Lewis Superacidic Tellurenyl Cation-Induced Electrophilic Activation of an Inert Carborane


Abstract: The aryltellurenyl cation [2-(tBuNCH)C₆H₄Te]+, a Lewis superacid, and the weakly coordinating carborane anion [CB₁₁H₁₃]−, an extremely weak Brønsted acid (pKₐ = 131.0 in MeCN), form an isolable ion pair complex [2-(tBuNCH)C₆H₄Te][CB₁₁H₁₃], in which the Brønsted acidity (pKₐ = 7.4 in MeCN) of the formally hydridic B–H bonds is dramatically increased by more than 120 orders of magnitude. The electrophilic activation of B–H bonds in the carborane moiety gives rise to a proton transfer from boron to nitrogen at slightly elevated temperatures, as rationalized by the isolation of a mixture of the zwitterionic isomers 12- and 7-[2-(tBuNCH)C₆H₄Te(CB₁₁H₁₃)] in ratios ranging from 62:38 to 80:20.

Main-group elements mediating bond activation of small molecules and catalytic transformations have attracted considerable attention in recent years.[1] That holds particularly for the cooperative reactivity of Lewis acids and Lewis bases that are restricted to form energetically favourable donor–acceptor complexes. Amongst those, the most prominent are arguably the frustrated Lewis pairs (FLPs), in which bulky substituents prevent the formation of stable (and unreactive) donor-acceptor bonds. Besides FLPs, there is a growing number of regular, yet reactive Lewis pairs that are capable of activating small molecules.[2]

The aryltellurenyl cation, [2-(tBuNCH)C₆H₄Te]+ (I), containing an imino donor functionality can be regarded as an intramolecular regular N−Te Lewis pair, however, the intramolecularly coordinating 2-tert-butyl-iminomethylphenyl group compensates the electron deficiency at the tellurium atom only insufficiently (Figure 1).[3] Despite the N-donor coordination and the aromatic character of the five-membered C₆Te ring, I is a highly electrophilic Lewis superacid that gives rise to ion pairs even with weakly coordinating anions (WCAs).[f] These ion pairs [2-(tBuNCH)C₆H₄Te][X] (IX = [O₃SCF₃]−, [SbF₆]− and [AlOC-(CF₃)₃]−) show significant Te−O and Te−F interactions in the solid state, whereas in nonpolar solvents the electrolytic dissociation remains incomplete. In an effort to obtain an essentially isolated [2-(tBuNCH)C₆H₄Te]+ (I) cation, we turned our attention to an alternative WCA, namely, the closo-carborane anion [CB₁₁H₁₃]−, which is known as robust entity with a very low reactivity.[4] However, the salt metathesis reaction of 2-(tBuNCH)C₆H₄TeCl (II)[5] with Ag[CB₁₁H₁₃][6] provided again a contact ion pair [2-(tBuNCH)C₆H₄Te][CB₁₁H₁₃] (1), which was isolated as yellow crystals in 99% yield (Scheme 1, Figure 2).[7] In the solid state, the dative N−Te bond (2.088(2) Å) of 1 is shorter than that of (tBuNCH)C₆H₄Te[O₃SCF₃] (2.113(1) Å), but longer than those of (tBuNCH)C₆H₄Te[SbF₆] (2.076(2) Å) and [2-(tBuNCH)C₆H₄Te][AlOC-(CF₃)₃] (2.044(2) Å).

Figure 1. Resonance formula representations and electrostatic potential (ESP) of the Lewis superacid [2-(tBuNCH)C₆H₄Te]+ (I).
BuNCH)C₆H₄TeCl (II) and Ag[CB₁₁H₁₂] and further transformations.

As further reactivity studies showed, 1 is in fact only metastable and susceptible to further transformations at slightly elevated temperatures, both in CH₂Cl₂ and the solid state. Gentle heating of 1 in inert solvents produced a mixture of two isomeric dinuclear donor-acceptor complexes [(tBuNCH)C₆H₄Te·D][CB₁₁H₁₂] (2a, D = THF) and (2b, D = DMAP) in ratio 80 : 20, which were isolated as mixed orange crystals in 49 % yield (Scheme 1, Figure 2).

In the presence of the donor molecules THF and DMAP, the reaction of 2-(tBuNCH)C₆H₄TeCl (II) with Ag[CB₁₁H₁₂] directly afforded the mononuclear donor-acceptor complexes [(tBuNCH)C₆H₄Te·D][CB₁₁H₁₂]₃ (D = THF) and (4, D = DMAP) as yellowish crystals in 95 % and 83 % yield (Scheme 1, Figure 2).

It is worth noting that heating of the DMAP complex 4 in THF did not provide any hint of further transformation as the Lewis acidity is attenuated in comparison to 1. On the other hand, prolonged heating of the THF complex 3 in THF quantitatively provided mixtures of the isomers 5a and 5b (Scheme 1).

Scheme 1. Reaction of 2-(tBuNCH)C₆H₄TeCl (II) with Ag[CB₁₁H₁₂] and further transformations.
Thermodynamic measurements based on \(^1\)H NMR integration within transformation of 3 upon heating at various temperatures in [D₆]THF proved its first-order kinetics (Figures S28 and 29) with the following activation parameters: \(\Delta G^\ddagger = 118.4 \text{ kJ mol}^{-1}\); \(\Delta H^* = 114.9 \text{ kJ mol}^{-1}\); \(\Delta S^* = -11.8 \text{ J mol}^{-1} \text{ K}^{-1}\). The most straightforward way providing the quantitative yield of the zwitterionic species 5a and 5b (in a ratio of 62:38) was heating of complex 3 in the solid state at 140 °C for 2.5 h, which effectively removes the THF (details in the Supporting Information). The formation of 5a and 5b (donors D in case of 2a(2b)) may be rationalized by hydrogen transfer from the B–H functions in the B12 and B7 positions\(^{10}\) of the closo-carborane anion \([\text{CB}_6\text{H}_{11}]^-\) to the lone pair of the N atom in 1, upon which a Te–B12(B7) bond is formed. This hydrogen transfer is facilitated by the cooperative reactivity of the intramolecular regular N–Te Lewis pair. While the Lewis acidic Te site reverses the formal polarity of the B–H bond from hydridic to protic, the Lewis basic N-atom serves as a final proton acceptor within its gradual transfer from the Te atom to the N atom (for the DFT based mechanism, see below). Thus, the Lewis super acid \([\text{BuNCH})_2\text{Te}]^+\) (I) has activated the closo-carborane ion \([\text{CB}_6\text{H}_{11}]^-\), which serves as a proton donor. In fact, such a bond arrangement gives a unique insight into a long unresolved issue of electrophilic activation of closo-[\text{CB}_6\text{H}_{11}]^- (see below).\(^6\) This process is accompanied not only by a significant change in color from light-yellow (3) to dark red, but also by a dramatic change in the \(\delta(\text{Te})\) values\(^{11}\) reflecting the transition of the cationic Te\(^\dagger\) site to neutral in the zwitterionic 5a\(\text{Te}^{3}\) by the Te–B12(B7) bond formation. Consequently, the boron atom at the B12 position of the free \([\text{CB}_6\text{H}_{11}]^-\) anion of 3 resonating in \(^{11}\)B NMR at ~7.3 ppm is high-field shifted upon formation of Te–B12 bond in compound 5a to ~11.5 ppm. While the unsubstituted B12 atom in case of 5b containing Te–B7 bond resonates slightly more low-field at ~5.8 ppm, the signal of boron atom at the B7 position is shifted to high field from \(\delta(\text{Te}) = 13.7 \text{ ppm in 3 to } \delta(\text{Te}) = 17.3 \text{ ppm.}\) Interestingly, both Te–B12 and Te–B7 atoms in 5a and 5b are in \(^{11}\)B NMR significantly low-field shifted (\(\Delta\delta \sim 7 \text{ ppm} \) in comparison to analogously monoiodo substituted derivatives of closo-carbadodecaborate.\(^{10}\)) In the solid state 5a\(\text{Te}^{3}\) features a weak intramolecular hydrogen bond of the type N–H–Te (N–H: 0.860(2) Å, H–Te (2.568(1) Å, N–Te: 3.320(1) Å), in which Te serves as unprecedented hydrogen bond acceptor. This bonding situation is a result of the 5a\(\text{Te}^{3}\) formation mechanism (see below) enforcing the E configuration of the protonated imino \(\text{CH}≡\text{NH}^+\) moiety for both products, which is manifested by observation of typical \(J(\text{H}^+,\text{H})\) values (acquired in CDCl\(_3\)) of 17.3 and 17.4 Hz, respectively. Although the intramolecular hydrogen bond of the type N–H–Te was found in the solid state, the coupling constant \(J(\text{N}^+\text{H}^-) = 85.3 \text{ Hz for both 5a and 5b in the solution spectra lies in range for protonated imines.}^{17}\) Similarly, despite the fact that both 5a and 5b contain such bonding interaction, FTIR is showing no shift of the N–H bond \(\nu\) vibration in the solid state sample (5a: 3244 cm\(^{-1}\); 5b: 3295 cm\(^{-1}\)) in comparison to adducts 2a and 2b (3244 cm\(^{-1}\) and 3297 cm\(^{-1}\) having no N–H–Te interaction. Finally, deprotonation of 5a\(\text{Te}^{3}\) was achieved upon addition of triethylamine, which afforded a mixture of \([\text{Et}_3\text{NH}][12-(\text{tBuNCH})\text{C}_6\text{H}_3\text{Te}]\).
CB₁₁H₁₁ [6a] and [Et₃NH][12-(2-(tBuNCH))C₆H₆Te]CB₁₁H₁₁ [6b] in the same molar ratio as given by parent compounds 5a(5b), which was isolated as orange oil in quantitative yield (Scheme 1). The deprotonation was shown to have a significant effect on the shielding of the nitrogen atom, as the signal with value of δ(NO) = –172.1 ppm acquired in [D₆]THF for 5a(5b) is shifted to low field for 6a and 6b up to –35.4 and –32.8 ppm, respectively. Despite the assessable lone pair of the N atom in the 6a(6b) for coordination of Te atom, we can conclude that in this case no N–Te interaction is present, as δ(NO) for these compounds approaches the value of δ(NO) for the unsubstituted parent Schiff base, namely (tBuNCH)C₆H₆ (–24.3 ppm; [D₆] THF).

In an effort to shed light on the activation of the closo-carborane anion by the Lewis superacidic aryltellurenyl cation, two contact ion pairs, namely, 1 resembling the B12–H–Te connectivity found in the solid state, and the by 7.6 kJ mol⁻¹ less stable isomer 1’ featuring a B7–H–Te connectivity, were fully optimized in the gas phase (Figure 3a). The calculated B–Te distances of 1 (2.858 Å) and 1’ (2.867 Å) are significantly shorter than the experimentally observed distance of 1 (3.410(2) Å). As a result of the contact to adjacent Te atom, the B–H bond lengths of 1 (1.234) and 1’ (1.229) are substantially longer than those of the free closo-carborane anion (1.194 and 1.193 Å). The B–H stretching upon Te coordination is accompanied by a dramatic increase of the Brønsted acidity. As expected for a weakly coordinating anion, the calculated pKₐ value of the free closo-carborane (131.0) in MeCN is extremely high, rendering it an extremely weak acid. The pKₐ values of 1 (7.4) and 1’ (7.2) are dramatically smaller by more than 120 units. These pKₐ values compare well with that of HCl (7.9) in MeCN.[18] Thus, the Lewis superacidic aryltellurenyl cation, [2-(tBuNCH)C₆H₆Te]⁺ (I) induces an electrophilic activation of the 12- or 7-B–H bond in the closo-carborane ion[16] which seems to be instrumental for the bond activation and the proton transfer to the N atoms of 5a and 5b. The proton transfer from 1’ to 5a is associated with an energy gain of 193.3 kJ mol⁻¹ and most likely proceeds via a concerted wagging motion involving the transition state TS with double triangular arrangement of N, Te and B12–H, which accounts for an activation barrier of 118.1 kJ mol⁻¹ (Figure 3a). Such a value of activation barrier is in great agreement with the experimental one (ΔG°298 = 118.4 kJ mol⁻¹) as discussed above. The AIM bond topology of TS reveals a curved Te–H(B) bond path, indicating the onset of Te–B bond formation (Figure 3b).[19–21] With an electron density (ED, ρ(r)) of 0.59 e Å⁻³ and considerably negative total energy over ED ratio (H/ρ(r)) of –0.38 a.u., covalent bonding aspects of the Te–H contact in the TS are much higher than in 1 (ρ(r) = 0.34, H/ρ(r) = –0.21 a.u.) and 5a (ρ(r) = 0.23, H/ρ(r) = –0.14 a.u.). This is supported by the NCI, which shows a ring-shaped and red-colored NCI basin enclosing the Te–H and Te–B bonding axes, in contrast to the disc-shaped and blue-colored NCI basin in 1 and 5 (Figure 3d). In accordance with a H(Te)B arrangement, the ED within the corresponding ELI–D basin is

Figure 3. a) Calculated gas-phase structures, relative energies and pKₐ values of 1, 1’, TS, and 5a. b) The atoms-in-molecules (AIM) topology, c) iso-surface representation of the electron localizability indicator (ELI–D) and d) the noncovalent interaction (NCI) index of the TS.
distributed over the atoms as follows: H = 53%, Te = 26%, and B = 22%, compared to the bisynaptic contact mode in 1 (H = 16%, Te = 4%, B = 80%). In 5a, only the N (77%) and now prohit (23%) atoms contributions are relevant, supporting a coordinate Te–H bonding mode (Figure 3c).

In summary, the aryllometlen cation [2–(tBuNCH)CtHtHtH] (I), and the weakly coordinating closo-carborane anion [CbH2(H)2]– give rise to a metastable contact ion pair [2–(tBuNCH)CtHtHtH]2+ [2–(tBuNCH)CtHtHtH]– (1), in which the B–H bond in the 12- or 7-position of closo-[CbH2(H)2]– is activated by the proximity of a Lewis superacid cation, the Brønsted acidity of the Lewis superacidic cation, the Brønsted acidity of the contact ion pair. The proton transfer and the formation of 12-[2–(tBuNCH)CtHtHtH]2+ [2–(tBuNCH)CtHtHtH]– is activated by the proximity of a Lewis superacid cation, the Brønsted acidity of the Lewis superacidic cation, the Brønsted acidity of the contact ion pair. The proton transfer and the formation of 12-[2–(tBuNCH)CtHtHtH]2+ [2–(tBuNCH)CtHtHtH]– is activated by the proximity of a Lewis superacid cation, the Brønsted acidity of the Lewis superacidic cation, the Brønsted acidity of the contact ion pair. The proton transfer and the formation of 12-[2–(tBuNCH)CtHtHtH]2+ [2–(tBuNCH)CtHtHtH]– is activated by the proximity of a Lewis superacid cation, the Brønsted acidity of the Lewis superacidic cation, the Brønsted acidity of the contact ion pair.

Acknowledgements

The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support. The pKf values were calculated within the frames of Project 19-03-00755 supported by the Russian Foundation for Basic Research (RFBR). The authors L.D. and M.H. thank the Czech Science Foundation (grant no. 18-10222 S). A.L. thanks the University of Hradec Králové for a support. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: bond activation · boron · carboranes · Lewis superacids · tellurium