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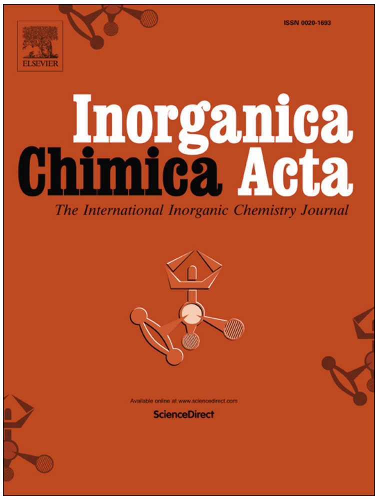

Research paper

Synthesis of N-heterocyclic nitrenium (NHN) ions and related donor systems: Coordination with d^{10}-metal ions

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Synthesis of N-heterocyclic nitrenium (NHN) ions and related donor systems: Coordination with d^{10}-metal ions

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Keyword

N-heterocyclic carbene, nitrenium ion, pincer ligand, selone, tellurium

Abstract

The synthesis of three new NNN- and CNC type N-heterocyclic nitrenium (NHN) ion based pincer ligands is reported from 1,3-di-(2´-bromoethyl)-triazolium bromide (**5**). The reaction of **5** with ammonium hexafluorophosphate followed by two equivalent of pyrrolidine/diethylamine afforded NHN ions (**10a** and **10b**). The reaction of **5** with N-butylbenzimidazole (**6**) afforded nitrenium ion **7**, where the chelating arms have benzimidazole based carbene carbons. In an attempt to synthesize hybrid NHN ligand containing soft tellurium donor in the chelating arm, 1-(2´-bromoethyl)-benzotriazole, was first reacted with *in situ* generated NaTePh to afford tellurated benzotriazol (**13**). However, when compound **13** was treated with methyl iodide, an unexpected methylation underwent at tellurium center to afford compound **14**. Reaction of **7** with $Hg(OAc)_2$ and **10a** with CuI afforded complex **8** and **11** respectively. Both these complexes are characterized by NMR (^1H, ^{13}C), HRMS and CHN analysis. The Natural Bond Order (NBO) calculations and Atoms in Molecules (AIM) analyses sufficiently substantiate the presence of interaction between triazolium N atom with metal centre. The reaction of N,N´-disubstituted benzimidazoles, **17a-17b** with *in situ* generated Na_2Se_2 in the presence of potassium *tert*-butoxide at room temperature afforded two novel benzimidazoline-2-chalcogenones (**18a** and **18b**). Nitrenium ion (**10a-10b**), tellurated benzotriazole (**13** and **14**) and selone **18a** are authenticated by single crystal X-ray diffraction studies.

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Introduction

Carbenes, after the pioneering work by Wanzlick[1] and successful isolation of the first stable N-heterocyclic carbene (NHC) by Arduengo,[2] have garnered significant attention and become an important class of compounds with respect to their intriguing and uncommon bonding and structural properties.[3] Carbenes are defined as neutral compounds containing a divalent carbon atom with a six-electron valence shell, which consequently make them highly reactive in nature. With their unambiguous role as ancillary ligands for complexation with metals, the coordination chemistry of carbenes and their reactivity have reached enviable position across many fields of organic and organometallic chemistry.[4] The extraordinarily expanded portfolio displayed by NHC motivated the researchers to urge for the exploration of its isovalent analogous forms. Consequently, main-group carbene analogues, like NHC, have flourished in almost all aspects of organometallic chemistry and they have been ubiquitously used in various metal based chemistry.[5] In both NHC and main-group carbene analogues, it possess one lone pair of electron which can take part in σ-bonding during coordination with metal (Figure 1a). At the same time, empty *p*-orbital in carbenoid center can accept electron from the metal (Figure 1b).

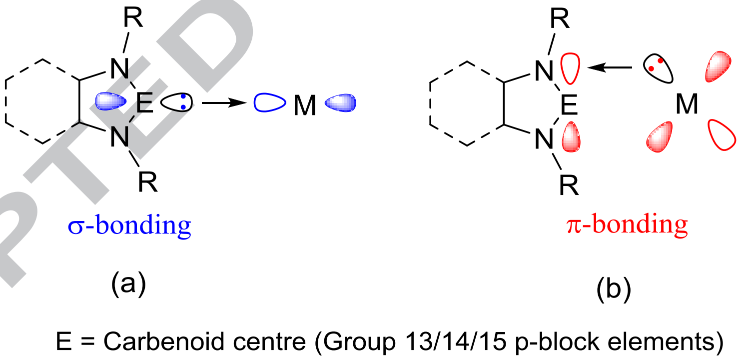

Figure 1. Bonding picture of NHC and analogues with metals

However, despite close analogy, the nitrogen analogue of NHC, known as N-heterocyclic nitrenium (NHN) ion and their metal complexes remained elusive for a long time and are still not well-explored.[6] The main stumbling block of NHN as a ligand is the presence of positive charge at the periphery *i.e.* triazolium ion, which in turn offers poor coordination to the metal center. Although not prevalent, there is limited literature available which deals with the ligation of cationic ligand to a transition metal.[7] In these complexes, the bonding between the metals and

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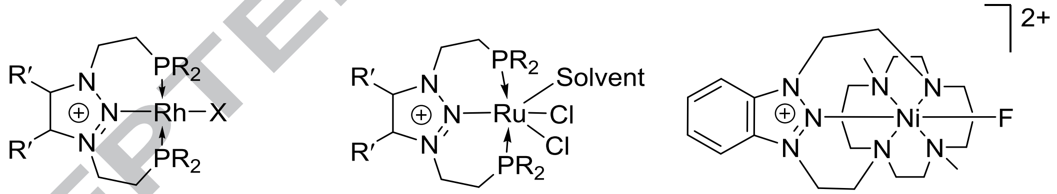
ligands can be best explained by solely considering the metal to ligand *π*-back donation ($M\rightarrow L^*$) (Figure 1b) in to account. However, in the case of NHN, the weaker *π*-acceptor ability of cationic N atom makes this kind of bonding theoretically less feasible. Gandelman *et al.* in 2011,[8] pioneered the coordination chemistry of NHN by reporting Rh(I) and Ru(II) complexes, **1**-**3** (Chart 1) of nitrenium ion-based PNP-pincer ligand wherein they have incorporated two phosphine chelating arms to a triazolium ring, which eventually bring the metal close to the nitrogen center, thus allowing the otherwise unconventional coordination mode possible. Subsequently, they have expanded the coordination chemistry of nitrenium ions to Pd, Pt, Mo and Ag metals.[9] From the Density Functional Theory (DFT) calculations, they inferred that the nitrenium ions are relatively weak σ-donors and reasonably π-acceptor. Ray and co-workers[10] have studied the redox properties of nickel(I) complex of nitrenium ion, **4**. Interestingly, in the complex they have observed a bent coordination mode of the nitrenium ion to the Ni(I) center, similar to a nitrosyl ion. This is caused by the presence of a nonbonding electron pair in the sp^2 hybrid orbital of nitrenium nitrogen. While still in its infancy, the novel chemistry of nitrenium ion sincerely demands design and development of new ligand family to get detail insight into their unusual bonding facets with metals and probable applications in contemporary coordination chemistry.



1 R′ = -CHCH-, R = Ph, X = Cl

2 R′ = H, R = *i*-Pr
3 R′ = -CHCH-, R = Ph

4

Chart 1. Examples of nitrenium ions and their coordination complexes.

As it is abundantly clear that most of the literature reports on coordination chemistry of nitrenium ions are based on PNP-type ligands and variation of nitrenium ion based ligands are rather scarce. In this context, we have envisaged to develop new NNN, CNC- type NHN ligands which contain, in particular, pyrrole, N,N-dimethylamine, imidazole based carbenes as auxiliary arms. We have further attempted to explore the ligation behavior of the synthesized nitrenium ions with transition metal, in particular with d^{10} metal precursors (*vide infra*). While trying to

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synthesize ‘hybrid’ NHN ligand where the auxiliary arms contain soft donor atom such as tellurium, the reaction did not proceed as desired and resulted in unexpected ternization at tellurium center (*vide infra*).

Like other carbene analogues/derivatives, the group 16 (chalcogens) derivatives of NHC, commonly known as chalcogenones (Chart 2), have also gained significant attention in complementary organometallic chemistry. The first chalcogenone, benzimidazolin-2-selone was reported by Warner in 1963 by reacting *o*-phenylenediamine with carbon diselenide.[11a] The corresponding sulphur analogues (thiones) and tellurium analogues (tellones) were introduced by Ansell *et al*. and Arduengo *et al*. respectively.[11b-c] Similar to parent NHCs, the corresponding chalcogen adducts are also expected to contribute to the metal-selenium bond by their both σ-donating as well as π-acceptor properties. Ganter *et al*. have recently incorporated ^{77}Se NMR spectroscopy as an efficient method for the assessment of the π-acceptor strength of selones.[11d] By covering a wide range of ^{77}Se chemical shifts of a series of selone derivatives, they have reported that with an increase of π-acidity led to the downfield shifts of the ^{77}Se NMR signals. It is worth mentioning that, with various modified synthetic protocols and with their interesting bonding properties and versatile reactivity, selones have become an important ancillary ligand in metal based chemistry with respect to their catalysis, antithyroid activity, demercuration activity, and sensing toward transition metal ions.[11e-r]

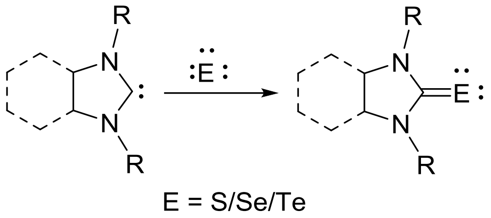

Chart 2. Group 16 adducts of NHC.

Our group has long standing interest on the coordination chemistry and reactivity of selones.[12] In a recent development, we have synthesized a series of selone metal complexes and demonstrated that these complexes could act as excellent transmetallating agent with stronger σ-donating ligands like phosphines.[12j] As an extension of our previous work on selones, this article also features the synthesis of two new selone based pincer compounds.

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Results and Discussion

In order to synthesize the NHN based pincer ligands, N, N´-disubstituted benzotriazolium bromide salt, **5** was first prepared from benzotriazole by following the reported procedure.[8] Synthesis of **5** involved multi-step reaction sequences. In detail, benzotriazole was first treated with potassium *tert*-butoxide to afford potassium benzotriaazolate. In subsequent steps, potassium benzotriaazolate was treated with two equivalents of 2-bromoethanol followed by the reaction with HBr in presence of acetic acid to afford 1,3-di-(2´-bromoethyl)-triazolium bromide, **5**. When compound **5** was treated with N-butylbenzimidazole, **6** (synthesized by the reaction of benzimidazole with *n*-butyl bromide in presence of 30% NaOH and TBAB),[12a] it resulted in the formation of the desired NHN-based pincer ligand **7**, where the chelating arms were benzimidazole based carbenes (Scheme 1). When the free NHN ligand **7** was treated with mercuric acetate [$Hg(OAc)_2$], it resulted in the isolation of metal complex **8**. From the optimized geometry (Figure S1, Supporting Information), it was observed that there is no interaction between the nitrenium ion and Hg centre (*vide infra*). It is probably due to the large size of the chelating ring. In an attempt to synthesize NHN ligands which can form six-membered chelating ring after metalation compound **5** was first treated with ammonium hexafluorophosphate to give compound **9**. Compound **9** was then treated with pyrrolidine/dimethylamine to afford NHN derivatives **10a** and **10b**. To explore the coordination chemistry of synthesized NHN pincer ligand with transition metals, compound **10** was reacted with equimolar amount of copper(I) iodide in dry dichloromethane. This immediately yielded a precipitate of compound **11**. Quantum chemical computations confirmed the coordination between nitrenium ion and Cu metal centre in complex **11** (*vide infra*).

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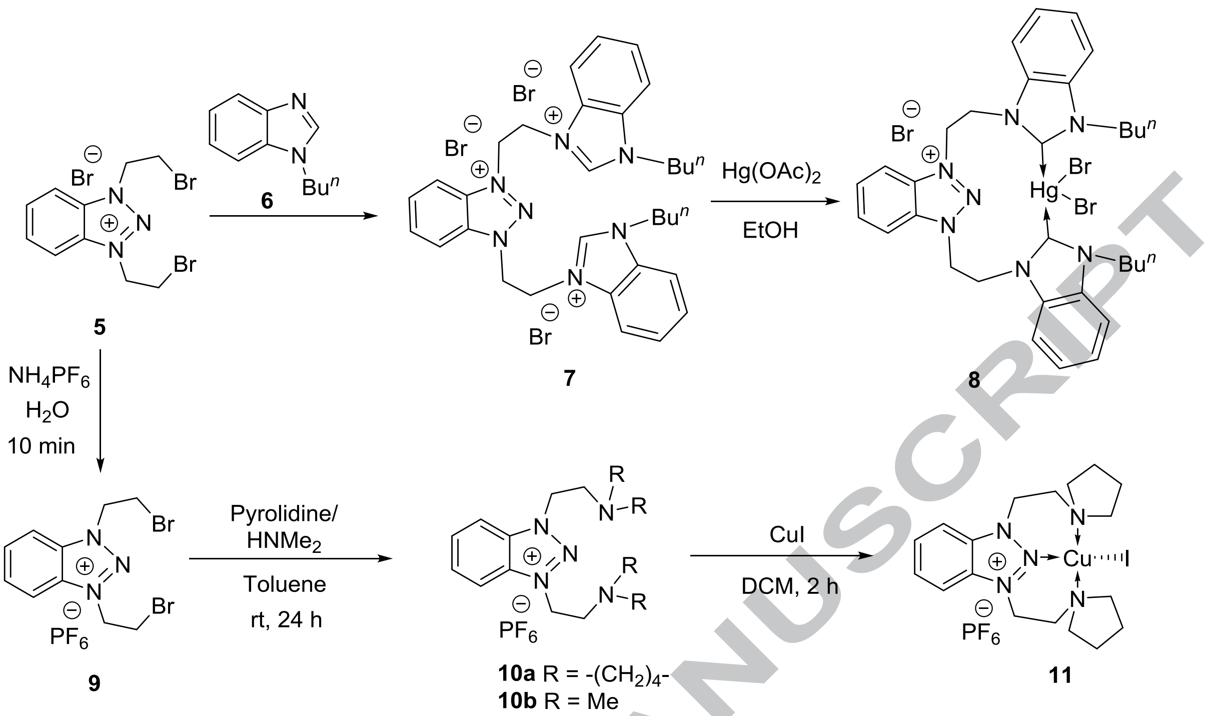

Scheme 1. Synthesis of nitrenium ion based pincer ligands and complexes.

In the ^{1}H NMR spectrum of compound **7**, the singlet resonance at 9.37 ppm corresponded to the two carbene protons. The two multiplets observed in the aromatic region corresponded to the four benzotriazole protons and eight benzimidazole protons. The two signals observed at 5.61 and 5.27 ppm could be assigned to methylene spacers (-CH$_2$-CH$_2$-) spacer between benzotriazole and benzimidazole rings. The four signals for *n*-butyl group were observed in the expected aliphatic region. In ^{1}H NMR spectrum of compound **8**, the disappearance of characteristic signal for carbene proton at 9.37 ppm indicated the ligation of the free ligand **7** with the metal. The signal for carbene carbon appeared at 141.38 ppm in ^{13}C NMR spectrum of compound **7**. A slight downfield shift (142.96 ppm) was observed in the ^{13}C NMR spectrum of compound **8** which might be due to the de-shielding effect caused by the *σ*-donation from the carbene carbon to the metal center. The C$\underline{H}_2$ protons attached to nitrenium moiety did not show any change in chemical shifts for ligand **7** as well as its metal complex **8** (5.61 ppm for **7** and 5.62 ppm for **8**). However, a considerable downfield shift was observed in the chemical shift for C$\underline{H}_2$ attached to the carbene moiety of complex **8** (5.50 ppm) as compared to the free ligand, **7** (5.27 ppm). In the ^{1}H NMR spectra of compound **10a** and **10b**, two sets of peaks were observed in the aromatic region corresponding to the benzotriazole ring protons. The chemical shifts at 5.00 ppm and 3.18

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ppm for compound **10a** could be assigned to the methylene spacers. The corresponding chemical shifts for compound **10b** were observed at 5.41 ppm and 3.99 ppm respectively. For compound **10a**, the pyrrolidine protons showed two resonances at 2.53 ppm and 1.67 ppm. The corresponding –$NC\underline{H}_3$ protons for compound **10b** were observed as a single resonance at 2.94 ppm. In compounds **10a** and **10b**, the anionic *entity* i.e., the potassium hexafluorophosphate (PF_6^-) ion showed two set of ^{19}F NMR resonances at (-71.31, -72.82 ppm) and (-72.03, -73.54 pp) respectively. The corresponding ^{31}P NMR resonance showed a septet centered at -141.16 and -144.64 ppm respectively. In the ^1H NMR spectrum of metal complex **11**, all the signal appeared broad, which might be attributed to the coordination of the ligand to the metal. All the aliphatic protons showed considerable downfield shift (5.33, 3.55, 2.94 and 1.78 ppm) as compared to free ligand **10a** (5.00, 3.18, 2.53 and 1.67 ppm). The ^{19}F NMR spectrum for complex **11**, PF_6^- ion showed resonance at -69.21 and -71.10 ppm. The corresponding ^{31}P NMR resonance showed a septet centered at -144.24 ppm.

The identity of the new ligands and the corresponding metal complexes could be established by High Resolution Electrospray Ionization Mass Spectrometry (HRMS). In the mass spectra, taken in the positive ion mode, the molecular ion peaks at *m*/z 173.6139 ($[M\text{-}3Br]^{3+}$) (**7**), 882.1231 (Calc. 882.1235 $[M\text{-}Br]^+$) (**8**), 314.2339 (Calc. 314.2339 $[M\text{-}PF_6]^+$), (**10a**) 262.2027 (Calc. 262.2027 $[M\text{-}PF_6]^+$), (**10b**), 504.0684 (Calc. 504.0680 $[M\text{-}PF_6]^+$), (**11**) substantiated the formation of the respective compounds. It is worth mentioning that the observed patterns in HRMS for the compounds were in agreement with the simulated isotopic patterns.

In an attempt to synthesize hybrid NHN ligand where the chelating arm contained soft Te donor, benzotriazole was treated with 1,2-dibromoethane in presence of NaOH and TBAB to afford 1-(2´-bromoethyl)-benzotriazole, **12**. Compound **12** on reaction with *in situ* generated NaTePh afforded tellurated benzotriazol, **13** (Scheme 2). To synthesize NHN ligand, when the second N-alkylation of compound **13** was attempted with methyliodide, an unexpected ternisation takes place at tellurium center to afford compound **14** instead of expected hybrid NHN pincer ligand.

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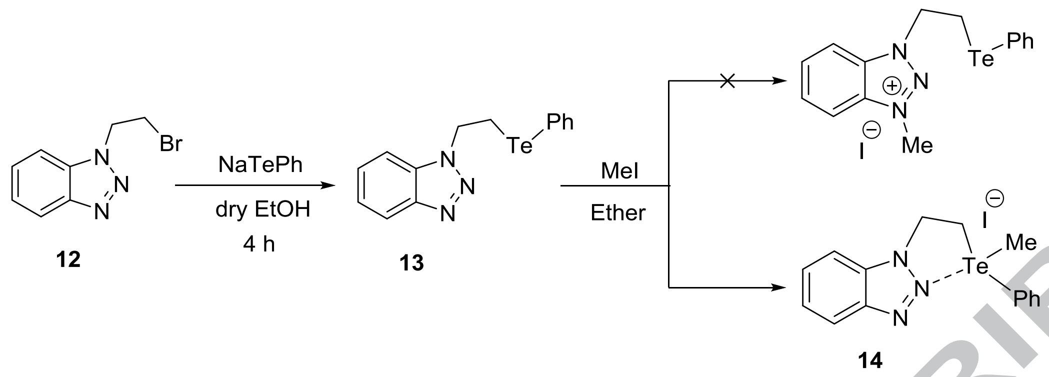

Scheme 2. Attempted synthesis of Te containing hybrid, NHN based pincer ligand and synthesis of tellurated benzotriazole derivatives, **13** and **14**.

In the ^{1}H NMR spectra of compounds **13** and **14**, the chemical shifts were in agreement with the expected values. In detail, the chemical shifts for the benzotriazole ring protons and phenyl protons for both the compounds appeared in the region 8-7 ppm. For compound **13**, the methylene protons showed resonances at 4.95 and 3.36 ppm respectively. The corresponding signals for compound **14** were observed at 5.01 and 3.42 ppm respectively. The methyl protons for compound **14** showed resonance at 2.18 ppm. In ^{13}C NMR spectrum of compound **13**, tellurium satellites are observed for $CH_2\underline{C}H_2Te$ at 6.54 and 5.13 ppm ($^2J_{C\text{-}Te}$ = 705 Hz). The ^{125}Te NMR (proton coupled) spectrum for **13** showed a triplet at 483.9 ppm ($^3J_{Te\text{-}H}$ = 95 Hz) because of the coupling with neighboring $-CH_2-$ protons. In the ^{13}C NMR spectrum of **14**, a highly shielded resonance was observed at -22.84 ppm corresponding to Te-$\underline{C}H_3$. The ^{125}Te NMR signal for compound **14** is significantly downfield shifted than that of compound **13** and appeared at 606.3 ppm due to the presence of positive charge on the tellurium atom. In the HRMS spectrum of compound **13**, the molecular ion peak observed at *m*/z 376.0062 corresponded to $[M+Na]^+$ species (Calc. 376.0064). In the HRMS spectrum of compound **14**, the molecular ion peak observed at *m*/z 368.0405 corresponded to the $[M-I]^+$ species (Calc. 368.0402).

X-ray Crystallographic Studies

The molecular structure of **10a** is shown in figure 2(a). The asymmetric unit contains two molecules of **10a** with one additional water of crystallization. Out of the two molecules present in the asymmetric units, one of the pyrroldine nitrogen atoms of one molecule undergoes protonation while other nitrogen atoms are unaffected. The protonation might be occurred due to the presence of traces of HBr from the previous reaction step. The molecule with protonated

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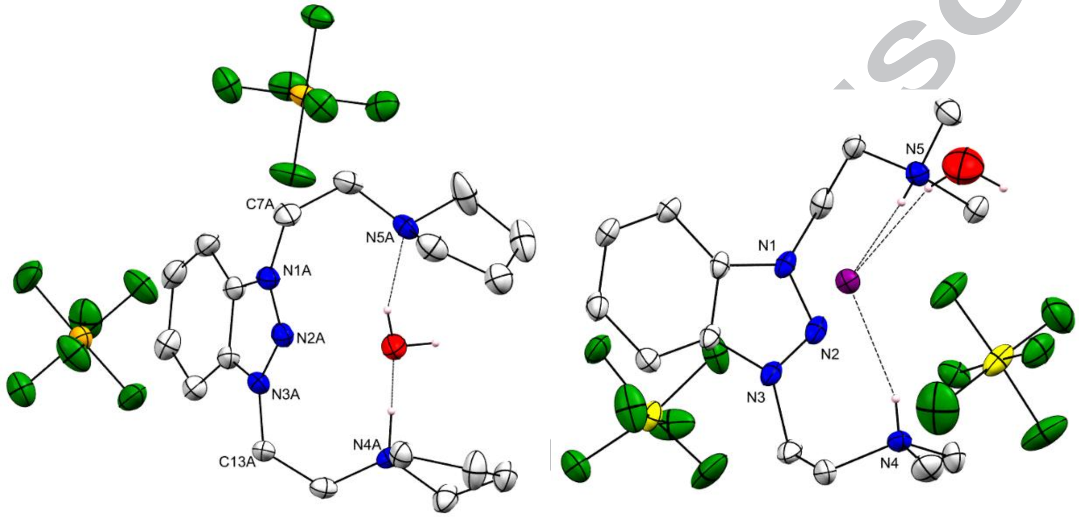
pyrrolidine side arm has been considered here for discussion. In the molecular structure of **10a**, the benzotriazole ring and two the methylene carbons attached to the triazole nitrogen atoms reside in the same plane. Interestingly, the molecule adopts a conformation in which the two flanking arms are directed in the same direction with respect to the central benzotriazoline ring. A water molecule was observed to be trapped between both the flanking arms wherein the one of its H-atoms was involved in H-bonding to one of the pyrrolidine N-atom with a distance of 1.999 Å. At the same time, oxygen atom is involved in hydrogen bonding with N4A-<u>H</u> hydrogen with a distance of 1.769 Å.



(a) (b)

Figure 2. ORTEP diagrams of (a) compound **10a** and (b) compound **10b** plotted with 50% probability thermal ellipsoids.

The molecular structure of compound **10b** is shown in Figure 2(b). The molecular structure of **10b** is similar to **10a** with respect to the orientation of the flanking arms around the central plane. However, both the amine nitrogen atoms from the side arms undergo protonation and the total of three positive charges on the molecule are balanced by one bromide and two hexafluorophospate counter anions. Like compound **10a**, there is also a water of crystallisation present in compound **10b**. The bromide ion is involved in hydrogen bonding to both -N-<u>H</u> atoms of the side arms with distance of 2.489 Å (N4-<u>H</u>···Br) and 2.425 Å (N5-<u>H</u>···Br). Again, the bromide ion is also involved in hydrogen bonding with one of the hydrogen atoms of the water molecule with a distance of 2.616Å.

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The ORTEP views of compounds **13** and **14** are shown in Fig 3(a) and Fig 3(b) respectively. Like the previous two compounds, in the molecular structures of **13** and **14**, the benzotriazole ring and the methylene carbon from the side arm are positioned in the same plane. In compound **13**, the geoemtry around Te center is V-shaped with C8-Te1-C9 bond angle of 92.6(2)°. The Te-C9 bond distance is 2.124(6) Å, which is significantly shorter than the Te-C8 bond distance of 2.153(4) Å. Both these distnaces are in good agreement with related compound, namely 1-(4-methoxyphenyltelluromethyl)-1*H*-benzotriazole[Te-C(aryl) = 2.117(3)Å; Te-C(alkyl) = 2.159(3) Å].[13] In case of compound **14**, the geometry around Te atom is distorted trigonal pyramidal with C8-Te1-C15, C8-Te1-C9 and C15-Te1-C9 bond angle of 90.79(13)°, 97.67(13)° and 97.05(12)° repectively. The Te-C9 bond distance is 2.129(3) Å, whereas the Te-C8 bond distance is 2.165(3) Å. Both distances are comparable with the corresponding distances observed in **13**. The Te1-C15 distance is observed to be 2.137(3) Å. Interestingly, in compound **14**, two week interactions from Te center; one intramolecular interactions with triazolium nitrogen, N2 with Te1···N2 distance of 2.919(3) Å and one intermolecular interaction with iodide anion with Te1···I1 distance of 3.5010(4) Å, are observed.

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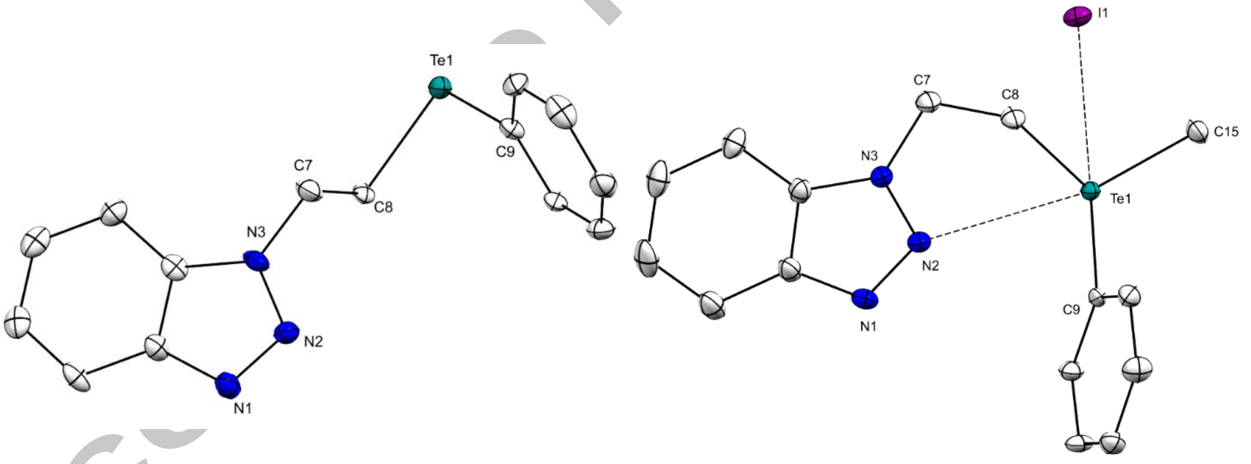

(a) **(b)**

Figure 3. ORTEP diagram of (a) compound **13** and (b) compound **14** plotted with 50% probability thermal ellipsoids.

Computational Studies

Since single crystals could not be obtained for the complexes of nitrenium ions, to get a better understanding of the nature of the nitrenium ion-metal bond, electronic structure calculations

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have been carried out using Gaussian09 package[14] by employing DFT method. Geometry optimizations were carried out using MPW1PW91 method,[15] 6-311g(d)[16] basis set for C, H, N, Br, P, F and Se, Lanl2dz[17] basis set for Hg and TZVP[18] basis set for Cu. In the optimized structure of compound **8**, the carbene to mercury coordination is observed, however, there is no interaction between nitrenium ion and Hg centre (Figure S1, Supporting Information). In the optimized structure of compound **11**, N8-Cu, N12-Cu and N15-Cu bond lengths are 2.17920, 2.19028 and 2.19989 Å respectively, which are shorter than the sum of covalent radii of copper (1.52 Å) and nitrogen (0.68 Å). It indicates that there is a proper coordination between nitrenium ion and copper metal center (N→Cu) (Figure 4a). To further support the presence of N→Cu bond, Atom in Molecule (AIM) analysis was carried out by using AIM2000[19] on the wave function file generated from Gaussian09. Topological properties of electron density at the N···M bond critical point (*bcp*) were investigated using Bader's theory of atoms in molecule (AIM) as implemented in AIM2000 package. Distinct bond critical points associated with N-M interaction were identified in all compounds, thus indicating the presence of N-M interaction. The parameters obtained from AIM are in full agreement with those obtained from NBO analysis.[20] The values of bond critical point (ρ), Laplacian (∇^2) and total energy density (*H*) and of the N→Cu are given in Table 1. In compound **11**, the total electron density at N8···Cu bond critical point is 0.054, which is very close to N12···Cu (0.057) and N15···Cu (0.059) indicating that N8···Cu, N12···Cu and N15···Cu bonds are real coordination bonds. This observation is further supported by NBO analysis. From NBO analysis, it can be observed that in compound **11** there is donation of lone pair from N8, N12 and N15 to LP* of Cu to form formal coordination bonds. The energies associated with these interactions are 14.6, 10.4 and 12.6 kcal/mol respectively. These indicate the presence of similar bonds between all three nitrogens and copper. The energy values indicating the possible interaction of N8, N12 and N15 with Cu, are given in Table S2(SI).

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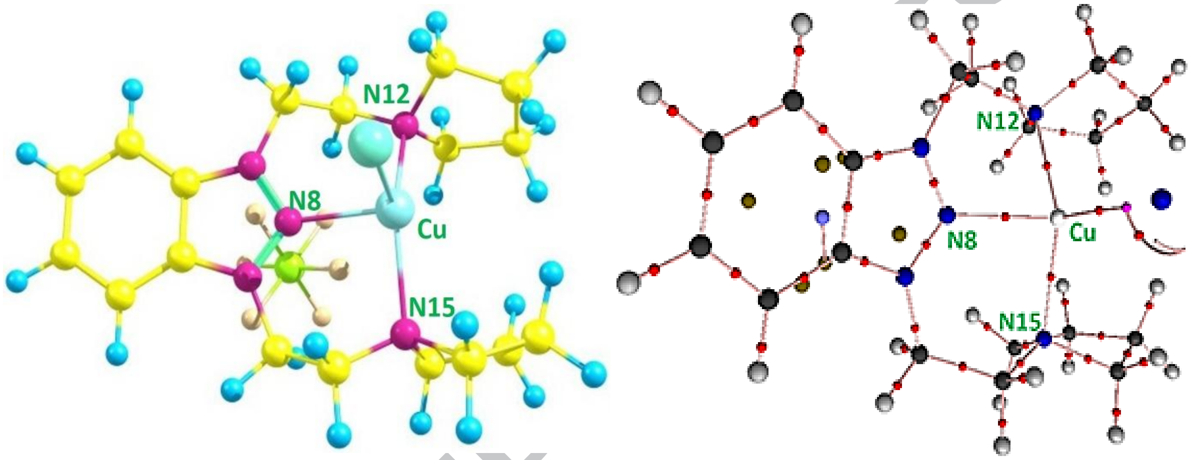
Table 1. Total electron density ($\rho_{bcpN\cdots M}$), Laplacian value ($\nabla^2_{bcpN\cdots M}$) and total energy density ($H_{bcpN\cdots M}$) at bond critical points of N-M bonds in compound **11**.

Bond	$\rho_{bcpN\cdots M}$	$\nabla^2_{bcpN\cdots M}$	$H_{bcpN\cdots M}$
N8-Cu	0.054	-0.071	0.0044
N12-Cu	0.057	-0.065	0.0076
N15-Cu	0.059	-0.067	0.0083



(a) (b)

Figure 4. (a) Optimized structure and (b) molecular Graph of compound **11** showing the bond critical points.

Selones **18a-18b** were synthesised in ca. 70-75% yield by following the reported procedure (Scheme 3). First benzimidazole (**15**) was *N*-alkylated by 2-bromo-1-ethanol/3-bromo-1-propanol in presence of 30% NaOH solution and a phase-transfer catalyst (tetrabutylammonium bromide, TBAB). Subsequent quaternization of **16a-16b** by another equivalent of 2-bromo-1-ethanol/3-bromo-1-propanol afforded N,N´-disubstituted benzimidazole, **17a-17b**. These benzimidazolium salts when reacted with *in situ* generated Na_2Se_2 in presence of potassium *tert*-butoxide at room temperature, afforded selones, **18a-18b**.

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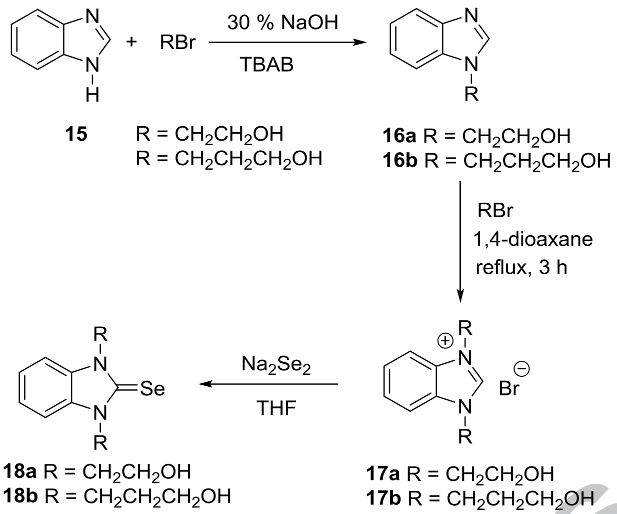

Scheme 3. Synthesis of selones **22 -23**.

Compounds **18a-18b** were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR signal for the acidic NC<u>H</u>N proton present in salts **17a** and **17b** were absent in the corresponding chalcogenone derivatives. In ^{77}Se NMR spectrum, compound **18a** showed a single resonance at 66.4 ppm, while a chemical shift of 33.2 ppm was observed for compound **18b**. Both these chemical shifts are in agreement with the values reported for similar benzimidazole based selone derivatives.[12a-b]

The single crystals of compound **18a** were obtained by slow evaporation of a chloroform/hexane solution of the compound. In the molecular structure of **18a** (Figure 4), the benzimidazole ring, selenium atom and the methylene carbon connected to the N atoms of the imidazole ring, are in the same plane. The C and Se atom sit on the crystallographically imposed C_2 axis of symmetry, wherein the two O-atoms of the flanking arms are *trans*-oriented with respect to the core plane. The geometry around the carbene carbon is planar trigonal. The C-Se distance is found to be 1.834 (4) Å, which is in accordance with C-Se bond length of similar compounds reported in the literature.[12a] This bond distance is on the longer side for a double bond but shorter than expected for a C-Se single bond. However, a detailed DFT calculation performed by Manjare *et al.*,[12a] wherein Wiberg bond indexes and Natural Population Analysis (NPA) have been taken in to account, unambiguously inferred that the donor-acceptor bonding mode in C-Se bond not only comprises of a σ donation from the carbene, but also significant π back-bonding from selenium, which confirmed the double bond character of C-Se bond.

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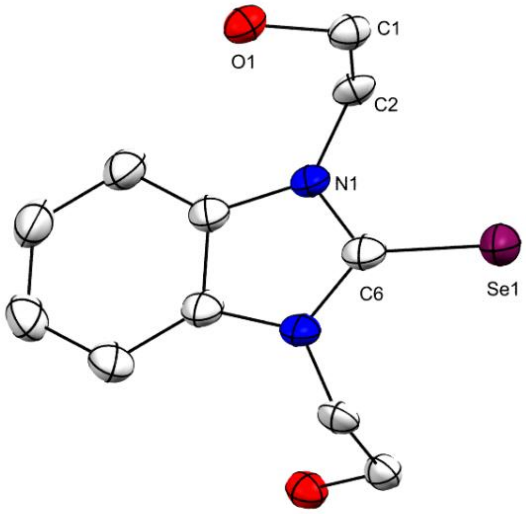

Figure 4. Molecular structure of selone, **18a**.

Conclusion

In summary, we have successfully synthesized new NNN- and CNC type N-heterocyclic nitrenium ion (NHN) within a tridentate pincer scaffold. However, when the synthesis of hybrid NHN ligand where the chelating arm contains soft Te donor is attempted, methylation took place at Te center instead of at triazole nitrogen and afforded telluronium cation. The molecular structure of the synthesized NHN ligands reveal that in both the cases, the triazole ring and the methylene carbons connected to the triazole nitrogen atoms are in the same plane, while both the flanking arms rest in the same side of the core plane. The reactions of the synthesized nitrenium ions with d^{10} metal precursors have also been explored. The common spectroscopic techniques (^{1}H, ^{13}C NMR), mass spectrometry authenticated the ligation of the nitrenium ions to the metal centre. However, due to the unavailability of the single crystal structures of the same, the direct coordination of the metal to triazolium centre remains obscure. Nevertheless, Natural Bond Order (NBO) calculations and Atoms in Molecules (AIM) analyses adequately substantiate the presence of interaction between triazolium N with the Cu metal centre.

Experimental Section

All the manipulations were executed under a nitrogen or argon atmosphere using standard Schlenk techniques unless otherwise noted. Solvents were purified and dried by standard

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procedures and were distilled prior to use. ^{1}H (400 MHz, 500 MHz), ^{11}B NMR (128 MHz), ^{13}C NMR (100.56 MHz, 126 MHz), ^{19}F NMR (376 MHz), ^{31}P NMR (161 MHz, 202 MHz), ^{77}Se NMR (76 MHz, 95 MHz) and ^{125}Te (126 MHz, 158 MHz) nuclear magnetic resonance spectra were recorded on Bruker AV 400 and/or Bruker AV 500 spectrometers at 25 °C. Chemical shifts are cited with respect to Me_4Si as an internal standard for ^{1}H and ^{13}C, 85% H_3PO_4 for ^{31}P, tetrafluorotoluene for ^{19}F, Me_2Se for ^{77}Se and Me_2Te for ^{125}Te as external standards. Elemental analyses were performed on a Carlo Erba Model 1106 elemental analyser. The ESI mass spectra were recorded on a Q-tof micro (YA-105) mass spectrometer. The single crystal X-ray diffraction measurements were performed on a Rigaku Saturn 724 diffractometer and an Oxford Diffraction Gemini diffractometer. The data were corrected for Lorentz, polarization, and absorption effects. The structures were determined by routine heavy-atom methods using SHELXS 97[21] and Fourier methods and refined by full-matrix least squares with the anisotropic non-hydrogen atoms and hydrogen atoms with fixed isotropic thermal parameters of 0.07 Å^2 using the SHELXL 97[22] program. The hydrogens were partially located from difference electron density maps, and the rest were fixed at predetermined positions. Scattering factors were from common sources.[23]

Synthesis of compound 7 A mixture of compound **5** (1.00 g, 2.42 mmol) and *n*-butylbenzimidazole (**6**) (0.84 g, 4.83 mmol) in 30 mL dry 1,4-dioxane was stirred at 90 °C for 24 h. A white precipitate of compound **7** appeared. The precipitate was washed with ethyl acetate and diethyl ether. The product was purified by recrystallization from methanol. Yield: 1.76 g (96%). ^{1}H NMR (400 MHz, D_2O): δ (ppm) 9.37 (s, 2H), 7.93-7.86 (m, 6H), 7.77-7.64 (m, 6H), 5.61 (t, *J* = 5.44 Hz, 4H), 5.27 (t, *J* = 5.44 Hz, 4H), 4.35 (t, *J* = 7.30 Hz, 4H), 1.77 (q, *J* = 7.42 Hz, 4H), 1.21 (sext, *J* = 7.56 Hz, 4H), 0.87 (t, *J* = 7.36 Hz, 4H); ^{13}C NMR (100 MHz, D_2O): δ (ppm) 141.38 (NCN), 135.36, 133.10, 131.28, 130.73, 127.94, 127.80, 114.17, 112.83, 112.50, 50.43, 47.40, 45.44, 30.54, 19.16, 12.84; ESI-MS (positive mode): $[(C_{32}H_{40}N_7)\text{-}H]^{3+}$ *m/z* = 173.6139 (observed), 173.7750 (calculated).

Synthesis of compound 8 Compound **7** (0.20 g, 0.26 mmol) was dissolved in dry ethanol and to this was added to a solution of mercuric acetate (0.08 g, 0.26 mmol) in dry ethanol. A white precipitate appeared soon after the addition. The reaction mixture was kept for stirring for 12 h. The precipitate was filtered and washed with ethanol to get pure compound **8** Yield: 0.18 g

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(72%). ^{1}H NMR (400 MHz, DMSO): δ (ppm) 8.44-8.42 (m, 2H), 8.04-8.01 (m, 4H), 7.77-7.68 (m, 4H), 5.62 (t, *J* = 5.93 Hz, 4H), 5.50 (t, *J* = 5.93 Hz, 4H), 4.59 (t, *J* = 7.52 Hz, 4H), 1.56 (q, *J* = 7.57 Hz, 4H), 1.31 (sext, *J* = 7.61 Hz, 4H), 0.87 (t, *J* = 7.25 Hz, 6H); ^{13}C NMR (100 MHz, DMSO): δ (ppm) 142.96 (NCN), 135.10, 131.60, 130.90, 130.60, 126.92, 113.89, 113.71, 113.67, 49.96, 46.58, 44.95, 30.56, 19.01, 13.44; ESI-MS (positive mode): $[C_{32}H_{38}N_7Br_2Hg]^+$ *m/z* = 882.1231 (observed), 882.1234 (calculated).

Synthesis of compound 9 Compound **5** (1.00 g, 2.42 mmol) was dissolved in 5 ml water and ammonium hexaflorophosphate (0.43 g, 2.66 mmol) was added to it. An immediate precipitation of compound **9** occurred, which was separated by filtration followed by washing with 2 ml water. Yield: 1.16 g (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.52-8.50 (m, 2H), 8.07-8.05 (m, 2H), 5.59 (t, *J* = 5.40 Hz, 4H), 4.19 (t, *J* = 5.40 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 134.86, 131.57, 114.29, 52.87, 29.81; ^{19}F NMR (100 MHz, $CDCl_3$): δ (ppm) -73.05, -74.58; ^{31}P NMR (100 MHz, $CDCl_3$): δ (ppm) -140.70 (sep), ESI-MS (positive mode): $[C_{10}H_{12}N_3Br_2]^+$ *m/z* = 333.9374 (observed), 333.9372 (calculated).

Synthesis of compound 10a Compound **9** (0.50 g, 1.04 mmol) was suspended in toluene and pyrrolidine (0.19 g, 2.61 mmol) was added to it. Slowly compound **9** gets dissolved and the color of the solution turns yellow. After stirring at rt for 24 h a light yellow precipitate of pure compound **10a** appeared, which was separated by filtration.Yield: 0.48 g (67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08-8.03 (m, 2H), 7.84-7.80 (m, 2H), 5.00 (t, *J* = 5.85 Hz, 4H), 3.18 (t, *J* = 5.85 Hz, 4H), 2.53 (t, *J* = 3.16 Hz, 6H), 1.67 (t, *J* = 3.16 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 135.54, 131.91, 113.98, 54.27, 54.14, 51.62, 24.04; ^{19}F NMR (100 MHz, $CDCl_3$): δ (ppm) -72.31, -72.82; ^{31}P NMR (100 MHz, $CDCl_3$): δ (ppm) -141.16 (sep), ESI-MS (positive mode): $[C_{18}H_{28}N_5]^+$ *m/z* = 314.2339 (observed), 314.2339 (calculated).

Synthesis of compound 10b Compound **10b** was prepared using the method similar to that used for compound **10a**. The reagents used were compound **9** (0.50 g, 1.04 mmol) and diethylamine (0.12 g, 2.61 mmol). Yield: 0.23 g (53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29-8.28 (m, 2H), 8.09-8.08 (m, 2H), 5.41 (t, *J* = 5.85 Hz, 4H), 3.99 (t, *J* = 5.85 Hz, 4H), 2.94 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.11, 133.60, 118.32, 114.63, 55.03, 48.05, 43.86; ^{19}F NMR (100 MHz, $CDCl_3$): δ (ppm) -72.03, -73.54; ^{31}P NMR (100 MHz, $CDCl_3$): δ (ppm) -144.64 (sept), ESI-MS (positive mode): $[C_{14}H_{24}N_5]^+$ *m/z* = 262.2027 (observed), 262.2026 (calculated).

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Synthesis of compound 11 Compound **10a** (0.50g, 1.09 mmol) was dissolved in dry dichloromethane and to it was added cuprous iodide (0.21g, 1.09 mmol). A yellow precipitate of the product appeared after stirring the reaction mixture at rt for 30 min. The precipitate was soluble in CH_3CN and DMSO. Yield: 0.48 g (68%). ^1H NMR (400 MHz, CH_3CN): δ (ppm) 8.48-8.46 (m, 2H), 8.06-8.04 (m, 2H), 5.33 (broad, 4H), 3.55 (broad, 4H), 2.94 (broad, 8H), 1.78 (broad, 8H); ^{13}C NMR (100 MHz, CH_3CN): δ (ppm) 134.03, 131.44, 113.17, 51.83, 30.10, 19.03, 12.71; ^{19}F NMR (100 MHz, $CDCl_3$): δ (ppm) -69.21, -71.10; ^{31}P NMR (100 MHz, $CDCl_3$): δ (ppm) -144.24 (sep), ESI-MS (positive mode): $[C_{18}H_{28}N_5CuI]^+$ m/z = 504.0684 (observed), 504.0680 (calculated).

Synthesis of compound 13 Diphenyl ditelluride (0.45g, 1.11 mmol) was dissolved in dry ethanol in N_2 atmosphere. Two equivalents of $NaBH_4$ (0.09g, 2.22 mmol) were added to it. The reaction mixture started to become colorless and it was stirred at rt for 30 min. Then compound **12** (0.50g, 2.22 mmol) was added to the colorless reaction mixture. The reaction mixture was further stirred at rt for 2 hr, worked up with dichloromethane to get pure compound **13**. Yield: 0.54 g (76%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02-8.01 (m, 1H), 7.74-7.73 (m, 2H), 7.45-7.42 (m, 1H), 7.35-7.31 (m, 3H), 7.23-7.20 (m, 2H), 4.95 (t, J = 7.85 Hz, 4H), 3.36 (t, J = 7.85 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 146.01, 139.13, 132.70, 129.62, 128.51, 127.40, 124.00, 120.17, 110.33, 109.18, 50.25, 6.54, 5.84, 5.13; ^{125}Te NMR (126 MHz, $CDCl_3$): δ (ppm) 484.9 (t); ESI-MS (positive mode): $[(C_{14}H_{13}N_3Te)+Na]^+$ m/z = 376.0062 (observed), 376.0064 (calculated).

Synthesis of compound 14 Compound **13** (0.20g, 0.57 mmol) was dissolved in diethyl ether. Methyl iodide (0.08g, 0.57 mmol) was added to it. The reaction mixture was stirred in closed vessel for 48 h. The white precipitate was filtered off followed by the washing with dichloromethane to remove the unreacted starting material. The product was further purified by recrystallization from methanol. Yield: 0.26 g (91%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94-7.92 (m, 1H), 7.76-7.63 (m, 2H), 7.59-7.52 (m, 1H), 7.51-7.43 (m, 1H), 7.36-7.33(m, 1H), 7.28-7.26 (m, 3H), 5.01(m, 4H), 3.42 (m, 4H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.22, 130.29, 128.90, 128.10, 124.84, 120.23, 118.25, 111.00, 50.74, 7.12; ^{125}Te NMR (126 MHz, $CDCl_3$): δ (ppm) 606.2 (s); ESI-MS (positive mode): $[C_{15}H_{16}N_3Te]^+$ m/z = 368.0405 (observed), 368.0402 (calculated).

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Synthesis of compound 16a To a round-bottomed flask containing benzimidazole (**15**) (10.00 g, 84.75 mmol), was added 30% aq. NaOH (66 mL) and tetrabutylammonium bromide 1.0 g followed by 2- bromoethanol (6 mL, 6.00 mol) at rt. The mixture was stirred at rt for 3 h. Then it was poured in to 100 ml water and extracted with chloroform (40 mL × 3), The organic layer was separated, dried over anhydrous Na_2SO_4 and was evaporated to dryness to give a red coloured liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.73 (s,1H), 7.48(d, 1H), 7.33(d, 1H), 7.19(m, 2H), 4.2 (t,3H), 4.0 (t,3H); ^{13}C NMR (125MHz, $CDCl_3$): δ (ppm) 130.8, 130.3, 120.3, 110.9, 110.6, 110.0, 140.4., 60.0, 40.8.

Synthesis of compound 17a A solution of 2-bromoethanol (2.9 mL, 5.07 g, 40.00 mmol) and compound **16a** (6.5 g, 40.00 mmol) in 1, 4-dioxane (40 mL) were refluxed under nitrogen atmosphere for 3 h. After the completion of reaction, the solvent was removed and the solid residue was washed with ethyl acetate (3×20 mL) to get compound **17a** as a white solid and was used for the next step without any further purification.

Synthesis of selone 18a: To salt **17a** (1.13 g, 3.80 mmol) in THF, was added *in situ* generated Na_2Se_2 at rt under nitrogen atmosphere and the reaction mixture was stirred for 2h at rt. Solid KO^tBu (0.43 g, 3.80 mmol) was added to the reaction mixture and stirred further for additional 5-7 h. After completion of reaction, the reaction was quenched by adding water (50 mL), and extracted with dichloromethane (3×25 mL), dried over Na_2SO_4, and the solvent is removed *in vacuo* to afford selone **18a**. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.38 (m, 2H), 7.30 (m, 2H), 4.64 (t, 2H), 4.11 (t, 2H); ^{77}Se NMR (76MHz, CDCl3): δ (ppm) 66.4 ppm. ESI-MS (positive mode): $[(C_{11}H_{14}N_2O_2Se)+Na]^+$ *m/z* = 309.0121 (observed), 309.0118 (calculated).

Synthesis of compound 17b: In a round-bottom flask containing benzimidazole (**15**) (5.00 g, 42.37 mmol), was added 30% aq. NaOH (33 mL) and tetrabutylammonium bromide (0.50 g), followed by the addition of 3- bromopropanol (3.75 mL, 42.37 mol) at rt. The mixture was stirred at rt for 3 h, henceforth the reaction mixture was poured in to 100 ml water and extracted with chloroform (40 mL × 3). The organic layer was separated, dried over anhydrous Na_2SO_4 and was evaporated to dryness to give a red colored liquid of compound **16b**. The compound was used further without purification. A solution of 3-bromopropanol (3.15 g, 22.71 mmol) and

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compound **16b** (4.00 g, 22.71 mmol) in 1, 4-dioxane (40 mL) was refluxed under nitrogen atmosphere for 3 h. After the completion of reaction, the solvent was removed and the solid residue was washed with ethyl acetate (3×20 mL) to get compound**17b** as a white solid and was used for the next step without any further purification.

Synthesis of selone 18b: To salt **17b** (1.37 g, 4.00 mmol) in THF, was added *in situ* generated Na_2Se_2 at rt under nitrogen atmosphere and the reaction mixture was stirred for 2h at rt. KO^tBu (0.60 g, 4.00 mmol) was added to the reaction mixture and stirred further for additional 5-7 h. After completion of reaction, the reaction was quenched by adding water (50 mL), and extracted with dichloromethane (3×25 mL), dried over Na_2SO_4, and the solvent was removed *in vacuo* which afforded the title compound as an off white solid. ^1H NMR (500, MHz, MeOD): δ (ppm) 8.2(s, 1H), 6.8(m, 2H), 6.4(m, 2H), 3.5(2H), 2.3(4H), 1.9(4H), 0.9(4H); ^{13}C NMR (125MHz, $CDCl_3$): δ (ppm) 141.03, 131.47, 126.98, 113.28, 58.24, 44.39, 30.76, ^{77}Se NMR (76MHz, CDCl3): δ (ppm) 33.2 ppm. ESI-MS (positive mode): $[(C_{13}H_{18}N_2O_2Se)+Na]^+$ *m/z* = 337.0437 (observed), 337.0431 (calculated).

Supporting Information

NMR spectra, ESI-MS spectra, single crystal X-ray analysis are given as Supporting Information; X-ray structural parameters are given in Table S1 (**10a** and **10b**, **13**, **14** and **18a**). CCDC 1870798 - 1870802 (Compounds **10b**, **18a**, **13**, **10a** and **14** respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Notes

The authors declare no conflict of interest.

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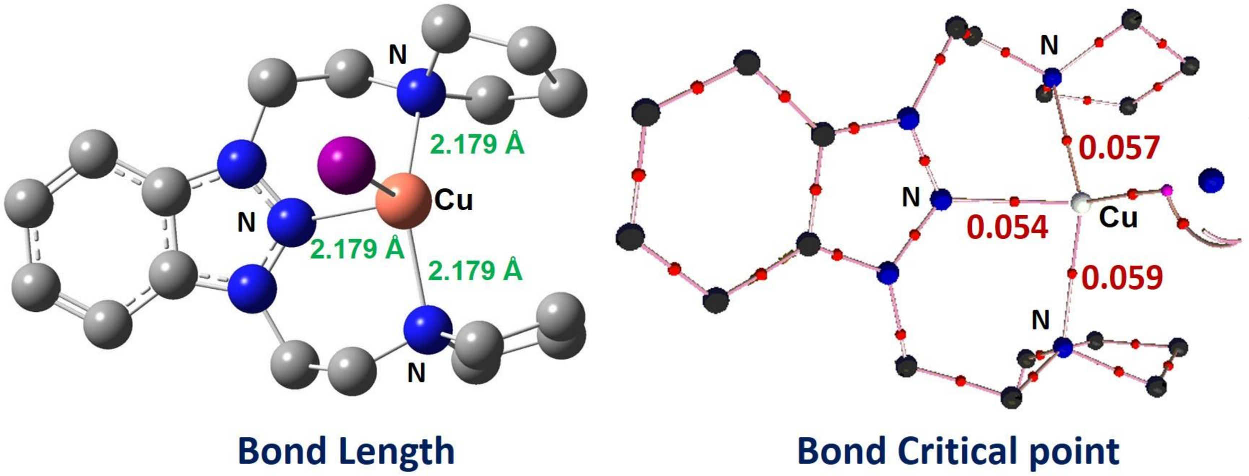

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Highlights

- New NNN- and CNC type N-hetrocyclic nitrenium ions (NHN) within tridentate pincer scaffold are reported.
- The attempted synthesis of hybrid NHN ligand containing soft Te atom in the auxiliary arms results in the formation of telluronium cation where the N atom from the triazole ring makes five membered chelating ring by intramolecular N···Te secondary bonding interaction.
- The Natural Bond Order (NBO) calculations and Atoms in Molecules (AIM) analyses on the metal complexes adequately substantiate the presence of interaction between triazolium N with metal centre.
- Synthesis of two new selone based OSeO type pincer ligands is reported.