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Linear Cu(I) chalcogenones: synthesis and application in borylation of unsymmetrical alkynes†‡

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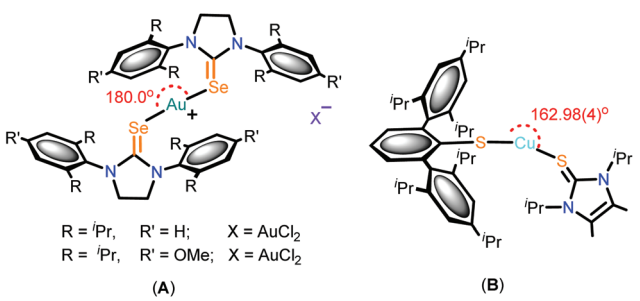
The syntheses and structures of copper(I) chalcogenone complexes are described. The homoleptic mononuclear copper(I) complexes $[(IPr{=}E)_2Cu]ClO_4$, IPr=E, 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-thione (**1**) and 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-selone (**2**); $[(IMes{=}E)_2Cu]ClO_4$, IMes=E, 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-thione (**3**) and 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-selone (**4**); $[(IPr{=}E)_2Cu]BF_4$, E = S (**5**); E = Se (**6**) and $[(IMes{=}E)_2Cu]BF_4$, E = S (**7**); E = Se (**8**) are formed from the reduction of copper(II) to copper(I) with the corresponding imidazoline-2-chalcogenones. X-ray structure analyses of seven compounds (**1–3** and **5–8**) show that the copper(I) ion is in a perfect linear coordination, while **4** is in *quasi*-linear geometry. Molecules **2**, **4**, **6** and **8** are the first structurally characterized homoleptic copper(I) selone complexes. The optical and thermal properties of imidazoline-2-chalcogenones and their copper(I) derivatives are investigated. These complexes are able to act as catalysts in regioselective borylation of numerous unsymmetrical alkynes, yielding synthetically useful vinylboronates. Among catalysts **1–8**, catalyst **4** is highly selective towards the regioselective boron addition of 1-phenyl-1-propyne.

Introduction

The focus on copper chalcogenide chemistry is experiencing continuous growth over the last few decades owing to their novel properties and significant applications.[1,2] The properties of copper chalcogenides are mainly controlled by the chalcogen sources. For example, recent work has also shown the active role of the decade old ligand system imidazoline-2-chalcogenones for this endeavor.[3–6] Notably, imidazoline-2-chalcogenone ligands have the potential to serve as ligands with copper in medicine.[3] Some other potential applications of this imidazoline-2-chalcogenone ligand supported copper include its use as a precursor for nanomaterial synthesis and as a co-ligand in catalysis. Recently shape and phase controlled copper-selenide nanoflakes were reported using 1-*n*-butyl-3-ethylimidazolium methylselenite and copper sulphate.[4] Besides, imidazoline-2-thione tethered copper catalysts were demonstrated for highly regioselective boron addition to internal alkynes.[5] This catalytic study represents the first and only report available to understand the role of imidazoline-2-chalcogenone in catalysis as a co-ligand. In this process the catalytic reactions were carried out using *in situ* generated catalysts. The isolation of the catalyst from the catalytic reaction mixture led to a tri coordinated copper imidazoline-2-thione complex with planar metal geometry. Although copper exists in a different coordination mode with imidazoline-2-chalcogenones,[2d,6] homoleptic two coordinated copper complexes of imidazoline-2-chalcogenones have not been reported. Recent efforts have revealed that it is possible to isolate two co-



Scheme 1 Known linear/quasi-linear homoleptic group 9-imidazoline-2-chalcogenone complexes.

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†In this paper "chalcogenones or heavier chalcogens" represent the molecules with "S and Se". Therefore "O and Te" (*i.e.* molecules with C=O–Cu and C=Te–Cu bond) should not be considered for the current discussion.

‡Electronic supplementary information (ESI) available: FT-IR, NMR and Tables S1 and S2 for **1–9**. CCDC 1407359–1407366. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02320c

ordinated homoleptic imidazoline-2-selone gold complexes $[(IPr{=}Se)_2Au][AuCl_2]$, 1,3-bis(2,6-diisopropyl-phenyl)-imidazoline-2-selone and $[(IPr^{OMe}{=}Se)_2Au][AuCl_2]$, IPr^{OMe} = 1,3-bis-(2,6-diisopropyl-4-methoxyphenyl)-imidazoline-2-selone, using more π accepting imidazoline-2-selone ligands (Scheme 1, **A**).[7] However, only one *quasi*-linear homoleptic copper imidazoline-2-chalcogenone complex is known (Scheme 1, **B**).[8] Molecule **B** has been isolated using a relatively less π accepting thione ligand.

However, these recent efforts have not answered the critical questions necessary to clearly realize the formation of linear dicoordinated coinage metal complexes involving imidazoline-2-chalcogenones. For example, do "homoleptic two coordinated" intermediates exist in the catalytic process? How essential is the "more π accepting imidazoline-2-selone" to isolate the homoleptic two coordinated coinage metal derivatives? In order to address these above challenges, we have isolated the homoleptic two coordinated copper imidazoline-2-thione/selone complexes using relatively less π accepting imidazoline-2-thiones/selones and studied their role in the regioselective borylation of alkynes.

Experimental

Materials and methods

All manipulations were carried out under an 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 an argon atmosphere prior to use.[9] Unless otherwise stated, the chemicals were purchased from commercial sources. IPrHCl, IPr=S, IPr=Se, IMesHCl, IMes=S, and IMes=Se were prepared as previously reported.[10] $Cu(ClO_4)_2{\cdot}6H_2O$ and $Cu(BF_4)_2$ hydrate were purchased from Sigma Aldrich and used as received. 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. 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 using the Euro EA-300 elemental analyzer. The crystal structures of **1–8** were analyzed 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 **1**, **3** and **5**, measured at 298 K) in inert oil under an argon atmosphere. Using Olex2,[11] the structure was solved with the ShelXS[12] 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. 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. Structures **1** and **5** contain solvent accessible voids of 143 Å^3 and 144 Å^3, respectively. These residual voids in the structure may be due to the disordered counter ion density. The counter ions in structures **1**, **2**, **5** and **6** are disordered. CCDC 1407359–1407366 contains the supplementary crystallographic data for this paper.

Caution

Perchlorate salts of metal salts and complexes are potentially explosive. Only small amounts of material should be prepared and handled with great care; particular caution must be exercised when they are dried under vacuum.

Synthesis of $[(IPr{=}S)_2Cu]ClO_4$ (1)

A mixture of IPr=S (0.100 g, 0.238 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.106 g, 0.286 mmol) in methanol (5 mL) was refluxed at 80 °C for 12 h. The clear reaction mixture was brought to room temperature to result in the colorless crystals of **1** in 2 days. Yield: 73% (based on $Cu(ClO_4)_2{\cdot}6H_2O$). M.p.: 258–260 °C (dec.). Elemental analysis calcd (%) for $C_{54}H_{72}ClCuN_4O_4S_2$ (1002.4): C, 64.58; H, 7.23; N, 5.58; Found: C, 64.08; H, 7.19; N, 5.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.34 (t, 2H, CH_{para}), 7.20–7.18 (d, 4H, CH_{meta}), 7.10 (s, 2H, ImH), 2.35–2.28 (sept, 4H, ^{i}PrCH), 1.16–1.15, 1.13–1.11 (d, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.07 (NCN), 145.63 (ImC), 131.66, 131.48, 124.99, 122.10 (ArC), 28.91 (^{i}PrCH), 24.16, 23.30 (CH_3) ppm. FT-IR (neat): $\bar{\nu}$ = 2933(s), 2839(m), 1554(w), 1458(s), 1424(m), 1379(s), 1334(m), 1214(m), 1180(w), 1094(s) (Cl–O), 981(s), 938(s), 803(s) cm^{-1}.

Synthesis of $[(IPr{=}Se)_2Cu]ClO_4$ (2)

2 was prepared in the same manner as described for **1** using IPr=Se (0.100 g, 0.213 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.095 g, 0.256 mmol) in methanol (5 mL). Yield: 70% (based on $Cu(ClO_4)_2{\cdot}6H_2O$). M.p.: 276–278 °C (dec.). Elemental analysis calcd (%) for $C_{54}H_{72}ClCuN_4O_4Se_2$ (1098.2): C, 59.06; H, 6.61; N, 5.10; Found: C, 58.56; H, 6.71; N, 5.08. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.39 (t, 2H, CH_{para}), 7.23–7.22 (d, 4H, CH_{meta}), 7.20 (s, 2H, ImH), 2.34–2.28 (sept, 4H, ^{i}PrCH), 1.20–1.19, 1.12–1.10 (d, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.21 (NCN), 145.50 (ImC), 132.44, 131.55, 124.98, 123.86 (ArC), 28.96 (^{i}PrCH), 24.24, 23.32 (CH_3) ppm. FT-IR (neat): $\bar{\nu}$ = 2961(s), 2871(m), 1519(w), 1454(s), 1351(s), 1324(m), 1214(m), 1182(w), 1076(s) (Cl–O), 967(s), 804(s), 750(s) cm^{-1}.

Synthesis of $[(IMes{=}S)_2Cu]ClO_4$ (3)

3 was prepared in the same manner as described for **1** using IMes=S (0.100 g, 0.297 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.132 g, 0.356 mmol) in methanol (5 mL). Yield: 74% (based on $Cu(ClO_4)_2{\cdot}6H_2O$). M.p.: 263–265 °C (dec.). Elemental analysis

calcd (%) for $C_{42}H_{48}ClCuN_4O_4S_2$ (834.2): C, 60.34; H, 5.79; N, 6.70; Found: C, 60.14; H, 5.87; N, 6.59. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 4H, Im*H*), 6.94 (s, 8H, CH_{meta}), 2.25 (s, 12H, CH_{3para}), 1.95 (s, 24H, CH_{3ortho}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.02 (*C*=S), 141.08, 134.95, 131.63, 130.10, 121.21 (Ar*C*), 21.10 (*p*-*C*H_3), 17.59 (*o*-*C*H_3) ppm. FT-IR (neat): $\bar{\nu}$ = 3169(w), 1607(m), 1554(w), 1481(s), 1442(m), 1374(s), 1232(m), 1095(s), 1072(s) (Cl–O), 925(w), 844(w), 735(s) cm^{-1}.

Synthesis of [(IMes=Se)$_2$Cu]ClO$_4$ (4)

4 was prepared in the same manner as described for **1** using IMes=Se (0.100 g, 0.260 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.116 g, 0.312 mmol) in methanol (5 mL). Yield: 67% (based on $Cu(ClO_4)_2{\cdot}6H_2O$). M.p.: 278–280 °C (dec.). Elemental analysis calcd (%) for $C_{42}H_{48}ClCuN_4O_4Se_2$ (930.0): C, 54.26; H, 5.20; N, 6.03; Found: C, 54.06; H, 5.18; N, 5.93. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 4H, Im*H*), 6.94 (s, 8H, CH_{meta}), 2.24 (s, 12H, CH_{3para}), 1.95 (s, 24H, CH_{3ortho}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.28 (*C*=S), 141.12, 134.81, 132.56, 130.09, 123.04 (Ar*C*), 21.23 (*p*-*C*H_3), 17.69 (*o*-*C*H_3) ppm. FT-IR (neat): $\bar{\nu}$ = 1602(m), 1549(w), 1480(s), 1443(m), 1363(s), 1230(m), 1038(s) (Cl–O), 926(w), 845(w), 735(s) cm^{-1}.

Synthesis of [(IPr=S)$_2$Cu]BF$_4$ (5)

5 was prepared in the same manner as described for **1** using IPr=S (0.100 g, 0.238 mmol) and $Cu(BF_4)_2$ (0.068 g, 0.286 mmol) in methanol (5 mL). Yield: 69% (based on $Cu(BF_4)_2$). M.p.: 296–298 °C (dec.). Elemental analysis calcd (%) for $C_{54}H_{72}BCuN_4F_4S_2$ (991.6): C, 65.40; H, 7.32; N, 5.65; Found: C, 64.86; H, 7.18; N, 5.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (t, 2H, CH_{para}), 7.33–7.32 (d, 4H, CH_{meta}), 7.21 (s, 2H, Im*H*), 2.65–2.55 (sept, 4H, ^{i}PrC*H*), 1.40–1.38, 1.20–1.18 (d, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.99 (*C*=S), 145.63, 131.62, 131.50, 124.97, 122.11 (Ar*C*),), 28.90 (^{i}Pr*C*H), 24.13, 23.30 (*C*H_3) ppm. ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$): δ = −0.98 ppm. ^{19}F{^{1}H} NMR (376.4 MHz, $CDCl_3$): δ = −154.30 ppm. FT-IR (neat): $\bar{\nu}$ = 3540(b), 2963(s), 1632(m), 1556(w), 1462(s), 1375(s), 1257(w), 1214(w), 1040(s) (B–F), 939(w), 802(m), 746(s), 693(s), 570(m) cm^{-1}.

Synthesis of [(IPr=Se)$_2$Cu]BF$_4$ (6)

6 was prepared in the same manner as described for **1** using IPr=Se (0.100 g, 0.213 mmol) and $Cu(BF_4)_2$ (0.060 g, 0.256 mmol) in methanol (5 mL). Yield: 77% (based on $Cu(BF_4)_2$). M.p.: 260–262 °C (dec.). Elemental analysis calcd (%) for $C_{54}H_{72}BCuN_4F_4Se_2$ (1085.4): C, 59.75; H, 6.69; N, 5.16; Found: C, 59.66; H, 6.72; N, 5.21. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.57 (t, 2H, CH_{para}), 7.38–7.36 (d, 4H, CH_{meta}), 7.14 (s, 2H, Im*H*), 2.56–2.46 (sept, 4H, ^{i}PrC*H*), 1.28–1.26, 1.15–1.14 (d, 24H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.21 (*C*=Se), 145.50, 132.44, 131.55, 124.99, 123.86 (Ar*C*),), 28.96 (^{i}Pr*C*H), 24.25, 23.32 (*C*H_3) ppm. ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$): δ = −0.99 ppm. ^{19}F{^{1}H} NMR (376.4 MHz, $CDCl_3$): δ = −154.14 ppm. FT-IR (neat): $\bar{\nu}$ = 3552(b), 2963(m), 1631(m), 1554(w), 1462(m), 1425(m), 1359(s), 1212(w), 1176(w), 1044(s) (B–F), 939(m), 803(s), 749(s), 689(m) cm^{-1}.

Synthesis of [(IMes=S)$_2$Cu]BF$_4$ (7)

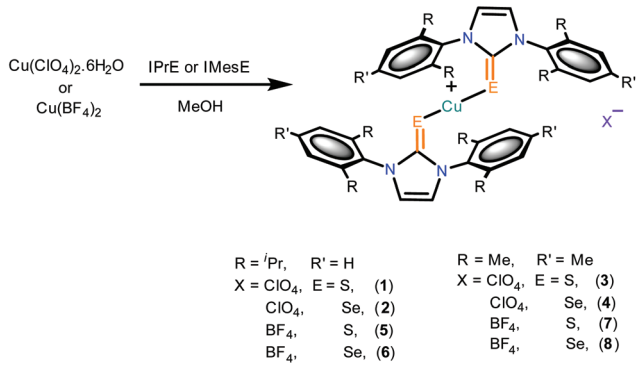
7 was prepared in the same manner as described for **1** using IMes=S (0.100 g, 0.297 mmol) and $Cu(BF_4)_2$ (0.085 g, 0.356 mmol) in methanol (5 mL). Yield: 75% (based on $Cu(BF_4)_2$). M.p.: 288–290 °C (dec.). Elemental analysis calcd (%) for $C_{42}H_{48}BCuN_4F_4S_2$ (823.3): C, 61.27; H, 5.88; N, 6.80; Found: C, 61.06; H, 5.18; N, 5.93. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (s, 4H, Im*H*), 6.94 (s, 8H, CH_{meta}), 2.28 (s, 12H, CH_{3para}), 1.94 (s, 24H, CH_{3ortho}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.94 (*C*=S), 141.05, 134.96, 131.66, 130.08, 121.23 (Ar*C*), 21.10 (*p*-*C*H_3), 17.57 (*o*-*C*H_3) ppm. ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$): δ = −0.97 ppm. ^{19}F{^{1}H} NMR (376.4 MHz, $CDCl_3$): δ = −154.13 ppm. FT-IR (neat): $\bar{\nu}$ = 3531(b), 1632(m), 1552(w), 1480(m), 1442(m), 1374(s), 1287(m), 1231(m), 1028(s) (B–F), 923(w), 842(w), 733(s), 691(s), 602(s), 570(m) cm^{-1}.

Synthesis of [(IMes=Se)$_2$Cu]BF$_4$ (8)

8 was prepared in the same manner as described for **1** using IMes=Se (0.100 g, 0.260 mmol) and $Cu(BF_4)_2$ (0.075 g, 0.312 mmol) in methanol (5 mL). Yield: 63% (based on $Cu(BF_4)_2$). M.p.: 235–237 °C (dec.). Elemental analysis calcd (%) for $C_{42}H_{48}BCuN_4F_4Se_2$ (917.2): C, 55.00; H, 5.28; N, 6.11; Found: C, 54.86; H, 5.23; N, 5.98. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (s, 4H, Im*H*), 7.02 (s, 8H, CH_{meta}), 2.36 (s, 12H, CH_{3para}), 2.02 (s, 24H, CH_{3ortho}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.07 (*C*=Se), 141.06, 134.81, 132.58, 130.06, 123.08 (Ar*C*), 21.23 (*p*-*C*H_3), 17.67 (*o*-*C*H_3) ppm. ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$): δ = −1.01 ppm. ^{19}F{^{1}H} NMR (376.4 MHz, $CDCl_3$): δ = −153.76 ppm. FT-IR (neat): $\bar{\nu}$ = 3525(b), 1630(m), 1550(w), 1480(m), 1448(m), 1369(s), 1288(m), 1234(m), 1022(s) (B–F), 825(w), 793(w), 735(w), 689(s), 566(m) cm^{-1}.

1–8 catalyzed regioselective boron addition to unsymmetrical alkynes

The catalytic reactions were carried out under very mild conditions using newly synthesized copper(I) catalysts (**1–8**) for the regioselective boron addition of unsymmetrical alkynes in THF using a previously reported synthetic procedure.[5] Copper(I) complex (0.050 mmol) was taken in a Schlenk flask along with NaO^t-Bu (0.100 mmol) in THF (0.40 mL) under the brisk flow of nitrogen. After the mixture was stirred at room temperature for 30 min, bis(pinacolato)diboron (B_2pin_2) (0.55 mmol) in THF (0.30 mL) was added. The reaction mixture was stirred further for 20–30 min. Then, alkyne (0.50 mmol) was added, followed by MeOH (1 mmol). The Schlenk flask was washed with THF (0.40 mL), sealed, and allowed to stir at room temperature. The progress of the reaction was monitored by TLC. After the completion, 5–10 mL hexane was added and the reaction mixture was filtered through Celite and concentrated. The products were purified by column chromatography to produce an oily liquid. The fading of the starting materials and appearance of the products were conveniently examined by ^{1}H NMR spectroscopy.



Scheme 2 Synthesis of **1–8**.

Results and discussion

Synthesis and characterization of 1–8

The linear mononuclear copper(I) thiones and selones, **1–8**, were isolated in excellent yield from the reduction of the corresponding copper(II) salts using imidazoline-2-thiones/selones (Scheme 2). The reduction of copper(II) to copper(I) using imidazoline-2-chalcogenones, R=E (E = S, Se and Te) is a rare reaction. Only two reports demonstrate the reduction of Cu^{2+} to Cu^{+} using chalcogenones. The first Cu^{2+} to Cu^{+} reduction was demonstrated by Brumaghim and co-workers.[3b] Later, the reduction of $CuCl_2$ using 2,6-bis{[*N*-isopropyl-*N*′-methylene]-imidazoline-2-thione}-pyridine or 2,6-bis{[*N*-isopropyl-*N*′-methylene]triazole-2-thione}pyridine was reported.[13]

The formation of **1–8** was confirmed by elemental analysis, FT-IR, multinuclear (^{1}H, ^{13}C, ^{11}B and ^{19}F) NMR, UV-vis, TGA and single crystal X-ray diffraction techniques. All these compounds are soluble in common organic solvents like CH_2Cl_2, $CHCl_3$, acetone, THF, and acetonitrile. In ^{13}C NMR, the carbene carbon chemical shift values of **1–8** were upfield shifted (about δ = 5–8 ppm) from those of the corresponding ligands IPr=E and IMes=E, respectively. This could be due to the decrease in the π-acceptance nature of the carbene carbon upon coordination. In the ^{1}H NMR, the signals of protons, which are in weak interaction with counter anions, are clearly shuffled. The FT-IR spectra of **1–8** showed stretching frequencies in the range of 1022 to 1094 cm^{-1} for uncoordinated perchlorate/tetra fluoro borate anions. In addition, the tetra fluoro borate complexes (**4–8**) were further confirmed by ^{19}F and ^{11}B NMR spectroscopy. The ^{11}B NMR spectra of **5–8** showed a sharp signal in the range of −0.97 to −1.01 ppm and ^{19}F NMR spectra of **5–8** showed a sharp signal in the range of 153.76 to 154.30 ppm. The solid state structures of **1–8** were further confirmed by single crystal X-ray diffraction study.

Single crystal X-ray structure of 1–8

The molecules **1–3** and **5–8** crystallized in the monoclinic space group, *C*2/*c*, while molecule **4** crystallized in the orthorhombic space group, $P2_12_12_1$ (Fig. 1–4). The crystallographic data for **1–8** are furnished in Tables S1 and S2 (see ESI‡). The

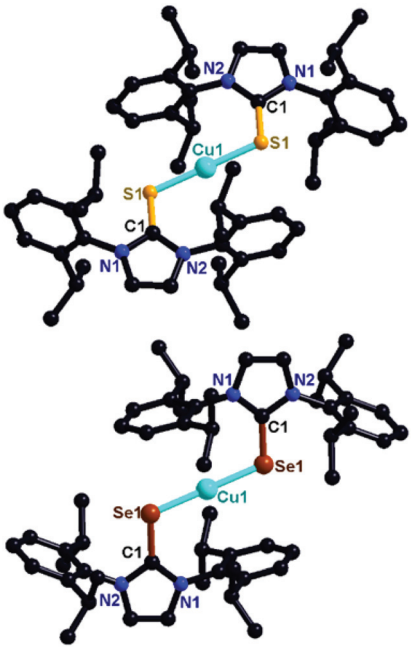


Fig. 1 Top: Molecular structure of **1**. Hydrogen atoms and perchlorate counter ions have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–S(1), 1.702(4), S(1)–Cu(1), 2.1468(9), C(1)–S(1)–Cu(1), 109.44(13), N(1)–C(1)–N(2), 106.5(3), N(1)–C(1)–S(1), 123.0(3), N(2)–C(1)–S(1), 130.5(3), S(1)–Cu(1)–S(2), 180.0. Bottom: Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.857(4), Se(1)–Cu(1), 2.2680(5), C(1)–Se(1)–Cu(1), 105.09(14), N(1)–C(1)–N(2), 105.6(4), N(1)–C(1)–Se(1), 131.5(3), N(2)–C(1)–Se(1), 123.0(3), Se(1)–Cu(1)–Se(2), 180.0.

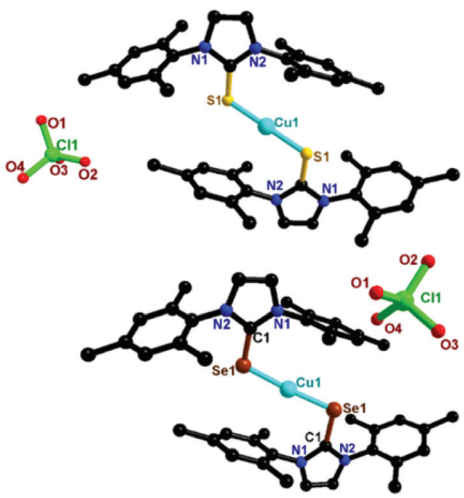


Fig. 2 Top: Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–S(1), 1.701(3), S(1)–Cu(1), 2.1434(7), C(1)–S(1)–Cu(1), 107.19(9), N(1)–C(1)–N(2), 106.1(2), N(1)–C(1)–S(1), 123.6(2), N(2)–C(1)–S(1), 130.3(2), S(1)–Cu(1)–S(2), 180.0. Bottom: Molecular structure of **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.864(5), Se(1)–Cu(1), 2.2513(9), Se(1′)–Cu(1), 2.2513(9), Se(1′)–Cu(1), 2.2475(9), C(1)–Se(1)–Cu(1), 103.23(15), N(1)–C(1)–N(2), 106.8(4), N(1)–C(1)–Se(1), 122.9(4), N(2)–C(1)–Se(1), 130.3(4), Se(1)–Cu(1)–Se(2), 176.29(4).

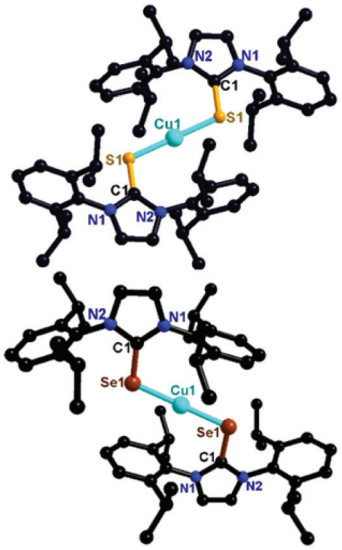
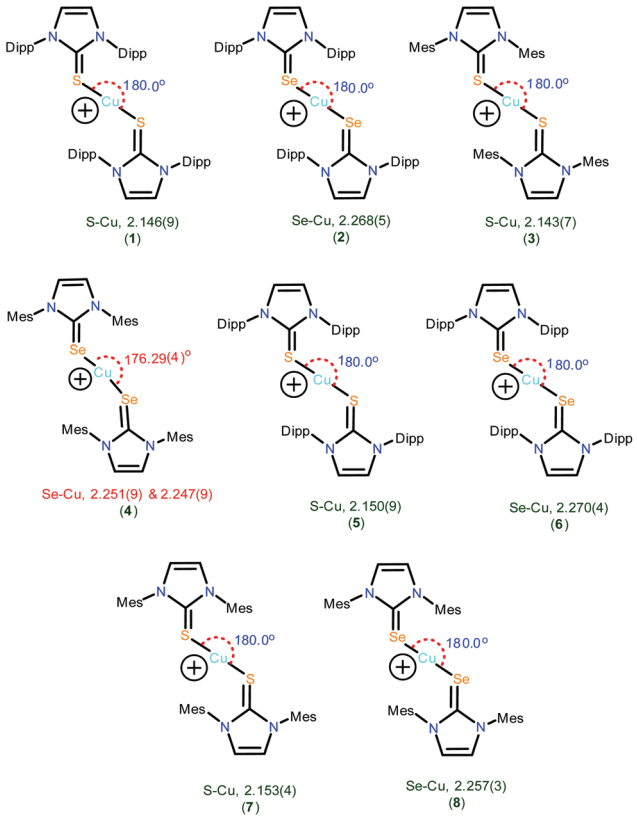


Fig. 3 Top: Molecular structure of **5**. Hydrogen atoms and tetra fluoro borate counter ions have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–S(1), 1.700(4), S(1)–Cu(1), 2.1501(9), C(1)–S(1)–Cu(1), 109.65(13), N(1)–C(1)–N(2), 106.3(3), N(1)–C(1)–S(1), 123.0(3), N(2)–C(1)–S(1), 130.7(3), S(1)–Cu(1) –S(2), 180.0. Bottom: Molecular structure of **6**. Hydrogen atoms and tetra fluoro borate counter ions have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.862(4), Se(1)–Cu(1), 2.2705(4), C(1)–Se(1)–Cu(1), 105.07(13), N(1)–C(1)–N(2), 106.4(3), N(1)–C(1)–Se(1), 131.0(3), N(2)–C(1)–Se(1), 122.6(3), Se(1)–Cu(1)–Se(2), 180.0.



Scheme 3 Vital bond lengths [Å] and angles [°] of compounds **1–8**.

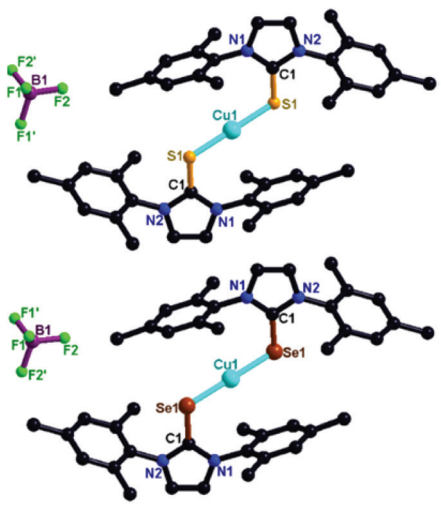


Fig. 4 Top: Molecular structure of **7**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–S(1), 1.705(18), S(1)–Cu(1), 2.1536(4), C(1)–S(1)–Cu(1), 106.70(6), N(1)–C(1)–N(2), 106.10(15), N(1)–C(1)–S(1), 130.08(14), N(2)–C(1)–S(1), 123.79(14), S(1)–Cu(1) –S(2), 180.0. Bottom: Molecular structure of **8**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Se(1), 1.860(3), Se(1)–Cu(1), 2.2576(3), C(1)–Se(1)–Cu(1), 103.04(7), N(1)–C(1)–N(2), 106.0(2), N(1)–C(1)–Se(1), 131.31(19), N(2)–C(1)–Se(1), 123.66(18), Se(1)–Cu(1)–Se(2), 180.0.

molecular drawings with selected bond lengths and bond angles are reported in Scheme 3. As shown in Fig. 1–4, the molecules **1–8** are distinct monomers. Molecules **1–8** are isolated as homoleptic cations with the corresponding anions. **1–3** and **5–8** are rare examples of structurally characterized perfect linear homoleptic copper(I) chalcogenone derivatives, while **4** is in quasi-linear geometry.

The copper(I) center in **1–8** is coordinated with two imidazoline-2-thiones/selones and the valency is satisfied by one perchlorate/tetra fluoro borate counter anion. Such linearly coordinated copper(I) compounds are very rare. In particular, only two nonlinear copper(I) thione derivatives $[Cu(dptu)_2](SO_4)_{0.5}$ (dptu = *N*,*N*′-diphenylthiourea) (S–Cu–S is 162.18(2)°) and [Cu(SAr*)(S=C(N^{i}Pr)$_2$(CMe)$_2$)] (Ar*S = 2,6-bis(2,4,6-triisopropylphenyl)benzenethiolate) (S–Cu–S is 162.98(4)°) were reported with the thiourea type of ligands (*vide supra*, Scheme 1, **B**).[14] Among coinage metals, only linearly coordinated gold(I) imidazoline-2-chalcogenone complexes are known (*vide supra*, Scheme 1). However, few non-imidazole ligands coordinated quasi-linear or linear group 9 thio derivatives, $[Ph_4P][Cu(SC\{O\}Me)_2]$ (176.6(2)°), $[NEt_4][Cu(SAd)_2]$ (Ad = adamantanyl) (180°), *fac*-[Mn(CN^{t}Bu)(CO)$_3${(PPh$_2$)$_2$C(H)SC(S)NMe$_2$}]$_2$Cu][BF$_4$] (180°), $[Ph_4P][Ag(SC\{O\}Me)_2]$ (178.9(5)°) and $[Ph_4P][Ag(SC\{O\}Ph)_2]$ (161.1(4)°) were reported.[15,16]

The C=S bond lengths and C=Se bond lengths are increased upon coordinating with copper compared to their

corresponding ligands IPr=S (1.670(3) Å), IMes=S (1.675(18) Å), IPr=Se (1.822(4) Å), and IMes=Se (1.830(6) Å) (Scheme 3).[10] The Cu–S bond lengths in **1**, **3**, **5** and **7** are almost comparable to that of $[NEt_4][Cu(SAd)_2]$ (Ad = adamantanyl) (2.147(1) Å).[15] The E–Cu–E bond angle in **1–3** and **5–8** is exactly 180°, while molecule **4** is in quasi-linear form with a Se–Cu–Se angle of 176.29(4)°. Such linear and quasi-linear thio derivatives of copper complexes are limited, which are known to exist with different types of thio ligands.[15,16] Thus Cu–E bond lengths in **1–3** and **5–8** are comparable, while Cu–Se bond lengths in **4** are not comparable (Cu(1)–Se(1), 2.251(9) Å and Cu(1)–Se(1′), 2.248(9) Å).

The absence of interaction between the copper center and the counter ion is evidenced from the molecular packing of **1–8** (see ESI‡). In addition, the extensive C–H···F type of interaction is observed for tetra fluoro borate complexes, **5–8**.

UV-vis solid and solution state absorption study of 1–8

The solution state UV-vis absorption spectra of **1–8** were recorded in $CHCl_3$ (Fig. 5(I) and 5(III)). In solution state UV-vis absorption spectra, IPr=S ($\mathbf{L_1}$), IPr=Se ($\mathbf{L_2}$), IMes=S ($\mathbf{L_3}$), IMes=Se ($\mathbf{L_4}$), and **1–8** show nearly comparable absorption patterns. The absorption band observed around 240–250 nm can be attributed to the $\pi \rightarrow \pi^*$ transition, while the absorption band observed around 260–310 nm can be assigned to the $n \rightarrow \pi^*$ transition. In general, the absorption intensity of **1–8** is considerably lower (hypochromic) along with the bathochromic shift compared to the corresponding chalcogenone ligands. As shown in Fig. 5(II) and 5(IV), the solid state UV-vis absorption spectra of **1–8** are not comparable to the solution state absorption spectra of **1–8**. In the case of solid state absorption spectra, the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are merged together to give a broad absorption band.

TGA analysis of 1–8

The thermal stability of molecules **1–8** is analyzed by TGA. Fig. 6 reveals the thermal breakdown pathway of **1–8** based on thermal investigation under a flowing nitrogen atmosphere (10 °C min^{-1}, 30–900 °C). Complexes **1–5** show enough stability till 370–390 °C then a sudden weight loss in a single step in the region of 40–70%, which can be attributed to the decomposition of organic moieties. Subsequently, a gradual weight loss was observed till 850 °C with 9–12% residue for the metal chalcogenides. Whereas complex **2** displayed an extreme stability till 370 °C and showed a gradual weight loss till 850 °C with 12% residue. Complexes **6–8** were fairly stable up to 400 °C and showed a gradual decrease till 800 °C but complex **6** lost its weight gradually up to 600 °C and remained unchanged till 900 °C with 18% residue. The black residues

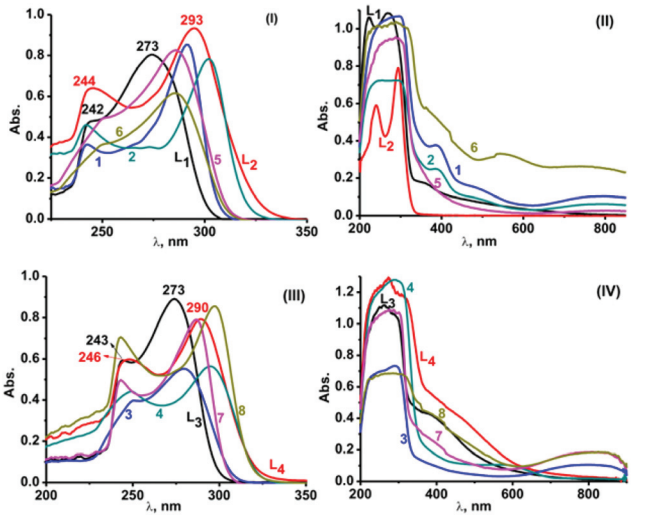


Fig. 5 (I) Solution state UV-vis spectra of (IPr=S) L_1, (IPr=Se) L_2, **1**, **2**, **5** and **6** in $CHCl_3$ at 25 °C (1.8×10^{-5} M). (II) Solid state UV-vis spectra of (IPr=S) L_1, (IPr=Se) L_2, **1**, **2**, **5** and **6**. (III) Solution state UV-vis spectra of (IMes=S) L_3, (IMes=Se) L_4, **3**, **4**, **7** and **8** in $CHCl_3$ at 25 °C (1.8×10^{-5} M). (IV) Solid state UV-vis spectra of (IMes=S) L_3, (IMes=Se) L_4, **3**, **4**, **7** and **8**.

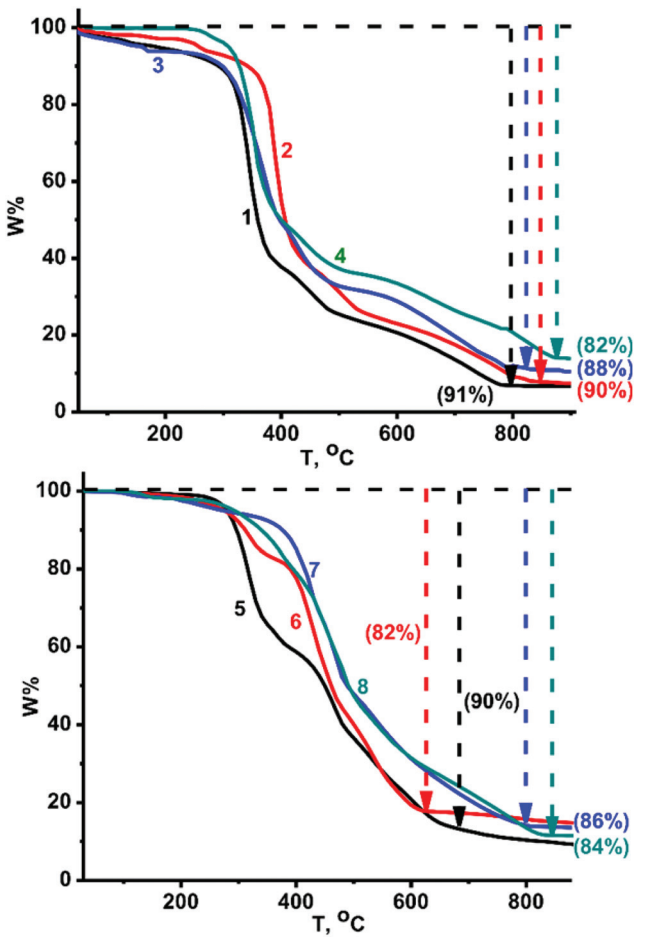


Fig. 6 TGA curve of **1–4** (top) and **5–8** (bottom) from 30 to 900 °C under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. **1** residual wt 9%, calc. wt 10%; **3** residual wt 12%, calc. wt 12%; **5** residual wt 10%, calc. wt 9% and **7** residual wt 14%, calc. wt 12%. **2** residual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

obtained from the thione compounds (**1**, **3**, **5** and **7**) were almost in accord with the calculated values for the copper monosulfide (CuS). Similarly, the residues obtained from the selone compounds (**2**, **4**, **6** and **8**) were in accord with the calculated values for the copper monoselenide (CuSe).

Copper(I) catalyzed borylation of unsymmetrical alkynes

The copper(I) mediated selective borylation of alkynes is considered to be one of the key reactions in multistep organic synthesis.[17,18] The catalytic reaction was demonstrated with copper using NHC[17] or phosphine[18] as the ligand. For example, the imidazole chalcogenone supported copper catalysts for the borylation of alkynes are rare.[5,18d] Thus, molecules **1–8** are used as catalysts for the regioselective borylation of alkynes under mild conditions (Table 1). The borylation of 1-phenyl-1-propyne using bis(pinacolato)diboron in THF was probed in the presence of MeOH as a proton source at ambient temperature using catalysts **1–8** (Scheme 4). The catalysts **1–8** are active towards the borylation of 1-phenyl-1-propyne over a period of 24 h to 36 h. Among **1–8**, catalyst **4** is very active (yield, 96%) and highly regioselective (100% major product) (Table 1, entry 4). The catalyst **2** shows poor selectivity (Table 1, entry 2), while catalyst **6** gives poor conversion (Table 1, entry 6). Notably, the regioselectivity (98%–100% major product) of **3** (entry 3), **5** (entry 5), **7** (entry 7) and **8** (entry 8) is appreciable, however the yield is considerably lower than entry 4. In order to understand the role of ancillary ligands, the catalytic reaction was performed using only IMes=Se (entry 9), $Cu(ClO_4)_2{\cdot}6H_2O$ (entry 10), $Cu(BF_4)_2{\cdot}H_2O$ (entry 11) and IMes=Se/$Cu(ClO_4)_2{\cdot}6H_2O$ (entry 12). As expected, no catalytic reaction was noticed in the presence of IMes=Se (entry 9). The reaction was very slow in the case of $Cu(ClO_4)_2{\cdot}6H_2O$ with poor yield (entry 10). Interestingly, the regioselectivity and yield are nearly comparable for $Cu(BF_4)_2{\cdot}H_2O$ (entry 11) and IMes=Se/$Cu(ClO_4)_2{\cdot}6H_2O$ (entry 12). Therefore, the well defined catalyst **4** (entry 4) is more active than the *in situ* catalyst (entry 12).

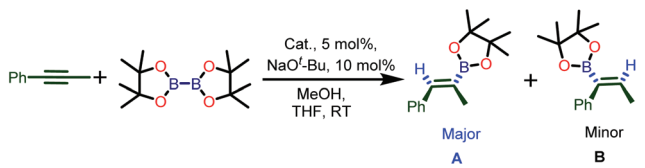
Subsequently, the temperature and solvent choice was optimized using catalyst **4** (Table 2). The regioselectivity and yield are not appreciable when the reaction was carried out using **4** in THF at 75 °C (Table 2, entry 2) or in 1,4-dioxane at 25 °C (Table 2, entry 3) or in hexane at 25 °C (Table 2, entry 4). The mid polar solvents like toluene, diethyl ether and dichloromethane gave considerable selectivity with good yield (Table 2, entries 5–7, respectively). Therefore the best possible conversion and regioselectivity can be obtained using catalyst **4** in THF at room temperature (Table 1, entry 4 and Table 2, entry 1). As proposed in Scheme 5, the nucleophilic attack by the Bpin anion takes place at the electrophilic centre; this followed by protonation led to an expected product. The most efficient catalysis of **4** can be attributed to the high Lewis acidity of the copper centre: *i.e.*, poor σ donor and strong π accepting nature of the ligand coordinated with the strong cationic nature of the metal center.[7]

Consequently, the scope of catalyst **4** was analyzed for unsymmetrical alkynes (Table 3). The aromatic alkynes like phenyl acetylene, 1-phenyl-1-butyne and ethyl 3-phenylpropiolate gave 100% selectivity with very good yield (Table 3, entries 1 and 2 for product **A** and entry 3 for product **B**).[19] Whereas

Table 1 Regioselective borylation of 1-phenyl-1-propyne using **1–8**[a]

E	Catalyst	Time (h)	Selectivity[b] (%) A	B	SMC[b] (%)	Y[c] (%)
1	**1**	24	90	10	90	80
2	**2**	36	86	14	75	70
3	**3**	24	99	01	74	68
4	**4**	24	100	ND	>99	96
5	**5**	36	100	ND	64	62
6	**6**	36	94	06	40	38
7	**7**	24	98	02	76	70
8	**8**	36	99	01	90	82
9	IMes=Se	48	0	0	NR	NR
10	$Cu(ClO_4)_2{\cdot}6H_2O$	48	99	01	45	40
11	$Cu(BF_4)_2{\cdot}H_2O$	36	98	02	65	60
12	IMes=Se and $Cu(ClO_4)_2{\cdot}6H_2O$	36	94	06	70	64

[a] Reaction conditions: 0.50 mmol 1-phenyl-1-propyne, 0.55 mmol bis(pinacolato)diboron, 5 mol% copper(I) catalyst, 10 mol% NaO^tBu and 1.0 mmol MeOH were used at room temperature. E – entry. [b] % based on ^1H NMR spectroscopy. [c] % isolated yield by column chromatography, NR – no reaction, ND – not detected, SMC – starting material conversion and Y – yield.

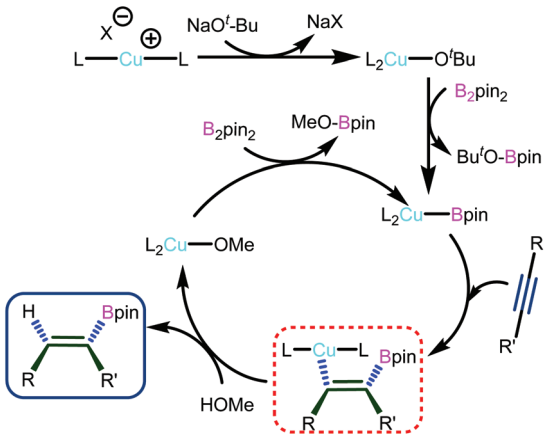


Scheme 4 Regioselective borylation of 1-phenyl-1-propyne using **1–8**.

Table 2 Optimization of regioselective borylation of 1-phenyl-1-propyne by **4** in 24 h[a]

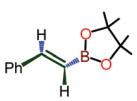
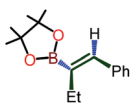
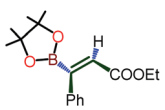
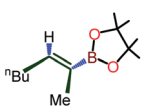
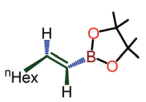
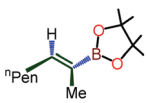
E	Solvent	*T* (°C)	Selectivity[b] (%) A	B	SMC[b] (%)	Y[c] (%)
1	THF	25	100	ND	>99	96
2	THF	75	95	05	76	70
3	1,4-Dioxane	25	90	10	37	35
4	Hexane	25	90	10	46	40
5	Toluene	25	98	02	85	78
6	Et_2O	25	95	05	90	85
7	CH_2Cl_2	25	99	01	80	76

[a] Reaction conditions: 0.50 mmol 1-phenyl-1-propyne, 0.55 mmol bis(pinacolato)diboron, 5 mol% copper(I) catalyst (**4**), 10 mol% NaO^tBu and 1.0 mmol MeOH were used in 1.0 mL of solvent. E – entry. [b] % based on ^1H NMR spectroscopy. [c] % isolated yield by column chromatography, ND – not detected, SMC – starting material conversion and Y – yield.



Scheme 5 Plausible reaction pathway shows the nucleophilic attack by the Bpin anion from the less hindered side followed by protonation.

Table 3 Regioselective borylation of unsymmetrical alkynes by **4** at 25 °C in THF[a]

E	Starting material	Major product	Selectivity[b] (%) A	B	SMC[b] (%)	Y[c] (%)
1	H—≡—Ph		100	ND	75	69
2	Ph—≡—Et		100	ND	82	78
3	Ph—≡—C(=O)OEt		ND	100	80	72
4	^{n}Bu—≡		78	22	85	76
5	Hex^n—≡—H		85	15	90	80
6	Pen^n—≡		90	10	95	82

[a] Reaction conditions: 0.50 mmol alkyne, 0.55 mmol bis(pinacolato)-diboron, 5 mol% copper(I) catalyst (**4**), 10 mol% NaO^t-Bu and 1.0 mmol MeOH were used in 1.0 mL of THF at room temperature for 24 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 aliphatic alkynes like 2-hexyne, 1-octyne and 2-octyne gave considerably less selectivity compared to aromatic alkynes (Table 3, entries 4–6). However, the product yields for both aliphatic and aromatic alkynes are comparable.

Conclusions

Copper(I) thione (**1**, **3**, **5** and **7**) complexes along with rare homoleptic two coordinated copper(I) selone (**2**, **4**, **6** and **8**) complexes were synthesized and structurally characterized. The molecules **1–8** were isolated by copper(II) to copper(I) reduction with chalcogenones. The molecules **1–3** and **5–8** are in perfect linear geometry, while **4** is in quasi-linear geometry. These newly isolated molecules **1–8** were used as catalysts for boron addition to alkynes. The catalysts **1–8** were active for regioselective boron addition to alkynes. Moreover, (i) we assume that the homoleptic two coordinated intermediate does not exist in the catalytic process, (ii) the π accepting nature of imidazoline-2-chalcogenone does play a small role in isolating homoleptic two coordinated coinage metal derivatives, (iii) complex **4** showed the best catalytic activity, (iv) the well-defined catalyst is much more active than the *in situ* generated catalyst, for example catalyst **4**, (v) IMes=Se based copper(I) complexes (**4** and **8**) were more selective and efficient than **3** and **5–7**, and (vi) the high Lewis acidity of the copper centre in **4** enhances the catalytic activity. The excellent selectivity of the reactions at room temperature, especially with **4**, makes this strategy viable for the borylation of symmetrical/unsymmetrical alkynes. Nevertheless the investigation towards highly selective catalysts with reduced reaction time is in progress.

Acknowledgements

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Notes and references

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