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Dicationic Tellurium Analogues of the Classic N-Heterocyclic Carbene

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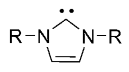
Dedicated to Professor J. Peter Guthrie on the occasion of his retirement

Abstract: The synthesis and comprehensive characterization of the first dicationic tellurium analogues of N-heterocyclic carbenes (NHCs) has been reported, in both the +2 and +4 oxidation states. For the +2 oxidation state, a base-stabilized form of $TeCl_2$ is used as the starting material. The dications are isolated by means of halide metathesis and the solid-state structures confirm the previously calculated diimine bonding arrangement. For Te^{IV}, a diamine is used in a high-yielding dehydrohalogen coupling reaction from $TeCl_4$. The dicationic NHC analogue is isolated in a base-stabilized form through halide abstraction and subsequent coordination by pyridine.

Keywords: carbene analogues · heterocycles · N ligands · polycations · tellurium

Introduction

The discovery of an isolable N-heterocyclic carbene (NHC; **1**) by Arduengo and co-workers has been recognized as one of the most significant achievements in synthetic chemistry within the past 20 years.[1,2]



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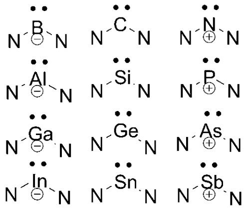
N-heterocyclic carbenes are renowned for being strong σ-donors for elements spanning the periodic table and are known to act as ideal ligands for some of the most important transition-metal catalysts (i.e. Grubbs 2nd-generation olefin metathesis catalyst).[3–5] Following the discovery of isolable NHCs, chemists have endeavored to synthesize *p*-block analogues of NHCs featuring main-group elements (other than carbon) at the central position. These compounds have been reported for many of the elements from groups 13–15 and have shown a rich chemistry complementary to and divergent from NHCs. Known examples are shown schematically in Scheme 1, with the syntheses generally relying on a diazabutadiene (DAB) α-diimine ligand. Depending on the periodic group of the central atom a charge may be imposed on the molecule, negative for group 13,[6–10] neutral for group 14,[11–13] and cationic for group 15.[14–17]



Scheme 1. Schematic diagram of known NHC analogues from groups 13–15.

In all cases similar geometries are calculated and observed experimentally for the N-heterocycles.[18] The E−N bonds are somewhat shortened from single standard bond lengths, with a decreasing difference moving down the groups. This observation is usually attributed as reflecting the occupancy of the formally empty *p*-orbital by the lone pairs on the flanking nitrogen atom, giving partial multiple-bond character to the E−N bonds and an octet of electrons about the central element.[19] Less effective orbital overlap for the heavier congeners decreases the importance of this effect. Therefore, short C−C and long N−C endocyclic bonds are observed, consistent with double and single-bond character, respectively (Scheme 2).

The optimized geometries and electronic structures of the dicationic S, Se, and Te analogues display striking differences relative to those from groups 13–15. The N−C bond lengths are short, averaging 1.32 Å, consistent with an N−C double bond. The C−C bond is longer, at 1.40 Å, approaching the distance observed in the free diazabutadiene (DAB) ligands. These two pieces of data suggest a diimine framework is retained. The Ch−N bonds are not shortened from typical single bond lengths. The electron localization function (ELF) for the chalcogen compounds reveals two mono-

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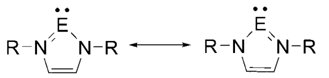
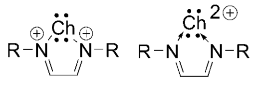


Scheme 2. Resonance structures for NHCs and their *p*-block analogues (charges omitted).

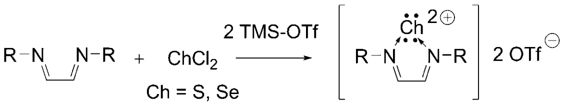
synapic basins about the central element, consistent with two lone pairs of electrons, and assignment of the +2 oxidation state, rather than +4 for the group 16 atoms. The ELF for all other *p*-block analogues (except for Sb) gives the expected single lone pair about the central atoms. Combined, these findings indicate that group 16 carbene analogues (Scheme 3) of type **2** should be considered as either chalcadiazolium dications (**2a**), or coordination complexes between a diazabutadiene ligand and a Ch^{2+} dication (**2b**), and thus are only structural mimics of the ubiquitous NHC.



2a **2b**
Ch = S, Se, Te

Scheme 3. Bonding representations for group 16 carbene analogues.

Our past efforts have resulted in the synthesis of the sulfur and selenium derivatives with a coordination/halide abstraction protocol (Scheme 4). The experimentally determined metrical parameters agreed well with the calculated values, confirming that the diimine bonding motif was retained, and ligand exchange reactions were demonstrated, which indicated that **2b** is a reasonable bonding model.[20–23] We have also synthesized a related tellurium derivative; however, covalent bonds were observed between the tellurium center and the triflate counterions, giving a neutral compound.[24]

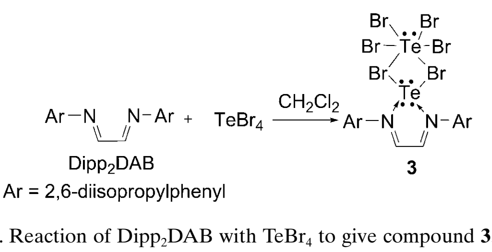


Scheme 4. Synthesis of Ch^{II} NHC analogues through a coordination/halide abstraction strategy.

The binary chlorides were used as the starting reagents; however, SCl_2 and $SeCl_2$ are both unstable with respect to disproportionation.[25] That said, SCl_2 may be stored for months at a low temperature (−30 °C), and $SeCl_2$ may be synthesized and stored for approximately one day, making both materials relatively easy to use. The corresponding binary halides for tellurium are only known as transient species in the gas phase, and are essentially unobtainable for practical synthetic purposes.[26,27] Coordination by Lewis bases allows for TeX_2 to be stabilized and stored.[28–34] Recently a few groups have used this strategy to deliver this otherwise unstable electrophilic Te^{II} source.[35–37] Therefore, the proposed synthetic route to the tellurium NHC analogues is coordination by a DAB ligand to TeX_4, followed by reduction and halide abstraction to give the dication. We have previously demonstrated the coordination of the *tert*-butyl-DAB ligand to $TeBr_4$; in this case, reduction was spontaneous upon attempted halide abstraction giving a 1,2,5-telluradiazolium cation, due to the facile elimination of *tert*-butylbromide.[38,39] Use of aryl or secondary alkyl-substituted diazabutadiene ligands should reduce the propensity for elimination of a side group. The isolation of the tellurium NHC analogue has been identified as a challenge,[40] and in this context we now report the synthesis of dicationic Te^{II} N-heterocycles, by using a coordination/halide abstraction pathway, relying on a 2,2′-bipyridine sequestered source of $TeCl_2$. An alternate route, based on a diamine ligand allowed for isolation of a Te^{IV} N-heterocycle in a base-stabilized form, representing the first isovalent and isostructural dicationic analogue of an N-heterocyclic carbene.

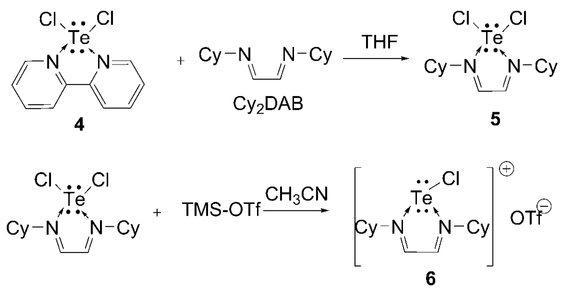
Results and Discussion

Synthesis of dicationic Te^{II} carbene analogues: For tellurium, attempts to reduce $TeCl_4$ concomitant with ligation by $Dipp_2DAB$ (Dipp = 2,6-diisoproylphenyl) were met with abysmal failure, with large amounts of Te^0 immediately produced. Therefore, initial coordination of the ligand to the tetrahalide was attempted. The direct reaction of $Dipp_2DAB$ with one stoichiometric equivalent of $TeBr_4$ in CH_2Cl_2 resulted in the precipitation of a dark-red solid over a period of four hours. The powder was found to be highly insoluble in a variety of organic solvents, but was sufficiently soluble in CD_3CN for ^1H NMR spectroscopy, which revealed a set of resonances consistent with a single product containing intact $Dipp_2DAB$. The diagnostic signals arising from the "backbone" protons were found at $\delta = 9.84$ ppm, significantly downfield from $Dipp_2DAB$ ($\delta = 7.99$ ppm), which is characteristic for the generation of a highly charged compound. Single crystals were grown from a CH_3CN solution of the bulk powder held at −30 °C, and subsequent X-ray diffraction studies revealed a Te^{II} center in the N,N-chelate of the $Dipp_2DAB$ ligand, bridging to a $[TeBr_6]$ dianion in the solid state, giving an overall neutral molecule (**3**; Scheme 5).



Scheme 5. Reaction of $Dipp_2DAB$ with $TeBr_4$ to give compound **3**.

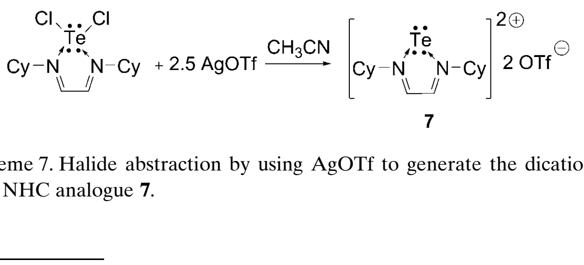
Spontaneous reduction of chalcogen tetrahalides in the presence of DAB ligands has been previously observed for both selenium and tellurium.[38,39] Hexahalochalcogenide anions are generally undesirable, as they are readily available sources of halides.[41] Unfortunately, all attempts at metathesis of $[TeBr_6]^{2-}$ were unsuccessful, so a synthetic route was sought avoiding its incorporation (Scheme 6).



Scheme 6. A ligand exchange reaction transferring $TeCl_2$ to Cy_2DAB and halide abstraction by using TMSOTf to give monocationic heterocycle **6**.

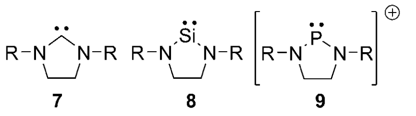
The 2,2′-bipyridine chelate of $TeCl_2$ (**4**) has been demonstrated to be a stable and viable source of $TeCl_2$.[35] Attempted ligand exchange with $Dipp_2DAB$ resulted in no reaction, but the 1:1 stoichiometric reaction of the more Lewis basic Cy_2DAB (Cy = cyclohexyl) with **4** resulted in the immediate deposition of a dark-yellow powder. The yellow powder was found to be completely insoluble in organic solvents, precluding analysis through NMR spectroscopy, similar to what had been found for the $SeCl_2$-Cy_2DAB adduct.[21] In that case, addition of two stoichiometric equivalents of TMSOTf (TMSOTf = trimethylsilyl trifluoromethanesulfonate) gave the dicationic heterocycle. Under the assumption that the $TeCl_2$-Cy_2DAB adduct (**5**) had been generated, a halide abstraction reaction was carried out with an excess of TMSOTf, which after workup gave a bright-yellow powder. The ^1H NMR spectrum of the redissolved powder showed that the diagnostic backbone resonances were $\delta = 9.68$ ppm. A mass spectrum of a sample of the bulk powder revealed an isotope pattern consistent with the presence of tellurium and chlorine ($[M]^+ = 385$). X-ray diffraction studies on single crystals grown from a CH_3CN solution of the bulk powder through vapor diffusion of Et_2O revealed a monocationic tellurium-centered heterocycle bearing a single chlorine atom paired with a triflate anion (**6**).

The use of the stronger halide abstraction reagent AgOTf under identical conditions gives a compound containing a ^1H NMR spectroscopic resonance for the backbone protons signal at $\delta = 9.90$ ppm, shifted downfield from the monocation. The synthesis of the dicationic tellurium **7** NHC analogue was confirmed by X-ray crystallographic studies on single crystals grown from a CH_3CN solution of the bulk powder (Scheme 7).

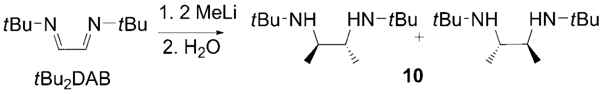


Scheme 7. Halide abstraction by using AgOTf to generate the dicationic Te^{II} NHC analogue **7**.

Synthesis of dicationic Te^{IV} carbene analogues: Efforts to generate a group 16 carbene analogue in the +4 oxidation state (and therefore isostructural and isovalent to an NHC) necessitated a different synthetic strategy. Fully saturated amine ligands have been used to generate *p*-block NHC analogues for groups 14–15, and the parent NHC is also known with a saturated backbone (**7**–**9**).[42] While these are no longer formally 6-π-electron aromatic compounds, only a small drop in stability is observed. The critical π donation from the flanking nitrogen atoms into the otherwise empty *p*-orbital on the central atom remains for the fully saturated analogues.



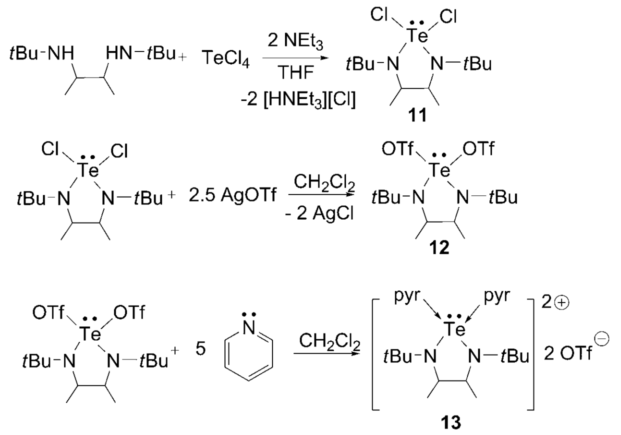
Recently West and co-workers reported a facile synthesis of a saturated derivative of the $t$$Bu_2DAB$ ligand (**10**) by means of a carbolithiation reaction with MeLi, followed by an aqueous workup (Scheme 8).[43]



Scheme 8. West's synthesis of amine **10**.

The diamine is isolated and used as a racemic mixture of the *R*,*R* and *S*,*S* enantiomers, which is not represented in the succeeding drawings for simplicity. The 1:1 stoichiometric reaction of **10** with $TeCl_4$ in the presence of two equivalents of NEt_3 in THF at −78 °C resulted in the formation of a yellow slurry. After warming to room temperature, the solids were removed by centrifugation and the THF was removed from the supernatant to give a yellow powder. The ^1H NMR spectrum of the powder revealed a single set of peaks, consistent with intact ligand. The diagnostic protons are a quartet from the endocyclic backbone protons, which were found at $\delta = 4.05$ ppm (c.f. $\delta = 2.44$ ppm for free **10**). One resonance was observed in the $^{125}Te\{^1H\}$ NMR spectrum at $\delta = 1557$ ppm. Single crystals were grown from a CH_2Cl_2 solution of the bulk powder through vapor diffusion with *n*-hexane, and X-ray diffraction studies revealed a Te^{IV}-centered heterocycle with the two chlorine atoms bound to the tellurium atom (**11**, Scheme 9).

To generate the target dication, a methathesis reaction was performed on **11** by using two stoichiometric equivalents of AgOTf, which gave a yellow powder after workup. ^1H NMR spectroscopy of a redissolved sample revealed a distinct downfield shift for the diagnostic protons ($\delta = 4.40$ ppm). It is noteworthy that the corresponding signal for the neutral silylene ($\delta = 2.81$ ppm) is found at much higher



Scheme 9. Synthetic pathway to base-stabilized Te^{IV} NHC analogue **13**.

field.[43] There was also a downfield shift relative to **11** for the resonance in the $^{125}Te\{^1H\}$ NMR spectrum to $\delta =$ 1823 ppm. These data pointed to a successful metathesis reaction, which was confirmed by X-ray crystallography of single crystals grown from the bulk powder. However, rather than a dicationic heterocycle, the triflates were found to be weakly bound to the Te center, giving an overall neutral molecule (**12**).

To displace the triflates from the Te center, five stoichiometric equivalents of pyridine were added to **12**. There was an immediate upfield shift of the singlet in the $^{125}Te\{^1H\}$ NMR spectrum to $\delta = 1736$ ppm, consistent with coordination of a Lewis base to the tellurium center. A sample of the isolated powder redissolved in $CDCl_3$ for ^1H NMR spectroscopy showed that the heterocycle was intact; the diagnostic quartet was virtually unchanged from **12**. The signals arising from pyridine were shifted slightly downfield from free pyridine and integrated for two pyridine molecules relative to the heterocycle. Single crystals suitable for X-ray crystallography were grown from a concentrated pyridine/Et_2O solution of the bulk powder held at −30 °C overnight, which confirmed the identity of the material as **13**. Compound **13** can be considered a base-stabilized dicationic Te^{IV} analogue of an N-heterocyclic carbene with a single stereochemically active lone pair of electrons.

X-ray crystallography: Compounds **3**, **6**, **7**, and **11**–**13** have been characterized by single-crystal X-ray diffraction studies. Views of the formula units are shown in Figures 1–6, and refinement details may be found in Table 1.

Compound **3** (Figure 1) contains Te−N bond lengths of 2.146(7) Å, approximately 0.1 Å longer than those calculated in the optimized structure with −Ph nitrogen substituents.[18] The Te−N bonds are much shorter than those found in a related TeI_2 chelate of a DAB ligand (2.40 Å), reflecting weaker interactions with the anion.[34] The geometry about the tellurium center in the chelate is square planar (Σ angles=359.9°), consistent with an AX_3E_2 electron pair

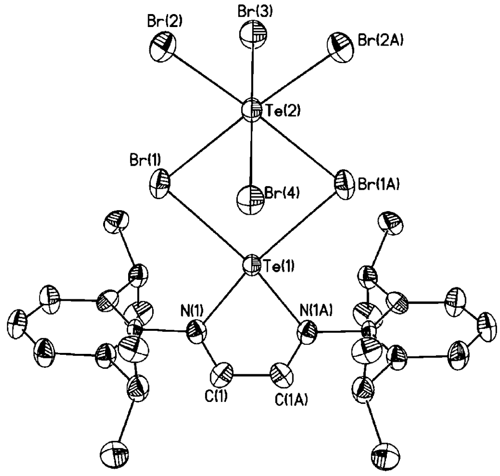


Figure 1. Solid-state structure of **3**: Ellipsoids are displayed to the 50 % probability level. Hydrogen atoms and MeCN solvate are omitted. Selected bond lengths [Å] and angles [°]:Te(1)−N(1): 2.146(7), Te(1)−Br(1): 2.8534(11), Te(2)−Br(1): 2.9929(11), Te(2)−Br(2) 2.5313(11), Te(2)−Br(3): 2.6828(15), Te(2)−Br(4): 2.6742(15), N(1)−C(2): 1.286(10), C(2)−C(2A): 1.421(16); N(1)-Te(1)-N(1A): 74.4(4).

Table 1. Single-crystal X-ray diffraction structural and refinement details.

	3	**6**	**7**	**11**	**12**	**13**
empirical formula	$C_{36}H_{51}Br_6N_7Te_2$	$C_{15}H_{24}Cl_1F_3N_2O_3S_1Te_1$	$C_{16}H_{24}F_6N_2O_6S_2Te_1$	$C_{12}H_{26}Cl_2N_2Te_1$	$C_{14}H_{26}F_6N_2O_6S_2Te_1$	$C_{35}H_{41}F_6N_5O_6S_2Te_1$
F_w	1316.50	532.47	646.09	396.85	624.09	933.45
crystal system	orthorhombic	monoclinic	Triclinic	monoclinic	orthorhombic	triclinic
space group	*Pnma*	$P2_1/n$	$P-1$	$P2_1/c$	*Pbca*	$P-1$
a [Å]	27.2439(9)	6.757(1)	14.640(3)	8.210(1)	8.4746(5)	14.971(3)
b [Å]	16.6918(5)	23.223(5)	14.815(3)	16.395(3)	16.5761(9)	17.522(4)
c [Å]	10.6181(3)	13.129(3)	22.623(5)	12.1987(3)	33.566(2)	18.034(4)
α [°]	90	90	82.03(3)	90	90	68.89(3)
β [°]	90	101.48(3)	79.33(3)	106.77(3)	90	81.73(3)
γ [°]	90	90	89.77(3)	90	90	67.46(3)
V [$Å^3$]	4828.6(3)	2019.0(7)	4774.2(17)	1673.9(6)	4715.2(5)	4083(1)
ρ_{calcd} [$mg\,m^{-3}$]	1.811	1.752	1.798	1.575	1.758	1.518
$R[I>2\sigma I]$[a]	0.0648	0.0328	0.0808	0.0488	0.0667	0.0505
$wR2(F^2)$[b]	0.1934	0.1068	0.1919	0.1400	0.1677	0.1553

[a] $R(F[I>2\sigma(I)]) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR(F^2 \text{ [all data]}) = [\Sigma w(F_o^2-F_c^2)^2]^{1/2}$; $S(\text{all data}) = [\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$ (n = no. of data, p = no. of parameters varied. [b] $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ in which $P = (F_o^2+2F_c^2)/3$ and a and b are constants suggested by the refinement program.

geometry, and the assignment of the +2 oxidation state for the central tellurium. The N–C bonds are short and the C–C bond is long, confirming retention of the diimine bonding motif.

The Te–Br bonds from the tellurium in the chelate to the bridging bromides are long (2.853(1) Å) relative to a standard Te–Br bond (2.6 Å), but are even further to the Te^{IV} center in the TeBr$_6$ unit (2.993(1) Å).[32] Therefore, the compound can be considered as either a tellurium-centered dication interacting strongly with a [TeBr$_6$] dianion in the solid state or as a TeBr$_2$–DAB chelate in which the TeBr$_2$ acts as Lewis base to TeBr$_4$. Based on the ^{1}H NMR spectrosopcic data, the backbone protons are shifted too far downfield for a ChX$_2$–DAB chelate (c.f. SeBr$_2$–Dipp$_2$DAB $\delta = 8.16$ ppm).[35] However, the fact that the Te–Br bonds to the Te^{II} center are shorter than those to the Te^{IV} center indicates that the complex cannot be considered a dication, and the bromides are best described as simply bridging in the solid state. Tellurium-125 NMR spectroscopy would be able to determine the nature of the anion in solution, unfortunately **3** is not sufficiently soluble for ^{125}Te{^{1}H} NMR spectroscopic studies, and decomposes if held in solution, precluding lengthy acquisition time. The solid-state structure of **6** (Figure 2) reveals a T-shaped environment about the tellurium center, consistent with an AX$_3$E$_2$ electron pair geometry and the assignment of the +2 oxidation state for tellurium. The Te–N bond *trans* to the chloride (Te(1)–N(1) 2.152 Å) is slightly longer than the Te(1)–N(2) bond (2.090(3) Å). The structure of compound **6** also provides evidence for the successful synthesis of the TeCl$_2$–Cy$_2$DAB complex **5**, which could not be confirmed by spectroscopic methods.

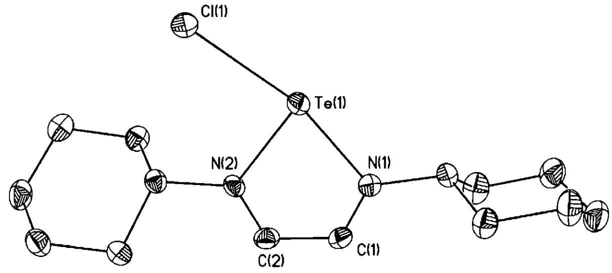


Figure 2. Solid-state structure of **6**: Ellipsoids are displayed to the 50% probability level. Hydrogen atoms and the triflate anion are omitted. Selected bond lengths [Å] and angles [°]: Te(1)–N(1): 2.152, Te(1)–N(2): 2.090(3), Te(1)–Cl(1): 2.553(1); N(1)-Te(1)-Cl(1): 165.35(8), N(2)-Te(1)-N(1): 74.8(1), N(2)-Te(1)-Cl(1): 90.53(9).

The Te–N bonds in **7** (Figure 3) average 2.08 Å, shorter than those found in the monocation, and slightly longer than the calculated values for the idealized dication bearing –Ph N substituents. The C–N and C–C bonds are again consistent with double and single-bond functionalities, respectively. There are short contacts in the solid state between the tellurium center and oxygen atoms from two of the triflate anions. The Te–O contacts average 2.57 Å, with a range between 2.49–2.66 Å, significantly longer than the standard Te–O single bond length of 1.95 Å; shorter distances of 2.42 Å have been described as merely solid-state contacts.[44] The nature of the compound in solution is revealed by the ^{19}F{^{1}H} NMR chemical shift of the –CF$_3$ group in the triflate. For **7**, one sharp resonance was found at $\delta = -78.5$ ppm in MeCN. This can be compared with an ionic standard ([NOct$_4$][OTf]: $\delta = -78.5$ ppm (MeCN)) and covalent standards (MeOTf: $\delta = -75$ ppm; TMSOTf: $\delta = -77.6$ ppm (MeCN)), which indicates that **7** exists in an ionic form in solution, driven by the strong trans effect of the Cy$_2$DAB ligand.

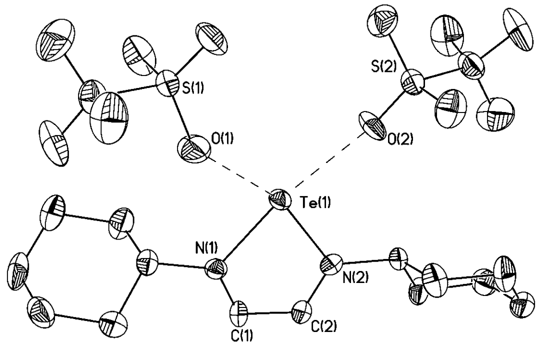


Figure 3. Solid-state structure of **7**: Ellipsoids are displayed to the 50% probability level. Hydrogen atoms are omitted, and one of four independent molecules in the asymmetric unit is shown. Selected bond lengths [Å]: Te(1)–N(1): 2.074(6), Te(1)–N(2): 2.079(6), N(1)–C(1): 1.285(9), C(1)–C(2): 1.43(1), Te(1)–O(1): 2.549(6), Te(1)–O(2): 2.602(6).

The solid-state structure of **11** (Figure 4) features a disphenoidal AX$_4$E bonding arrangement about the tellurium center, consistent with the tellurium carrying one lone pair of electrons and the assignment of the +4 oxidation state. The Te–N bonds are 1.94 Å, significantly shorter than those in **3**, **6**, and **7**, reflective of the stronger bonding with the formally dianionic ligand. The Te–Cl bonds (2.60 Å) are typical of Te–Cl single bonds.

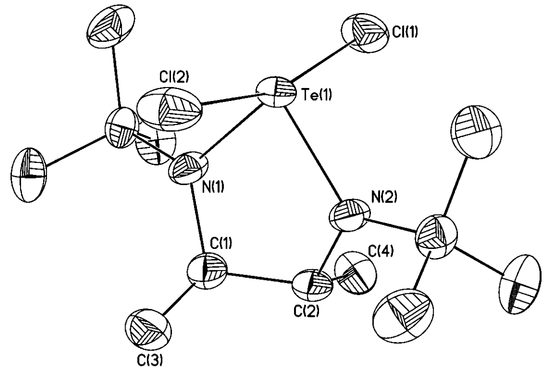


Figure 4. Solid-state structure of **11**: Ellipsoids are displayed to the 50% probability level. Hydrogen atoms and MeCN solvate are omitted. Selected bond lengths [Å] and angles [°]: Te(1)–N(1): 1.944(4), Te(1)–N(2): 1.947(4), Te(1)–Cl(1): 2.590(2), Te(1)–Cl(2): 2.613(2); Cl(1)-Te(1)-Cl(2): 164.6(5), N(1)-Te(1)-N(2): 84.3(2).

The Te–N bonds in compound **12** (Figure 5) are only slightly shorter than those in **11**, unlike that which is observed for the diimine complexes. This is due to the lack of any substituents *trans* to the nitrogen atoms, within the disphenoidal bonding arrangement. The Te–O bonds average 2.34 Å and are much longer than a typical Te–O bond, reflecting the weak nucleophilicty of the OTf anions, and the ease with which they are displaced by pyridine. Despite the weak bond, the Te–O interactions are retained in solution, based on the clear difference in the ^{19}F{^{1}H} NMR chemical shift from ionic triflate ($\delta = -77.6$ ppm, c.f. [NOct$_4$][OTf]: $\delta = -79.0$ ppm (CH$_2$Cl$_2$)), **12** cannot be represented as a dicationic compound.

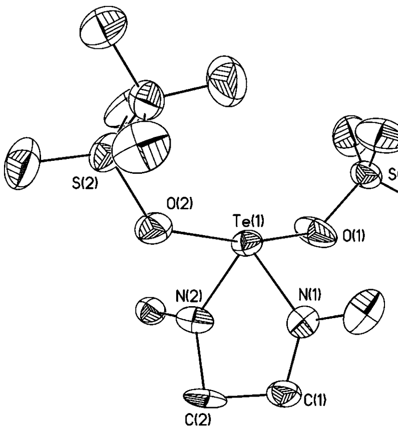


Figure 5. Solid-state structure of **12**: Ellipsoids are displayed to the 50% probability level, methyl groups and hydrogen atoms are omitted. One portion of the disordered NCCN backbone portion is shown. Selected bond lengths [Å] and angles [°]: Te(1)–N(1): 1.900(8), Te(1)–N(2): 1.908(9), Te(1)–O(1): 2.358(7), Te(1)–O(2): 2.332(7); O(2)-Te(1)-O(1): 166.2(3), N(1)-Te(1)-N(2): 86.1(4).

The pyridine ligands replace the OTf anions in compound **13** (Figure 6). The Te–N bonds from the pyridine are 2.333(4) and 2.393(4) Å for Te(1)–N(3) and Te(1)–N(4), respectively, longer than the endocyclic Te–N bonds, which are virtually unchanged from the other two derivatives at 1.96 Å. The disphenoidal geometry about tellurium is retained for the coordination complex. There is little to compare the pyridine–tellurium bonds with, as this is only the fourth example of any monodentate pyridine-type donor bound to any tellurium, and the first for Te^{IV}. Two of the other reports involve hemilabile complexes of Te^{II} thiolates with bridging 4,4′-bipyridine ligands containing very long Te–N contacts of ~2.8 Å.[45,46] The other example is a dicationic homoleptic Te^{II} complex with four 4-dimethylaminopyridine ligands in a square-planar arrangement, featuring Te–N bonds of ~2.3 Å.[24]

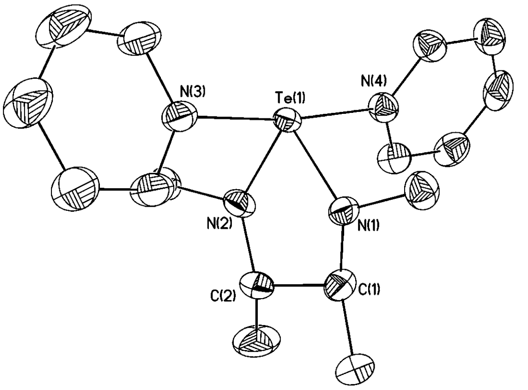


Figure 6. Solid-state structure of **13**: Ellipsoids are drawn to the 50% probability level, methyl groups on the *tert*-butyl groups, hydrogen atoms, pyridine solvate, and triflate anions are omitted. . Selected bond lengths [Å] and angles [°]: Te(1)–N(1): 1.958(4), Te(1)–N(2): 1.955(4), Te(1)–N(3): 2.333(4), Te(1)–N(4): 2.393(4); N(2)-Te(1)-N(4): 172.8(1), N(2)-Te(1)-N(1): 86.4(2).

Conclusion

Synthetic, structural, and spectroscopic studies of tellurium NHC analogues have been conducted. For the unsaturated derivatives, the solid-state structures confirmed theoretical predictions, in that the chalcogen atoms adopt the +2 oxidation state, and the diimine framework of the ligand is retained. Use of a nonredox active diamine ligand allowed for the isolation of a Te^{IV} N-heterocycle, and the generation of the first dicationic Ch^{IV} NHC analogue, which was stabilized by coordination of a Lewis base (pyridine).

Experimental Section

General: Manipulations were performed in an N$_2$-filled MBraun Labmaster 130 glove box in 4 dr vials affixed with Teflon lined screw caps or by using standard Schlenk techniques. Dichloromethane, THF, Et$_2$O, CH$_3$CN, *n*-pentane, and *n*-hexane were obtained from Caledon Laboratories and dried by using an MBraun SPS with appropriate drying agents. Pyridine was obtained from Caledon, dried over CaH$_2$, and distilled. The dried solvents were stored in Strauss flasks under an N$_2$ atmosphere or over 4 Å molecular sieves in a glove box. Solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, dried by stirring for 3 days over CaH$_2$, distilled prior to use, and stored in the glove box over 4 Å molecular sieves. Tellurium tetrachloride, TeBr$_4$, TMSOTf, AgOTf, and 2,2′-bipyridine were purchased from Alfa Aeasar and used as received. The Dipp$_2$DAB, Cy$_2$DAB, and diamine **10** were prepared according to literature procedures.[42,43,47] NMR spectra were recorded on an INOVA 400 MHz spectrometer. Tellurium-125 NMR spectra were referenced to Me$_2$Te ($\delta = 0.00$ ppm by using H$_2$TeO$_4$ in D$_2$O; $\delta = 712$ ppm). Fluorine-19 NMR spectra were referenced to CFCl$_3$ ($\delta = 0.00$ ppm by using C$_6$H$_5$CF$_3$ $\delta = -63.7$ ppm) ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced relative to Me$_4$Si by using the resonances from within the NMR spectroscopic solvents.[48] Samples for FT-Raman spectroscopy were packed in capillary tubes, flame-sealed, and data were collected by using a Bruker RFS 100/S spectrometer, with a resolution of 4 cm^{-1}. FTIR spectra were collected on samples as KBr pellets by using a Bruker Tensor 27 spectrometer, with a resolution of 4 cm^{-1}. Decomposition/melting points were recorded in flame-sealed capillary tubes by using a Gallenkamp Variable Heater. All mass spectrometry measurements were collected by Mr. Doug Hairsine by using an electrospray ionization Micromass LCT spectrometer. Suitable single crystals for X-ray diffraction studies were individually selected under oil (Paratone-N), mounted on nylon loops, and immediately placed in a cold stream of N$_2$ (150 K). Data were collected on a Bruker Nonius Kappa CCD X-ray diffractometer or a Bruker APEX II CCD X-ray diffractometer by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The solution and subsequent refinement of the data were performed by using the SHELXTL suite of programs.[49] CCDC-625896 (**3**), -775711 (**6**), -775712 (**7**), -775713 (**11**), -775714 (**12**), and -775715 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Decomposition is observed within a few days if these compounds are allowed to stand in the solid state at room temperature under a N_2 atmosphere. No decomposition was observed when they were stored at −30 °C.

Synthesis of 3: $Dipp_2DAB$ (0.0504 g, 0.134 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred slurry of $TeBr_4$ (0.060 g, 0.134 mmol) in CH_2Cl_2 (5 mL) at room temperature, resulting in the formation of a red/brown slurry. The reaction mixture was allowed to stir for 3.5 h over which time a red precipitate formed. The reaction mixture was centrifuged and the precipitate washed with CH_2Cl_2 (2×10 mL). The supernatant was decanted and the volatiles were removed in vacuo to give **3** as a dark-red powder. Yield: 0.037 g, 50%; d.p. 161 °C; ^1H NMR (CD_3CN): $\delta = 9.91$ (s, 2H), 7.54 (t, $^3J_{H-H} = 6.80$ Hz, 2H), 7.45 (d, $^3J_{H-H} = 7.20$ Hz, 4H), 2.60 (sept, $^3J_{H-H} = 6.80$ Hz, 4H), 1.31 (d, $^3J_{H-H} = 6.80$ Hz, 9H), 1.25 ppm (d, $^3J_{H-H} = 6.80$ Hz, 9H); ESI-MS: m/z: 585 $[M+Br]^+$.

Synthesis of 5: A solution of Cy_2DAB (0.046 g, 0.211 mmol; THF 5 mL) was added to a slurry of **4** (0.075 g, 0.211 mmol; THF 5 mL), resulting in a color change of the slurry from green to orange. After five minutes, the mixture was centrifuged and the supernatant decanted. The solids were washed with Et_2O (3×5 mL) and dried in vacuo to give **5** as a dark-yellow powder. Yield: 0.086 g, 97%; d.p. 170 °C.

Synthesis of 6: Neat TMSOTf (60 uL, 0.332 mmol) was added to a slurry of **5** (0.064 g, 0.153 mmol; CH_3CN 5 mL) and stirred for 30 min. Diethyl ether (15 mL) was added to give a yellow precipitate. The supernatant was decanted, the precipitate washed with Et_2O (2×10 mL), and dried in vacuo to give **6** as a bright-yellow powder. Yield: 0.05 g, 61%; d.p. solid turns black 120–145 °C; ^1H NMR (CD_3CN): 9.69 (s, 2H), 4.86 (m, 2H, cyclohexyl C-H), 2.17–1.09 ppm (cyclohexyl CH_2); $^{19}F\{^1H\}$ NMR (CH_3CN): −78.5 ppm; ESI-MS m/z: $[M]^+$ 385.

Synthesis of 7: A slurry of **5** (0.086 g, 0.207 mmol; CH_3CN 10 mL) was added to solid AgOTf (0.400 g, 1.56 mmol) and stirred for 2 h. The mixture was centrifuged and gave a yellow solution over a white solid. The supernatant was decanted, and then Et_2O was added to the supernatant to give a light-yellow precipitate. The solution was decanted and the solids washed with Et_2O (3×10 mL) and then dried in vacuo to give **7** as a light-yellow powder. Yield: 0.125 g, 93%; d.p. 195–200 °C;^1H NMR (CD_3CN): $\delta = 9.84$ (s, 2H), 4.95 (m, 2H, cyclohexyl C−H), 2.20–1.26 ppm (cyclohexyl CH_2); $^{13}C\{^1H\}$ NMR (CD_3CN): $\delta = 160.0$, 70.0, 36.5, 26.0, 25.0 ppm; $^{19}F\{^1H\}$ NMR (CH_3CN): $\delta = -78.5$ ppm; ESI-MS: m/z: $[MOTf_2-H]^+$ 645, $[M-C_6H_{11}]^+$ 264.

Synthesis of 11: A solution of **10** (0.470 g, 2.35 mmol; THF 10 mL) and NEt_3 (0.66 mL, 4.7 mmol) was added to a stirred −65 °C solution of $TeCl_4$ (0.632 g, 2.35 mmol; THF 25 mL) to give a yellow slurry. After 1 h, the solution was allowed to warm to room temperature and filtered to give a yellow solution. The solvent was removed in vacuo and gave a dark-yellow powder. The material was redissolved in CH_2Cl_2 (10 mL) and *n*-pentane (5 mL) was added. The mixture was centrifuged and the supernatant decanted. The solvent was removed from the supernatant in vacuo to give **11** as a yellow powder. Yield: 0.705 g, 76%; d.p. solid browns at 100 °C; ^1H NMR ($CDCl_3$): $\delta = 4.05$ (q, $^3J_{H-H} = 6.6$ Hz, 2H), 1.58 (s, 18H), 1.53 ppm (d, $^3J_{H-H} = 6.6$ Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 69.7$, 59.5, 31.5, 22.5 ppm; $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): $\delta = 1557$ ppm.

Synthesis of 12: A solution of **11** (0.235 g, 0.591 mmol; CH_2Cl_2 10 mL) was added to an aluminum-foil-wrapped vial containing solid AgOTf (.305 g, 1.18 mmol). The vial was then carefully wrapped in additional aluminum foil and allowed to stir for 16 h, after which time, the mixture was centrifuged. The bright-yellow supernatant was decanted and CH_2Cl_2 removed under reduced pressure to give **12** as a bright-yellow powder. Yield: 0.270 g, 73%; d.p. 110–120 °C; ^1H NMR ($CDCl_3$): $\delta = 4.40$ (q, $^3J_{H-H} = 6.6$ Hz, 2H), 1.61 (s, 18H), 1.49 ppm (d, $^3J_{H-H} = 6.6$ Hz, 6H); $^{13}C\{^1H\}$ NMR (CH_2Cl_2): $\delta = 70.1$, 61.8, 30.8, 21.9 ppm; $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): $\delta = 1823$ ppm; $^{19}F\{^1H\}$ NMR (CH_2Cl_2): $\delta = -77.6$ ppm.

Synthesis of 13: Pyridine (90 uL, 1.12 mmol) was added to a solution of **12** (0.150 g, 0.240 mmol; CH_2Cl_2 5 mL), which resulted in a color change from bright yellow to pale yellow. Diethyl ether (5 mL) and *n*-pentane (5 mL) were then added to give a yellow precipitate. The mixture was cooled to −30 °C for 1 h. The solution was then decanted, the solid washed with Et_2O (2×5 mL), and then dried in vacuo to give **13** as a light-yellow powder. Yield: 0.098 g, 52%; d.p. 110 °C; ^1H NMR ($CDCl_3$): $\delta = 8.65$ (d, $^3J_{H-H} = 4.4$ Hz, 4H), 7.73 (t, $^3J_{H-H} = 8.0$ Hz, 2H), 7.35 (d, $^3J_{H-H} = 8.0$ Hz, 4H), 4.40 (q, $^3J_{H-H} = 6.6$ Hz, 2H), 1.62 (s, 18H), 1.46 ppm (d, $^3J_{H-H} = 6.6$ Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 148.6$, 138.2, 124.9, 70.5, 61.9, 31.2, 22.1 ppm; $^{125}Te\{^1H\}$ NMR (CH_2Cl_2): $\delta = 1736$ ppm; $^{19}F\{^1H\}$ NMR (CH_2Cl_2): $\delta = -78.7$ ppm.

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