Te–Te and Te–C bond cleavage reactions using a monovalent gallanediyl†

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LGa (L = [(2,6-i-Pr2-C6H3)NC(Me)]2CH) reacts with elemental tellurium with formation of the Te-bridged compound [LGa–μ-Te]2, whereas the reactions with Ph2Te and i-Pr2Te occurred with cleavage of the Te–Te and Te–C bond, respectively, and subsequent formation of LGa(TePh)2 and LGa(i-PrTe)i-Pr. 1–3 were characterized by heteronuclear NMR (1H, 13C, 125Te) and IR spectroscopy and their solid state structures were determined by single crystal X-ray analyses.

Introduction

Univalent LGa containing the sterically crowded β-diketiminate ligand (L = [(2,6-i-Pr2-C6H3)NC(Me)]2CH)† adopts a monomeric structure in the solid state and in solution. The gallium valence shell contains two bond pairs, a lone pair and an empty p-orbital. Therefore, LGa can react as electrophilic and nucleophilic reagent at the gallium atom. Computational calculations predicted that LGa is a good σ-donor but a poor π-acceptor due to the low energy and high s-character of the HOMO, and the large energy difference (95.3–110 kcal mol−1) between the HOMO and the rather diffuse acceptor 4p-orbital (LUMO+1).2–4 The σ-donor capacity of LGa was experimentally demonstrated for instance with the synthesis of the Lewis acid–base adduct LGa–B(C6F5)3, and other p- or d-block metal complexes as well as with the synthesis of a large variety of (late) transition metal complexes.6 The latter were shown to be promising reagents for the activation of small molecules such as ethylene and have been used as precursors for the formation of heterometallic clusters,7,8 which in part can be described as molecular models for alloys.

While the coordination chemistry of LGa has been developed to a far greater extent compared to that of its lighter homologue LAl, its use in the transformation of unsaturated organic substrates has not9–11 which most likely results from the weaker reducing properties of LGa. However, LGa was found to react with E–X bonds via insertion of the Ga(i) centre and subsequent formation of covalent Ga–E bonds.12 This reaction pathway was used for cluster formation reactions via oxidative insertion/reductive elimination processes. The synthesis of molecular gallium–tin intermetallic clusters upon reaction of LGa with SnCl213 as well as two galla-dibis-muthenes containing covalent Ga–Bi single-bonds and Bi≡Bi double bonds, which were obtained from the reactions of LGa with Bi(OR)3 (R = O2SCF3, C6F5)14 represent remarkable experimental “snapshots” of these reactions. The cluster compounds can be considered as isolated reaction intermediates on the way to full reduction to tin metal and bismuth metal, respectively. The syntheses of these complexes demonstrate the promising potential of LGa to serve as selective reducing agent in the preparation of metalloid clusters and subvalent “metastable” compounds.

In addition to these interesting studies on the synthesis of intermetallic compounds, the capability of LGa in bond activation reactions was also studied. LGa was reacted with a large variety of compounds containing different element–element bonds including dihydrogen15 as well as electronically unsaturated molecules such as N2O, organic azides N3R and elemental sulphur. Many of these reactions were performed in order to synthesize compounds containing multiple bonds to gallium. However, reactions of LGa with N2O or S8 yielded the oxo- or sulfido bridged dimers [LGa–μ-E]2 (E = O, S),16 while its reaction with N3SiMe3 proceeded with formation of a cyclic gallium tetrazole and a gallium imide/azide compound. The most-likely formed reaction intermediate, a monomeric gallium imide LGa≡NR,17 was finally synthesized by reaction of LGa with the sterically encumbered azide Ar*N3 (Ar* = 2,6-Trip2-C6H3, Trip = 2,4,6-i-Pr3-C6H2) and structurally characterized by single crystal X-ray diffraction.18

Our long-term interest in the reactivity of low-valent organo-metallics of group 12 to 16 elements prompted us to start investigations on the general reactivity of LM (M = Al, Ga, In)
toward group 15 compounds such as BiEt$_3$ as well as tetraalkyldistibanes and dibismuthanes Et$_4$E$_2$ (E = Sb, Bi). These reactions were found to proceed with cleavage of the Bi–C as well as E–E bond and subsequent formation of LM(Et)BiEt$_2$ and LM(Et$_2$)$_3$, respectively, in which the Ga atom is oxidized from the formal oxidation state +1 to +III. Moreover, oxidative addition reactions of monovalent Ga(0) compounds, as well as E methyl groups of the C$_3$N$_2$Ga rings (1.35 ppm), were not intense enough. The $^{13}$C NMR spectrum shows more distinct methyl protons of the i-Pr groups in 3 are magnetically inequivalent, leading to six doublets (1.87, 1.61, 1.34, 1.31, 1.08, 0.67 ppm) in the $^1$H NMR spectrum. The six methine protons of the i-Pr groups appear as four septets (4.16, 3.82, 3.42, 1.04 ppm) with the integral ratios of 2:1:2:1, respectively. Integrals of 2 H belong to the i-Pr methylene groups of the L ligand. The γ-CH and two methyl groups of the C$_3$N$_2$M ring are in the mirror plane and exhibit only single resonances at 4.67 and 1.51 ppm, respectively. The $^{13}$C/$^1$H NMR spectrum of 3 shows the expected 19 signals and some of them were tentatively assigned to the i-Pr carbons atoms in 3 in the Experimental section. Elemental analyses (C, H, N) of 1–3 confirm the structural compositions and their analytical purity nature. Furthermore, the NMR ($^1$H, $^{13}$C, $^{125}$Te) and IR spectroscopic details are in accordance with the proposed formulations of 1–3.

1–3 are stable in solution and no reduction/decomposition occurs even at 90 °C in C$_6$D$_6$. Despite that the first Te–C bond cleavage of i-Pr$_2$Te occurred smoothly at room temperature, the second Te–C bond couldn’t be cleaved by reaction with an additional equivalent of LGa. In contrast, we successfully cleaved the Te–C and Te–Te bonds of Ph$_2$Te$_2$ upon reaction with an equimolar amount of the Lewis acid–base adduct LGa→B(C$_6$F$_5$)$_3$ in C$_6$D$_6$, which yielded an yellow-orange solution at room temperature within three days. The $^1$H NMR spectrum of the reaction mixture shows the presence of four different types of γ-CH protons with different integral ratios (Fig. S11f) and the spectral comparison evidences the presence of traces of 1 (4.57, 3.39 ppm) and 2 (4.76, 3.62 ppm) along with two unknown compounds. Prolonged storage of the reaction mixture (10 days) at room temperature led to pale yellow crystals of 1. During this period the peaks corresponding to 2 gradually decreased. Unfortunately, our efforts to isolate the major component of the reaction mixture (see Fig. S12f) failed since the solution is highly sensitive and decomposes to oily substances. According to the $^1$H NMR pattern, the Ga atom in the major product has three different substituents.

Single crystals of 1 were grown separately in benzene and toluene solutions. 1a is the solvent-free compound (obtained from the 1:1 reaction of Ph$_2$Te$_2$ and LGa→B(C$_6$F$_5$)$_3$) and crystallises in the monoclinic space group P2$_1$/c, while 1b is its toluene hemi-solvate (obtained from the 1:1 reaction of Te and LGa), which crystallises in the monoclinic space group C2/m. Single crystals of 2 were obtained from a freshly prepared n-hexane solution upon storage at room temperature.

### Results and discussion

Equimolar amounts of LGa were reacted with elemental tellurium, diphenylditellane Ph$_2$Te$_2$ and diisopropyltellane i-Pr$_2$Te in toluene at ambient temperature, yielding the Te-bridged dimer [LGa–Pr$_2$Te]$_2$. As well as LGa(SePh)$_2$ and LGa(i-Pr)TePr$_3$, respectively (Scheme 1). 1–3 are moisture sensitive, yellow to pale yellow crystalline solids but moderately stable toward air. 1 is sparingly soluble in benzene, toluene and n-hexane whereas 2 and 3 are soluble in these solvents.

The $^1$H and $^{13}$C NMR spectra of 1–3 show the characteristic resonances of the organic entities. $^1$H NMR spectral pattern of 1 and 2 are similar to those of LGa and C$_2$ symmetric molecules related to the β-diketiminato ligands. They exhibit single resonances for the γ-CH (4.59 ppm, 1; 4.76 ppm, 2) and two methyl groups of the C$_3$N$_2$Ga rings (1.35 ppm 1; 1.50 ppm 2). The methyl protons of the isopropyl substituents and methine protons appear as two doublets (1.13 & 1.10 ppm 1; 1.48 & 1.08 ppm 2) and a septet (3.33 ppm 1; 3.62 ppm 2), respectively. Due to its low solubility, the $^{13}$C and $^{125}$Te NMR resonances of 1 were not intense enough. The $^{13}$C NMR spectrum of 2 shows 14 signals including the characteristic resonances due to the γ-CH (99.22 ppm) backbone carbon atom, both β-C atoms atoms of the C$_3$N$_2$Ga ring (170.63 ppm) and the methine (29.36 ppm) and methyl carbon atoms of isopropyl groups (27.01, 25.44 ppm). Compound 3 shows more distinct $^1$H and $^{13}$C NMR patterns than 1 and 2. Due to the presence of three different substituents at the Ga atom and a hindered rotation about the N–C bonds, the i-Pr groups in 3 are magnetically inequivalent, leading to six doublets (1.87, 1.61, 1.34, 1.31, 1.08, 0.67 ppm) in the $^1$H NMR spectrum. The six methine protons of the i-Pr groups appear as four septets (4.16, 3.82, 3.42, 1.04 ppm) with the integral ratios of 2:1:2:1, respectively. Integrals of 2 H belong to the i-Pr methylene groups of the L ligand. The γ-CH and two methyl groups of the C$_3$N$_2$M ring are in the mirror plane and exhibit only single resonances at 4.67 and 1.51 ppm, respectively.

#### Scheme 1 Synthesis of 1–3.

![Scheme 1 Synthesis of 1–3.](image-url)
while single crystals of 3 were grown from saturated toluene solutions at 5 °C. 2 and 3 crystallise in the orthorhombic space groups Pbca (2) and Pnma (3). Fig. 1-3 show the solid state structures of 1a, 2 and 3 and the selected bond lengths and bond angles are given at the figure captions. Table 1 summarises the crystal data and details of the structural determinations.

The Ga atoms in 1a, 1b, 2 and 3 each adopt slightly distorted tetrahedral coordination spheres.† The six-membered GaN2C3 rings show boat-type conformations, in which the Ga atoms are significantly out of plane (deviation from best plane of the ligand’s backbone: 0.521(3) Å 1a, 0.5853(19) and 0.560(2) Å 1b, 0.721(5) Å 2, 0.6309(18) Å 3) The average Ga-N bond length (1.981(2) Å 1a, 1.992(2) Å 1b, 1.961(4) Å 2, 1.9739(10) Å 3) and N-Ga-N bond angle (94.92(10)° 1a; 95.38(6)° 1b; 97.45(15)° 2; 95.66(5)° 3) as observed for 1, 2 and 3 are almost identical to that of LGa, for which an average Ga-N distance of 2.054(2) Å and a N-Ga-N bond angle of 87.56(5)° was reported. The Te–Ga–Te angles (98.88(2)° 1a; 100.39(1)° 1b; 113.59(2)° 2) and C-Ga–Te bond angles (105.84(5)° 3) are smaller compared to the N-Ga-N bond angles. The Ga–Te bond lengths (2.5777(4), 2.5898(4) Å 1a, 2.5809(2), 2.5909(2) Å 1b, 2.5586(5), 2.6076(6) Å 2, 2.114(5), Te(2)–C(31) 2.144(4), N(1)–C(1) 1.342(6), N(2)–C(3) 1.335(4), C(1)–C(2) 1.377(6), C(2)–C(3) 1.406(6), N(1)–Ga(1)–N(2) 97.45(15), N(1)–Ga(1)–Te(1) 110.65(11), N(2)–Ga(1)–Te(1) 114.06(11), N(1)–Ga(1)–Te(2) 110.98(12), N(2)–Ga(1)–Te(2) 109.00(11), Te(1)–Ga(1)–Te(2) 113.587(19), C(1)–C(2)–C(3) 130.5(4), N(1)–C(1)–C(2) 123.5(4), N(2)–C(3)–C(2) 122.7(4).

†The crystallographic data of 1a, 1b, 2 and 3 (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1040132 (1a), CCDC-1040134 (1b), CCDC-1040133 (2) and CCDC-1040135 (3).
θ bonds observed in Ga{TeSi(SiMe₃)₃}₃ (av. 2.496(6) Å)⁴² as well as bond lengths in the range from 2.67 to 2.76 Å were obtained from the reaction of base-stabilized gallanes [R₂Ga₂(μ-OOCCH₃)₂] (2.534 Å) ²⁹ as well as the base-stabilized compounds LGa(TePh)₃ (L = NMe₅, PCy₃), which were obtained from the reaction of base-stabilized gallanes [LGaH₃] with Ph₂Te₂ and which also contain fourfold-coordinated Ga atoms and twofold-coordinated Te atoms, show comparable Ga–Te bond distances of 2.580(1) Å and 2.597(2) Å, respectively.³⁰ In contrast, the Ga–Te bonds in the [MeGa(TePh)₃]³⁺ monocation of [[Me₃P₂]₄Cu[MeGa(TePh)₃]] is slightly elongated (2.640(3) Å).³¹ The same holds for the Ga–Te bonds in four structurally characterized Ga₄Te₆ heterocubanes, which range from 2.67 to 2.72 Å,²⁻³⁵ as well as in dimeric compounds of the general type [R₂Gaµ-TeR₂], for which Ga–Te bond lengths in the range from 2.67 to 2.76 Å were reported.³⁶⁻³⁹ In contrast, slightly shorter Ga–Te bond lengths were reported for [[(Me₅C₅)₄Cu]₂] (2.552(4) Å),¹⁰ [(Me₅C₅)₂]₂GaTe₂Si(SiMe₃)₃ (2.535(1) Å),⁴¹ whereas the Ga–Te bonds observed in Ga[TesSi(SiMe₃)₃]₂ (av. 2.496(6) Å)⁴² as well as in Tp²GaTe (2.422(1)) (Tp² = tris(3,5-di-tert-butylpyrazolyl) hydroborato), to date the only compound containing a terminal Ga–Te double bond, are significantly shortened.⁴¹

Reactions of trivalent group 13 compounds (MR₃, MH₃; M = Al, Ga, In) with elemental chalcogens E or chalcogen sources such as R₄P=E (E = O, S, Se, Te) typically occur with insertion of the chalcogen atom into the M–E bond and subsequent formation of dimeric [[R₂M-µ-ER₂]₃] or tetrameric [[RME]₄] compounds, whereas divalent (R₄M₂) as well as monovalent group 13 compounds RM (M = Al, Ga, In, Tl) react with Te double bond, are significantly shortened.⁴³

Conclusions

LGa was found to selectively insert into the Te–Te bond of diphenylditellane Ph₂Te₂ as well as on Te–C bond of diisopropyltellane i-Pr₂Te, resulting in the formation of LGa(TePh)₃, LGa[i-Pr]Te[i-Pr] and LGa[i-Pr]Te[i-Pr]₃. Moreover, its reaction with elemental tellurium yielded the Te-bridged compound [LGaµ-Te]₃. ¹ We are currently investigating reactions of the somewhat stronger reducing agent LAI with various group 16 precursors. A previous report showed that LAI reacted with elemental sulfur...
with subsequent formation of \([\text{La}][\mu-\text{S}_2]_2\), containing an unusual \(\text{Al}_2\text{S}_6\) ring.\(^5^2\)

**Experimental**

All manipulations were performed in an atmosphere of purified argon using standard Schlenk and glove-box techniques. Toluenes were dried and concentrated to a THF suspension (1.0 g, 7.84 mmol) at 0 °C. After stirring at room temperature for 2 h, a solution of isopropyl bromide (1.976 g, 16.06 mmol, 1.5 mL) in THF (10 mL) was added. The reaction mixture was additionally stirred at room temperature for 2 h and the mixture was filtered through a glass frit. The solvents were removed under reduced pressure (500 mbar) and i-Pr\(_2\)Te was distilled at 45 °C (10 mbar). Yield: 72% (1.20 g).

**Synthesis of i-Pr\(_2\)Te.** Et\(_2\)BHLLi ("superhydride", 1.0 M in THF, 16.06 mmol, 16.1 mL) was added dropwise to a THF (50 mL) suspension of \(\text{Te}(1.0 \text{ g}, 7.84 \text{ mmol})\) at 0 °C. After stirring at room temperature for 2 h, a solution of isopropyl bromide (1.976 g, 16.06 mmol, 1.5 mL) in THF (10 mL) was added. The reaction mixture was additionally stirred at room temperature for 2 h and the mixture was filtered through a glass frit. The solvents were removed under reduced pressure (500 mbar) and i-Pr\(_2\)Te was distilled at 45 °C (10 mbar). Yield: 72% (1.20 g).

**Synthesis of \(\text{Ph}_2\text{Te}\).** A mixture of elemental tellurium (0.0393 g, 0.254 mmol) and \(\text{Ph}_2\text{Te}_2\) (0.168 g, 0.41 mmol) in toluene (2 mL) was added dropwise to a well-stirred toluene (2 mL) soln of LGa (0.2 g, 0.41 mmol). The reaction mixture was stirred at room temperature for 3 h and stored at −30 °C to give a clear yellow solution. The solution was then concentrated to 1 mL, layered with 1 mL of n-hexane and stored at −30 °C to give an analytically pure crystalline precipitate of 2. Single crystals suitable for X-ray diffraction analysis were grown from n-hexane solution. 0.13 g of 2 was dissolved in 4 mL of warm n-hexane and stored at room temperature for 1 day to give yellow crystals suitable for X-ray diffraction analysis. Yield: 73% (0.269 g).

**Synthesis of 3.** A mixture of i-Pr\(_2\)Te (0.068 g, 50 µL, 0.318 mmol) and LGa (0.155 g, 0.318 mmol) in 2 mL of toluene was stirred at ambient temperature for 24 h. The clear solution was concentrated to 1 mL and stored at 5 °C for 3 days to give a large amount of 2 as pale yellow blocks. Yield: 76% (0.169 g).

**Synthesis of 1.** A mixture of elemental tellurium (0.0393 g, 0.308 mmol) and LGa (0.150 g, 0.308 mmol) in 20 mL of toluene was stirred at ambient temperature for 3 days. The reaction mixture was centrifuged and either precipitate was extracted twice with 10 mL of hot toluene. Combined filtrates were concentrated to 10 mL and stored at −30 °C for 3 days to afford analytically pure 1 as pale yellow crystals. Yield: 61% (0.115 g).

**Synthesis of 2.** A solution of \(\text{Ph}_2\text{Te}_2\) (0.168 g, 0.41 mmol) in toluene (2 mL) was added dropwise to a well-stirred toluene (2 mL) soln of LGa (0.2 g, 0.41 mmol). The reaction mixture was stirred at room temperature for 3 h and stored at −30 °C to give a clear yellow solution. The solution was then concentrated to 1 mL, layered with 1 mL of n-hexane and stored at −30 °C to give yellow crystals suitable for X-ray diffraction analysis. Yield: 73% (0.269 g).

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tures of 1–3 are shown in Fig. 1–3. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on \( F^2 \) (SHELXL-97).\(^{54,55}\) Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). The toluene molecule of 1b is disordered via \( 2/m \) symmetry. Further solvent molecules that could not be modelled sufficiently were removed by a PLATON/SQUEEZE run.\(^{56}\) The crystal quality of 2 was rather low consequently the quantitative results of the model should be carefully assessed. The resolution of the data of 3 was high enough to show a mismatch of the calculated position of H2 and the residual electron density. Consequently H2 was refined freely with its displacement parameter constrained to be 1.2 times \( U_{eq} \) of the connected C atom. Other hydrogen atoms were refined using a riding model or rigid methyl groups.

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