Journal Pre-proofs


Research paper

# Ferrocenylated Chalcogen (Se and Te)-Containing N-Heterocyclic Carbenes: Selenones, Silver and Palladium Complexes

Rodary Gonzalez, Ramón Azpiroz, Pankaj Sharma, Claudia P. Villamizar C, Bertin Anzaldo, Francisco J. Pérez-Flores, Ruben Alfredo Toscano

PII: S0020-1693(19)32002-X
DOI: https://doi.org/10.1016/j.ica.2020.119531
Reference: ICA 119531

To appear in: *Inorganica Chimica Acta*

Received Date: 19 December 2019
Revised Date: 12 February 2020
Accepted Date: 12 February 2020

Please cite this article as: R. Gonzalez, R. Azpiroz, P. Sharma, C.P. Villamizar C, B. Anzaldo, F.J. Pérez-Flores, R. Alfredo Toscano, Ferrocenylated Chalcogen (Se and Te)-Containing N-Heterocyclic Carbenes: Selenones, Silver and Palladium Complexes, *Inorganica Chimica Acta* (2020), doi: https://doi.org/10.1016/j.ica.2020.119531

# Fe
## Palladium Complexes

Rodary Gonzalez,[a] Ramón Azpiroz,[a] Pankaj Sharma,[a*] Claudia P. Villamizar C,[a] Bertin Anzaldo,[a] Francisco J. Pérez-Flores,[a] Ruben Alfredo Toscano [a]

[a] Instituto de Química Universidad Autónoma de México UNAM, Cd., Universitaria, PO Box 04510, Ciudad de México, México. *E-mail: pankajsh@servidor.unam.mx*

**Keywords:** Ferrocenyl Chalcogen • N-Heterocyclic Carbene• Selenones

**Abstract:** New Ferrocenylated Chalcogen (Se and Te)-Containing imidazolium salts have been synthesized. These imidazolium salts have been used as precursors for the synthesis of ferrocenyl-NHC selenones, silver NHC and ionic palladium (II) complexes where the imidazolium ligand act as the cation. For the synthesis of Pd $NHC_{(Se,\ CNHC)}$ complex from appropriate imidazolium salts, the route of the silver carbene transfer reaction has been adopted and the ligand shows bidentate coordination through (Se, $C_{NHC}$) atoms. All the compounds have been fully characterized by multinuclear NMR, mass spectrometry and X-ray diffraction. Molecular structures of ferrocenyl chalcogenide imidazolium salts present intra and inter cation/anion interactions. Interestingly, $^{77}$Se NMR studies of ionic palladium complexes with ferrocenyl chalcogenide imidazolium cation do not present Se coordination to Palladium in solution. The bond distance between $C_{NHC}$ and selenium atom in both the selenones is similar to other reported imidazolium selenones where this bond has a double bond character.

## Introduction

*N*-Heterocyclic carbenes (NHCs) and their main group element adducts have been the subject of extensive investigations for the last three decades in coordination chemistry and homogenous catalysis.[1,2] The great interest on NHCs as ligands in comparison to classical phosphines is due to their easy accessibility and modulation of their substituents which modify their electronic and steric properties.[3] Recently, the functionalization of imidazole ring with donor atoms such as N,[4] P[5] O,[6] and relatively less explored with donor atoms S[7] or Se[8], provide new interesting bidentate[4a, 4c, 5b, 5c, 5d, 5f, 6, 7] and tridentate[4b, 4d, 5a, 5e, 7] ligands. The presence of donor groups on the pendant arm with free conformational arrangement around the metal stimulates hemilabile or labile interactions. Hemilability is an important concept in catalysis to stabilize intermediates and promote catalytic transformations by generating coordination sites that lead to interaction with substrates.[9] In the family of NHCs, the functionalization of the imidazole moiety with ferrocenyl substituents shows unique properties due to sterically cylindrical shape and its donor capacity to stabilize and increase the electronic properties of the NHCs.[10] Precedent for the introduction of additional heteroatom donors (sulfonate, carbonate, pyranyl and pyridyl groups) on the side-arm of ferrocenyl substituted-NHCs structures are very scarce.[11] To our knowledge, there is no report available on ferrocenyl substituted-NHC ligands based on organo- selenium and tellurium, so it appears interesting to explore in this area. Recently, the use of heavier organochalcogens as ligands in organometallic chemistry has received special attention in comparison to organophosphorus ligands because of their low toxicity, air and moisture sensitivity, higher thermal stability and their capacity to stimulate intra- and intermolecular interactions.[12] In particular organoselenium ligands present comparable electron-donating ability as organophosphorus ligands and led to the synthesis of many transition metal complexes, which can serve as catalysts for a variety of C-C cross-coupling reactions.[13]

The selection of a carbene for a specific purpose requires detailed knowledge of its stereoelectronic properties. Recently, reports have appeared on Se-N-Heterocyclic Carbene (Se-NHC) adducts (selenoureas or selones) to observe the donor abilities of NHC ligands.[14] The assessment of the ligand properties of NHCs, Tolman electronic parameter (TEP) has become the most frequently used parameter which reflects the overall ligand properties.[15] However, this parameter does not give much idea of the σ-donating and π-accepting nature of a particular NHC. NMR methods also have been used that provide an insight into the π-acceptor strength of NHCs. The π-acceptor strengths of the NHCs within the NHC–Se adducts or NHC–phosphinidene adducts were determined by measuring the $^{31}$P NMR chemical shifts and the $^{77}$Se NMR chemical shifts.[16] In principle, N-heterocyclic carbenes nucleophilic character is transferred onto the exocyclic selenium atom which affords Se-donor ligands, that can act themselves as ligands toward main group elements and transition metal complex fragments. These N-heterocyclic carbene selenone derivatives have also received increasing attention because of their structural relevance to methimazole and selenoneine.

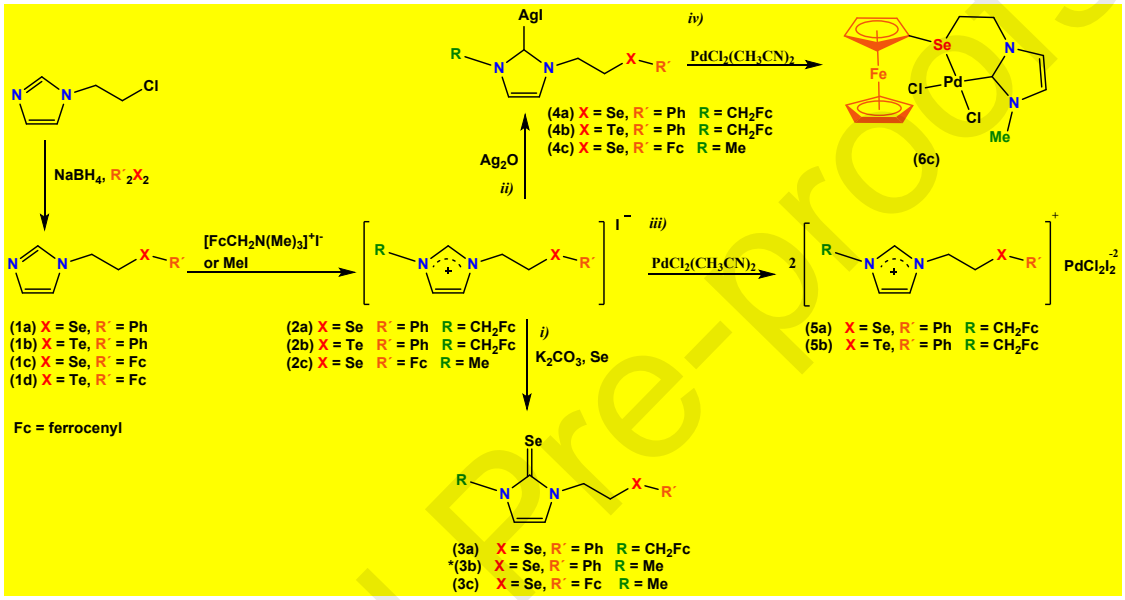
Apart from this, a vast variety of NHC-transition.metal complexes bearing different substituents on the side-arm of imidazole fragment have been prepared using different synthetic methods including a) the isolation of free NHCs prior to the reaction with transition metal,[17] or metalloid,[18] b) *in situ* generation via reaction of imidazolium salt with an external base,[19] c) the use of imidazolium salts with suitable basic transition metal[20] and d) transmetallation with other organometallic species.[21] The

use he preparation of transition metal NHCs complexes.

In continuation to our search for new organoselenium and tellurium ligands,[22] herein we describe the synthesis of some new ferrocenyl-NHCs salts (**2a-c**) containing organochalcogen donor (Se and Te) on the side-arm of NHC moiety, their selones derivatives and complexation with Ag(I) and Pd(II) metals.

**Results and Discussion**

**Synthesis of *N*-PhXCH$_2$CH$_2$ImH and *N*-FcXCH$_2$CH$_2$ImH (1a-d).** Synthesis of *N*-PhXCH$_2$CH$_2$ImH {X= Se (**1a**) and Te (**1b**)} and *N*-FcXCH$_2$CH$_2$ImH {Fc = ferrocene, X = Se, (**1c**) and Te (**1d**)} was carried out starting from 1-chloroethylimidazole and sodium organoselenide (NaSePh for **1a** and NaSeFc for **1c**), or sodium organoteluride (NaTePh for **1b** and NaTeFc for **1d**) in ethanol which was obtained *in situ* and under nitrogen atmosphere by the reduction and consecutive cleave of PhX-XPh or FcX-XFc (X = Se, Te), respectively. The desired compounds were obtained as a yellow oil. *N*-PhSeCH$_2$CH$_2$ImH (**1a**) has already been reported earlier in the literature,[8b] however *N*-PhTeCH$_2$CH$_2$Im (**1b**), *N*-FcSeCH$_2$CH$_2$ImH (**1c**) and (**1d**) are unknown.




**Scheme 1.** Synthetic methodology for the preparation of new ferrocenyl imidazolium chalcogenide salts (**2a**-**c**) from starting precursors (**1a**-**d**). Compounds (**2a-c**) resulted excellent reactants for the preparation of: *i)* new selenones (**3a**-**c**) (*Compound 3b was synthesized from an imidazolium salt as reported in the literature [8b]) *ii)* new silver NHC complexes (**4a-c**) and *iii)* new ionic palladium imidazolium complexes (**5a,b**). *iv)* new palladium NHC complex (**6c**).

The $^1$H NMR spectra of **1a**, **b** in $CDCl_3$ and **1c,d** in acetone-$d_6$ at room temperature show the proton NCHN at ~ δ 7.4 ppm as a singlet and =CHN protons at ~ δ 7.0 and δ 6.8 ppm as broad signals. The N-$CH_2$ and X-$CH_2$ (X = Se, Te) protons appear at ~ δ 4 ppm and at ~ δ 3 ppm respectively, as triplets ($J_{H\text{-}H} \approx 7$ Hz). Additionally, for compound **1a** $^{77}$Se NMR shows a broad singlet at δ 284.0 ppm which is in accordance with selenium atom connected to alkyl fragment.[23] For compound **1c**, the resonance corresponding to the selenium atom appears a higher field (δ 180.0 ppm), which is due to the higher electron donating ability of the ferrocenyl group. $^{13}$C NMR spectra of these compounds are in accordance with the proposed structure.

**Synthesis of ferrocenyl imidazolium chalcogenide salts.** The imidazolium salts (**2a-c**) were prepared by the reaction of 1-substituted imidazoles (**1a-c**) with N-trimethylaminomethyl ferrocenium iodide or with methyliodide and were isolated as yellow solids in good yields. In general, the $^1$H NMR spectra of **2a**-**c** at room temperature showed characteristic resonances of NCHN proton at ~ δ 9.5 ppm, suggesting the high acidity of this proton.[25] All compounds showed three signals corresponding to the ferrocenyl moiety at ~ δ 4.5-4.0 ppm, two doublets of doublets for 4H protons of linked cyclopentadienyl fragment and one singlet for symmetrical 5H protons of ferrocene. Also, a signal at ~ δ 5.2 ppm corresponds to methylene protons of **2a,b** and a singlet at δ 4.07 ppm for methyl group of **2c**. Interestingly, a slightly downfield shift ~ Δδ = 0.3 ppm was observed for N-$CH_2$ and X-$CH_2$ group (X = Se, Te) protons for the imidazolium salts (**2**) in comparison to their precursors (**1**). This observation suggests the presence of C-H···I interactions, as reported earlier in the literature.[26] A similar downfield shift was observed in $^{13}$C spectra. This downfiled shift is also due to the formation of imidazolium salt with a deprotected N-$\underline{C}H_2$ carbon.

Single crystals of **2b** were grown by slow evaporation of saturated solution in acetonitrile and the solid-state structure was determined by single crystal X-ray diffraction studies. Figure 1 reports the ORTEP view along with selected bond lengths and angles of the imidazolium compound. To the best of our knowledge, this is the first structurally characterized imidazolium compound bearing an aliphatic chain containing telluroether fragment as a substituent. The imidazolium cation **2b** presents N(1)-C(2)-N(3) angle of 109.5(4)°. In addition, the skeleton involving the Te1 displays C(19)-Te(1)-C(18) angle of 96.32(19)°. The other bond lengths and bond angles observed are of similar magnitude as reported earlier for other imidazolium salts and organochalcogen compounds.[8b, 27]

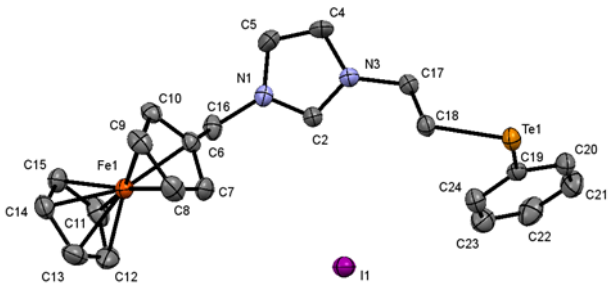



**Figure 1**. Molecular structure of **2b** depicted with 30% thermal ellipsoids. Hydrogens atoms have been omitted for clarity. Selected Bonds lengths (Å): Te(1)-C(19), 2.121(5); Te(1)-C(18), 2.138(5); N(1)-C(2), 1.314(7); N(1)-C(16), 1.484(7); N(3)-C(2), 1.330(6); N(3)-C(17), 1.478(7); N(1)-C(5), 1.367(7); N(3)-C(4), 1.370(7); C(6)-C(16), 1.487(7); C(17)-C(18), 1.493(7); Bond angles(°): C(19)-Te(1)-C(18), 96.3(2); C(2)-N(1)-C(16), 124.8(4); C(2)-N(3)-C(17), 125.8(4); N(1)-C(16)-C(6), 112.7(4); Te(1)-C(18)-C(17), 113.2(3); N(3)-C(17)-C(18), 111.6(4); N(1)-C(2)-N(3), 109.4(4); Bond torsion (°): Te(1)-C(18)-C(17)-N(3), 178.6(3); C(19)-Te(1)-C(18)-C(17), -64.2(4); C(6)-C(16)-N(1)-C(2), 90.7(6).

When considering the 3D packing of **2b**, intra and inter cation/anion interactions were detected.[6e, 26] A shorter intra cation/anion interaction involving imidazolium ring and iodide atom {H(1)···I(1), 2.867 Å} were observed and, the positive charge is localized around the imidazole (Figure 2A) ring. In accordance with NMR observations, intra cation/anion interactions between μ-$CH_2$ and aromatic ring with iodide atom were detected {H(18)···I(1), 3.141 Å; H(24)···I(1), 3.132 Å}. It is to be noted that the presence of inter cation/anion CH···I interactions generate chains of molecules growing parallel to {H(7)···I(1), 3.028 Å} axis (Figure 2B). In addition, these chains are joined together by CH···C interactions rendering chains affording the 3D packing {H(8)···C(20), 2.859 Å; H(17)···C(10), 2.874 Å} (Figure 2C). These interactions are driven by the packing and electrostatic effect of acidic protons that stabilize the structure.

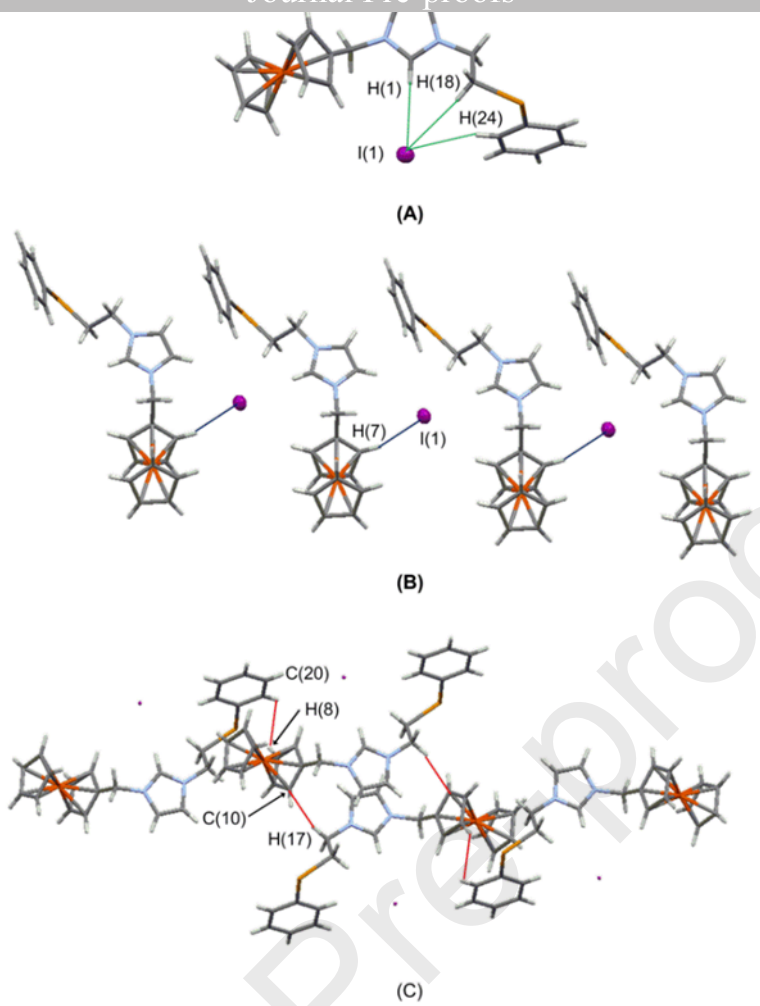



**Figure 2**. (**A**) Representation of intra cation/anion CH···I interactions (green) of **2b**. (**B**) CH···I inter cation/anion interactions (blue) between adjacent molecules forming chains along an {H(7)···I(1), 3.028 Å}. (**C**) View of CH-C contacts (red) detected in 3D packing structure {H(8)···C(20), 2.859 Å; H(17)···C(10), 2.874 Å}.

**Synthesis of ferrocenyl NHC selenones.** New selenones (**3a**-**c**) were obtained as yellow solids, in good isolated yields by the reaction of imidazolium salts (**2a,c**) with elemental selenium and potassium carbonate in anhydrous acetonitrile at room temperature. The disappearance of acidic NCHN proton in $^{1}$H NMR and the appearance of chemical shift at ~δ 156 ppm in $^{13}$C NMR for compounds **3a,c** confirms the formation carbene bonded to Selenium. Moreover, the presence of two chemical shifts in $^{77}$Se NMR spectra confirmed the presence of two different selenium atoms (see supporting information).

The structures of (*N*-PhSeCH$_2$CH$_2$)(*N*´-CH$_2$Fc)ImSe (**3a**) and (*N*-FcSeCH$_2$CH$_2$)(*N*´-CH$_3$)ImSe (**3c**) were confirmed by X-ray diffraction studies and crystals were obtained by slow evaporation of acetonitrile solution of the title compounds (Figures 3 and 4). The asymmetric unit of selenone **3c** contains two crystallographically independent molecules showing similar bond angles and lengths, thus only one of the two molecules is discussed herein (see Supporting Information). Both selenones (**3a,c**) present similar angles between the carbene atom and the nitrogen atoms of imidazole {N(1)-C(12)-N(2), 105.7(2)°; N(4)-C(31)-N(3), 106.1(2)°} and between selenium atom and adjacent carbon atoms of pendant arm fragment {C(17)-Se(2)-C(16), 101.58(9)°; C(19)-Se(3)-C(29), 97.2(3)}. The distance between carbene and selenium atom in both the selenones {Se(1)-C(12), 1.840(2); Se(4)-C(31), 1.847(7) Å} are similar to other reported imidazolium selenones[14] This bond distance is similar to the distances observed in alkylidenes with a more doble bond character and not with single bond character as observed for organometallic NHC carbenes.[28]

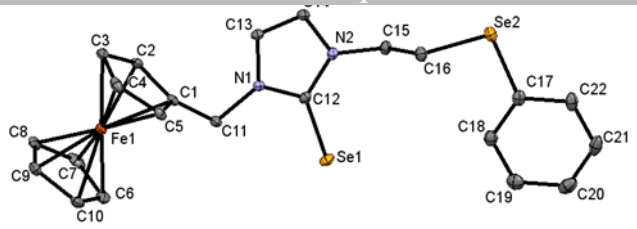



**Figure 3**. Molecular structure of **3a** depicted with 30% thermal ellipsoids. Hydrogens atoms have been omitted for clarity. Bonds lengths (Å): Se(2)-C(17), 1.917(2); Se(2)-C(16), 1.955(2); Se(1)-C(12), 1.840(2); N(2)-C(15), 1.460(3); N(1)-C(11), 1.473(3); C(1)-C(11) 1.494(3); C(12)-N(1) 1.356(3); C(12)-N(2), 1.362(3); N(1)-C(13), 1.383(3); N(2)-C(14), 1.381(3); C(15)-C(16), 1.512(3); Bond angles (°): C(17)-Se(2)-C(16), 101.58(9); Se(1)-C(12)-N(2), 126.8(2); Se(1)-C(12)-N(1), 127.5(2); C(12)-N(1)-C(11), 124.2(2); C(12)-N(2)-C(15), 126.0(2); N(2)-C(15)-C(16); 111.0(2); C(15)-C(16)-Se(2), 111.8(1); N(1)-C(11) C(1), 111.5(2); N(1)-C(12)-N(2), 105.7(2); Bond torsion(°): Se(2)-C(16)-C(15)-N(2) -169.7(1); C(1)-C(11)-N(1)-C(12), 170.0(2); C(17)-Se(2)-C(16)-C(15), -91.6(2); Se(1)-C(12)-N(1)-C(11), -2.4(3); Se(1)-C(12)-N(2)-C(15), -2.8(3).

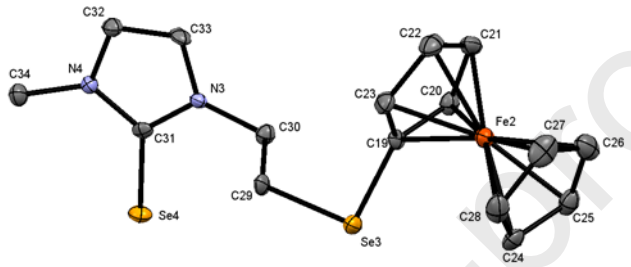



**Figure 4**. Molecular structure of **3c** depicted with 30% thermal ellipsoids. Hydrogens atoms have been omitted for clarity. Bond lengths (Å): Se(3)-C(19), 1.900(1); Se(3)-C(29), 1.952(9); Se(4)-C(31), 1.847(7); N(3)-C(30), 1.447(9); N(4)-C(34), 1.459(4); C(31)-N(4), 1.348(9); C(31)-N(3), 1.348(8); N(4)-C(32), 1.372(9); N(3)-C(33), 1.382(9); C(30-C(29), 1.51(1); Bond angles(°): C(19)-Se(3)-C(29), 97.2(3); Se(4)-C(31)-N(3), 127.0(5); Se(4)-C(31)-N(4), 126.8(5); C(31)-N(4)-C(34), 125.3(6); C(15)-N(1)-C(14), 125.0(6); N(3)-C(30)-C(29), 109.9(6); C(30)-C(29)-Se(3), 112.6(5); N(4)-C(31)-N(3), 106.1(2) Bond torsion (°): Se(3)-C(29)-C(30)-N(3), 173.3(4); C(19)-Se(3)-C(29)-C(30), 64.7(5); Se(2)-C(15)-N(2)-C(18), 2(1); Se(2)-C(15)-N(1)-C(14), -9(1).

**Synthesis of Silver NHC complexes**. The yellow monocarbene silver iodides (**4a-c**) complexes were synthesized by the reaction of imidazolium iodides **2a**-**c** with silver (I) oxide in dry $CH_2Cl_2$. These complexes are stable in air and moisture, but their dichloromethane solutions are slightly sensitive. Molecular ion peak (M-I; *m/z* = 607) observed in the mass spectra of **4b** confirms the presence of the ferrocenyl-NHC silver complex. In $^{1}$H NMR spectra, disappearance of NCHN proton signal for silver-NHC complexes**(4)** in comparison to their imidazolium salts **(2)** precursors confirm the formation silver-NHC complexes Additionally, a slight upfield shift was observed for olefinic =CHN protons at ~ δ 6.8 and 6.7 ppm in comparison to their precursor imidazolium salts (~ δ 7.4 and 7.2 ppm). In $^{13}$C NMR spectra for these complexes, a characteristic signal at ~ δ 182 ppm was observed for the silver carbene carbon. Finally, no significant difference was observed in $^{77}$Se NMR spectra between **4a** and **4c** (δ 274.1 and 173.4 ppm respectively) and imidazolium salt **2a** and **2c** (δ 277.4 and 175.4 ppm respectively) which confirm the non-coordination of selenium to the central silver atom.

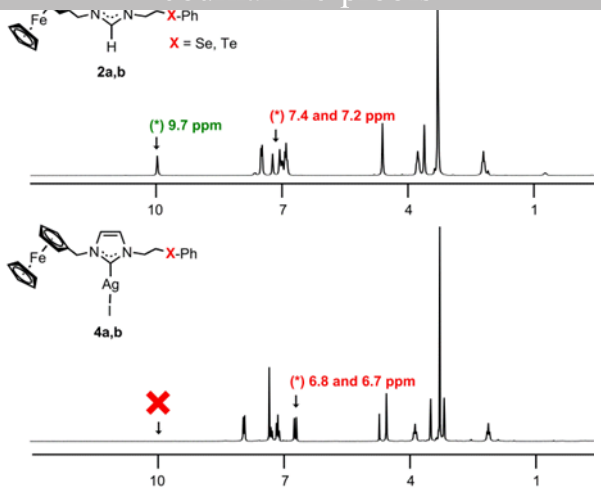



**Figure 5.** $^{1}$H NMR spectra of **2a,b** and **4a,b**.

**Synthesis of Palladium NHC complexes.** On adding the imidazolium salts (**2a,b**) to a solution of palladium (II) acetate, the desired palladium carbene complex could not be obtained which may be due to the strong steric hindrance of ferrocenyl moiety of the imidazolium with iodo ligands. However, reaction of imidazolium salts (**2a,b**) with $PdCl_2(CH_3CN)_2$ in 2:1 ratio, allowed the preparation of the corresponding air stable ionic palladium complexes $[(N\text{-PhXCH}_2\text{CH}_2)(N'\text{-CH}_2\text{Fc})\text{ImH}]^+ [(PdCl_2I_2)]^{-2}{}_{1/2}$ {X = Se (**5a**) , Te (**5b**)}[29] in good yields. These ionic complexes were isolated as red solids. The $^{1}$H NMR spectrum of **5a-b** showed NCHN proton resonance at ~ δ 10.2 ppm, which is slightly downfield (Δδ = 0.3) in comparison to NCHN proton of **2a-b** (Figure 6). The opposite chemical shift trend was observed in the $^{13}$C NMR spectrum where NCHN carbon of **5a-b**, appears at δ 134.3 and 138.3 ppm, respectively. These chemical shift differences may be due to the type of counter anion and the interactions involved between $PdCl_2I_2^{2-}$ and imidazolium ring. Interestingly, there is no difference in the $^{77}$Se NMR spectra of **2a** and **5a**, showing the non-coordination of the selenium atom to palladium. On the other hand in the mass spectra of **5a,** the detected ion peak at *m/z* = 305 and at *m/z* = 451 confirm the presence of palladate anion (MS (FAB$^-$) *m/z*: 305 $[PdCl_2I_2]^-$ and imidazolium cation (HRMS (FAB) found *m/z* 451.0376) and is in agreement with the ionic structure.

For the synthesis of Pd complex **6** from appropriate imidazolium salts (**4c**), the route of the silver carbene transfer reaction has been adopted and thereby, the reaction of $(N\text{-FcSeCH}_2\text{CH}_2)(N'\text{-Me})\text{ImAgI}$ **4c** with $PdCl_2(CH_3CN)_2$ in anhydrous acetonitrile resulted in the formation of $FcSeEtImMePdCl_2$ (**6**) as a red solid. $^{1}$H NMR spectra of palladium complex showed four diastereotopic protons at δ 4.56, 3.52, and 2.32 ppm as a multiplet chemical shift. In the $^{77}$Se NMR spectra, selenium atom appears at δ 162.3 ppm as a broad signal, ~10-20 ppm at the higher field in comparison to the selenium chemical shift of organoselenium compounds **2-4**. These all evidence suggests the ligand coordinate to palladium with selenium and carbene and thus forming a six-membered chelate ring. Moreover in $^{1}$H NMR and $^{13}$C NMR spectra, the cyclopentadienyl moiety of ferrocene linked to selenium display four signals at δ 4.28, 4.28, 4.09, and 3.73 ppm as multiplets and δ 70.7, 70.2, 69.8, and 69.3 ppm respectively. The asymmetry of the cyclopentadienyl ring suggests the presence of intramolecular Pd-Se coordinative bond.[30]

The molecular structure of **6** was determined by X-ray crystallography (Figure 7). The palladium atom presents a slightly distorted square planar geometry {Se(1)-Pd(1)-Cl(2), 86.06(4); Se(1)-Pd(1)-C(15), 89.7(2); Cl(1)-Pd(1)-C(15), 92.0(2); Cl(2)-Pd(1)-Cl(1), 93.07(6)} with four coordination sites occupied by carbene and selenium atom precedent of bidentate ligand and two chlorine atoms in *cis* positions, respectively. Only one intramolecular interaction was detected between the H(5) proton of the ferrocene with the $C_{N\underline{C}N}$ carbon of the imidazole, {H(5) ··· C(15), 2,814 Å}, which could also be the reason for the loss of the symmetry of the Cp ring observed in $^{1}$H and $^{13}$C NMR spectra (Figure 8). Palladium-Selenium bond lengths of complex **6** {Se(1)-Pd(1), 2.3808(7) Å} and the distance between palladium atom and carbene {C(15)-Pd(1 ), 1.970(6) Å} are consistent with earlier reported values.[23]

**Conclusions**

New imidazolium species containing the ferrocenyl and the organochalcogenide fragment as pendant arm (**2**) have been revealed as the efficient precursors for the synthesis of new ferrocenyl NHC selenones (**3**), silver NHC (**4**) and ionic palladium complexes containing imidazolium species as cations (**5**). Moreover, silver NHC complexes (**4**) have been efficient transmetallating agents to afford new palladium NHC complex (**6**). The solid-state structure of ferrocenyl chalcogenide imidazolium salts presents intramolecular interactions between acidic NCHN and μ-$CH_2$ protons with iodide atom which are

in [redacted] ate polymeric chains of alternating cations and anions, are described. $^{77}$Se NMR spectra of ionic palladium complexes species showed a unique chemical shift similar to imidazolium salts (**2** *vs* **5**). However, in palladium NHC complex **6** selenium atom appeared ~ 10-20 ppm a higher field. This is clear evidence of coordination of selenium atom to palladium center in comparison to non-coordination of selenium pendant arm fragment into ionic palladium species. The stereochemistry of **6**, was finally confirmed by X-ray structural analysis which is in agreement with NMR studies. These new silver and palladium complexes bearing the ferrocenyl NHC and chalcogenide pendent arm fragments are potentially catalyst in many organic transformations so they will be studied in future studies.

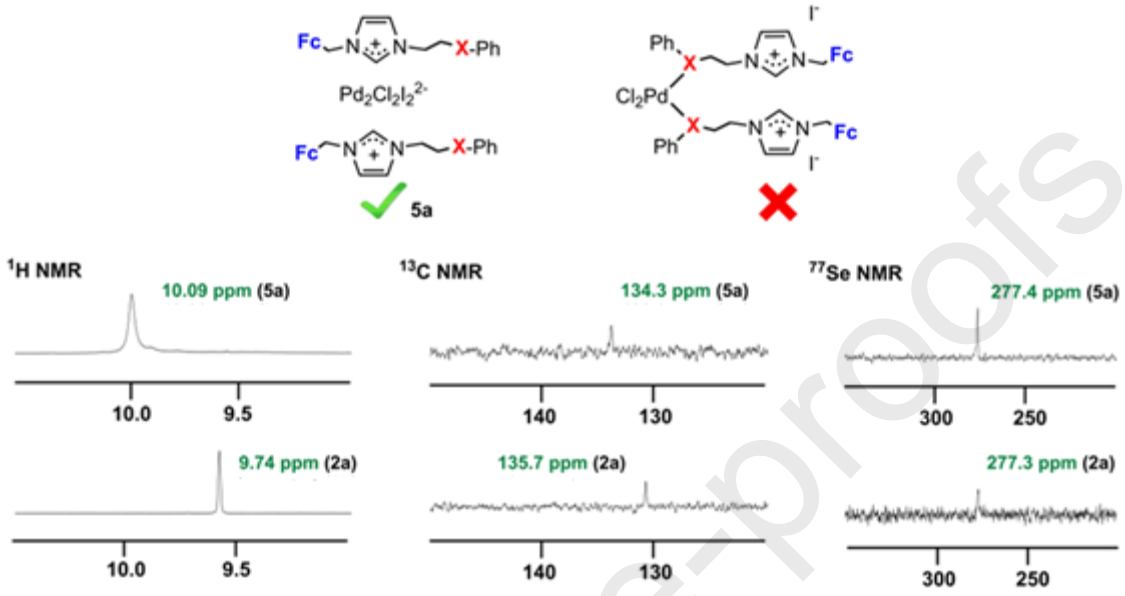



**Figure 6**. $^{1}$H, $^{13}$C and $^{77}$Se NMR spectra for compounds **2a** and **5a** in $CDCl_3$.

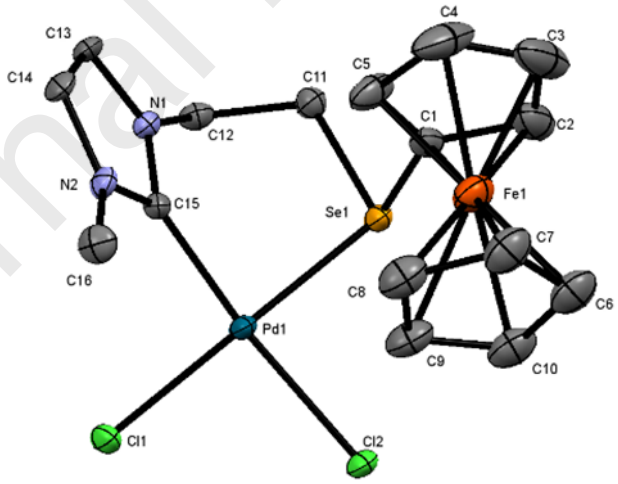



**Figure 7**. Molecular structure of **6c** with 30% thermal ellipsoids. Hydrogens atoms have been omitted for clarity. Bond lengths (Å): C(15)-Pd(1 ), 1.970(6); Pd(1)-Cl(2), 2.374(2); Se(1)-Pd(1), 2.3808(7); Pd(1)-Cl(1), 2.338(2); C(1)-Se(1), 1.901(8); Se(1)-C(11), 1.961(5); C(15)-N(1), 1.344(7); C(15)-N(2), 1.348(9); N(1)-C(12), 1.462(8); C(13)-C(14), 1.333(9); C(12)-C(11), 1.511(8); C(16)-N(2), 1.465(7); Bond angles(°): C(1)-Se(1)-C(11), 96.6(3); N(1)-C(15)-Pd(1), 125.5(4); N(2)-C(15)-Pd(1), 128.8(4); N(1)-C(15)-N(2), 105.6(5); C(15)-N(1)-C(12), 123.9(5); C(15)-N(2)-C(16), 126.2(5); Se(1)-Pd(1)-C(15), 89.7(2); Cl(2)-Pd(1)-Cl(1), 93.07(6); Se(1)-Pd(1)-Cl(2), 86.06(4); Cl(1)-Pd(1)-C(15), 92.0(2).

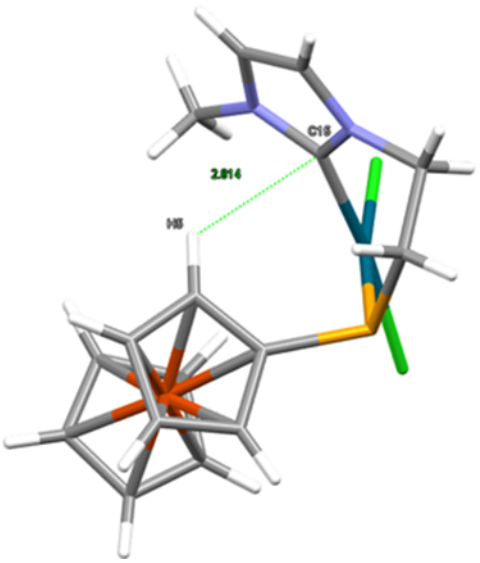



**Figure 8.** Representation of intramolecular interaction between H(5)···$C_{NCN}$ C (15) of **6c**.

**Experimental**

**General Information.** All reactions and manipulations were carried out by using Schlenk-type techniques. Dimethylaminomethyl ferrocene, $Ph_2X_2$ (X = Se, Te) and silver (I) oxide were purchased from commercial sources and were used as received. (Ferrocenylmethyl)trimethylammonium iodide and $PdCl_2(CH_3CN)_2$ were synthesized according to the literature.[31] Organic solvents were dried by standard procedures and distilled under nitrogen prior to use. $^1$H and $^{13}$C{1H} spectra were recorded either on a Bruker 300 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks ($^1$H, $^{13}$C{1H}). All chemical shifts (δ) are reported in ppm and coupling constants, J, are given in Hz to apparent peak multiplications. Spectral assignments were achieved by a combination of $^1$H-$^1$H COSY, and $^1$H-$^{13}$C HSQC/HMBC experiments. The splitting patterns are indicated as follows abbreviations: singlet (*s*), doublet (*d*), doublet of doublet (*dd*), triplet (*t*), quartet (*q*), multiplet (*m*) and broad (br). Mass spectra were obtained using a JEOL JMS-SX102A instrument with m-nitrobenzyl alcohol as the matrix (FAB+ mode), and a JEOL JMS-AX505-A (EI mode at 70 eV). DART analyses were recorded on a Jeol AccuTOF JMS-T100LC mass spectrometer. Elemental compositions were calculated within an uncertainty of 5 ppm by using the program installed in the computer system.

The X-ray diffraction data collection and refinement parameters for compounds **2b**, **3a**, **3c** and **6c** were recorded by Bruker Smart APEX spectrometer using graphite monochromated Mo$K_\alpha$ radiation (0.71073 Å) at 298°K. Data reduction was carried out with the APEX2 software.[32] The structures were solved by SHEXS and refined using SHELX-2016 and 2018.[33] Non-hydrogen atoms were refined anisotropically. H atoms were positioned geometrically and refined with isotropic displacement parameters according the riding model.). Crystal data for the structural analysis is given in Table 1. The CIF file containing complete information on the studied structure was deposited in Cambridge Crystallographic Data Centre deposition number:1983258, 1956452, 1950575 and 1928553 (E-mail: deposit@ccdc.cam.ac.uk), and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

**Synthesis of *N*-PhSeCH$_2$CH$_2$ImH.(1a)** A solution of diphenyldiselenide (0.624g, 2.0 mmol) in ethanol (30 mL) was treated with sodium borohydride (0.151g, 4.0 mmol) and the mixture was further stirred for 30 min. When it became colorless, a solution of 1-(2-chloroethyl)-1*H*-imidazole (0.522g, 4.0 mmol) in ethanol (10 mL) was added with constant stirring for 12 h under nitrogen. Water was added to the solution (40 mL) and was extracted with dichloromethane (4 x 25 mL). The extract was washed with water (2 x 25 mL), dried over anhydrous sodium sulphate and evaporated under reduced pressure to afford the desired compound as yellow oil. Yield (0.956g, 95%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.46 (d, $J_{H\text{-}H}$ = 8.0, 2H, $H_{o\text{-}Ph}$), 7.40 (s, 1H, NC<u>H</u>N), 7.28 (t, $J_{H\text{-}H}$ = 6.8, 1H, $H_{p\text{-}Ph}$), 7.26 (dd, $J_{H\text{-}H}$ = 8.0, 6.8, 2H, $H_{m\text{-}Ph}$), 7.00 and 6.85 (both br, 2H, =C<u>H</u>N), 4.10 (t, $J_{H\text{-}H}$ = 7.0, 2H, N-C<u>H</u>$_2$), 3.11 (t, $J_{H\text{-}H}$ = 7.0, Se-C<u>H</u>$_2$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 298 K): δ 137.0 (s, N<u>C</u>HN), 133.4 (s, $C_{o\text{-}Ph}$), 129.6 (s, $C_{p\text{-}Ph}$), 129.5 (s, $C_{m\text{-}Ph}$), 128.3 (s, $C_{q\text{-}Ph}$), 127.8 and 118.6 (both s, =<u>C</u>HN), 46.9 (s, N-<u>C</u>H$_2$), 28.0 (s, Se-<u>C</u>H$_2$). $^{77}$Se NMR (57 MHz, $CDCl_3$, 298 K): δ 284.0. MS (DART) *m/z*: 253 $[M+H]^+$, 225, 185. HRMS (DART) *m/z* calcd for $C_{11}H_{13}N_2Se$ $[M+H]^+$ 253.0244, found 253.0241.

**Sy** ith sodium borohydride (0.151g, 4.0 mmol) and the mixture was further stirred for 30 min. When it became colorless, a solution of 1-(2-chloroethyl)-1*H*-imidazole (0.522g, 4.0 mmol) in ethanol (10 mL) was added under nitrogen and was heated with constant stirring for 3 h at 90 °C. Water was added to the solution (40 mL) and was extracted with dichloromethane (4 x 25 mL). The extract was washed with water (2 x 25 mL), dried with anhydrous sodium sulphate and evaporated under reduced pressure to afford the desired compound as yellow oil. Yield (1.056g, 87%). $^{1}$H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.66 (d, $J_{H-H}$ = 7.7, 2H, $H_{o-Ph}$), 7.37 (s, 1H, NC<u>H</u>N), 7.27 (t, $J_{H-H}$ = 6.7, 1H, $H_{p-Ph}$), 7.16 (dd, $J_{H-H}$ = 7.7, 6.7, 2H, $H_{m-Ph}$), 6.95 and 6.80 (both br, 2H, =C<u>H</u>N), 4.18 (t, $J_{H-H}$ = 7.4, 2H, N-C<u>H</u>$_2$), 3.07 (t, $J_{H-H}$ = 7.4, 2H, Te-C<u>H</u>$_2$). $^{13}$C{$^{1}$H} NMR (75 MHz, $CDCl_3$, 298 K): δ 139.0 (s, $C_{o-Ph}$), 136.7 (s, N<u>C</u>HN), 129.7 (s, $C_{p-Ph}$), 129.5 (s, $C_{m-Ph}$), 128.4 and 118.2 (both s, =<u>C</u>HN), 110.2 (s, $C_{q-Ph}$), 48.9 (s, N-<u>C</u>H$_2$), 7.9 (s, Te-<u>C</u>H$_2$). ). $^{125}$Te NMR (94.67 MHz, acetone-$d_6$, 298 K): δ 455.13. MS (DART) *m/z*: 303 [M+H]+, 275, 235. HRMS (DART) *m/z* calcd for $C_{11}H_{13}N_2Te$ [M+H]$^+$ 303.0141, found 303.0149.

**Synthesis of *N*-FcSeCH$_2$CH$_2$ImH**. (**1c**) A solution of diferrocenyldiselenide (0.15g, 0.2841 mmol) in ethanol (40 mL) was treated with sodium borohydride (0.0434g, 1.1364 mmol) and the mixture was further stirred at 90°C for 1 h. When the color changes, a solution of 1-(2-chloroethyl)-1H-imidazole (0.0739g, 0.5682 mmol) in ethanol (5 mL) was added with constant stirring for 6 h at 90°C under nitrogen. Water was added to the solution (40 mL) and was extracted with dichloromethane (4 x 25 mL). The extract was dried with anhydrous sodium sulfate and evaporated under reduced pressure to afford the desired compound as an orange oil. Yield (0.1442g, 70.5%). $^{1}$H NMR (300 MHz, acetone-$d_6$, 298 K): δ 7.41 (s, 1H, NC<u>H</u>N), 6.94 and 6.76 (both br, 2H, =C<u>H</u>N), 4.19 and 4.12 (both br, 4H, $Fc_A$), 4.06 (t, $J_{H-H}$ = 7.0, 2H, N-C<u>H</u>$_2$), 4.05 (s, 5H, $Fc_B$), 2.82 (t, $J_{H-H}$ = 7.0, 2H, Se-C<u>H</u>$_2$). $^{13}$C NMR (75 MHz, acetone-$d_6$, 298 K): δ 137.1 (s, N<u>C</u>HN), 128.7 and 118.7 (both s, =<u>C</u>HN), 75.1 and 69.8 (both s, $Fc_B$), 69.7 (s, $C_{q-Fc}$), 69.1 (s, $Fc_A$), 46.7 (s, N-<u>C</u>H$_2$), 29.3 (s, Se-<u>C</u>H$_2$). $^{77}$Se NMR (57 MHz, acetone-$d_6$, 298 K): δ 180.07. MS (DART) *m/z*: 361 [M+H]$^+$, 265. **HRMS:** Found 360.9904 calcd. For $C_{15}H_{17}FeN_2Se$ 360.9906.

**Synthesis of *N*-FcTeCH$_2$CH$_2$ImH**. (**1d**) A solution of diferrocenylditelluride (0.15g, 0.2381 mmol) in ethanol (30 mL) was treated with sodium borohydride (0.0367g, 0.9526 mmol) and the mixture was further stirred for 1 h. When the color changes, a solution of 1-(2-chloroethyl)-1H-imidazole (0.0619g, 0.4763 mmol) in ethanol (5 mL) was added under nitrogen and was heated with constant stirring for 5 h at 90 °C. Water was added to the solution (40 mL) and was extracted with dichloromethane (4 x 25 mL). The extract was dried with anhydrous sodium sulfate and evaporated under reduced pressure to afford the desired compound as yellow solid. Yield (0.156g, 80%). $^{1}$H NMR (300 MHz, acetone-$d_6$, 298 K): δ 7.51 (s, 1H, NC<u>H</u>N), 7.05 and 6.88 (both br, 2H, =CHN), 4.36 and 4.27 (both dd, $J_{H-H}$ = 1.8, 1.8, 4H, $Fc_A$), 4.28 (t, $J_{H-H}$ = 7.8, 2H,N-C<u>H</u>$_2$), 4.16 (s, 5H, $Fc_B$), 2.97 (t, $J_{H-H}$ = 7.8, 2H,Te-C<u>H</u>$_2$). $^{13}$C NMR (100 MHz, acetone-$d_6$, 298 K): δ 136.8 (s, N<u>C</u>HN), 128.8 and 118.4 (both s, =<u>C</u>HN), 79.3 and 71.3 (both s, $Fc_A$), 69.05 (s, $Fc_B$), 48.6 (s, N-<u>C</u>H$_2$), 42.4 (s, $C_{q-Fc}$), 8.23 (s, Te-<u>C</u>H$_2$). $^{125}$Te NMR (94.67 MHz, acetone-$d_6$, 298 K): δ 289.85. MS (DART) *m/z*: 409 [M+H]$^+$ **HRMS:** Found .410.9817 calcd. For $C_{15}H_{17}N_2Te$ 410.9803. Elemental Analysis Calcd for $C_{15}H_{16}FeN_2Te$: C, 44.18; H, 3.96; N, 6.87. Found: C, 44.39; H, 4.04; N, 6.38.

**General procedure for the synthesis of ferrocenyl-chalcogen-imidazolium salts**. A solution of (ferrocenylmethyl)trimethylamonium iodide (6.50 mmol) was reacted with the appropriate 1-substituted imidazole derivative (7.00 mmol) in anhydrous MeCN (20 mL) and the reaction mixture was refluxed for 24 h. After this period, the cooled solution was poured into water (10 mL) and extracted with chloroform (4 x 25 mL). The organic phase was washed with water (2 x 20 mL), dried with $MgSO_4$ and evaporated under reduced pressure to give an orange oil.

**Synthesis of (*N*-PhSeCH$_2$CH$_2$)(*N*´-CH$_2$Fc)ImH$^+$I$^-$.(2a)**. This compound was prepared according to the general procedure and it was isolated as orange oil. Yield (3.46 g, 85%). $^{1}$H NMR (300 MHz, $CDCl_3$, 298 K) δ 9.74 (s, 1H, NCHN), 7.43 (dd, $J_{H-H}$ = 7.5, 2.2, 2H, $H_{o-Ph}$), 7.33 and 7.15 (both t, $J_{H-H}$ = 2.0, 2H, =C<u>H</u>N), 7.24 (dd, $J_{H-H}$ = 7.5, 6.3, 2H, $H_{m-Ph}$), 7.23 (t, $J_{H-H}$ = 6.3, 1H, $H_{p-Ph}$), 5.29 (s, 2H, Fc-C<u>H</u>$_2$), 4.54 (t, $J_{H-H}$ = 6.5, 2H, N-C<u>H</u>$_2$), 4.45 and 4.25 (both dd, $J_{H-H}$ = 1.5, 1.5, 4H, $Fc_A$), 4.24 (s, 5H, $Fc_B$), 3.39 (t, $J_{H-H}$ = 6.5, 2H, Se-C<u>H</u>$_2$). $^{13}$C{$^{1}$H} NMR (75 MHz, $CDCl_3$, 298 K): δ 135.7 (s, N<u>C</u>HN), 133.3 (s, $C_{o-Ph}$), 129.7 (s, $C_{m-Ph}$), 128.0 (s, $C_{p-Ph}$), 127.6 (s, $C_{q-Ph}$), 122.3 and 121.2 (both s, =<u>C</u>HN), 78.2 (s, $C_{q-Fc}$), 69.9 and 69.7 (both s, $Fc_A$), 69.3 (s, $Fc_B$), 50.1 (s, Fc-<u>C</u>H$_2$), 50.0 (s, N-<u>C</u>H$_2$), 27.2 (s, Se-<u>C</u>H$_2$). $^{77}$Se NMR (57 MHz, CDCl3, 298 K): δ 277.4. HRMS (FAB) *m/z* calcd for $C_{22}H_{23}N_2FeSe$ [M-I]+ 451.0376, found 451.0376.

**Synthesis of (*N*-PhTeCH$_2$CH$_2$)(*N*´-CH$_2$Fc)ImH$^+$I$^-$.(2b)**. This compound was prepared according to the general procedure and it was isolated as orange oil. Yield (3.82 g, 80%). $^{1}$H NMR (300 MHz, $CDCl_3$, 298 K) δ 9.64 (s, 1H, NC<u>H</u>N), 7.61 (d, $J_{H-H}$ = 7.4, 2H, $H_{o-Ph}$), 7.40 and 7.26 (both br, 2H, =C<u>H</u>N), 7.22 (t, $J_{H-H}$ = 7.1, 1H, $H_{p-Ph}$), 7.14 (dd, $J_{H-H}$ = 7.4, 7.1, 2H, $H_{m-Ph}$), 5.27 (s, 2H, Fc-C<u>H</u>$_2$), 4.59 (t, $J_{H-H}$ = 6.8, 2H, N-C<u>H</u>$_2$), 4.46 and 4.20 (both br, 4H, $Fc_A$), 4.20 (s, 5H, $Fc_B$), 3.32 (t, $J_{H-H}$ = 6.8, 2H, Te-C<u>H</u>$_2$). $^{13}$C{$^{1}$H} NMR (75 MHz, $CDCl_3$, 298 K): δ 138.6 (s, $C_{o-Ph}$), 134.9 (s, N<u>C</u>HN), 129.7 (s, $C_{m-Ph}$), 128.3 (s, $C_{p-Ph}$), 122.1 and 121.6 (both s, =<u>C</u>HN), 110.9 (s, $C_{q-Ph}$), 78.6 (s, $C_{q-Fc}$), 69.8 (s, $Fc_A$), 69.2 (s, $Fc_B$), 51.8 (s, N-<u>C</u>H$_2$), 50.0 (s, Fc-<u>C</u>H$_2$), 7.9 (s, Te-<u>C</u>H$_2$). HRMS (FAB) *m/z* calcd for $C_{22}H_{23}N_2FeTe$ [M-I]+ 501.0273, found 501.0278.

**Sy** 1-substituted imidazole derivative (7.00 mmol) in anhydrous MeCN (20 mL) and the solution was refluxed for 24 h. After this period, the cooled solution was poured into water (10 mL) and extracted with chloroform (4 x 25 mL). The organic phase was washed with water (2 x 20 mL), dried with MgSO4 and evaporated under reduced pressure to give orange solid.[1]H NMR (300 MHz, acetone-$d_6$, 298 K): δ 9.44 (t, $J_{H-H}$ = 1.6, 1H, NCHN), 7.80 and 7.70 (both dd, $J_{H-H}$ = 1.8, 1.6, 2H, =CHN), 4.58 (t, $J_{H-H}$ = 6.9, 2H, N-$CH_2$), 4.36 and 4.25 (both, dd, $J_{H-H}$ = 1.7, 1.9, 4H, $Fc_A$), -4.17 (s, 5H, $Fc_B$), 4.07 (s ,3H, Me), 3.18 (t, $J_{H-H}$ = 6.9, 2H, Se-$CH_2$). $^{13}$C NMR (75 MHz, acetone-$d_6$, 298 K): δ 137.8 (s, NCHN), 124.5 and 123.4 (both s, =CHN), 76.2 and 70.7 (both s, $Fc_A$), 70.1 (s, $Fc_B$), 69.9 (s, $C_{q\text{-}Fc}$), 50.9 (s, N-$CH_2$), 36.7 (s, Me), 28.7 (s, Se-$CH_2$) $^{77}$Se NMR (57 MHz, acetone-$d_6$, 298 K): δ 175.40. FAB MS *m/z*: $[M+H]^+$ 375.

**General procedure for the synthesis of ferrocenyl NHC selenones.** To a solution of the corresponding imidazolium iodide (1.3332mmol) in anhydrous acetonitrile (10 mL), elemental Se (1.3332mmol) and potassium carbonate (1.3332 mmol) were added. Then, the mixture was stirred at room temperature for 24 h. After this period, the solution was filtered and the filtrate was evaporated under reduced pressure and washed with hexane to give yellow solid.

**Synthesis of (*N*-PhSeCH$_2$CH$_2$)(*N*´-CH$_2$Fc)ImSe.(3a)** This compound was prepared according to the general procedure using (*N*-PhSeCH$_2$CH$_2$)(*N*´-CH$_2$Fc)ImH$^+$I$^-$.(2a) as a reactant. The compound **(3a)** was isolated as a yellow solid Yield 95 % (1.07369 g)**.** $^1$H NMR) (400 MHz, acetone-$d_6$, 298 K): 7.62-7.54 (m, 2H, $H_{m\text{-}Ph}$), 7.31-7.22 (m, 3H, $H_{o,p\text{-}Ph}$), 7.15 and 7.08 (both d, 2H, =CHN), 5.08 (s, 2H, Fc-$CH_2$), 4.49 and 4.16 (both dd, 4H, $Fc_A$), 4.39 (t, $J_{H-H}$ = 7.15, 2H, N-$CH_2$), 4.23 (s, 5H, $Fc_B$), 3.38 (t, $J_{H-H}$ = 7.2, 2H, Se-$CH_2$). $^{13}$C NMR (75 MHz, acetone-$d_6$, 298 K): δ: 156.5 (s, $C_{NCN}$), 132.6 (s,$C_{o\text{-}Ph}$), 130.3 (s, $C_{q\text{-}Ph}$), 130.1 (s, $C_{m\text{-}Ph}$), 127.6 (s, $C_{p\text{-}Ph}$), 120.3 (s, $C_{=CHN}$), 119.2 (s, $C_{=CHN}$), 83.7 (s, $C_{q\text{-}Fc}$), 70.3 and 69.1 (both s, $C_{FcA}$), 69.5 (s, $C_{FcB}$), 50.4 (s, N-$CH_2$), 49.1 (s, Fc-$CH_2$), 25.4 (s, Se-$CH_2$). $^{77}$Se NMR (57 MHz, acetone-$d_6$, 298 K) δ: 268.46 (s, Se-$CH_2$), 14.68 (s, Se-$C_{NHC}$). DART-MS *m/z*: 530 $[M+H]^+$**. HRMS:** Found 528.9548 calcd. $C_{22}H_{23}FeN_2Se_2$ 528.9549.

**Synthesis of (*N*-PhSeCH$_2$CH$_2$)(*N*´-CH$_3$)ImSe.(3b)** This compound was prepared according to the general procedure using (*N*-PhSeCH$_2$CH$_2$)(*N*´-CH$_3$)ImH$^+$I$^-$.[8b] as a reactant. The compound **(3b)** was isolated as a yellow solid. Yield (0.5640g, 93%) $^1$H NMR (300 MHz, acetonitrile-$d_3$, 298 K): δ 7.53 (d, $J_{H-H}$ =7.4, 2H, $H_{o\text{-}Ph}$), 7.29-7.20 (m, 3H, $H_{m,p\text{-}Ph}$), 6.98 and 6.92 (both d, $J_{H-H}$ = 2,3, 2H, =CHN), 4.30 (t, $J_{H-H}$ = 7.3, 2H, N-$CH_2$), 3.52 (s, 3H, Me), 3.30 (t, $J_{H-H}$ = 7.3, 2H, Se-$CH_2$). $^{13}$C NMR (75 MHz, acetonitrile-$d_3$, 298 K): δ 155.94 (s, Se-$C_{NHC}$), 132.54 (s, $C_{o\text{-}Ph}$), 129.9 (s, $C_{m\text{-}Ph}$), 127.54 (s, $C_{p\text{-}Ph}$), 122.3 (s, $C_{q\text{-}Ph}$), 120.6 and 120.1 (both s, =CHN), 50.3 (s, N-$CH_2$), 37.0 (s, Se-$CH_2$), 25.5 (s, Me). $^{77}$Se NMR (57 MHz, acetonitrile-$d_3$, 298 K): δ 268.7 (s, Se-$CH_2$), 32.6 (s, Se-$C_{NHC}$). DART-MS *m/z*: 347 $[M+H]^+$. **HRMS:** Found 344.9580 calcd. For $C_{12}H_{15}N_2Se_2$ 344.9573.

**Synthesis of (*N*-FcSeCH$_2$CH$_2$)(*N*´-CH$_3$)ImSe.(3c)** This compound was prepared according to the general procedure using (*N*-FcSeCH$_2$CH$_2$)(*N*´-CH$_3$)ImH$^+$I$^-$ **(2c)** as a reactant. The compound **(3c)** was isolated as a yellow solid. Yield (0.5640g, 93% $^1$H NMR) (400 MHz, acetone-$d_6$, 298 K): δ 7.08 and 7.06 (both d, $J_{H-H}$ = 2.3, 2H, =CHN), 4.27 and 4.11 (both dd, $J_{H-H}$ = 1.6, 1.8, 4H, $Fc_A$), 4.17 (t, $J_{H-H}$ = 7.5, 2H, N-$CH_2$), 4.05 (s, 5H, $Fc_B$), 3.47 (s, 3H, Me), 2.91(t, $J_{H-H}$ = 6.9, 2H, Se-$CH_2$). $^{13}$C NMR (100 MHz, acetone-$d_6$, 298 K): δ 156.2 (s, Ag-$C_{NHC}$), 119.7 and 119.2 (both s, =CHN), 74.6 and 69.5 (both s, $Fc_A$), 70.5 (s, $C_{q\text{-}Fc}$), 69.2 (s, $Fc_B$), 69.17 (s, C-d), 49.7 (s, N-$CH_2$), 36.0 (s, Me), 26.5 (s, Se-$CH_2$). $^{77}$Se NMR (57 MHz, acetone-$d_6$, 298 K): δ 170.4 (s, Se-$CH_2$), 11.5 (s, Se-$C_{NHC}$). DART-MS *m/z*: 455 $[M+H]^+$. **HRMS:** Found 452.9249 Calcd. $C_{12}H_{15}N_2Se_2$ 452.9236. Elemental Analysis Calcd for $C_{16}H_{19}FeN_2Se_2$: C, 42.51; H, 4.01; N, 6.20. Found: C, 41.97; H, 4.14; N, 5.95.

**General procedure for the synthesis of Ag(I)-ferrocenyl-chalcogen-NHC-complexes.** A solution of 1-ferrocenylmethyl-3-(phenyl-chalcogen-ethyl)imidazolium iodide (0.5 mmol) in anhydrous dichloromethane (20 mL) was added $Ag_2O$ (0.5 mmol) and stirred at room temperature in the dark. After this period, the solution was filtered and evaporated under reduced pressure to yellow-orange oil. The addition of hexane (10 mL) precipitates the desired compound. The corresponding solid was collected by filtration and dried at room temperature.

**Synthesis of (*N*-PhSeCH$_2$CH$_2$)(*N*´-CH$_2$Fc)ImAgI (4a).** This compound was prepared according to the general procedure and was isolated as yellow solid. Yield (280 mg, 81%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.32 (d, $J_{H-H}$ = 6.0, 2H, $H_{o\text{-}Ph}$), 7.11 (dd, $J_{H-H}$ = 6.0, 6.0, 2H, $H_{m\text{-}Ph}$), 7.09 (t, $J_{H-H}$ = 6.0, 1H, $H_{p\text{-}Ph}$), 6.83 and 6.77 (both br, 2H, =CHN), 5.03 (s, 2H, Fc-$CH_2$), 4.33 (t, $J_{H-H}$ = 5.8, 2H, N-$CH_2$), 4.26 and 4.07 (both br, 4H, $Fc_A$), 4.13 (s, 5H, $Fc_B$), 3.22 (t, $J_{H-H}$ = 5.8, 4H, Se-$CH_2$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 298 K): δ 181.5 (s, Ag-$C_{NHC}$), 132.8 (s, $C_{o\text{-}Ph}$), 129.4 (s, $C_{m\text{-}Ph}$), 128.9 (s, $C_{q\text{-}Ph}$), 127.3 (s, $C_{p\text{-}Ph}$), 121.2 and 120.3 (both s, =CHN), 82.1 (s, $C_{q\text{-}Fc}$), 69.4 and 68.9 (both s, $Fc_A$), 69.1 (s, $Fc_B$), 51.8 (s, N-$CH_2$), 51.6 (s, Fc-$CH_2$), 29.2 (s, Se-$CH_2$). $^{77}$Se NMR (57 MHz, $CDCl_3$, 298 K): δ 274.6.

**Synthesis of (*N*-PhTeCH$_2$CH$_2$)(*N*´-CH$_2$Fc)ImAgI. (4b)** This compound was prepared according to the general procedure and was isolated as yellow solid. Yield (310 mg, 84%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.72 (d, $J_{H-H}$ = 7.2, 2H, $H_{o\text{-}Ph}$), 7.24 (t, $J_{H-H}$ = 7.2, 1H, $H_{p\text{-}Ph}$), 7.11 (dd, $J_{H-H}$ = 7.2, 7.2, 2H, $H_{m\text{-}Ph}$), 6.82 and 6.78 (both br, 2H, =CHN), 5.17 (s, 2H, Fc-$CH_2$), 4.65 (t, $J_{H-H}$ = 6.9, 2H, N-$CH_2$), 4.37 and 4.07 (both br, 4H, $Fc_A$), 4.21 (s, 5H, $Fc_B$), 3.34 (t, $J_{H-H}$ = 6.9, 2H, Te-$CH_2$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 298 K): δ

 $C_{q\text{-}Fc}$), 69.5 and 68.9 (both s, $Fc_A$), 69.1 (s, $Fc_B$), 52.4 (s, N-$\underline{C}H_2$), 51.6 (s, Fc-$\underline{C}H_2$), 13.6 (s, Te-$\underline{C}H_2$). MS (FAB) *m/z*: 607 $[M\text{-}I]^+$

**Synthesis of (*N*-FcSeCH$_2$CH$_2$)(*N*´-Me)ImAgI. (4c)** This compound was prepared according to the general procedure and it was isolated as yellow solid. Yield (280 mg, 73%)$^1$H NMR (300 MHz, acetone-$d_6$, 298 K): δ 7.38 and 7.32(both br, 2H, =C$\underline{H}$N), 4.46 (t, $J_{H\text{-}H}$ = 6.9, 2H, N-C$\underline{H}_2$), 4.34 and 4.18 (both dd, $J_{H\text{-}H}$ = 1.6, 1.8, 4H, $Fc_A$), 4.16 (s, 5H,$Fc_B$), 3.91 (s, 3H, Me), 3.09 (t, $J_{H\text{-}H}$ = 6.9, 2H, Se-C$\underline{H}_2$). $^{13}$C NMR (75 MHz, acetone-$d_6$, 298 K): δ 182.46 (s, Ag-$C_{NHC}$), 123.5 and 122.4 (both s, =$\underline{C}$HN), 75.8 and 70.5 (both s, $Fc_A$), 71.1 (s, $C_{q\text{-}Fc}$), 70.1 (s, $Fc_B$), 52.7 (s, N-$\underline{C}H_2$), 39.0 (s,Me), 30.9 (s, Se-$\underline{C}H_2$), $^{77}$Se NMR (57 MHz, acetone-$d_6$, 298 K): δ 173.4.

General procedure for the synthesis of palladate ferrocenyl-chalcogen-NHC complexes. A solution of the corresponding ferrocenyl-chalcogen-NHC (6.50 mmol) was treated with $PdCl_2(CH_3CN)_2$ (3.25 mmol) in anhydrous $CHCl_3$ (5 mL). The crude reaction mixture was evaporated under reduced pressure to give red oil.

**Synthesis of [(*N*-PhSeCH$_2$CH$_2$)(*N*´-CH$_2$Fc)ImH]$^+$ $PdCl_2I_2^{-2}{}_{1/2}$ (5a)** This compound was prepared according to the general procedure and it was isolated as red oil. Yield (3.91 g, 91%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K) δ 10.09 (s, 1H, NCHN), 7.38 (dd, $J_{H\text{-}H}$ = 7.5, 2.2, 2H, $H_{o\text{-}Ph}$), 7.31 and 7.09 (both t, $J_{H\text{-}H}$ = 2.0, 2H, =CHN), 7.18 (dd, $J_{H\text{-}H}$ = 7.5, 6.3, 2H, $H_{m\text{-}Ph}$), 7.16 (t, $J_{H\text{-}H}$ = 6.3, 1H, $H_{p\text{-}Ph}$), 5.23 (s, 2H, Fc-$CH_2$), 4.52 (t, $J_{H\text{-}H}$ = 6.5, 2H, N-$CH_2$), 4.38 and 4.16 (both dd, $J_{H\text{-}H}$ = 1.5, 1.5, 4H, $Fc_A$), 4.17 (s, 5H, $Fc_B$), 3.38 (t, $J_{H\text{-}H}$ = 6.5, 2H, Se-$CH_2$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 298 K): δ 134.3 (s, NCHN), 133.3 (s, $C_{o\text{-}Ph}$), 127.6 (s, $C_{m\text{-}Ph}$), 125.9 (s, $C_{p\text{-}Ph}$), 125.8 (s, $C_{q\text{-}Ph}$), 120.5 and 119.0 (both s, =CHN), 76.6 (s, $C_{q\text{-}Fc}$), 67.8 and 67.6 (both s, $Fc_A$), 67.3 (s, $Fc_B$), 48.1 (s, Fc-$CH_2$), 48.0 (s, N-$CH_2$), 27.9 (s, Se-$CH_2$). $^{77}$Se NMR (57 MHz, $CDCl_3$, 298 K): δ 277.3. MS (FAB) *m/z*: 430 $[PdCl_2I]^-$.HRMS (FAB) *m/z* calcd for $C_{22}H_{23}N_2FeSe$ $[M\text{-}PdCl_2I_2]$+ 451.0376, found 451.0376.

**Synthesis of. [(*N*-PhTeCH$_2$CH$_2$)(*N*´-CH$_2$Fc)ImH]$^+$ $PdCl_2I_2^{-2}{}_{1/2}$ (5b)** This compound was prepared according to the general procedure and was isolated as orange oil. Yield (4.06 g, 87%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K) δ 10.23 (s, 1H, NCHN), 7.82 (d, $J_{H\text{-}H}$ = 7.6, 2H, $H_{o\text{-}Ph}$), 7.58 and 7.18 (both br, 2H, =CHN), 7.32 (t, $J_{H\text{-}H}$ = 7.2, 1H, $H_{p\text{-}Ph}$), 7.21 (dd, $J_{H\text{-}H}$ = 7.6, 7.2, 2H, $H_{m\text{-}Ph}$), 5.28 (s, 2H, Fc-$CH_2$), 4.75 (t, $J_{H\text{-}H}$ = 6.8, 2H, N-$CH_2$), 4.45 and 4.22 (both br, 4H, $Fc_A$), 4.23 (s, 5H, $Fc_B$), 3.70 (t, $J_{H\text{-}H}$ = 6.8, 2H, Te-$CH_2$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 298 K): δ 138.3 (s, $C_{o\text{-}Ph}$), 135.8 (s, NCHN), 129.7 (s, $C_{m\text{-}Ph}$), 129.4 (s, $C_{p\text{-}Ph}$), 122.3 and 121.2 (both s, =CHN), 114.6 (s, $C_{q\text{-}Ph}$), 78.7 (s, $C_{q\text{-}Fc}$), 69.8 and 69.7 (both s, $Fc_A$), 69.2 (s, $Fc_B$), 50.3 (s, N-$CH_2$), 49.9 (s, Fc-$CH_2$), 17.9 (s, Te-$CH_2$).

**Synthesis of (*N*-FcSeCH$_2$CH$_2$)(*N*´-CH$_3$)ImPdCl$_2$ (6c).** A solution of (*N*-FcSeCH$_2$CH$_2$)(*N*´-Me)ImAgI (**4c**) (3.25 mmol) was treated with $PdCl_2(CH_3CN)_2$ (3.25 mmol) in anhydrous acetonitrile (5 mL). The crude reaction mixture was evaporated under reduced pressure to give red oil which was purified on a celite column using a 95/5 ethyl acetate-hexane (95:5) mixture. The resulting solid was filtered and dried at room temperature. $^1$H NMR (300 MHz, acetonitrile-$d_3$, 298 K) δ 7.16 and 7.10 (both d, $J_{H\text{-}H}$ = 1.9, 2H, =CHN), 4.56 (m, 2H, N-C$\underline{H}_2$), 4.28, 4.28, 4.09, and 3.73 (all m, 4H, $Fc_A$), 4.47 (s, 5H, $Fc_B$), 4.11 (s, 3H, Me), 3.53 and 2.32 (both m, 2H, Se-C$\underline{H}_2$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 298 K): δ 151.3 (s, Pd-$C_{NHC}$), 125.0 and 123.3 (both s, =CHN), 72.9 (s, $C_{q\text{-}Fc}$), 70.7, 70.2, 69.8, and 69.3 (all s, $Fc_A$), 69.3 (s, $Fc_B$), 52.1 (s, N-$\underline{C}H_2$), 39.2 (s, Me), 37.4 (s, Se-$\underline{C}H_2$). $^{77}$Se NMR (57 MHz, acetonitrile-$d_3$, 298 K): δ 162.3. DART-MS *m/z*: 589 [M+H+Cl]+. HRMS: Found 551.8519 Calcd. $C_{16}H_{18}Cl_2FeN_2PdSe$ 551.8529.

**Table 1.** Crystallographic data for compounds **2b, 3a, 3c** and **6c**

| Compound | **2b** | **3a** | **(3c)** | **6c** |
|---|---|---|---|---|
| Moiety formula | $C_{22}H_{23}FeN_2Te_1I$ | $C_{22}H_{22}FeN_2Se_2$ | $C_{16}H_{18}FeN_2Se_2$ | $C_{16}H_{18}Cl_2FeN_2PdSe$ |
| Mr | 625.77 | 528.19 | 452.09 | 635.36 |
| Temp | 298 k | 150 K | 150 K | 250 K |
| λ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P21/c | P21/c | C2 | P21/c |
| Cell | a = 8.8989(14) Å | a = 14.0188(6) Å | a = 38.635(2) Å | a = 191490(8) Å |
| | b = 23.167(4) Å | b = 10.0612(4) Å | b = 7.5167(4) Å | b = 8.1857(4) Å |
| | c = 11.1057(16) Å | c = 14.3661(5) Å | c = 11.6786(6) Å | c = 14.8480(5) Å |
| | α = 90° | α = 90° | α = 90° | α = 90° |
| | β = 101.824(5)° | β = 97.348(1)° | β = 104.075° | β = 112.553(2)° |
| | γ =90° | γ = 90° | γ = 90° | γ = 90° |
| Volume (Å$^3$) | 2241.0 (6) | 2009.64 (14) | 3289.7 (3) | 2149.41 (16) |
| Z | 4 | 4 | 8 | 4 |
| $D_{cal}$ (g/cm$^3$) | 1.855 | 1.746 | 1.826 | 1.963 |
| M (mm$^{-1}$) | 3.335 | 4.382 | 5.337 mm-1 | 3.707 |

| | | | | |
|---|---|---|---|---|
| $R_1[I>2\sigma(I)]$ | 0.0481 | 0.0228 | 0.0380 | 0.0481 |
| Transmission factor | min = 0.294 | min = 0.2096 | min = 0.625 | min = 0.313 |
| | max = 0.417 | max = 0.286 | max = 0.726 | max = 0.752 |
| reflns number total | 6297 | 3680 | 5964 | 3937 |
| reflns number gt | 4249 | 3339 | 5236 | 2879 |

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgments**

We thank DGAPA-UNAM for financial support (PAPIIT IN209020) and CONACyT (Fellowship 915760).

**References**

[1] (a) J. M. Praetorius, C. M. Crudden, *Dalton Trans.* **2008**, 4079-4094. (b) A. J. Arduengo, L. I. Iconaru, *Dalton Trans.* **2009**, 6903-6914. (c) L. Mercs, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903-1912. (d) W. Liu, R. Gust, *Chem. Soc. Rev.* **2013**, *42*, 755-773. (e) R. Visbal, M. C. Gimeno, *Chem. Soc. Rev.* **2014**, *43*, 3551-3574. (f) D. Zhang, G. Zi, *Chem. Soc. Rev.* **2015**, *44*, 1898-1921. (g) A. Di Giuseppe, R. De Luca, R. Castarlenas, J. J. Pérez-Torrente, M. Crucianelli, L. A. Oro, *Chem. Commun.* **2016**, *52*, 5554-5557. (h) L. Rubio-Pérez, M. Iglesias, J. Muharriz, V. Polo, V. Passarelli, J. J. Pérez-Torrente, L. A. Oro, *Chem. Sci*. **2017**, *8*, 4811-4822. (i) A. Iturmendi, L. Rubio-Pérez, J. J. Pérez-Torrente, M. Iglesias, L. A. Oro, *Organometallics* **2018**, *37*, 3611-3618. (j) R. Azpiroz, A. Di Giuseppe, A. Urriolabeitia, V. Passarelli, V. Polo, J. J. Pérez-Torrente, L. A. Oro, R. Castarlenas, *ACS Catal*., **2019**, *9*, 9372-9386.

[2] (a) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606-5655. (b) A. T. Biju, Kuhl, N. Gloris, F. Acc. *Chem. Res.* **2011**, *44*, 1182-1195. (c) S. J. Ryan, L. Candish, D. W. Lupton, *Chem. Soc. Rev*. **2013**, *42*, 4906-4917. (c) Y. Du, Y. Wang, X. Li, Y. Shao, G. Li, R. D. Webster, Y. R. Chi, *Org. Lett*. **2014**, *16*, 5678-5681. (c) J. C. A. Flanagan, E. J. Kang, N. I. Strong, R.M. Waymouth, *ACS Catal*. **2015**, *5*, 5328-5332. (c) R. S. Menon, A. T. Biju, V. Nair, Beilstein *J. Org. Chem*. **2016**, *12*, 444-461. (d) D. Janssen-Müller, M. Fleige, D. Schlüns, M. Wollenburg, C. G. Daniliuc, J. Neugebauer, F. Gloris, *ACS Catal*. **2016**, *6*, 5735-5739. (e) L. Wang, L. Sun, M. Blümel, R. Puttreddy, A. Peuronen, K. Rissanen, Enders, D. *Angew. Chem. Int. Ed.* **2017**, *56*, 8516-8521.

[3] (a) A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo, S. P. Nolan, *Organometallics* **2003**, *22*, 4322-4326. (b) S. Würtz, F. Glorius, *Acc. Chem. Res.* **2008**, *41*, 1523-1533. (c) H. Clavier, S. P. Nolan, *Chem. Commun*. **2010**, *46*, 841-861. (d) D. J. D. Wilson, S. A. Couchman, J. L. Dutton, *Inorg. Chem*. **2012**, *51*, 7657-7668.

[4] (a) A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, S. Kleinhenz, M. B. Hursthouse, *Chem. Commun.* **2000**, 1247-1248. (b) E. Fogler, E. Balaraman, Y. Ben-David, G. Leitus, L. J. W. Shimon, D. Milstein, *Organometallics* **2011**, *30*, 3826-3833. (c) K. Y. Wan, A. J. Lough, R. H. Morris, *Organometallics* **2016**, *35*, 1604-1612. (d) L. Le, J. Liu, T. He, D. Kim, E. J. Lindley, T. N. Cervarich, J. C. Malek, J. Pham, M. R. Buck, A. R. Chianese, *Organometallics* **2018**, *37*, 3286-3297.

[5] (a) S. Gaillard, J. L. Renaud, *Dalton Trans* **2013**, *42*, 7255-7270. (b) C. A. Wheaton, J. P. J. Bow, M. Stradiotto, *Organometallics* **2013**, *32*, 6148-6161. (c) P. Ai, A. A. Danopoulos, P. Braunstein, *Organometallics* **2015**, *34*, 4109-4116. (d) P. Ai, A. A. Danopoulos, P. Braunstein, *Dalton Trans* **2016**, *45*, 4771-4779. (e) T. Simler, S. Choua, A. A. Danopoulos, P. Braunstein *Dalton Trans* **2018**, *47*, 7888-7895. (f) K. Takahashi, K. Cho, A. Iwai, T. Ito, N. Iwasawa, *Chem. Eur. J.* **2019**, *25*, 1-6.

[6] (a) P. L. Arnold, M. S. Sanford, S. M. Pearson, *J. Am. Chem. Soc*. **2009**, *131*, 13912-13913. (b) A. Meyer, Y. Unger, A. Poething, T. Strassner, *Organometallics* **2011**, *30*, 2980-2985. (c) L. Busetto, M. C. Cassani, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni, G. Solinas, *Organometallics* **2011**, *30*, 5258-5272. (d) M. Iglesias, M. Pérez-Nicolás, P. J. Sanz-Miguel, V. Polo, F. J. Fernández-Alvarez, J. J. Pérez-Torrente, L. A. Oro, *Chem. Commun.* **2012**, *48*, 9480-9482. (e) A. Vellé, A. Cebollada, R. Macías, M. Iglesias, M. Gil-Moles, P. J. Sanz-Miguel, *ACS Omega* **2017**, *2*, 1392-1399. (f) M. O. Karatas, A. Di Giuseppe, V. Passarelli, B. Alici, J. J. Pérez-Torrente, L. A. Oro, I. Özdemir, R. Castarlenas, *Organometallics* **2018**, *37*, 191-202.

[7] (a) M. Bierenstiel, E. D. Cross, Cord. *Chem. Rev*. **2011**, *255*, 574-590. (b) D. Yuan, H. V. Huynh, *Molecules* **2012**, *17*, 2491-2517.

[8] (a) H. Joshi, K. N. Sharma, V. V. Singh, P. Singh, A. K. Singh, *Dalton Trans* **2013**, *42*, 2366-2370. (b) K. N. Sharma, H. Joshi, A. K. Sharma, O. Prakash, A. K. Singh, *Organometallics* **2013**, *32*, 2443-2451. (c) Rishu, B. Prashanth, D. Bawari, U. Mandal, A. Verma, A. R. Choudhury, S. Singh, *Dalton Trans* **2017**, *46*, 6291-6302.

[9] P. Braunstein, F. Naud, *Angew. Chem. Int. Ed*. **2001**, *40*, 680-699.

[10] F. Camponovo, A. Togni, *Eur J. Inorg. Chem*. **2005**, 347-356. (c) U. E. I. Horvath, G. Bentivoglio, M. Hummel, H. Schottenberger, K. Wusrt, M. J. Nell, C. E. J. van Rensburg, S. Cronie, H. G. Raubenheimer, *New. J. Chem*. **2008**, *32*, 533-539. (d) P. He, Y. Du, S. Wang, C. Cao, X. Wang, G. Pang, Y. Z. Shi, *Anorg. Allg. Chem.* **2013**, *639*, 1004-1000. (e) S. Ibáñez, M. Poyatos, L. N. Dawe, D. Gusev, E. Peris, *Organometallics* **2016**, *35*, 2747-2758. (f) J. K. Muenzner, B. Biersack, A. Albrecht, T. Rehm, U. Lacher, W. Milius, A. Casini, J.-J. Zhang, I. Ott, V. Brabec, O. Stuchlokova, I. C. Andronache, L. Kaps, D. Schuppan, R. Schobert, *Chem. Eur. J.* **2016**, *22*, 18953-18962. (g) D. Kale, G. Rashinkar, A. Kumbhar, R. Salunkhe, *React Funct Polym.* **2017**, *116*, 9-16.

[11] (a) Q. Li, X. Li, J. Yang, H.-B. Song, L.-F. Tang, *Polyhedron* **2013**, *59*, 29-37. (b) Z.-M. Su, H.-M. Ye, X.-X. Zhu, L.-L. Xie, S. Bai, Y.-F. Yuan, *J. Organomet. Chem*. **2014**, *750*, 162-168. (c) C. Thie, C. Bruhn, U. Siemeling, *Eur. J. Inorg. Chem.* **2015**, 5457-5466. (d) V. Bui-Thi-Tuyet, G. Trippé-Allard, J. Ghilane, H. Randriamahazaka, *ACS Appl. Mater. Interfaces* **2016**, *8*, 28316-28324.

[12] (a) S. K. Tripathi, U. Patel, D. Roy, R. B. Sunoj, H. B. Singh, G. Wolmershauser, R. J. Butcher, *J. Org. Chem.* **2005**, *70*, 9237-9247. (b) A. J. Mukherjee, S. S. Zade, H. B. Singh, R. B. Sunoj, *Chem. Rev.* **2010**, *110*, 4357-4416. (c) C. A. Bayse, A. Pavlou, *Org. Biomol. Chem*. **2011**, *9*, 8006-8015. (d) S. M. Mali, T. F. Schneider, A. Bandyopadhyay, S. V. Jadhav, D. B. Werz, H. N. Gopi, *Crys. Growth Des*. **2012**, *12*, 5643-5648. (e) V. P. Singh, J.-f. Poon, R. J. Butcher, L. Engman, *Chem. Eur. J.* **2014**, *20*, 12563-12571. (f) S. Hayashi, K. Matsuiwa, N. Nishizawa, W. Nakanishi, *J. Org. Chem*. **2015**, *80*, 11963-11976. (g) P. S. Camacho, D. McKay, D. M. Dawson, C. Kirst, J. R. Yates, T. F. G. Green, D. B. Cordes, A. M. Z. Slawin, J. D. Woollins, S. E. Ashbrook, *Inorg. Chem.* **2016**, *55*, 10881-10887.

[13] (a) A. Molter, F. Mohr, Coord. *Chem. Rev*. **2010**, *254*, 19-45. (b) M. Godoi, M. W. Paixao, A. L. Braga, *Dalton Trans*. **2011**, *40*, 11347-11355. (c) A. Kumar, G. K. Rao, F. Salem, A. K. Singh, *Dalton Trans.* **2012**, *41*, 11949-11977. (d) A. Kumar, G. K. Rao, S. Kumar, A. K. Singh, *Organometallics* **2014**, *33*, 2921-2943. (e) M. Azizpoor, M. J. Willans, B. K. Najafabadi, T. I. Levchenko, J. F. Corrigan, *Dalton Trans*. **2015**, *44*, 8267-8277. (f) A. Pop, C. Bellini, R. Suteu, V. Dorcet, T. Roisnel, J.-F. Carpentier, A. Silvestru, Y. Sarazin, *Dalton Trans*. **2017**, *46*, 3179-3191.

[14] (a) M. Carla, Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, P. Grimaldi, F. Isaia, F. Leji, V. Lippolis, G. Verani, *Eur. J. Inorg. Chem.* **2004**, 2363-2368. (b) D. J. Nelson, F. Nahra, S. R. Patrick, D. B. Cordes, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2014**, *33*, 3640-3645. (c) M. M. Kimani, D. Watts, L. A. Graham, D. Rabinovich, G. P. A. Yap, J. L. Brumaghim, *Dalton Trans* **2015**, *44*, 16313-16324. (d) M. C. Aragoni, M. Arca, A. J. Blake, L. Copolovici, F. Isaia, V. Lippolis, A. Pop, C. Silvestru, J. P. Tidey and R. A. Varga, *New J. Chem.*, **2019**, *43*, 11821-11831.

[15] (a) D. G. Gusev, *Organometallics* **2009**, *28*, 6458-6461. (b) D. G. Gusev, E. Peris, *Dalton Trans* **2013**, *42*, 7359-7364. (c) P. R. Sultane, G. Ahumada, D. Janser-Müller, C. W. Bielawski, *Angew. Chem. Int. Ed*. **2019**, *58*, 16320-16325.

[16] (a) A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, *Organometallics* **2013**, *32*, 5269–5272. (b) O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed*. **2013**, *52*, 2939–2943. (c) R. R. Rodrigues, C. L. Dorsey, C. A. Arceneaux, T. W. Hudnall, *Chem. Commun*. **2014**, *50*, 162–164. (d) D. J. Nelson, A. Collado, S. Manzini, S. Meiries, A. M. Z. Slawin, D. B. Cordes, S. P. Nolan, *Organometallics* **2014**, *33*, 2048–2058.

[17] W. A. Herrmann, C. Köcher, L. J. Gooβen, G. R. J. Artus, *Chem. Eur. J*. **1996**, *2*, 1627-1636.

[18] I. Alkorta, J. Elguero, *J. Heterocyclic Chem*. **2019**, *56*, 359-370.

[19] (a) W. P. Fehlhammer, T. Bliss, U. Kernbach, I. Brüdgam, *J. Organomet. Chem.* **1995**, *490*, 149-153. (b) A. M. Voutchkova, L. N. Appelhans, A. R. Chianese, R. H. Crabtree, *J. Am. Chem. Soc*. **2005**, *127*, 17624-17625. (c) E. Chardon, G. Dahm, G. Guichard, S. Bellemin-Laponnaz, *Inorganica Chimica Acta*, **2017**, *467*, 33-38.

[20] (a) M. T. Zamora, M. J. Ferguson, R. Mcdonald, M. Cowie, *Organometallics*, **2012**, *31*, 5463-5477. (b) M. V. Jimenez, J. Fernández-Tornos, J. J. Pérez-Torrente, F. J. Modrego, P. Garcia-Orduña, L. A. Oro, *Organometallics*, **2015**, *34*, 926-940.

[21] (a) S. Hameury, P. de Frémont, P.-A. R. Breuil, H. Olivier-Bourbigou, P. Braunstein, *Dalton Trans*. **2014**, *43*, 4700-4710. (b) T. Simler, P. Braunstein, A. A. Danopoulos, *Angew. Chem. Int. Ed*. **2015**, *127*, 13895-13899. (c) F. Nahra, A. Gomez-Herrera, C. S. J. Cazin, *Dalton Trans*. **2017**, *47*, 628-631. (d) M. H. Yu, H. H. Yang, Y. C. Gu, B. H. Wang, F. C. Liu, I. J. B. Lin, G. H. Lee, *J. Organomet. Chem*. **2019**, *887*, 12-17.

[22] R. Azpiroz, P. Sharma, F. J. Pérez-Flores, R. Gutierrez, G. Espinosa-Pérez, F. Lara-Ochoa, *J. Organomet. Chem*. **2017**, *848*, 196-206.

[23] . A. Bayse, *Inorg. Chem*. **2004**, *43*, 1208-1210.

[24] J. Howarth, J.-L. Thomas, K. Hanlon, D. McGuirk, *Synth. Commun*. **2000**, *30*, 1865-1878.

[25] , *J. Org. Chem*. **2013**, *78*, 5723-5730. (c) M. Hans, J. Lorkowski, Demonceau, A. L. Delaude, *Beilstein J. Org. Chem*. **2015**, *11*, 2318-2325.

[26] (a) C. Xu, J.-F. Gong, S.-F. Yue, Y. Zhu, Y.-J. Wu, *Dalton Trans.* **2006** 4730-4739. (b) H. Matter, M. Nazaré, S. Güssregen, D. W. Will, H. Schreuder, A. Bauer, M. Urmann, K. Ritter, M. Wagner, V. Wehner, *Angew. Chem. Int. Ed*. **2009**, *48*, 2911-2916. (c) C. Xu, Z.-Q. Wang, Y.-P. Zhang, X.-M. Dong, X.-Q. Hao, W.-J. Fu, B.-M. Ji, M.-P. Song, *Eur. J. Inorg. Chem.* **2011** 4878-4888. (d) D. Trzybinski, A. Sikorski, *CrystEngComm* **2013**, *15*, 6808-6818. (e) C. Xu, H.-M. Li, Z.-Q. Xiao, Z.-Q. Wang, S.-F. Tang, B.-M. Ji, X.-Q. Hao, M.-P. Song, *Dalton Trans.* **2014**, *43*, 10235-10247. (f) K. Y. Suponitsky, N. I. Burakov, A. L. Kanibolotsky, V. A. Mikhailov, *J. Phys. Chem. A.* **2016**, *120*, 4179-4190.

[27] P. Sharma, N. Rosas, A. Cabrera, A. Toscano, M. Silva, D. Pérez, L. Velasco, J. Pérez, R. Gutierrez, *J. Organomet. Chem*. **2005**, *690*, 3286-3291.

[28] L. Palacios, X. Miao, A. Di Giuseppe, S. Pascal, C. Cunchillos, R. Castarlenas, J. J. Pérez-Torrente, F. J. Lahoz, P. H. Dixneuf, L. A. Oro, *Organometallics* **2011**, *30*, 5208-5213.

[29] E. Silarska, A. M. Trzeciak, *J. Mol. Cat. A: Chem*. **2015**, *408*, 1-11.

[30] S. Jing, C. P. Morley, C. A. Webster, M. Di Vaira, *Eur. J. Inorg. Chem*. **2008**, 5067-5075.

[31] (a) T. Goseki, M.-a. Hirai, T. Kakimoto, I. Hayakawa, *J. Polym.Sci*. **2012**, 1-10. (b) M. A. Andrews, T. C. T. Chang, C. W. F. Cheng, T. J. Emge, K. P. Kelly, T. F. Koetzle, *J. Am. Chem. Soc*. **1984**, *106*, 5913-5920.

[32]. APEX2 Software Package, Bruker AXS Inc., USA, Madison, (2005).

[33]. G. M. Sheldrick, Acta Cryst, 2015, A71, 3-8.

# Ferrocenylated Chalcogen (Se and Te)-Containing N-Heterocyclic Carbenes: Selenones, Silver and Palladium Complexes

Rodary Gonzalez,[a] Ramón Azpiroz,[a] Pankaj Sharma,[a*] Claudia P. Villamizar-Caballero,[a] Bertín Anzaldo,[a] Francisco J. Pérez-Flores,[a] Alfredo Ruben. Toscano [a]

[a] Instituto de Química Universidad Autónoma de México UNAM, Cd., Universitaria, PO Box 04510, Ciudad de México, México. *E-mail: pankajsh@servidor.unam.mx* México. *E-mail: pankajsh@servidor.unam.mx*

**Conflicts of interest**

There are no conflicts to declare.

**CRediT author statement**

**Rodary Gonzalez:** Methodology, validation, Writing - Review and editing; **Ramón Azpiroz.**: Methodology, validation, Writing- Original draft preparation a Pankaj Sharma,: conceptualization, Investigation, supervision; ***Claudia P. Villamizar C****:* investigation, methodology, Writing - Review and editing; **Bertin Anzaldo**: methodology, Validation; **Francisco J. Pérez-Flores:** data curation; Ruben Alfredo Toscano: data curation.

## Highlights

- New Ferrocenylated Chalcogen (Se and Te)-Containing imidazolium salts.
- Molecular structures of ferrocenyl-NHC selenones, silver NHC and ionic palladium (II) complexes
- New palladium(II)- Ferrocenylated Chalcogen containing NHC complex by silver carbene transfer reaction