Lewis acidic telluronium cations: enhanced chalcogen-bond donor properties and application to transfer hydrogenation catalysis

Benyu Zhou and François P. Gabbaï*

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, United States of America

ABSTRACT: We describe the synthesis and structures of *o*-$C_6F_4(TeMes)_2$ (**1**) and *o*-$C_6F_4(TeAr^F)_2$ (**2**, Ar^F = 3,5-$(CF_3)_2C_6H_3$)). two new two bifunctional tellurides featuring an electron-withdrawing backbone. While **2** resisted methylation, **1** reacted with $Me_3O{\cdot}BF_4$ in CH_2Cl_2 to afford *o*-C_6F_4(TeMes)(TeMeMes) ([**3**]$^+$), a mixed valent telluride/telluronium cation isolated as a tetrafluoroborate salt. Although attempts to methylate the second telluride have been unsuccessful, [**3**]$^+$ readily catalyzes the hydrogenation of 2-phenyl-quinoline with Hantzsch ester. Comparison with simple telluronium cations including $[Ar^F{}_2TeMe]^+$ and $[MesAr^FTeMe]^+$ confirms that the catalytic activity of these compounds originates from the presence of a tetravalent, cationic tellurium center.

Over the past decades, the field of Lewis acid chemistry has witnessed the emergence of saturated acceptors that interact with Lewis basic partners through the formation of secondary interactions.[1] One of the most potent classes of such saturated acceptors is based on tellurium (Te) derivatives that interact with donors to form "chalcogen-bonded" complexes of type **A** (Chart 1).[1-2] The donor-acceptor interaction formed in these complexes displays greater stability than typical halogen bonds involving electron deficient iodides because of the greater Lewis acidity of Te derivatives. Moreover, the presence of two substituents in Te(II) derivatives provides access to a broader chemical space in which the strength of the donor-acceptor interactions, their compatibility with different environments, and the arrangement of the electron acceptors within supporting molecular scaffolds can be adjusted by simple synthetic variations.

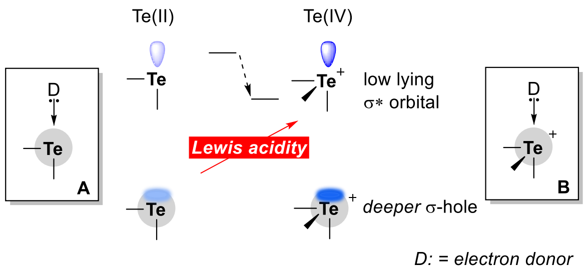


Chart 1. Schematic representation of "chalcogen-bonded" complexes of type **A** and **B** and origin of the increase in Lewis acidity upon oxidation of a telluride into a telluronium.

This atypical, chalcogen-centered, hypervalent bonding mode draws increasing attention, especially in the areas of anion sensing[3] and organocatalysis.[2g, 2h] To our knowledge, all applications considered by the community favor derivatives where the Te atom is in the divalent state. Based on the understanding that increasing the charge and valence of a saturated acceptor can enhance its Lewis acidity, we made the hypothesis that the D:→Te interactions could be strengthened by oxidation of the chalcogen atom into a tetravalent cation as in complexes of type **B** (Chart 1).[4] This hypothesis is based on the notion that the increased valence and charge of the chalcogen atom would: i) lower the energy of the accepting σ* orbitals; ii) result in a deeper σ-hole (Chart 1). While we have obtained validation for our approach in the realm of anion sequestration and transport,[4] we have not investigated the use of the cationic chalcogen bond donors as promoters of organic reactions. We were also intrigued by the possibility of accessing bifunctional systems, reasoning that the acceptor properties of such systems might be enhanced by cooperative as we have recently observed for bifunctional antimony Lewis acids.[5]

We first synthesized *o*-$C_6F_4(TeMes)_2$ (**1**) and *o*-$C_6F_4(TeAr^F)_2$ (**2**, Ar^F = 3,5-$(CF_3)_2C_6H_3$) by reaction of *o*-$Li_2C_6F_4$ with the corresponding ditelluride at -78°C (Figure 1). ^{19}F NMR spectroscopy confirmed the presence of a tetrafluoro-*o*-phenylene unit in both products as indicated by the detection of resonances at -106.8 and -153.0 ppm for **1** and -105.3 and -148.2 ppm for **2**. In the case of **2**, the Ar^F groups give rise to another ^{19}F NMR resonance corresponding to the CF_3 groups. These compounds are air-stable. Their solid-state structure confirms the presence of two Te atoms spaced by 3.736(1) Å in **1** (Figure 1) and 3.579(1) Å in **2** (see SI). Having confirmed the identity of these compounds, we investigated their methylation. While **2** failed to react with $Me_3O{\cdot}BF_4$ due to its electron deficiency and steric encumbrance, we found that a reaction occurred in the case of the more electron-rich derivative **1**, leading to the formation of the *o*-C_6F_4(TeMes)(TeMeMes) ([**3**]$^+$), a mixed valent telluride/telluronium cation (Figure 1). The structure of [**3**][BF_4] shows a shortening of the Te-Te distance from 3.736(1) Å in **1** to 3.515 (1) Å in [**3**]$^+$, indicative of Te(II)→Te(IV) bonding as confirmed by Natural Bond Orbital analysis (Figure 1). This interaction tames the nucleophilicity of the Te(II) center as indicated by the reluctance of [**3**]$^+$ to undergo further methylation. In the ^{1}H NMR spectrum, the methyl group appears as a doublet ($J_{H\text{-}F}$ = 3.5 Hz), displaying the expected ^{125}Te satellites spaced by $^2J_{Te\text{-}H}$ = 33.5 Hz.[4b] Consistent with the presence of a Te(II)→Te(IV) interactions, we note that the two ^{125}Te resonances of [**3**]$^+$ are flanked by satellites separated by $J_{Te\text{-}Te}$ = 527

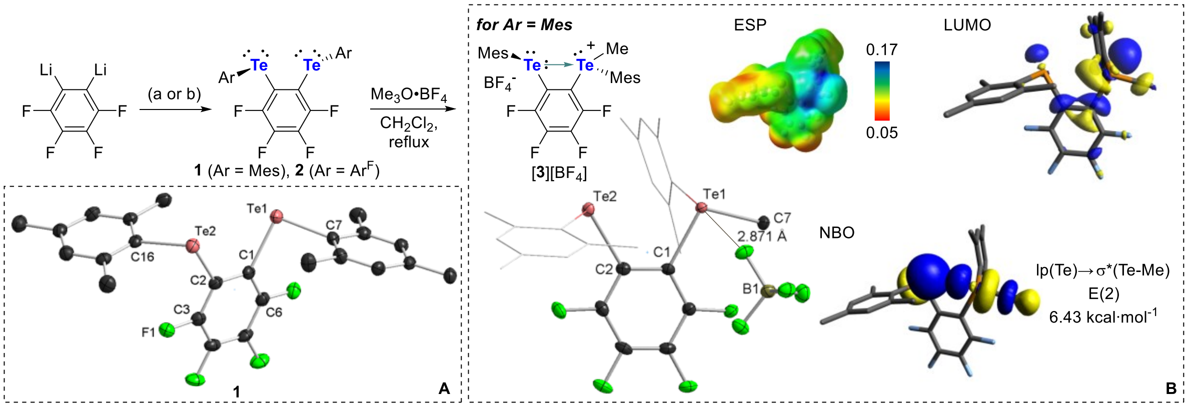
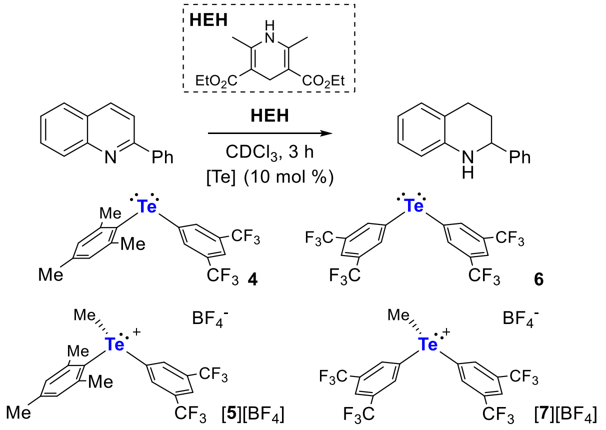


Figure 1. Synthesis of **1**, **2** and [**3**]BF$_4$] (a: Mes$_2$Te$_2$, THF, -78°C; b: (3,5-(CF$_3$)$_2$C$_6$H$_3$)$_2$Te$_2$, Et$_2$O, -78°C). Inset **A** shows the crystal structure of **1**. Inset **B** shows the crystal structure of [**3**]$^+$ as the BF$_4^-$ salt. The ESP map of [**3**]$^+$ (color scale is at a.u.), its LUMO contour plot (isovalue = 0.001) and the contour plot of the NBOs (isovalue = 0.05) involved in the Te(II)→Te(IV) are also included. When shown, the thermal ellipsoids in the crystal structures are set at the 50% probability level and the H atoms are omitted.

Hz. This value is smaller than that measured for [1-(PhTe)-8-PhMeTe)-naphthalene]$^+$ (1093 Hz) and [1-(PhTe)-8-PhMeTe)-acenaphthalene]$^+$ (946 Hz) whose backbones support shorter Te-Te interactions than in [**3**]$^+$.[6] In the structure, the BF$_4^-$ counter anion forms a secondary interaction or chalcogen bond with the telluronium ion, confirming the increased Lewis acidity of the Te(IV) center. DFT calculations followed by a visualization of the electrostatic potential (ESP) map show that oxidation leads to an accentuated σ-hole on the Te(IV) center (Figure 1). This σ-hole expectedly coincides with the LUMO of the compound which has Te-C σ* parentage.

Returning to one of the primary intents of this study, we tested the activity of the above-mentioned derivatives for the reduction of quinolines using Hantzsch ester (Scheme 1). This simple reaction is often used to benchmark the catalytic activity of saturated acceptors based on group 15 and 16 elements.[7, 5b, 8] We first tested the neutral bifunctional tellurides **1** and **2** (Table 1 - entries 1 and 2). We only observed conversion in the case of **2**, in line with its more electron-deficient structure and lower steric crowding around the Te atoms. However, the reaction proved to be slow, only reaching 8% after 3 hours when the reaction was carried out in CDCl$_3$ with a catalyst loading of 10 mol%. By contrast, we found that [**3**][BF$_4$] smoothly promoted this reaction suggesting that its enhanced chalcogen bond donor properties or synonymously its higher Lewis acidity boosts its catalytic activity in this reaction. To more firmly correlate the enhancement in catalytic activity to the oxidation of the Te center, we endeavoured to compare the activity [**3**][BF$_4$] to that of less structurally complex telluride and telluronium cations. We selected **4** and [**5**][BF$_4$] as well as **6** and [**7**][BF$_4$] which were prepared using protocols that we recently described for electron-deficient tellurides and telluronium cations.[4b] These four new derivatives, which have been characterized using conventional means (see SI), are air-stable and can be stored on the benchtop for extended periods of time. Our survey of these four additional compounds shows that the telluronium cations [**5**][BF$_4$] and [**7**][BF$_4$] are active catalysts (entries 5 and 7) while **4** and **6** induced hardly any conversion within the 3 h time frame chosen in this study (entries 4 and 6). The higher activity of [**5**][BF$_4$] and [**7**][BF$_4$] fortifies the notion that the oxidative methylation of the Te center is responsible for the higher catalytic activity of these salts. It has been recently proposed that Lewis acid catalysts may acidify Hantzsch ester thus promoting protonation of the quinoline in the rate-determining step of the reaction.[9] Another mechanistic suggestion involves activation of the quinoline electrophile by coordination of the nitrogen to the Lewis acid.[8] Since both pathways would benefit from a more potent Lewis acid, we propose that the lower σ* orbitals and deeper σ-holes of the telluronium cations are at the origin of the rate acceleration observed with the oxidized derivatives.

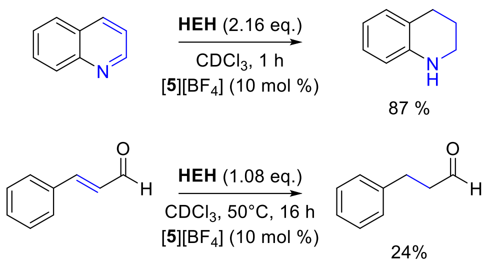


Scheme 1. Transfer hydrogenation of 2-phenyl-quinoline and structures of additional Te-based catalysts.

Table 1. Compilation of the results obtained for the transfer hydrogenation of 2-phenyl-quinoline using Hantzsch ester.

Entry	Catalyst ([Te])	Time	Conv.
1	**1**	3 h	< 1%
2	**2**	3 h	8%
3	[**3**][BF$_4$]	3 h	96%
4	**4**	3 h	< 1%
5	[**5**][BF$_4$]	3 h	95%
6	**6**	3 h	6%
7	[**7**][BF$_4$]	3 h	91%

To conclude this study we decided to survey additional substrates using [**5**][BF$_4$] as a catalyst. When used in CDCl$_3$ with a loading of 10 mol%, we found that quinoline was readily hydrogenated, reaching a conversion of 87% within 1 h (Scheme 2). The C=C bond of *trans*-cinnamaldehyde proved harder to reduce as indicated by the limited conversion of 24% observed after 16 h at an elevated temperature (Scheme 2). These additional reactions, which did not proceed in the absence of the catalyst, show that telluronium-based catalysts may be effective in meditating the transfer hydrogenation of a larger range of substrates.



Scheme 2. Transfer hydrogenation of quinoline and *trans*-cinnamaldehyde using [**5**][BF_4] as the catalyst.

While we have previously demonstrated that telluronium cations display enhanced anion binding and anion transport properties compared to their neutral divalent precursors, this communication shows that the same electronic effects, as summarized in Chart 1, elicit greater catalytic activity in the transfer hydrogenation of 2-phenyl-quinoline using Hantzsch ester. Our results also document the synthetic difficulties associated with the synthesis of dicationic bis(telluronium) derivatives displaying short Te-Te separations and electron-withdrawing ligands.[6b, 10]

ASSOCIATED CONTENT

Supporting Information

Additional experimental and computational details. Crystallographic data in cif format. Optimized structures in xyz format. These materials are available free of charge via the Internet at http://pubs.acs.org.

Accession Codes

CCDC 2081831-2081833 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

François P. Gabbaï – Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States. **orcid**.org/0000-0003-4788-2998. Email: francois@tamu.edu

Authors

Benyu Zhou – Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States.

Author Contributions

BZ carried out all experiments and drafted the manuscript. BZ and F.P.G conceived the study.

Notes

The authors declare no competing financial interest.

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