Group 13/15 Heterocycles

A Versatile Metathesis Reaction for the Formation of Labile Bonds between Group 13 and Group 15 Atoms**

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Dedicated to Professor Peter Jutzi on the occasion of his 65th birthday

Although Group 13/Group 15 compounds have been intensely studied for some decades, no generally applicable synthetic pathway for the formation of M–E bonds (M = Al–Tl; E = N–Bi) is known to date. Dihydrogen- and saltelimination reactions as well as metathesis reactions with organolithium reagents are well-established methods for the formation of M–NR₂ and M–PR₂ bonds, but they are generally ineffective for the synthesis of compounds containing the heaviest Group 13/15 elements (M = In, Tl; E = Sb, Bi). To date, dehydrosilylation reactions represent the most versatile reaction pathway for the generation of this type of compound.^[1] The activation energy is low, thus allowing the reaction to be performed at low temperature. Additionally, the tendency of silyl-substituted compounds of the type

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 R_2ESiMe_3 to undergo redox reactions is rather low compared to that of organolithium compounds, R_2ELi . Unfortunately, this reaction pathway cannot be used for the synthesis of In–E and Tl–E compounds because of the instability of the required dialkylindium hydrides R_2InH and dialkylthallium hydrides R_2TIH .^[2] Consequently, we became interested in an alternative route to Group 13/15 compounds, in particular those compounds that contain the heaviest elements of both groups. Herein, we report a new metathesis reaction, which is used for the synthesis of the previously unknown heterocycles of the type [{ $Me_2ME(SiMe_3)_2$ }.].

[{Me₂AlBi(SiMe₃)₂}]^[3] reacts with the Lewis acid–base adduct [Me₃In–dmap]^[4] (dmap = 4-dimethylaminopyridine) at -50° C with the formation of [Me₃Al–dmap] and [Me₂In-Bi(SiMe₃)₂]₃ (1). We believe this reaction to proceed through the cleavage of the Al–Bi heterocycle by the reaction with the strong Lewis base dmap. The subsequent coordination of InMe₃ results in the formation of [dmap–Al(Me₂)Bi(SiMe₃)₂– InMe₃],^[5] which undergoes fragmentation with Al–Bi and In– Me bond breakage to give 1 and [Me₃Al–dmap] (Scheme 1).



Scheme 1. Synthesis of the six-membered In-Bi heterocycle 1.

Compound 1 is heat labile and sensitive towards oxygen and water. Whereas isolated 1 can be stored in the dark at -30°C for several weeks, it decomposes in solution at temperatures above -30°C within minutes with the formation of Bi₂(SiMe₃)₄, InMe₃, and elemental In and Bi. Consequently, NMR spectra (¹H, ¹³C) were recorded at -40 °C in [D₈] toluene. Both spectra show only two resonances arising from the InMe₂ and SiMe₃ groups, as observed for the corresponding AlBi^[3] and GaBi heterocycles.^[6] The mass spectrum of 1 only shows decomposition fragments, thus indicating the lability of 1. Single crystals of 1 were obtained from a toluene solution at -60 °C (Figure 1). Compound 1 crystallizes in the monoclinic space group $P2_1/n$ (No. 14)^[7] and is isostructural to [{Me₂AlBi(SiMe₃)₂]₃]^[3] and [{Me₂GaBi-(SiMe₃)₂]₃].^[6] The central structural feature of this first organometallic In-Bi compound^[8] is the nonplanar sixmembered In₃Bi₃ ring. Both the In and the Bi atoms adopt distorted tetrahedral environments, in which the average endocyclic Bi-In-Bi bond angle (101.1°) is significantly smaller than the average In-Bi-In bond angle (127.1°). The In-Bi bond lengths range from 2.903(1) to 2.935(1) Å (av 2.915 Å), which is about 0.15 Å longer than the corresponding M-Bi bond lengths in [{Me₂AlBi(SiMe₃)₂]₃] $(av 2.774 \text{ Å})^{[3]}$ and $[\{Me_2GaBi(SiMe_3)_2\}_3]$ $(av 2.762 \text{ Å}).^{[6]}$ However, this increase in bond length is less pronounced than was expected because of the increase of the covalent radii of the In atom (1.44 Å) compared to Al (1.25 Å) and Ga (1.26 Å) atoms.^[9]



Figure 1. Solid-state structure of 1. Selected bond lengths [Å] and angles [°]: Bi1-In1 2.907(1), Bi1-In2 2.903(1), Bi2-In2 2.914(1), Bi2-In3 2.911(1), Bi3-In1 2.935(1), Bi3-In3 2.920(1), Bi1-Si1 2.628(2), Bi1-Si2 2.622(2), In1-C1 2.182(7), In1-C2 2.165(8), Bi2-Si3 2.637(2), Bi2-Si4 2.635, In2-C3 2.162(8), In2-C4 2.171(8), Bi3-Si5 2.639(2), Bi3-Si6 2.642(2), In3-C5 2.180(8), In3-C6 2.195(8); In1-Bi1-In2 123.0(1), In2-Bi2-In3 129.1(1), In1-Bi3-In3 129.2(1), Bi1-In1-Bi3 99.7(1), Bi1-In2-Bi2 99.4(1), Bi2-In3-Bi3 104.2(1), C1-In1-C2 126.9(3), Si1-Bi1-Si2 102.3(1), C3-In2-C4 125.6(3), Si3-Bi2-Si4 100.1(1), C5-In3-C6 116.6(3), Si5-Bi3-Si6 101.6(1).

Detailed studies on the reactivity of $[\{Me_2AlE(SiMe_3)_2\}_x]$ (E = P, As, Sb, Bi) towards $[Me_3M$ -dmap] (M = Ga, In) clearly demonstrated that the described reaction pathway is generally applicable for the formation of heterocycles of the type $[\{Me_2ME(SiMe_3)_2\}_x]$ (M = Ga, In; E = P, As, Sb, Bi).^[10] The presence of the Lewis base dmap was found to be essential, as the reactivity of $[\{Me_2AlE(SiMe_3)_2\}_x]$ is significantly increased owing to the initial formation of Lewis base stabilized, monomeric $[R_2E-AlR_2(dmap)]$. This is also known for organolithium reagents, whose reactivity increases in the presence of donor solvents (disaggregation and formation of RLi(donor)).^[11] Comparable results have been reported by Driess et al. on the reactivity of $[(iBu)_2AlPH_2]_3$, which was found to be a mild PH₂-transfer reagent in coordinating solvents such as THF.^[12]

In an attempt to explore the synthetic potential of this new metathesis reaction, we focused our interest on the synthesis of TIE heterocycles [{ $R_2TIER'_2$ }]. To date, heterocycles of this type are completely unknown owing to the high oxidation potential and the low thermal resistance of TI^{III} compounds and because dialkylthallium hydrides R_2TIH are not available. Our initial studies on the reactions of [{ Me_2AIE -(SiMe₃)₂}] (E = P, As)^[13] with [Me₃TI-dmap]^[4] resulted in the formation of the corresponding four-membered TIE heterocycles [{ $Me_2TIP(SiMe_3)_2$ }] **2** and [{ $Me_2TIAs(SiMe_3)_2$ }] **3** in good yields (Scheme 2).

1/2 [{Me₂AIE(SiMe₃)₂}₂] + [Me₃TI-dmap] - [Me₃AI-dmap]

1/2 [{Me₂TIE(SiMe₃)₂}₂] $\begin{array}{c} 2, E = P, T = 0^{\circ}C \\ 3, E = As, T = -30^{\circ}C \end{array}$

Scheme 2. Synthesis of the four-membered Tl–E heterocycles 2 (E=P) and 3 (E=As).

The presence of a triplet in the ³¹P NMR spectrum of **2** with a ¹*J*_{TI,P} coupling constant of 2462 Hz proves the formation of a TI–P heterocycle.^[14] The ¹H and ¹³C NMR spectra of **2** and **3** each show a doublet arising from the TIMe₂ groups (**2**: ²*J*_{TI-H} = 317 Hz, ¹*J*_{TI-C} = 2391 Hz; **3**: ²*J*_{TI-H} = 313 Hz, ¹*J*_{TI-C} = 2304 Hz), whereas the SiMe₃ groups only show a singlet. The mass spectra of **2** and **3** do not show the molecular ion peaks. The mass spectrum of **2** shows the presence of two fragments at *m*/*z* 557 [(Me₃Si)₂PTIP(SiMe₃)₂]⁺ and *m*/*z* 395 [MeTIP(SiMe₃)₂]⁺) that contain a TI–P bond, whereas the mass spectrum of **3** only shows decomposition fragments.

Crystals of 2 and 3 suitable for single-crystal X-ray diffraction analyses were obtained from solutions in toluene at -30 °C (2) and -60 °C (3) (Figure 2). Compounds 2 and 3



Figure 2. Solid-state structures of **2** (above) and **3** (below): Selected bond lengths [Å] and angles [°]. **2**: TI1-P1 2.695(2), TI1-P1A 2.688(2), P1-Si1 2.246(2), P1-Si2 2.245(2), TI1-C7 2.198(5), TI1-C8 2.210(5); TI1-P1-TI1A 95.5(1), P1-TI1-P1A 84.5(1), C7-TI1-C8 122.3(2), Si1-P1-Si2 109.0(1). **3**: TI1-As1 2.781(1), TI1-As1A 2.743(1), As1-Si1 2.334(2), As1-Si2 2.338(2), TI1-C7 2.192(6), TI1-C8 2.202(6); TI1-As1-TI1A 96.7(1), As1-TI1-As1A 83.3(1), C7-TI1-C8 124.6(3), Si1-As1-Si2 108.5(1).

are isostructural and crystallize in the triclinic space group $P\bar{1}$ (No. 2).^[15] The central structural units of **2** and **3** are the fourmembered planar Tl_2E_2 rings. The Tl- and P- or As-atoms each adopt distorted tetrahedral environments. To date, only two Lewis acid–base adducts containing a Tl^{III} center with a Tl–P bond have been structurally characterized. The Tl–P σ bond in **2** (2.688(1), 2.695(1) Å) is significantly shorter than the dative Tl–P bond observed in the intramolecularly

stabilized adduct [Tl{o-(Ph2PCH2)C6H4]3] (2.795 Å) as well as in [(Me₃SiCH₂)₃Tl-P(SiMe₃)₃] (2.992 Å).^[16] Compound **3** is the first organometallic compound that contains a Tl-As bond. Consequently, the Tl-As bond lengths (2.743(1), 2.781(1) Å) can only be compared with the Tl-As bond lengths in Zintl anions such as [TaAs₄Tl₂]⁵⁻ (2.74–2.88 Å).^[17] The average Tl-C bond lengths (2: 2.204 Å, 3: 2.197 Å) are almost the same as those in [Me₃Tl-dmap] (2.180 Å).^[4] The endocyclic E-Tl-E bond angles are smaller than the Tl-E-Tl bond angles, as is generally observed for four-membered heterocycles of the type $[\{Me_2ME(SiMe_3)_2\}_2].^{[18]}$ However, the differences within the thallium heterocycles 2 (P-Tl-P = 84.5(1)° versus Tl-P-Tl = 95.5(1)°) and **3** (As-Tl-As = $83.1(1)^{\circ}$ versus Tl-As-Tl = $96.7(1)^{\circ}$), are significantly more pronounced than in analogous heterocycles containing the lighter elements of Group 13.

The synthesis of the heat-labile heterocycles **1–3** provides evidence for the preparative potential of this new synthetic pathway and extends the methods available for the formation of Group 13/Group 15 atom bonds. The driving force of the described reaction is the formation of the stable Lewis acid– base adduct [Me₃Al–dmap]. Because of the excellent reactivity of the starting Al/Group 15 atom heterocycles of the type [{Me₂AlE(SiMe₃)₂}_x] and the mild reaction conditions (low temperature), this metathesis reaction has a promising potential for the formation of compounds containing yet unknown bonds between Group 15 atoms and atoms of other elements.

Experimental Section

1: A suspension of $[\{Me_2AlBi(SiMe_3)_2\}_3]$ (0.41 g, 0.33 mmol) in toluene (10 mL) at -50 °C was combined with $[Me_3In-dmap]$ (0.28 g, 1.0 mmol) dissolved in toluene (5 mL). The resulting brownish suspension was allowed to warm to -30 °C over 30 min. Thereafter, the suspension was quickly warmed until a clear solution was formed, which was then stored at -60 °C. Colorless crystals of **1** were obtained after 24h. Yield: 0.15 g, 0.10 mmol, 30%. M.p. 68–73 °C (decomp). ¹H NMR (300 MHz, $[D_8]$ toluene, -40 °C): $\delta = 0.62$ (s, 6H; InMe₂), 0.70 ppm (s, 18H; SiMe₃). ¹³C{¹H} NMR (75 MHz, $[D_8]$ toluene, -40 °C): $\delta = -1.1$ (InMe₂), 6.8 ppm (SiMe₃). MS (EI, 12 eV, 50 °C) m/z (%) = 428 (13) [Bi(SiMe₃)_3]^+, 282 (13) [BiSiMe₃]^+, 145 (65) [InMe₂]^+, 131 (100) [Si_2Me_5]^+, 73 (39) [SiMe_3]^+.

2: A suspension of [{Me₂AlP(SiMe₃)₂]₂] (0.23 g 0.5 mmol) in toluene (10 mL) at 0°C was combined with [Me₃Tl-dmap] (0.37 g, 1.0 mmol) dissolved in toluene (5 mL). The resulting clear solution was stirred for an additional 30 min and stored at -30°C. Colorless crystals of **2** were obtained after 24 h. Yield: 0.33 g, 0.28 mmol, 56%. M.p. 107-111°C (decomp). ¹H NMR (300 MHz, C₆D₆, 30°C): $\delta = 0.35$ (s, 18H; SiMe₃), 1.00 ppm (d, ²J_{Tl-H}=317 Hz, 6H; TlMe₂). ¹³C{¹H} NMR (75 MHz, C₆D₆, 30°C): $\delta = 5.0$ (s; SiMe₃), 12.8 ppm (d, ¹J_{Tl-C}=2391 Hz; TlMe₂). ³¹P{¹H} NMR (120 MHz, C₆D₆, 30°C): $\delta = -234$ ppm (t, ¹J_{Tl-P}=2462 Hz). MS (EI, 12 eV, 75°C) *m/z* (%) = 557 (5) [(Me₃Si)₂PTIP(SiMe₃)₂]⁺, 416 (26) [P₄(SiMe₃)₄]⁺, 401 (100) [P₄(SiMe₃)₃(SiMe₂)]⁺, 313 (24) [P₄(SiMe₃)(SiMe₂)]⁺, 203 (7) Tl⁺, 178 (36) [HP(SiMe₃)₂]⁺, 163 (5) [P(SiMe₃)(SiMe₂)]⁺, 73 (25) [SiMe₃]⁺.

3: A suspension of $[\{Me_2AlAs(SiMe_3)_2\}_2]$ (0.28 g, 0.5 mmol) in toluene (10 mL) at -30 °C was combined with $[Me_3TI-dmap]$ (0.37 g, 1.0 mmol) dissolved in toluene (5 mL). The resulting slightly brown suspension was stirred for 30 min, then warmed quickly until a clear solution was formed, and finally stored at -60 °C. Colorless crystals of **3** were obtained after 24 h. Yield: 0.29 g, 0.32 mmol, 64%. M.p. 118–

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121 °C (decomp, darkening above 70 °C). ¹H NMR (300 MHz, [D₈]toluene, -10 °C): $\delta = 0.32$ (s, 18 H; SiMe₃), 0.97 ppm (d, ²J_{TI-H} = 313 Hz, 6 H; TIMe₂). ¹³C{¹H} NMR (75 MHz, [D₈]toluene, -10 °C): $\delta = 4.3$ (s; SiMe₃), 12.4 ppm (d, ¹J_{TI-C} = 2304 Hz; TIMe₂). MS (EI, 12 eV, 150 °C) m/z (%) = 442 (76) [As₂(SiMe₃)₄]⁺, 354 (11) [As₂(SiMe₃)₂(SiMe₂)]⁺, 339 (11) [As₂(SiMe₃)(SiMe₂)₂]⁺, 294 (30) [(As(SiMe₃)₃]⁺, 266 (61) [As₂(SiMe₂)₂]⁺, 233 (24) [TIMe₂]⁺, 203 (9) TI⁺, 131 (15) [Si₂Me₅]⁺, 73 (100) [SiMe₃]⁺.

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- [15] **2**: $C_{16}H_{48}P_2Si_4Tl_2$, $M_r = 823.58$, colorless crystal $0.40 \times 0.30 \times$ 0.20 mm; triclinic, space group $P\bar{1}$ (No. 2); a = 9.2585(2), b =9.5727(2), c = 9.6569(3) Å, $\alpha = 77.581(1)$, $\beta = 81.497(1)$, $\gamma =$ 64.991(2)°, $V = 755.92(3) \text{ Å}^3$; Z = 1; $\mu = 10.910 \text{ mm}^{-1}$; $\rho_{\text{calcd}} =$ 1.809 g cm⁻³; 10498 reflections $(2\theta_{max} = 55^{\circ})$, 3378 unique $(R_{int} = 0.049)$, 109 parameters; largest max./min. in the final difference Fourier synthesis: 1.709 e Å⁻³/-2.514 e Å⁻³; max./ min. transmission 0.1589/0.0846; $R_1 = 0.029$ ($I > 2\sigma(I)$), $wR_2 =$ 0.072. **3**: $C_{16}H_{48}As_2Si_4Tl_2$, $M_r = 911.48$, colorless crystal $0.40 \times$ 0.35×0.30 mm; triclinic, space group $P\bar{1}$ (No. 2); a = 9.2985(4), b = 9.4604(3), c = 9.7580(4) Å, $\alpha = 78.332(2), \beta = 82.125(2), \gamma =$ 66.191(2)°, $V = 767.64(5) \text{ Å}^3$; Z = 1; $\mu = 12.779 \text{ mm}^{-1}$; $\rho_{\text{calcd}} =$ 1.972 g cm⁻³; 6618 reflections ($2\theta_{max} = 55^{\circ}$), 3321 unique ($R_{int} =$ 0.055), 109 parameters; largest max./min. in the final difference Fourier synthesis: 2.177 e Å⁻³/-3.042 e Å⁻³; max./min. transmission 0.1311/0.0639; $R_1 = 0.038$ ($I > 2\sigma(I)$), $wR_2 = 0.093$. CCDC-213920 (1), CCDC-213921 (2), and CCDC-213922 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
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