Metal complexes of selenophosphinates from reactions with $(R_2PSe)_2Se$: $[M(R_2PSe_2)_n]$ ($M = Zn^{II}, Cd^{II}, Pb^{II}, In^{III}, Ga^{III}, Cu^{I}, Bi^{III}, Ni^{II}$; $R = {}^iPr$, Ph) and $[Mo^{V}_2O_2Se_2(Se_2P^iPr_2)_2]$

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The reactions of bis(dialkylselenophosphinyl)selenide with a series of metals have been investigated: synthesis of several metal selenophosphinate complexes and their structures are reported.

The coordination chemistry of dithiophosphinate complexes has been well explored and the complexes' potential as single-source precursors (SSPs) for metal sulfide thin films has been shown.[1] There are no reports in the literature for a structurally characterized isolated selenophosphinate such as $(R_2PSe)_2Se$, and only a few reports on their metal complexes. The methods reported in the literature for the preparation of selenophosphates or selenophosphinates are not always reproducible.[2]

In this paper, we report the reactions of bis(dialkylselenophosphinyl)selenide $(R_2PSe)_2Se$ with a range of metals resulting in novel and facile syntheses of metal dialkyldiselenophosphinato complexes, and the complexes' characterization in solution and solid state.

The compound $(R_2PSe)_2Se$ ($R = {}^iPr$, Ph) was prepared by the reaction of NEt_3 with ${}^iPr_2PCl$, $HSiCl_3$ and Se in toluene (see accompanying communication).[3] The reaction of this compound with different metal salts was then carried out in methanolic solutions to give the metal complexes as precipitates which were subsequently recrystallized from dichloromethane or toluene before further analyses. The complexes are soluble in chloroform, toluene or dichloromethane. All are stable at room temperature under open atmosphere for months which makes them potentially useful as SSPs for the deposition of metal selenide thin films or nanoparticles.

The copper complex **1** is based on the tetramer $[Cu_4({}^iPr_2P\,Se_2)_4]$ (Fig. 1). None of the ligands are chelating, all four ligands are bridging. One of the seleniums is bound to phosphorus and copper only whilst the other selenium is bonded to two copper atoms and one phosphorus atom in each ligand. Each Cu is bonded to three Se atoms, giving overall a cubane structure. The Se–Cu–Se bond angles range from 128.733(2) to 101.419(2)° to give a distorted trigonal planar geometry at each Cu centre. The Cu–Se bond distances range from 2.437(5) to 2.369(5) Å. The dithiocarbamato or dithiophosphinato ligands chelate to the copper centre as expected.[4,5]

In an analogous reaction, molybdenum complex **2** $[Mo_2O_2Se_2(Se_2P^iPr_2)_2]$ is formed. In a dimeric structure, each ligand chelates to one Mo atom and the two Mo atoms are doubly bridged by two selenium atoms (Fig. 2). The geometry around Mo is distorted square pyramidal. The structure is similar to that of $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(S_2CNPr_2)_2]$.[6]

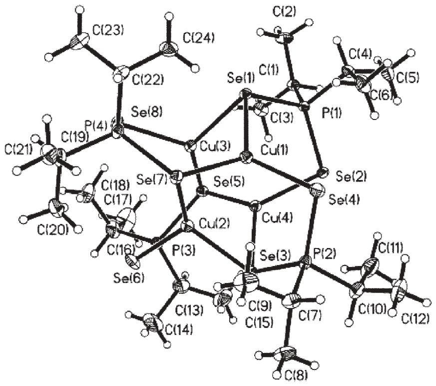

Fig. 1 Thermal ellipsoid plot (50% probability) of the structure of **1**. Selected bond distances (Å) and angles (°): Cu(1)–Se(1), 2.401(5); Cu(1)–Se(7), 2.425(5); Cu(1)–Se(4), 2.437(5); Cu(2)–Se(7), 2.369(5); Cu(2)–Se(3), 2.387(5); Cu(2)–Se(6), 2.409(5); Cu(3)–Se(5), 2.388(5); Cu(3)–Se(1), 2.392(5); Cu(3)–Se(8), 2.407(5); Cu(4)–Se(2), 2.398(5); Cu(4)–Se(3), 2.398(5); Cu(4)–Se(5), 2.409(5); Se(1)–Cu(1)–Se(7), 120.29(2); Se(1)–Cu(1)–Se(4), 124.63(2); Se(7)–Cu(1)–Se(4), 110.56(2); Se(7)–Cu(2)–Se(3), 124.99(2); Se(7)–Cu(2)–Se(6), 128.73(2); Se(3)–Cu(2)–Se(6), 101.42(2); Se(5)–Cu(3)–Se(8), 121.48(2); Se(1)–Cu(3)–Se(8), 111.91(2); Se(2)–Cu(4)–Se(5), 113.64(2); Se(3)–Cu(4)–Se(5), 120.61(2).

The indium complex **3** shows (Fig. 3) the expected $[In({}^iPr_2PSe_2)_3]$ molecule. All three diselenophosphinate ligands are chelating to form three four membered rings (Se–P–Se–In) with In–Se bond distances range from 2.729(6) to 2.768(6) Å. The geometry on indium is trigonally distorted octahedral due to the

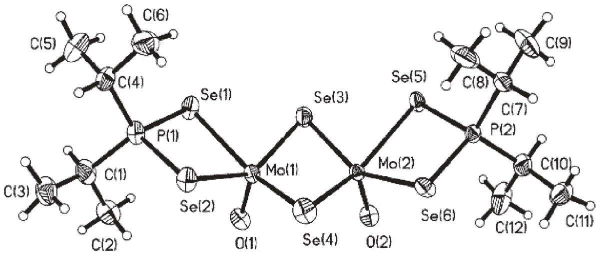

Fig. 2 Thermal ellipsoid plot (50% probability) of the structure of **2**. Selected bond distances (Å) and angles (°): Mo(1)–O(1), 1.656(7); Mo(1)–Se(3), 2.434(1); Mo(1)–Se(4), 2.451(2); Mo(1)–Se(2), 2.587(1); Mo(1)–Se(1), 2.606(1); Mo(2)–O(2), 1.663(7); Mo(2)–Se(3), 2.441(1); Mo(2)–Se(4), 2.454(2); Mo(2)–Se(6), 2.595(1); Mo(2)–Se(5), 2.596(1); O(1)–Mo(1)–Se(3), 109.00(2); O(1)–Mo(1)–Se(4), 105.70(2); Se(3)–Mo(1)–Se(4), 105.77(5); O(1)–Mo(1)–Se(2), 107.70(2); Se(3)–Mo(1)–Se(2), 140.93(6); Se(4)–Mo(1)–Se(2), 76.46(5); O(1)–Mo(1)–Se(1), 103.0(3); Se(3)–Mo(1)–Se(1), 78.64(4); Se(4)–Mo(1)–Se(1), 147.43(6); Se(2)–Mo(1)–Se(1), 80.46(4).

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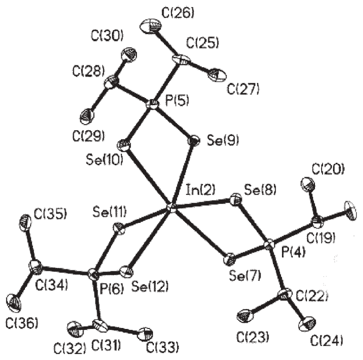

Fig. 3 Thermal ellipsoid plot (50% probability) of the structure of **3**. Selected bond distances (Å) and angles (°): In(2)–Se(9), 2.729(6), In(2)–Se(8), 2.733(6); In(2)–Se(12), 2.742(6); In(2)–Se(7), 2.752(6); In(2)–Se(10), 2.767(6); In(2)–Se(11), 2.768(6); Se(9)–In(2)–Se(8), 96.34(2); Se(9)–In(2)–Se(12), 164.280(2), Se(8)–In(2)–Se(12), 96.16(2); Se(9)–In(2)–Se(7), 96.87(2); Se(8)–In(2)–Se(7), 80.31(2); Se(12)–In(2)–Se(7), 94.60(2); Se(9)–In(2)–Se(10), 80.84(2); Se(8)–In(2)–Se(10), 88.88(2); Se(12)–In(2)–Se(10), 89.91(2); Se(7)–In(2)–Se(10), 168.67(2); Se(9)–In(2)–Se(11), 89.42(2); Se(8)–In(2)–Se(11), 169.47(2); Se(12)–In(2)–Se(11), 79.79(2); Se(7)–In(2)–Se(11), 90.27(2); Se(10)–In(2)–Se(11), 100.77(2).

restricted bite angle of the chelating diselenophosphinate ligand. The structure is similar to those reported for $[In(Ph_2PSe_2)_3]$[7] or the sulfur analogue $[In(Ph_2PS_2)_3]$.[8]

The structure of $[Ga(^iPr_2PSe_2)_3]$ (**4**) (Fig. 4) has a four coordinate gallium centre in contrast to the six coordinate indium. Until recently[9] all of the reports on structurally characterized pairs of analogues In/Ga tris(chelates) with (O, O′) or (S, S′) ligands have been shown to be isostructural.[10,11] The first such structure of a gallium complex was reported by us for tris(di-isobutyldithiophosphinato) gallium(III) $[Ga(Ph_2PS_2)_3]$.[9] The structure consists of one chelating and two pendant di-isopropyldiselenophosphinate ligands in a distorted tetragonal geometry. The bite angle of the chelating ligand (90.42(15)°) is considerably larger than that of the indium complex (80.84(19), 80.31(16), 79.79(16)°) and the tetrahedral angle between the sulfur atoms of the two pendant ligands is 115.97(16)°. The bond distances between Se–Ga in chelating ligand (2.446(4) Å and 2.451(4) Å) are larger than those of the pendant ligands (2.396(5), 2.385 (4) Å) which shows that the negative charge is localized on a single donor atom in pendant ligands. We have also analysed the X-ray structure of $[Ga(Ph_2PSe_2)_3]$ which showed similar coordination and will be reported later.

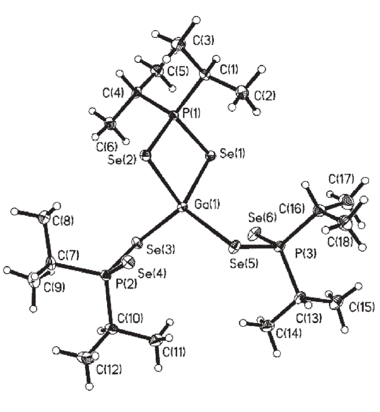

Fig. 4 Thermal ellipsoid plot (50% probability) of the structure of **4**. Selected bond distances (Å) and angles (°): Ga(1)–Se(5), 2.385(4); Ga(1)–Se(3), 2.396(5); Ga(1)–Se(2), 2.446(4); Ga(1)–Se(1), 2.451(4); Se(5)–Ga(1)–Se(3), 115.97(2); Se(5)–Ga(1)–Se(2), 115.89(2); Se(3)–Ga(1)–Se(2), 110.75(1); Se(5)–Ga(1)–Se(1), 112.49(2); Se(3)–Ga(1)–Se(1), 108.32(1); Se(2)–Ga(1)–Se(1), 90.42 (2).

The compounds **5–18** were prepared in a similar way.† It is worth noting that $(R_2PSe)_2Se$ (R = ^iPr, Ph) breaks its phosphorus selenium bond in each case and acts as a source of dialkylselenophosphinate anion $[R_2PSe_2]^-$. In the copper complex the ligand is bridging, in the molybdenum complex chelating and bridging, in the indium complex chelating only and in the gallium complex only one is chelating whilst the other two are pendant.

All these complexes are potentially useful single source precursors. Preliminary chemical vapour deposition experiments of Cu, Mo, Cd and Zn complexes produce high quality thin films and nanoparticles. Detailed deposition studies on these complexes are under way and will be reported else where.

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Notes and references

† All the reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. All chemicals were bought from Aldrich Chemical Company Limited and used as received. Solvents were distilled prior to use. NMR spectra were obtained with chloroform-D6 solution using a Bruker AC300 FTNMR instrument. Elemental analysis was performed by the University of Manchester micro-analytical laboratory. Single crystal X-ray crystallography measurements were made using graphite monochromated Mo Kα radiation on a Bruker APEX diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares on F^2.[12] All calculations were carried out using the SHELXTL package.[13] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were placed in calculated positions, assigned isotropic atoms. CCDC numbers, 282910 (**1**), 282909 (**2**), 291036 (**3**), 291037 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603198f

$(^iPr_2PSe)_2Se$ **(A)** and $(Ph_2PSe)_2Se$ (**B**) were prepared as discussed in the preceding paper.[3]

$[Cu_4(^iPr_2PSe_2)_4]$ (**1**). In a typical experiment the solution of $CuCl_2$ (1.0 g, 7.5 mmol) in 20 ml MeOH was added dropwise to a solution of $(^iPr_2PSe)_2Se$ **(A)** (7 g, 15 mmol) in 100 ml of MeOH. The mixture was stirred for 1 h at room temperature under atmospheric pressure, forming a light yellow precipitate, which was filtered, washed with MeOH and re-crystallized in dichloromethane to obtain light yellow crystals of **1** (6.6 g, yield 65%). Mp 230–235 °C. Elemental analysis (found: C, 21.94; H, 4.30; P, 9.01; calc. for $C_{24}H_{56}P_4Se_8Cu_4$: C, 21.28; H, 4.17; P, 9.15%;) ^1H NMR δ = 1.35 ppm (ddd, 12H, J = 7.0 Hz, J = 19.2 Hz, J = 26.1 Hz, 2 × $CH(CH_3)_2$), 2.44 ppm (dq, 2H, J = 5.5 Hz, J = 14.1 Hz, 2 × $CH(CH_3)_2$).

$[Mo_2O_2Se_2(^iPr_2PSe_2)_2]$ (**2**). We followed the process of making **1** but used $MoCl_5$ (2.05 g, 7.5 mmol), and obtained brown crystals of **2** (4.2 g, yield 37%). Mp 295–300 °C. Elemental analysis (found: C, 16.00; H, 2.88; Mo, 20.92%; calc. for $C_{12}H_{28}O_2P_2Se_6Mo_2$: C,15.47; H, 3.03; Mo, 20.59%)

$[In(^iPr_2PSe_2)_3]$ (**3**). We followed the process of making **1** but used $InCl_3$ (1.1 g, 5 mmol), to obtain light yellow crystals of **3** (2.5 g, yield 53.1%). Mp 183 °C. Elemental analysis (found: C, 23.09; H, 4.37; P, 10.22; In, 12.02%; calc. for $C_{18}H_{42}P_3Se_6In$: C, 23; H, 4.5; P, 9.88; In 12.21%; ^1H NMR δ = 1.37 ppm (dd, 36H, J = 6.8 Hz, J = 20.4 Hz, 6 × $CH(CH_3)_2$) , 2.24 ppm (dq, 6H, J = 2.7 Hz, J = 6.9 Hz, 6 × $CH(CH_3)_2$).

$[Ga(^iPr_2PSe_2)_3]$ (**4**). We followed the process of making **1** but used $GaCl_3$ (0.88 g, 5 mmol), and obtained light yellow crystals of **4** (2.8 g, yield 62.6%). Mp 180 °C. Elemental analysis (found: C, 24.19; H, 4.71; P, 9.99; Ga, 7.58%; calc. for $C_{18}H_{42}P_3Se_6Ga$: C, 24.16; H, 4.73; P, 10.38; Ga 7.79%; ^1H NMR δ = 1.31 ppm (dd, 36H, J = 6.9 Hz, J = 20.2 Hz, 6 × $CH(CH_3)_2$), 2.29 ppm (dq, 6H, J = 6.8 Hz, J = 11.7 Hz, 6 × $CH(CH_3)_2$).

$[Pb(^iPr_2PSe_2)_2]$ (**5**). We followed the process of making **1** but used $Pb(CH_3COO)_2$ (2.9 g, 7.5 mmol), and obtained yellow crystals of **5** (3.6 g, yield 63.4%). Mp 140 °C. Elemental analysis (found: C, 19.07; H, 3.58; P, 7.69; Pb, 26.67%; calc. for $C_{12}H_{28}P_2Se_4Pb$: C, 19.03; H, 3.73; P, 8.18; Pb, 27.36%; ^{1}H NMR δ = 1.29 ppm (dd, 24H, J = 6.8 Hz, J = 20.3 Hz, 4 × CH(CH_3)$_2$), 2.16 ppm (dq, 4H, J = 6.8 Hz J = 12.1, 4 × CH(CH$_3$)$_2$).

[Zn(^{i}Pr$_2$PSe$_2$)$_2$] (6). We followed the process of making **1** but used ZnCl$_2$ (1.02 g, 7.5 mmol), and obtained colourless crystals of **6** (2.5 g, yield 54.3%). Mp 120 °C. Elemental analysis (found: C, 23.49; H, 4.46; P, 10.29; Zn, 10.48%; calc. for $C_{12}H_{28}P_2Se_4Zn$: C, 23.42; H, 4.59; P,10.06; Zn, 10.62%; ^{1}H NMR δ = 1.25 ppm (dd, 24H, J = 6.8 Hz, J = 20.7 Hz, 4 × CH(CH_3)$_2$), 2.17 ppm (dq, 4H, J = 6.9Hz, J = 11.1Hz, 4 × CH(CH$_3$)$_2$).

[Cd(^{i}Pr$_2$PSe$_2$)$_2$] (7). We followed the process of making **1** but used CdCl$_2$ (1.37g, 7.5 mmol), and obtained colourless crystals of **7** (3.0 g, yield 60.3%). Mp 200 °C. Elemental analysis (found: C, 22.69; H, 4.32; P, 9.39; Cd, 16.37%; calc. for $C_{12}H_{28}P_2Se_4Cd$: C, 21.75; H, 4.26; P, 9.35; Cd, 16.97%; ^{1}H NMR δ = 1.27 ppm (dd, 24H, J = 6.8 Hz, J = 20.5 Hz, 4 × CH(CH_3)$_2$), 2.17 ppm (dq, 4H, J = 6.8 Hz, J = 11.4 Hz, 4 × CH(CH$_3$)$_2$).

[Bi(Se$_2$P^{i}Pr$_2$)$_3$] (**8**). We followed the process of making **1** but used Bi(NO$_3$)·5H$_2$0 (2.4 g, 5 mmol), to obtain orange crystals of **8** (3.1 g, yield 61.0%). Mp 172 °C. Elemental analysis (found: C, 20.33; H, 3.94; P, 7.56%; calcd for $C_{18}H_{42}P_3Se_6Bi$: C, 20.90; H, 4.09; P, 8.98%); ^{1}H NMR δ = 1.30 ppm (dd, 36H, J = 6.8 Hz J = 20.5 Hz, 6 × CH(CH_3)$_2$), 2.23 ppm (dq, 6H, J = 6.9 Hz, J = 11.5 Hz, 6 × CH(CH$_3$)$_2$).

[Co(Se$_2$P^{i}Pr$_2$)$_2$] (**9**). We followed the process of making **1** but used CoCl$_2$·6H$_2$O (1.77 g, 7.5 mmol) , to obtain light green crystals of **9** (2.0 g, yield 66.2%). Mp 275 °C. Elemental analysis (found: C, 24.04; H, 4.72; P, 10.08%; calc. for $C_{12}H_{28}P_2Se_4Co$: C, 23.67; H, 4.64; P, 10.17%); ^{1}H NMR δ = 1.37 ppm (dd, 24H, J = 6.8 Hz, J = 20.4 Hz, 4 × CH(CH_3)$_2$), 2.16 ppm (m, 4H, 4 × CH(CH$_3$)$_2$).

[Ni(Se$_2$P^{i}Pr$_2$)$_2$] (**10**). We followed the process of making **1** but used Ni(NO$_3$)$_2$·6H$_2$0 (2.18 g, 7.5 mmol), to obtained green crystals of **10** (2.1 g, yield 69.1%). Mp 173–175 °C. Elemental analysis (found: C, 23.88; H, 4.58; P, 9.92%; calc. for $C_{12}H_{28}P_2Se_4Ni$: C, 23.67; H, 4.64; P, 10.17%); ^{1}H NMR δ = 1.40 ppm (m, 12H, CH(CH_3)$_2$), 2.10 ppm (m, 2H, CH(CH$_3$)$_2$).

[In(Ph$_2$PSe$_2$)$_3$] (**11**). The solution of InCl$_3$ (1.1 g, 5 mmol) in 20 mL MeOH was added dropwise to solution of (Ph$_2$PSe)$_2$Se **(B)**(9.1 g, 15 mmol) in 150 ml of MeOH. The mixture was stirred for 1 h at room temperature under atmospheric pressure forming a light yellow precipitate, which was filtered, washed with MeOH and re-crystallized in dichloromethane to obtain yellow crystals of **11** (3.8 g, yield 66.6%). Mp 187 °C. Elemental analysis (found: C, 36.68; H, 2.56; P, 8.21; In, 9.63%; calc. $C_{36}H_{30}P_3Se_6In$: C, 37.79; H, 2.64; P, 8.12; In 10.04%). ^{1}H NMR δ = 7.43 ppm (m, 18H, 6 × *p*-Ph and 6 × *m*-Ph), 7.89 ppm (ddd, 12H, J = 2.0 Hz, J = 7.5 Hz, J = 15.4 Hz, 6 × *o*-Ph).

[Pb(Ph$_2$PSe$_2$)$_2$] (**12**). We followed the process of making **11** but used Pb(CH$_3$COO)$_2$·3H$_2$O (2.9 g, 7.5 mmol), and obtained yellow crystals of **12** (4.5 g, yield 67.2%). Mp 235 °C. Elemental analysis (found: C, 32.48; H, 2.24; P, 6.40; Pb, 22.47%; calc. for $C_{24}H_{20}P_2Se_4Pb$: C, 32.27; H, 2.26; P, 6.93; Pb, 23.19%); ^{1}H NMR δ = 7.39 ppm (m, 4H, 4 × *p*-Ph), 5.51 ppm (m, 8H, 4 × *m*-Ph), 7.85 ppm (m, 8H, 4 × *o*-Ph).

[Zn(Ph$_2$PSe$_2$)$_2$] (**13**). We followed the process of making **11** but used ZnCl$_2$ (1.02 g, 7.5 mmol), and obtained light yellow crystals of **13** (3.5 g, yield 62.1%). Mp 302 °C. Elemental analysis (found: C, 38.52; H, 2.59; P, 8.20; Zn, 8.48%; calc. for $C_{12}H_{20}P_2Se_4Zn$: C, 38.35; H, 2.68; P, 8.24; Zn, 8.70%); ^{1}H NMR δ = 7.44 ppm (m, 12H, 4 × *p*-Ph and 4 × *m*-Ph), 7.87 ppm (ddd, 8H, J = 3.9 Hz, J = 7.1 Hz, J = 8.9 Hz, 4 × *o*-Ph).

[Cd(Ph$_2$PSe$_2$)$_2$] (**14**). We followed the process of making **11** but used CdCl$_2$ (1.37 g, 7.5 mmol), and obtained light yellow crystals of **14** (4.0 g, yield 66.7%). Mp 309 °C. Elemental analysis (found: C, 36.11; H, 2.52; P, 7.48; Cd, 13.93%; calc. for $C_{24}H_{20}P_2Se_4Cd$: C, 36.09; H, 2.52; P, 7.76; Cd, 14.08%); ^{1}H NMR δ = 7.43 ppm (m, 12H, 4 × *p*-Ph and 4 × *m*-Ph), 7.88 (m, 8H, 4 × *o*-Ph).

[Ga(Ph$_2$PSe$_2$)$_3$] (**15**). We followed the process of making **11** but used GaCl$_3$ (0.88 g, 5 mmol), and obtained yellow crystals of **15** (3.6 g, yield 65.5%). Mp 241 °C. Elemental analysis (found: C, 39.56; H, 2.76; P, 8.74; Ga 5.76%; calc. for $C_{36}H_{30}P_3Se_6Ga$: C, 39; H, 2.75; P, 8.45; Ga, 6.34%); ^{1}H NMR δ = 7.33 ppm (m, 18H, 6 × *p*-Ph and 6 × *m*-Ph), 7.76 ppm (dd, 12H, J = 6.9 Hz, J = 15.1 Hz, 6 × *o*-Ph).

[Bi(Ph$_2$PSe$_2$)$_3$] (**16**). We followed the process of making **11** but used Bi(NO$_3$)$_3$·6H$_2$0 (2.4 g, 5 mmol), and obtained orange crystals of **16** (3.9 g, yield 63.5%). Mp 203 °C. Elemental analysis (found: C, 34.67; H, 2.38; P, 7.53%; calc. for $C_{36}H_{30}P_3Se_6Bi$: C, 34.92; H, 2.44; P, 7.50%). ^{1}H NMR δ = 7.39 ppm (dd, 6H, J = 2.8 Hz, J = 7.6 Hz, 6 × *p*-Ph) 7.45 ppm (ddd, 12H, J = 3.2 Hz, J = 5.9 Hz, J = 7.4 Hz, 6 × *m*-Ph), 7.85 ppm (dd, 12H, J = 7.0 Hz, J = 15.4 Hz, 6 × *o*-Ph).

[Ni(Ph$_2$PSe$_2$)$_2$] (**17**). We followed the process of making **11** but used Ni(NO$_3$)$_2$·6H$_2$0 (2.18 g, 7.5 mmol), and obtained green crystals of **17** (3.3 g, yield 60%). Mp 220 °C. Elemental analysis (found: C, 38.67; H, 2.77; P, 8.29%; calc. for $C_{24}H_{20}P_2Se_4Ni$: C, 38.70; H, 2.71; P, 8.32%).

[Co(Ph$_2$PSe$_2$)$_2$] (**18**). We followed the process of making **11** but used CoCl$_2$·6H$_2$0 (1.77 g, 7.5 mmol), and obtained green crystals of **18** (3.0 g, yield 57%). Mp 302 °C. Elemental analysis (found: C, 39.14; H, 2.98; P, 8.03%; calc. for $C_{24}H_{20}P_2Se_4Co$: C, 38.69; H, 2.71; P, 8.31%).

Crystal data for **1**: $C_{24}H_{56}Cu_4P_4Se_8$, M_r = 1354.41, monoclinic, space group *P*2(1)/*n*, a = 12.9380(16) Å, b = 17.527(2) Å, c = 18.617(2) Å, α = 90, β = 91.453(2), γ = 90, V = 4220.3(9) Å^3, Z = 4, $\rho_{calculated}$ = 2.132 g cm^{-3}, μ= 9.056 mm^{-1}, T = 100(2) K. λ = 0.71073 Å. Reflections collected/unique = 35597/9770 [R(int) = 0.0276], final R indices [$I > 2\sigma(I)$], $R1$= 0.0309, w$R2$ = 0.0590.

Crystal data for **2**: $C_{12}H_{28}Mo_2O_2P_2Se_6$, M_r = 931.92, monoclinic, space group *P*2(1)/*c*, a = 11.5073(12) Å, b = 14.1178(15) Å, c = 16.0926(17) Å, α = 90, β = 97.671(2), γ = 90, V = 2591.0(5) Å^3, Z = 4, $\rho_{calculated}$ = 2.389 g cm^{-3}, μ = 9.525 mm^{-1}, T = 100(2) K. λ = 0.71073 Å. Reflections collected/unique = 15944/6046 [R(int) = 0.0889], final R indices [$I > 2\sigma(I)$], $R1$= 0.1043, w$R2$ = 0.1299.

Crystal data for **3**: $C_{18}H_{42}InP_3Se_6$, M_r = 940.01, monoclinic, space group *P*2(1)/*n*, a = 15.925(3) Å, b = 10.4450(17) Å, c = 37.635(6) Å, α = 90, β = 92.853(3), γ = 90 , V = 6252.3(18) Å^3, Z = 8, $\rho_{calculated}$ = 1.997 g cm^{-3}, μ = 7.901 mm^{-1}, T = 100(2) K. λ = 0.71073 Å. Reflections collected/unique = 52875/14861 [R(int) = 0.0789], final R indices [$I > 2\sigma(I)$], $R1$ = 0.0523, w$R2$ = 0.0602.

Crystal data for **4**: $C_{18}H_{42}GaP_3Se_6$, M_r = 894.91, monoclinic, space group *P*2(1)/*c*, a = 8.7140(12) Å, b = 20.684(3) Å, c = 16.941(2) Å, α = 90, β = 99.457(2), γ = 90 , V = 3012.0(7) Å^3, Z = 4, $\rho_{calculated}$ = 1.974 g cm^{-3}, μ = 8.330 mm^{-1}, T = 100(2) K. λ = 0.71073 Å. Reflections collected/unique = 25581/7111 [R(int) = 0.0309], final R indices [$I > 2\sigma(I)$], $R1$ = 0.0297, w$R2$ = 0.0541.

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