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Bismuth(III)dichalcogenones as Highly Active Catalysts in Multiple C–C Bond Formation Reactions

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Thirteen new bismuth(III) dichalcogenones derivatives of triflates and halides were synthesized and structurally characterized. The mono, di, tetra and hepta nuclear complexes were isolated with different bismuth(III) coordination environments. These newly isolated bismuth(III)dichalcogenones were characterized by multi nuclear NMR, FT-IR, UV-vis, TGA and single crystal X-ray diffraction techniques. These complexes were tested for the synthesis of symmetrical triaryl- or triheteroarylmethanes and the catalysts were found to be highly active. In particular, the selone complexes were relatively more active than thione complexes. Subsequently, the scope of the catalytic reactions were further explored with different substituents.

Introduction

The N-heterocyclic carbene (NHC) analogues of imidazoline-2-chalcogenone metal complexes have shown the promising features in catalysis[1] and structural chemistry[2-4] due to their tuneable σ-donor and π-accepting nature (Chart 1).[5] Notably, the catalytic efficiency of metal-imidazoline-2-chalcogenone complexes is better than metal-NHC complexes (Chart 2).[6-11]

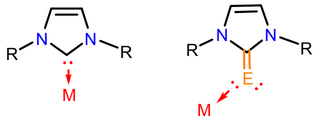

Chart 1. The N-heterocyclic carbene (NHC) analogues of imidazoline-2-chalcogenone.

For example, the regioselective borylation of internal alkyne in presence of copper chalcogen complexes [(**IME**)$_2$CuCl; **IME** = 1,3-dimethylimidazoline-2-chalcogenone; **E** = O, S and Se] has proved to be more active than that of NHC-Cu.[7] The thione gold(I) complexes [(**IMesS**)AuCl and (**S^Imine$_{tBu}$**)AuCl; **IMesS** = 1,3-dimesitylimidazole-2-thione, **S^Imine$_{tBu}$** = 1-[1-(2,6-dimethylphenylimino)*tert*-butyl]-3-(mesityl)imidazole-2-thione] mediated hydroamination of phenylacetylene with substituted anilines have shown comparable catalytic activity with Au-NHC [(**IMes**)AuCl].[8] The iridium complexes, {[(ppy)$_2$**L$_2$**Ir]PF$_6$, [(ppy)$_2$**L$_3$**Ir]PF$_6$, [(btpy)$_2$**L$_2$**Ir]PF$_6$ and [(btpy)$_2$**L$_3$**Ir]PF$_6$; **L$_2$** = **mbit**, **L$_3$** = **mbis**, ppy = 2-phenylpyridinato and btpy = 2-(2′-benzothienyl)pyridinato}, catalysed oxidative coupling of benzylamine to imine under visible-light have depicted the much superior catalytic activity than NHC-Ir catalysts.[9a] The selone supported pincer type Pd(II) complexes[10a] have found to be comparable with the most efficient NHC-Pd catalysts for the Heck coupling.[10b-d] **IPrE** and **IMesE** (**IPrE** = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-chalcogenone and **IMesE** = 1,3-dimesitylimidazole-2-chalcogenone) complexes of copper(I) depicted the best regioselective borylation of unsymmetrical alkynes compared to Cu-**IPr** catalyst.[11]

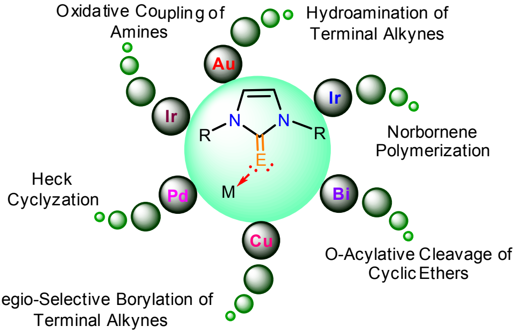

Chart 2. Known catalytic reactions of imidazoline-2-chalcogenone supported metal complexes.[6-11,12b]

Notably, NHC complexes of bismuth are rare in the literature due to highly polar nature of bond between carbene carbon and bismuth.[12] Moreover the catalytic applications of bismuth-NHC's are not reported yet. Thus, the imidazoline-2-chalcogenone bismuth(III) complexes could be the ideal replacement for bismuth-NHC's. Recently, we demonstrated the first catalytic application of NHC–Bi analogue of monoimidazoline-2-chalcogenone derivatives for *O*-acylative

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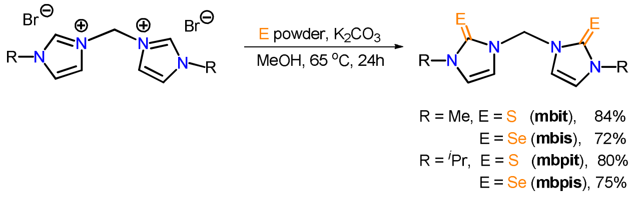
Electronic Supplementary Information (ESI) available: [^{1}H NMR, ^{13}C NMR, FT-IR, Solid-state fluorescence spectra and Table S1]. See DOI: 10.1039/x0xx00000x cleavage of cyclic ethers.[12b] In addition, the 1,3-di*iso*propylimidazole-2-thione supported bismuth(III) iodide complex was demonstrated for the trans-metalation reactions with Hg and Pd.[13] Similarly, 1,3-dibutyl-benzimidazole-2-selone supported bismuth(III) iodide complex was employed as a single source precursor for the preparation of Bi_2Se_3 nanoparticles.[14]

Although the catalytic role of Bi(III)-monochalcogenone complexes were evidenced, the catalytic applications of bismuth-dicarbene analogues of Bi(III)-diimidazole chalcogenones have not been reported yet. Therefore, we presumed that the structurally modified diimidazole chalcogenones with higher or lower degrees of flexibility and suitable reaction conditions can led to the structurally well characterized Bi(III)-diimidazole chalcogenone catalysts. In this paper, we report a series of new organo dichalcogenones supported bismuth(III) complexes (**1**-**13**) with variable coordination environments. The catalysts **1**-**13** were tested for the triaryl- or triheteroarylmethanes synthesis.[15] These new catalysts were highly active towards multiple C–C bond formation reactions with excellent functional group tolerance.

Results and discussion

The organo dichalcogenones (**mbit**, **mbis**, **mbpit** and **mbpis**) ligands were synthesized in very good yields by treating 3,3'-methylenebis(1-methyl-1*H*-imidazol-3-ium) bromide (for **mbit** and **mbis**) or 3,3'-methylenebis(1-isopropyl-1*H*-imidazol-3-ium) bromide (for **mbpit** and **mbpis**) with elemental chalcogen powder in the presence of potassium carbonate (Scheme 1).[16]

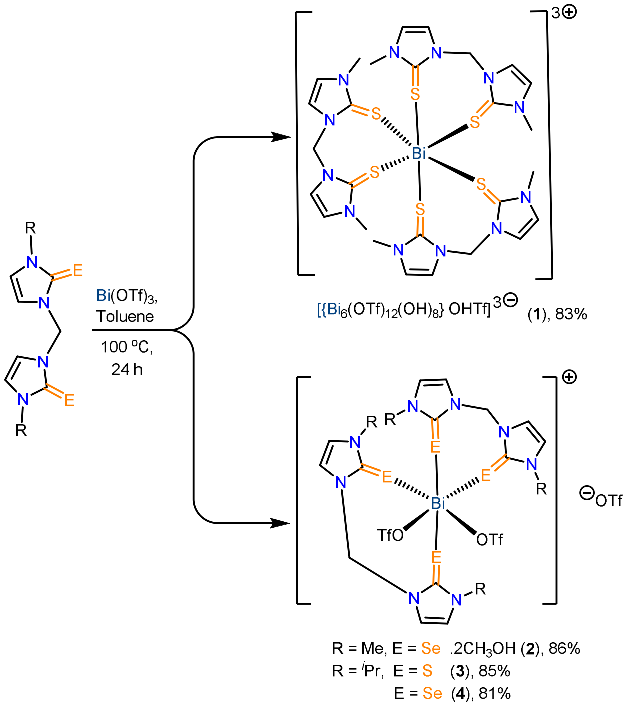


Scheme 1. Synthesis of **mbit, mbis, mbpit** and **mbpis**.

Organo dichalcogenone ligands were treated with corresponding bismuth(III) salts to isolate bismuth(III) chalcogenone derivatives **1-13** (Scheme 2 and 3). The formation of complexes **1-13** were confirmed by FT-IR, multinuclear (^1H, ^{13}C and ^{19}F) NMR, UV-vis, TGA and single crystal X-ray diffraction analysis techniques.

Mononuclear bismuth(III) chalcogenone complexes, 1-4

The mononuclear bismuth(III) chalcogenones **1-4** were derived from the reaction between bismuth(III) triflate and an equimolar quantity of organo dichalcogenones in toluene (Scheme 2). The analytically pure complexes, **1-4** were isolated as orange red precipitate in excellent yield. The single crystals suitable for X-ray analysis were grown at ambient temperature over a period of 2 days by dissolving the crude compounds in methanol and acetonitrile mixture.



Scheme 2. Synthesis of monomeric bismuth(III) chalcogenone complexes **1**-**4**.

The solid state structures of **1-4** were further confirmed by single crystal X-ray diffraction techniques. The cationic salt **1** crystallized in trigonal space group, *R-3c*. **1** is a rare homoleptic tricationic mononuclear bismuth(III) thione (Fig. 1). Charge of the complex is balanced by trianionic hexanuclear bismuth(III) hydroxo-triflato cluster. Similar such hexanuclear bismuth clusters were reported with bis(trifluoromethanesulfonyl)amide $[(NTf_2)^-]$ counter ion.[17d] The core structure of hexanuclear bismuth cluster in **1** can be comparable with the known $[Bi_6(O)_4(OH)_4(H_2O)_6](NTf_2)_6)$.[17d] In mononuclear unit, three **mbit** ligands were coordinated with bismuth(III) centre in slightly distorted octahedral geometry. Bismuth(III) centre with deca coordination was found in $[Bi_6(OH)_8(OTf)_{12}]^{3-}$ counter ion,[17] in which bismuth forms four bonds with triply bonded bridging oxygen, two bonds with oxygens of bridging triflate units in bidentate fashion and one bond with oxygen of terminal triflate unit in monodentate fashion, besides each metal shows three metal···metal bonds. The Bi–μ_3–OH bond lengths in **1** found to be 2.277(0) to 2.896(1) Å and shorter Bi–O bond distances are also observed between Bi(2)–O(1) (2.207(0)), Bi(2)–O(4) (2.180(1)), Bi(3)–O(4) (2.203(0)) and Bi(2)–O(4') (2.215(0)). These values are in good agreement with the known Bi–μ_3–OH bond distances for $[Bi_6O_4(OH)_4(NO_3)_6(H_2O)_2]\cdot H_2O$ with 2.250(8) to 2.600(8) Å and are almost comparable with the values reported for $[Bi_6(O)_4(OH)_4(H_2O)_6](NTf_2)_6)$ with 2,297(14) to 2.557(16) Å. The basic unit of Bi_6 counter ion contains 14 atoms cage with 12 tetragons made of two bismuth and two oxygen atoms. Furthermore, the weak metal···metal interactions are also been perceived between metal centres with bond lengths of d$_{Bi-Bi}$ = 3.65(1)-3.72(1) Å (*i.e.,* Bi$_1$–Bi$_1$ 3.675(1) Å, Bi$_1$–Bi$_2$ 3.650(1) Å, Bi$_1$–Bi$_2$ 3.724(1) Å and Bi$_2$–Bi$_2$ 3.689(1) Å). The Bi···Bi distances can be consider as elongated Bi–Bi single bond interactions, since the distances are slightly longer than the sum of covalent radii of Bi atoms (∑r$_{cov}$= 3.04 Å). However, Bi···Bi distances are within the range of van der Waals interactions (∑r$_{vdW}$ = 4.80 Å).[18]

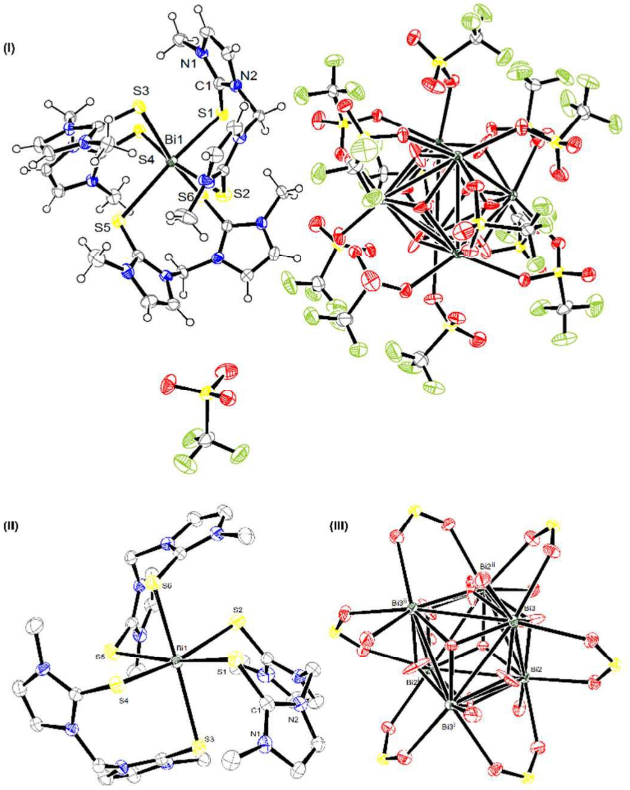


Fig. 1 (I) The solid state structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–S(1), 1.717(8), C(6)–S(2), 1.697(8), C(10)–S(3), 1.689(7), C(15)–S(4), 1.709(7), C(19)–S(5), 1.703(8), C(24)–S(6), 1.708(7), S(1)–Bi(1), 2.700(17), S(2)–Bi(1), 2.879(2), S(3)–Bi(1), 2.894(19), S(4)–Bi(1), 2.755(19), S(5)–Bi(1), 3.013(2), S(6)–Bi(1), 2.703(18), S(3)–Bi(1)–S(6), 165.46(5), N(1)–C(1)– N(2), 106.3(6), N(1)–C(1)–S(1), 126.3(6), N(2)–C(1)–S(1), 127.3(6), Bi(2)–Bi(3), 3.650(4), Bi(3)–Bi(3'), 3.675(5). (II) [Bi(**mbit**)$_3$]$^{3+}$ cationic unit. Counter ions and hydrogens have been omitted for clarity. (III) Mode of triflate coordination in Bi$_6$. Cationic unit and some part of triflate moiety have been omitted for clarity.

The salt **2** crystallized in triclinic space group, *Pī*, while **3** and **4** crystallized in monoclinic space group, *P2$_1$/n*. The X-ray analysis revealed that the monocationic salts **2**-**4** are isostructural (Fig. 2-4). Besides, **2** crystallized with two methanol molecules in its lattice. The metal centre in **2**-**4** adopts a slightly distorted octahedral geometry. The equatorial positions around bismuth(III) centre in **2**-**4** were occupied by two triflate units and two chalcogen centres from two ligands.

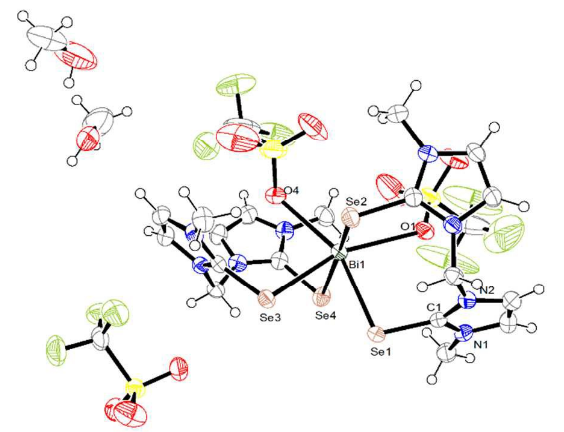


Fig. 2) The solid state structure e of **2.** Hydrogen atoms in **2** have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.881(8), C(6)–Se(2), 1.875(7), C(10)–Se(3), 1.875(8), C(15)–Se(4), 1.879(8), Se(1)–Bi(1), 2.767(8), Se(2)–Bi(1), 2.885(9), Se(3)–Bi(1), 2.771(8), Se(4)–Bi(1), 2.953(9), O(1)–Bi(1), 2.676(6), O(4)–Bi(1), 2.690(6), Se(2)–Bi(1)–Se(4), 169.50(3), N(1)–C(1)–N(2), 107.7(7), N(1)–C(1)–Se(1), 124.1(6), N(2)–C(1)–Se(1), 127.7(6).

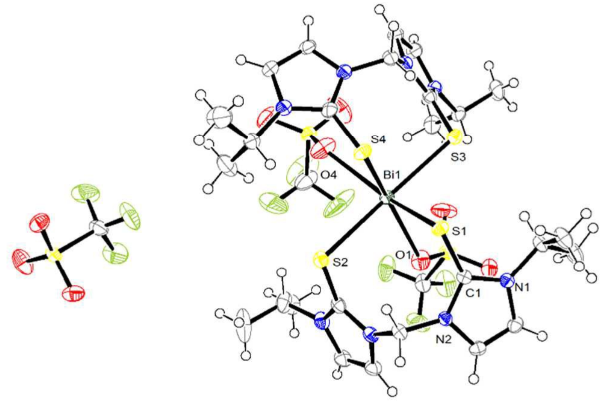


Fig. 3) The solid state structure of **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–S(1), 1.730(4), C(5)–S(2), 1.705(4), C(14)–S(3), 1.712(3), C(18)–S(4), 1.727(4), S(1)–Bi(1), 2.624(8), S(2)–Bi(1), 2.840(9), S(3)–Bi(1), 2.778(9), S(4)–Bi(1), 2.676(8), O(1)–Bi(1), 2.590(3), O(4)–Bi(1), 2.692(4), S(2)–Bi(1)–S(3), 166.69(3), N(1)–C(1)– N(2), 107.5(3), N(1)–C(1)–S(1), 125.0(3), N(2)–C(1)–S(1), 127.1(3).

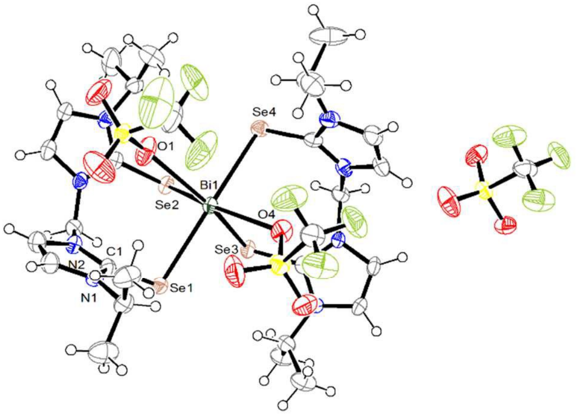


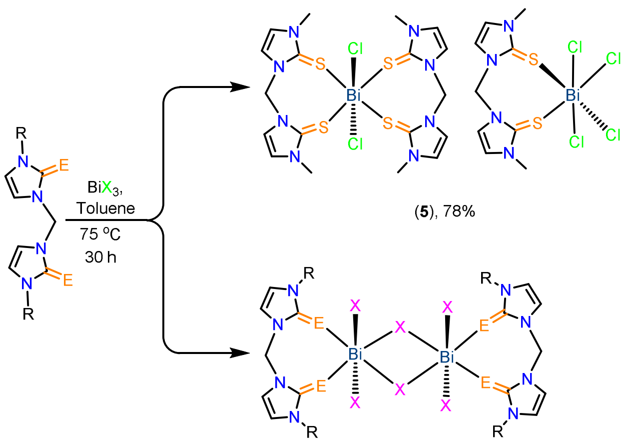
Fig. 4 Molecular structure of **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.867(6), C(8)–Se(2),

1.878(6), C(14)–Se(3), 1.872(7), C(21)–Se(4), 1.867(7), Se(1)–Bi(1), 2.889(8), Se(2)–Bi(1), 2.785(7), Se(3)–Bi(1), 2.737(7), Se(4)–Bi(1), 2.938(8), O(1)–Bi(1), 2.729(6), O(4)–Bi(1), 2.646(5), Se(1)–Bi(1)–Se(4), 164.80(2), N(1)–C(1)–N(2), 106.7(5), N(1)–C(1)–Se(1), 126.9(5), N(2)–C(1)–Se(1), 126.1(5).

The C=S bond distances in **1** are slightly longer than that of **3**. The C=S bond distances in **1** are almost comparable with known monomeric bismuth(III) chalcogenones.[12b] Similarly, the E=Bi bond distances are considerably shorter than the former report.[12b] However the axially coordinated bonds are slightly elongated than equatorial bonds as expected for an octahedral molecule. Slight up-field shift is observed in ^{1}H and ^{13}C NMR values for **1**-**4** compared to corresponding ligands. In ^{13}C NMR, C=E carbon chemical shift value observed at δ 163 (**1**), 156 (**2**), 161 (**3**) and 155 (**4**). In FT-IR, a weak signal appeared at 1376-1395 cm^{-1} range for uncoordinated S=O stretching frequency and a strong signal appeared at 1216-1224 cm^{-1} range for coordinated S=O stretching frequency of triflate unit. C=E stretching frequency signal appeared at 1160-1168 cm^{-1} for the complexes **1**-**4**.

Binuclear bismuth(III) chalcogenone complexes

The binuclear bismuth(III) chalcogenones **5**-**12** were isolated by treating an equimolar quantity of organo dichalcogenone ligands with bismuth(III) halides in toluene (Scheme 3). Analytically pure yellow precipitates were produced from bismuth(III) chloride reactions, while yellowish orange precipitates were isolated from bismuth(III) bromide reactions. The single crystals of **5**-**12** were grown at ambient temperature over a period of 2-3 days by dissolving the crude samples in hot acetonitrile. Compounds **5**-**12** are soluble only in methanol, acetonitrile and dimethyl sulfoxide. The bismuth(III) centre adopts octahedral geometry in **5**-**12**. However, the **5** exist as ion pairs, in which both the bismuth(III) centres adopt in octahedral geometries with diverse coordination environment. One of the bismuth(III) centre in **5** is coordinated with two **mbit** ligands and two chlorine ligands, while another bismuth(III) centre is surrounded by one **mbit** ligand and four chlorine ligands. The FT-IR stretching frequency values for C=E (1162-1198 cm^{-1}) confirmed the complex formation. The ^{1}H NMR chemical shift values of complexes **5**-**13** are almost similar to that of corresponding ligands. The ^{13}C NMR spectra of **5**-**13** showed 1-3 ppm up-field shift for C=E carbon due to the complexation.



R = Me, E = S, X = Br (**6**), 82%
E = Se, X = Cl (**7**), 75%
X = Br (**8**), 77%
R = ^{i}Pr, E = S, X = Cl .CH$_3$CN (**9**), 72%
X = Br .CH$_3$CN (**10**), 74%
E = Se, X = Cl .CH$_3$CN (**11**), 78%
X = Br .CH$_3$CN (**12**), 87%

Scheme 3 Synthesis of binuclear bismuth(III) chalcogenone complexes **6**-**12**.

Single crystal X-ray structure of 5-12

The solid state structures of **5**-**12** were further confirmed by single crystal X-ray diffraction analysis. **5**-**8** crystallized in monoclinic space group (*C2/c* for **5**, *C2/m* for **7**, *P2$_1$/c* for **6**, and *P2$_1$/n* for **8**, (Fig. 5 and 6). **9**, **10**, **11** and **12** crystallized in the tetragonal space group, *P4$_2$/ncm* (Fig. 7 and 8). The monocationic salt **5** is a rare homo nuclear salt, which is in contrast with known mononuclear bismuth(III) **mbit** complex.[4a] In **5**, the cationic bismuth(III) unit co-exist with an anionic bismuth(III) unit, in which one bismuth centre is coordinated with two **mbit** units and two chlorine atoms, while another bismuth centre is coordinated with one **mbit** ligand and four chlorine atoms (Fig. 5 top).

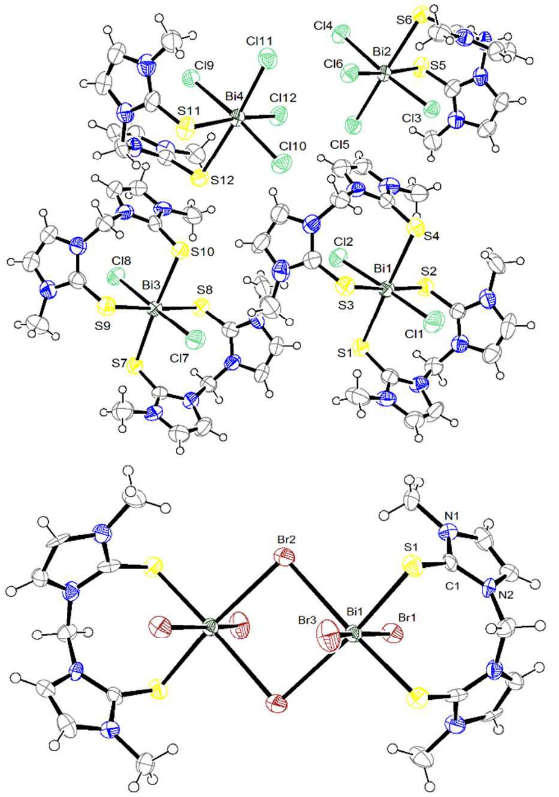


Fig. 5 Top: The solid state structure of **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (^{o}): C(1)–S(1), 1.731(12), S(1)–Bi(1), 2.822(3), S(2)–Bi(1), 2.876(3), S(3)–Bi(1), 2.806(3), S(4)–Bi(1), 2.804(3), Bi(1)–Cl(1), 2.629(3), Bi(1)–Cl(2), 2.657(3), Bi(2)–Cl(3), 2.660(3), Bi(2)–Cl(4), 2.685(3), Bi(2)–Cl(5), 2.666(3), Bi(2)–Cl(6), 2.655(2), C(1)–S(1)–Bi(1), 99.9(4), S(2)–Bi(1)–S(3), 175.88(5), N(1)–C(1)– N(2), 108.9(10), N(1)–C(1)–S(1), 125.4(9), N(2)–C(1)–S(1), 125.6(9). Bottom: Molecular structure of **6**. Disordered solvent molecule has been omitted for clarity. Selected bond lengths (Å) and angles (^{o}): C(1)–S(1), 1.705 (12), C(6)–S(2), 1.707(13), S(1)–Bi(1), 2.687(3), S(2)–Bi(1), 2.697(4), Bi(1)–Br(1), 2.788(14), Bi(1)–Br(2), 3.169(2), Bi(1)–Br(2'), 3.086(15), Bi(1)–Br(3), 2.812(16), C(1)–S(1)–Bi(1), 103.4(4), C(6)–S(2)–Bi(1), 102.9(5), N(1)–C(1)– N(2), 106.2(11), N(3)–C(6)– N(4), 106.1(11), N(1)–C(1)–S(1), 126.6(10), N(2)–C(1)–S(1), 127.1(9), N(3)–C(6)–S(2), 128.2(9), N(4)–C(6)–S(2), 125.1(10).

In contrast to **5**, the molecules **6**-**12** are isostructural. **6**-**12** exist as dinuclear complex (Fig. 5 bottom, and Fig 6-8). In which each bismuth centre adopts octahedral geometry with one organo dichalcogen ligand, two terminal halogens and two bridging halogens. The bridging Bi–X bond distances are slightly elongated compared to terminal Bi–X bonds, as reported earlier for binuclear complexes.[12b] In addition, the elongation of C=E bond distances were observed after complexation. The C=E and E–Bi bond distances are almost consistent with the literature.[4,12b] However, the structural parameters of molecules **7** and **8** are not considered for the current discussion because of the structural disorderness. The solid state structures of **7** and **8** were considered only to elucidate the coordination modes of ligand with metal precursors.

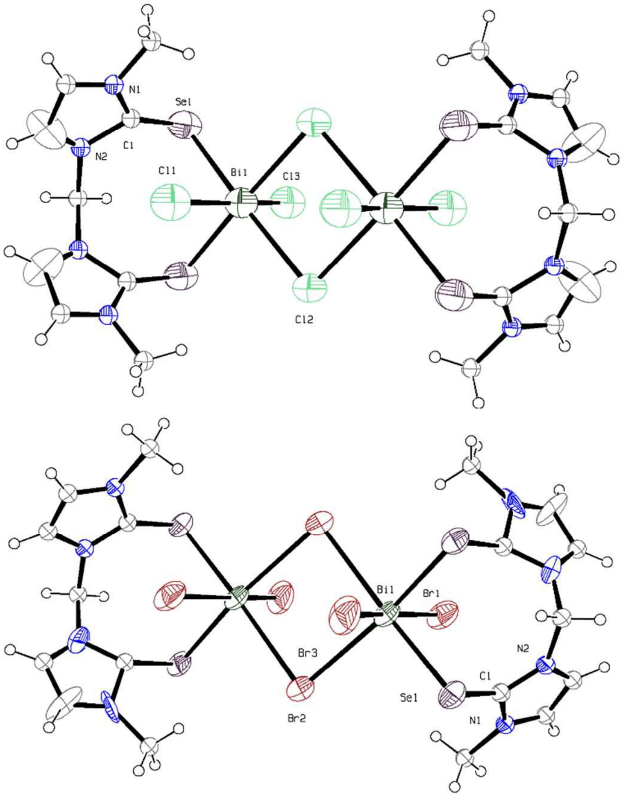


Fig. 6 Top: Molecular structure of **7**. Bottom: Molecular structure of **8**.

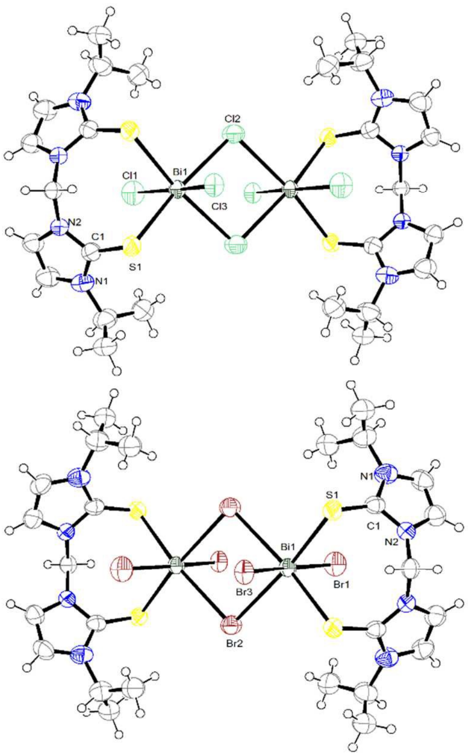


Fig. 7 Top: Molecular structure of **9**. Disordered solvent molecule has been omitted for clarity. Selected bond lengths (Å) and angles (^{o}): C(1)–S(1), 1.707(6),

S(1)–Bi(1), 2.746(15), Bi(1)–Cl(1), 2.608(3), Bi(1)–Cl(2), 2.892(15), Bi(1)–Cl(3), 2.709(2), C(1)–S(1)–Bi(1), 105.6(2), N(1)–C(1)– N(2), 105.6(6), N(1)–C(1)–S(1), 128.4(5), N(2)–C(1)–S(1), 125.7(5). Bottom: Molecular structure of **10**. Disordered solvent molecule has been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–S(1), 1.702(8), S(1)–Bi(1), 2.755(19), Bi(1)–Br(1), 2.743(14), Bi(1)–Br(2), 3.020(8), Bi(1)–Br(3), 2.870(13), C(1)–S(1)–Bi(1), 106.4(2), N(1)–C(1)– N(2), 105.2(7), N(1)–C(1)–S(1), 129.4(6), N(2)–C(1)–S(1), 125.3(6).

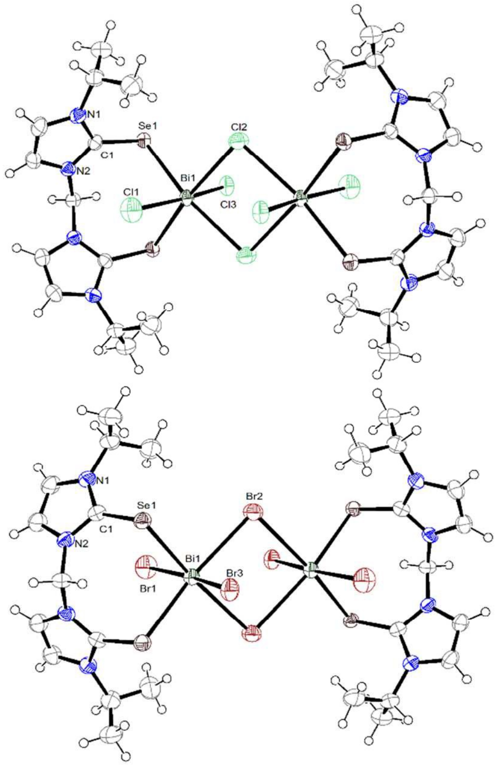
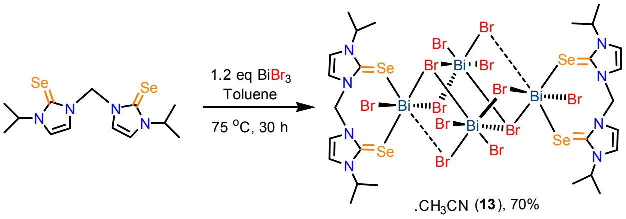


Fig. 8 Top: Molecular structure of **11**. Disordered solvent molecule has been omitted for clarity. Selected bond lengths (Å) and angles (o): C(1)–Se(1), 1.869(4), Se(1)–Bi(1), 2.828(5), Bi(1)–Cl(1), 2.623(2), Bi(1)–Cl(2), 2.914(11), Bi(1)–Cl(3), 2.732(17), C(1)–Se(1)–Bi(1), 102.84(13), N(1)–C(1)– N(2), 106.1(4), N(1)–C(1)–Se(1), 128.0(3), N(2)–C(1)–Se(1), 125.7(3). Bottom: Molecular structure of **12**. Disordered solvent molecule has been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.873(5), Se(1)–Bi(1), 2.834(5), Bi(1)–Br(1), 2.751(9), Bi(1)–Br(2), 3.038(5), Bi(1)–Br(3), 2.889(8), C(1)–Se(1)–Bi(1), 103.27(14), N(1)–C(1)– N(2), 106.0(4), N(1)–C(1)–Se(1), 127.7(4), N(2)–C(1)–Se(1), 126.0(3).

Tetranuclear bismuth(III) chalcogenone complex

A tetra nuclear bismuth(III) selone complex **13** was isolated by treating **mbpis** ligand with 1.2 equivalents of bismuth(III) bromide in toluene (Scheme 4). Compound **13** is soluble only in acetonitrile and dimethyl sulfoxide. Single crystals of **13** were grown at ambient temperature in hot acetonitrile solution. In ^{1}H NMR spectrum, a slight down field shift was observed for imidazole protons and CH_2 protons attached between two imidazole moieties upon complexation. Similarly, ^{13}C NMR spectrum showed the notable up-field shift (5 ppm) for C=Se carbon, indicating the complex formation. Additionally, the strong stretching frequency value for C=E appeared at 1183 cm^{-1} in FT-IR.



.CH_3CN (**13**), 70%

Scheme 4 Synthesis of tetranuclear bismuth(III) selone complex **13**.

Single crystal X-ray structure of 13

The solid state structure of **13** was further confirmed by single crystal X-ray diffraction technique. Molecule **13** is a tetra nuclear cluster, which crystallized in monoclinic space group, $P2_1/c$ (Fig. 9). Structure can be consider as a fused double open cube tetramer bridged by Bi–Br bonds. Interestingly, the tetrameric Bi–Br cluster is coordinated by the neutral selone ligand **mbpis**. The geometry around each bismuth atom is octahedral with different coordination environments. The coordination environment of Bi_1 is fulfilled by one terminal and three bridging Br donors as well as **mbpis**, whereas the Bi_2 is surrounded by two terminal and four bridging Br donors. The Bi–Br bond lengths to the terminal Br donors are relatively shorter (ranging from 2.664(12) to 2.721(11) Å) than those to the bridging Br donors (ranging from 2.665(13) to 3.270(0) Å). Even the environment around Br centres varies widely. In **13**, there are six terminal, four doubly bridged, and two triply bridged Br ligands. This type of discrete tetrameric bismuth chloride[19] and iodide[14] clusters were reported; however, **13** is the first example for bismuth bromide cluster.[20]

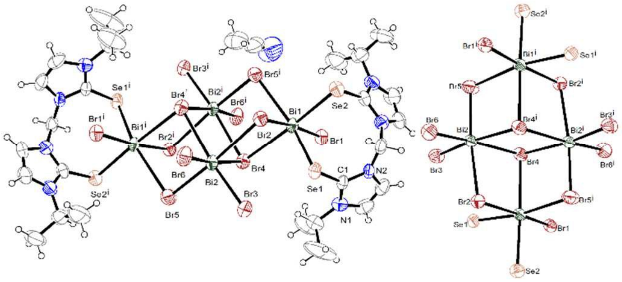


Fig. 9 (i) Molecular structure of **13**. Disordered solvent molecule has been omitted for clarity. Selected bond lengths (Å) and angles (o): C(1)–Se(1), 1.874(9), C(8)–Se(2), 1.865(11), Se(1)–Bi(1), 2.735(12), Se(2)–Bi(1), 2.829(12), Bi(1)–Br(1), 2.721(11), Bi(1)–Br(2), 2.963(11), Bi(1)–Br(4), 3.081(11), Bi(1)–Br(5), 3.270(0), Bi(2)–Br(2), 3.071(11), Bi(2)–Br(3), 2.664(12), Bi(2)–Br(4), 3.161(12), Bi(2)–Br(4’), 3.166(12), Bi(2)–Br(5), 2.760(13), Bi(2)–Br(6), 2.665(13), C(1)–Se(1)–Bi(1), 99.8(3), C(8)–Se(2)–Bi(1), 98.7(3), N(1)–C(1)– N(2), 108.5(9), N(1)–C(1)–Se(1), 125.4(7), N(2)–C(1)–Se(1), 126.6(8), N(3)–C(8)–Se(2), 127.1(8), N(4)–C(8)–Se(2), 126.2(9). (ii) Core double open cubic tetramer (Bi_4Br_{12}) entity in molecule **13**, ligand part has been omitted for clarity.

TGA analysis of 1–13

The thermal stability of complex**1**-**13** was analysed by TGA. Fig. 10 reveals the thermal breakdown pathway of **1**-**13** based on thermal investigation under nitrogen atmosphere (10 °C min^{-1}, 30–900 °C). Bismuth(III) triflate complexes **1**-**4** depicted enough stability till 380-390 °C. Then a sudden weight loss (35-

45%) is observed in a single step, which can be attributed to the decomposition of organic moieties. The cationic salts **2**-**4** showed a similar pattern in decomposition and the residual weights are almost matching with the calculated amounts for bismuth(III) sulphide. In contrast to the cationic salts **2**-**4**, tricationic salt **1** showed slight deviation in decomposition and left with the 25% residue, which can be bismuth(III) sulphide (18% calculated weight). Thus, this confirms the structural diversity between **1** and **2**-**4**.

Likewise, the molecules **5**-**8** are thermally stable up to 350-360 °C. Molecules **6**-**8** show gradual weight loss till 700-720 °C with 78-90% weight loss. Whereas cationic salt **5** lost its weight in two step with 25% residual weight, which can be attributed to the calculated weight for Bi_2S_3. Similarly, molecules **6** and **7** are left with the calculated amount of residues of corresponding mono chalcogenides. In the same way the residual weight of **8** is comparable with the calculated weight of $BiSe_2$.

Besides, the molecules **9**-**13** also showed enough stability still 300-320 °C. Compounds **9** and **11** decomposed in step wise manner to give 17% residual weight due to the formation of BiS_2 and $BiSe_2$, respectively. The molecules **10**, **12** and **13** drop their weight in a single step with almost 10% residual weight, in which the residues of **10** and **12** are equal to the calculated weight of corresponding mono chalcogenides. The residual weight of **13** is matching with the calculated amount for $BiSe_2$.

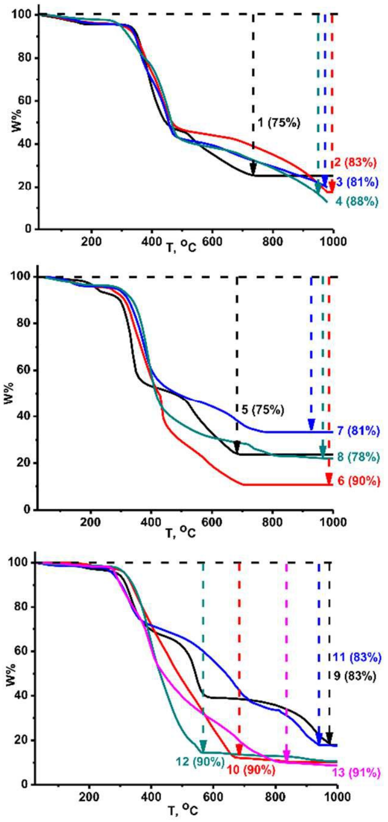


Fig. 10 TGA curve of **1**–**4** (top) and **5**–**8**(bottom) from 30 to 900 °C under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. **1** residual wt 25%, calc. wt 18%; **2** residual wt 17%, calc. wt 18%; **3** residual wt 19%, calc. wt 19%, **4** residual wt 12%, calc. wt 16%. **5** residual wt 25%, calc. wt 26%; **6** residual wt 10%, calc. wt 16%; **7** residual wt 19%, calc. wt 30%, **8** residual wt 22%, calc. wt 30%, **9** residual wt 17%, calc. wt 15%. **10** residual wt 10%, calc. wt 13%; **11** residual wt 17%, calc. wt 21%; **12** residual wt 10%, calc. wt 14% and **13** residual wt 9%, calc. wt 12%.

UV-vis solid and solution state absorption study

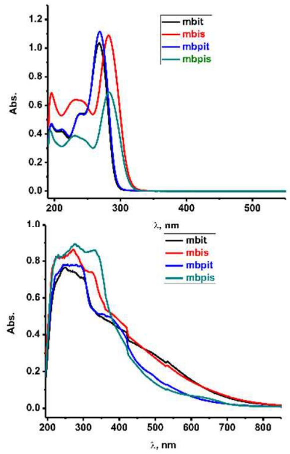


Fig. 11 Top: Solution state UV-vis spectra of organo dichalcogenones in acetonitrile at 25 °C (1.38 x 10^{-5} M). Bottom: Solid state UV-vis spectra of organo dichalcogenones.

The solution state UV-vis absorption spectra of organo dichalcogenones and their corresponding complexes **1**–**13** were studied (Fig. 11 (Top) and Fig. 12) at ambient temperature. In solution state UV-vis absorption spectra of **mbit**, **mbis**, **mbpit** and **mbpis**, and **1**–**13** showed nearly the comparable absorption patterns for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (200-320 nm). The absorption bands observed around 340–550 nm can be attributed to the ligand to metal charge transitions, which further supports the complex stability in solution.

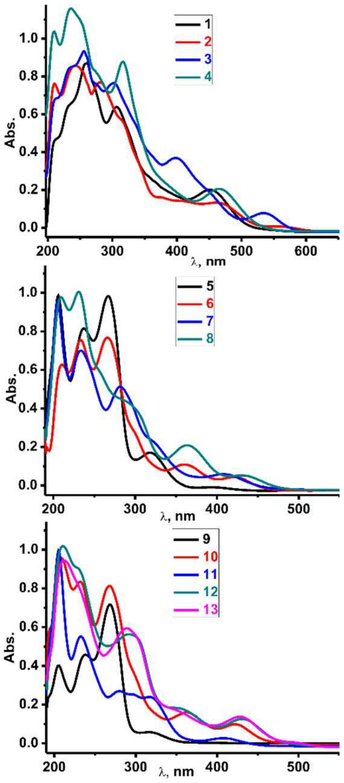
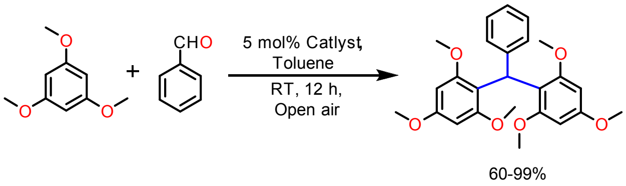


Fig. 12 Solution state UV-vis spectra of complexes **1**-**13** in acetonitrile at 25 °C (1.38×10^{-5} M).

The solid state UV-vis absorption spectra of ligands shows the broad absorption signals in contrast to the solution UV-vis spectra for π→π* and n→π* transitions (Fig. 11, Bottom). Complexes **1**-**13** showed the broad absorption band in their solid state UV-vis spectra. The molecule **1** shows high intense broad spectrum compared to other mono nuclear complexes **1**-**4**. Among **5**-**8, 5** showed the distinct signals in solid UV-vis spectra compared to **6**-**8**. In the case of complexes **9**-**13**, the broad spectra was observed with variable intensities (See Supporting Information, Fig. S44).

Catalysts 1-13 promoted triaryl and tryheteroaryl methane synthesis

The synthetic methodologies to isolate the symmetrical triaryl- or triheteroarylmethane scaffolds have attracted much attention in medicinal organic chemistry.[15] The formerly reported methods for this synthesis are mostly multi-step processes and involves synthetically challenging conditions.[21] More recently, these triaryl- or triheteroarylmethanes were isolated as by-products from electron-rich arenes with carbamates mediated by $Bi(OTf)_3$.[22] However, the straight forward synthetic routes for the isolation of these symmetrical triaryl- or triheteroarylmethanes are rare.[23,24] In particular, the NHC or imidazole chalcogenone supported bismuth catalysts for the synthesis of triaryl- or triheteroarylmethanes are not reported yet. Thus, molecules **1**–**13** are used as catalysts for the synthesis of symmetrical triaryl- or triheteroarylmethanes under very mild conditions (Scheme 5, Table 1). In a pilot experiment, 1,3,5-trimethoxy benzene was treated with benzaldehyde in the presence of newly isolated catalysts **1**-**13** (5 mol% based on the aldehyde) in toluene (Scheme 5, Table 1) under ambient condition. The target compound 2,2'-(phenylmethylene)bis(1,3,5-trimethoxybenzene) was isolated in 60-99% yield. The catalysts **1**-**13** are active towards the synthesis of triaryl- or triarylmethanes. Besides, this reaction is established in very mild reaction conditions for the triarylmethane synthesis with considerable yield compared to literature.[23,24] Catalyst **1** depicted the excellent activity with >99% starting material conversion within 12 h (entry 1). Notably, the bismuth(III) triflate catalysts **1**-**4** showed very good conversion and yield (entry 1-4), compared to bismuth(III) halides (entry 5-12). In contrast, the tetra nuclear catalyst **13** gave appreciable conversion and yield (entry 13). This may be due to the presence of more numbers of Lewis acidic centres. In order to understand the role of ancillary ligand, the catalytic reaction was performed using only **mbit** (entry 18), $Bi(OTf)_3$ (entry 14), $BiCl_3$ (entry 15) and $BiBr_3$ (entry 16). As expected, no catalytic reaction was noticed in the presence of **mbit** (entry 18). The poor yield was obtained in the case of $BiCl_3$ (entry 15) and $BiBr_3$ (entry 16), while slightly better yield was observed with $Bi(OTf)_3$ (entry 14). However, the conversion and yield were less than the catalyst **1**. Interestingly, the yield is nearly comparable with bismuth(III) halide complexes (**5**-**12**) when the same experiment was performed with *in-situ* generated catalyst (entry 17).



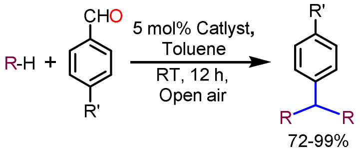
Scheme 5 Synthesis of triarylmethanes by bismuth(III) complexes.

Table 1 Synthesis of triarylmethane using **1**-**13**[a]

E	Catalyst	SMC[b] (%)	Y[c] (%)
1	**1**	>99	98
2	**2**	78	73
3	**3**	74	70
4	**4**	80	78
5	**5**	68	62
6	**6**	72	64
7	**7**	69	65
8	**8**	70	63
9	**9**	68	64
10	**10**	72	68
11	**11**	65	60
12	**12**	72	68
13	**13**	82	80
14	$Bi(OTf)_3$	58	52
15	$BiCl_3$	46	42
16	$BiBr_3$	48	46
17	$Bi(OTf)_3$ and **mbit**	64	61
18	**Mbit**	ND	ND

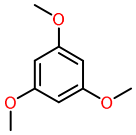
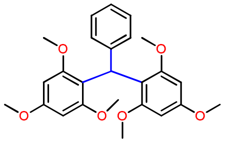
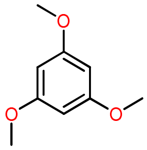
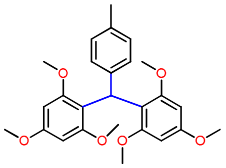
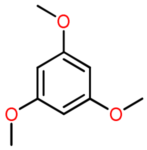
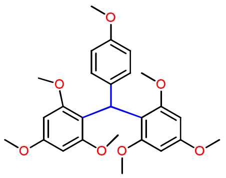
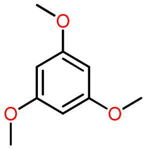
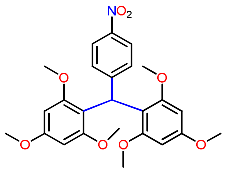
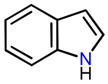
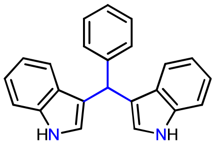
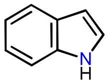
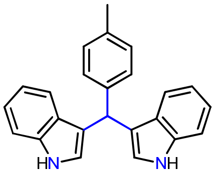
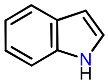
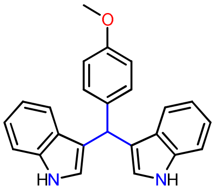
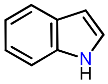
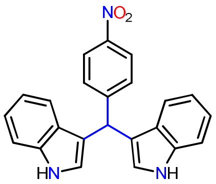
[a]Reaction conditions: 0.10 mmol 1,3,5-trimethoxy benzene, 0.05 mmol benzaldehyde, 5 mol% bismuth (III) catalyst and 1 mL of toluene were used at room temperature for 12 h. E – entry, [b]% based on ^{1}H NMR spectroscopy. [c]% isolated yield by column chromatography, ND–not detected, SMC–starting material conversion and Y–yield.

The efficiency of catalyst **1** can be attributed to the strong Lewis acidic nature of metal centres, in which the metal coordinated to the poor σ-donor and strong π accepting **mbit** ligand with triflate counter ion. Subsequently, the substrate scope was analysed by using catalyst **1**. 1,3,5-trimethoxy benzene and indole were separately subjected to numerous aldehydes in the presence of catalyst **1** (Scheme 6, Table 2). The substitutional effect was observed when we utilize the electron withdrawing (entry 4 and 8, Table 2) as well as electron donating substituents at various positions (entry 2, 3, 6 and 7) of aryl aldehydes. 4-Nitro benzaldehyde produces higher yields than 4-methyl and 4-methoxy substituted benzaldehydes (entry 2, 3, 6 and 7) with both 1,3,5-trimethoxy benzene and indole. This may be due to the existence of high electrophilicity at the aldehyde centre in nitro substituted benzaldehyde.



Scheme 6 Synthesis of triaryl- or triheteroarylmethanes by catalyst **1**[a]. [a]Reaction conditions: 0.10 mmol electron rich arene, 0.05 mmol aromaticaldehyde, 5 mol% bismuth (III) catalyst **1** and 1 mL of toluene were used at room temperature for a fixed time 12 h.

Table 2 Evaluation of scope of catalyst **1**.[a]

E	R	R'	Product	Y (%)[b]
1		H		99
2		Methyl		80
3		Methoxy		72
4		Nitro		88
5		H		80
6		Methyl		78
7		Methoxy		74
8		Nitro		85

[a]Reaction conditions: 0.10 mmol arene, 0.05 mmol aromaticaldehyde, 5 mol% bismuth (III) catalyst **1** and 1 mL of toluene were used at room temperature for a fixed time 12 h, [b]% isolated yield by column chromatography, E – entry.

The solid state structures of 2,2'-((4-nitrophenyl)methylene)bis(1,3,5-trimethoxybenzene) and 3,3'-((4-nitrophenyl)methylene)bis(1*H*-indole) have been additionally elucidated unambiguously by single crystal X-ray diffraction analysis (Fig. 13). Colourless crystals of 2,2'-((4-nitrophenyl)methylene)bis(1,3,5-trimethoxybenzene) were obtained at ambient temperature from its saturated chloroform solution, while brown coloured crystals were obtained for 3,3'-((4-nitrophenyl)methylene)bis(1*H*-indole) under the same set of crystallization conditions. The former molecule has been crystallized in triclinic space group, $P\bar{1}$, while the later has been crystallized in monoclinic space group, *I2/a*.

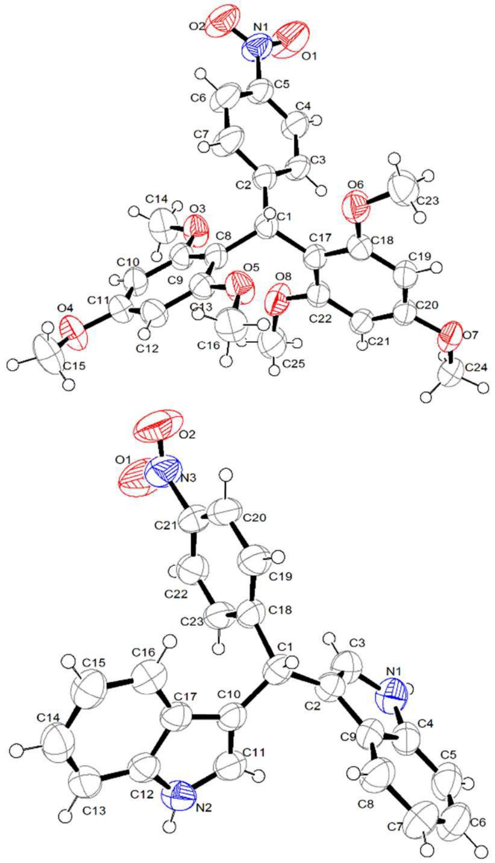


Fig. 13 Top: Solid state structure of 2,2'-((4-nitrophenyl)methylene)bis(1,3,5-trimethoxybenzene). Solvent *n*-hexane molecule has been omitted for clarity. Bottom: 3,3'-((4-nitrophenyl)methylene)bis(1*H*-indole). New C–C bonds and nitro group have been labelled for clarity. Crystallographic data of these molecules have been furnished in supporting information Table S2.

Experimental

Materials

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were purchased from commercial sources and purified according to standard procedures and freshly distilled under an argon atmosphere prior to use.[25] Unless otherwise stated, the chemicals were purchased from commercial sources. 3,3'-methylenebis(1-methyl-1*H*-imidazole-2(3*H*)-thione (**mbit**), 3,3'-methylenebis(1-methyl-1*H*-imidazole-2(3*H*)-selone (**mbis**), 3,3'-methylenebis(1-isopropyl-1*H*-imidazole-2(3*H*)-thione (**mbpit**) and 3,3'-methylenebis(1-isopropyl-1*H*-imidazole-2(3*H*)-selone (**mbpis**) ligands were synthesized as reported.[16] Sulphur powder, Selenium powder, $BiCl_3$, $BiBr_3$ and $Bi(OTf)_3$ were purchased from Sigma Aldrich and used as received.

Instrumentation

FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV-vis spectra were recorded on a T90+ UV-visible spectrophotometer. Thermogravimetric analysis (TGA) was performed using a TASDT Q600, Tzero-press. Elemental analyses were performed by the Euro Vector EA-300 elemental analyser. The matching EA data was not observed in the case of compounds **1**-**4** due to the presence of fluorine in the compounds. Similarly, a minor variation in the found elemental analysis value was reported compared to the calculated elemental analysis value for **9**-**13** due the presence of solvent in the lattice. The 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. The crystal structures of **1–13** were analysed on an Oxford Xcalibur 2 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 a low temperature (150 K) (except for **5**-**12**, 2,2'-((4-nitrophenyl)methylene)bis(1,3,5-trimethoxybenzene) and 3,3'-((4-nitrophenyl)methylene)bis(1*H*-indole); measured at 293 K) in inert oil under an argon atmosphere. Using Olex2,[26] the structures were solved with the ShelXS[27] 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 the calculated positions riding on their carrier atoms. No restraint was imposed on any of the compounds. Molecules **9**-**13** were crystallized (Fig. 7-9) along with one acetonitrile solvent molecule, in which three methyl protons were not fixed due to disorderness. However the data quality is good enough to show the coordination mode of metal centre. Similarly, the molecules **7** (Final R indexes [all data] R_1 = 0.2094, wR_2 = 0.5458) and **8** (Final R indexes [all data] R_1 = 0.2597, wR_2 = 0.6719) gave poor data set due to the absence of diffraction above 85° in 2Theta for **7** and high-angle reflections as well as a beta angle of about 140 degrees for **8**. Therefore, **7** and **8** were not submitted to CSD (Fig. 6). The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)2 + bP]$), where $P = (\max(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R_1 and wR_2 were $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$, respectively. CCDC 1440442-1440447 (for structures **1**-**6**) and 1440450-1440456 (for structures **9**-**13**) contains the supplementary crystallographic data for this paper. 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.

Synthesis of $[(\mathbf{mbit})_3Bi](OTf)[Bi_6(OTf)_{12}(\mu_3\text{-}OH)_8]$ (1)

Bismuth(III) triflate (0.13 g, 0.19 mmol) was added to a stirred solution of **mbit** (0.05 g, 0.19 mmol) in toluene (1 mL) under argon atmosphere at ambient temperature.

Subsequently, the reaction mixture was stirred at 100 °C for 24 h. The reaction mixture was filtered, the orange precipitate was collected, re-dissolved in methanol and acetonitrile mixture to result the deep red crystals of **1** at ambient temperature after 2-3 days. Yield: 83% (Based on $Bi(OTf)_3$). M.p., 245-247 °C (decomposed). ^1H NMR (DMSO, 400 MHz): δ 7.38 (d, 6H, Im*H*), 7.11-7.10 (d, 6H, Im*H*), 6.12 (s, 6H, NC*H*$_2$), 3.45 (s, 18H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 162.60 (*C*=S), 118.71 (Im-*C*H), 117.58 (Im-*C*H), 55.98 (N-*C*H$_2$), , 34.46 (*C*H$_3$) ppm. ^{19}F NMR (DMSO, 400 MHz): δ -77.73 (*C*F$_3$) ppm. FT-IR (neat, $\bar{\upsilon}$): 3131(w), 1574(m), 1474(w), 1395(m) (S=O), 1287(s), 1224(s), 1168(s) (C=S), 1098(w), 1020(s), 758(m), 704(w), 669(w), 631(s), 572(s), 515(m) cm^{-1}.

Synthesis of $[(mbis)_2(OTf)_2Bi](OTf).2CH_3OH$ (2)

2 was prepared as described for **1** using **mbis** (0.05 g, 0.14 mmol) and bismuth(III) triflate (0.09 g, 0.14 mmol) in toluene (2 mL). Yield: 86% (Based on $Bi(OTf)_3$). M.p., 198-200 °C (decomposed). ^1H NMR (DMSO, 400 MHz): δ 7.79-7.78 (d, 4H, Im*H*), 7.36-7.35 (d, 4H, Im*H*), 6.36 (s, 4H, NC*H*$_2$), 4.11 (br, 2H, O*H*), 3.58 (s, 6H, C*H*$_3$OH), 3.18 (s, 12H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 156.02 (*C*=Se), 121.09 (Im-*C*H), 119.83 (Im-*C*H), 59.05 (N-*C*H2), 48.56 (*C*H$_3$-OH), 36.52 (*C*H3) ppm. ^{19}F NMR (DMSO, 400 MHz): δ -77.77 (*C*F$_3$) ppm. FT-IR (neat, $\bar{\upsilon}$): 3119(m), 1629(m), 1573(m), 1478(m), 1383(m) (S=O), 1216(s), 1162(s) (C=Se), 1016(s), 751(s), 697(w), 628(s), 571(s), 515(m) cm^{-1}.

Synthesis of $[(mbpit)_2(OTf)_2Bi](OTf)$ (3)

3 was prepared as described for **1** using **mbpit** (0.05 g, 0.16 mmol) and bismuth(III) triflate (0.11 g, 0.16 mmol) in toluene (2 mL). Yield: 85% (Based on $Bi(OTf)_3$). M.p., 268-270 °C (decomposed). ^1H NMR (DMSO, 400 MHz): δ 7.46-7.45 (d, 4H, Im*H*), 7.26 (d, 4H, Im*H*), 6.18 (s, 4H, NC*H*$_2$), 4.88-4.78 (m, 4H, NC*H*$_2$), 1.28-1.27 (d, 24H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 161.41 (*C*=S), 118.38 (Im-*C*H), 114.22 (Im-*C*H), 55.39 (N-*C*H$_2$), 48.51 (N-*C*H), 21.07 (*C*H$_3$) ppm. ^{19}F NMR (DMSO, 400 MHz): δ -77.75 (*C*F$_3$) ppm. FT-IR (neat, $\bar{\upsilon}$): 3161(w), 3129(w), 3102(w), 1642(w), 1567(m), 1448(m), 1412(m), 1378(m) (S=O), 1292(m), 1222(s), 1201(s), 1167(s) (C=S), 1086(m), 1015(s), 882(w), 759(s), 687(m), 632(s), 575(s), 518(m) cm^{-1}.

Synthesis of $[(mbpis)_2(OTf)_2Bi](OTf)$ (4)

4 was prepared as described for **1** using **mbpis** (0.05 g, 0.12 mmol) and bismuth(III) triflate (0.08 g, 0.12 mmol) in toluene (2 mL). Yield: 81% (Based on $Bi(OTf)_3$). M.p., 189-191 °C (decomposed). ^1H NMR (DMSO, 400 MHz): δ 7.87 (d, 4H, Im*H*), 7.51-7.50 (d, 4H, Im*H*), 6.42 (s, 4H, NC*H*$_2$), 5.02-4.92 (m, 4H, NC*H*), 1.33-1.31 (d, 24H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 155.07 (*C*=Se), 120.62 (Im-*C*H), 116.55 (Im-*C*H), 58.33 (N-*C*H$_2$), 50.84 (N-*C*H), 21.20 (*C*H$_3$) ppm. ^{19}F NMR (DMSO, 400 MHz): δ -77.76 (*C*F$_3$) ppm. FT-IR (neat, $\bar{\upsilon}$): 3105(m), 2984(w), 1623(w), 1566(m), 1464(m), 1407(m), 1376(m) (S=O), 1219(s), 1160(s) (C=Se), 1080(w), 1020(s), 881(w), 757(m), 737(m), 678(w), 631(s), 571(s), 514(m) cm^{-1}.

Synthesis of $[(mbit)_2BiCl_2][($*mbit*$)BiCl_4]$ (5)

To a stirred solution of **mbit** (0.05 g, 0.19 mmol) in toluene (1 mL), bismuth(III) chloride (0.06 g, 0.19 mmol) was added at ambient temperature. The reaction mixture was stirred at 75 °C for 30 h. The reaction mixture was filtered, the orange precipitate was collected then dissolved in hot acetonitrile to isolate the deep red crystals of **5** at ambient temperature after 2-3 days. Yield: 78% (Based on $BiCl_3$). M.p., 212-214 °C (decomposed). Elemental Analysis for $C_{27}H_{36}Bi_2Cl_6N_{12}S_6$ (1351.72): Calcd. C, 23.99; H, 2.68; N, 12.43; Found: C, 24.1; H, 2.8; N, 12.4. ^1H NMR (DMSO, 400 MHz): δ 7.41-7.40 (d, 6H, Im*H*), 7.12-7.11 (d, 6H, Im*H*), 6.14 (s, 6H, NC*H*$_2$), 3.66 (s, 18H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 162.61 (*C*=S), 118.72 (Im-*C*H), 117.64 (Im-*C*H), 56.01 (N-*C*H$_2$), 34.51 (*C*H$_3$) ppm. FT-IR (neat, υ): 3123(m), 2990(w), 2943(w), 1603(m), 1568(s), 1466(s), 1433(w), 1393(s), 1319(m), 1230(s), 1222(s), 1162(s) (C=S), 1088(m), 1046(w), 1018(m), 966(w), 819(w), 753(s), 734(s), 702(s), 765(s) cm^{-1}.

Synthesis of $[(mbit)Bi(Br)_2(\mu_2\text{-}Br)]_2$ (6)

6 was prepared as described for **5** using **mbit** (0.05 g, 0.19 mmol) and bismuth(III) bromide (0.09 g, 0.19 mmol) in toluene (2 mL). Elemental Analysis for $C_{18}H_{24}Bi_2Br_6N_8S_4$ (1378.08): Calcd. C, 15.69; H, 1.76; N, 8.13; Found: C, 15.5; H, 1.7; N, 8.1. Yield: 82% (Based on $BiBr_3$). M.p., 206-208 °C (decomposed). ^1H NMR (DMSO, 400 MHz): δ 7.44 (d, 4H, Im*H*), 7.17 (d, 4H, Im*H*), 6.18 (s, 4H, NC*H*$_2$), 3.55 (s, 12H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 161.18 (*C*=S), 119.25 (Im-*C*H), 118.01 (Im-*C*H), 56.23 (N-*C*H$_2$), 34.68 (*C*H$_3$) ppm. FT-IR (neat, $\bar{\upsilon}$): 3155(w), 3092(w), 3007(w), 1566(s), 1465(s), 14276(m), 1391(s), 1328(w), 1228(s), 1206(s), 1166(s) (C=S), 1089(m), 1065(w), 1044(m), 1018(w), 967(w), 825(w), 776(s), 753(s), 732(s), 701(s), 664(s), 608(w), 582(w) cm^{-1}.

Synthesis of $[(mbis)Bi(Cl)_2(\mu_2\text{-}Cl)]_2$ (7)

7 was prepared as described for **5** using **mbis** (0.05 g, 0.14 mmol) and bismuth(III) chloride (0.05 g, 0.14 mmol) in toluene (2 mL). Yield: 75% (Based on $BiCl_3$). M.p., 228-230 °C (decomposed). Elemental Analysis for $C_{18}H_{24}Bi_2Cl_6N_8Se_4$ (1298.95): Calcd. C, 16.64; H, 1.86; N, 8.63; Found: C, 16.5; H, 1.9; N, 8.6. ^1H NMR (DMSO, 400 MHz): δ 7.79 (d, 4H, Im*H*), 7.38-7.37 (d, 4H, Im*H*), 6.36 (s, 4H, NC*H*$_2$), 3.58 (s, 12H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 155.83 (*C*=Se), 121.20 (Im-*C*H), 119.91 (Im-*C*H), 59.08 (N-*C*H$_2$), 36.59 (*C*H$_3$) ppm. FT-IR (neat, $\bar{\upsilon}$): 3156(w), 3110(m), 2948(w), 1632(s), 1568(s), 1471(s), 1392(s), 1318(m), 1228(s), 1198(m) (C=Se), 1141(s), 1091(m), 1021(w), 752(s), 697(m), 656(m), 545(m) cm^{-1}.

Synthesis of $[(mbis)Bi(Br)_2(\mu_2\text{-}Br)]_2$ (8)

8 was prepared as described for **5** using **mbis** (0.05 g, 0.14 mmol) and bismuth(III) bromide (0.06 g, 0.14 mmol) in toluene (2 mL). Yield: 77% (Based on $BiBr_3$). M.p., 210-211 °C (decomposed). Elemental Analysis for $C_{18}H_{24}Bi_2Br_6N_8Se_4$ (1565.66): Calcd. C, 13.81; H, 1.55; N, 7.16; Found: C, 13.8; H, 1.6; N, 7.0. ^1H NMR (DMSO, 400 MHz): δ 7.81-7.80 (d, 4H, Im*H*), 7.40 (d, 4H, Im*H*), 6.39 (s, 4H, NC*H*$_2$), 3.60 (s, 12H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 155.16 (*C*=Se), 121.41 (Im-*C*H), 120.07 (Im-*C*H), 59.19 (N-*C*H$_2$), 36.67 (*C*H$_3$) ppm. FT-IR (neat, $\bar{\upsilon}$): 3156(w), 3108(m), 1599(m), 1567(s), 1470(s), 1432(w), 1389(m), 1317(m), 1226(s), 1196(s) (C=Se), 1139(s), 1089(m), 1067(w), 1041(w), 1019(w), 741(s), 697(m), 650(m), 605(w) cm^{-1}.

Synthesis of [(mbpit)Bi(Cl)$_2$(μ_2-Cl)]$_2$.CH$_3$CN (9)

9 was prepared as described for **5** using **mbpit** (0.05 g, 0.16 mmol) and bismuth(III) chloride (0.05 g, 0.16 mmol) in toluene (2 mL). Yield: 72% (Based on BiCl$_3$). M.p., 238-240 °C (decomposed). Elemental Analysis for $C_{28}H_{43}Bi_2Cl_6N_9S_4$ (1264.64): Calcd. C, 26.59; H, 3.43; N, 9.97; Found: C, 26.5; H, 3.3; N, 9.8. ^{1}H NMR (DMSO, 400 MHz): δ 7.48-7.47 (d, 4H, Im*H*), 7.25-7.24 (d, 4H, Im*H*), 6.20 (s, 4H, NC*H*$_2$), 4.90-4.80 (m, 4H, NC*H*), 2.07 (s, 3H, C*H*$_3$CN), 1.29-1.28 (d, 24H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 160.36 (*C*=S), 117.31 (Im-*C*H), 116.87 (Im-*C*H), 113.03 (*C*N), 54.27 (N-*C*H$_2$), 47.41 (N-*C*H), 19.95 (*C*H$_3$), 0.00 (*C*H$_3$CN) ppm. FT-IR (neat, $\bar{\upsilon}$): 3191(m), 2976(m), 1567(s), 1458(s), 1413(s), 1374(s), 1350(m), 1306(m), 1229(s), 1212(s), 1190(s) (C=S), 1136(m), 1082(m), 1008(w), 882(w), 778(m), 744(s), 681(m), 547(w) cm^{-1}.

Synthesis of [(mbpit)Bi(Br)$_2$(μ_2-Br)]$_2$.CH$_3$CN (10)

10 was prepared as described for **5** using **mbpit** (0.05 g, 0.16 mmol) and bismuth(III) bromide (0.07 g, 0.16 mmol) in toluene (2 mL). Yield: 74% (Based on BiBr$_3$). M.p., 218-219 °C (decomposed). Elemental Analysis for $C_{28}H_{43}Bi_2Br_6N_9S_4$ (1531.34): Calcd. C, 21.96; H, 2.83; N, 8.23; Found: C, 21.8; H, 2.8; N, 8.1. ^{1}H NMR (DMSO, 400 MHz): δ 7.48 (d, 4H, Im*H*), 7.25 (d, 4H, Im*H*), 6.20 (s, 4H, NC*H*$_2$), 4.90-4.80 (m, 4H, NC*H*), 2.07 (s, 3H, C*H*$_3$CN), 1.29-1.28 (d, 24H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 160.28 (*C*=S), 117.31 (Im-*C*H), 116.84 (Im-*C*H), 113.05 (*C*N), 54.28 (N-*C*H$_2$), 47.41 (N-*C*H), 19.94 (*C*H$_3$), 0.00 (*C*H$_3$CN) ppm. FT-IR (neat, $\bar{\upsilon}$): 3157(m), 3094(m), 2978(m), 2874(w), 1564(s), 1491(w), 1459(m), 1441(w), 1413(s), 1374(s), 1349(m), 1307(m), 1229(m), 1211(m), 1191(s) (C=S), 1135(m), 1082(m), 1009(w), 956(w), 882(w), 779(m), 735(s), 702(s), 681(s), 636(m), 570(w), 520(m) cm^{-1}.

Synthesis of [(mbpis)Bi(Cl)$_2$(μ_2-Cl)]$_2$.CH$_3$CN (11)

11 was prepared as described for **5** using **mbpis** (0.05 g, 0.12 mmol) and bismuth(III) chloride (0.04 g, 0.12 mmol) in toluene (2 mL). Yield: 78% (Based on BiCl$_3$). M.p., 208-209 °C (decomposed). Elemental Analysis for $C_{28}H_{43}Bi_2Cl_6N_9Se_4$ (1452.22): Calcd. C, 23.16; H, 2.98; N, 8.68; Found: C, 23.0; H, 2.8; N, 8.5. ^{1}H NMR (DMSO, 400 MHz): δ 7.87 (d, 4H, Im*H*), 7.49 (d, 4H, Im*H*), 6.42 (s, 4H, NC*H*$_2$), 5.02-4.92 (m, 4H, NC*H*), 2.08 (s, 3H, C*H*$_3$CN), 1.33-1.31 (d, 24H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 154.07 (*C*=Se), 119.41 (Im-*C*H), 116.81 (Im-*C*H), 115.29 (*C*N), 57.11 (N-*C*H$_2$), 49.63 (N-*C*H), 20.01 (*C*H$_3$), 0.00 (*C*H$_3$CN) ppm. FT-IR (neat,$\bar{\upsilon}$): 3094(m), 2974(w), 2931(w), 1594(m), 1562(s), 1441(s), 1405(s), 1369(s), 1291(m), 1208(s), 1181(s) (C=Se), 1131(m), 1073(m), 1008(w), 881(w), 776(w), 731(s), 672(s), 618(m), 521(m) cm^{-1}.

Synthesis of [(mbpis)Bi(Br)$_2$(μ_2-Br)]$_2$.CH$_3$CN (12)

12 was prepared as described for **5** using **mbpis** (0.05 g, 0.12 mmol) and bismuth(III) bromide (0.06 g, 0.12 mmol) in toluene (2 mL). Yield: 87% (Based on BiBr$_3$). M.p., 220-222 °C (decomposed). Elemental Analysis for $C_{28}H_{43}Bi_2Br_6N_9Se_4$ (1718.92): Calcd. C, 19.56; H, 2.52; N, 7.33; Found: C, 19.4; H, 2.5; N, 7.2. ^{1}H NMR (DMSO, 400 MHz): δ 7.89-7.88 (d, 4H, Im*H*), 7.59-7.58 (d, 4H, Im*H*), 6.45 (s, 4H, NC*H*$_2$), 5.00-4.90 (m, 4H, NC*H*), 2.08 (s, 3H, C*H*$_3$CN), 1.34-1.32 (d, 24H, CH$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 152.06 (*C*=Se), 119.92 (Im-*C*H), 116.77 (Im-*C*H), 115.88 (*C*N), 57.45 (N-*C*H$_2$), 49.97 (N-*C*H), 20.00 (*C*H$_3$), 0.00 (*C*H$_3$CN) ppm. FT-IR (neat, $\bar{\upsilon}$): 3085(m), 2975(w), 1564(s), 1459(s), 1408(s), 1371(s), 1346(m), 1308(m), 1225(m), 1206(s), 1183(m) (C=Se), 1137(w), 1076(m), 1006(w), 879(m), 737(s), 673(m), 628(m), 538(m) cm^{-1}.

Synthesis of [(mbpis)Bi$_2$(Br)$_3$(μ_2-Br$_2$)(μ_3-Br)]$_2$.CH$_3$CN (13)

13 was prepared as described for **5** using **mbpis** (0.05 g, 0.12 mmol) and bismuth(III) bromide (0.07 g, 0.15 mmol) in toluene (2 mL). Yield: 70% (Based on BiBr$_3$). M.p., 228-229 °C (decomposed). Elemental Analysis for $C_{28}H_{43}Bi_4Br_{12}N_9Se_4$ (2616.31): Calcd. C, 12.85; H, 1.66; N, 4.82; Found: C, 12.7; H, 1.6; N, 4.7. ^{1}H NMR (DMSO, 400 MHz): δ 7.93-7.92 (d, 4H, Im*H*), 7.64 (d, 4H, Im*H*), 6.52 (s, 4H, NC*H*$_2$), 5.02-4.92 (m, 4H, NC*H*$_2$), 2.08 (s, 3H, C*H*$_3$CN), 1.36-1.34 (d, 24H, C*H*$_3$) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 150.51 (*C*=Se), 120.27 (Im-*C*H), 116.77 (Im-*C*H), 116.38 (*C*N), 57.70 (N-*C*H$_2$), 50.21 (N-*C*H), 20.12 (*C*H$_3$), 0.00 (*C*H$_3$CN) ppm. FT-IR (neat, $\bar{\upsilon}$): 3087(m), 2976(m), 1564(s), 1459(s), 1408(s), 1370(s), 1346(m), 1308(m), 1225(s), 1205(s), 1183(s) (C=Se), 1136(w), 1119(w), 1076(m), 1044(w), 1008(w), 954(w), 881(m), 738(s), 674(s), 626(m), 543(m) cm^{-1}.

Catalysts 1-13 promoted triaryl- or tryheteroaryl methanes synthesis

The newly synthesized bismuth(III) catalysts (**1**-**13**) were used for the synthesis of triaryl and tryheteroaryl methanes under very mild conditions. Bismuth(III) complex (0.05 mmol) was taken in a test tube along with arene or heteroarene (0.10 mmol) in toluene (0.50 mL) under ambient condition. Subsequently, the mixture was stirred at room temperature for 2-3 min. Aldehyde (0.05 mmol) was added. Test tube wall was washed with toluene (0.50 mL) then allowed to stir at room temperature (Scheme 5 and 6). The progress of reaction was continuously monitored by TLC. After completion of the reaction, the crude mixture was purified by silica gel column chromatography to produce an expected product (eluent: gradient mixture of EtOAc/petroleum ether). The disappearance characteristic signals of starting materials and the appearance of characteristic peaks of products were conveniently surveyed by ^{1}H NMR spectroscopy. The spectral data obtained for the isolated products are in excellent agreement with the reported data.

Conclusions

In conclusion, we have successfully isolated thirteen new structurally interesting bismuth(III) chancogenone complexes by treating bismuth(III) triflate/halides with organo dichalcogenone ligands (**mbit**, **mbis**, **mbpit** and **mbpis**). Some of these molecules are rare in the literature with new structural topologies and versatile coordination modes. The bismuth(III) centre in **1**-**13** adopt the distorted octahedral geometry with bidentate chalcogenone ligands. Besides, the catalytic properties of **1**-**13** were tested for multiple C–C bond formation reactions. Catalysts **1**-**13** were very active towards coupling of electron rich arenes with substituted aldehydes to yield triaryl- or triheteroaryl methanes in excellent yield. The catalytic strength of **1**-**13** is almost comparable. However, (i) the mononuclear complex **1** displays the best catalytic activity, (ii) bismuth(III) triflate complexes (**1**-**4**) were highly efficient than bismuth(III) halide complexes (**5**-**12**), (iii) the catalytic activity of tetra nuclear bismuth(III) bromide complex (**13**) is comparable with triflate complexes (**1**-**4**). This may be due to the presence of strong Lewis acidic centres, (iv) catalyst **1** showed a wide range of functional group tolerance, and (v) the selone–bismuth complexes displayed the better activity than thione analogues. The better catalytic activity of mononuclear complex **1** compared to **2**-**13**, can be attributed to the presence of co-ordinately unsaturated bismuth(III) centres in **1**. Besides, the investigation towards most efficient stereospecific catalysts under similar strategy is in progress.

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Thirteen new bismuth(III) dichalcogenone derivatives with diversified structural motifs were successfully isolated and used as potential catalysts for the synthesis of triaryl- or triheteroarylmethanes.