A monotopic aluminum telluride with an Al–Te double bond stabilized by N-heterocyclic carbenes

Daniel Franz¹, Tibor Szilvasi², Elisabeth Irran¹ & Shigeyoshi Inoue¹

Aluminum chalcogenides are mostly encountered in the form of bulk aluminum oxides that are structurally diverse but typically consist of networks with high lattice energy in which the chalcogen atoms bridge the metal centres. This makes their molecular congeners difficult to synthesize because of a pronounced tendency for oligomerization. Here we describe the isolation of the monotopic aluminum chalcogenide \((L^{\text{Dip}})\text{AlTe}(L^{\text{Et}})_2\) \((L^{\text{Dip}} = 1,3-(2,6\text{-diisopropylphenyl})\text{-imidazolin}-2\text{-imine}, L^{\text{Et}} = 1,3\text{-diethyl}-4,5\text{-dimethyl-}
\text{imidazolin}-2\text{-ylidene})\). Unique features of \((L^{\text{Dip}})\text{AlTe}(L^{\text{Et}})_2\) are the terminal position of the tellurium atom, the shortest aluminum–tellurium distance hitherto reported for a molecular complex and the highest bond order reported for an interaction between these elements, to the best of our knowledge. At elevated temperature \((L^{\text{Dip}})\text{AlTe}(L^{\text{Et}})_2\) equilibrates with dimeric \({(L^{\text{Dip}})\text{AlTe}(L^{\text{Et}})}_2\) in which the chalcogen atoms assume their common role as bridges between the metal centres. These findings demonstrate that \((L^{\text{Dip}})\text{AlTe}(L^{\text{Et}})_2\) comprises the elusive Al–Te double bond in the form of an N-heterocyclic carbene-stabilized species.

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Aluminum is the third most abundant element in the earth’s crust surpassed in quantity only by oxygen and silicon and it is most often found among the elements of the group 13 family. The metal is easily oxidized and mostly encountered in the form of aluminum oxides, which are ionic compounds with high lattice energies. The structural diversity of aluminum oxides has led them to be used in a variety of applications in science and technology1–3. Among the heavier aluminum chalcogenides, tellurium compounds are explored the least, which is mainly due to this element’s low abundance on our planet. Applications of aluminum tellurides in chemical synthesis have barely been reported4; however, attention to the heaviest non-radioactive chalcogen has intensified lately because of its use for electronic devices5,6. Considering the general importance of inorganic aluminum chalcogenides to applied research, it is of prime interest to understand the aggregation processes that create the bulk materials from single atoms and to clarify the nature of the chemical bond between the elements. Theoretical calculations, as well as low-temperature matrix isolation techniques have been used to get an initial insight into the ultrafast bond formations involved in those processes, but these methods have considerable limitations7–9. One of the best methods to overcome these limitations is to study well-defined molecular complexes that are stable in the condensed phase at ambient temperatures. Astonishingly, complexes of the general formula R–Al=E (I, Fig. 1, R = monoanionic ligand, E = chalcogen) with a double bond between the elements are scarcely found in the literature10 and oligomeric compounds (RAIE)n (n = 2, 3, 4, ...) dominate the field11–15.

Interestingly, the double-bonded species could be regarded as a molecular mimic of an elusive intermediate in the processes of aggregation and polymerization that may lead to bulk inorganic aluminum chalcogenides reminiscent of the formation of macromolecular polyolefins from monomolecular vinyl precursors. An apparent explanation for the high reactivity of I is the electropositive nature of the aluminum atom, which renders the Al=E moiety a highly polarized Lewis acid–base pair. In consequence, the combination of an electrophilic site at the Al centre and a nucleophilic lone pair located at the chalcogen atom results in self-oligomerization. By the use of unchanged electron pair donor ligands, one can decrease the Lewis acidity of the metal centre to thermodynamically stabilize the Al=E functionality, a technique often complemented by the addition of a Lewis acid that binds to the chalcogen atom. This results in donor–acceptor-stabilized complexes of type II (Fig. 1). Further stabilization can be achieved by introduction of an additional Lewis base (III, Fig. 1).

This technique has led to the isolation of a monoaluminoxane complex of the highly unstable R–Al=E functionality, for which two Lewis bases and one Lewis acid were used to stabilize the Al and O atom, respectively16. Though donor–acceptor stabilization is an elaborate and useful synthetic tool to generate complexes with considerable multiple bond character, the steric and electronic stabilization at the terminal chalcogen atom of R–Al=E species significantly limits the investigation of their reactivity. In this work, we describe the monatomic aluminum telluride (L3DipN)AlTe(L3Et)2 (3, L3Dip = 1,3-(2,6-diisopropylphenyl)-imidazolin-2-imine, L3Et = 1,3-diethyl-4,5-dimethyl-imidazolin-2-ylidene), an electron-precise aluminum chalcogenide that bears a terminal atom of the group 16 family. The unique bonding situation of 3 results in the shortest aluminum–tellurium distance and the highest bond order reported for this type of molecular complex. Furthermore, 3 dimerizes to ([L3DipN]AlTe(L3Et))2 (5) at elevated temperature. We interpret these results in terms of an Al=Te double bond to be present in 3.

Results

Synthesis of the monatomic aluminum telluride 3. The synthesis of the aluminum telluride 3 starts out with the previously reported17,18 dimeric aluminum dihydride 1 (Fig. 2). The introduction of tellurium to the system was accomplished by addition of two equivalents of the convenient tellurium transfer reagent 4Bu2P=Te (4Bu2 = n-butyly) to produce the aluminum ditelluride 2 via a dehydrogenative three-electron redox process in which the chalcogen is reduced from the oxidation state of +2 to −1. An X-ray study on 2 revealed that the four-membered Al2N2 ring is decorated with a bridging ditelluride group. Though we could not obtain crystals of sufficient quality to allow for the discussion of structural parameters, the connectivity as in the structural formulation 2 was verified (Supplementary Fig. 16).

The Al–Te–Te–Al structural motif is without precedence in the literature. Notably, it resembles the Al–Te–Al moiety reported for a pyrazolato aluminum telluride, wherein one tellurium atom bridges the aluminium centres19.

Bicyclic systems, such as the Al2N2Te2 moiety in 2, obviously possess high ring strain because the geometry imposes internal bond angles significantly <109.5°, which aggravates typical tetrahedral coordination. Thus, it seemed reasonable that the cycle might be prone to the cleavage by nucleophilic attack at the metal centres to furnish a monatomic aluminum–tellurium complex. We chose N-heterocyclic carbene (NHC) as a nucleophile because NHCs are strong σ-electron pair donors that have proven viable for the taming of numerous elusive main group element compounds on a molecular level20–24. Indeed, the reaction of the ditelluride 2 with two equivalents of LEt yielded the monatomic telluride 3 (Fig. 2). During this dehydrogenative redox process, the tellurium atom is further reduced to the −2 oxidation state with concomitant formation of dihydrogenated NHC (LEt(H2), hydrogenated at the formerly carbenoid atom). The abstraction of hydrogen from iminoboranes using NHC to produce NHC(H2) had been previously investigated25.

The single-crystal X-ray analysis unambiguously shows that the aluminum centre in 3 is bonded to one imino group, two NHC ligands and a terminal tellurium atom (Fig. 3a). The aluminum centre is coordinated in a distorted tetrahedral manner with the chalcogen atom tilted away from the bulkier diisopropylphenyl (Dip) moieties of the imino group towards one of the sterically less hindered carbene ligands. The Al–Te bond length was determined to be 2.5130(14) Å, which is decreased in comparison with the typical range found for molecular aluminum tellurides with four-coordinate aluminum atoms (2.562–2.750 Å)11,15,26–28. Remarkably, the Al–Te distance in 3 is even shorter than the 2.549(1) Å found for the ditopic Te[Al(CH(SiMe3)2)3]2 with three-coordinate aluminium centres that marked the hitherto shortest AlTe contact reported for a molecular complex29.

The terminal position of the tellurium atom in 3 is a unique finding because chalcogens commonly function as bridging ligands in aluminum compounds or are coordinated to another

![Figure 1 | General types of molecular group 13 metal chalcogenides with double-bond character.](image-url)
Selected bond lengths (Å) and bond angles (°) are provided in Table 1 for the molecules adjacent in the crystal lattice for clarity. Thermal ellipsoids are at the 30% probability level.

Figure 2 | Synthetic overview for this work. Conversion of dimeric aluminum dihydride 1 via ditelluride 2 to monotopic aluminum telluride 3 and its dimerization via intermediate 4 to tellurium-bridged 5 (Dip = 2,6-diisopropylphenyl, LEt = 1,3-diethyl-4,5-dimethyl-imidazolin-2-ylidene). (i) Toluene, rt, 48 h. (ii) Benzenes, rt, 48 h. (iii) Benzenes, 80 °C, 22 h; rt = ambient temperature.

Figure 3 | Ellipsoid plots derived from single-crystal X-ray diffraction data. Molecular structures of 3 (a) and 5 (b) in the solid state. Hydrogen atoms, isopropyl groups and non-N-bonded methyl groups have been omitted for reasons of clarity. Thermal ellipsoids are at the 30% probability level. Selected bond lengths (Å) and bond angles (°): 3: Al–Tel = 2.5130(14), Al–N1 = 1.804(4), Al–C28 = 2.084(5), Al–C37 = 2.077(5), N1–C1 = 1.259(6); Tel–Al–N1 = 118.34(14), Tel–Al–C28 = 102.65(13), Tel–Al–C37 = 119.08(14), Al–N1–C1 = 139.8(4). 5: Al–Tel = 2.6143(14), Al–Tel′ = 2.6143(14), Al–N1 = 1.765(5), Al–C28 = 2.086(5), N1–C1 = 1.253(7); Al–Tel–Al′ = 80.86(5), Tel–Al–Tel′ = 99.14(5), N1–Al–Tel = 115.83(15), N1–Al–Tel′ = 121.13(16), Al–N1–C1 = 164.3(4).

Lewis acid. The closest distance between an aluminum and a tellurium centre in 3 of molecules adjacent in the crystal lattice amounts to 7.31 Å.

Theoretical study of monotopic aluminum telluride 3. We calculated a Wiberg Bond Index (WBI) of 1.20 for the AlTe bond in 3, which indicates significant double-bond character, particularly, if the strong polarization along the AlTe vector is taken into account (selected natural population analysis (NPA) charges for 3: Al = +1.24, Te = −0.95). Notably, it is commonly acknowledged that WBI values have a tendency to underestimate bond orders for heavier main group element bonds. For comparison the WBI_{AlTe} for the ditopic Te(Al(CH(SiMe3)2)2)_2 (vide supra) was calculated using the same theoretical method as for 3 and found to be smaller than one (0.91). This suggests that a trigonal-planar coordination environment of the aluminum centre is not a prerequisite for relevant AlTe double-bond character. Moreover, the WBI_{AlTe} of 1.20 for 3 is in line with that reported for the highly polarized Ge=O double bond in a germanone (WBI_{GeO} = 1.252) and the Si=O double bond in a sila-urea (WBI_{SiO} = 1.29), respectively.30,31 Remarkably, the two latter compounds bear trigonal-planar-coordinate metal centres. The molecular orbital analysis of 3 reveals the highest occupied molecular orbital (HOMO) to comprise a lone pair with π-symmetry that is primarily located at the tellurium atom (Fig. 4). The HOMO−1 shows a π-symmetric orbital lobe expanding between the aluminum and the tellurium centre that hints towards an interaction of higher bond order between these atoms. An expected AlTe σ-bond is observed in the HOMO−3 (Supplementary Fig. 21). Antibonding π-interaction among the phenyl rings of the Dip groups is found for the lowest unoccupied molecular orbital (LUMO), which suggests that electron donation to 3 would preferably start out at the ligand system rather than the metal site.

Natural Resonance Theory (NRT) investigation of 3 reveals a major contribution (77%) of resonance structures that feature an Al=Te double bond (that is, 3) and only a minor share (23%) of zwiterionic species with an Al−Te single bond as 3A or 3B (Fig. 5). This result is in accordance with a recent NRT study on NHC-stabilized sila-acylium ions that are isoelectronic to the aluminum telluride 3 (ref. 32). Interestingly, though solid batches of 3 can be stored in an inert atmosphere for weeks the compound decomposes in deuterated tetrahydrofurane solution.

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within few days to yield the protonated iminato ligand (L4DippNH, Supplementary Fig. 6).

**Thermal dimerization of 3 to tellurium-bridged 5.** When we heated a solution of 3 in benzene dimerization to 5 occurred (Fig. 2) in which the four-membered Al₂Te₂ cycle shows the chalcogen-bridged connectivity pattern common for complexes of aluminum with group 16 ligand atoms. Monitoring the process with NMR spectroscopy in C₆D₆ solution revealed that the system equilibrates at 80 °C in about 24 h with the dimer (5) and the monomer (3) coexisting in an approximate ratio of 1:1 (Supplementary Figs 11 and 12). After 5 has been isolated and stripped from solvent, it decomposes at ambient temperature within hours to a considerable degree (Supplementary Figs 13 and 14). Presumably, the stability of 5 depends on the presence of 3 and free NHC in solution. In comparison with monoprotic 3, the Al–Te distances in 5 are expanded and amount to 2.6143(14) and 2.6211(15) Å (Fig. 3b). This increase in bond length corresponds to the significantly lower calculated bond index of the AlTe double bond is underlined.

DFT analysis of the possible reaction mechanism for the transformation of 3 into 5 revealed intermediate complex 4 (Fig. 2) with a three-coordinate aluminum centre. The formation of 4 from 3 is a barrierless process that is usual for NHCl-coordinated main group element structures and underlines the donor–acceptor-bonding mode in NHC–Al bonds. The dissociated pair of complex 4 and free L4 is only 15.0 kcal mol⁻¹ higher in Gibbs free energy than its precursor 3, while a comparably low energy gain of 2.9 kcal mol⁻¹ is obtained in the overall process of forming the dimer 5 and free L4 from 3 (Supplementary Fig. 22). This small difference in the thermodynamic stabilities of 3 and 5 allows for assuming dynamic equilibrium between the two compounds that explains that 3 does not fully convert into 5 on heating.

**Discussion**

As a consequence of the terminal position of the tellurium atom in 3, the AlTe bond order is markedly increased with respect to complexes in which the chalcogen atom assumes a bridging position. Backed by the results of our theoretical study (WBI, NPA and NRT), we presume that 3 represents the elusive R–Al = Te species (vide supra) in the form of an NHCl-stabilized congener. Though the aluminum centre in 3 is four-coordinate, the WBIₐₙₜₑ is comparable to those of polarized metal chalcogen double bonds. Upon thermal dimerization of 3 into 5, the WBIₐₙₜₑ of the dimer is vastly decreased, which again underlines the importance of a terminal chalcogen atom for a bond order larger than one. Consequently, an Al = Te double bond is unlikely to be found for complexes following the approach of donor–acceptor stabilization (type II, III; Fig. 1). The calculated intermediate in the process of dimerization, that is, 4, which bears a three-coordinate aluminum centre exhibits a higher WBIₐₙₜₑ than 3 (Supplementary Table 1). There is no experimental proof for its existence, but it is conceivable that the isolation of a more stable congener to 4 may be accomplished by the use of bulkier NHCl ligands. However, our conversions of the ditelluride 2 with imidazolin-2-ylidenes more sterically congested than L4 did not yield respective analogues to neither 3 nor 4 or 5.

The isolation of the monoprotic aluminum telluride 3 markedly contributes to the field of aluminum element multiple bonds that are surprisingly unexplored to date. The thermal transformation of 3 into dimeric 5 may serve as a simplified model on the molecular level that could contribute to the elucidation of the complex process of how isolated atoms aggregate to three-dimensional networks in bulk aluminum chalcogenides.

**Methods**

**Experimental.** All experiments and manipulations were carried out under dry oxygen-free nitrogen using a Schlenk Line or an MBraun Glove Box Workstation containing an atmosphere of purified nitrogen. Glass junctions were coated with the polytetrafluoroethylene (PTFE)-based grease Merkel Tribolton III. Solvents were dried by standard methods and freshly distilled before the use. NMR spectra were recorded on a Bruker Avance 400 or an Avance III 500 spectrometer. Chemical shift values (δ) are given in parts per million and are referenced to (residual) solvent signals (¹H) and (¹C)NMR. s = singlet, br = broadened, d = doublet, t = triplet, sept = septet, n.o. = not observed, n.r. = not resolved.

L(DippNH)₂Al₂Te₂ (1), L₄Et₂₄ and 1½ were synthesized according to the published procedures. Reagents purchased from commercial sources were used as received if not stated otherwise. High-resolution mass spectrometry (HRMS) was performed on a Thermo Fisher Scientific LTQ Orbitrap XL machine using an atmospheric-pressure chemical ionization (APCI) or an electrospray ionization (ESI)
ion source and positive detection mode. Elemental analyses (via combustion) were carried out by the microanalytical laboratory of the Institut für Chemie, Technische Universität Berlin. The content of selected NMR spectra see Supplementary Figs 1–14. For NMR spectroscopic characterization of LE₄(H₂)₅e⁺ observed in some instances that the substance was covered with a thin layer of

**Computational.** Geometry optimizations were carried out at 897-D/Def2-31G(d) (Al: cc-pVTZ, Te: cc-pV TZ-P) level of theory in all cases[a]–[a]. All stationary points were verified via frequency calculations. All analyses (WBI, NPA, NRT and orbital) occurred at the same level. In case of the reaction mechanism calculation, accurate single-point energy calculations at cc-pVTZ/Def2-31G(d) were performed[b]. Thermodynamic corrections were calculated at 353 K to model reaction conditions. Benzene solvent was considered via the polarizable continuum model, in the framework of the solution model based on density method[c]. All calculations were carried out with the GAUSSIAN 09 program package[d]. For geometries optimized structures of 2–5 see Supplementary Figs 17–20 (depiction) and Supplementary Tables 2–5 (cartesian geometry).

**Synthesis and isolation of ([L²⁵N]AlN{H(5)}Te₂)(2).** In a Glove Box Workstation, a 25 ml Schlenk flask equipped with a PTFE-coated magnetic stirrer bar was charged with [L²⁵N]AlN{H(5)}Te₂ (1, 898 mg, 1.04 mmol) and [863但是他 didn’t provide the proper context or the final text is incomplete. It looks like the document is a mix of different scientific papers, and it is not clear what the main topic is or what the complete text should be. Let's try to piece together the information we have:

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Elemental analysis calculated (%) for C$_2$H$_{10}$Al$_2$N$_{10}$Te$_2$: 1418.86; C 60.95, H 7.39, N 9.87; found: C 60.86, H 7.55, N 9.81; the analyte was provided wrapped in silver foil.

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