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Anionic Bismuth(III) chloride cluster with diselenide countercations: Application in C-S cross coupling reactions

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ABSTRACT

The first weakly coordinating anion (WCA) with reactive p-block cation (rPBC) type of $[(Bi_4Cl_{16})^{4-}\{(LSeSeL)^{2+}\}_2]$, L = 1,3-bis(2-benzhydryl-4,6-dimethylphenyl)-1H-imidazole-2(3H), ion pair is reported. The tetranuclear anionic bismuth(III) cluster shows a new type of ladder structure with two different types of Bi(III) coordination modes. In the solid state structure, the tetranuclear bismuth(III) cluster is sandwiched by two diselenide cations through hydrogen bonding interactions. Besides, this ion pair has been efficaciously employed as catalyst in C-S cross-coupling reactions under optimized reaction condition. This ion pair depicted a wide range of substrate scope with different thiols and aryl halides.

1. Introduction

The N-heterocyclic carbene (NHC) analogues of chalcogenones (S, Se, Te), have depicted the upsurge growth in the field of organometallic chemistry owing to their potential applications in supramolecular [1], medicinal [2] and materials chemistry [3–6]. Especially, the oxidation of imidazole selone is known as the pivotal reaction in the metabolism of several biological process [7]. Such oxidation of 1,3-disubstituted imidazole was carried out under suitable conditions using suitable oxidizing agents such as 7,7',8,8'-tetracyano-*p*-quinodimethane [8] or I_2 [9,10] or Te or ICl or IBr [8,11] or Br_2 [12–14] or HCl/air [15–17]. Several 1,3- disubstituted imidazole diselenide dications have been isolated and most of them are structurally characterized [18]. However, the metal catalyzed oxidation of 1,3-disubstituted imidazole selone or thione has not been realized until 2011 [19]. The first triflate salts of 1,3-disubstituted imidazole disulfide dications or diselenide dications have been derived using $Cu(OTf)_2$ [20]. Later, the oxidative reaction of sterically crowded IPrSe or IPr'Se ($IPr = \{(HCN(C_6H_3\text{-}i Pr_2\text{-}2,6))_2C\}$; $IPr' = [(HC)_2\{N(C_6H_3\text{-}i Pr_2\text{-}2,6)\}\{NCH_2C(O)OMe\}C]$ by $Bi(OTf)_3$ or $Cu(-ClO_4)_2 \cdot 6H_2O$ was reported to isolate $[(IPr)Se]_2^{2+}\{^-OTf\}_2]$ or $[(IPr')Se]_2^{2+}\{\text{-}O_4Cl\}_2]$, respectively [21]. Although the metal salt route to imidazole diselenide dication is well established, the weakly coordinating anion (WCA) with reactive p-block cations (rPBC) class of pair is not known [22].

Thus, we now report the isolation of first bismuth tetra anionic salt as WCA with semi-super bulky bis-1,3-diimidazole diselenide as rPBC from the direct oxidation of 1,3-bis(2-benzhydryl-4,6-dimethylphenyl)-1H-imidazole-2(3H)-selenone (**1**) by $BiCl_3$. In addition, the application of WCA-rPBC pair in C-S cross coupling reactions are demonstrated.

2. Results and discussion

2.1. Synthesis and characterization of 1 and 2

Organo imidazolin-2-selone ligand **1** with spatially defined steric impact was synthesized in very good yield from the reaction between 1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazolium chloride and elemental selenium powder in the presence of activated K_2CO_3 in methanol (Scheme 1) [23]. In solution state, **1** adopts two different conformations with 2:1 ratio. The mixture of two conformations was obtained in deuterated chloroform solution. However, the identity of each rotamer was very complicated. In NMR analysis, ^1H and ^{13}C spectra gave complicated splitting and related information due to free rotation around C-N bond slowing the interchange between conformations. The rotamers of the ligand was confirmed by FT-IR, multinuclear (^1H and ^{13}C) NMR, and TGA. In molecule **1**, the FTIR stretching frequency for C = Se was located at 1266 and 1167 cm^{-1}. Upon seleniation, the ^1H NMR signal for the

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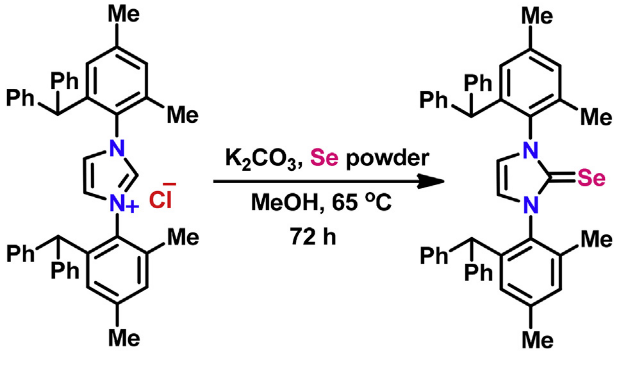


1

Scheme 1. Synthesis of **1**.

acidic N(CH)N protons (around $\delta = 10.5-12.0$) present in 1,3-bis(2-benzhydryl-4,6-dimethylphenyl)-1H-imidazolium chloride was absent in imidazolin-2-selone (**1**). In ^{13}C NMR, the carbene carbon attached to selenium shows two signals at $\delta = 159.1$ and 158.1.

Subsequently, the tetra nuclear bismuth(III) selone complex **2** was synthesized from the reaction between $BiCl_3$, and an equimolar quantity of organo selone (**1**) in toluene at room temperature (Scheme 2). The complex **2** was isolated as orange red precipitate with good yield. **2** is soluble in highly polar organic solvents like methanol, acetonitrile and dimethyl sulfoxide, while insoluble in dichloromethane, chloroform and petroleum ether. **2** is stable under ambient condition. The ^{1}H NMR chemical shift values of **2** are almost similar to that of **1**.

The ^{13}C NMR chemical shift value of *C*=Se in **2** showed δ 1–3 upfield shift compared to that of **1.** The solid state structure of **2** was further confirmed by single crystal X-ray diffraction technique. The suitable single crystals for the X-ray analysis of **2** were isolated from the saturated solutions of acetonitrile at room temperature (Table 1). The X-ray crystallographic analyses of **2** suggests that the *syn* conformer is preferred in the solid state due to intermolecular interactions [23].

2 is a rare example for the weakly coordinating anion (WCA) with reactive p-block cations (rPBC) class of pair. The tetra anionic tetranuclear bismuth(III) chloride cluster, $[Bi_2Cl_{16}]^{4-}$ is stabilized by the two diselenide counter cations (Fig. 1). Interestingly, $[Bi_2Cl_{16}]^{4-}$ in **2** shows an unusual structural motive with two different types of coordination environment around bismuth(III) centers.

The possible mechanism for the formation of $[Bi_4Cl_{16}]^{4-}$ can be rationalized through the formation of edge-edge dimer $[Bi_2Cl_8]^{2-}$ from Ψ-square-based pyramidal $[BiCl_4]^{-}$ unit with retention of lone-pair electrons (Scheme 3) [24]. Further dimerization of $[Bi_2Cl_8]^{2-}$ anions could lead to the formation of $[Bi_4Cl_{16}]^{4-}$anions, which got trapped by two semi-super bulky diselenide cations. Though few $[Bi_4Cl_{16}]^{4-}$ clusters have been reported with cations like $[Mg(MeCN)_6]_2$ [24a], N,N,N′,N′,N″,N″-hexamethylguanidinium ion [24b], 1-butylpyridinium cation [24c], and $(Ph_4P)_4$ [24d], in all these cases Bi(III) centers are in a distorted octahedral geometry with six chloride ions (Type A cluster, Scheme 3). The major structural difference between the known $[Bi_4Cl_{16}]^{4-}$ cluster vs present $[Bi_4Cl_{16}]^{4-}$ cluster is that the lack of two μ^2 bridging chloride ions in **2** to result a new type of $[Bi_4Cl_{16}]^{4-}$ structural motif with lone pair elections (Type B cluster, Scheme 3). The distance between Bi(1) and Cl(3)/Cl(4) is 3.008 Å, which is slightly far from the Bi–Cl bond distance found in **2.** Thus, $[Bi_2Cl_{16}]^{4-}$ ion in **2** is in ladder structure and this can be considered as dimerized $[Cl_3Bi(\mu^2Cl)(\mu^3Cl)BiCl_3]_2$ through μ^3 bridging chloride ligands. The geometry of each Bi(1) center is penta coordinated by three terminals, one doubly bridged and one triply bridged chloride ions. The geometry of Bi(1) can be described as square pyramidal geometry. The Bi(2) center in **2** is fulfilled by three terminal, two doubly bridged and one triply bridged chloride ions. The geometry of Bi(2) can be considered as octahedral. The diselenide fragment Se–Se is connected by two semi bulky imidazole ligands. The terminal Bi−Cl bond distances around Bi(1) and Bi(2) are not comparable. The Bi(1)−Cl(7) depicts the shortest bond distance while Bi(2)−Cl(1) shows the longest bond distance. The terminal Bi−Cl bond lengths are shorter than the bridging Bi−Cl bond distances. The Se–Se bond lengths in **2** is 2.345(12) Å, which is slightly shorter than the presciently reported $[\{(HCN(Me))_2C\text{-}Se\}_2]^{2+}[\{^{-}OTf\}_2]$ 2.360(7) Å [25], $[\{(HCN(Me))_2CSe\}_2]^{2+}\{I\}_2]$ (2.434(2) Å), $[\{(HCN(Me))_2CSe\}_2Cl]^{+}\{I_3\}]$ (2.440(2) Å) [26] and [$IPrSe(OTf)_2]_2$ 2.427(5) Å [21]. The C−Se bond lengths in **2** is comparable and slightly shorter than IPr*Se (1.942(16) Å) [27]. As shown in Fig. 2, the WCA and rPBC are held together through C−H ···Cl (2.727(1) and 2.837(1) Å) and Se ···N (2.782(1)-2.849(1) Å) hydrogen bonding interactions. The WCA, $[Bi_2Cl_{16}]^{4-}$ is sandwiched by two rPBC diselenides (Fig. 3).

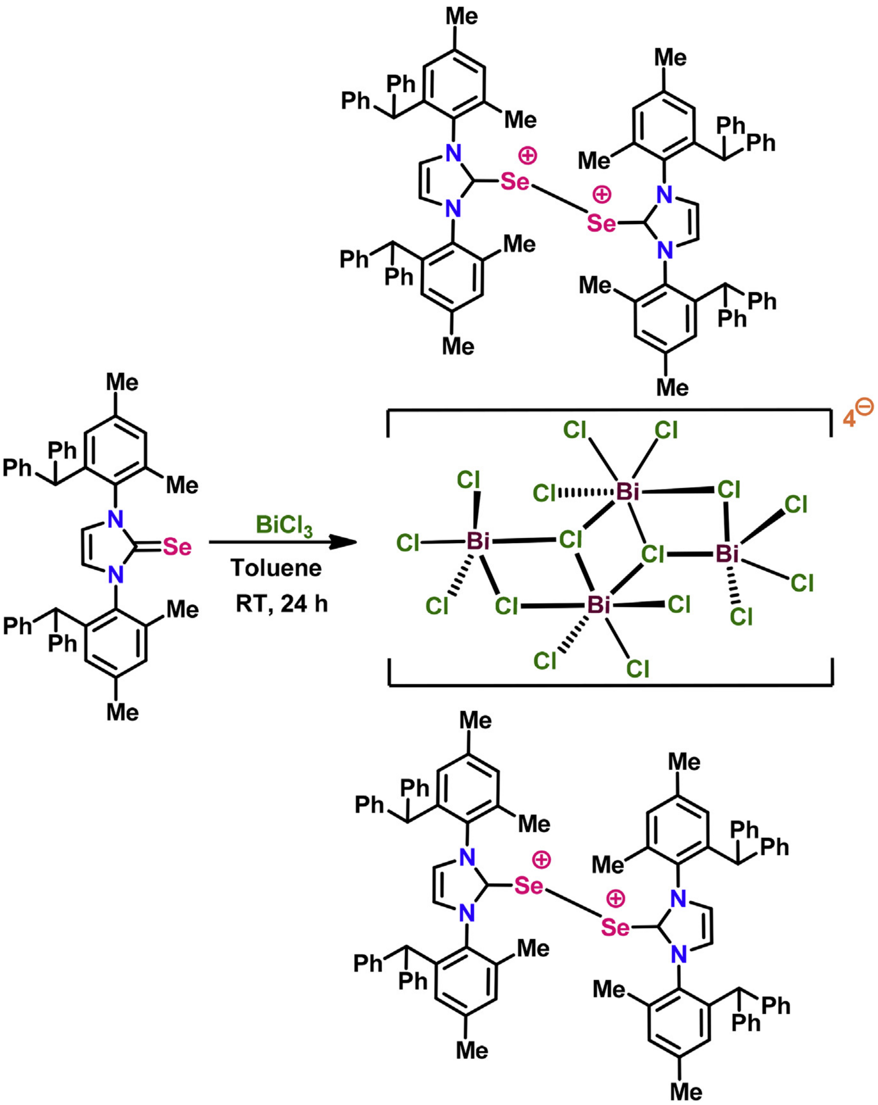
2.1.1. Thermogravimetric analysis

Stability of **2** was accomplished by thermogravimetric analysis (TGA) and compared with **1** (Fig. 4). **1** depicted a clear two stage weight losses from 290 °C to 440 °C with 79% weight loss then 21% weight loss from 440 °C to 620 °C, which can be attributed to the decomposition of organic moieties followed by selenium. The molecule **2** showed considerable stability till 290 °C then gradual weight loss till 770 °C with 84% weight loss due to the decomposition of organic moieties. The remaining 16% residue can be attributed to the Bi_2Se_3 material.

2.2. Catalysis

2.2.1. C-S cross coupling reactions

Transition metal catalyzed cross-coupling reactions have found widespread popularity in synthetic chemistry [28]. The C–S bond plays an important role in numerous compounds for biological and pharmaceutical applications as well as for the precursor based materials chemistry [29–39]. The traditional methods for C–S bond formation often employs the harsh conditions [29h]. For example, the coupling of thiolates with aryl halides takes place in hexamethylphosphoramide at 200 °C. The reduction of sulfoxide/sulfone is carried out with strong reducing agents like DIBAL-H and $LiAlH_4$ [40,41]. To overcome such drawbacks, considerable research on the development of catalytic systems for the C–S cross-coupling of thiols with aryl halides have been developed. In 1978, Migita and co-workers reported the first C−S cross-coupling of aryl halides with thiols using tetrakis(triphenylphosphine)-palladium as catalyst [30]. Later, several metal catalysts in which palladium [31], nickel [32], cobalt [33], copper [34], rhodium [35], indium [36], zinc [37] and bismuth [42] serve as the metal sources in combination with appropriate ligands have been developed. Out of these metals, the main group bismuth is more attractive over other metals owing to its benign nature. Of-late, the applications of bismuth compounds in organic transformations have been extensively investigated [43,44]. Notably, the catalytic applications of bismuth selone compounds are very scarce in the literature. Recently, we have demonstrated the first catalytic application of NHC–Bi analogue of monoimidazoline-2-chalcogenone derivatives of Bi(III) for *O*-acylative cleavage of cyclic ethers [45]. Subsequently, the bismuth(III) dichalcogenones derivatives of triflates and halides were isolated and observed to be highly active catalysts in synthesis of triaryl- or triheteroarylmethanes [46]. Based on the above fact, the expansion of bismuth chemistry has aroused interest in recent years for various organic transformations [43,46,47].



2

Scheme 2. Synthesis of **2**.

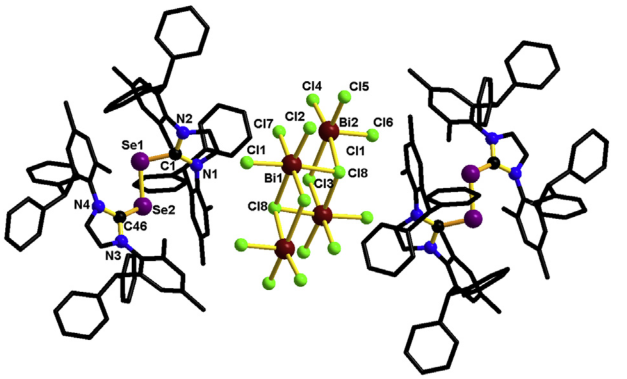
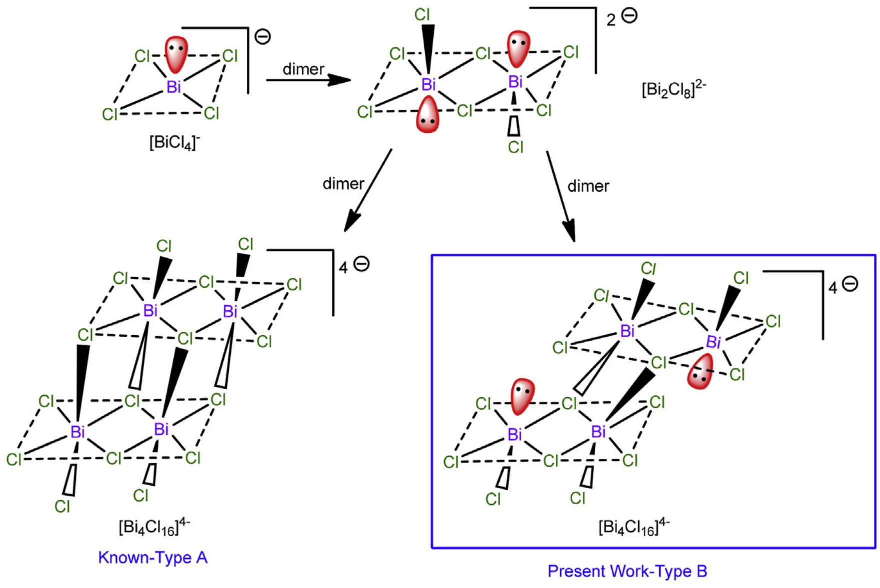


Fig. 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): C(1)–Se(1), 1.894(8), Se(1)–Se(2) 2.345(12), Bi(1)–Cl(7) 2.489(3), Bi(1)–Cl(6) 2.545(2), Bi(1)–Cl(8) 2.542(2), Bi(2)–Cl(2) 2.527(3), Bi(2)–Cl(3) 2.685(2), Bi(2)–Cl(4) 2.557(2), Bi(2)–Cl(5) 2.747(2), Bi(2)–Cl(1) 2.927(2), Cl(6)–Bi(1)–Cl(8) 92.33(7), Cl(6)–Bi(1)–Cl(7) 93.74(10), Cl(3)–Bi(2)–Cl(5) 174.53(8), Cl(1)–Bi(2)–Cl(5) 84.23(7), Cl(2)–Bi(2)–Cl(5) 90.25(9), N(1)–C(1)–N(2) 107.1(7), N(1)–C(1)–Se(1) 122.22(6). C(1)–Se(1)–Se(2) 99.1(3).

Thus, **2** was used as catalyst in C-S cross coupling reactions and explore the scope of the catalyst. To optimize the reaction condition, the cross coupling reaction of 1-bromo-4-nitrobenzene and thiophenol was chosen as a model reaction (Scheme 4). The effect of catalyst loading and reaction time on C-S cross coupling reaction were investigated. Thus, the reaction was performed with different catalytic amounts ranging from 2 to 12 mol % at different time intervals (Fig. 5). The best conversion was obtained with 10 mol % catalytic loading within 16 h. Besides, the effect of base and the choice of solvent for C-S cross coupling reactions were examined using catalyst **2**. After screening with KO^{t}Bu, KOH, NaO^{t}Bu and K_2CO_3, NaO^{t}Bu was found to be the best base (Table 2). Among toluene, 1,4-dioxane, MeCN and THF, MeCN seems to be best choice. Thus, it appears that the C-S cross coupled product can be isolated in good yield from the reaction between thiophenol and aryl halides in the presence of L-proline (10 mol%) and NaO^{t}Bu (2eq) in CH_3CN at 85 °C.

The cross coupling reaction between 1-bromo-4-nitrobenzene and thiophenol was performed without catalyst **2** but in the presence of L-proline (10 mol %) and NaO^{t}Bu (2eq) in CH_3CN at 85 °C,



Scheme 3. Possible mechanism for the formation of $[Bi_4Cl_{16}]^{4-}$.

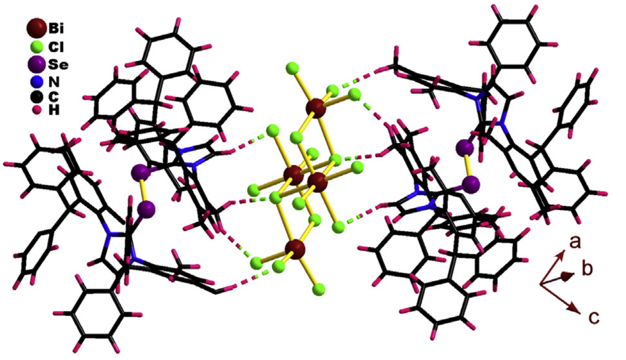


Fig. 2. The C—H ⋯ Cl and Se ⋯N bonding interactions between WCA and rPBC in **2**.

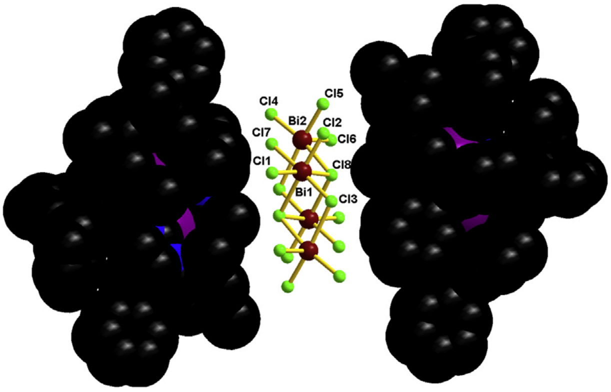


Fig. 3. Space filling modal of **2.**

which resulted in lower yield of the desired product (35%). Moreover, the above cross coupling reaction under same condition but in a mixture of solvents CH_3CN and H_2O (1:1), gave poor yield. The cross coupling reaction between 1-bromo-4-nitrobenzene and thiophenol with catalyst $BiCl_3$, L-proline (10 mol %) and NaO^{t}Bu (2eq) in CH_3CN at 85 °C gave moderate conversion (42%).

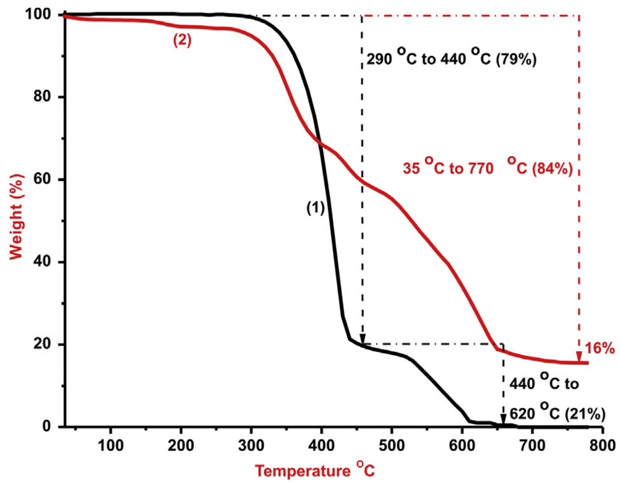
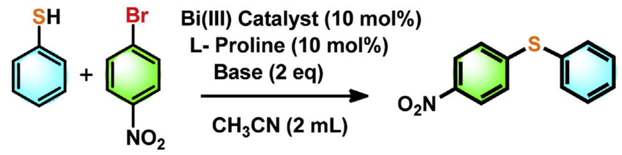


Fig. 4. TGA curves of **1** and **2** from 35 °C to 800 °C recorded with heating rate of 10 °C min^{-1} under nitrogen atmosphere.

In order to expand the scope of the present protocol, the C-S cross coupling reactions were performed with different thiols and aryl halides under optimized conditions (Table 3). The reaction of 4-chlorothiophenol with 1-bromo-4-nitrobenzene and 1-bromo-2-nitrobenzene afforded the corresponding (4-chlorophenyl)(2-nitrophenyl)sulfane and 4-chlorophenyl)(4-nitrophenyl)sulfane in 89% and 80% yield, respectively (Table 3, Entries 1 and 2). The reaction of 4-chlorothiophenol with 4-bromobenzonitrile resulted the 4-((4-chlorophenyl)thio)benzonitrile in very good yield (Table 3, Entry 4). Interestingly, the aryl halides with electron withdrawing groups (Cl, Br and I) (Table 3, Entries 3, 4, 5 and 9) gave good yield than aryl halides with electron donating substituents (Table 3, Entries 8 and 11). The coupling of mercaptobenzonitrile with 1-bromo-4-nitrobenzene gave the coupled product in 84% yield (Table 3, Entry 6). The coupling of 4-chlorobenzonitrile with benzene thiol underwent smoothly to provide the 4-(phenylthio) benzonitrile product in 85% yield (Table 3, Entry 10). Noteworthy that the isolated yield under the present synthetic methodology is more convenient and more economic under mild reaction

Table 1
Crystallographic data, details of data collection and structure refinement parameters for **2**.

Parameters	2
Empirical formula	$C_{180}H_{160}Bi_4Cl_{16}N_8Se_4$
Formula weight	4154
Temperature (K)	150
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	15.1171(5)
b/Å	15.3407(3)
c/Å	19.2555(5)
α/°	76.864(2)
β/°	82.029(2)
γ/°	87.196(2)
Volume (Å^3)	4305.9(2)
Z	2
ρ_{calc}/mg mm^{-3}	1.6020
Absorption coefficient (μ/mm^{-1})	5.221
F(000)	2023.1
Reflections collected	90373
R_{int}	0.1080
GOF on F^2	1.044
R_1 ($I > 2\sigma(I)$)	0.0709
wR_2 ($I > 2\sigma(I)$)	0.1913
R_1 values (all data)	0.0940
R_2 values (all data)	0.2110



Scheme 4. **2** catalyzed C-S cross coupling reaction between 1-bromo-4-nitrobenzene and thiophenol.

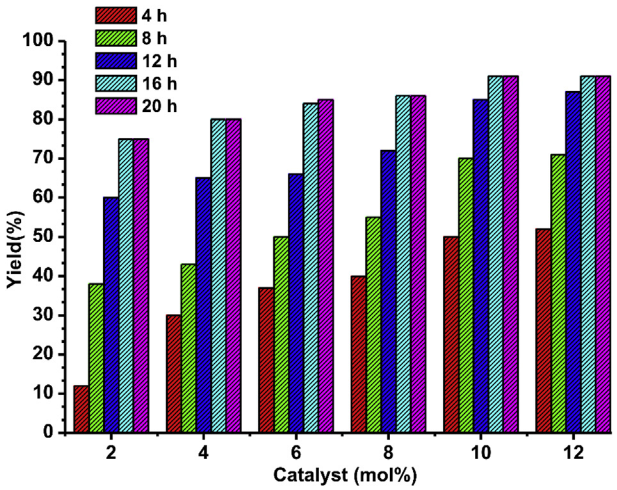


Fig. 5. Effect of catalyst mol % (2–12 mol%) with respect to time (4–20 h) on C-S cross coupling reaction between 1-bromo-4-nitrobenzene with thiophenol.

conditions compared to the previous literature report [48]. The detailed mechanism of the reaction is not clear at this stage as cited for most of the examples [23], however the efforts are underway to explore the reaction mechanism.

3. Conclusions

In conclusion, we have reported the synthesis and structural characterization of first rPBC and WCA model of semi-super bulky bis-1,3-diimidazole diselenide and tetranuclear bismuth anionic salt from the direct reaction of $BiCl_3$ with the 1,3-bis(2-benzhydryl-4,6-dimethylphenyl)-1H-imidazole-2(3H)-selenone. The solid state structure of **2** reveals that WCA, $[Bi_2Cl_{16}]^{4-}$ is held together by two rPBC diselenides through C—H ···Cl and Se ···N hydrogen bonding interactions. Interestingly, $[Bi_2Cl_{16}]^{4-}$ in **2** shows an unusual structural motive with two different types of coordination environment around bismuth(III) centers. The $[Bi_2Cl_{16}]^{4-}$ ion in **2** exist in ladder structure. Subsequently **2** was successfully employed for the C-S cross coupling reaction of aryl halides and thiols under acetonitrile medium. The present catalytic system best owed the C-S cross coupling reactions with broad scope of thiols together with aryl halides. Indeed, the out-come of the current work will significantly endow towards the exploration and growth of bismuth chalcogenide chemistry for the synthesis of thioethers. Further explorations in this direction are in progress.

Table 2
Effect of base and solvent on C-S cross coupling reaction of 1-bromo-4-nitrobenzene with thiophenol[a].

Entry	Base	Solvent	Temp (°C)	Yield (%)[b]
1	KO*t*Bu	1,4-dioxane	101	48
2	NaO*t*Bu	1,4-dioxane	101	65
3	KOH	1,4-dioxane	101	51
4	K_2CO_3	1,4-dioxane	101	65
5	NaO*t*Bu	THF	66	62
6	KO*t*Bu	THF	66	51
7	KOH	THF	66	50
8	K_2CO_3	THF	66	62
9	NaO*t*Bu	Toluene	110	41
10	KOH	Toluene	110	48
11[c]	**NaO*t*Bu**	**CH_3CN**	**85**	**89**
12	KOH	CH_3CN	85	75
13	K_2CO_3	CH_3CN	85	67
14[d]	NaO*t*Bu	CH_3CN	85	29
15[e]	NaO*t*Bu	CH_3CN	85	56
16[f]	NaO*t*Bu	CH_3CN	85	69

[a] Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), thiophenol (1 mmol), NaO^tBu (2 equiv.), L-proline (10 mol %), solvent (5 mL) and catalyst (10 mol %) for 16 h.

[b] Isolated yield after column chromatography.

[c] Better optimization condition.

[d] Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), thiophenol (1 mmol), NaO^tBu (2 equiv.), L-proline (10 mol %) and solvent (5 mL) for 48 h (absence of catalyst).

[e] Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), thiophenol (1 mmol), NaO^tBu (2 equiv.), L-proline (10 mol %), solvent (5 mL) and catalyst (5 mol %) for 24 h.

[f] Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), thiophenol (1 mmol), NaO^tBu (2 equiv.), L-proline (10 mol %), solvent (5 mL) and catalyst (7 mol %) for 24 h.

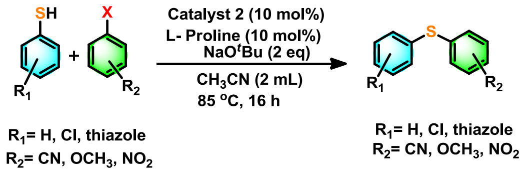
4. Experimental section

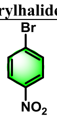
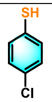
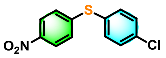
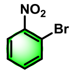
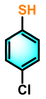
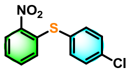
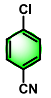
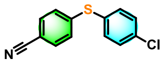
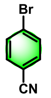
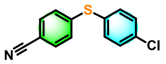
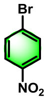
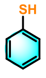
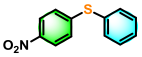
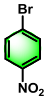
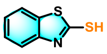
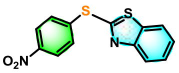
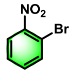
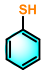
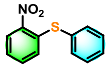
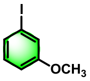
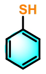
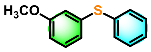
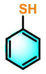
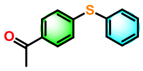
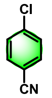
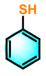
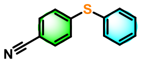
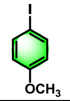
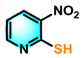
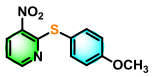
4.1. General comments

The reactions were carried out in oven dried glassware with magnetic stirrer and without inert gas protection. The commercial chemicals were used as purchased. **1** was prepared according to the earlier proclaimed methods [23]. FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. Microanalyses of carbon, hydrogen and nitrogen were carried out using a Euro EA - CHNSO Elemental Analyzer. Thermogravimetric analysis (TGA) was performed using a TASDT Q600, Tzero-press. NMR spectra were recorded on Bruker Ultrashield-400 spectrometers at 25 °C unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as

Table 3

C-S cross coupling of thiophenols with aryl halides catalyzed by **2.**[a]



S. No	Arylhalides	Thiols	Product	Yield (%)[b]
[b]1				89
2				80
[c]3				76
[d]4				83
5				89
6				84
7				84
8				78
9				80
10				85
11				72

[a] Reaction conditions: Aryl halides (1.2 mmol), thiophenols (1 mmol), NaO^{t}Bu (2 equiv.), catalyst (10 mol %) and L-proline (10 mol %) in CH$_3$CN for 16 h at 85 °C.

[b] Entry number, isolated yield after column chromatography (%).

[c] Reaction conditions: 4-chlorobenzonitrile (1.2 mmol), 4-chlorothiophenol (1 mmol), NaO^{t}Bu (2 equiv.), catalyst (10 mol %) and L-proline (10 mol %) in CH$_3$CN for 16 h at 85 °C.

[d] Reaction conditions: 4-bromobenzonitrile (1.2 mmol), 4-chlorothiophenol (1 mmol), NaO^{t}Bu (2 equiv.), catalyst (10 mol %) and L-proline (10 mol %) in CH$_3$CN for 16 h at 85 °C.

[a] Reaction conditions: Aryl halides (1.2 mmol), thiophenols (1 mmol), NaO^{t}Bu (2 equiv.), catalyst (10 mol %) and L-proline (10 mol %) in CH$_3$CN for 16 h at 85 °C.

[b] Entry number, isolated yield after column chromatography (%).

[c] Reaction conditions: 4-chlorobenzonitrile (1.2 mmol), 4-chlorothiophenol (1 mmol), NaO^{t}Bu (2 equiv.), catalyst (10 mol %) and L-proline (10 mol %) in CH$_3$CN for 16 h at 85 °C.

[d] Reaction conditions: 4-bromobenzonitrile (1.2 mmol), 4-chlorothiophenol (1 mmol), NaO^{t}Bu (2 equiv.), catalyst (10 mol %) and L-proline (10 mol %) in CH$_3$CN for 16 h at 85 °C.

internal standards. Single crystals of complex suitable for the single crystal X-ray analysis were obtained from their reaction mixture at room temperature and the suitable single crystals for X-ray structural analysis were mounted at room temperature (150 K) in inert oil under an argon atmosphere. The crystal structure of **2** was measured on an Oxford Xcalibur 2 diffractometer. Using Olex2 [49] the structure was solved with the ShelXS [50] structure solution program using Direct Methods and refined with the olex2. refine refinement package using Gauss-Newton minimization. Absorption corrections were performed on the basis of multi-scans. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement in calculated positions riding on their carrier atoms. No restraint has been made for any of the compounds. **2** gave both “A” level and “B” level alerts due to improper convergence of the refinement and variation in residual density. Attempts to rectify these issues were not fruitful. CCDC 1881751 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

*4.2. Synthesis of **2***

A mixture of **1** (100 mg, 1 mmol) and BiCl$_3$ (65.19 mg, 1 mmol) in toluene (5 mL) was stirred for 24 h at room temperature to yield the pale red precipitate. The reaction mixture was filtered, the precipitate was washed with hexane (2 × 5 mL) and then the precipitate was dried and dissolved in acetonitrile to isolate the pale red crystals of **2**. Yield 82% (based on BiCl$_3$). M.p.: 180–183 °C. CHN analysis for $C_{180}H_{164}N_8Se_4Cl_{16}Bi_4$ (MW: 4158.29) (%): Calcd. C, 51.99; H, 3.98; N, 2.69. Found C, 52.2; H, 4.1; N, 2.7.^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.34–7.13 (20H, m, Ar-*H*), 6.89–6.76 (4H, m, Ar-*H*), 6.52–6.22 (2H, s, N(C*H*)$_2$N), 5.47–5.43 (2H, s, C*H*(Ph$_2$), 2.23 (6H, s, C*H*$_3$), 1.99 (6H, s, C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 157.2, 156.3, (*C-Se*), 143.4, 143.2, 141.8, 140.5, 134.7, 138.5, 137.3, 135.8, 135.6, 134.0, 129.7, 129.4129.2, 128.8, 128.3, 128.1, 128.0126.4, 125.4, (C_{Ar}), 51.01, 50.9 (*C*HPh$_2$), 20.9, 17.8 (*C*H$_3$). FT-IR (cm^{-1}, neat): 3020 (bw), 2358 (m), 1952 (bw), 1694 (m), 1597 (m), 1547 (m), 1483 (s), 1341 (bw), 1243 (m), 1159 (m), 1078 (m), 1032 (m), 858 (m), 739 (s), 698 (s), 628 (m).

4.3. General procedure for Bi(III)-selone catalyzed C-S cross coupling reactions

A mixture of thiophenol (1 mmol), aryl halide (1.2 mmol), L–proline (10 mol%) and **2** (10 mol%) in acetonitrile (5 mL) was stirred at 85 °C. The reaction mixture was monitored by TLC until all thiophenol was found consumed. The reaction mixture was extracted with ethyl acetate and water, the organic layer was separated then washed with NaCl and dried with anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure using the rotatory evaporator. The crude product was purified by column chromatography (5:95 of ethyl acetate and hexane) to isolate the yellow solid.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.01.017.

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