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## Sequential Bi–C bond activation reactions of BiEt<sub>3</sub> via insertion reactions of RE {R = HC[C(Me)N(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]<sub>2</sub>; E = Al, Ga, In}†‡

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**Two of the Bi–C bonds of BiEt<sub>3</sub> are sequentially activated by mono-valent RM {R = HC[C(Me)N(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]<sub>2</sub>; M = Al, Ga, In}. The first Bi–C bond activation leads to the formation of insertion complexes, [RMET(BiEt<sub>2</sub>)] (M = Al 1; Ga 2; In 3), whereas the consecutive second activation proceeds through a reductive elimination of RMEt<sub>2</sub> (M = Al 4, Ga 5), elemental Bi and BiEt<sub>3</sub>.**

Univalent group 13 diyls RM (M = Al, Ga, In; R = halides, Cp\*, diketiminates, terphenyl, ...) have been found to attract widespread interest from the days of their discovery and spectacular new research fields in modern inorganic chemistry have been developed in the last two decades.<sup>1</sup> The fundamental work of Schnöckel *et al.* led to the isolation of meta-stable M<sup>I</sup> halides, which smoothed the way to obtain univalent group 13 complexes as well as metalloid Al and Ga clusters by controlling the disproportionation reaction of M<sup>I</sup> in the presence of suitable organic ligands.<sup>2</sup> In contrast, Uhl, Roesky, Jutzi, Power, Robinson and others independently synthesized RM compounds using standard reduction reactions and investigated their diverse reactivity toward a number of unsaturated organic functional groups, such as olefins, diketones, isocyanides, azobenzene, azides and small molecules such as O<sub>2</sub>, S<sub>8</sub>, P<sub>4</sub>, N<sub>2</sub>O and carbenes.<sup>3,4</sup> Moreover, the Fischer group predominantly uses the metal centered lone pair of RM as an “exotic σ-donor” in the formation of late transition metal based molecular compounds and clusters *via* substitution of weakly bonded ligands.<sup>5</sup> The redox behavior of RM was found to play a crucial role in both small molecule activation and in intermetallic compounds/cluster formation reactions. In addition, Lewis acid–base adducts of univalent group 13 metals were explored.<sup>6</sup> Our general interest in weak

metal–metal bonds<sup>7</sup> and Lewis acid–base interactions<sup>8</sup> prompted us to focus our attention on the reactions of univalent (RM) and trivalent (R'<sub>3</sub>E) complexes of group 13 and 15 elements, both of which have different kinds of electron lone pairs. The question was whether these complexes simply behave as donor–acceptor derivatives and, if so, what are the orbital contributions, or do they offer further reactions? We herein report on the reactions of the mono-valent group 13 complexes RM {R = HC[C(Me)N(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]<sub>2</sub>; M = Al, Ga, In} with BiEt<sub>3</sub>.

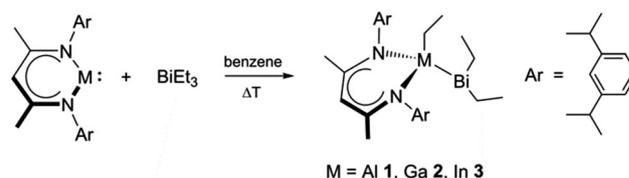
RM initially reacts with BiEt<sub>3</sub> *via* insertion into one of the Bi–C bonds to yield [RMET(BiEt<sub>2</sub>)] (E = Al 1; Ga 2; In 3) (Scheme 1). The yields of 1–3 strongly depend on the reaction temperature and heating time as they normally decompose under harsh conditions. The presence of a slight excess of BiEt<sub>3</sub> improves the yield of 3. 1–3 are moisture sensitive but moderately stable in air, decompose at elevated temperatures but are quite stable in solution and in the solid state at ambient temperature under an inert gas atmosphere.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of 1–3 show the characteristic resonances of the organic substituents. Due to the presence of two different substituents at M (Et, BiEt<sub>2</sub>), the resonances due to the *i*-Pr groups of the β-diketimate ligand are magnetically inequivalent. The <sup>1</sup>H NMR spectra display two septets and four doublets for the two sets of methine and diastereotopic methyl groups of the isopropyl substituents, respectively. In contrast, the γ-H and two methyl groups of the C<sub>3</sub>N<sub>2</sub>M ring are in the mirror plane and exhibit only single resonances in the <sup>1</sup>H NMR spectra. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectral patterns of 1–3 are comparable to those reported for similar β-diketimate group 13 complexes.<sup>9</sup>

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† Dedicated to Prof. M. Jansen on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available: Experimental procedure and characterization of 1–5 including crystallographic data for 1–3 and 5. CCDC 1011108 (1), 1011107 (2), 1011105 (3), and 1011106 (5). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc05028b



Scheme 1 Formation of [RMET(BiEt<sub>2</sub>)].



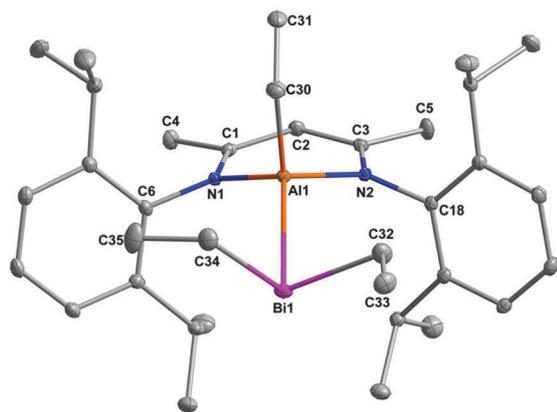


Fig. 1 Molecular structure of RAlEt(BiEt<sub>2</sub>) (**1**). H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level.

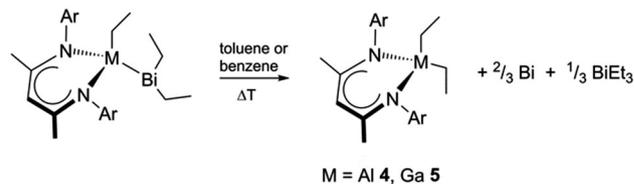
The molecular structures of **1–3** were unambiguously confirmed using single crystal X-ray analyses. Suitable crystals of **1–3** were obtained from saturated solutions in *n*-hexane upon storage at  $-30\text{ }^{\circ}\text{C}$  after 24 h. Since the conformations in **1–3** are roughly the same, only the molecular structure of **1** is presented (Fig. 1). Crystal data and the details of the structure determination are summarized in the ESI,<sup>†</sup> while selected bond lengths and bond angles are given in Table 1.

**1** and **2** crystallize in the triclinic space group  $P\bar{1}$  and **3** in the monoclinic  $P2_1/n$ . Each of the group 13 metals in **1** to **3** adopts a distorted tetrahedral geometry, whereas the Bi atom shows a pyramidal coordination sphere. As was pointed out by Power, there is a possibility for the conjugation of the lone pair of Bi with the empty orbital on the group 13 elements (Al, Ga and In).<sup>10</sup> However, due to its large inversion barrier and the high *s*-orbital contribution of the electron lone pair, the Bi atom adopts a pyramidal coordination sphere without any  $\pi$ -interaction. The C<sub>3</sub>N<sub>2</sub>M rings in the starting reagents RM are planar, whereas the metal atoms M in **1–3** are out of plane (deviation from the best plane of the ligand backbone 0.6097(18) Å **1**, 0.616(3) Å **2**, 0.876(3) Å **3**). The bite angles of the chelating organic ligand R are 95.84(6)<sup>°</sup> (**1**), 93.39(9)<sup>°</sup> (**2**) and 86.72(7)<sup>°</sup> (**3**), respectively. The two independent M–N distances in **1–3** are virtually the same [1.9250(14), 1.9262(15) (**1**); 1.997(2), 2.012(2) (**2**); 2.210(2), 2.212(2) (**3**)] and the Bi–M–C<sub>ethyl</sub> angles

Table 1 Selected bond lengths [Å] and angles [°] of **1–3**<sup>a</sup>

	<b>1</b>	<b>2</b>	<b>3</b>
M1–Bi1	2.7549(6)	2.6959(3)	2.8535(2)
M1–C30(34)*	1.9716(18)	1.980(3)	2.197(3)
M1–N1	1.9262(15)	2.012(2)	2.212(2)
M1–N2	1.9250(14)	1.997(2)	2.210(2)
Bi1–C32	2.292(2)	2.293(3)	2.280(3)
Bi1–C34(30)*	2.2914(19)	2.282(3)	2.283(3)
N1–M1–N2	95.84(6)	93.39(9)	86.72(7)
Bi1–M1–C30(34)*	109.56(6)	113.47(8)	133.43(7)
C32–Bi1–C34(30)*	93.29(8)	93.63(12)	92.93(13)
C34(30)*–Bi1–M1	93.33(5)	94.66(9)	95.19(10)
C32–Bi1–M1	92.72(5)	92.83(8)	95.50(9)
M1–N1–C1–C3	18.91	17.66	–25.15

<sup>a</sup> (30)\*, (34)\* compound **3** C atom labelling.



Scheme 2 Formation of RMEt<sub>2</sub>, Bi and BiEt<sub>3</sub>.

of **1–3** are 109.56(6)<sup>°</sup>, 113.47(8)<sup>°</sup> and 133.43(7)<sup>°</sup>, respectively. The M–Bi bond distances [2.7549(6) (**1**); 2.6959(3) (**2**); 2.8535(2) (**3**)] are comparable to the sum of the respective covalent radii (covalent radii of Al = 1.26 Å; Ga = 1.24 Å; In = 1.42 Å; Bi = 1.51 Å)<sup>11</sup> and agree well with those observed in M–E  $\sigma$ -bonded trimers [Me<sub>2</sub>MBi(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (M = Al, 2.774 Å; Ga, 2.762 Å; In, 2.915 Å) and the monomers [(dmap)R<sub>2</sub>AlBi(SiMe<sub>3</sub>)<sub>2</sub>] (R = Me, 2.755(2) Å; Et, 2.750(2) Å; dmap = 4-dimethylamino pyridine).<sup>12</sup>

**1–3** further react at elevated temperatures upon activation of the second ethyl group at the Bi atom and the quantitative formation of RMEt<sub>2</sub> (E = Al **4**; Ga **5**), BiEt<sub>3</sub> and elemental bismuth (Scheme 2) occurs. For instance, pure **1** and **2** react in toluene solution upon heating at 90 °C for 5 h (**4**) and 120 °C for 15 h (**5**), respectively. EDX and PXRD analyses of the solid precipitates confirm the formation of the Bi metal (Fig. S16 and S17, ESI<sup>†</sup>). The <sup>1</sup>H NMR spectra of the reaction mixtures show the presence of BiEt<sub>3</sub> and **4** or **5**, respectively, in molar ratios of 1:3 (Fig. S13 and S14, ESI<sup>†</sup>). Although RInEt(BiEt<sub>2</sub>) (**3**) also follows the same reductive pathway in the beginning, the sensitivity of RIn toward heat and light makes the reaction pathway more complex. RInEt<sub>2</sub> is initially formed, but further decomposition reaction occurs.

**5** was isolated in a large-scale experiment and fully characterized using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and single-crystal X-ray diffraction. The molecular structure of **5** (Fig. S21, ESI<sup>†</sup>) is closely related to the analogous derivatives, RGAx<sub>2</sub> (X = Cl, I, Me).<sup>13</sup> The formation of 1/3 equivalent of BiEt<sub>3</sub> with respect to **4** and **5**, respectively, as well as Bi metal in the reaction mixture apparently shows the formation of a redox-active low-valent [BiEt]<sub>x</sub> reaction intermediate, which consequently undergoes disproportionation at high temperature (BiEt → 2/3Bi + 1/3BiEt<sub>3</sub>). Similar reductive elimination of Cp\*H has been reported for Cp\*<sub>2</sub>AlH and Cp\*<sub>2</sub>AlH<sub>2</sub> (Cp\* = C<sub>5</sub>Me<sub>5</sub>).<sup>14</sup> Furthermore, RGA was shown to undergo comparable insertion reactions with group 13 and group 14 alkyl complexes.<sup>15</sup> However, the controlled decomposition of (hetero)multimetallic complexes into low valent metal complexes – a mechanism following Schnöckel's route in the synthesis of metalloid Al and Ga cluster complexes using metastable Al<sup>I</sup> and Ga<sup>I</sup> halides – is still very rare.

The selective activation of Bi–C bonds by low-valent group 13 complexes RM (M = Al, Ga, In) was established as new synthetic method for the synthesis of intermetallic compounds of heavier main-group metals containing a metal–metal bond. The specific reaction sequence occurs with the formation of stable intermediates of the type RM(Et)BiEt<sub>2</sub> **1–3**, which upon heating react leading to the formation of the low-valent [BiEt]<sub>x</sub> species. The reaction has a promising potential for the general synthesis of similar intermetallic complexes through consecutive bond activations.



1–3 are rare examples of structurally characterized heavier main-group 13/15  $\sigma$ -bonded derivatives and the controlled disproportionation reaction of the low-valent  $[\text{BiEt}]_x$  intermediate in the presence of stabilizing agents is currently under active investigation.

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