Anion chelation via double chalcogen bonding: The case of a bis-telluronium dication and its application in electrophilic catalysis via metal-chloride bond activation

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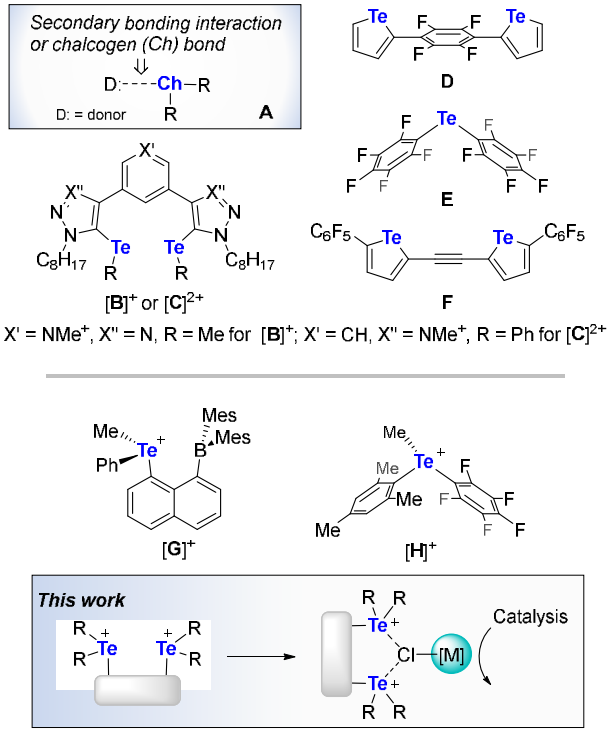
ABSTRACT: Telluronium cations have long been known to engage their counter anions via secondary interactions. Yet, this property has rarely been exploited for anion binding. Motivated by such applications, we have now synthesized a bis-telluronium dication ([**3**]$^{2+}$) that was obtained as a tetrafluoroborate salt by reaction of 2,7-di-*tert*-butyl-9,9-dimethylxanthene-4,5-diboronic acid with phenoxatellurine difluoride and $BF_3{\cdot}OEt_2$. As confirmed by the formation of Te-(μ-BF_4)-Te bridges in the structure of [**3**][BF_4]$_2$, [**3**]$^{2+}$ functions as a bidentate Lewis acid toward anions. [**3**][BF_4]$_2$ has also been converted into the more exposed [**3**][$BArF_{24}$]$_2$ ([$BArF_{24}$]$^-$ = [B(3,5-(CF_3)$_2$$C_6H_3$)$_4$]$^-$). The latter, which readily ionizes Ph_3CCl, displays a chloride anion binding constant that exceeds that of a monofunctional model compound by almost four orders of magnitude. The unique properties of this new bis-telluronium dication are further highlighted by its ability to activate Ph_3PAuCl and *cis*-(Ph_3P)$_2$$PtCl_2$ in $CHCl_3$, leading to catalytic systems highly active in the cycloisomerization of propargylamide or enyne substrates.

The ability of divalent group 16 compounds (**A**, Chart 1) to engage in secondary bonding interactions[1] with electron-rich species has been exploited extensively in the area of supramolecular chemistry and catalysis.[2] The stability of these secondary bonding interactions, often described as chalcogen bonds (ChB), tracks with the Lewis acidity of the chalcogen atom and augments as the group is descended, reaching a maximum at tellurium.[1c, 2c, 3] These unique electron-acceptor properties have gained increasing recognition as illustrated by a series of recent reports on the use of tellurium(II) derivatives for the complexation and transport of anions[4] and for the activation of organic substrates.[3] These studies have shown that the chalcogen bond formed by these tellurium(II) derivatives can be particularly strong, especially in the presence of electron-withdrawing substituents as in the case of [**B**]$^+$,[4h] [**C**]$^{2+}$,[3a] **D**,[4g] **E**,[4d, 4f, 4i] and **F** (Chart 1).[4i] The neutral or charged electron-withdrawing substituents present in these derivatives enhance the development of electropositive regions (called σ holes) on the chalcogen atom, opposite from, but not always strictly alligned with, the R-Te bonds.[5] These effects are concomitant with an increase of the chalcogen parentage of the Te-R σ* orbital thus elevating the dative character of the secondary interaction.[6]

Aiming to increase further the stability of the secondary bonding interactions formed by tellurium acceptors, we proposed a strategy that rests on tetravalent tellurium derivatives.[7] We were swayed in this research direction by the pioneering work of Gutmann, who showed that $TeCl_4$ stands on the upper echelons of his chloride anion affinity scale.[8] Another impetus came from the knowledge that telluronium cations readily associate with their counteranions.[7] With these precedents as a backdrop, we

Chart 1. Top: The chalcogen bonding concept and examples of Te(II) ChB donors. Bottom: Examples of cationic Te(IV) ChB donors and objective of this work.



introduced molecules such as [**G**]$^+$ and [**H**]$^+$ (Chart 1) for application in anion sequestration and transport, respectively.[9] When compared to their divalent counterparts, these telluronium cations display deeper σ holes and stabilized σ* orbitals, leading to an increase in their Lewis acidity or chalcogen bonding abilities.[9b] Similar effects are also responsible for the advantageous properties displayed by iodonium[10] or stibonium[11] cations which exhibit greater halogen- or pnictogen-bond donor properties, respectively, than their neutral counterparts. Encouraged by these early results and realizing that additional benefits could derive from the juxtaposition of two telluronium cations in a bifunctional motif, we have now decided to investigate the synthesis of bis-telluronium dications as bidentate Lewis acids (Chart 1).[12] This contribution describes an original incarnation of this idea along with a demonstration that such bidentate ChB donors can be used for activation of C-Cl and M-Cl bonds (M = Au, Pt), with application in electrophilic organometallic catalysis.

To reduce the steric profile and increase the stability of the telluronium units, we decided to consider the cyclized phenoxatellurine (**1**) as an elementary building block.[13] This compound was first converted into **1**-F_2 by reaction with *N*-fluorobenzenesulfonimide (NFSI) and CsF and allowed to react with $PhB(OH)_2$ and $BF_3{\cdot}OEt_2$ to afford [**2**][BF_4] in 85% yield (Figure 1).[14] Under analogous conditions, 2,7-di-*tert*-butyl-9,9-dimethylxanthene-4,5-diboronic acid was easily converted into [**3**][BF_4]$_2$, a large-bite bidentate Lewis acid,[15] which was isolated in 70% yield. The ^{1}H NMR spectra of [**2**][BF_4] and [**3**][BF_4]$_2$ show distinct resonances in CD_3CN in the 7.45-8.08 ppm range, which can be assigned to the phenoxatellurinium units. Realizing that the coordination of the tetrafluoroborate anions (*vide infra*) may limit the Lewis acidity of these telluronium cations, we also generated [**2**][$BArF_{24}$] and [**3**][$BArF_{24}$]$_2$ ([$BArF_{24}$]$^-$ = [B(3,5-$(CF_3)_2C_6H_3)_4$]$^-$) by salt metathesis.

Single crystals of [**2**][BF_4] and [**3**][BF_4]$_2$ could be readily obtained, allowing for the determination of their solid-state structures (Figure 1). In all cases, the phenoxatellurinium unit adopts a slightly folded geometry as indicated by the dihedral angle α (α = 37.9° for [**2**][BF_4], α =12.7° and 31.6° for [**3**][BF4]$_2$) formed by the two o-phenylene units. The tellurium atoms adopt a trigonal pyramidal geometry as indicated by the C-Te-C angles which fall within the 90.8(1)°-95.2(1)° and 89.7(6)°-98.1(3)° range for [**2**][BF_4] and [**3**][BF_4]$_2$, respectively. In both salts, the [BF_4]$^-$ counter anions form short Te-F contacts with the tellurium atom, indicating the presence of secondary or chalcogen bonding interactions (Figure 1).[9b] In [**3**][BF_4]$_2$, the tetrafluoroborate anions link the two telluronium centers through the formation of a unique Te-(μ-BF_4-κ^1(F),κ^1(F′))-Te' bridging motifs, illustrating the bidentate character of [**3**]$^{2+}$. Additionally, we noted that each tellurium atom interacts with two tetrafluoroborate anions along approximately perpendicular directions. Such a feature indicates that the Lewis acidic tellurium centers of this structure act as biaxial ChB donors, thus mimicking the properties of iodonium cations as biaxial halogen bond donors.[10a]

Both [**2**]$^+$ and [**3**]$^{2+}$ have been computationally investigated. As illustrated in Figure 2, these calculations show that the LUMO and LUMO+1 of [**2**]$^+$ have σ*(Te-C) character in agreement with the multidirectional ChB donor properties of the telluronium center, as previously noted in the case of [$(C_6F_5)_2$TeMe]$^+$.[9b] The same situation is seen in the case of [**3**]$^{2+}$ for which the LUMO, LUMO+1, LUMO+2, and LUMO+3 also have σ*(C-Te) character. We will note that these orbitals are closely spaced energetically

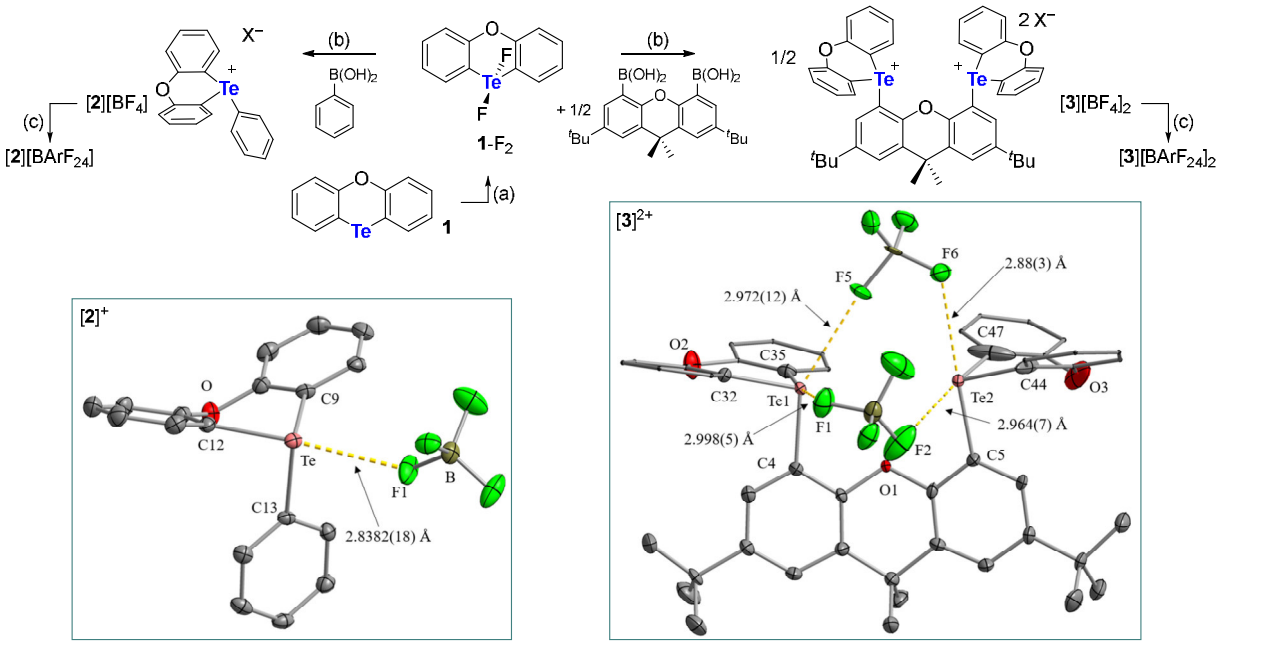


Figure 1. Synthesis and structures of the telluronium salts. Synthetic details: (a): 1 equiv. of NFSI and 2 equiv. of CsF in CH_2Cl_2, 0°C to r.t.; (b): 1) 1 equiv. of $BF_3{\cdot}OEt_2$ per Te atom in CH_2Cl_2, 0°C to r.t. 2) excess of $NaBF_4$ in CH_2Cl_2/H_2O; (c): 1 equiv. of Na[$BArF_{24}$] per Te atom in CH_2Cl_2, r.t. The structures are shown with thermal ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

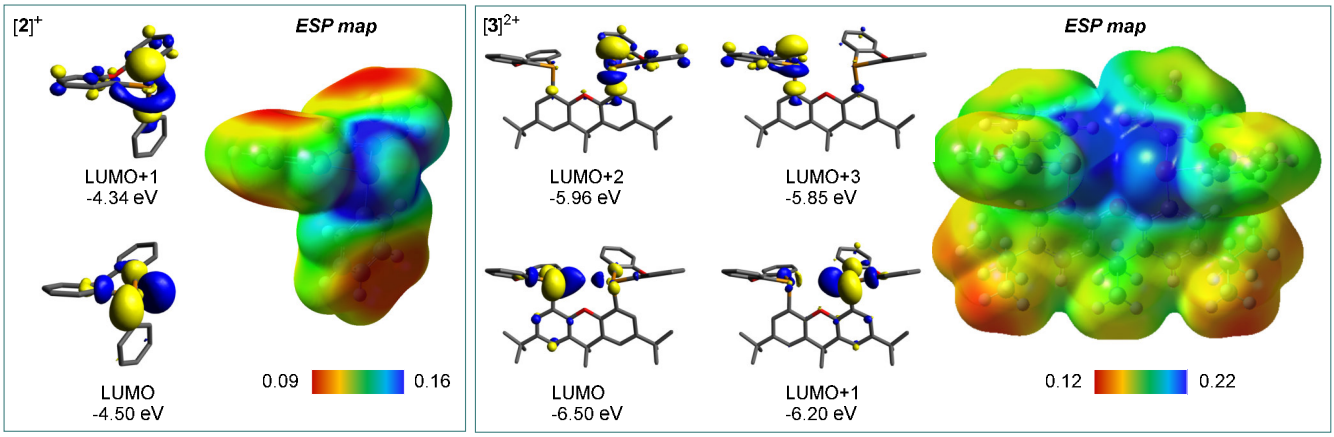


Figure 2. Contour and energies of the LUMOs of [**2**]$^{+}$ and [**3**]$^{2+}$ (isosurface value: 0.05 a.u.). The ESP map of each cations are also shown (isosurface value = 0.001 a.u.).

, indicating that all sites will display similar Lewis acidity. Consistent findings emerge from an inspection of the electrostatic potential maps of these derivatives which show the expected σ holes, at positions coinciding with the σ*(Te-C) orbitals (Figure 2). In the case of [**3**]$^{2+}$, the convergence of the telluronium units creates an area of elevated positive potential spanning the two tellurium atoms and defining the bidentate Lewis acidic pocket.

Building on these initial results, we became eager to quantify the Lewis acidity of these compounds towards an anionic substrate such as the chloride anion. To this end, we tested the ability of [**2**][$BArF_{24}$] and [**3**][$BArF_{24}$]$_2$ to ionize Ph_3CCl (Figure 3).[16] UV-vis monitoring afforded the equilibrium constant K_{rel} = 14.5 for [**3**][$BArF_{24}$]$_2$ and $1.58\times10^{-3}$for [**2**][$BArF_{24}$]. The four-order-of-magnitude difference observed in the binding constants of these derivatives shows that [**3**]$^{2+}$ is significantly more Lewis acidic than [**2**]$^{+}$. We assign this higher affinity to the

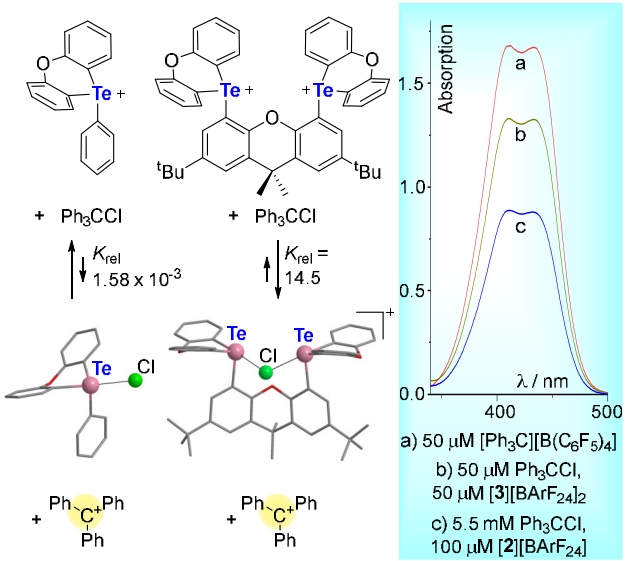


Figure 3. Left: Equilibrium established upon combining the telluronium cations with Ph_3CCl. Right: UV-Vis spectra of the corresponding mixtures along with that of [Ph_3C][$B(C_6F_5)_4$] which was used as a standard.

dicationic nature of [**3**]$^{2+}$ as well as its ability to form a chloride chelate as suggested by the optimized geometry of [**3**-μ_2-Cl]$^{+}$ (Figure 3). Such a multidentate binding mode is reminiscent of that displayed by other high-affinity polytopic chloride anion receptors.[17] The high Lewis acidity of [**3**]$^{2+}$ also comes to light using Ph_3PO as a probe.[18] Indeed, ^{31}P NMR measurements in CH_2Cl_2 show a larger deshielding of the phosphorus resonance upon addition of [**3**][$BArF_{24}$]$_2$ to Ph_3PO ($\Delta\delta$ = 7.9 ppm for a 6 mM 1:1 mixture) than with [**2**][$BArF_{24}$] ($\Delta\delta$ = 6.1 ppm for a 6 mM of 1:1 mixture).

To highlight the unique properties of the telluronium cations described herein, we investigated their use as activators in transition metal-based catalysis. While pnictogen and halogen bond donors have been used in this context,[19] related efforts with ChB donors have not been previously visited. We first tested the ability of [**2**][$BArF_{24}$] and [**3**][$BArF_{24}$]$_2$ to activate Ph_3PAuCl using the cycloisomerization of 4-fluoro-N-(propyl-2-yn-1-yl)benzamide (**4**) into **5** as a test reaction (Scheme 1, Table 1 entry 1 and 2).[20] A notably higher activity was observed with [**3**][$BArF_{24}$]$_2$, providing initial evidence for the superiority of the bifunctional motif. Encouraged by this result, we attempted the more challenging generation of electrophilic platinum catalysts,[19c, 21] by activation of Pt(II)-Cl bonds. With this in mind, we chose *cis*-$(Ph_3P)_2PtCl_2$ as

Scheme 1. Cycloisomerization reaction of propargyl amide 4 and of 1,6-enyne 6 using Ph_3AuCl and *cis*-$(Ph_3P)_2PtCl_2$ as precatalysts.

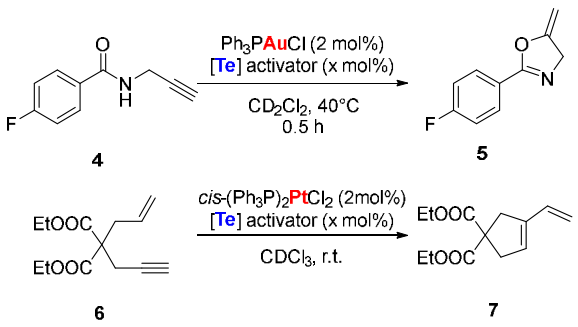


Table 1. Catalytic profile for the cyclization reaction of 4 and 6.

Entry	Precat.[a] / loading (mol%)	Activator / loading (mol%)	Sub. [b]	Time (min)	Conv. [c] (%)
1	[Au] / 2	[**2**][$BArF_{24}$] / 4	4	30	36
2	[Au] / 2	[**3**][$BArF_{24}$]$_2$ / 2	4	30	95
3	[Pt] / 2	[**3**][$BArF_{24}$]$_2$ / 2	6	10	12
4	[Pt] / 2	[**3**][$BArF_{24}$]$_2$ / 4	6	10	96
5	[Pt] / 2	[**2**][$BArF_{24}$] / 8	6	10	6
6	[Pt] / 2	Na[$BArF_{24}$] / 2	6	10	3
7	[Pt] / 2	Na[$BArF_{24}$] / 4	6	10	18
8	[Pt] / 2	-	6	60	<1
9	-	[**3**][$BArF_{24}$]$_2$ / 4	6	60	<1

[a]Precat. = precatalyst: [Au] = Ph_3AuCl, [Pt] = *cis*-$(Ph_3P)_2PtCl_2$; [b]Sub. = substrate. [c]Conv. = conversion measured by ^1H NMR spectroscopy.

a precatalyst and the cycloisomerization of enyne **6** into **7**, as a benchmark reaction (Scheme 1, Table 1). The reaction was first attempted with a 2 mol% loading of *cis*-$(Ph_3P)_2PtCl_2$ and [**3**][$BArF_{24}$] in dry $CDCl_3$. Under these conditions, the reaction proceeded slowly, only reaching 12% conversion after 1 h (entry 3). The activity significantly improved when the loading of [**3**][$BArF_{24}$]$_2$ was increased to 4 mol%. Indeed, under this condition, the reaction was essentially complete (> 95% conversion) after only 10 min (entry 4). Prior studies have shown that platinum dichloride precatalysts necessitate two equivalents of chloride abstractors for proper activation,[21b] supporting the notion that each equivalent of [**3**]$^{2+}$ abstracts a single chloride anion. The unique properties of [**3**][$BArF_{24}$]$_2$ as an activator are further highlighted by a comparison with its monofunctional analog since activation of *cis*-$(Ph_3P)_2PtCl_2$ (2 mol %) with [**2**][$BArF_{24}$] (8 mol %) led to only 6% conversion after 10 min and only 11% after 1 h (entry 5). The distinctly superior ability of [**3**][$BArF_{24}$]$_2$ to activate the platinum catalyst is again ascribed to its dicationic nature and its chloride chelating ability. The use of Na[$BArF_{24}$]as an activator only led to low conversions even when used in a two-fold excess with respect to the precatalyst concentration (entries 6 and 7). Finally, the platinum precatalyst or [**3**][$BArF_{24}$]$_2$ alone were inactive (entries 8 and 9). The lack of activity observed with [**3**][$BArF_{24}$]$_2$ alone indicates that catalysis occurs at the platinum center.

In summary, we show that the enforced juxtaposition of the telluronium moieties in [**3**]$^{2+}$ leads to favorable cooperative effects illustrated by the chelation of two tetrafluoroborate anions in [**3**][BF_4]$_2$ and by the elevated chloride anion affinity of [**3**]$^{2+}$. At the same time, the lipophilicity of the backbone enhances the solubility of this doubly charged species. These properties have significant consequences in the realm of C-Cl and M-Cl (M = metal) bond activations. The latter is illustrated by the use of [**3**]$^{2+}$ as a catalyst activator. These results open a new chapter in the application of ChB in anion complexation and catalysis; they also showcase the potential that telluronium cations hold as Lewis acidic sites in polydentate chalcogen-bond donor constructs.

ASSOCIATED CONTENT

Supporting Information

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

Accession Codes

CCDC 2081070-2081071 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.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. (a) Alcock, N. W., Secondary Bonding to Nonmetallic Elements. In *Advances in Inorganic Chemistry and Radiochemistry*, Emeléus, H. J.; Sharpe, A. G., Eds. Academic Press: 1972; Vol. 15, pp 1-58; (b) Vargas-Baca, I.; Chivers, T., Weakly bonding interactions in organochalcogen chemistry. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000,** *164*, 207-227; (c) Cozzolino, A. F.; Elder, P. J. W.; Vargas-Baca, I., A survey of tellurium-centered secondary-bonding supramolecular synthons. *Coord. Chem. Rev.* **2011,** *255*, 1426-1438; (d) Scilabra, P.; Terraneo, G.; Resnati, G., The chalcogen bond in crystalline solids: A world parallel to halogen bond. *Acc. Chem. Res.* **2019,** *52*, 1313-1324; (e) Fourmigué, M.; Dhaka, A., Chalcogen bonding in crystalline diselenides and selenocyanates: From molecules of pharmaceutical interest to conducting materials. *Coord. Chem. Rev.* **2020,** *403*, 213084; (f) Sudha, N.; Singh, H. B., Intramolecular coordination in tellurium chemistry. *Coord. Chem. Rev.* **1994,** *135*, 469-515.

2. (a) Breugst, M.; von der Heiden, D.; Schmauck, J., Novel noncovalent interactions in catalysis: A focus on halogen, chalcogen, and anion-π bonding. *Synthesis* **2017,** *49*, 3224-3236; (b) Mahmudov, K. T.; Kopylovich, M. N.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L., Chalcogen bonding in synthesis, catalysis and design of materials. *Dalton Trans.* **2017,** *46*, 10121-10138; (c) Gleiter, R.; Haberhauer, G.; Werz, D. B.; Rominger, F.; Bleiholder, C., From noncovalent chalcogen–chalcogen interactions to supramolecular aggregates: Experiments and calculations. *Chem.*

Rev. **2018,** *118*, 2010-2041; (d) Selvakumar, K.; Singh, H. B., Adaptive responses of sterically confined intramolecular chalcogen bonds. *Chem. Sci.* **2018,** *9*, 7027-7042; (e) Lim, J. Y. C.; Beer, P. D., Sigma-hole interactions in anion recognition. *Chem* **2018,** *4*, 731-783; (f) Bamberger, J.; Ostler, F.; Mancheño, O. G., Frontiers in halogen and chalcogen-bond donor organocatalysis. *ChemCatChem* **2019,** *11*, 5198-5211; (g) Vogel, L.; Wonner, P.; Huber, S. M., Chalcogen bonding: an overview. *Angew. Chem. Int. Ed.* **2019,** *58*, 1880-1891; (h) Strakova, K.; Assies, L.; Goujon, A.; Piazzolla, F.; Humeniuk, H. V.; Matile, S., Dithienothiophenes at work: Access to mechanosensitive fluorescent probes, chalcogen-bonding catalysis, and beyond. *Chem. Rev.* **2019,** *119*, 10977-11005; (i) Biot, N.; Bonifazi, D., Chalcogen-bond driven molecular recognition at work. *Coord. Chem. Rev.* **2020,** *413*, 213243; (j) Ho, P. C.; Wang, J. Z.; Meloni, F.; Vargas-Baca, I., Chalcogen bonding in materials chemistry. *Coord. Chem. Rev.* **2020,** *422*, 213464.

3. (a) Wonner, P.; Dreger, A.; Vogel, L.; Engelage, E.; Huber, S. M., Chalcogen bonding catalysis of a nitro-michael reaction. *Angew. Chem. Int. Ed.* **2019,** *58*, 16923-16927; (b) Wonner, P.; Steinke, T.; Vogel, L.; Huber, S. M., Carbonyl activation by selenium- and tellurium-cased chalcogen bonding in a michael addition reaction. *Chem. Eur. J.* **2020,** *26*, 1258-1262.

4. (a) Garrett, G. E.; Gibson, G. L.; Straus, R. N.; Seferos, D. S.; Taylor, M. S., Chalcogen bonding in solution: interactions of benzotelluradiazoles with anionic and uncharged lewis bases. *J. Am. Chem. Soc.* **2015,** *137*, 4126-4133; (b) Lim, J. Y. C.; Marques, I.; Thompson, A. L.; Christensen, K. E.; Félix, V.; Beer, P. D., Chalcogen Bonding Macrocycles and [2]Rotaxanes for Anion Recognition. *J. Am. Chem. Soc.* **2017,** *139*, 3122-3133; (c) Borissov, A.; Marques, I.; Lim, J. Y. C.; Félix, V.; Smith, M. D.; Beer, P. D., Anion recognition in water by charge-neutral halogen and chalcogen bonding foldamer receptors. *J. Am. Chem. Soc.* **2019,** *141*, 4119-4129; (d) Lee, L. M.; Tsemperouli, M.; Poblador-Bahamonde, A. I.; Benz, S.; Sakai, N.; Sugihara, K.; Matile, S., Anion transport with pnictogen bonds in direct comparison with chalcogen and halogen bonds. *J. Am. Chem. Soc.* **2019,** *141*, 810-814; (e) Steinke, T.; Wonner, P.; Engelage, E.; Huber, S. M., Catalytic Activation of a Carbon–Chloride Bond by Dicationic Tellurium-Based Chalcogen Bond Donors. *Synthesis* **2021**, doi:10.1055/a-1372-6309; (f) Benz, S.; Poblador-Bahamonde, A. I.; Low-Ders, N.; Matile, S., Catalysis with pnictogen, chalcogen, and halogen bonds. *Angew. Chem. Int. Ed.* **2018,** *57*, 5408-5412; (g) Navarro-García, E.; Galmés, B.; Velasco, M. D.; Frontera, A.; Caballero, A., Anion Recognition by Neutral Chalcogen Bonding Receptors: Experimental and Theoretical Investigations. *Chem. Eur. J.* **2020,** *26*, 4706-4713; (h) Lim, J. Y. C.; Liew, J. Y.; Beer, P. D., Thermodynamics of Anion Binding by Chalcogen Bonding Receptors. *Chem. Eur. J.* **2018,** *24*, 14560-14566; (i) Garrett, G. E.; Carrera, E. I.; Seferos, D. S.; Taylor, M. S., Anion recognition by a bidentate chalcogen bond donor. *Chem. Commun.* **2016,** *52*, 9881-9884.

5. Politzer, P.; Murray, J. S., σ-Hole Interactions: Perspectives and Misconceptions. *Crystals* **2017,** *7*, 212.

6. Glodde, T.; Vishnevskiy, Y. V.; Zimmermann, L.; Stammler, H.-G.; Neumann, B.; Mitzel, N. W., The nature of chalcogen-bonding-type tellurium–nitrogen interactions: A first experimental structure from the gas phase. *Angew. Chem. Int. Ed.* **2021,** *60*, 1519-1523.

7. (a) Collins, M. J.; Ripmeester, J. A.; Sawyer, J. F., CP/MAS tellurium-125 NMR in solids: an example of 125Te-35,37Cl J coupling. *J. Am. Chem. Soc.* **1987,** *109*, 4113-4115; (b) Klapötke, T. M.; Krumm, B.; Mayer, P.; Polborn, K.; Ruscitti, O. P., The reactivity of perfluoroaryltellurium(IV) dihalides towards cyanide, crystal structures of $(C_6F_5)_3TeCl$ and $C_6F_5TeTeC_6F_5$. *J. Fluorine Chem.* **2001,** *112*, 207-212.

8. Baaz, M.; Gutmann, V.; Kunze, O., Die Chloridionenaffinitäten von Akzeptorchloriden in Acetonitril, 1. Mitt.: Lösungszustand und Bildungsgleichgewichte der Triphenylchlormethankomplexe. *Monatsh. Chem.* **1962,** *93*, 1142-1161.

9. (a) Zhao, H. Y.; Gabbaï, F. P., A bidentate Lewis acid with a telluronium ion as an anion-binding site. *Nat. Chem.* **2010,** *2*, 984-990; (b) Zhou, B.; Gabbaï, F. P., Redox-controlled chalcogen-bonding at tellurium: impact on Lewis acidity and chloride anion transport properties. *Chem. Sci.* **2020,** *11*, 7495-7500.

10. (a) Heinen, F.; Engelage, E.; Cramer, C. J.; Huber, S. M., Hypervalent Iodine(III) Compounds as Biaxial Halogen Bond Donors. *J. Am. Chem. Soc.* **2020,** *142*, 8633-8640; (b) Mayer, R. J.; Ofial, A. R.; Mayr, H.; Legault, C. Y., Lewis Acidity Scale of Diaryliodonium Ions toward Oxygen, Nitrogen, and Halogen Lewis Bases. *J. Am. Chem. Soc.* **2020,** *142*, 5221-5233; (c) Seidl, T. L.; Stuart, D. R., An Admix Approach To Determine Counter Anion Effects on Metal-Free Arylation Reactions with Diaryliodonium Salts. *J. Org. Chem.* **2017,** *82*, 11765-11771.

11. (a) Park, G.; Brock, D. J.; Pellois, J.-P.; Gabbaï, F. P., Heavy Pnictogenium Cations as Transmembrane Anion Transporters in Vesicles and Erythrocytes. *Chem* **2019,** *5*, 2215-2227; (b) Ke, I.-S.; Myahkostupov, M.; Castellano, F. N.; Gabbaï, F. P., Stibonium Ions for the Fluorescence Turn-On Sensing of F^- in Drinking Water at Parts per Million Concentrations. *J. Am. Chem. Soc.* **2012,** *134*, 15309-15311; (c) Hirai, M.; Myahkostupov, M.; Castellano, F. N.; Gabbaï, F. P., 1-Pyrenyl- and 3-Perylenyl-antimony(V) Derivatives for the Fluorescence Turn-On Sensing of Fluoride Ions in Water at Sub-ppm Concentrations. *Organometallics* **2016,** *35*, 1854-1860; (d) Robertson, A. P. M.; Burford, N.; McDonald, R.; Ferguson, M. J., Coordination Complexes of Ph_3Sb^{2+} and Ph_3Bi^{2+}: Beyond Pnictonium Cations. *Angew. Chem. Int. Ed.* **2014,** *53*, 3480-3483.

12. (a) Hudnall, T. W.; Chiu, C.-W.; Gabbaï, F. P., Fluoride ion recognition by chelating and cationic boranes. *Acc. Chem. Res.* **2009,** *42*, 388-397; (b) Galbraith, E.; James, T. D., Boron based anion receptors as sensors. *Chem. Soc. Rev.* **2010,** *39*, 3831-3842; (c) Wade, C. R.; Broomsgrove, A. E. J.; Aldridge, S.; Gabbaï, F. P., Fluoride Ion Complexation and Sensing Using Organoboron Compounds. *Chemical Reviews* **2010,** *110*, 3958-3984; (d) Bowman-James, K.; Bianchi, A.; Garcia-Espana, E.; Editors, *Anion Coordination Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA: 2012; p 559 pp; (e) Zhao, H.; Leamer, L. A.; Gabbaï, F. P., Anion capture and sensing with cationic boranes: on the synergy of Coulombic effects and onium ion-centred Lewis acidity. *Dalton Trans.* **2013,** *42*, 8164-8178; (f) Busschaert, N.; Caltagirone, C.; Van Rossom, W.; Gale, P. A., Applications of Supramolecular Anion Recognition. *Chem. Rev.* **2015,** *115*, 8038-8155; (g) Gale, P. A.; Howe, E. N. W.; Wu, X.; Spooner, M. J., Anion receptor chemistry: Highlights from 2016. *Coord. Chem. Rev.* **2018,** *375*, 333-372; (h) Schweighauser, L.; Wegner, H. A., Bis‐Boron Compounds in Catalysis: Bidentate and Bifunctional Activation. *Chem. Eur. J.* **2016,** *22*, 14094-14103; (i) Niermeier, P.; Blomeyer, S.; Bejaoui, Y. K. J.; Beckmann, J. L.; Neumann, B.; Stammler, H.-G.; Mitzel, N. W., Bidentate Boron Lewis Acids: Selectivity in Host–Guest Complex Formation. *Angew. Chem. Int. Ed.* **2019,** *58*, 1965-1969.

13. Mostaghimi, F.; Lork, E.; Hong, I.; Roemmele, T. L.; Boeré, R. T.; Mebs, S.; Beckmann, J., The reaction of phenoxatellurine with single-electron oxidizers revisited. *New J. Chem.* **2019,** *43*, 12754-12766.

14. Matano, Y.; Begum, S. A.; Miyamatsu, T.; Suzuki, H., A new and efficient method for the preparation of bismuthonium and telluronium salts using aryl- and alkenylboronic acids. First observation of the chirality at bismuth in an asymmetrical bismuthonium salt. *Organometallics* **1998,** *17*, 4332-4334.

15. (a) Yang, M.; Hirai, M.; Gabbaï, F. P., Phosphonium-stibonium and bis-stibonium cations as pnictogen-bonding catalysts for the transfer hydrogenation of quinolines. *Dalton Trans.* **2019,** *48*, 6685-6689; (b) Hirai, M.; Gabbaï, F. P., Squeezing Fluoride out of Water with a Neutral Bidentate Antimony(V) Lewis Acid. *Angew. Chem. Int. Ed.* **2015,** *54*, 1205-1209; (c) Chen, C.-H.; Gabbaï, F. P., Fluoride Anion Complexation by a Triptycene-Based Distiborane: Taking Advantage of a Weak but Observable C–H···F Interaction. *Angew. Chem. Int. Ed.* **2017,** *56*, 1799-1804; (d) Hirai, M.; Cho, J.; Gabbaï, F. P., Promoting the Hydrosilylation of Benzaldehyde by Using a Dicationic Antimony-Based Lewis Acid: Evidence for the Double Electrophilic Activation of the Carbonyl Substrate. *Chem. Eur. J.* **2016,** *22*, 6537-6541.

16. Baaz, M.; Gutmann, V.; Kunze, O., Die Chloridionenaffinitäten von Akzeptorchloriden in Acetonitril, 1. Mitt.: Lösungszustand und Bildungsgleichgewichte der

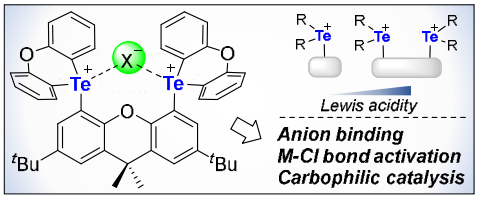
Triphenylchlormethyankomplexe. *Mon. Chem.* **1962,** *93*, 1142-1161.

17. (a) Liu, Y.; Zhao, W.; Chen, C.-H.; Flood, A. H., Chloride capture using a C–H hydrogen-bonding cage. *Science* **2019,** *365*, 159-161; (b) Liu, Y.; Sengupta, A.; Raghavachari, K.; Flood, A. H., Anion Binding in Solution: Beyond the Electrostatic Regime. *Chem* **2017,** *3*, 411-427.

18. Yang, M.; Tofan, D.; Chen, C.-H.; Jack, K. M.; Gabbaï, F. P., Digging the Sigma-Hole of Organoantimony Lewis Acids by Oxidation. *Angew. Chem. Int. Ed.* **2018,** *57*, 13868-13872.

19. (a) Wolf, J.; Huber, F.; Erochok, N.; Heinen, F.; Guérin, V.; Legault, C. Y.; Kirsch, S. F.; Huber, S. M., Activation of a Metal-Halogen Bond by Halogen Bonding. *Angew. Chem. Int. Ed.* **2020,** *59*, 16496-16500; (b) Jones, J. S.; Gabbaï, F. P., Activation of an Au-Cl Bond by a Pendent Sb^{III} Lewis Acid: Impact on Structure and Catalytic Activity. *Chem. Eur. J.* **2017,** *23*, 1136-1144; (c) You, D.; Gabbaï, F. P., Unmasking the Catalytic Activity of a Platinum Complex with a Lewis Acidic, Non-innocent Antimony Ligand. *J. Am. Chem. Soc.* **2017,** *139*, 6843-6846.

TOC graphic



20. (a) Hashmi, A. S. K.; Weyrauch, J. P.; Frey, W.; Bats, J. W., Gold Catalysis: Mild Conditions for the Synthesis of Oxazoles from N-Propargylcarboxamides and Mechanistic Aspects. *Org. Lett.* **2004,** *6*, 4391-4394; (b) Weyrauch, J. P.; Hashmi, A. S. K.; Schuster, A.; Hengst, T.; Schetter, S.; Littmann, A.; Rudolph, M.; Hamzic, M.; Visus, J.; Rominger, F.; Frey, W.; Bats, J. W., Cyclization of Propargylic Amides: Mild Access to Oxazole Derivatives. *Chem. Eur. J.* **2010,** *16*, 956-963.

21. (a) Fürstner, A.; Stelzer, F.; Szillat, H., Platinum-Catalyzed Cycloisomerization Reactions of Enynes. *J. Am. Chem. Soc.* **2001,** *123*, 11863-11869; (b) Talley, M. R.; Stokes, R. W.; Walker, W. K.; Michaelis, D. J., Electrophilic activation of alkynes for enyne cycloisomerization reactions with in situ generated early/late heterobimetallic Pt–Ti catalysts. *Dalton Trans.* **2016,** *45*, 9770-9773; (c) You, D.; Yang, H.; Sen, S.; Gabbaï, F. P., Modulating the σ-Accepting Properties of an Antimony Z-type Ligand via Anion Abstraction: Remote-Controlled Reactivity of the Coordinated Platinum Atom. *J. Am. Chem. Soc.* **2018,** *140*, 9644-9651.