Journal of Cluster Science (2024) 35:13–22
https://doi.org/10.1007/s10876-023-02458-z

ORIGINAL PAPER

Scrambling of Metal Precursors: A Strategy to Synthesize Trinuclear $[M_3(\mu\text{-Se})_2(dppe)_3]^{2+}$ (M = Ni, Pd) and Pentanuclear $[Pd_5(\mu_3\text{-Se})_4(dppe)_4]^{2+}$ Coordination Clusters

Atharva Yeshwant Kulkarni[1] · **Saili Vikram Lokhande**[1] · **Afsar Ali Siddiki**[1] · **Rohit Singh Chauhan**[1] ·
Raymond J. Butcher[2]

Received: 14 April 2023 / Accepted: 7 June 2023 / Published online: 20 June 2023

Abstract

Reaction of $[PdCl_2(dppe)]$ with two equivalents of the sodium salt of pyridyl selenolate afforded *cis* configured complex $[Pd\{2\text{-}SeC_5H_3(5\text{-}R)N\}_2(dppe)]$ (R = H, Me). The latter complexes on reacting with two equivalent of $[NiCl_2(dppe)]$ yielded an edge centered trinuclear complex $[Ni_3(\mu\text{-Se})_2(dppe)_3]Cl_2$ (**2**) and homometallic pentanuclear aggregates of composition $[Pd_5(\mu_3\text{-Se})_4(dppe)_4][BPh_4]_2$ (**3**). Interplaying the same reaction in 1:2 molar ratio with $[Ni(SeC_5H_4N)_2(dppe)]$ and $[PdCl_2(dppe)]$, resulted in trinuclear compounds $[M_3(\mu\text{-Se})_2(dppe)_3]^{2+}$ (M = Ni, Pd) and an unidentified insoluble matrix. All the synthesized complexes were characterized by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$ NMR, IR and microanalysis. The molecular structure of the complex $[Pd\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppe)]$ and $[Pd_5(\mu_3\text{-}Se)_4(dppe)_4][BPh_4]_2$ were established through single crystal X-ray analysis. In complex $[Pd_5(\mu_3\text{-}Se)_4(dppe)_4][BPh_4]_2$, the palladium metals occupied the corner of square pyramidal geometry and the Pd···Pd distance within the dimeric unit is 3.1087 Å whereas the axial palladium-equatorial distance are 3.363 Å and 3.067 Å.

Keywords Coordination cluster · NMR · Single crystal

Introduction

The term "cluster" is described as the complex containing two or more metal atoms having direct and substantial metal-metal bonding. An involvement of numerous metals made this field interesting and quite popular [1–4]. Among the various class of cluster, 'coordination clusters' are a compound in which neighbouring metal centres are separated through non-metal atom. The presence of chalcogens in coordination clusters has made this field evolving due to geometrical evolution [5, 6], rich co-ordinations [7–9] and their tuneable physical properties like electrical conduction, magnetic behaviour and catalysis etc. [3, 10, 11]. Till today, a variety of coordination clusters have been reported ranging from nuclearity 3 to 9 but group 10 cluster complexes are limited due to their favourable planar geometry.

Prof. T. S. Hor synthesized a binuclear complex $[M_2(\mu\text{-E})(P\text{-}P)_n]$ (E = S, Se; n = 2, 4, P-P = dppe, PPh_3) which act as a metallophilic ligand to provide a binding site for incoming metal precursors [12–14]. On applying this strategy, various homonuclear [15, 16] as well as heteronuclear clusters [17, 18] have been isolated. High nucleophilicity and instability of the core "M_2E_2" (M = S, Se; M = Pd, Pt) makes this route quite inconvenient. Further new strategies have been explored in which $[MCl_2(dppe)]$ (M = Pd, Pt) is treated with Na_2E/NaEH (E = S, Se, Te) under refluxing condition to obtain edge sharing as well as corner sharing complexes $[M_3(\mu\text{-E})_2(P\text{-}P)_n]$ (E = S, Se; P-P = PPh_3, n = 6; dppe, n=3) with 10-12 % yield [19–22]. Reports related to tetranuclear and higher nuclearity is still limited in number [8]. Very few cases have been documented in which structurally characterised trinuclear $[Pd_3Se(SePh)_3(PPh_3)_3]Cl$ as well as hexanuclear $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6]$ complex has been yielded through the interplay of metal $[(PdCl_2(PPh_3)_2]$ to ligand ($PhSe^-$) molar ratio of 2:1 and 1:2 respectively [23]. Similar isostructural species $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6]$,

✉ Rohit Singh Chauhan
rohit.chauhan@somaiya.edu

[1] Department of Chemistry, K. J. Somaiya College of Science and Commerce, Vidyavihar, Mumbai 400077, India

[2] Department of Chemistry, Howard University, Washington, DC 20059, USA

$[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ were also isolated on performing an oxidative addition reaction between $[Pd(PPh_3)_4]$ with Ar_2Te_2 (Ar = Ph, Th) in chlorinated solvents [24].

Recently, our group has explored the reactivity of mononuclear $[M(SeC_5H_4N)_2(dppe)]$ (M = Ni, Pt) towards diamagnetic precursor $[M(OAc)_2]$ (Zn, Cd etc.) and obtained an adduct product $[\{Pt(SeC_5H_4N)_2(dppp)\}MCl_2]$ (M= Zn, Cd) [25] whereas the tetranuclear complex $[\{Ni_2(\kappa^2\text{-}SeC_5H_4N)_2(\mu\text{-}OCH_3)_2CdCl_2\}_2]$ was isolated in case of nickel in quantitatively good yield at room temperature. The outcome of the thermal studies for complex $[\{Ni_2(\kappa^2\text{-}SeC_5H_4N)_2(\mu\text{-}OCH_3)CdCl\}_2]$ corresponds the dissociation at 220 °C and pXRD pattern indicates the formation of both NiSe and CdSe phase. To investigate further this complex was thermolyzed to obtain the heterostructures of Ni-Se/Cd-Se through solvothermal method [26]. The presence of rigid backbone (framed by chelated phosphane ligand) and availability of chalcogen and pyridyl nitrogen provide the binding sites for incoming substrate as building block. With this prospect, we thought to explore the *cis* configured mononuclear complex $[M\{2\text{-}SeC_5H_3(5\text{-}R)N\}_2(dppe)]$ (M = Ni, Pd) (Fig. 1) as a building block to synthesize high nuclearity complexes at an ambient temperature. The outcomes of our findings are discussed herein.

Experimental

Chemical

All the reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Solvents used during the reactions were purified and dried by applying standard procedures [27]. The compound $NiCl_2{\cdot}6H_2O$, $PdCl_2$ and 1,2-bis(diphenylphosphino)ethane were procured from Sigma Aldrich and used without further purification. The metal precursor complexes $[MCl_2(dppe)]$ (M = Ni, Pd) [28], $[Ni(2\text{-}SeC_5H_4N)_2(dppe)]$ [29] and the ligands $(SeC_5H_4N)_2$

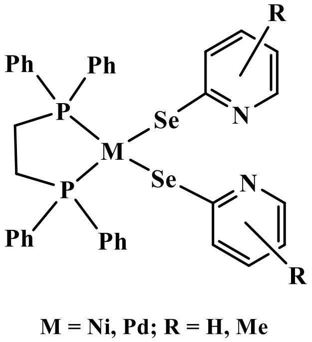


Fig. 1 Structure of mononuclear bis mono-nuclear complex $[M\{2\text{-}SeC_5H_3(5\text{-}R)N\}_2(dppe)]$ (R = H, Me; M = Ni, Pd)

[30], $[\{SeC_5H_3(5\text{-}Me)N\}_2]$ [31] were prepared according to literature procedures.

Instrumentation

The ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra were recorded on a Bruker Avance-III spectrometer operating at 600.17, 150.1, 242.95, 114.46 MHz, respectively at 298K. ^{1}HNMR and $^{13}C\{^1H\}$ spectra were referenced with the solvent peak of chloroform at δ 7.26 ppm, externally to 85% H_3PO_4 (0.00 ppm) for ^{31}P NMR, and externally to Ph_2Se_2 (δ 463 ppm relative to Me_2Se) in $CDCl_3$ for $^{77}Se\{^1H\}$ NMR. FTIR spectra of solid complexes were studied using KBr pellet on PerkinElmer FTIR model spectrophotometer over a range of 4000–400 cm^{-1}. Elemental analyses were carried out on a Thermo Fischer EA1112 CHNS analyzer.

Single crystal X-ray data for $[Pd\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppe)]$ (**1b**) and $[Pd_5(\mu_3\text{-}Se)_4(dppe)_4]^{2+}$ (**3**) were collected at 100K, on using a SuperNova, dual with diffraction source micro-focus sealed X-ray tube, Mo-K_α radiation (λ = 0.71073 Å) and synchrotron (λ = 0.41032 Å), respectively. Intensity data were collected using ω steps CCD area detector images spanning at least a hemisphere o reciprocal space. The crystal structures of the complexes **1b** and **3** were solved using SHELXT [32]. Numerical absorption correction was done by gaussian integration over a multifaceted crystal model for $[Pd\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppe)]$ (**1b**) whereas semiempirical absorption from equivalents was applied for complex $[Pd_5(\mu_3\text{-}Se)_4(dppe)_4]^{2+}$ (**3**). All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in calculated positions. Molecular structures of complex **1b** and **3** were generated using Mercury 2020.3.0 [33]. In case of complex $[Pd_5(\mu_3\text{-}Se)_4(dppe)_4](BPh_4)$ (**3**), Some of the phenyl rings had disorder and SQUEEZE was used for disordered solvent. Crystallographic and structural determination data are listed in Table 1.

Syntheses of Complexes

Synthesis of $[Pd(2\text{-}SeC_5H_4N)_2(dppe)]$ (1a)

To a toluene-methanol solution (10 cm^3) of $NaSeC_5H_4N$ [freshly prepared an *in situ* from $\{SeC_5H_4N\}_2$ (45 mg, 0.12 mmol) and $NaBH_4$ (10 mg, 0.26 mmol)], $[PdCl_2(dppe)]$ (98 mg, 0.12 mmol) was added and the resultant mixture stirred for 5 h at room temperature. The solvents were evaporated in vacuo and the compound was washed with hexane and diethyl ether. The residue was extracted with acetone and passed through a celite column to afford yellow crystals of title compound. (Yield: 87 mg, 67%; m.p.:176 °C (dec.)). Anal. Calcd. for $C_{36}H_{32}N_2P_2PdSe_2$: C, 52.69; H, 3.93; N, 3.42%. Found: C, 52.70; H, 3.94; N, 3.34%. IR (KBr, cm^{-1}):

Table 1 Crystallographic and structural determination data for [Pd{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)] (**1b**) and [Pd$_5$(μ$_3$-Se)$_4$(dppe)$_4$][BPh$_4$]$_2$ (**3**)

Complex	[Pd{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)] (**1b**)	[Pd$_5$(μ$_3$-Se)$_4$(dppe)$_4$][BPh$_4$]$_2$ (**3**)
Chemical formula	$C_{38}H_{36}N_2P_2PdSe_{1.97}$	$C_{152}H_{136}B_2P_8Pd_5Se_4$
Formula wt.	844.97	3079.82
Crystal size (mm^3)	0.235 × 0.198 × 0.126	0.09 × 0.05 × 0.03
Wavelength (Å)	0.71073	0.41032
Crystal system	Monoclinic	Monoclinic
Space group	C 2/c	C 2/c
Unit cell dimensions		
a (Å)	31.4488(12)	36.526(3)
b (Å)	15.2053(5)	16.5000(11)
c (Å)	17.5195(6)	31.413(2)
α (°)	90	90
β (°)	108.4450(10)	122.166(2)
γ (°)	90	90
Volume (Å^3)	7947.2(5)	16026(2)
ρ_{cacld}.	1.412 g/cm^3	1.276 mg/m^3
Z	8	4
μ (mm^{-1})/F(000)	2.406/3376	1.011 /6176
Limiting indices	$-39 \le h \le 39$	$-43 \le h \le 44$
	$-19 \le k \le 19$	$-20 \le k \le 20$
	$-21 \le l \le 21$	$-38 \le l \le 38$
θ for data collection(min/max°)	4.142 / 52.816	0.813 /14.636
No of reflections collected	70422	188856
No of independent reflection (R_{int})	8133(0.0608)	14855(0.1043)
Data/restraints/parameters	8133/0/410	14855/528/833
Final R$_1$, wR$_2$ indices ($I > 2\sigma I$)	0.0270/0.0598	0.0486, 0.1241
R$_1$, wR$_2$ (all data)	0.0390, 0.0640	0.0835, 0.1504
Goodness of fit on F^2	1.019	1.009

1567 (s), 1545 (m), 1483 (w), 1434 (s, coupled), 1401 (s), 1266 (w), 1101 (s), 1077 (m), 1026 (w), 980 (m), 874 (w), 738 (m), 687 (s), 648 (m), 617 (m), 529 (s), 480 (m), 461 (s).^{1}H NMR (CDCl$_3$) δ: 2.29 (br, $^1J_{P–H}$ = 18 Hz, 4H, –PCH$_2$), 6.82 (t, $^1J_{H–H}$ = 3.4 Hz, 2H, C$_5$*H*$_4$N), 7.28–7.24 (m, Ph+C$_5$*H*$_4$N, 10H), 7.43–7.35 (m, Ph, 8H), 7.82–7.74 (m, Ph, 8H), 8.49 (d, ^{1}J = 4.2 Hz, 2H, C$_5$H$_4$N); ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 29.57 (d, $^1J_{P–C}$ = 39 Hz), 117.5, 128.53, 128.92, 130.86, 133.58 (d, $^1J_{c–p}$ =19.9 Hz), 148.02, 161.49; ^{31}P{^{1}H} NMR (CDCl$_3$) δ: 53.5; ^{77}Se{^{1}H}NMR (CDCl$_3$) δ: 263.7 ppm (d, $^2J_{P–Se}$ = 95.35 Hz).

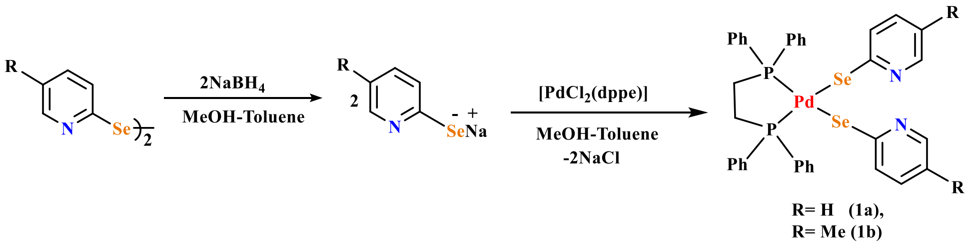
Synthesis of [Pd{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)] (1b)

An acetone suspension of [PdCl$_2$(dppe)] (100 mg, 0.17 mmol) was added to a toluene-methanol solution (10 cm^3) of NaSeC$_5$H$_3$(5-Me)N [freshly prepared an *in situ* from [SeC$_5$H$_3$(5-Me)N]$_2$ (60 mg, 0.17 mmol) and NaBH$_4$ (13.3 mg, 0.35 mmol)]. The reaction mixture was stirred for 5 h at room temperature and the solvents were evaporated *in vacuo*. The product was extracted with acetone and passed through a celite column to yield red crystals of compound **1b**. (Yield: 110 mg, 73%; m.p.:180 °C (dec.)). Anal. Calcd. for C$_{38}$H$_{36}$N$_2$P$_2$PdSe$_2$: C, 53.89; H, 4.28; N, 3.31%. Found: C, 53.58; H, 4.12; N, 3.28%. IR (KBr, cm^{-1}): 2628 (m), 2427 (m), 2311 (m), 2271 (m), 2200 (m), 1450 (s), 1436 (s), 1362 (m), 1187 (m), 1101 (s), 1095 (s), 1024 (m), 983 (s), 875 (m), 818 (m), 746 (m), 712 (m), 691 (s), 525 (s), 439 (s). ^{1}H NMR (CDCl$_3$) δ: 2.11 (s, 6H, C*H*$_3$), 2.26 (d, $^1J_{P–H}$ = 30 Hz, 4H, –PCH$_2$), 6.62 (d, ^{1}J = 5.4Hz, 2H), 7.29–7.37 (m, 10H, Ph), 7.39–7.44 (m, 10H, Ph), 7.78–7.75 (m, 2H, Ph), 8.92 (br, 2H, C$_5$H$_4$N); ^{13}C{^{1}H} NMR (CDCl$_3$) δ: 3.2, 17.8, 126.9, 128.5, 129.3, 130.9, 131.6, 132.9, 133.6, 134.6, 148.4; ^{31}P{^{1}H}NMR (CDCl$_3$) δ: 52.60 ppm; ^{77}Se{^{1}H} NMR (CDCl$_3$) δ: 263.09 ppm (d, $^2J_{P–Se}$ = 95.54 Hz).

Synthesis of [Ni$_3$(μ-Se)$_2$(dppe)$_3$]Cl$_2$ (2) and [Pd$_5$(μ$_3$-Se)$_4$(dppe)$_4$][BPh$_4$]$_2$ (3)

(i) A dichloromethane solution (15 cm^3) of [Pd(2-SeC$_5$H$_4$N)$_2$(dppe)] (60 mg, 0.07 mmol) was added to a solution of [NiCl$_2$(dppe)] (77 mg, 0.15 mmol) in same

Scheme 1 Reactions of $[PdCl_2(dppe)]$ with sodium salt of pyridyl selenolates.



solvent and stirred for 2 hours. The resulting mixture was treated with $NaBPh_4$ (50 mg, 0.15 mmol) and the stirring was continued for 24 hours at room temperature. The ensuing solution was filtered through G3 assembly and the filtrate was concentrated to minimum volume and kept for crystallization at − 5 °C, to obtain red crystals of $[Ni_3(\mu\text{-}Se)_2(dppe)_3]Cl_2$ (**2**) (Yield: 21 mg, 13.5%, m.p.: 212°C (dec)). Anal. Calcd. for $C_{78}H_{72}Cl_2P_6Ni_3Se_2$: C, 58.57; H, 4.54%. Found: C, 58.45; H, 4.52%. IR (KBr, cm^{-1}): 2570 (m), 2481 (m), 2350 (m), 2310 (s), 2080 (w), 1914 (s), 1880 (m), 1869 (w), 1716 (m), 1669 (m), 1653 (s), 1647 (m), 1635 (w), 1584 (s), 1506 (s), 1481 (m), 1457 (w), 1436 (w), 1418 (m), 1339 (s), 1319 (m), 1307 (s), 1267 (m), 1235 (s), 1187 (w), 1122 (w), 1102 (m), 1071 (m), 1027 (s), 998 (m), 921 (s), 877 (m), 817 (s), 762 (m), 740 (s), 730 (m), 718 (w), 713 (w), 701 (w), 654 (m), 616 (s), 483 (s), 478 (m), 408 (s). ^1H NMR ($CDCl_3$) δ: 2.54 (br, 12H, P–CH_2), 7.12–7.42 (m, 12H, Ph), 7.45–7.55 (m, 24H, Ph), 7.72 (br, 24H, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 30.62 ppm, and yellow crystals of compound $[Pd_5(\mu_3\text{-}Se)_4(dppe)_4][BPh_4]_2$ (**3**) (Yield: 13 mg, 28.9%, m.p.: 292°C (dec)); Anal. Calcd. for $C_{152}H_{136}B_2P_8Pd_5Se_4$: C, 59.22; H, 4.32%. Found: C, 59.12; H, 4.22%. IR (KBr, cm^{-1}): 3340 (br), 3053 (m), 1658 (m), 1481 (s), 1434 (s), 1413 (m), 1305 (w), 1097 (m), 1081 (s), 1038 (m), 997 (s), 878 (m), 837 (s), 830 (m), 742 (w), 687 (s), 556 (m), 521 (s), 465 (s), 461 (s); ^1H NMR ($CDCl_3$) δ: 2.51 (d, $^1J_{P\text{–}H}$ = 42 Hz, 8H, –PCH_2), 7.15 (t, $^1J_{H\text{–}H}$ = 12 Hz, 8H), 7.34–7.38 (m, 40H, Ph), 7.49 (br, 40H, Ph), 7.56 (br, 40H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 27.7, 128.8, 130.7, 130.8, 130.9, 131.8, 132.1, 133.6, 167.2; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 42.9 ppm.

(ii) Similarly, $[Pd\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppe)]$ (50 mg, 0.06 mmol) along with $[NiCl_2(dppe)]$ (63.24 mg, 0.12 mmol) and $NaBPh_4$ (41 mg, 0.12 mmol) resulted in red crystals of $[Ni_3(\mu\text{-}Se)_2(dppe)_3]Cl_2$ (**2**) (Yield: 19 mg, 12.2%, m.p.: 212°C (dec)). Anal. Calcd. for $C_{78}H_{72}Cl_2P_6Ni_3Se_2$: C, 58.55; H, 4.54%. Found: C, 58.35; H, 4.51%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 31.73 ppm, and yellow crystals of compound $[Pd_5(\mu_3\text{-}Se)_4(dppe)_4][BPh_4]_2$ (**3**) (Yield: 10 mg, 22.2%, m.p.: 292°C (dec)). Anal. Calcd. for $C_{152}H_{136}B_2P_8Pd_5Se_4$: C, 59.28; H, 4.41%. Found: C, 59.16; H, 4.36%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 42.9 ppm.

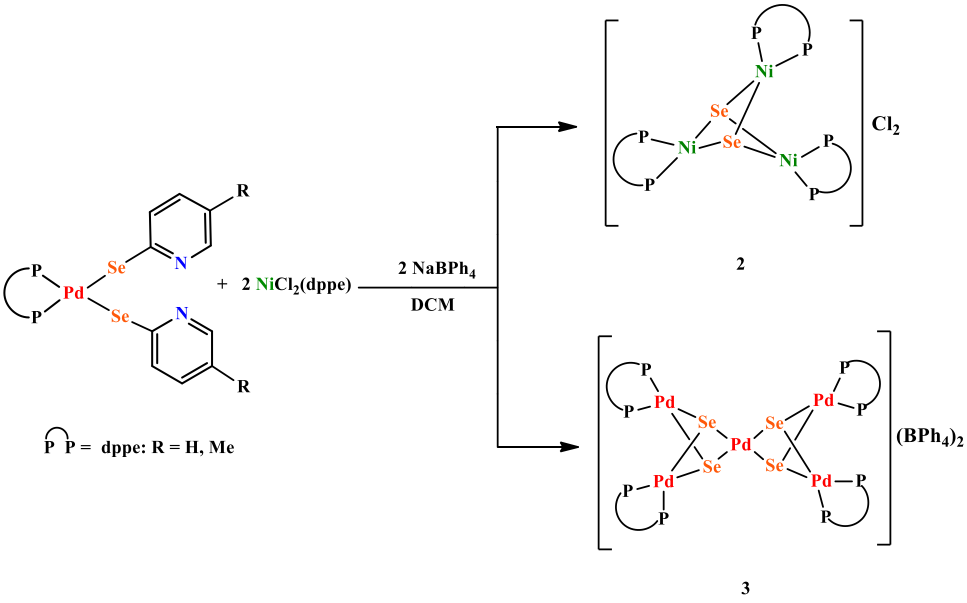
Synthesis of $[Ni_3(\mu\text{-}Se)_2(dppe)_3]Cl_2$ (2) $[Pd_3(\mu\text{-}Se)_2(dppe)_3][BPh_4]_2$ (4)

A dichloromethane solution (15 cm^3) of $[Ni(2\text{-}SeC_5H_4N)_2(dppe)]$ (50 mg, 0.06 mmol) was added to a suspension of $[PdCl_2(dppe)]$ (75 mg, 0.13 mmol) in the same solvent. To the latter resulting mixture, $NaBPh_4$ (45 mg, 0.13 mmol) was added and stirred for 24 hours at room temperature. Mixture was reduced *in vacuo* and powder was extracted with dichloromethane to yield red crystals of compound $[Ni_3(\mu\text{-}Se)_2(dppe)_3]Cl_2$ (**2**) (Yield: 16 mg, m.p.: 215°C (dec)). Anal. Calcd. for $C_{78}H_{72}Cl_2P_6Ni_3Se_2$: C, 58.55; H, 4.54%. Found: C, 58.39; H, 4.50%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 30.2 ppm and orange crystals of $[Pd_3(\mu\text{-}Se)_2(dppe)_3][BPh_4]_2$ (**4**) (yield 22 mg, 10.9%, m.p.: 292 °C (dec.)). Anal. Calcd. for $C_{126}H_{112}B_2P_6Pd_3Se_2$: C, 65.45; H, 4.89%. Found: C, 65.21; H, 4.46%. IR (KBr, cm^{-1}): 2984 (w), 2678 (m), 2311 (s), 2109 (m), 2054 (w), 1967 (m), 1894 (m), 1879 (w), 1748 (w), 1696 (m), 1669 (w), 1654 (s), 1635 (m), 1584 (s), 1570 (w), 1559 (w), 1540 (s), 1507 (m), 1470 (w), 1457 (m), 1496 (s), 1185 (m), 1161 (m), 1103 (m), 1072 (m), 1027 (s), 998 (w), 986 (w), 921 (m), 841 (m), 819 (w), 748 (m), 717 (w), 705 (s), 689 (m), 654 (m), 616 (w), 557 (w), 484 (s), 397 (m), 375 (w), 369 (m). ^1H NMR ($CDCl_3$) δ: 2.5 (d, $^1J_{P\text{–}H}$ = 42 Hz), 7.43–7.36 (m, 28H, Ph), 7.43 (br, 26H, Ph), 7.56–7.50 (m, 27H, Ph), 7.84 (br, 24H, Ph); $^{13}C\{^1H\}$NMR ($CDCl_3$) δ: 29.7, 117.1, 119.3, 129.2, 132.3, 133.6, 134.2, 148, 161.5; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 50.3; $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ: − 134.3 ppm.

Results and Discussion

The reaction of $[PdCl_2(dppe)]$ with two equivalents of the sodium salt of pyridyl selenolate (freshly prepared by reductive cleavage of Se–Se bond of corresponding dipyridyl diselenide through $NaBH_4$) resulted in the *cis* configured complex $[Pd\{2\text{-}SeC_5H_3(5\text{-}R)N\}_2(dppe)]$ (R = H (**1a**); Me (**1b**)) (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of complex $[Pd(2\text{-}SeC_5H_4N)_2(dppe)]$ (**1a**) and $[Pd\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppe)]$ (**1b**) displayed a single resonance at 53.5 and 52.5 ppm respectively. Jain et.al reported that a similar reaction with pyrimidyl selenolate derivatives on extracting with

Scheme 2 Reaction of [Pd{2-SeC_5H_3(5-R)N}$_2$(dppe)] with [$NiCl_2$(dppe)].



the dichloromethane afforded selenido bridged trinuclear complex [Pd_3(μ-Se)$_2$(dppe)$_3$]$^{2+}$ due to nucleophilic attack of the chlorinated solvent on the Se–C bond [34]. The ^{77}Se{^{1}H} NMR spectrum of complex [Pd{2-SeC_5H_3(5-R)N}$_2$(dppe)] (R = H/**1b**, Me/**1b**) showed a single resonance at ~ 263 ppm with a coupling constant ~ 95 Hz which in good conformity with reported values [35].

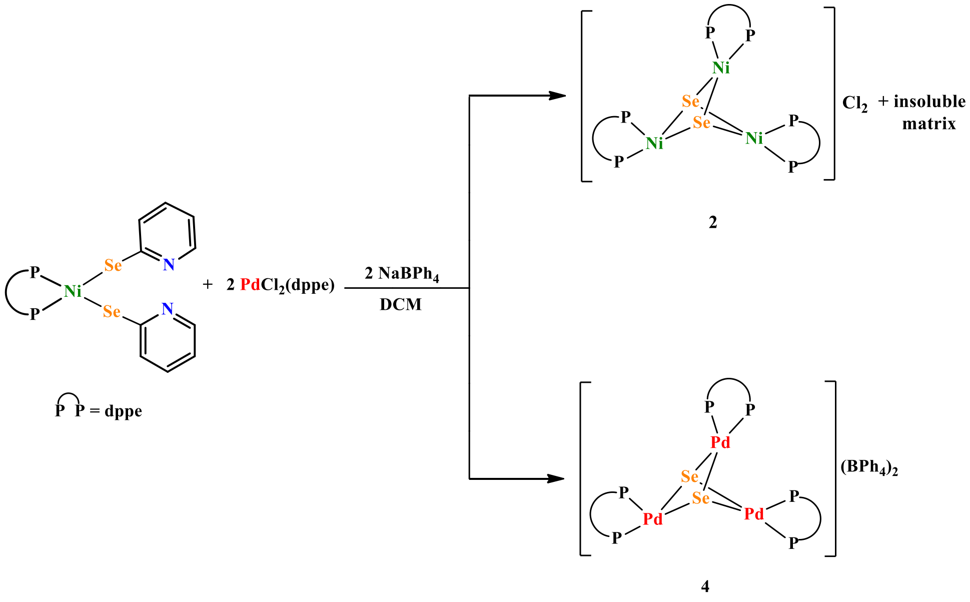
The reaction between [Pd(SeC_5H_4N)(dppe)] and two equivalents of [$NiCl_2$(dppe)] afforded two different complexes. Among them the red crystals referred to a complex having a composition [Ni_3(μ-Se)$_2$(dppe)$_3$]Cl_2 (**2**), whereas the yellow one belongs to pentanuclear compound [Pd_5(μ$_3$-Se)$_4$(dppe)$_4$][BPh_4]$_2$ (**3**) (Scheme 2). The formation of latter mentioned complexes can be explain with the help of two different in situ reactions. First step involves the scrambling of metals (exchange of Ni and Pd), followed by the cleavage of Se–C bond due to the nucleophilic attack of dichloromethane. The main aim was to isolate heteronuclear cluster core of Pd_2Ni/Ni_2Pd. Contrary to our expectations, pentanuclear as well as trinuclear homonuclear complexes were obtained. The presence of only one resonance signal in complex at 42.9 ppm in ^{31}P{^{1}H} NMR spectrum indicates magnetic equivalence of all phosphorous nuclei present in the pentanuclear cluster [Pd_5(μ$_3$-Se)$_4$(dppe)$_4$][BPh_4]$_2$. A notable shielded behaviour of peak is expected due to high metal content compared to trinuclear complex [Pd_3(μ-Se)$_2$(dppe)$_3$]$^{2+}$ (E = Se, Te). Second product of the reaction [Ni_3(μ-Se)$_2$(dppe)$_3$]$^{2+}$ showed a resonance at 31.5 ppm which is in good agreement with reported values. Both complex [Ni_3(μ-Se)$_2$(dppe)$_3$]Cl_2 (**2**) and [Pd_5(μ$_3$-Se)$_4$(dppe)$_4$][BPh_4]$_2$ (**3**) were also synthesized through the reaction between [Pd(5-MeSepy)$_2$(dppe)] and two moles of [$NiCl_2$(dppe)]. Differ to our finding Nakagawa and co-workers have elegantly demonstrated the reaction of ditolyl-ditelluride with [Cp*Ir(CO)$_2$] to isolate an expected mononuclear complex [Cp*Ir(CO)(TeTol)$_2$] which on further treatment with the latter tellurolate complex with [M(PPh$_3$)$_4$] (M = Pd, Pt) yielded a trinuclear heterometallic cluster having formula [{Cp*Ir(CO)}(μ$_3$-Te)$_2${MTol(PPh$_3$)}$_2$] (M = Pd, Pt) [36].

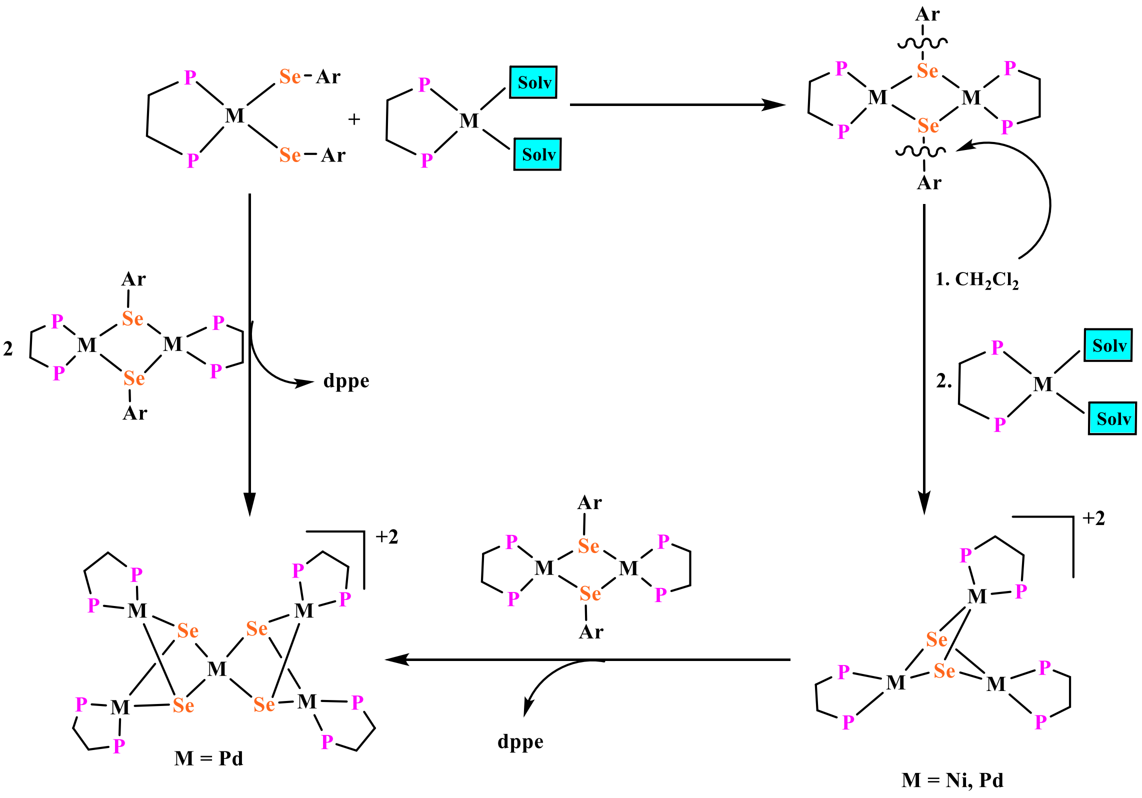
On switching the mole ratio between [$PdCl_2$(dppe)] and [Ni(SeC_5H_4N)(dppe)] in 2:1, afforded trinuclear complexes [M_3(μ-Se)$_2$(dppe)$_3$]$^{2+}$ (M = Ni, Pd) as well as an unidentified insoluble matrix (Scheme 3). The ^{31}P{^{1}H} NMR spectra of complexes [Ni_3(μ-Se)$_2$(dppe)$_3$]Cl_2 (**2**), [Pd_3(μ-Se)$_2$(dppe)$_3$][BPh_4]$_2$ (**4**), displayed a single resonance at 30.2 ppm and 50.3 ppm respectively and an appearance of single resonance signal in [M_3(μ-Se)$_2$(dppe)$_3$]$^{2+}$ (M = Ni, Pd) accounts that all the phosphorous atoms present in both the complexes are magnetically equivalent in nature. The formations of latter complexes were further corroborated by structure with help of single crystal X-ray diffraction. Due to poor R values their structures are not discussed here.

Reaction Pathways

The formation of binuclear complex of composition [Pd_2(μ-SeR)$_2$(SeR)$_2$(PR'$_3$)$_2$] is well reported in literature which were obtained through an oxidative addition of diorgano-diselenides to zero valent Palladium derivatives such as [Pd(PPh$_3$)$_4$], Pd_2(dba)$_3$/PR'$_3$ [37]. The resulting nucleophilic "M_2Se_2" core, on treating with an electrophilic chlorinated solvent afforded cleavage of Se–C bond to obtain trinuclear complex [Ni_3(μ-Se)$_2$(dppe)$_3$]Cl_2 (**2**) (Scheme 4) [38]. The complexes of later composition i.e. [Pd_5(μ$_3$-Se)$_4$(dppe)$_4$][BPh_4]$_2$ can be explained by

Scheme 3 Reaction of $[Ni(SeC_5H_4N)_2(dppe)]$ with $[PdCl_2(dppe)]$.





Scheme 4 Plausible mechanism for the formation of various clusters from mononuclear compounds [M = Ni, Pd; Ar = C_5H_4N, $C_5H_3(5\text{-}Me)N$]

considering an *in situ* formation of metallophilic ligand "M_2Se_2" (M= Pd) which on dimerization followed by addition of one equivalent of monomer unit resulted rare example of pentanuclear complex $[Pd_5(\mu_3\text{-}Se)_4(dppe)_4][BPh_4]_2$ (**3**). Secondly, it is also possible that trinuclear complex $[Pd_3(\mu\text{-}Se)_2(dppe)_3)]^{2+}$ on reacting with binuclear complex $[Pd_2(\mu\text{-}Se)_2(dppe)_2]^{2+}$ core resulted a pentanuclear complex (Scheme 4) [21, 22]. However, Hor and their co-workers reported that reaction of $[Pt_2(\mu\text{-}E)_2(dppe)_2]$ (E= S, Se) with $[PdCl_2(dppe)]$ in 1:1 molar ratio resulted range of product

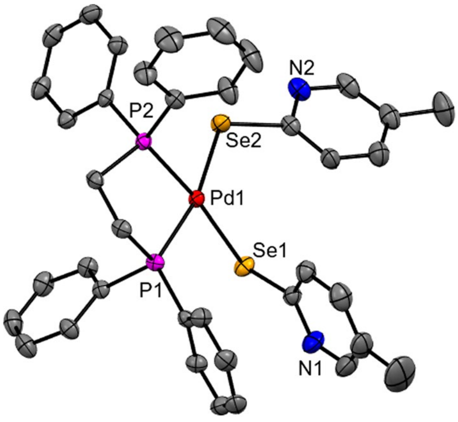


Fig. 2 Crystal structure of [Pd{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)] (**1b**) drawn from mercury. Hydrogen atoms are omitted for clarity. The ellipsoids were drawn at the 25% probability.

composition [Pd$_x$Pt$_{3-x}$(dppe)$_3$(μ-E)]$^{2+}$ (x = 1 to 1.5; E = S, Se) [39]. An attempt to isolate pentanuclear aggregates was also performed but examples of homonuclear moiety are limited in number. In few cases heterometallic pentanuclear clusters [M{Pt$_2$(μ-E)$_2$(dppe)]$^{+2}$ (M = Zn, Cd, Hg; E = S, Se) had obtained through treatment of [Pt$_2$(μ-E)$_2$(dppe)$_2$]$^{2+}$ precursor with respective metal perchlorates in 2:1 molar ratio respectively.

Crystal Structure

The molecular structures of [Pd{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)] (**1b**) and [Pd$_5$(μ$_3$-Se)$_4$(dppe)$_4$][BPh$_4$]$_2$ (**3**) have been established by Single Crystal X-ray diffraction analysis (Figs. 2 and 3). Selected interatomic parameters of the complex [Pd{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)] (**1b**) and [Pd$_5$(μ$_3$-Se)$_4$(dppe)$_4$]$^{2+}$ (**3**) are summarized in Tables 2 And 3, respectively.

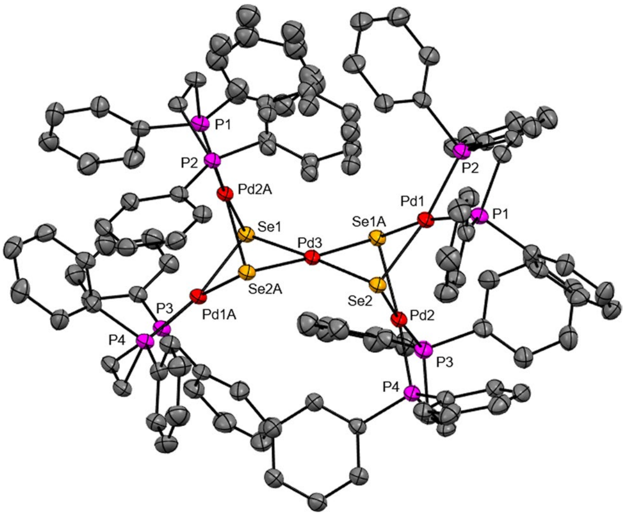


Fig. 3 Crystal structure of [Pd$_5$(μ$_3$-Se)$_4$(dppe)$_4$][BPh$_4$]$_2$ (**3**) drawn from mercury. Counter-anion and hydrogen atoms are omitted for clarity. The ellipsoids were drawn at the 25% probability.

Table 2 Selected bond lengths (Å) and angles (°) of [Pd{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)] (**1b**)

Pd(1)–P(1)	2.2891(6)	Pd(1)–P(2)	2.2779(6)
Pd(1)–Se(1)	2.4729(3)	Pd(1)–Se(2)	2.4709(3)
Se(1)–C(6)	1.893(3)	Se(2)–C(7)	1.910(3)
P(1)–Pd(1)–P(2)	85.39(2)	Se(1)–Pd(1)–Se(2)	96.481(11)
P(1)–Pd(1)–Se(1)	91.049(17)	P(2)–Pd(1)–Se(2)	85.956(17)
P(1)–Pd(1)–Se(2)	166.924(19)	P(2)–Pd(1)–Se(1)	173.026(19)

Cis configured mononuclear complex [Pd{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)] (**1b**) has adopted a distorted square planar geometry, where co-ordination core has defined through 'P$_2$Se$_2$' donor atoms. The bond distances Pd(1)-Se(1)/Pd(2)-Se(2) are 2.4729(3) and 2.4709(3) Å in compound [Pd{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)] (**1b**) are slightly elongated compared to the compound [Pd{4-SeC$_5$H$_4$N}$_2$(dppe)] (Pd–Se 2.4750–2.4777 Å) [40] while, Pd–P bond lengths (2.2779–2.2891 Å) are slightly longer compared to [Pd(SePh)$_2$(dppe)] (Pd–P = 2.270–2.274 Å) [41] and [Pd(SeTh)$_2$(dppe)] (Pd–P = 2.265–2.274 Å) [42]. The chelate bond angle P(1)–Pd(1)–P(2) is [85.39°(2)] is acute in nature as consequence opposite bond angle Se(1)–Pd(1)–Se(2) is get opened to 95.56°(3) to accommodate the pyridyl ring which is deviated from the plane.

Pentanuclear palladium cluster [Pd$_5$(μ$_3$-Se)$_4$(dppe)$_4$][BPh$_4$]$_2$ crystallizes in monoclinic fashion, in which two dinuclear units "[Pd$_2$(Se$_2$(dppe)$_2$]" are coordinated to palladium Pd(3) via bridging selenium atoms [Se(1), Se(1A), Se(2), Se(2A)] of dinuclear unit. The cluster is centrosymmetric in nature as Pd$_2$Se$_2$ coordination planes pass through common [PdSe$_4$]$^{2-}$ plane of axis. Palladium atoms in complex [Pd$_5$(μ-Se)$_4$(dppe)$_4$]$^{2+}$ occupy at corner of headed fused two triangles. The side of the triangles Pd(1A)···Pd(2A)/Pd(1A)···Pd(3) and Pd(2A)···Pd(3) are 3.109/3.363/3.062 Å (Fig. 4a) which are in the range of Van der Waals radii of palladium atoms to show weak metallophilic interaction among them. The distance between two asymmetric fragment [Pd$_2$(μ-Se)$_2$(dppe)$_2$]$^{2+}$ is 5.632 Å, which is higher than interaction range. The neighbouring Se(1)···Se(2A) bond distance (within asymmetric unit) 3.261 Å and Se(1)···Se(1A)/Se(2)···Se(2A) (between asymmetric fragment) is 3.644 Å (Fig. 4b) corresponds to close fragment and comparable to [Ni$_3$(μ-Se)$_2$(dppe)$_3$]$^{2+}$ (Se···Se = 3.1 Å). The bond angle present in the core of "[Pd$_2$Se$_2$(dppe)$_2$]" i.e. Pd(1)–Se(1A)–Pd(2) and Pd(2)–Se(2)–Pd(1) is 77.97° and 78.36° which is shorter than reported higher congeners of pentanuclear cluster [Pd$_5$(μ$_3$-Te)$_4$(dppe)$_4$]$^{2+}$ (79.32° and

Table 3 Selected bond lengths (Å) and angles (°) of $[Pd_5(\mu_3\text{-}Se)_4(dppe)_4]^{2+}$ (**3**)

Pd(1)–P(1)	2.2520 (16)	Pd(1)–P(2)	2.2572(16)
Pd(2)–P(3)	2.2825(16)	Pd(2)–P(4)	2.2788(16)
Pd(1A)–P(3)	2.2825(16)	Pd(1A)– (4)	2.2788(16)
Pd(2A)– (2)	2.2520 (16)	Pd(2A)–P(1)	2.2572(16)
Pd(1)–Se(1A)	2.4767(7)	Pd(1)–Se(2)	2.4620(7)
Pd(2)–Se(1A)	2.4648(7)	Pd(2)–Se(2)	2.4586(7)
Pd(1A)–Se(1)	2.4648(7)	Pd(1A)–Se(2A)	2.4586(7)
Pd(2A)–Se(1)	2.4767(7)	Pd(2A)–Se(2A)	2.4620(7)
Pd(3)–Se(1A)	2.444(7)	Pd(3)–Se(2)	2.4472(7)
Pd(3)–Se(2A)	2.4471(7)	Pd(3)–Se(1)	2.444(7)
P(1)–Pd(1)–P(2)	86.96(6)	P(4)–Pd(2)–P(3)	85.78(6)
P(3)–Pd(1A)–P(4)	85.78(6)	P(1)–Pd(2A)–P(2)	86.96(6)
Se(1A)–Pd(1)–Se(2)	82.63(2)	Se(1A)–Pd(2)–Se(2)	82.94(2)
Se(2A)–Pd(1A)–Se(1)	82.94(2)	Se(2A)–Pd(2A)–Se(1)	82.63(2)
Se(1A)–Pd(1)–P(2)	174.18(5)	Se(2)–Pd(1)–P(1)	176.25(5)
Se(1A)–Pd(2)–P(3)	97.89(5)	Se(2)–Pd(2)–P(4)	95.15(5)
Se(2A)–Pd(1A)–P(4)	95.15(5)	Se(1)–Pd(1A)–P(3)	97.89(5)
Se(2A)–Pd(2A)–P(2)	174.18(5)	Se(1)–Pd(2A)–P(1)	174.18(5)
Pd(1)–Se(1A)–Pd(2)	77.97(2)	Pd(1)–Se(2)–Pd(2)	78.36(2)
Pd(1A)–Se(2A)–Pd(2A)	78.36(2)	Pd(1A)–Se(1)–P(2A)	77.97(2)
Pd(3)–Se(1A)–Pd(1)	86.47(2)	Pd(3)–Se(1A)–Pd(2)	77.17(2)
Pd(3)–Se(2)–Pd(1)	77.17(2)	Pd(3)–Se(2)–Pd(2)	86.54(2)
Pd(3)–Se(2A)–Pd(1A)	86.54(2)	Pd(3)–Se(2A)–Pd(2A)	77.17(2)
Pd(3)–Se(1)–Pd(2A)	86.47(2)	Pd(3)–Se(1)–Pd(1A)	76.95(2)
Se(1A)–Pd(3)–Se(2)	83.60(2)	Se(2)–Pd(3)–Se(2A)	96.59(4)
Se(2A)–Pd(3)–Se(1)	83.60(2)	Se(1)–Pd(3)–Se(1A)	96.38(3)
Se(1A)–Pd(3)–Se(2A)	176.853(16)	Se(1)–Pd(3)–Se(2)	176.855(16)

79.64°) [43] and greater than heterometallic cluster $[Pt\{[Pd(dppe)]_2(\mu_3\text{-}Te)_2\}_2]^{2+}$ (78.02° and 78.14°) (Table 4) [44].

The Pd–Se bond lengths are ranging between 2.444(7) and 2.4767(7) Å which are quite close to $[Pd_3Se(SePh)_3(PPh_3)_3]Cl$ (Pd–Se = 2.4477–2.4584 Å) [23] and $[Pd_3(\mu\text{-}Se)_2(dppe)_3]^{2+}$ (Pd–Se = 2.4425(5)–2.4785(5) Å) [45]. The bond angles Se(1A)–Pd(1)–Se(2), 82.63° and Se(2)–Pd(2)–Se(1A) (82.94) are acute in nature which as a consequence opened up the opposite bond angle P(2)–Pd(1) P(1) and P(3)–Pd(2)–P(4).

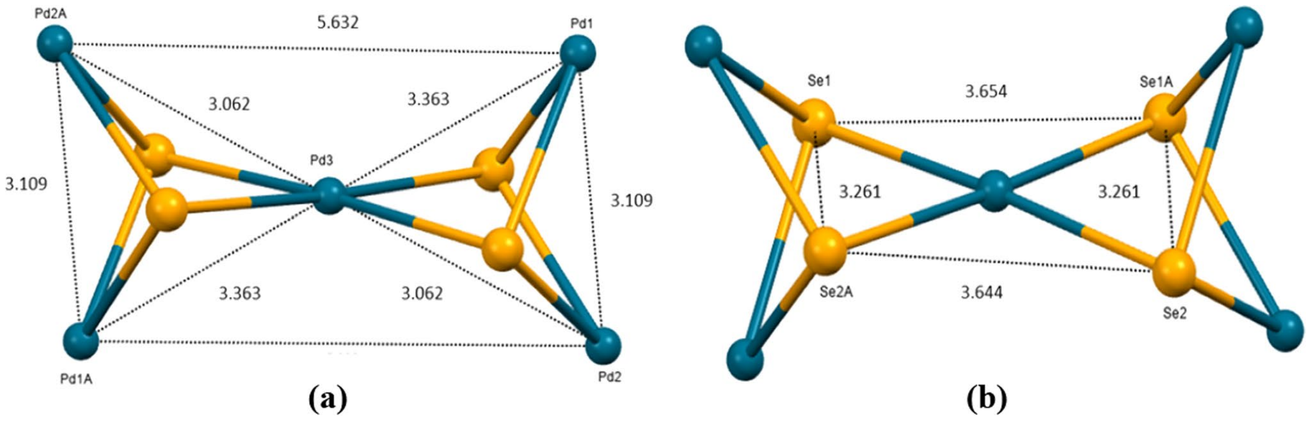


Fig. 4 **a** Pd···Pd interaction (**b**) Se···Se interaction in pentanuclear cluster having $[Pd_5(\mu_3\text{-}Se)_4]$ core.

Table 4 Comparative prospects of selected Pd–E bond length (Å) and bond angles (°) in complexes $[M\{[Pd(dppe)]_2(\mu_3\text{-}E)_2\}_2]^{2+}$ (M = Pd, Pt and E = Se, Te)

S.N	Complex	Pd–E (Å)	Pd–P (Å)	E···E (Å)	Pd–M–Pd (°)	References
1.	$[Pd\{[Pd(dppe)]_2(\mu_3\text{-}Se)_2\}_2]^{2+}$	2.4586–2.4767	2.250–2.2825	3.654	177.71	Our work
2.	$[Pd\{[Pd(dppe)]_2(\mu_3\text{-}Te)_2\}_2]^{2+}$	2.609–2.619	2.260–2.293	3.424	177.31	[42]
3.	$[Pt\{[Pd(dppe)]_2(\mu_3\text{-}Te)_2\}_2]^{2+}$	2.599–2.636	2.260–2.295	3.938	175.45	[43]

Conclusion

In current study, an attempt has been made to synthesize high nuclearity homonuclear aggregates ranging from trinuclear to pentanuclear coordination clusters. The formation of such complexes took place mainly due to the high nucleophilicity of bridging core and scrambling of metal precursor. In order to obtain this homometallic clusters *cis* configured mononuclear complexes $[M(SeC_5H_3(3\text{-}R)N)_2(dppe)]$ (M = Ni, Pd) plays a significant role as building block. The presence of selenium and pyridyl nitrogen in mononuclear complex opens an opportunity to synthesize series of complexes by coordinating *cis* configured mononuclear complexes and main group metal, transition metal precursor etc. and explore their properties. The discussed strategies provide direction to isolate the clusters through green approach avoiding high temperature and high boiling solvents. The geometrical richness of such complexes would assist to evolve more such complexes and their coordination. As a futuristic note, new direction would open up for the material chemist and physician to synthesise the binary materials of composition M_XSe_Y (M = Ni, Pd) through single source molecular precursor method which had promising electronic and magnetic property.

Supporting Information

CCDC 2235870, 2210436 contains the supplementary data for **1b** and **3**. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk, 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

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10876-023-02458-z.

Acknowledgements One of the authors Dr. Afsar Ali Siddiki is thankful to DST-SERB for providing grant TARE/2022/000220 to carry out this work. AYK is thankful to Kamlesh Sathpute from IIT Ropar for carrying out the single crystal XRD studies. RJ acknowledge sincere gratitude to Advanced Photon Source (APS) located at Argonne National Laboratory for mounting the crystal at their facility. ChemMatCARS Sector 15 is supported by the National Science Foundation under grant number NSF/CHE-1834750. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

Author Contributions AK: Methodology and investigating, SL: data curation, AAS: writing the draft, RSC: conceptualization, supervision, review and editing, RB: characterization.

Funding One of the author Afsar Ali is thankful to DST-SERB for providing the TARE grant (TARE/2022/000220) to carry out this work.

Data Availability Data can be used free of cost available in electronic supplementary information.

Declarations

Competing interests The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this finding.

Ethical approval Not applicable.

References

1. R. D. Adams and V. P. Fedin (2015). *J. Clust. Sci.* **26**, 1–2.
2. M. N. Sokolov, N. G. Naumov, P. P. Samoylov, and V. P. Fedin, Clusters and cluster assemblies, in *Comprehensive Inorganic Chemistry II*, 2nd ed. (Elsevier, Amsterdam, 2013), pp 271–310.
3. A. Bencini and S. Midollini (1992). *Coord. Chem. Rev.* **120**, 87.
4. V. K. Jain, R. S. Chauhan, in V. Lippolis, C. Santi, E. J. Lenardão and A. L. Braga (eds.), *Metal Chalcogenolates: Synthesis and Application in Material Chemistry* (RSC, 2023), pp. 58–82.
5. V. K. Jain (2020). *Dalton. Trans.* **49**, 8817.
6. R. S. Chauhan and N. Shivran (2017). *RSC. Adv.* **87**, 2017.
7. R. S. Chauhan (2020). *New. J. Chem.* **44**, 2689.
8. J. Masternak, M. Z. Machnik, M. Kowalik, A. W. Jabłońska, P. Rogala, A. Adach, and B. Barszcz (2016). *Coord. Chem. Rev.* **327–328**, 242.
9. V. K. Jain and L. Jain (2010). *Coord. Chem. Rev.* **254**, 2848.
10. R. Xu, in R. Xu, W. Pang and Q. Huo (eds.), *Introduction: Modern Inorganic Synthetic Chemistry* (Elsevier, Amsterdam, 2011), pp. 1–7.
11. C. N. Cechin, B. N. Cabral, F. Bublitz, B. Bortolotto, G. D. Silveria, L. M. Carvalho, R. Caegnelutti, U. Abram, S. Nakagaki, E. S. Lang, and B. Tirloni (2021). *New J. Chem.* **45**, 19255.
12. J. L. Shott, M. B. Freeman, N. A. Saleh, D. S. Jones, D. W. Paley, and C. Bejger (2017). *Inorg. Chem.* **56**, 10984.
13. B. C. White, W. Henderson, T. S. Hor, and B. Nicholson (2013). *Inorg. Chim. Act.* **394**, 146.

14. J. L. Yeo, J. J. Vittal, W. Henderson, and T. S. Hor (2002). *Inorg. Chem.* **41**, 1194.
15. S. W. Fong, T. S. Hor, S. M. Devoy, B. A. Waugh, B. K. Nicholson, and W. Henderson (2004). *Inorg. Chim. Act.* **357**, 2081.
16. A. J. Touchton, G. Wu, and T. W. Hayton (2020). *Small* **17**, 2003133.
17. H. Liu, A. L. Tan, Y. Xu, K. F. Mok, and T. S. Hor (1997). *Polyhedron.* **16**, 377.
18. J. Ruiz, V. Rodíguez, A. Pérez, G. López, and D. Bautista (2004). *J. Organomet. Chem.* **689**, 2080.
19. B. C. White, D. Harrison, W. Henderson, B. K. Nicholson, and T. S. Hor (2010). *Inorg. Chim. Act.* **363**, 2387.
20. K. Matsumoto, K. Takahashi, S. Hada, and Y. Nakao (1999). *Polyhedron.* **18**, 1811.
21. K. Matsumoto, N. Saiga, S. Tanaka and S. Ooi (1991). *Dalton. Trans*.
22. K. Matsumoto, K. Takahashi, M. Ikuzawa, H. Kimoto, and S. Okeya (1998). *Inorg. Chim. Act.* **281**, 174.
23. M. S. Hannu-Kuure, K. Paldán, R. Oilunkaniemi, R. Laitinen, and M. Ahlgrén (2003). *J. Organomet. Chem.* **687**, 538.
24. R. Oilunkaniemi, R. Laitinen, and M. Ahlgrén (2000). *J. Organomet. Chem.* **595**, 232.
25. R. S. Chauhan, N. Shivran, A. Slawin, and J. D. Woollins (2017). *J. Organomet. Chem.* **830**, 181.
26. R. S. Chauhan, S. Nigam, S. Ansari, A. Tyagi, L. Singla, A. R. Choudhary, and C. L. Prajapat (2021). *J. Organomet. Chem.* **949**.
27. A. I. Vogel, B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell (eds.), *Textbook of Practical Organic Chemistry*, 5th edn. (ELBS Publication, 1989), pp. 1–1513.
28. R. Sanger (1977). *Dalton Trans*. https://doi.org/10.1039/DT9770001971.
29. R. S. Chauhan, D. Oza, S. Nigam, A. Tyagi, S. Ansari, R. J. Butcher, S. Yadav, and C. Dash (2022). *J. Mol. Struct.* **1248**.
30. A. S. Hodage, C. P. Prabhu, P. P. Phadnis, A. Wadawale, K. I. Priyadarshani, and V. K. Jain (2012). *J. Organomet. Chem.* **720**, 19.
31. K. K. Bhasin, V. K. Jain, H. Kumar, S. Sharma, S. K. Mehta, and J. Singh (2006). *Syn. Commun.* **33**, 977.
32. G. M. Sheldrick (2015). *Acta Crystallogr.* **71**, 3.
33. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, and P. A. Wood (2020). *J. Appl. Crystallogr.* **53**, 226.
34. R. S. Chauhan, R. K. Sharma, G. Kedarnath, D. B. Cordes, A. M. Z. Slawin, and V. K. Jain (2012). *J. Organomet. Chem.* **717**, 180.
35. K. V. Vivekananda, S. Dey, A. Wadawale, N. Bhuvanesh, and V. K. Jain (2013). *Dalton Trans.* **42**, 14158.
36. T. Nakagawa, H. Seino, S. Nagao, and Y. Mizobe (2006). *Angew. Chem. Int. Ed.* **45**, 7758.
37. R. S. Chauhan, G. Kedarnath, A. Wadawale, A. M. Castro, R. A. Perez, V. K. Jain, and W. Kaim (2010). *Inorg. Chem.* **49**, 4179.
38. J. Chatt and D. M. P. Mingos (1970). *J Chem Soc A*. https://doi.org/10.1039/J19700001243.
39. M. Capdevila, Y. Carraasco, W. Clegg, R. A. Coxall, P. G. Duarte, A. L. Lledós, and J. A. Ramírez (1999). *Dalton. Trans.* **17**, 3103.
40. S. Dey, K. V. Vivekananda, and N. Bhuvanesh (2018). *Eur. J. Inorg. Chem.* **2018**, 3579.
41. A. Singhal, V. K. Jain, A. Varghese, and E. R. Tiekink (1999). *Inorg. Chim. Acta* **285**, 190.
42. M. Risto, E. M. Jahr, M. S. Hannu-Kuure, R. Oilunkaniemi, and R. Laitinen (2007). *J. Organomet. Chem.* **692**, 2193.
43. K. Matsumoto, C. Nishitani, M. Tadokoro, and S. Okeya (1996). *Dalton Trans*. https://doi.org/10.1039/DT9960003335.
44. K. Nishitani, T. Sizhuka, K. Matsumoto, S. Okeya, and H. Kimoto (1998). *Inorg. Chem. Commun.* **1**, 325.
45. L. B. Kumbhare, V. K. Jain, and R. J. Butcher (2006). *Polyhedron* **25**, 3159.