (11.51); N, 11.10 (11.42%). $^1$H NMR (300 MHz, 297 K, $C_6D_6$), δ −0.09 (s, 9 H, $AlCH_3$), 1.09 [d, 12 H, NCH($CH_3$)$_2$, *J* 1.9 Hz], 1.59 [s, 6 H, C(4)$CH_3$ and C(5)$CH_3$], 5.46 (spt, 2 H, NCH); $^{13}$C NMR, δ −0.54 ($AlCH_3$), 9.41 [C(4)]$CH_3$ and C(5)$CH_3$], 21.16 [NCH($CH_3$)$_2$], 50.81 (NCH), 124.74 [C(4) and C(5)]. IR (KBr, Nujol, cm$^{-1}$): 3184w, 2722s, 2666s, 1634w, 1308s, 1227m, 1178s, 1116m, 1079m, 1030w, 974w, 906w, 845w, 770s, 721s, 696s, 622m, 573m, 548w, 524m. **2b**: the synthetic procedure affording **2b** proceeded in a fashion similar to that described for **2a**. Yield 95%. Mp 110 °C. Calc. (found) for $C_{14}H_{29}GaN_2$: C, 56.98 (55.94); H, 9.91 (9.90); N, 9.49 (9.89%). $^1$H NMR (300 MHz, 297 K, $C_6D_6$), δ −0.10 (s, 9 H, $GaCH_3$), 1.13 [d, 12 H, NCH($CH_3$)$_2$, *J* 1.9 Hz], 1.67 [s, 6 H, C(4)$CH_3$ and C(5)$CH_3$], 5.40 (spt, 2 H, NCH); $^{13}$C NMR, δ 0.03 ($GaCH_3$), 10.02 [C(4)$CH_3$ and C(5)$CH_3$], 21.80 [NCH($CH_3$)$_2$], 51.25 (NCH), 125.20 [C(4) and C(5)], 176.78 [C(2)]. IR (KBr, Nujol, cm$^{-1}$): 3186w, 2727m, 2671w, 1632w, 1301m, 1220s, 1179s, 1143m, 1113m, 1082m, 1026w, 899w, 756s, 726s, 660w, 552w, 527s.

‡ *Molecular structures*: X-ray intensity data for **2a** were collected on a Siemens P4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) at 21 °C. Cell parameters and an orientation matrix for data collection were obtained from a least-squares analysis of the setting angles of 25 carefully centred reflections in the range $15.0 < 2\theta < 30.0°$. The space group was determined to be orthorhombic $Pmn2_1$ (no. 31) [though *Pmnm* (no. 59) was also consistent with the systematic absences] due to the successful refinement of the data.

*Crystal data* for **2a**: $a = 9.912(5)$, $b = 10.300(2)$, $c = 16.908(3)$ Å, $U = 1726(1)$ Å$^3$ and $D_c = 0.971$ g cm$^{-3}$ for $Z = 4$. The structure was solved by direct methods and refined, based upon 1157 observed reflections, using the SHELXTL[14] system of computer programs. Refinement converged at $R = 0.039$, $R_w = 0.110$ using the $F^2$ refinement. Data collection and refinement for **2b** proceeded in a fashion similar to that described for **2a**. *Crystal data* for **2b**: $a = 9.890(3)$, $b = 10.286(4)$, $c = 16.869(4)$ Å, $U = 1716(9)$, $D_c = 1.142$ g cm$^{-3}$, $Z = 4$, orthorhombic, space group $Pmn2_1$ (no. 31). Refinement ($F^2$) converged at $R = 0.055$, $wR_2 = 0.136$. The molecular structure of **2a** is shown in Fig. 1. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/275.

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