**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, 1, 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(PhTe)2, 2 and LGa(i-Pr)Te(i-Pr)3, 3. 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 LGaÆB(C₆F₅)₃.⁵ 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 not,⁹ 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 SnCl₄,¹³ 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 NR,¹⁷ was finally synthesized by reaction of LGa with N₂O or Sn₅ yielded the oxo- or sulfido bridged dimers [LGa–μ-E]₂ (E = O, S),¹⁶ while its reaction with N₅SiMe₅ 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-Trpp₂C₆H₃, Trip₂ = 2,4,6-i-Pr₂C₆H₃) and structurally characterized by single crystal X-ray diffraction.¹⁸

Our long-term interest in the reactivity of low-valent organometallics 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 BiEt₃ as well as tetraalkyldistibanes and dibismuthanes Et₄E₂ (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(ET₂)₂ and LM[ET₃]₂, respectively, in which the Ga atom is oxidized from the formal oxidation state +I to +III. Moreover, oxidative addition reactions of monovalent Zn(i) compounds, germynes and stannylenes as well as distibanes and dibismuthanes with dichalcogenanes were reported by us. In addition, insertion reactions of elemental chalcogenos into metal–metal bonds were observed in reactions with tetraalkyldistibanes and -dibismuthanes. We herein report on the reactions of LGa with elemental tellurium as well as diphenylditellane Ph₂Te₂ and diisopropyltellane i-Pr₂Te, which proceeded with Te–Te and Te–C bond cleavage and subsequent formation of compounds containing direct Ga–Te σ-bonds.

Results and discussion

Equimolar amounts of LGa were reacted with elemental tellurium, diphenylditellane Ph₂Te₂ and diisopropyltellane i-Pr₂Te in toluene at ambient temperature, yielding the Te-bridged dimer [LGa-µ-Te₂] (1) as well as LGa(TePh)₂ (2) and LGa(i-Pr)Te(µ-Pr) (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 ¹H and ¹³C NMR spectra of 1–3 show the characteristic resonances of the organic entities. ¹H NMR spectral pattern of 1 and 2 are similar to those of LGa and LGa, which crystallises in the monoclinic space group P2₁/n. Due to its low solubility, the ¹³C and ¹²⁵Te NMR resonances of 1 were not intense enough. The ¹³C 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 C₃N₂Ga 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 ¹H and ¹³C 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 ¹H 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 methine groups of the L ligand. The γ-CH and two methyl groups of the C₃N₂M ring are in the mirror plane and exhibit only single resonances at 4.67 and 1.51 ppm, respectively. The ¹³C(¹H) 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 (¹H, ¹³C, ¹²⁵Te) 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 C₆D₆. Despite that the first Te–C bond cleavage of i-Pr₂Te 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 Ph₂Te₂ upon reaction with an equimolar amount of the Lewis acid-base adduct LGa→B(C₆F₅)₃ in C₆D₆, which yielded an yellow-orange solution at room temperature within three days. The ¹H 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 ¹H 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 Ph₂Te₂ and LGa→B(C₆F₅)₃) and crystallises in the monoclinic space group P2₁/n, 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/n. Single crystals of 2 were obtained from a freshly prepared n-hexane solution upon storage at room temperature,
while single crystals of 3 were grown from saturated toluene solutions at 5 °C. 2 and 3 crystallise in the orthorhombic space groups Pnma (2) and Cmcm (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 GaN₃C₃ 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; 1.9793(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(6)° was reported.1 The Te–Ga–Te (98.88(2)° 1a; 100.39(1)° 1b; 113.59(5)° 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; 2.5892(2), 2.5909(2) Å 1b; 2.5586(2), 2.6076(2) Å 2; 2.5929(4) Å 3) are comparable to those reported for [K(OEt)₂][[PhTe₃]Ga[N(2,6-i-Pr₂-C₆H₄)-C(H)₃]] (2.5785(12), 2.6577(10) Å).²⁵ The Te-bridged dimers

‡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).
Table 1  Crystallographic data of 1a, 1b, 2, and 3

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<td>M</td>
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<td>2.287−1.586</td>
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R₁ = ∑||Fₒ| − |F₁||/∑|Fₒ||, wR₂ = (∑[w(F₁² − F国际在线的文献。
with subsequent formation of \([\text{LA}][\mu-\text{S}])_2], containing an unusual \(\text{AlS}_6\) ring.\(^{52}\)

**Experimental**

All manipulations were performed in an atmosphere of purified argon using standard Schlenk and glove-box techniques. Toluenes and hexane were dried using a mBraun Solvent Purification System. THF was carefully dried over Na/K. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. Anhydrous nature of the solvents was verified by Karl Fischer titration. The \(^1\text{H}\) (300 MHz), \(^{13}\text{C}\)\(^{(1)}\text{H}\) (75.5 MHz) and \(^{125}\text{Te}\) NMR (95 MHz) (δ in ppm) spectra were recorded using a Bruker Avance DPX-300 spectrometer. The \(^1\text{H}\) and \(^{13}\text{C}\)\(^{(1)}\text{H}\) spectra were referenced to internal \(\text{C}_{6}\text{D}_{6}\text{H}(\text{H}: \delta = 7.154); \(^{13}\text{C}\): \(\delta = 128.39)\) and \(\text{C}_{6}\text{D}_{5}\text{CHD}_{2}\) (\(\text{H}: \delta = 2.09); \(^{13}\text{C}\): \(\delta = 20.40). \(^{125}\text{Te}\) NMR spectra were referenced to \(\text{Na}_2\text{TeO}_3\) in D\(_2\)O.

**Synthesis of i-Pr\(_2\)Te.** \(\text{Et}_2\text{BHLi ("superhydride"), 1.0 M in THF, 16.06 mmol, 16.1 mL) was added drop wise to a THF (50 mL) suspension of \(\text{Te}(1.0 \text{ g}, 7.84 \text{ mmol}) at 0^\circ\text{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). \(^1\text{H}\) NMR (\(\text{C}_6\text{D}_{6}\), 300 MHz): \(\delta 3.18\) (sept, \(\text{CH}-(\text{CH}_3)_2\), 2 H), 1.50 (d, \(\text{CH}(\text{H})_2\), 12 H). \(^{13}\text{C}\) NMR (\(\text{C}_6\text{D}_{6}\), 75 MHz): \(\delta 28.00\) (\(\text{CH}(\text{H})_2\)), 10.57 (\(\text{CH}(\text{H})_2\)).

**Synthesis of 1.** A mixture of elemental tellurium (0.0393 g, 0.218 mmol) and LGa (0.155 g, 0.318 mmol) in 2 mL of toluene was stirred at ambient temperature for 3 days to give a yellow solution. The solution was then concentrated to 1 mL, layered with 1 mL of \(n\)-hexane and stored at \(-30^\circ\text{C}\) to give analytically pure crystalline precipitate of 1. 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). Anal. Calcd for \(\text{C}_{14}\text{H}_{25}\text{Ga}_{2}\text{Te}_2\): C, 54.96; H, 5.73; N, 3.12. Found: C, 55.30; H, 5.81; N, 3.13.

**Synthesis of 2.** A solution of \(\text{Ph}_2\text{Te}_2\) (0.068 g, 0.41 mmol) in toluene (2 mL) was added dropwise to a well-stirred toluene (2 mL) solution of LGa (0.2 g, 0.41 mmol). The reaction mixture was stirred at room temperature for 3 h to give a clear yellow solution. The solution was then concentrated to 1 mL, layered with 1 mL of \(n\)-hexane and stored at \(-30^\circ\text{C}\) to give 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). Anal. Calcd for \(\text{C}_{14}\text{H}_{25}\text{Ga}_{2}\text{Te}_2\): C, 54.96; H, 5.73; N, 3.12. Found: C, 55.30; H, 5.81; N, 3.13. \(^1\text{H}\) NMR (300 MHz, \(\text{C}_6\text{D}_{6}\)): \(\delta 7.54\) (m, \(\text{H}, \text{Ph}\)), 7.18 (m, \(\text{C}_6\text{H}_3(\text{Pr})_2\)), 6.96 (m, \(\text{H}, \text{Ph}\)), 6.78 (m, \(\text{m}, \text{H}, \text{Ph}\)), 4.76 (s, \(\gamma\text{CH}^-, 1\) H), 3.62 (sept, \(\text{CH}(\text{H})_3\)), 1.50 (s, \(\text{ArNCCH}_2\)), 1.48 (d, \(\text{CH}(\text{H})_3\)), 1.20 (d, \(\text{CH}(\text{H})_3\)). \(^{13}\text{C}\) NMR (75.5 MHz, \(\text{C}_6\text{D}_{6}\)): \(\delta 170.63\) (\(\text{ArNC\_}\)), 145.36 (Ar), 141.58 (Ar), 128.91 (Ar), 128.21 (Ar), 126.81 (Ar), 125.47 (Ar), 108.69 (Ar), 99.22 (\(\gamma\text{CH}^-\)), 29.36 (\(\text{CH}(\text{H})_3\)), 27.01 (\(\text{CH}(\text{H})_3\)), 25.44 (\(\text{CH}(\text{H})_3\)), 24.67 (\(\text{ArNC\_}\)). \(^{125}\text{Te}\) NMR (95 MHz, \(\text{C}_6\text{D}_{6}\)): \(\delta -21.94\). IR (neat): \(\nu\) 3051 (w), 2962 (m), 2923 (w), 2863 (w), 1521 (m), 1460 (m), 1366 (m), 1311 (m), 1254 (m), 1169 (w), 1103 (w), 1014 (m), 935 (w), 861 (w), 797 (m), 727 (s), 689 (s), 636 (w), 531 (w), 451 (m) cm\(^{-1}\).
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). 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. The crystal quality of 1b was rather low consequently the quantitation of the model should be carefully assessed. 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.

Acknowledgements

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Notes and references