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Journal Name

ARTICLE

Facile Access to Zinc and Cadmium Selones: Highly Active Catalysts for Barbier Reactions in Aqueous Media

Chatla Naga Babu, Katam Srinivas and Ganesan Prabusankar*

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The syntheses and structures of five mononuclear zinc and cadmium selone complexes along with polynuclear cadmium selone 1D chain were described. The mononuclear homoleptic zinc selone complexes were the first examples of structurally characterized zinc(II) selone complexes. The spectral properties of zinc and cadmium selone derivatives were investigated. The interesting structural diversity, coordination geometry, variable chemical and thermal stability were observed for these zinc and cadmium selone compounds. Besides, the first metal selone mediated Barbier coupling was reported. These catalysts were highly active for Barbier coupling reactions in aqueous alcohol media. In addition, the scope of the catalytic reactions were further explored with eleven different aldehydes.

Introduction

Functionalized imidazoline chalcogenone organic spacers are one of the most promising chelating ligands due to their extraordinary binding affinity towards most metal ions, together with the chalcogenone centers for the wide range of biological, material and catalysis applications.¹⁻¹² Recently, the imidazoline chalcogenones have been employed as a potential ligands to replace the N-heterocyclic carbene's (NHC's) type ligands.⁶

transition metal complexes.⁸⁻¹²

For examples, the known imidazoline chalcogenone supported transition catalytic reactions are depicted in chart 1.⁸⁻¹² The catalytic efficiency of pincer type Pd(II) selone complexes⁷ for Heck coupling reaction was comparable with the most efficient NHC-Pd catalysts.¹³ The iridium complexes, $\{[(ppy)_2(mbis)Ir]PF_6\}$, $\{[(btpy)_2(mbis)Ir]PF_6\}$, $\{[(ppy)_2(mbit)Ir]PF_6\}$ and $\{[(btpy)_2(mbit)Ir]PF_6\}$; mbit = 1,1'-Dimethyl-3,3'-methyleneimidazoline thione; mbis = 1,1'-Dimethyl-3,3'-methyleneimidazoline selone; ppy = 2-phenylpyridinato and btpy = 2-(2'-benzothienyl)pyridinato, catalysed oxidative coupling of benzylamine to imine under visible-light were much superior than NHC-Ir catalysts.⁹ The catalytic efficiency of thione gold(I) complexes mediated hydroamination reaction was comparable with catalytic activity of Au-NHC complex.¹⁰ The regioselective borylation of internal alkyne in presence of copper imidazoline chalcogen complexes was more efficient than NHC-Cu complexes.¹¹ Similarly, the imidazoline chalcogen complexes of copper(I) depicted the best regioselective borylation of unsymmetrical alkyne compared to Cu-IPr catalyst.¹²

The similar class of cadmium and zinc chalcogenones is still in embryonic stage and their compounds are particularly rare.¹⁴ Moreover, the catalytic applications of cadmium and zinc chalcogenones are not explored yet. Herein, we report the first catalytic application of six new examples of cadmium and zinc selones, $\{[(L1')Cd(Cl)(NO_3)]\}$ (1), $\{[(L1')_4Cd]\{ClO_4\}_2 \cdot 2H_2O\}$ (2), $\{[(L1')_4Zn]^{2+}\{ClO_4\}_2^{2-}\}$ (3), $\{[(L2')CdCl_2]_n\}$ (4), $\{[(L2')Cd(Cl)]\{ClO_4\}\}$ (5) and $\{[(L2')_2Zn]\{ClO_4\}_2 \cdot 2H_2O\}$ (6), $L1' = 1-(2,6-diisopropylphenyl)-3-(2-methoxy-2-oxoethyl)-imidazoline$ selone; $L2' = 3-(2-methoxy-2-oxoethyl)-1-mesityl-imidazoline$ selone for the Barbier type reactions. These newly prepared catalysts are highly active towards Barbier type reactions with good functional group tolerances.

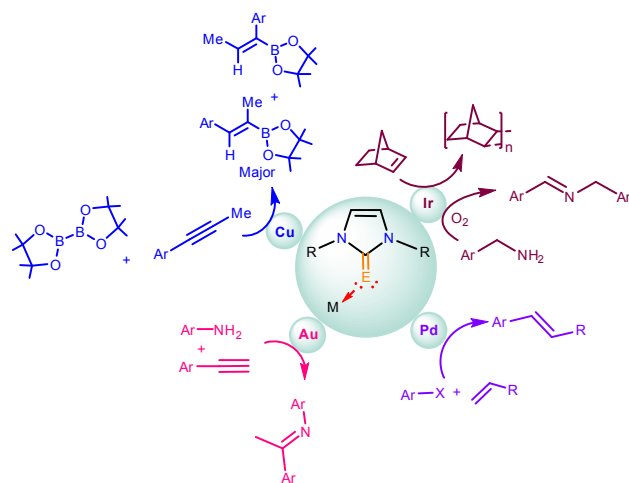


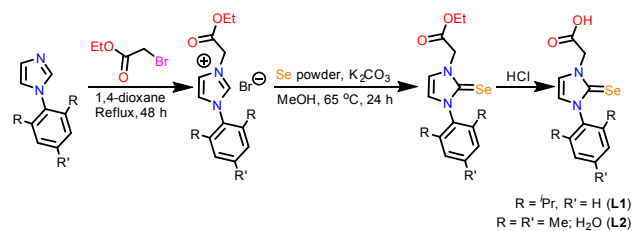
Chart 1. Known catalytic reactions of imidazoline-2-chalcogenone supported

^a Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Medak, TS, INDIA-502 285. Fax: +91 40 2301 6032; Tel: +91 40 2301 6089; E-mail: prabu@iith.ac.in.

† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [¹H NMR, ¹³C NMR, FT-IR and Table S1-S13]. See DOI: 10.1039/x0xx00000x

Results and discussion

The ester functionalized selones N-(2,6-diisopropylphenyl)-N'-acetic acid-imidazoline-selone (**L1**) and N-mesityl-N'-acetic acid-imidazoline-selone (**L2**) were isolated in very good yield by treating corresponding imidazolium salts with elemental selenium powder in the presence of potassium carbonate (Scheme 1).¹⁵



Scheme 1. Synthesis of **L1** and **L2**.

The crude products **L1** and **L2** were pure enough to carry out the next step. The formation of **L1** and **L2** were confirmed by elemental analysis, FT-IR and multinuclear NMR studies. In ¹³C NMR, NC(Se)N carbon in **L1** and **L2** appeared at δ 158.6 ppm and δ 158.9 ppm, respectively. The FT-IR spectrum of **L1** and **L2** showed the strong peaks (at 1775 cm⁻¹ and 1177 cm⁻¹ for **L1**; 1720 cm⁻¹ and 1250 cm⁻¹ for **L2**) for the presence of free carboxylate groups.¹⁶ The carboxylic acid O–H stretch appeared as a very broad band in the region from 3165–3080 cm⁻¹ for **L1** and 3470–3094 cm⁻¹ for **L2**. Molecular structures of **L1** and **L2** were further confirmed by single crystal X-ray diffraction method (Fig. 1). Molecules **L1** and **L2** crystallized in orthorhombic space group, *P2₁2₁2₁* and monoclinic space group, *P2₁/c* respectively (See supporting information I, Table S1–S12). The C–Se bond distances in **L1** and **L2** are comparable.

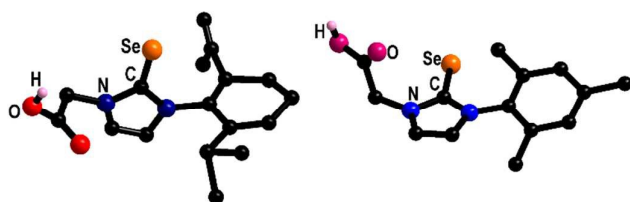
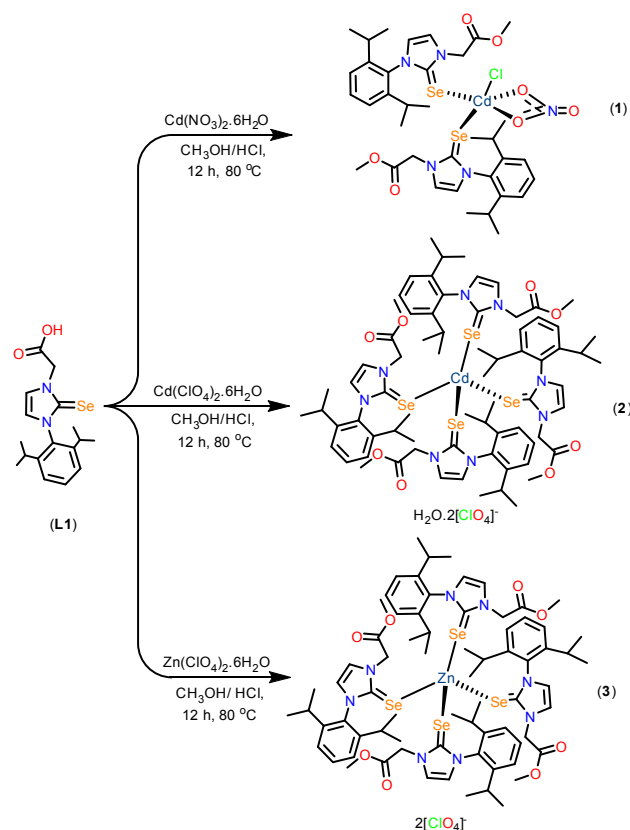


Fig 1. Left: Molecular structure of **L1**. Hydrogen atoms have been omitted for clarity. C–Se, 1.834(3) Å. Right: Molecular structure of **L2**. Hydrogen atoms and one water molecule have been omitted for clarity. C–Se, 1.835(3) Å.

Synthesis and characterization of 1-3

The discrete zinc selones^{14a} and cadmium selones^{14d} are rare. Only one structurally characterized molecule per zinc/cadmium was detected from the structural search by CSD version 5.36 updates (Feb 2015). The mononuclear cadmium complex, $(\mathbf{L1})\text{Cd}(\text{Cl})(\text{NO}_3)]$ (**1**), was synthesized from the reaction between cadmium(II) nitrate hexahydrate and **L1** (Scheme 2). Under similar condition, the homoleptic complexes $[\{(\mathbf{L1})_4\text{M}\}^{2+}\{\text{ClO}_4\}_2^{2-}]$ $\text{M} = \text{Cd}$ (**2**) and **Zn** (**3**), were isolated in good yield (Scheme 2). **1-3** were soluble in DMSO and insoluble in chloroform and acetone.



Scheme 2. Synthesis of **1-3**.

The formation of **1-3** were confirmed by elemental analysis, FT-IR, multinuclear (¹H and ¹³C) NMR, UV-vis and TGA. In ¹H NMR, the ester methyl group appeared at δ 3.70 ppm for **1** and **2**, while it was slightly upfield shifted (δ 3.63 ppm) for **3**. The ¹³C NMR chemical shift value of C=O and N-C(Se) carbons were virtually comparable (δ 167.71 (C=O) and 158.80 (C=Se) ppm for **1** and **2**; δ 167.70 (C=O) and 158.80 (C=Se) for **3**). The C=O and N-C(Se)-N carbons chemical shift values of **1-3** were nearly comparable with **L1**. The presence of ester moieties in **1-3** were confirmed by the characteristic stretching frequency of carbonyl group at 1748 cm⁻¹, 1762 cm⁻¹ and 1755 cm⁻¹, respectively.¹⁶ The free ClO₄⁻ ions in **2** and **3** were also witnessed by FT-IR. The FT-IR vibrations of ClO₄⁻ ions in **2** and **3** appeared at 1088 cm⁻¹ (for **2**) and 1111 and 1058 cm⁻¹ (for **3**), respectively.¹⁶ The solid state structures of **1-3** were further confirmed by single crystal X-ray diffraction technique.

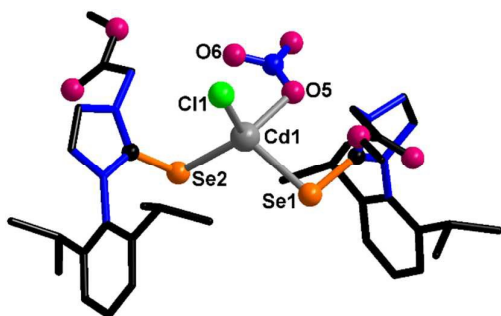


Fig 2. Molecular structure of **1**. Hydrogen atoms in **1** have been omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): C(1)–Se(1), 1.868(5), C(19)–Se(2), 1.882(6), Se(1)–Cd(1), 2.658(7), Se(2)–Cd(1), 2.631(7), Cl(1)–Cd(1), 2.509(16), O(5)–Cd(1), 2.270(5), O(6)–Cd(1), 2.847(102), Se(2)–Cd(1)–Se(1), 112.15(2), C(1)–Se(1)–Cd(1), 94.81(16), C(19)–Se(2)–Cd(1), 98.80(15), Cl(1)–Cd(1)–Se(1), 112.10(4), Cl(1)–Cd(1)–Se(2), 114.04(4), O(5)–Cd(1)–Se(1), 91.21(13), O(5)–Cd(1)–Se(2), 117.28(15), N(1)–C(1)–N(2), 107.2(5), N(1)–C(1)–Se(1), 126.0(4), N(2)–C(1)–Se(1), 126.8(4), N(3)–C(19)–N(4), 106.9(5), N(3)–C(19)–Se(2), 126.8(4), N(4)–C(19)–Se(2), 126.2(4).

Molecule **1** crystallized in the monoclinic space group, $P2_1/c$ (Fig. 2, Table S13). Molecule **1** is a tetra coordinated mononuclear complex. The coordination environment of Cd(II) in **1** is satisfied by selenium atoms of two **L1'**, chloride and nitrate moieties. The geometry of Cd(II) in **1** can be described as tetrahedral geometry. The Se(1)–Cd(1) (2.658(7) Å) bond length is considerably longer than that of Se(2)–Cd(1) (2.631(7) Å). The O(5)–Cd(1) bond length is 2.270(5) Å. The Se(2)–Cd(1)–Se(1), angle is 112.15(2) $^{\circ}$.

Molecules **2** and **3** crystallized in the cubic space group, $F-4_3c$ and the solid state structures are depicted in figure 3 (Table S13). Molecules **2** and **3** are isostructural. Thus, the structural features are discussed in common. Molecules **2** and **3** are a rare homoleptic dicationic complexes. The geometry of metal centre can be described as tetrahedral. The coordination environment of metal centre is accomplished by four selenium atoms of four **L1'** ligands. Molecule **3** is the first structurally characterized mononuclear zinc selenone with $ZnSe_4$ core, while **2** is a second example in the literature.^{14a} The Se(1)–Cd(1) (2.625(5) Å) bond distances in **2** are identical. Similarly, the Se(1)–Zn(1) (2.463(6) Å) bond distances in **3** are identical. As expected, the Se(1)–Zn(1) bond distances in **3** is considerably shorter than that of Se(1)–Cd(1) bond distances in **2**. The Se(1)–Zn(1)–Se(1) ($96.73(1)^{\circ}$) bond angles in **3** are nearly comparable with Se(1)–Cd(1)–Se(1) bond angles ($96.02(9)^{\circ}$) in **2**. The C(1)–Se(1)–Zn(1) ($107.09(1)^{\circ}$) bond angles in **3** are slightly wider than C(1)–Se(1)–Cd(1) ($106.60(1)^{\circ}$) bond angles in **2**.

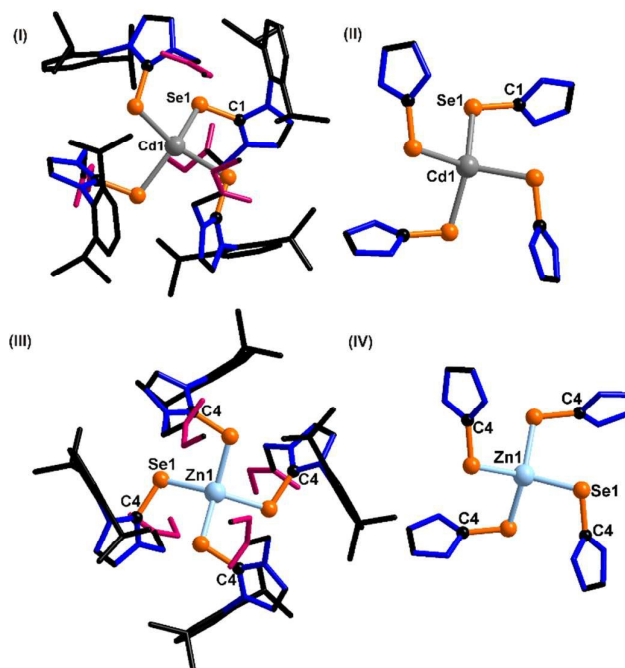
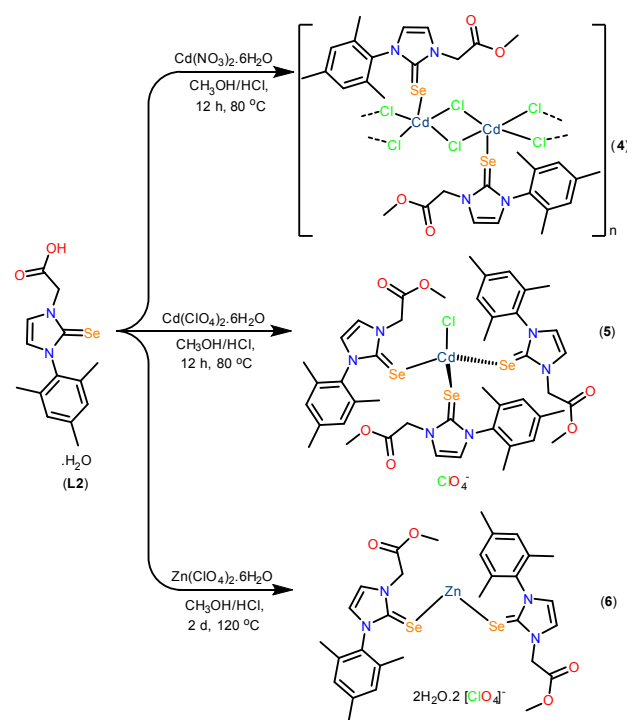


Fig 3. (I) Molecular structure of **2**. Hydrogen atoms and two perchlorate ions in molecule **2** have been omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): C(1)–Se(1), 1.850(5), Se(1)–Cd(1), 2.625(5), Se(1)–Cd(1)–Se(1), $96.02(9)$, C(1)–Se(1)–Cd(1), $106.60(1)$, N(1)–C(1)–N(2), $106.2(4)$, N(1)–C(1)–Se(1), $128.0(4)$, N(2)–C(1)–Se(1), $125.60(3)$; (II) The core unit of molecule **1** without substituents on imidazoline units; (III) Molecular structure of **3**. Hydrogen atoms and two perchlorate ions in molecule **3** have been omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): C(1)–Se(1), 1.866(6), Se(1)–Zn(1), 2.463(6), Se(1)–Zn(1)–Se(1), $96.73(1)$, C(1)–Se(1)–Zn(1), $107.09(1)$, N(1)–C(1)–N(2), $106.6(5)$, N(1)–C(1)–Se(1), $127.70(4)$, N(2)–C(1)–Se(1), $125.50(4)$; (IV) The core unit of molecule **3** without substituents on imidazoline units.

Synthesis and characterization of 4-6

Interestingly, the sterically less crowded ligand **L2** (compared to **L1**) under similar reaction condition as reported for the synthesis of **1-3**, gave completely new types of cadmium and zinc complexes, **4-6** (Scheme 3). The polynuclear complex **4**, mono nuclear cadmium(II) complex **5** and first two coordinated mononuclear homoleptic zinc selenone complex **6** were isolated in good yield. **4-6** were soluble in DMSO and insoluble in chloroform and acetone. **4-6** were characterized by elemental analysis, FT-IR, multinuclear (1H and ^{13}C) NMR, UV-vis, TGA and single crystal X-ray diffraction techniques. In FT-IR spectrum, uncoordinated perchlorate anions in **5** and **6** appeared at 1052 cm^{-1} and 1076 cm^{-1} , respectively.¹⁶ The ^{13}C NMR chemical shift values of C=O and N–C(Se)–N carbons for **4-6** were nearly comparable (δ 168.56 (C=O) and 158.88 (C=Se) for **L2**; δ 167.67 (C=O) and 159.00 (C=Se) ppm for **4**; δ 167.76 (C=O) and 158.88 (C=Se) for **5**; δ 167.67 (C=O) and 159.00 (C=Se) for **6**).



Scheme 3. Synthesis of 4-6.

The solid state structure of **4** was further confirmed by single crystal X-ray diffraction (Fig. 4). Molecule **4** crystallized in the monoclinic space group, $P2_1/c$ (Table S13). **4** is a 1D $[(L2')CdCl_2]_n$ complex. Cadmium centres are five coordinated by four bridging chlorides and one $L2'$. The geometry of $[Cd(Cl)_4(Se)]$ core in **4** can be considered as distorted square pyramid geometry (Fig. 4(II)). The Cd–Se bond distance is 2.656(5) Å. Four different Cd–Cl bond distances are observed in **4** and it varies from 2.524(1) Å to 2.732(9) Å. The Cd–Cl(1') (2.524(1) Å) bond distance is much shorter than that of Cd–Cl(1) (2.732(9) Å) bond distance. Similarly, the Cd–Cl(2) (2.536(9) Å) bond distance is much shorter than that of Cd–Cl(2') (2.703(1) Å) bond distance. The Cl–Cd–Cl angles varies from 93.05(3)° (Cl(2)'–Cd(1)–Cl(1)') to 171.95(3)° (Cl(2)'–Cd(1)–Cl(1)).

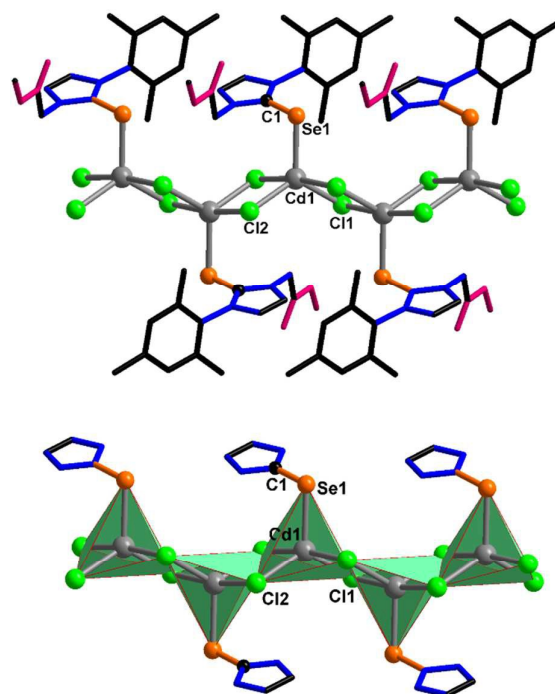


Fig 4. Top: Molecular structure of **4**. Hydrogen atoms in molecule **4** have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.873(4), Se(1)–Cd(1), 2.656(5), Cl(1)–Cd(1), 2.524(1), Cl(2)–Cd(1), 2.703(1), C(1)–Se(1)–Cd(1), 99.49(1), N(1)–C(1)–N(2), 106.4(4), N(1)–C(1)–Se(1), 126.6(3), N(2)–C(1)–Se(1), 127.0(3); Bottom: Polyhedron view of **4**.

Molecule **5** crystallized in the trigonal space group, $R-3$ (Table S13). **5** is a centrosymmetric structure with propeller shape structure. The C_3 symmetry axis can be imagined through Cl–Cd bond. Cadmium centre is tetra coordinated with tetrahedral geometry (Fig. 5(II)). The Se–Cd–Se angles are comparable (111.79(1)°). The geometry of cadmium is satisfied by three $L2'$ selenium atoms and one chloride ligand. The three ester groups are pointing towards chloride phase. The Cd–Se bond lengths are same (2.645(4) Å).

The colourless crystals of **6** were derived from the methanol mixture. Compound **6** crystallized in the tetragonal space group, $P4_322$ (Table S13). Molecule **6** can be described as “V” shape molecule, where the zinc centre is coordinated by two $L2'$ ligands (Fig. 5(II)). The Se(1)–Zn(1)–Se(1) bond angle is 103.05(5)°. Molecule **6** represents the first two coordinated homoleptic zinc selenide molecule. The $L2$ ligands are oriented in *trans* position with respect to SeZnSe plane. The orientation of two $L2'$ ligands are not on the same plane. The Zn–Se bond lengths are equal (2.328(10) Å). C–Se bond length is 1.895(6) Å.

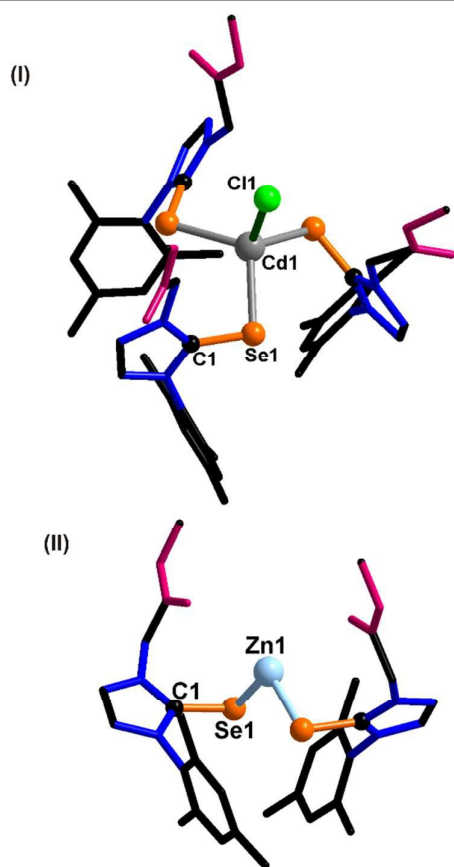


Fig 5. (I) Molecular structure of **5**. Hydrogen atoms, two water molecules and two perchlorate ion in molecule **5** have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.864(4), Se(1)–Cd(1), 2.645(4), Cl(1)–Cd(1), 2.456(1), Se(1)–Cd(1)–Se(1), 111.79(1), C(1)–Se(1)–Cd(1), 99.54(1), Cl(1)–Cd(1)–Se(1), 107.04(1), N(1)–C(1)–N(2), 106.28(3), N(1)–C(1)–Se(1), 125.0(3), N(2)–C(1)–Se(1), 128.7(3); (II) Molecular structure of **6**. Hydrogen atoms, two perchlorate ions and two water molecules in **6** have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.895(6), Se(1)–Zn(1), 2.328(10), C(1)–Se(1)–Zn(1), 96.20(17), Se(1)–Zn(1)–Se(1), 103.05(5), N(1)–C(1)–N(2), 108.0(5), N(1)–C(1)–Se(1), 125.2(5), N(2)–C(1)–Se(1), 125.2(5).

Structural comparison.

The molecules **2**, **3**, **5** and **6** are mononuclear cationic complexes, while **1** is a neutral mono nuclear complex and **4** is a poly nuclear 1D chain. Interestingly, the geometry of metal centres in **1-6** are completely diversified (Fig. 6). The C=Se bond lengths are not comparable among **1-6**. The C=Se bond distances are much longer than that of **L1** and **L2** due to strong σ donor ability of ligands. Similarly, the C=Se bond distances are much longer than that of an isolated carbon selenium double bond distances in CSe_2 (1.698 Å)¹⁷ and are closer to the sum of the single bond covalent radii of 1.94 Å.¹⁸ There are no unusual intermolecular interactions were observed. The observed Cd–Se bond lengths in **1** (2.658(7) Å), **2** (2.625(6) Å), **4** (2.656(0) Å) and **5** (2.645(4) Å) are slightly elongated than the previously observed Cd–Se bond lengths for $[\text{Cd}(\text{dmise})_4][\text{PF}_6]_2$ (dmise = N,N'-dimethyl-imidazoline-selone) (2.609(2) Å to 2.636(2) Å).^{14d} Similarly, the observed Zn–Se bond lengths in **3** (2.463(6) Å) and **6** (2.328(10) Å) are slightly shorter than Zn–Se bond lengths in $[\text{ZnCl}_2(\text{dmise})_2]$ (2.4691 to

2.4873 Å).^{14a} The Se–Cd–Se bond angles in **1** (112.15(2)), **2** (96.02(0)) and **5** (111.78(1)) are not comparable. The molecules **3** and **6** are the first examples of structural studied homoleptic zinc selone with ZnSe_4 and ZnSe_2 core, respectively.

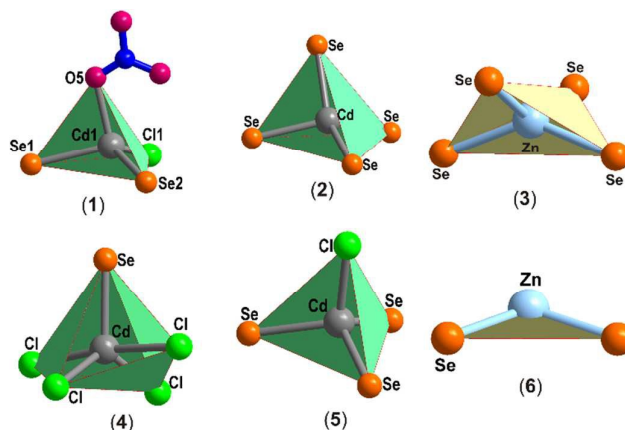
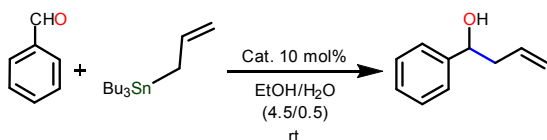


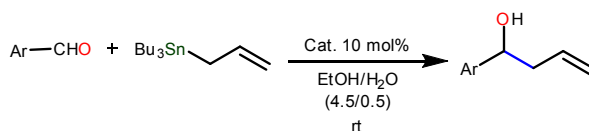
Fig 6. Polyhedron view of metal centers in **1-6**.

1-6 mediated Barbier coupling reactions.

Among known carbon-carbon bond formation reactions, the Barbier coupling process is a powerful tool in synthetic organic chemistry and is one of the most extensively studied fundamental carbon-carbon bond-forming reactions.¹⁹ Over the past decade, various metals such as zinc, cadmium, magnesium, lithium, indium, tin, and lead have been developed to facilitate such reactions.²⁰ Particularly, the development of allylation reactions in aqueous media has attracted great attention because of the easy handling and unique reactivity of the methodology. Thus in our present study we used our complexes **1-6** as catalysts for allylation of benzaldehyde with allyltributyltin in aqueous alcohol media. Initially, we have screened out the 10 mol% complexes **1-6** for allylation of benzaldehyde (1 equiv) with allyltributyltin (1.2 equiv) in aqueous alcohol media, $\text{H}_2\text{O}:\text{EtOH}$. These reactions were carried out for 30 min to obtain the desired product in very good yield (57%-98%) (Fig. 9). The catalytic efficiency of **1-6** is much superior than corresponding metal salts or zinc mediated transformations (Table 1, entries 1-5, 30-40%). Therefore the well-defined catalysts **1-6** are extremely active than metal salt catalyzed Barbier reactions in terms of time and yields (Table 1). To check the role of ancillary ligand, the catalytic reactions were carried out using only, **L1** or **L2** (without metal precursor) upto 24 h. Notably, the catalytic conversion is absent. Among the catalysts **1-6**, **1**, **5** and **6** were found to be very effective towards Barbier coupling process. Moreover, the catalytic conversion was absent when the reaction was analyzed using without catalyst. As of our knowledge, the present system is the first example for cadmium-catalyzed allylation of carbonyl compounds.



Scheme 4. Catalyst **1** mediated Barbier coupling in aqueous ethanol solution at room temperature.



Scheme 5. Catalyst **1** mediated Barbier coupling in aqueous ethanol media at room temperature in 30 min.

Table 1. Screening of metalsalts/metal mediated Barbier coupling in aqueous ethanol media.

| E | Cat. (10 mol%) | Time (min) | Isolated Yield (%) ^a |
|---|---|------------|---------------------------------|
| 1 | Cd(ClO ₄) ₂ ·6H ₂ O | 30 | 40 |
| 2 | Zn(ClO ₄) ₂ ·6H ₂ O | 30 | 32 |
| 3 | Cd(NO ₃) ₂ ·6H ₂ O | 30 | 38 |
| 4 | Zn(NO ₃) ₂ ·6H ₂ O | 30 | 34 |
| 5 | Zn powder | 30 | 30 |

^aIsolated yields by column chromatography, E; Entry.

Although, the product was obtained in excellent yield in 30 min, the yield was further improved by extending the reaction time for 2 h (Fig. 7). Interestingly, the catalytic efficiency of **2-4** was further improved about 22% upon increasing the reaction time from 30 min to 2 h. The catalytic efficiency of **1** is almost independent of the reaction time, while **5** (4%) and **6** (7%) showed a minor improvement. Therefore, catalyst **1** is relatively appreciable for Barbier coupling.

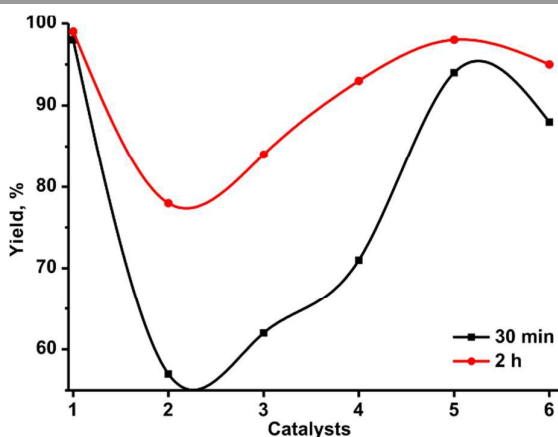


Fig 7. Catalysts **1-6** (10 mol%) mediated Barbier reaction of benzaldehyde with allyltributyltin in aqueous ethanol media in 30 min and 2 h. Yield was determined by ¹H NMR spectroscopy.

Subsequently, the catalytic reactions were extended with catalyst **1** for various aromatic carbonyl compounds (Scheme 5, Table 2). Furthermore, the functional group tolerance was evaluated for a range of substituted aromatic aldehydes (Scheme 5, Table 2) using catalyst **1**. The catalyst **1** gave considerable yields with good substrate scope (82-98). Notably, only the 2-nitrobenzaldehyde (Table 2, entry 7, 74%) depicted slightly lower yield compared to other examples.

Table 2. Evaluation of substrate scope with catalyst **1** in 30 min.

| E | Substrate | Product | Yield (%) ^a |
|----|-----------|---------|------------------------|
| 1 | | | 98 |
| 2 | | | 92 |
| 3 | | | 89 |
| 4 | | | 96 |
| 5 | | | 90 |
| 6 | | | 82 |
| 7 | | | 74 |
| 8 | | | 85 |
| 9 | | | 92 |
| 10 | | | 84 |
| 11 | | | 87 |

^aIsolated yields by column chromatography, E; Entry.

Experimental

General Considerations

All manipulations were carried out under argon atmosphere in a glove box using standard Schlenk techniques. The solvents were purchased from commercial sources and purified according to standard procedures and freshly distilled under argon atmosphere prior to use.²¹ Unless otherwise stated, the chemicals were purchased from commercial sources. 1-(2,6-diisopropylphenyl)-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-iumbromide and 3-(2-ethoxy-2-oxoethyl)-1-mesityl-1H-imidazol-3-ium bromide were prepared as previously reported.²² FTIR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV-vis spectra were measured on a T90+ UV-visible spectrophotometer. 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 internal standards. Elemental analyses were performed by the Euro EA-300 elemental analyzer. The crystal structures of **L1**, **L2**, $[(L1')_4Cd(Cl)(NO_3)]$ (**1**), $[(L1')_4Cd]^{2+}\{ClO_4\}_2^{2-}\cdot H_2O$ (**2**), $[(L1')_4Zn]^{2+}\{ClO_4\}_2^{2-}$ (**3**), $[(L2')_4CdCl_2]_n$ (**4**), $[(L2')_4Cd(Cl)]\{ClO_4\}$ (**5**) and $[(L2')_2Zn]\{ClO_4\}_2\cdot 2H_2O$ (**6**) were measured on an Oxford Super Nova X-ray diffractometer. Single crystals of complexes 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 150 K for **1**, **3** and **6** or at 293 K for **L1**, **L2**, **2**, **4** and **5** in inert oil. Using Olex2,²³ the structure was solved with the ShelXS²⁴ 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. The structural parameters of **L1** was not reported due to poor quality data (See supporting information). Molecule **1** showed "B" level alerts due to the high thermal parameter nature of nitrate moiety. Molecule **2** showed both "A" and "B" level alerts due to the disordered perchlorate moiety and due to isolated oxygen atom O(6) without hydrogen. Both "A" level alerts and "B" level alerts were received for disordered counter ions, water molecule and solvent accessible voids in structure **3**. In **3**, the electron density was not detected to locate the solvent molecules. Molecule **6** depicted both "A" and "B" level alerts due to short inter hydrogen interactions. 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. The function minimized was $[\sum w(F_o2 - F_c2)^2]$ ($w = 1/[\sigma^2(F_o2) + (aP)^2 + bP]$), where $P = (\max(F_o2, 0) + 2F_c2)/3$ with $\sigma^2(F_o2)$ from counting statistics. The functions $R1$ and $wR2$ were $(\sum ||F_o| - |F_c||)/\sum |F_o|$ and $[\sum w(F_o2 - F_c2)^2/\sum (wF_o4)]^{1/2}$, respectively. CCDC 1442188-1442194 contains the supplementary crystallographic data for **1-6** and **L2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via

www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Cautions

Selenium is toxic in large doses. The over dose of selenium casus skull and crossbones hazards (GHS06) and health hazards (GHS08). Must be handled with enough safety precautions. It should not be handled without splash goggles, lab coat, dust respirator, boots and gloves. Must be handled in the well ventilated fume hood to keep exposure to airborne contaminants below the exposure limit.

Synthesis of L1

A mixture of 1-(2,6-diisopropylphenyl)-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-iumbromide (0.50 g, 1.26 mmol), Se (0.12 g, 1.52 mmol) and K_2CO_3 (0.26 g, 1.90 mmol) in methanol (50 mL) was heated under reflux for 24 h then volatiles were removed under reduced pressure. The remaining solid was taken up in CH_2Cl_2 (2 X 30 mL), then the solution was filtered and dried under vacuum. Subsequently, the solid was treated with 12% HCl aqueous solution (30 mL), refluxed for 3 h then dried under vacuum to yield analytically pure **L1**. Yield: 73% (based on 1-(2,6-diisopropylphenyl)-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-iumbromide). M.p., 298 °C (decomp.). Elemental analysis calcd. (%) for $C_{17}H_{22}N_2O_2Se$ (366.08): C, 55.9; H, 6.1; N, 7.7; Found: C, 56.1; H 6.1; N 7.8. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.57 (d, 1H, Ar-*H*), 7.43 (dd, 2H, Im-*H*), 7.3 (d, 2H, Ar-*H*), 4.97 (s, 2H, CH₂), 2.39 (m, 2H, CH), 1.16 (d, 6H, CH₃), 1.06 (d, 6H, CH₃) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 168.59 (C=O), 158.58 (C=Se), 145.77(ArC), 134.41 (ArC), 129.66 (ImC), 123.78 (ImC), 121.46 (ArC), 121.15 (ArC), 50.24 (CH₂), 28.01 (CH), 24.15 (CH₃), 23.02 (CH₃) ppm. FT-IR (neat): $\bar{\nu}$ = 3165(w), 3080(s), 2964(s), 2926(w), 1775(vs), 1746(w), 1565(m), 1468(s), 1385(s), 1308(m), 1253(m), 1230(m), 1177(s), 1124(m), 1059(m), 961(w), 936(w), 809(s), 732(s), 655(m), 615(m), 577(w) cm⁻¹.

Synthesis of L2

L2 was prepared using the similar protocol used for **L1** by a mixture of 3-(2-ethoxy-2-oxoethyl)-1-mesityl-1H-imidazol-3-ium bromide (0.50 g, 1.42 mmol), Se (0.14 g, 1.70 mmol) and K_2CO_3 (0.29 g, 2.13 mmol) in methanol (50 mL). Yield: 81% (based on 3-(2-ethoxy-2-oxoethyl)-1-mesityl-1H-imidazol-3-ium bromide). M.p., 298 °C (decomp.). Elemental analysis calcd. (%) for $C_{14}H_{16}N_2O_2Se$ (324.03): C, 52.0; H, 5.0; N, 8.7; Found: C, 53.0; H 5.1; N 8.7. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.62 (s, 1H, Im-*H*), 7.36 (s, 1H, Im-*H*), 7.01 (s, 2H, Ar-*H*), 5.00 (s, 2H, CH₂), 2.29 (s, 3H, CH₃), 1.91 (s, 6H, CH₃) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 168.56 (C=O), 158.88 (C=Se), 145.77(ArC), 138.37 (ArC), 135.03 (ArC), 128.66 (ImC), 121.67 (ImC), 120.14 (ArC), 50.84 (CH₂), 20.83 (CH₃), 17.87 (CH₃) ppm. FT-IR (neat): $\bar{\nu}$ = 3470(s), 3360(w), 3162(w), 3132(w), 3094(w), 2917(w), 2855(w), 2474(w), 1918(w), 1720(vs), 1603(w), 1558(w), 1483(w), 1385(s), 1303(w), 1250(s), 1189(m), 1166(w),

1127(w), 975(s), 897(w), 860(w), 792(w), 715(w), 682(s), 623(w), 586(w), 530(w) cm^{-1} .

Synthesis of 1

To a mixture of **L1** (0.05 g, 0.27 mmol) and $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.17 g, 0.54 mmol), methanol (5 mL) was added under brisk flow of argon. The reaction mixture was allowed to stir at 80 °C for 12 h then brought to room temperature. Colorless crystals of **1** were obtained within 2 days under ambient conditions. Yield: 65% (based on $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). M.p., 234-236 °C. Elemental analysis calcd. (%) for $\text{C}_{36}\text{H}_{48}\text{CdClN}_5\text{O}_7\text{Se}_2$ (971.06): C, 44.6; H, 5.0; N, 7.2; Found: C, 45.0; H, 5.1; N, 7.3. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.57 (d, 1H, Ar-H), 7.45 (m, 2H, ImH), 7.31 (d, 2H, Ar-H), 5.06 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 2.39 (m, 2H, CH), 1.16 (d, 6H, 2CH_3), 1.06 (d, 6H, 2CH_3) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 167.71 (C=O), 158.80 (C=Se), 145.72 (ArC), 134.34 (ArC), 129.73 (ImC), 123.80 (ImC), 121.42 (ArC), 121.36 (ArC), 52.19 (OCH₃), 50.14 (CH₂), 28.04 (CH), 24.10 (CH₃), 23.02 (CH₃) ppm. FT-IR (neat): $\bar{\nu}$ = 3127(w), 3092(w), 2965(m), 2868(w), 1748(s), 1595(w), 1560(w), 1451(s), 1393(m), 1357(m), 1290(s), 1218(s), 1183(s), 1121(w), 1054(w), 1031(w), 988(w), 959(w), 803(m), 753(m), 698(m), 628(w), 577(w) cm^{-1} .

Synthesis of 2

Compound **2** was isolated as reported for **1** with a mixture of **L1** (0.05 g, 0.09 mmol), $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.06 g, 0.18 mmol) in methanol (5 mL). A large amount of colorless crystals of **2** were obtained within 12 h. Yield: 80% (based on $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). M.p., 248-250 °C. Elemental analysis calcd. (%) for $\text{C}_{72}\text{H}_{96}\text{CdCl}_2\text{N}_8\text{O}_{12}\text{Se}_4$ (1768.22): C, 49.0; H, 5.5; N, 6.4; Found: C, 50.0; H, 5.5; N, 6.4. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.56 (d, 1H, Ar-H), 7.45 (dd, 2H, ImH), 7.30 (d, 2H, Ar-H), 5.05 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 2.39 (m, 2H, CH), 1.16 (d, 6H, 2CH_3), 1.06 (d, 6H, 2CH_3) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 167.71 (C=O), 158.80 (C=Se), 145.73 (ArC), 134.34 (ArC), 129.72 (ImC), 123.80 (ImC), 121.41 (ArC), 121.32 (ArC), 52.19 (OCH₃), 50.14 (CH₂), 28.05 (CH), 24.09 (CH₃), 23.01 (CH₃) ppm. FT-IR (neat): $\bar{\nu}$ = 3504(w), 3136(w), 2963(m), 2929(w), 1762(s), 1710(w), 1622(w), 1559(w), 1463(s), 1391(w), 1360(w), 1311(w), 1219(s), 1186(w), 1088(vs), 989(w), 961(w), 929(w), 808(w), 754(m), 694(m), 620(s), 578(w), 534(w) cm^{-1} .

Synthesis of 3

Compound **3** was isolated as reported for **1** with a mixture of **L1** (0.05 g, 0.14 mmol) and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.09 g, 0.29 mmol) in methanol (5 mL). The colorless crystals of **3** were obtained within 12 h. Yield: 50% (based on $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). M.p., 243-245 °C (decomp.). Elemental analysis calcd. (%) for $\text{C}_{72}\text{H}_{96}\text{Cl}_2\text{N}_8\text{O}_{12}\text{Se}_4\text{Zn}$ (1718.25): C, 50.4; H, 5.6; N, 6.5; Found: C, 50.7; H, 5.8; N, 6.6. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.48 (d, 1H, Ar-H), 7.41 (dd, 2H, ImH), 7.23 (d, 2H, Ar-H), 4.98 (s, 2H, CH_2), 3.63 (s, 3H, CH_3), 2.45 (m, 2H, CH), 1.09 (d, 6H, 2CH_3), 1.00 (d, 6H, 2CH_3) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 167.70 (C=O), 158.80 (C=Se), 145.72 (ArC), 134.34 (ArC), 129.73 (ImC), 123.81 (ImC), 121.42 (ArC), 121.31 (ArC), 52.20 (OCH₃), 50.14 (CH₂), 28.04 (CH), 24.07 (CH₃), 23.00 (CH₃) ppm.

FT-IR (neat): $\bar{\nu}$ = 3217(w), 3170(w), 3125(w), 2959(m), 2923(s), 2956(m), 1755(s), 1626(m), 1519(w), 1462(s), 1432(m), 1378(s), 1300(m), 1220(s), 1177(m), 1111(s), 1058(s), 999(m), 954(m), 808(w), 783(w), 725(m), 697(m), 620(m), 581(w), 523(w) cm^{-1} .

Synthesis of 4

Compound **4** was isolated as reported for **1** with a mixture of **L2** (0.05 g, 0.09 mmol) and $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.06 g, 0.18 mmol) in methanol (3 mL). The colorless crystals of **4** were obtained within 2 days. Yield: 45% (based on $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). M.p., 230-232 °C. Elemental analysis calcd. (%) for $\text{C}_{30}\text{H}_{36}\text{Cd}_2\text{Cl}_6\text{N}_4\text{O}_4\text{Se}_2$ (1113.73): C, 32.4; H, 3.3; N, 5.0; Found: C, 33.0; H, 3.3; N, 5.1. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.64 (d, 1H, ImH), 7.41 (d, 1H, ImH), 7.01 (d, 2H, Ar-H), 5.08 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 1.90 (s, 6H, 2CH_3) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 167.67 (C=O), 159.00 (C=Se), 145.78 (ArC), 138.89 (ArC), 134.94 (ArC), 134.86 (ArC), 134.19 (ArC), 134.02 (ArC), 129.24 (ImC), 128.96 (ImC), 128.79 (ImC), 122.43 (ImC), 120.99 (ArC), 52.34 (OCH₃), 50.22 (CH₂), 20.59 (CH₃), 17.47 (CH₃) ppm. FT-IR (neat): $\bar{\nu}$ = 3402(m), 3161(w), 2956(w), 1749(s), 1615(m), 1557(w), 1436(s), 1293(s), 1214(s), 1030(m), 976(m), 862(w), 813(w), 748(m), 696(m), 583(w) cm^{-1} .

Synthesis of 5

Compound **5** was isolated as reported for **1** with a mixture of **L2** (0.05 g, 0.14 mmol) and $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.09 g, 0.29 mmol) in methanol (3 mL). The colorless crystals of **5** were obtained within 2 days. Yield: 54% (based on $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). M.p., 250-252 °C (decomp.). Elemental analysis calcd. (%) for $\text{C}_{45}\text{H}_{54}\text{CdCl}_2\text{N}_6\text{O}_{10}\text{Se}_3$ (1261.98): C, 42.9; H, 4.3; N, 6.7; Found: C, 43.2; H, 4.4; N, 6.7. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 7.56 (d, 1H, ImH), 7.31 (d, 1H, ImH), 7.01 (d, 2H, Ar-H), 5.04 (s, 2H, CH_2), 3.89 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 1.90 (s, 6H, 2CH_3) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 167.76 (C=O), 158.88 (C=Se), 145.78 (ArC), 138.37 (ArC), 135.03 (ArC), 128.66 (ImC), 121.67 (ImC), 120.14 (ArC), 52.24 (OCH₃), 50.05 (CH₂), 20.58 (CH₃), 17.47 (CH₃) ppm. FT-IR (neat): $\bar{\nu}$ = 3485(m), 3160(w), 3119(w), 3089(w), 2953(w), 1749(s), 1603(w), 1569(w), 1486(w), 1452(m), 1357(w), 1312(w), 1213(s), 1052(s), 976(m), 863(w), 776(w), 746(w), 695(w), 623(s), 591(w) cm^{-1} .

Synthesis of 6

A mixture of **L2** (0.05 g, 0.14 mmol) and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.09 g, 0.29 mmol) in methanol (5 mL) were loaded in a schlenk tube. Subsequently, the schlenk tube temperature was maintained at 120 °C for two days then slowly brought to room temperature. The colorless crystals of **6** were obtained within 12 h. Yield: 50% (based on $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). M.p., 210-212 °C (decomp.). Elemental analysis calcd. (%) for $\text{C}_{30}\text{H}_{36}\text{Cl}_2\text{N}_4\text{O}_{12}\text{Se}_2\text{Zn}$ (937.93): C, 38.4; H, 3.8; N, 6.0; Found: C, 38.9; H, 3.9; N, 6.1. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 8.16 (d, 1H, ImH), 7.94 (d, 1H, ImH), 7.18 (d, 2H, Ar-H), 5.22 (s, 2H, CH_2), 3.80 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 1.92 (s, 6H, 2CH_3) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 167.67 (C=O), 159.00 (C=Se), 138.69 (ArC), 134.94 (ArC), 134.02 (ArC), 128.79 (ImC),

122.43 (ImC), 120.99 (ArC), 52.34 (OCH₃), 50.22 (CH₂), 20.59 (CH₃), 17.47 (CH₃) ppm. FT-IR (neat): $\bar{\nu}$ = 3447(m), 3167(w), 1754(m), 1623(m), 1485(w), 1454(w), 1396(w), 136(w), 1217(w), 1076(s), 931(w), 853(w), 746(w), 700(w), 619(s), 584(w) cm⁻¹.

Reaction conditions for Barbier coupling reactions

Oven dried Schlenk was charged with catalysts (10 mol%), aromatic aldehyde (1 equiv) then dried under vacuum for 5 min. Solvent (5 mL) was added under nitrogen condition to the reaction mixture, evacuated for few seconds, loaded with nitrogen allyltributyltin (1.2 equiv) under nitrogen condition at room temperature. The reaction progress was monitored by TLC. The reaction mixture was diluted with water (10 mL) and DCM (10 mL). The organic phase was separated, washed with brine solution (10 mL), dried over an anhydrous sodium sulphate then the reaction mass was concentrated under reduced pressure to get crude compound. The crude compound was absorbed on silica gel (100-200 mesh) for purification then petroleum ether and 10% ethyl acetate/petroleum ether (200 mL) were poured on column to separate the final product.

Conclusions

In conclusion, here we investigated the reaction between zinc and cadmium salts with two different ester functionalized mono aryl substitute imidazoline selones along with variable steric effect at organic ligand. The mononuclear zinc and cadmium selone complexes (**1-3**, **5** and **6**) along with polynuclear cadmium selone 1D chain (**4**) were isolated. A novel structural topologies and versatile coordination properties were achieved by tuning steric effect on aryl group. The mononuclear homoleptic zinc selone complexes were the first structurally characterized zinc(II) selone complexes. The first catalytic application of imidazoline selones supported zinc and cadmium complexes were explored. The catalysts **1-6** were highly active for Barbier coupling reactions in aqueous alcohol media. The catalyst **1** was much more active than **2-6**. The potential role of imidazoline selone in carbon-carbon bond formation reactions was clearly justified in the catalytic demonstration. In addition, the scope of the catalytic reactions were further explored with eleven different aldehydes. The future studies on the reaction chemistry of these ligands and their coinage metal complexes toward organic transformations are underway in our laboratory.

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Graphical Abstract

The zinc and cadmium imidazoline selone complexes were synthesized and demonstrated as potential catalysts in Barbier coupling in aqueous alcohol media.

