ORGANOMETALLICS

Isolation of Homoleptic Dicationic Tellurium and Monocationic Bismuth Analogues of Non-N-Heterocyclic Carbene Derivatives

Rajesh Deka, Arup Sarkar, Ray J. Butcher, Peter C. Junk, David R. Turner, Glen B. Deacon,* and Harkesh B. Singh*



bismuthenium ion, $[(ppy)_2Bi]\cdotCl$, $[12]\cdotCl$, using the same aryl group. All of the synthesized compounds are unambiguously authenticated by single-crystal X-ray diffraction studies. DFT calculations [natural bond orbital (NBO), atoms in molecules (AIM), and electron localization function (ELF)] indicate that the stability of the non-NHC carbenoids relies on the σ -hole participation of the Te/Bi atom with the strong intramolecular coordination ability of the pyridyl N atom of the aryl substituent.

INTRODUCTION

Inspired by the extraordinary success of N-heterocyclic carbenes (NHCs), 1a in metal-based chemistry, significant research has been carried out in the last few decades to isolate and explore the reactivity of isovalent analogues of NHCs within *p*-block elements, collectively known as main-group NHC analogues (Chart 1).¹ The interesting molecular structures, versatile electronic properties, and reactivity associated with the main-group NHC analogues have offered abundant opportunities in main-group and coordination chemistry.¹ Compared to the group 14 and 15 NHC analogues of period 5, i.e., **1b–1d**, the isolation of group 16 NHC

Chart 1. NHC (1a) and Other Main-Group NHC Analogues of Period 5 (1b-1e)



analogues is very challenging, as the corresponding Te⁴⁺ cations are expected to be ambivalent in nature, i.e., being highly electrophilic and possessing a lone pair of electrons at the same time.^{2a} In a groundbreaking report, Ragogna and coworkers have utilized the strong σ -donating ability of the N atoms of the diazabutadiene α -diimine ligand motifs for the isolation of the Te analogues of NHC derivatives 1e.^{2b}

In the case of NHCs, while the steric properties can be easily fine-tuned by changing the substituents on the N atoms or by changing the size of the ring, the choices of modifying the electronic properties are limited.³ In this context, significant research has been undertaken lately to understand and explore the chemistry of "non-NHC" derivatives comprising a backbone other than imidazol-2-ylidenes. From the seminal work by Bertrand and co-workers, it is perceived that the non-NHC frameworks can exhibit promising electronic features and wide structural varieties which extend their applications in various fields of contemporary chemistry.³ Among the maingroup non-NHC analogues of groups 14–16, reports on the

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Scheme 1. Synthesis of Dicationic Tellurium Analogues of Non-NHC Derivatives, [4]·2ClO₄ and [5]·2OTf



heavier main-group analogues of group 15 and 16 non-NHC derivatives are still scarce even though the chemistry of group 14 analogues is well studied.⁴ Very recently, Beckmann and coworkers have reported the first examples of heavier group 15 analogues (Bi, Sb) of non-NHC derivatives, namely, the bismuthenium ion $[(2,6-\text{Mes}_2\text{C}_6\text{H}_3)_2\text{Bi}][\text{BAr}_4]$ and the stibenium ion $[(2,6-\text{Mes}_2\text{C}_6\text{H}_3)_2\text{Bi}][\text{BAr}_4]$ and the stibenium ion $[(2,6-\text{Mes}_2\text{C}_6\text{H}_3)_2\text{Sb}][\text{B}(\text{C}_6\text{F}_5)]$ [where Mes = 2,4,6-Me_3\text{C}_6\text{H}_2 and Ar = 3,5-(CF₃)₂C₆H₃] stabilized by bulky *meta*-terphenyl substituents and weakly coordinating anions.^{2a} The corresponding group 16 congeners have not been reported. It is worth mentioning that, in recent times, various cationic organotellurium and organobismuth compounds have received enormous attention because of their fascinating photoluminescence properties and promising applications in photocatalysis.⁵

Srivastava et al.^{6a} and Beckmann and co-workers^{6b} have independently utilized the intramolecular chalcogen bonding (IChB) approach for the isolation of diorganoiodotelluronium-(IV) cations. We envisaged that the metathesis reaction of these diorganoiodotelluronium(IV) cations with silver salts with noncoordinating anions might lead to the isolation of hitherto unknown Te analogues of non-NHC derivatives. Accordingly, iodobis [2 - (phenylazo)phenyl - C, N']tellureniumtriiodide^{6a} was treated with silver perchlorate in acetonitrile/methanol. However, the reaction did not afford the desired diorganotellurenium(IV) dication. We thought that, by utilizing stronger IChB interactions, the isolation of the desired diorganotellurenium(IV) dication could be achieved. In this context, we planned to use $[(ppy)_2TeI] \cdot I_3$, $[3] \cdot I_3$ [where ppy = 2-(2'-pyridyl)phenyl], as the precursor. It is worth mentioning that, by using a tellurium trichloride derivative of the same substrate, i.e., ppyTeCl₃, we have recently succeeded in the isolation of the first example of monomeric organotellurinic acid, wherein the lone pair of the N atom of the pyridylphenyl ring strongly participated with the Te center.⁷ Herein, by metathesis reaction of $[3] \cdot I_3$ with silver salts (AgClO₄ and AgOTf, Tf = O_2SCF_3), we report the first examples of stable, homoleptic dicationic tellurium analogues of "non-NHC" derivatives, namely, [(ppy)₂Te]·2ClO₄, [4]· $2ClO_4$, and $[(ppy)_2Te] \cdot 2OTf$, $[5] \cdot 2OTf$.

RESULTS AND DISCUSSION

Precursor $[3] \cdot I_3$ was synthesized by the oxidative addition of iodine with diorganotelluride (ppy)₂Te, 2.⁸ When $[3] \cdot I_3$ was

treated with an excess (ca. 5 equiv) of AgClO₄/AgOTf in acetonitrile solution at ambient temperature, the reaction resulted in the precipitation of silver iodide as an off-white solid. The precipitate was filtered off, and the resultant filtrate, on slow evaporation at ambient temperature, afforded stable, white crystalline solids of $[4] \cdot 2ClO_4 / [5] \cdot 2OTf$ in ca. 90% yield (Scheme 1). The ¹H and ¹³C NMR spectra of [4] 2ClO₄ and [5]·20Tf confirmed the purity of the compounds with characteristic signals and consistent integration values for the 2-(2'-pyridyl)phenyl moiety. Minute but perceptible changes in chemical shifts were observed for [4].2ClO4 and [5].2OTf in comparison to the precursor $[3] \cdot I_3$. In the ¹²⁵Te NMR spectra, $[4] \cdot 2ClO_4$ and $[5] \cdot 2OTf$ showed single resonances at δ = 1107 and 1114 ppm, respectively. While these chemical shift values are close to that of precursor $[3] \cdot I_3$ ($\delta = 1100$ ppm), they are significantly upfield shifted in comparison to the Te^{IV} NHC analogue, 1e, reported by Ragogna and coworkers (δ = 1736 ppm), as in the latter Te center was directly bonded to two N atoms.^{2b}

The molecular structure of $[3] \cdot I_3$ is represented in Figure 1. Defined by a C_2N_2I donor set, the geometry around the Te(IV) center is distorted trigonal bipyramidal, wherein the iodine and N1 atoms occupy the axial positions and the C11, C12, and N2 atoms occupy the equatorial positions.



Figure 1. Molecular structure of $[3] \cdot I_3$; thermal ellipsoids are set at the 50% probability level. Selected bond distances and angles (Å, deg): C1-Te 2.134(5), C12-Te 2.141(5), N1 \cdots Te 2.295(5), N2 \cdots Te 2.636(5), I1-Te 2.9158(5), I2-I3 2.9736(7), I3-I4 2.8779(7), C1-Te-C12 97.2(2), N1 \cdots Te \cdots N2 85.1(2), N1 \cdots Te-I1 167.7(1), N2 \cdots Te-I1 102.3(1), C1-Te-II 95.2(1), C12-Te-II 87.3(1), I2-I3-I4 177.06(2).



Figure 2. (a) Molecular structure of [4]·2ClO₄; thermal ellipsoids are drawn at the 50% probability level. Selected bond distances and angles (Å, deg): C1–Te 2.116(2), C12–Te 2.117(2), N1…Te 2.224(2), N2…Te 2.229(2), C1–Te–C12 92.68(9), C1–Te…N 77.04(8), C12–Te…N 77.37(8), N1…Te…N2 162.83(7). (b) Natural bond orbital (NBO) plot showing the $lp(N) \rightarrow p(Te)$ interaction, stabilization energy, $\Delta E = 122.5$, 122.5 kcal/mol. (c) Electron localization function (ELF) for [4]⁺ drawing in the plane containing N, Te, and C atoms.



Figure 3. (a) Electrostatic surface potential (ESP) map, $\rho = 0.001$ au, showing an enhanced σ -hole region antipodal to the C–Te bond in the absence of N \rightarrow Te IChB interactions. (b) ESP of [4]⁺ showing diminution of the σ -hole region due to the presence of N \rightarrow Te IChB interactions. ESPs have been drawn on the Hirshfeld surface with potential in the range from 0.175 au (red) to 0.210 au (blue). (c) Atoms in molecules (AIM) bond topology of [4]⁺.

Compound [3]·I₃ exhibits significantly stronger N…Te IChB interactions, as is evident from the corresponding N…Te distances of 2.295(5) and 2.636(5) Å, which are considerably shorter in comparison to that observed in similar iodotellurium(IV) cations, namely, $[(C_6H_5NNC_6H_4)_2TeI]$ ·I₃ [2.481(11) and 2.756(13) Å; 2.476(13) and 2.796(28) Å] and $[(8-Me_2NC_{10}H_6)_2TeI]$ ·I₃ [2.743(7) and 3.20(1) Å].⁶ The Te–I bond distance [2.9158(5) Å] and $\angle C$ –Te–C [95.2(1)°] in [3]·I₃ are in good agreement with those in $[(C_6H_5NNC_6H_4)_2TeI]$ ·I₃ [2.782(12)/2.778(15); 97.4(5)/95.5(6)°] and $[(8-Me_2NC_{10}H_6)_2TeI]$ ·I₃ [2.780(2) Å; 96.7(3)°].⁶

The molecular structures of $[4] \cdot 2\text{ClO}_4$ and $[5] \cdot 2\text{OTf}$ are significantly similar; hence, the structure of only $[4] \cdot 2\text{ClO}_4$ is described here (Figure 2a; see the Supporting Information for the structure of $[5] \cdot 2\text{OTf}$). The spatial arrangement of the Te(IV) center is distorted square pyramidal taking the lone pair of Te and N…Te IChB interactions into account. The donor set C_2N_2 makes a spirocyclic arrangement around the Te center with a C1–Te–C12 bond angle of 92.68(9)°, while both N atoms make a *transoid* angle of 162.83(7)°. In the Te^{IV} NHC analogue **1e**, the corresponding N–Te–N angle is significantly larger with an angle of 172.8(2)°.^{2b} The interesting feature in the structure of $[4] \cdot 2 \text{ClO}_4$ is the N··· Te IChB interactions, which make five-membered TeNC₃ rings with N···Te distances of 2.224(2) and 2.229(2) Å. These distances are significantly shorter than those observed in the precursor $[3] \cdot I_3$ [2.295(5) and 2.636(5) Å, *vide supra*]. The C-N-Te bond angles are 114.8(1) and 115.1(1)°. Both of the perchlorate anions are involved in weak interactions with the Te center with distances lying in the range 3.021(2)-3.115(2) Å, and these distances are well within the sum of the van der Waals radii of Te and O atoms [$\Sigma r_{vdw}(O, Te) = 3.49$ Å].⁹

To shed light on the electronic structure of a Te^{IV} cation and to understand the role of the N atoms of the 2-(2'pyridyl)phenyl on the stability of the synthesized compounds, DFT calculations were carried out using the Gaussian 0.9 (rev A.02) program¹⁰ (functional: B3PW91;¹¹ mixed basis set: Te, SDB-cc-pVTZ;¹² C/H/N/O, 6-31G**;¹³ Bi, cc-pVTZ-PP¹⁴). After a geometry optimization starting from the crystal coordinates, natural bond orbital (NBO) calculations were performed for cation [4]⁺.¹⁵ The NBO analysis treats each N– Te interaction in [4]⁺ as an $lp(N) \rightarrow p(Te)$ donor–acceptor interaction (Figure 2b). A stabilization energy of ~122 kcal/ mol of each N \rightarrow Te interaction inferred that they contributed significantly to the overall stability of the compound. The strong N \rightarrow Te IChB in [4]⁺ was further validated by electron localization function (ELF) calculation, wherein a continuum of elevated ELF values was observed along the N \rightarrow Te vectors (Figure 2c).¹⁶

To probe the effect of $N \rightarrow$ Te IChB interactions on the Te(IV) center in $[4]^+$, the electrostatic surface potential $(ESP)^{17}$ was calculated for $[4]^+$ and for a model compound wherein the pyridyl rings were rotated away from the Te center in such a way that no IChB was observed between the N and Te atoms. The ESP of the model compound showed a broad region of depleted electron density, known as the σ -hole region, antipodal to the C-Te bond (Figure 3a). It is worth mentioning that, in the case of group 14-16 compounds, along the extension of a covalent bond, a highly directional and localized region of depleted electron density (positive electrostatic potential) is observed, due to the anisotropic distribution of electron density, and is known as a σ -hole.¹ These σ -holes are responsible for various noncovalent interactions, such as chalcogen bonding (ChB), pnictogen bonding (PnB), and tetrel bonding (TrB) to name a few. The significant diminution of the original σ -hole in compound $[4]^+$ after N \rightarrow Te IChB (Figure 3b) unambiguously established the direct involvement of the σ -hole in chalcogen bonding with the lone pair of the nitrogen atom. To understand the nature of interaction between the N and Te atoms, an atoms in molecules (AIM) calculation has been carried out (Figure 3c).¹⁹ The analysis of the topological properties of the N…Te bond critical point (bcp), such as a low electron density, $\rho(r)$, value of 0.129 e Å⁻³, Laplacian of electron density, $\nabla^2_{\rho(r)}$, value of -0.018 e Å⁻³, a positive kinetic energy density over electron density ratio $[G(r)/\rho(r)]$ of 0.22 au, and a total energy density over electron density ratio $[H(r)/\rho(r)]$ of -0.66 au, infers a dominant electrostatic interaction between the two atoms. The "-G(r)/V(r)" value of 0.864 further suggests a predominantly ionic character of the N…Te interaction with a significant mixing of covalent character.²⁰ This is further corroborated by the natural population analysis (NPA) charge of -0.589 for each N atom and 1.785 for the Te atom.

In an attempt to synthesize the tricationic species (ppyTe³⁺), ppyTeCl₃,²¹ **6**, was treated with an excess of AgClO₄. However, the desired compound $[7]\cdot3ClO_4$ was not stable and the adventitious hydrolysis resulted in the formation of ditelluroxonium bis(perchlorate) [ppyTe(μ -O)]₂.2ClO₄, [**8**]· 2ClO₄ (Scheme 2). The ditelluroxonium cation [**8**]·2ClO₄ shows ¹²⁵Te NMR resonance at 1413 ppm.

Scheme 2. Isolation of $[8] \cdot 2ClO_4$ by the Attempted Synthesis of $[7] \cdot 3ClO_4$



The molecular structure of $[8] \cdot 2\text{ClO}_4$ is presented in Figure 4, which reveals a dimeric structure with a crystallographically imposed center of inversion. Each Te(IV) center is coordinated to one ppy ligand in *trans* orientation with respect to the other and forms a Te₂O₂ core with μ_2 -bridging oxygen atoms. The N…Te distance of 2.279(9) Å is significantly



Figure 4. Molecular structure of [8]·2ClO₄; thermal ellipsoids are set at the 50% probability level. Selected bond distances and angles (Å, deg): C-Te 2.11(1), N···Te 2.279(9), O1-Te 1.917(8), O2-Te 2.068(8), O11···Te 2.784(9), C-Te···N 76.0(4), O1-Te-O2 78.8(3), Te-O-Te 101.2(3).

longer than that in [4]·2ClO₄ [2.224(2) Å] but shorter than that in [3]·I₃ [2.295(5) Å]. The Te–O distances of 1.917(8) and 2.068(8) Å are in agreement with similar reported dimeric compounds, namely, $[Te(2,6-(Me_2NCH_2)(\mu-O)]_2 \cdot 2ClO_4$ [1.987(4) and 1.996(4) Å] and $[Te(6-Ph_2P(O)-Ace-5-)(\mu-O)]_2 \cdot 2OTf$ [1.920(3)–2.070(3) Å, Ace = acenaphthyl].²² The nonbonding distance between the two Te centers of 3.080(1) Å is significantly shorter than the sum of the van der Waal radii $[\Sigma r_{vdw}(Te, Te) = 3.98 \text{ Å}].^9$

To compare the structural parameters of the diorganodications $[4] \cdot 2ClO_4$ and $[5] \cdot 2OTf$ with the corresponding monocation $(ppy)_{3}Te^{+}$ and to explore the coordination ability of the Te center, ppyBr, 9^{23} was treated with "BuLi followed by TeCl_4 to afford $[(ppy)_3\text{Te}]\cdot\text{Br}$, $[10]\cdot\text{Br}$ (Scheme 3). Compound [10].Br showed ¹²⁵Te NMR resonance at 867 ppm, which is consistent with the value observed for similar reported triorganotelluronium(IV) cations, namely, triphenyltelluronium chloride (773 ppm) and tris(8-quinolinyl)telluronium chloride (669 ppm).²⁴ Interestingly, when [10]. Br was treated with K₂PdCl₄, a reverse transmetalation was observed, resulting in the formation of the Pd^{II} complex of chlorotelluronium cation, namely, [(ppy)₂TeCl]·[(ppy)-PdCl₂], 11. In the absence of any other possible explanation, the stronger N…Te IChB in [10].Br could be held responsible for the reverse transmetalation in contrast to the Gabbaï and co-workers report, wherein tris(8-quinolinyl) telluronium chloride on reaction with a Pd(II) precursor resulted in the formation of a 1:1 palladated complex with the telluronium ion acting as a σ -acceptor ligand.^{24b} In the ¹²⁵Te NMR spectrum, 11 showed single resonance at 1309 ppm.

In the molecular structure of [10]·Br (Figure 5a), the distortion from a regular octahedron is less $[\angle N-Te-C_{(trans)} 163.4(3)-165.7(3)^{\circ}]$ in comparison to that of the related compound, tris(8-quinolinyl)telluronium chloride $[\angle N-Te-C_{(trans)} 146.7(2)-147.8(2)^{\circ}]$.^{24b} Again, the N…Te IChB distances are significantly shorter [2.680(8)-2.689(7) Å] in comparison to tris(8-quinolinyl)telluronium chloride [2.950(5)-2.988(6) Å]. In the molecular structure of 11 (Figure 5b), the cationic entity, the halide site is mixed Cl/Br with occupancies of 0.908(8):0.092(8). Hence, the structure is described with respect to the Cl⁻ ligand. The spatial arrangement around the Te^{IV} center is similar to that of iodotelluronium cation, $[3] \cdot I_3$. In particular, the C-Te

Scheme 3. Synthesis of a Pd(II) Complex of Chlorotelluronium Cation, 11



Figure 5. Molecular structures of (a) [10]·Br and (b) 11; thermal ellipsoids are set at the 50% probability level. Selected bond distances and angles (Å, deg): For [10]·Br, C1–Te 2.152(9), C12–Te 2.13(1), C23–Te 2.152(7), N1···Te 2.688(7), N2···Te 2.680(8), N3···Te 2.647(8), C1–Te···N1 70.1(3), C12–Te···N2 70.4(3), C23–Te···N3 70.7(3), C1–Te···N2 164.3(3), C12–Te···N3 165.7(3), C23–Te···N1 163.4(3). For 11, C11A–Pd 2.02(1), C11B–Te 2.14(1), C22B–Te 2.15(1), N1A–Pd 2.03(1), N1B···Te 2.291(9), N2B···Te 2.67(1), Pd–Cl1 2.37(1), Pd–Cl2 2.49(2), Te–Cl1B 2.57(1), Pd···Te 3.738(1), N1A–Pd–Cl1A 81.5(4), N1A–Pd–Cl2 96.1(5), N1A–Pd–Cl1 173.2(5), C11A–Pd–Cl2 176.7(5), N1B–Te–C11B 76.6(4), N2B–Te–C22B 70.5(4), N1B–Te–Cl1B 167.3(4), N2B–Te–Cl1B 104.1(3). In the cationic entity, the halide site is mixed Cl/Br with occupancies of 0.908(8) (for Cl1B)/0.092(8) (for Br1B). In the anionic entity, the halide sites are mixed Cl/Br with occupancies of 0.874(9) (for Cl1)/0.126(9) (for Br1) and 0.781(9) (for Cl2)/0.219(9) (for Br2).

distances [2.15(1), 2.14(1) Å] and N···Te distances [2.291(9), 2.67(1) Å] in **11** are in good agreement with those observed in [**3**]·I₃. The \angle C-Te-C [94.7(4)°] in **11** is slightly smaller than that in [**3**]·I₃ [97.2(2)°]. In the anionic entity, the geometry around the Pd^{II} center is essentially square planar. The bond lengths and associated bond angles of the ppy and Cl ligands with the Pd^{II} center are in good agreement with the value observed in similar related dichlorido Pd(II) complexes.²⁵ Interestingly, an unsupported cation-anion interaction is exhibited between the Te^{IV} and Pd^{II} centers with a distance of 3.738(1) Å, which is shorter than the sum of van der Waals distances of the two atoms [Σr_{vdw} (Te, Pd) = 4.14 Å].⁹

To see the generality of the "ppy" group on stabilizing other main-group non-NHC analogues and to further explore the unique intramolecular interaction ability of the N atom of the ppy group, we went on to synthesize $(ppy)_2BiCl$, which was planned to be used for the metathesis reaction in a subsequent step to generate a cationic species. Interestingly, when **9** was treated with "BuLi followed by addition of $BiCl_3$, a facile autoionization took place, resulting in the formation of diorganobismuthenium chloride, $[(ppy)_2Bi^{III}]\cdotCl$, $[12]\cdotCl$ (Scheme 4). $[12]^+$ is only the second example of bismuthenium ion reported so far after the Beckmann and co-workers' donor free bismuthenium ion, $[(2,6-Mes_2C_6H_3)_2Bi][BAr_4]$ [where Mes = 2,4,6-Mes_2C_6H_2 and Ar = 3,5-(CF_3)_2C_6H_3], stabilized by bulky aryl substituents.^{2a}

An examination of the crystal structure of [12]·Cl indicates that, similar to [4]·2ClO₄ and [5]·2OTf, the coordination geometry of the Bi(III) center is distorted square pyramidal,

Scheme 4. Synthesis of the Diorganobismuthenium Chloride [12]·Cl



taking the lone pair of Bi and N…Bi intramolecular interactions into account (Figure 6a). The Bi(III) ion sits on a crystallographically imposed center of inversion, containing two ppy groups in a trans arrangement. The N…Bi distance of 2.467(5) Å is well within the sum of the van der Waals radii of the two elements $[\Sigma r_{vdw}(N, Bi) = 4.24 \text{ Å}]^9$ indicating the presence of strong N…Bi intramolecular interactions. The \angle C-Bi-C angle of 92.1(3)° is significantly smaller than that observed in $[(2,6-\text{Mes}_2C_6H_3)_2\text{Bi}][BAr_4] [116.69(9)^\circ]$ [where Mes = 2,4,6-Me₃C₆H₂ and Ar = 3,5-(CF₃)₂C₆H₃]² The NBO analysis indicates a strong $lp(N) \rightarrow p(Bi)$ donor-acceptor interaction in $[12]^+$, wherein each interaction contributes to the stability of the compound by $\Delta E = 60.12$ kcal/mol (Figure 6b). The ELF study on $[12]^+$ lends further support to the N \rightarrow Bi interaction, which shows a considerable degree of electron sharing between the N and Bi atoms (Figure 6c). It is noteworthy that, while comparing with the ELF of $[4] \cdot 2ClO_4$ (Figure 2c), the sharing of electrons between N and the element center in [12]·Cl is less, which might be attributed to



Figure 6. (a) Molecular structure of [12]·Cl; thermal ellipsoids are drawn at the 50% probability level. Selected bond distances and angles (Å, deg): C1–Bi 2.292(6), N1···Bi 2.467(5), C1–Bi–Cl' 92.1(3), N1···Bi···N1' 149.5(2), N1···Bi–Cl 71.65(19). (b) Natural bond orbital (NBO) plot of [12]⁺ showing the $lp(N) \rightarrow p(Bi)$ interaction, stabilization energy, $\Delta E = 60.12$ kcal/mol for each N \rightarrow Bi interaction. (c) ELF for [12]⁺ drawing in the plane containing N, Bi, and C atoms.



Figure 7. (a) ESP map, $\rho = 0.001$ au, showing the enhanced σ -hole antipodal to the C–Bi bond in the absence of N \rightarrow Bi intramolecular interactions. (b) ESP of $[12]^+$ showing diminution of the σ -hole region due to the presence of N \rightarrow Bi intramolecular interactions. ESPs have been drawn on the Hirshfeld surface with potential in the range from 0.08 au (red) to 0.115 au (blue). (c) AIM bond topology of $[12]^+$.

the differences in the size of Te^{IV} and Bi^{III} cations. This is further corroborated by the corresponding $N \rightarrow Te$ distance in [4]·2ClO₄ [2.224(2), 2.229(2) Å] and $N \rightarrow Bi$ distance in [12]·Cl [2.467(5) Å] (vide supra).

The ESP studies indicate a significant reduction in the σ hole region due to the presence of N \rightarrow Bi interaction (Figure 7b) in comparison to the model compound, wherein in the absence of N \rightarrow Bi interaction a large σ -hole region antipodal to the C-Bi bond is observed (Figure 7a). The analysis of the topological properties of the N \rightarrow Bi bcp indicates a predominant electrostatic interaction between the two atoms, as suggested by a low electron density, $\rho(r)$, value of 0.059 e Å⁻³, a slightly positive Laplacian of electron density, $\nabla^2_{\rho(r)}$, value of 0.159 e Å⁻³, a positive kinetic energy density over electron density ratio $[G(r)/\rho(r)]$ of 0.800 au, and a total energy density over electron density ratio $[H(r)/\rho(r)]$ of -0.125 au, a value close to 0 (Figure 7c). The predominant electrostatic nature of the N \rightarrow Bi interaction is further corroborated by the "-G(r)/V(r)" value of 0.07.

CONCLUSIONS

In conclusion, we have succeeded in isolating the first examples of robust, IChB stabilized Te analogues of non-NHC derivatives by metathesis reaction of diorganohalotelluronium-(IV) cations with AgClO₄/AgOTf. This novel series of compounds fills the missing link in the period 5 main-group analogues of non-NHC derivatives. The stability of the dicationic Te^{IV} non-NHC derivatives was achieved by exposing the σ -hole around the Te center to the N-lone pair of a rigid and planar pyridylphenyl ring. The active participation of the σ -hole with the lone pair of N-atoms through electrostatic interaction serves the purpose of attenuating the excessive electrophilicity around the Te^{IV} center, which is generally achieved by the strong σ -donating ability of the two N atoms in NHC derivatives. The generality of the phenylpyridyl ring on the stabilization of other main-group non-NHC analogues was further established by synthesizing intramolecular interactions stabilized bismuthenium cation. This is only the second example of this compound class and the first one to contain an intramolecularly coordinated substituent. Given the tremendous interest in NHCs and their analogues over the last few decades, this new family of compounds would be of significant interest with respect to their synthetic utility and reactivity.

EXPERIMENTAL SECTION

All manipulations were performed under a N_2 atmosphere using standard Schlenk techniques. Solvents were dried by following standard methods. The starting materials and solvents were purchased from commercial sources. $(ppy)_2$ Te was synthesized by the reaction of (ppy)HgCl with ppyTeCl₃ followed by the treatment with an excess of hydrazine hydrate.⁸ (ppy)TeCl₃ was synthesized following the reported procedure using (ppy)HgCl and TeCl₄.²¹ (*Caution:* Organomercury compounds are highly toxic. Perchlorate salts with organic ligands are potentially explosive. Adequate precaution should be taken while handling such compounds.) (ppy)Br was synthesized by the treatment of 2-phenylpyridine with $Pd(OAc)_2$ and NBS.²³ ¹H (400 and 500 MHz), ¹³C (100 and 125 MHz), and ¹²⁵Te (126 MHz, 158 MHz) NMR spectra were recorded on Bruker AV 400 MHz and Bruker AV 500 MHz spectrometers at 25 °C. The chemical shifts cited were referenced to TMS (¹H, ¹³C) as internal and Me₂Te (¹²⁵Te) as external standards. Electron spray mass spectra (ESI-MS) were performed on a Q-Tof micro (YA-105) mass spectrometer. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyzer. Infrared spectra were recorded on a PerkinElmer spectrometer.

Synthesis of Compound [3]·I₃. A solution of 2^8 (0.100 g, 0.228 mmol) in dry dichloromethane (15 mL) was cooled to 0 °C. A solution of iodine (0.115 g, 0.456 mmol) in carbon tetrachloride (15 mL) was added dropwise to it. After stirring at 0 °C for 1 h, the reaction mixture was filtered off and the solvent was removed under a vacuum to get a dark red solid of [3]·I₃. Red colored crystals of [3]·I₃ suitable for single-crystal diffraction analysis were obtained by slow evaporation of a chloroform solution of [3]·I₃ at room temperature. Yield 0.176 g (82%); mp 192–194 °C; ¹H NMR (500 MHz,

Yield 0.176 g (82%); mp 192–194 °C; ¹H NMR (500 MHz, DMSO- d_6) δ 9.26 (d, J = 5.6 Hz, 2H), 8.70 (d, J = 8.3 Hz, 2H), 8.57 (d, J = 7.9 Hz, 2H), 8.40 (d, J = 7.8 Hz, 2H), 8.26 (t, J = 7.8 Hz, 2H), 7.69–7.55 (m, 6H); ¹³C NMR (500 MHz, DMSO- d_6) δ 153.66, 143.61, 139.66, 134.21, 132.06, 130.99, 130.95, 127.30, 127.01, 123.67, 122.09; ¹²⁵Te NMR (126 MHz, DMSO- d_6) δ 1100; FT-IR (neat, cm⁻¹) 3051 (w), 1589 (m), 1481 (m), 1459 (w), 1437 (m), 1418 (m), 1301 (m), 1283 (m), 1259 (w), 1156 (m), 1103 (w), 1063 (vw), 1015 (m), 793 (w), 752 (s), 658 (vw), 642 (m), 627 (m); MS(ESI⁺), *m*/*z* Calcd for {3-I}⁺ (C₂₂H₁₆N₂Te), 438.05; Found, 438.07; Anal. Calcd for C₂₂H₁₆I₄N₂Te: C, 28.00, H, 1.71, N, 2.97; Found C, 28.13, H, 1.67, N, 3.09.

Synthesis of [4]·2ClO₄ and [5]·2OTf. To a solution of [3]·I₃ (0.040 g, 0.042 mmol) in acetonitrile (15 mL) was added silver salt [AgClO₄ (0.044 g, 0.211 mmol) for [4]·2ClO₄; AgOTf (0.054 g, 0.211 mmol) for [5]·2OTf]. The reaction mixture was stirred at room temperature for 2 h. This resulted in an off-white precipitate. The precipitate was filtered off. The resulting filtrate on slow evaporation afforded colorless crystalline solids of [4]·2ClO₄ and [5]·2OTf.

[4]·2ClO₄. Yield 0.023 g (88%); mp >300 °C; ¹H NMR (500 MHz, DMSO- d_6) δ 8.58–8.54 (m, 2H), 8.13 (dd, J = 11.8, 7.8 Hz, 4H), 7.97 (t, J = 7.0 Hz, 2H), 7.65–7.61 (m, 2H), 7.49 (dd, J = 10.8, 5.8 Hz, 2H), 7.42 (ddd, J = 15.0, 10.3, 4.3 Hz, 4H); ¹³C NMR (125 MHz, DMSO- d_6) δ 156.57, 150.35, 148.53, 141.95, 139.05, 138.48, 129.94, 128.79, 127.81, 124.10, 121.66; ¹²⁵Te NMR (126 MHz, DMSO- d_6) δ 1107; FT-IR (neat, cm⁻¹) 3064 (vw), 2922 (vw), 1606 (m), 1486 (w), 1463 (w), 1443 (w), 1309 (w), 1293 (vw), 1139 (s), 1112 (s), 1089 (s), 761 (m), 739 (w), 634 (m), 626 (m); MS(ESI⁺), *m/z* Calcd for {[4]ClO₄ + H}⁺ (C₂₂H₁₇ClN₂O₄Te), 537.97; Found, 537.98; Anal. Calcd for C₂₂H₁₆Cl₂N₂O₈Te: C, 41.62; H, 2.54; N, 4.41; Found C, 41.87; H, 2.22; N, 4.56.

[5]-207f. Yield 0.028 g (90%); mp >300 °C; ¹H NMR (500 MHz, DMSO- d_6) δ 8.59–8.55 (m, 2H), 8.15–8.08 (m, 4H), 7.98–7.93 (m, 2H), 7.64 (dd, J = 7.1, 1.2 Hz, 2H), 7.51–7.47 (m, 2H), 7.46–7.38 (m, 4H); ¹³C NMR (125 MHz, DMSO- d_6) δ 156.56, 150.35, 148.54, 141.95, 139.03, 138.49, 129.93, 128.79, 127.80, 124.09, 121.64; ¹²⁵Te NMR (126 MHz, DMSO- d_6) δ 1114; FT-IR (neat, cm⁻¹) 3054 (m), 3027 (m), 1600 (s), 1590 (s), 1483 (m), 1463 (m), 1438 (m), 1424 (m), 1306 (m), 1288 (m), 1261 (vw), 1171 (w), 1158 (w), 1105 (w), 1017 (m), 887 (w), 797 (w), 759 (s), 736 (m), 628 (m), 465 (m); MS(ESI⁺), *m*/*z* Calcd for {[5]OTf + H}⁺ (C₂₃H₁₇F₃N₂O₃STe), 587.99; Found, 587.96; Anal. Calcd for C₂₄H₁₆F₆N₂O₆S₂Te: C, 39.27; H, 2.20; N, 3.82; Found C, 39.41; H, 2.17; N, 4.16.

Synthesis of Compound [8]·2ClO₄. To a solution of 6^{21} (0.200 g, 0.514 mmol) in acetonitrile (15 mL) was added AgClO₄ (0.319 g, 1.542 mmol). The reaction mixture was stirred at room temperature for 2 h. This resulted in an off-white precipitate. The precipitate was filtered off. The resulting filtrate on slow evaporation at room temperature afforded a colorless crystalline solid of [8]·2ClO₄.

Yield 0.304 g (74%); mp >300 °C; ¹H NMR (500 MHz, DMSOd₆) δ 8.57 (d, J = 4.1 Hz, 2H), 8.12 (dd, J = 11.0, 8.0 Hz, 4H), 7.96 (td, J = 7.8, 1.6 Hz, 2H), 7.64 (d, J = 6.9 Hz, 2H), 7.49 (dd, J = 6.8, 5.1 Hz, 2H), 7.46–7.38 (m, 4H); ¹³C NMR (125 MHz, DMSO-d₆) δ 156.02, 149.80, 147.99, 141.40, 138.48, 137.94, 129.39, 128.24, 127.25, 123.54, 121.09; ¹²⁵Te NMR (157 MHz, DMSO-d₆) δ 1413; FT-IR (neat, cm⁻¹) 3077 (vw), 2918 (vw), 1603 (w), 1444 (s), 1308 (vw), 1141 (s), 1089 (s), 1053 (s), 914 (vw), 876 (m), 764 (m), 736 (w), 654 (w), 632 (m), 622 (m), 539 (vw), 498 (w); MS(ESI⁺), *m/z* Calcd for $\{[8]CIO_4\}^+$ ($C_{22}H_{16}CI_2N_2O_{10}Te_2$: C, 33.26, H, 2.03, N, 3.53; Found C, 33.07, H, 1.93, N, 3.71.

Synthesis of Compound [10]·Br. A stirred solution of 9^{23} (0.150 g, 0.643 mmol) in dry Et₂O (25 mL) was treated dropwise with 1.6 M solution of *n*-BuLi in hexane (0.482 mL, 0.772 mmol) at -78 °C for 30 min. An Et₂O (20 mL) solution of TeCl₄ (0.043 g, 0.160 mmol) was added to the reaction mixture at -78 °C. The reaction mixture was stirred for 14 h at room temperature. After completion of the reaction, the solvent was removed under a vacuum to get a light yellow solid, which is the mixture of [10]·Br and (ppy)₂Te. Dichloromethane (20 mL) was added to the solid, and the resulting reaction mixture was filtered through Celite. The filtrate was concentrated under a vacuum and washed with Et₂O (3 × 15 mL) which removed (ppy)₂Te, and this afforded the analytically pure solid of [10]·Br. Light yellow crystals of [10]·Br-2CHCl₃ suitable for single-crystal diffraction analysis were obtained by slow diffusion of hexane into CHCl₃ solution of [10]·Br.

Yield 0.284 g (66%); mp 156 °C; ¹H NMR (500 MHz, C₆D₆) δ 8.80 (dd, J = 7.9, 1.0 Hz, 3H), 8.41 (ddd, J = 4.9, 1.6, 0.9 Hz, 3H), 7.46 (dd, J = 7.8, 1.3 Hz, 3H), 7.27 (d, J = 8.2 Hz, 3H), 7.05–6.98 (m, 6H), 6.84 (td, J = 8.0, 1.4 Hz, 3H), 6.54 (ddd, J = 7.4, 4.9, 0.9 Hz, 3H); ¹³C NMR (125 MHz, C₆D₆) δ 156.81, 146.48, 141.35, 139.59, 137.07, 130.35, 127.53, 127.38, 122.52, 120.72, 112.75; ¹²⁵Te NMR (157 MHz, CDCl₃) δ 867; FT-IR (neat, cm⁻¹) 3051 (m), 1589 (s), 1476 (m), 1464 (m), 1434 (s), 1300 (m), 1157 (m), 1098 (m), 1071 (w), 1015 (w), 999 (m), 895 (w), 797 (m), 757 (s), 627 (m), 590 (w); MS(ESI⁺), m/z Calcd for [10]⁺ (C₃₃H₂₄N₃Te), 592.11; Found, 592.10; Anal. Calcd for C₃₃H₂₄BrN₃Te: C, 59.15, H, 3.61, N, 6.27; Found C, 58.97, H, 3.54, N, 6.39.

Synthesis of Compound 11. To a THF solution of [10]·Br (0.075 g, 0.118 mmol) was added a THF solution of K₂PdCl₄ (0.036 g, 0.112 mmol) at room temperature. The reaction mixture was stirred for 12 h. The solvent was removed under a vacuum to get a yellow solid. The solid was washed with CHCl₃ (3 × 15 mL) and Et₂O (3 × 15 mL) to afford the analytically pure solid of 11. Yellow crystals of 11 suitable for single-crystal diffraction analysis were obtained by slow diffusion of benzene into a DMSO solution of 11 at room temperature.

Yield 0.073 g (82%); mp 191 °C; ¹H NMR (400 MHz, DMSO- d_6) δ 9.27 (d, J = 5.6 Hz, 1H), 8.70 (d, J = 8.3 Hz, 1H), 8.60–8.54 (m, 2H), 8.40 (d, J = 8.0 Hz, 1H), 8.30–8.22 (m, 1H), 8.14 (dd, J = 12.7, 4.9 Hz, 2H), 8.00–7.94 (m, 1H), 7.69–7.56 (m, 4H), 7.50 (ddd, J = 7.4, 4.8, 1.0 Hz, 1H), 7.43 (dtd, J = 16.6, 7.3, 1.5 Hz, 2H); ¹³C NMR (400 MHz, DMSO- d_6) δ 156.49, 154.16, 148.38, 144.11, 141.95, 140.17, 139.03, 138.35, 134.71, 132.55, 131.45, 129.93, 128.72, 127.80, 127.74, 127.51, 124.17, 124.09, 122.60, 121.55; ¹²⁵Te NMR (400 MHz, DMSO- d_6) δ 1309; FT-IR (neat, cm⁻¹) 3061 (w), 2922 (s), 2852 (s), 1600 (m), 1578 (m), 1485 (w), 1466 (vw), 1439 (w), 1422 (w), 1304 (w), 1288 (w), 1273 (w), 1156 (w), 1017 (w), 790 (w), 757 (s), 739 (m), 661 (vw), 630 (w); MS(ESI⁺), m/z Calcd for [11-{(ppy)PdCl₂}]⁺ (C₂₂H₁₆ClN₂Te), 473.01; Found, 473.03.

Synthesis of [12]·Cl. A stirred solution of 9^{23} (0.100 g, 0.429 mmol) in dry Et₂O (20 mL) was treated dropwise with 1.6 M solution of *n*-BuLi in hexane (0.322 mL, 0.515 mmol) at -78 °C for 30 min. BiCl₃ (0.067 g, 0.212 mmol) was added to the reaction mixture and was stirred for 8 h. After completion of the reaction, the solvent was removed under a vacuum to get a white solid. Dichloromethane (20 mL) was added to the solid, and the resulting reaction mixture was filtered through Celite. The filtrate was concentrated under a vacuum to afford the analytically pure solid of [12]·Cl. Colorless crystals of

[12]·Cl suitable for single-crystal diffraction analysis were obtained by slow evaporation of a methanol solution of [12]·Cl at room temperature.

Ýield 0.169 g (71%); mp >300 °C; ¹H NMR (500 MHz, DMSOd₆) δ 8.99 (d, J = 4.7 Hz, 2H), 8.43 (d, J = 7.6 Hz, 2H), 8.38 (d, J = 8.2 Hz, 2H), 8.25 (t, J = 7.3 Hz, 2H), 7.90 (d, J = 7.2 Hz, 2H), 7.73– 7.69 (m, 2H), 7.52 (dt, J = 22.9, 7.0 Hz, 4H); ¹³C NMR (125 MHz, DMSO- d_6) δ 186.96, 161.65, 149.07, 145.28, 141.13, 138.19, 133.70, 130.15, 128.64, 124.67, 122.94; FT-IR (neat, cm⁻¹) 3051 (m), 3013 (m), 1625 (vw), 1594 (m), 1479 (m), 1420 (m), 1277 (vw), 1246 (vw), 1153 (w), 1102 (w), 1014 (m), 1000 (w), 902 (vw), 846 (vw), 805 (w), 761 (s), 737 (m), 729 (m), 635 (w), 553 (w); MS(ESI⁺), m/z Calcd for [12]⁺ (C₂₂H₁₆BiN₂), 517.11; Found, 517.13; Anal. Calcd for C₂₂H₁₆BiClN₂: C, 47.80; H, 2.92; N, 5.07; Found C, 47.56; H, 2.87; N, 5.26.

X-ray Crystallographic Study. The diffraction measurements for compounds [3]·I₃–[5]·20Tf and [8]·2ClO₄–[12]·Cl were performed on a Rigaku Saturn 724 diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.7107$ Å). The data collection was carried out by the standard ω -scan technique, and the data were evaluated and reduced by using *CrystalClear-SM* Expert software. The structures were determined by routine heavy-atom techniques using SHELXS-97²⁶ and Fourier methods and were refined by full-matrix least-squares with the anisotropic non-hydrogen atoms and hydrogen atoms with a fixed isotropic thermal parameter of 0.07 Å² using the SHELXL-97 program.²⁷ SQUEEZE was applied to the disordered solvent molecules in [10]·Br by using the PLATON program.²⁸

Computational Methodology. DFT calculations were carried out using the Gaussian 0.9 (rev D.02) program¹⁰ (functional: B3PW91;¹¹ mixed basis set: Te, SDB-cc-pVTZ;¹² C/H/N/O, 6-31G**;¹³ Bi, cc-pVTZ-PP¹⁴). Frequency calculations were calculated, and all of the structures were detected with minima such that no negative frequencies were observed. The topological analyses were carried out using Multiwfn software.²⁹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00698.

Spectroscopic data, crystallographic parameters, and packing diagrams for $[4] \cdot 2ClO_4$ and $[12] \cdot Cl$ (PDF) Cartesian coordinates for $[4] \cdot 2ClO_4$ and $[12] \cdot Cl$ (XYZ)

Accession Codes

CCDC 1949046–1949052 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 Authors

- Glen B. Deacon IITB-Monash Research Academy, Mumbai, India, and Monash University, Clayton, Australia; Email: glen.deacon@monash.edu
- Harkesh B. Singh Indian Institute of Technology Bombay, Mumbai, India, and IITB-Monash Research Academy, Mumbai, India; orcid.org/0000-0002-0403-0149; Email: chhbsia@chem.iitb.ac.in

Other Authors

Rajesh Deka – Indian Institute of Technology Bombay, Mumbai, India, IITB-Monash Research Academy, Mumbai, India, and Monash University, Clayton, Australia

Arup Sarkar – Indian Institute of Technology Bombay, Mumbai, India

Ray J. Butcher – Howard University, Washington, DC

Peter C. Junk – IITB-Monash Research Academy, Mumbai, India, and James Cook University, Townsville,

Australia; orcid.org/0000-0002-0683-8918 **David R. Turner** – IITB-Monash Research Academy, Mumbai, India, and Monash University, Clayton, Australia; orcid.org/0000-0003-1603-7994

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.9b00698

Notes

The authors declare no competing financial interest.

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