Reactivity of 5-methylpyridyl-2-selenolate with platinoid metal precursors: Isolation of tri and hexanuclear complexes via Se-Se and Se-C bond cleavage

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Abstract

A series of palladium (II) and platinum (II) selenolate complexes have been isolated depending upon the nature of the phosphine ligand. The substitution reaction of $[PdCl_2(PPh_3)_2]$ with two equivalents of $NaSeC_5H_3(5\text{-}Me)N$ resulted in the hexanuclear complex $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**1a**) whereas a chelated compound $[Pt\{\kappa\text{-}Se, \kappa\text{-}N: SeC_5H_3(5\text{-}Me)N\}\{SeC_5H_3(5\text{-}Me)N\}(PPh_3)]$ (**1b**) has been obtained in the case of $[PtCl_2(PPh_3)_2]$. However, chelated phosphine as an ancillary ligand with a similar reaction by using $[PtCl_2(P\cap P)]$ ($P\cap P$ = dppm, dppe) yielded *cis*-configured monomer $[Pt\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(P\cap P)]$. The trinuclear complexes $[M_3(\mu\text{-}Se)_3(dppp)_3]^{2+}$ [M = Pd (**2d**), Pt (**2e**)] were isolated by reactions of $[MCl_2(dppp)]$ (M = Pd, Pt) with $NaSeC_5H_3(5\text{-}Me)N$ via facile cleavage of Se-C bond in presence of chlorinated solvents. All the synthesized complexes have been characterized by elemental analyses, ^1H, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$ NMR spectroscopy. The molecular structure of complexes $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**1a**) and $[Pt\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppm)].C_6H_5CH_3$ (**2a**) were determined by single crystal X-ray diffraction analyses.

1. Introduction

A thirst to understand the reactivity of hybrid organoselenolate ligand systems has made this area of research quite intriguing. Within the plethora of organochalocogen chemistry, group 10 metal chalcogenolate complexes have attracted much attention due to their interesting structural motifs [1-3] and rich reactivities [4]. The promising relevance of derived complexes in cross coupling reactions [5, 6], material science [7] and electrocatalysis [8] has made this field evolving time to time.

Laitinen et al., have studied the reactions between $[M(PPh_3)_4]$/$[MCl_2(dppe)]$ (M = Pd, Pt) and Th_2E_2 (E = Se, Te). A variety of products viz. $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$, $[Pt_3Te_2(Th)(PPh_3)_5]Cl$, $[Pd_2(SeTh)_4(PPh_3)_2]$, $[Pt(SeTh)_2(PPh_3)_2]$, $[M(SeTh)_2(dppe)]$ (M = Pd, Pt) had been isolated depending upon the nature of phosphine as well as chalcogen atom [9-11]. The treatment of $[Pt_2X_2(\mu\text{-}Cl)_2(PR_3)_2]$ on NaEPy (E = S, Se) exclusively gave $[PtX(Epy)(PR_3)]_n$ (X = Cl or Ar; PR_3 = Pet_3, PMe_2Ph, $PMePh_2$ or PPh_3; n = 1,2). In chlorinated solvent, compounds showed dynamic equilibrium between $[Pt_2Cl_2(\mu\text{-}Spy)_2(PR_3)_2]$ and $[PtCl(\kappa\text{-}S,N\text{-}Spy)(PR_3)]$ [12]. However, the reaction of $[PdCl_2(PPh_3)_2]$ with NaSeAr (Ar = Ph, Th) resulted in a trinuclear $[Pd_3Se(SePh)_3(PPh_3)_3]$ and hexanuclear complex $[Pd_6Cl_2E_4(EAr)_2(PPh_3)_6]$ (Ar = Ph, Th). In contrast, a similar reaction with a platinum precursor is reported sluggish in nature and expected outcome obtained. In some of the cases, serendipitous isolation of complexes $[Pt(2\text{-}Te\text{-}C_5H_4N)_2Te(PPh_3)]$, $[Pt\{2\text{-}Te\text{-}C_5H_3(3\text{-}R)N\}_2(dppm)]$ (R = H, Me) and $[Pt_3(\mu\text{-}E)_2(P\cap P)_3]$ (E = Se, Te) has been reported [13-15]. The synthesis of $[PdI(TePy\text{-}2)(I_2TePy\text{-}2)_2]$ using diiodine adduct of bis-2-pyridylditelluride and a crude palladium powder was described by Ceching and collaborators [16]. The reaction of bis(4-pyridyl)diselenide/ditelluride with $[M(OTf)_2]$ (M = *cis*-$[Pt(PEt_3)_2]^{2+}$ or *cis*-$[Pd(dppe)]^{2+}$ yielded supramolecular Pd(II) and Pt(II) complexes having formula $[M(\mu_2\text{-}4,4'\text{-}py_2E_2)]_n(OTf)_{2n}$ (E = Se, Te) [17]. Moreover, these hybrid ligands were used to stabilize

macrocyclic complexes of the type $[Pd(P\cap P)(4\text{-}Sepy)]_nX_n$ (P∩P = dppe, dppf and Xantphos; n = 2, 4) which showed promising reactivity for Suzuki cross-coupling reactions [18]. In this sequential development, pyridyl dichalcogenide based ligands are well explored and competitive cleavage between E-E and E-C bond assisted in isolating coordination clusters which have intriguing electronic properties. Hence, the presence of soft chalcogen atom as well as hard nitrogen donor atom in the back bone of pyridyl selenolate ligand system made it quite interesting.

With this prospect, we studied the reactions of $[PdCl_2(P\cap P)]$ (P∩P = 2 PPh_3, dppm, dppe, dppp) with 5-methyl pyridyl-2-selenolate ligand systems and investigated the effect of phosphine on the nuclearity. The outcomes are discussed as herein.

2. Experimental

2.1 Chemicals

All the manipulations were carried out under nitrogen atmosphere using standard Schlenk line techniques. The solvents used during the course of reactions were distilled by standard procedures. Palladium(II) chloride, potassium tetrachloroplatinate(II), triphenyl phosphine, 1,1-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), sodium borohydride, were purchased from Sigma Aldrich and applied without purification. The precursor complex $[MCl_2(P\cap P)]$ (M = Pd, Pt; (P∩P) = 2 PPh_3, dppm, dppe, dppp) [20] and the ligand 5,5'-Dimethyl-2,2'-dipyridyl diselenide [21] were synthesized as reported in the literature.

2.2 Instrumentation

The ^1H, $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra were recorded on Bruker Avance-II spectrometer on scanning frequency 400, 161.96 and 76.3 MHz respectively. ^1H NMR spectra were referenced with the solvent peak of chloroform at δ = 7.26 ppm, externally to Ph_2Se_2 (δ = 463 ppm relative to Me_2Se) in $CDCl_3$ for $^{77}Se\{^1H\}$ NMR. FTIR spectra of 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 Fisher EA1112 CHNS analyzer.

The single crystal X-ray data for $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**1a**) and $[Pt\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppm)]$ (**2e**) were collected using Rigaku Oxford Diffraction Synergy S and Bruker D8 Venture diffractometer respectively. To determine structural parameters Cu-Kα (λ = 1.54184 Å) and Mo-Kα radiation (λ = 0.71073 Å) were used for complex **1a** and **2e**; respectively. Data acquisition as well as extraction of data was accomplished by utilizing Bruker Apex-3 and Bruker SAINT software packages using a narrow-frame algorithm (or CrysalisPro for those structures collected on the Synergy S diffractometer). The crystal structures were solved by utilizing Olex2 with the help of SHELXT [19] structure solution program by employing intrinsic phasing methods and crystal structure refinement was done with the SHELXL [20] refinement package by putting into use least squares minimization. Refinement of all non-hydrogen atoms were completed with the help of anisotropic thermal parameters. Molecular structure of complexes **1a** and **2a** were visualised using Mercury 2020.1.0 [20]. In case of complex $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**1a**), crystal quality was not the best and preliminary examination showed crystals of twinned nature. The crystallographic and structural determination data are given in **Table 1**.

Table 1: Crystallographic and structural determination data for $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**1a**) and $[Pt\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppm)].C_6H_5CH_3$ (**2a**)

Complex	$[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$	$[Pt\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppm)].C_6H_5CH_3$
Chemical formula	$C_{120}H_{102}Br_{0.87}Cl_{1.13}N_2P_6Pd_6Se_6$	$C_{81}H_{76}N_4P_4Pt_2Se_4$
Formula weight	2979.69	1935.35

Crystal size (mm^3)	0.136 X 0.072 X 0.026	0.231 X 0.201 X 0.098
Crystal system	monoclinic	monoclinic
Space group	P 21/n	P 21/n
Unit cell dimensions		
a(Å)	14.05760(10)	20.526(3)
b(Å)	22.5305(3)	13.8632(16)
c(Å)	17.7371(2)	27.118(3)
β(º)	96.4920(10)	93.048(4)
Volume ($Å^3$)	5581.75(11)	7705.8(15)
$\rho_{calcd.}$ (g/cm^3)	1.773	1.668
Z	2	4
μ (mm^{-1})/F(000)	11.681 / 2911	5.644 / 3768
Limiting indices	$-17 \leq h \leq 11$	$-25 \leq h \leq 25$
	$-28 \leq k \leq 27$	$-17 \leq k \leq 14$
	$-22 \leq l \leq 22$	$-33 \leq l \leq 34$
Θ for data collection (º)	3.184-77.857	2.417-26.473
No. of reflections collected	11370	64033
No. of independent reflections (R_{int})	11370 (0.1006)	15744 (0.0694)
Data/restraints/parameters	11370/1380/830	15744/0/798
Final R_1, wR_2 indices [$I>2\sigma I$]	0.1150, 0.2373	0.0418, 0.0946

R_1, wR_2 (all data)	0.1472, 0.2566	0.0667, 0.1049
Goodness of fit on F^2	1.163	1.034

2.3 Syntheses of complexes

2.3.1 Synthesis of $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**1a**)

A dichloromethane solution (15 cm^3) of $[PdCl_2(PPh_3)_2]$ (140 mg, 0.20 mmol) was added to a methanolic solution of $NaSeC_5H_3$(5-Me)N [freshly prepared *in situ* by the reaction of bis(5-methyl-2-pyridyl)diselenide (68 mg, 0.20 mmol) and $NaBH_4$ (15 mg, 0.40 mmol) in 10 cm^3 methanol. The resultant mixture was stirred for 7 hours at room temperature. The ensuing solution was passed through G-3 assembly and the filtrate was dried in *vacuo.* The residue was extracted in toluene which on slow evaporation gave red crystals of complex **1a** (Yield 65 mg, 11%) m.p.: 280°C (dec.). Anal. Calcd. for $C_{120}H_{102}N_2Br_{0.87}Cl_{1.13}Se_6P_6Pd_6$: C, 47.19; H, 3.40; N, 0.91% Found: C, 47.25; H, 3.42; N, 0.92%. IR (KBr, cm^{-1}): 3747 (m), 3405 (m), 3052 (m), 2921 (m), 2287 (w), 2168 (m), 2049 (w), 1982 (m), 1586 (m), 1432 (s), 1183 (m), 1092 (s), 691 (s), 534 (m), 418 (m). ^{1}H NMR ($CDCl_3$) δ: 1.96 (s, 6H, CH_3), 7.44-7.48 (m, 25H, Ph), 7.53-7.57 (m, 25H, Ph), 7.65-7.70 (m, 40H, Ph), 8.23 (s, 1H, C_5H_3N), 8.25 (s, 1H, C_5H_3N).

2.3.2 Synthesis of $[Pt\{\kappa\text{-}Se, \kappa\text{-}N: SeC_5H_3(5\text{-}Me)N\}\{SeC_5H_3(5\text{-}Me)N\}(PPh_3)]$ (**1b**)

To a methanolic solution (10 cm^3) of $NaSeC_5H_3$(5-Me)N [prepared *in situ* from reduction of bis(5-methyl-2-pyridyl)diselenide (86 mg, 0.25 mmol) by a methanolic solution (10 cm^3) of $NaBH_4$ (19 mg, 0.50 mmol)], a toluene suspension (5 cm^3) of $[PtCl_2(PPh_3)_2]$ (200 mg, 0.25 mmol) was added with stirring at room temperature which continued for 4 hours. The solvents were evaporated under vacuum and the residue was washed with diethyl ether followed by hexane to obtain titled complex (Yield 139 mg, 68.8%) m.p.: 219°C (dec.). Anal. Calcd. for $C_{30}H_{27}N_2Se_2PPt$: C, 45.07; H, 3.40; N, 3.50% Found: C, 45.11; H, 3.43; N, 3.48%. IR (KBr, cm^{-1}): 3345 (m), 3049 (m), 2916 (m), 2853 (w), 2320 (w), 2167 (w), 2113 (w), 2023

(w), 1984 (w), 1677 (w), 1584 (m), 1543 (w), 1450 (s), 1434 (s), 1355 (m), 1267 (m), 1184 (w), 1131 (m), 1088 (s), 997 (s), 943 (m), 821 (s), 744 (m), 694 (s), 541 (w), 508 (s), 456 (w). ^{1}H NMR ($CDCl_3$) δ: 1.99 (s, 3H, C*H*$_3$), 2.14 (s, 3H, C*H*$_3$), 7.31-7.38 (m, 13H, Ph), 7.64-7.68 (m, 8H, Ph), 8.02 (s, 1H, C_5H_3N), 8.06 (s, 1H, C_5H_3N); ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 7.21 ($^{1}J_{Pt-P}$ = 3819 Hz); ^{77}Se{^{1}H} NMR ($CDCl_3$) δ: 208, 102 ppm.

2.3.3 Synthesis of [Pt{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppm)] (**2a**)

A toluene suspension of [$PtCl_2$(dppm)] (150 mg, 0.23 mmol) was added to a methanolic solution of $NaSeC_5H_3$(5-Me)N [prepared *in situ* from reduction of bis(5-methyl-2-pyridyl)diselenide (79 mg, 0.23 mmol) by a methanolic solution (10 cm^3) of $NaBH_4$ (17 mg, 0.46 mmol)] in toluene-methanol mixture (20 cm^3) at room temperature for 4 hours. The reaction mixture was dried under vacuum and the product was extracted in acetone to afford a yellow solid of **2a**. (Yield: 139 mg, 66%) m.p. 205℃ (dec.). Anal. Calcd. for $C_{37}H_{34}N_2P_2Se_2Pt$: C, 48.22; H, 3.72; N, 3.04%; Found: C, 48.29; H, 3.80; N, 3.11%. IR (KBr, cm^{-1}): 3342 (s), 3047 (m), 2916 (m), 2227 (w), 2183 (w), 2082 (w), 1979 (w), 1951 (w), 1662 (w), 1583 (m), 1431 (s), 1356 (s), 1269 (m), 1129 (w), 1086 (s), 941 (m), 816 (m), 784 (m), 731 (m), 691 (s), 548 (w), 506 (m), 463 (m). ^{1}H NMR ($CDCl_3$) δ: 1.67 (br, 2H, -C*H*$_2$), 1.90 (s, 6H, C*H*$_3$), 7.28-7.33 (m, 5H, Ph), 7.38-7.44 (m, 14H, Ph), 7.78-7.83 (m, 5H, Ph), 8.7 (br, 2H, C_5H_3N); ^{31}P{^{1}H} NMR ($CDCl_3$) δ: -51.27 ppm ($^{1}J_{Pt-P}$ = 2691 Hz).

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

Prepared similar to method **2a** using bis(5-methyl-2-pyridyl)diselenide (89 mg, 0.26 mmol), sodium borohydride (20 mg, 0.52 mmol) and [$PdCl_2$(dppe)] (150 mg, 0.26 mmol) (Yield: 146 mg, 66%) m. p. 182℃ (dec.). Anal. Calcd. for $C_{38}H_{36}N_2Se_2P_2Pd$: 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

144 ($CDCl_3$) δ: 2.11 (s, 6H, C*H*$_3$), 2.26 (d, $^1J_{P-H}$ = 30 Hz, 4H, -CH_2), 6.62 (d, ^1J = 5.4 Hz, 2H),
145 7.29-7.37 (m, 10H, Ph), 7.39-7.44 (m, 10H, Ph), 7.78-7.55 (m, 2H, Ph), 8.92 (br, 2H, C_5H_3N);
146 $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 52.60 ppm; $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ: 263.09 ppm (d, $^2J_{P-Se}$ =
147 95.54 Hz)

148 *2.3.5 Synthesis of [Pt{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppe)]* (**2c**)

149 Prepared similar to method **2a** using bis(5-methyl-2-pyridyl)diselenide (82 mg, 0.24
150 mmol), sodium borohydride (18 mg, 0.48 mmol) and [$PtCl_2$(dppe)] (160 mg, 0.24 mmol)
151 (Yield: 152 mg, 66%) m.p. 191°C (dec.). Anal. Calcd. for $C_{38}H_{36}N_2Se_2P_2Pt$: C, 48.78; H, 3.88;
152 N, 2.99% Found: C, 48.71; H, 3.82; N, 2.97%. IR (KBr, cm^{-1}): 3342 (s), 3047(m), 2913 (m),
153 2111 (w), 1913 (w), 1654 (w), 1581 (m), 1545 (w), 1432 (s), 1356 (m), 1270 (m), 1130 (m),
154 1085 (s), 996 (s), 816 (s), 747 (m), 688 (s), 528 (s), 478 (m). ^1H NMR ($CDCl_3$) δ: 1.88 (br,
155 4H, -C*H*$_2$), 2.00 (s, 6H, C*H*$_3$), 7.30-7.39 (m, 12H, Ph), 7.74-7.83 (m, 12H, Ph), 8.28 (s, 2H,
156 C_5H_3N); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 45.06 ppm ($^1J_{Pt-P}$ = 3038 Hz).

157 *2.3.6 Synthesis of [Pd$_3$(μ-Se)$_2$(dppp)$_3$]Cl$_2$* (**2d**)

158 A benzene suspension of [$PdCl_2$(dppp)] (100 mg, 0.17 mmol) was added to a
159 methanolic solution (15 cm^3) of $NaSeC_5H_3$(5-Me)N [prepared *in situ* from reduction of bis(5-
160 methyl-2-pyridyl)diselenide (58 mg, 0.17 mmol) and $NaBH_4$ (13 mg, 0.34 mmol) in
161 methanol]. The reaction mixture was stirred for 4 hours at room temperature and dried under
162 vacuum. The residue was extracted in dichloromethane to obtained red crystals of complex
163 **2c**. (Yield: 81 mg, 27%) m. p. 279°C (dec.). Anal Calcd. for $C_{81}H_{78}Se_2P_6Cl_2Pd_3$: C, 54.49; H,
164 4.40%; Found: C, 54.42; H, 4.45%. IR (KBr, cm^{-1}): 3988 (w), 3913 (w), 3885 (w), 3726 (w),
165 3341 (s), 3046 (m), 2919 (m), 2166 (w), 1981 (w), 1655 (w), 1586 (w), 1433 (s), 1344 (m),
166 1271 (m), 1130 (w), 1092 (m), 997 (m), 943 (m), 823 (m), 743 (m), 693 (m), 511 (m), 431
167 (m). ^1H NMR ($CDCl_3$) δ: 1.63 (s, 12H, -C*H*$_2$), 1.71 (s, 6H, -C*H*$_2$), 7.34-7.48 (m 30H, Ph),
168 7.54-7.59 (m, 15H, Ph), 7.65-7.70 (m, 15H, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: -2.98 ppm.

169 *2.3.7 Synthesis of [$Pt_3(\mu\text{-}Se)_2(dppp)_3$]$Cl_2$* (**2e**)

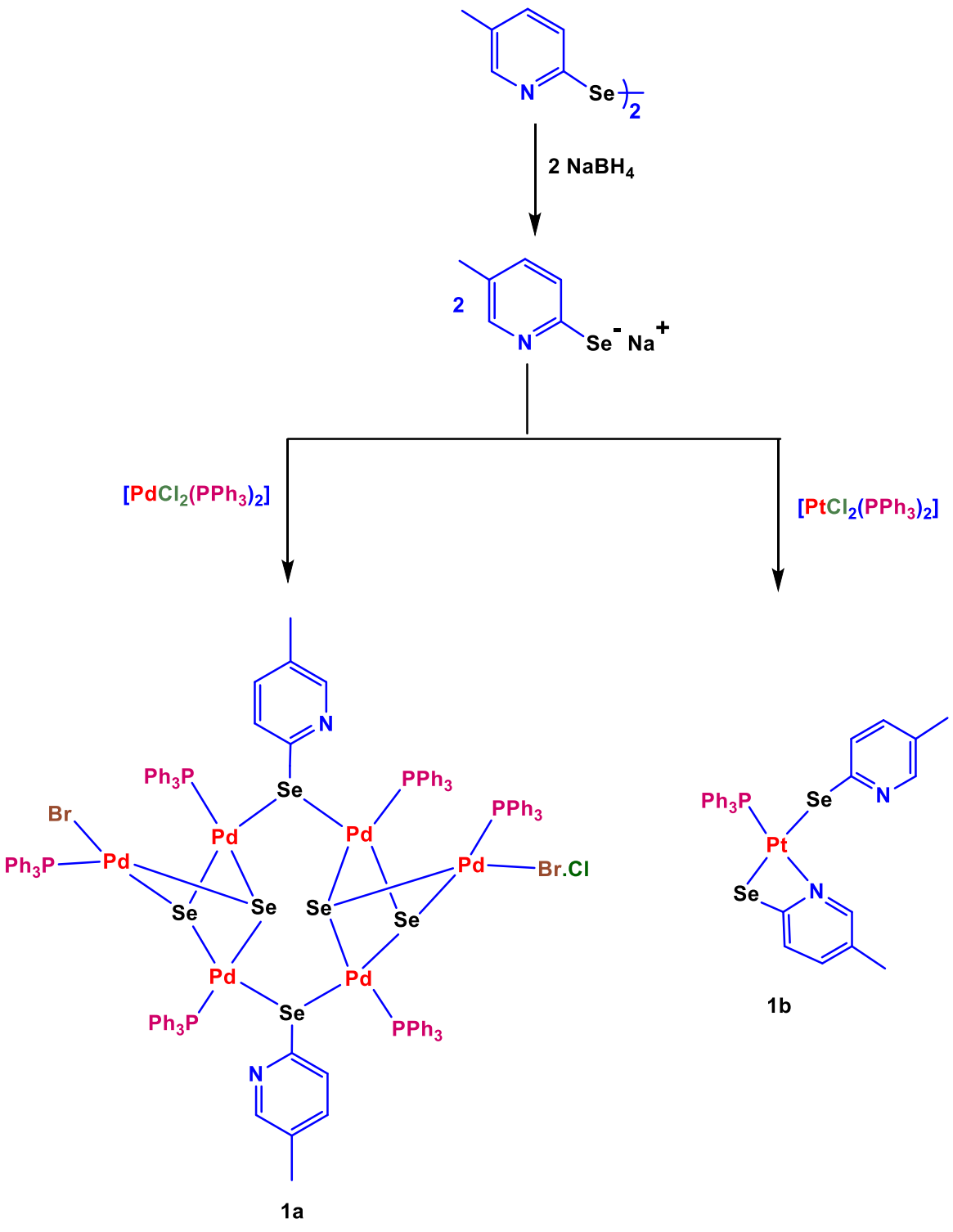
170 Compound **2e** was prepared similar to method **2d,** using bis(5-methyl-2-
171 pyridyl)diselenide (62 mg, 0.18 mmol), sodium borohydride (14 mg, 0.36 mmol) and
172 [$PtCl_2$(dppp)] (125 mg, 0.18 mmol) (Yield: 110 mg, 29%) m.p. 297°C (dec.). Anal. Calcd.
173 for $C_{81}H_{78}Se_2P_6Cl_2Pt_3$: C, 47.42; H, 3.83% Found: C, 47.48; H, 3.90%. IR (KBr, cm^{-1}): 3854
174 (w), 3639 (w), 3362 (s), 3049 (m), 2918 (m), 2319 (w), 2167 (w), 2033 (w), 1970 (m), 1623
175 (m), 1589 (m), 1433 (s), 1311 (w), 1273 (w), 1236 (w), 1186 (w), 1157 (m), 1099 (s), 972
176 (m), 919 (w), 835 (m), 795 (w), 747 (m), 694 (s), 511 (s). ^{1}H NMR ($CDCl_3$) δ: 1.69 (s, 12H,
177 -C*H*$_2$), 1.75 (s, 6H, -C*H*$_2$), 7.38-7.51 (m, 30H, ph), 7.66-7.71 (m, 15H, ph), 7.75-7.80 (m,
178 15H, ph); ^{31}P{^{1}H} NMR ($CDCl_3$) δ: -11.60 ppm ($^1J_{Pt\text{-}P}$ = 3007 Hz); ^{77}Se{^{1}H} NMR ($CDCl_3$)
179 δ: 127.7 ppm.

180 ## 3. Results and discussion

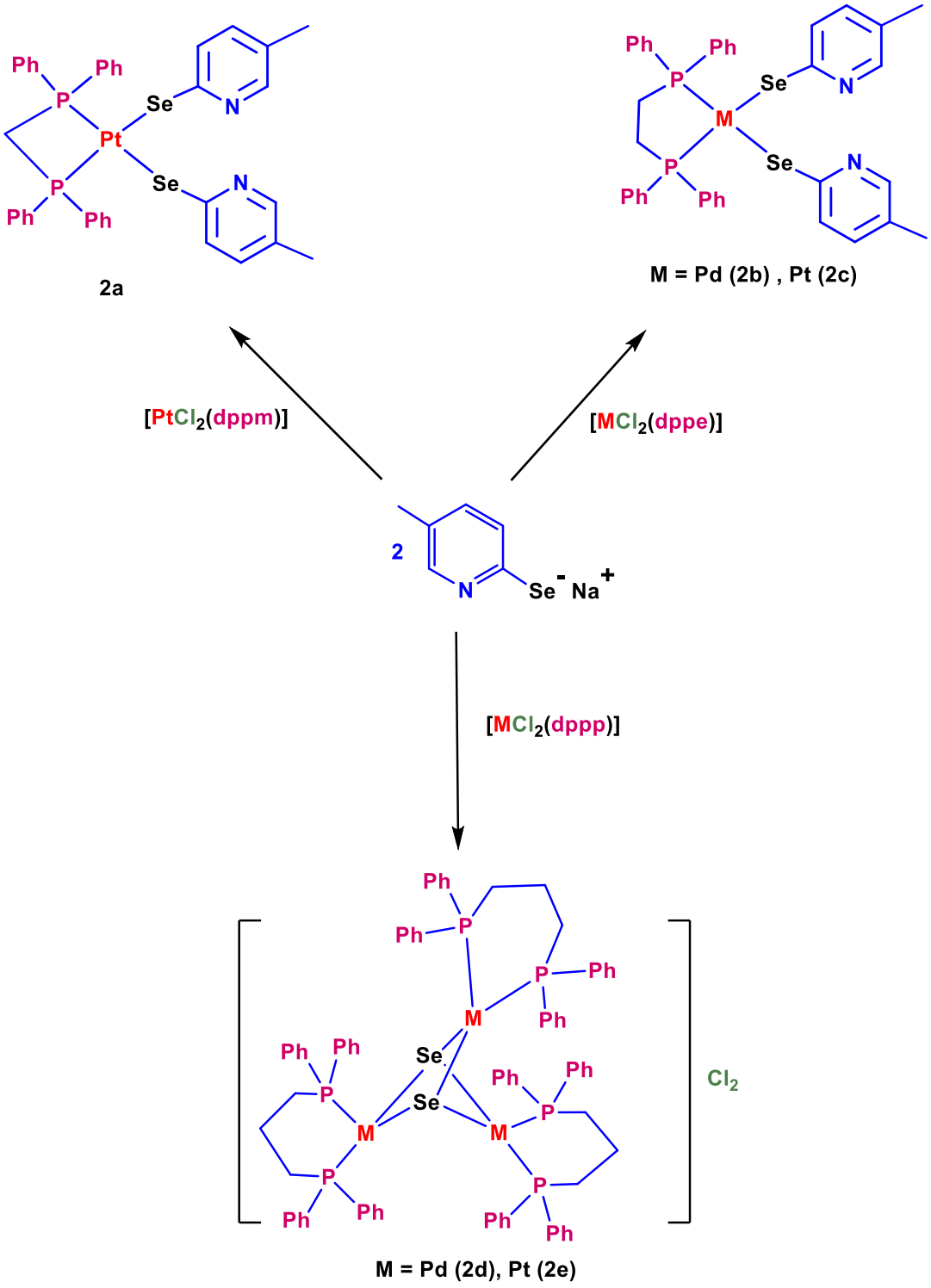
181 The treatment of [$PdCl_2(PPh_3)_2$] with two equivalents of $NaSeC_5H_3$(5-Me)N (freshly
182 prepared by reduction of 5-methyl-2-pyridyl)diselenide with $NaBH_4$ in methanol) resulted in
183 an unexpected hexanuclear species [$Pd_6Br_{0.87}Cl_{1.13}${2-SeC_5H_3(5-Me)}$_2(PPh_3)_6$] (**1a**) (**Scheme**
184 **1**). The IR spectrum showed all possible bands ranging from 3747 cm^{-1} to 418 cm^{-1}. The peak
185 at 3052 cm^{-1} corresponds to C−H stretching frequency and an absorption at 1092 cm^{-1} reflects
186 the C−C bond. The ^{31}P{^{1}H} NMR spectrum of complex **1a** displayed several resonances in
187 solution. Probably, complex **1a** disintegrates in solution into several species which makes the
188 spectrum inconclusive. M. S. Hannu-Kuure et al. reported similar findings for the formation
189 of [$Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6$] via treatment of [$PdCl_2(PPh_3)_2$] with $PhSe^-$ [21]. On the other
190 hand, by performing same reaction with [$PtCl_2(PPh_3)_2$], a chelated compound of composition
191 [Pt{κ-Se, κ-N: SeC_5H_3(5-Me)N}{SeC_5H_3(5-Me)N}(PPh_3)] (**1b**) was obtained. The
192 mentioned complex showed a resonance at δ = 7.21 ppm flanked by ^{1}J(Pt-P) coupling constant
193 of 3819 Hz in its ^{31}P{^{1}H} NMR spectrum and well in range to the reported values [22, 23].

Shielded chemical shift and higher coupling constant indicates the presence of pyrimidyl nitrogen *trans* to phosphine. An appearance of resonance at 208 ppm in $^{77}Se\{^{1}H\}$ NMR corroborated to chelating selenolate ligand trans to phosphorous atom whereas the peak at 102 ppm supported the non-chelated selenolate molecule.

The reaction of $[PtCl_2(P\cap P)]$ $NaSeC_5H_3(5\text{-}Me)N$ in 1:2 ratio gave *cis* configured mononuclear complex $[Pt\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppm)]$ (**2a**) which showed a singlet at δ = −51.27 ppm ($^{1}J_{Pt\text{-}P}$ = 2691 Hz) in $^{31}P\{^{1}H\}$ NMR spectrum (**Scheme 2**). S. Miranda and coworkers observed a signal at − 49.4 ppm ($^{1}J_{Pt\text{-}P}$ = 2800 Hz) for the complex *trans*-$[Pt(S\text{-}C_4H_3SN_2)_2(dppm)]$ [24]. Similar reaction with $[MCl_2(dppe)]$ (M = Pd, Pt) gave products of the type $[M\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppe)]$ [M = Pd (**2b**), Pt (**2c**)]. The $^{31}P\{^{1}H\}$ NMR spectrum of complexes **2b** and **2c** exhibited single resonances at δ = 52.60 and δ = 45.06 ppm respectively which are in good conformity to the earlier reported work [25]. However, changing the diphosphine with 1,3-bis(diphenylphosphino)propane (dppp) in $[MCl_2(dppp)]$ (M = Pd, Pt) afforded a selenido bridged trinuclear complexes $[Pd_3(\mu\text{-}Se)_2(dppp)_3]Cl_2$ (**2d**) and $[Pt_3(\mu\text{-}Se)_2(dppp)_3]Cl_2$ (**2e**) on extraction in dichloromethane. An identical behaviour has been observed for the formation of $[Pd_3(\mu\text{-}Se)_2(dppe)_3]^{2+}$ [26]. The prominent peaks at 1655 cm^{-1} and 1623 cm^{-1} are attributed to C=C stretching in IR spectra of complexes **2d** and **2e** respectively. The $^{31}P\{^{1}H\}$ NMR spectra of complex **2d** revealed one resonance at δ = −2.98 ppm suggesting the presence of chemically and magnetically equivalent phosphorus of the coordinated dppp. The peak at δ = −11.60 ppm has been observed for the $[Pt_3(\mu\text{-}Se)_2(dppp)_3]Cl_2$ (**2e**) and magnitude of $^{1}J_{Pt\text{-}P}$ coupling (3007 Hz) is significantly reduced compare to the value for $[PtCl_2(dppp)]$ ($^{1}J_{Pt\text{-}P}$ = 3420 Hz) but well matches with literature complex [15]. The selenido ligands also showed equivalence of all selenium nuclei as only one ^{77}Se resonance (δ = 127.7 ppm) has been found in $^{77}Se\{^{1}H\}$ NMR spectrum for complex **2e** which is quite deshielded as compared to 5,5'-Dimethyl-2,2'-dipyridyl diselenide.



Scheme 1: Reactions of $[MCl_2(PPh_3)_2]$ (M = Pd, Pt) with sodium salt of 5-methyl-2-pyridylselenolate



225

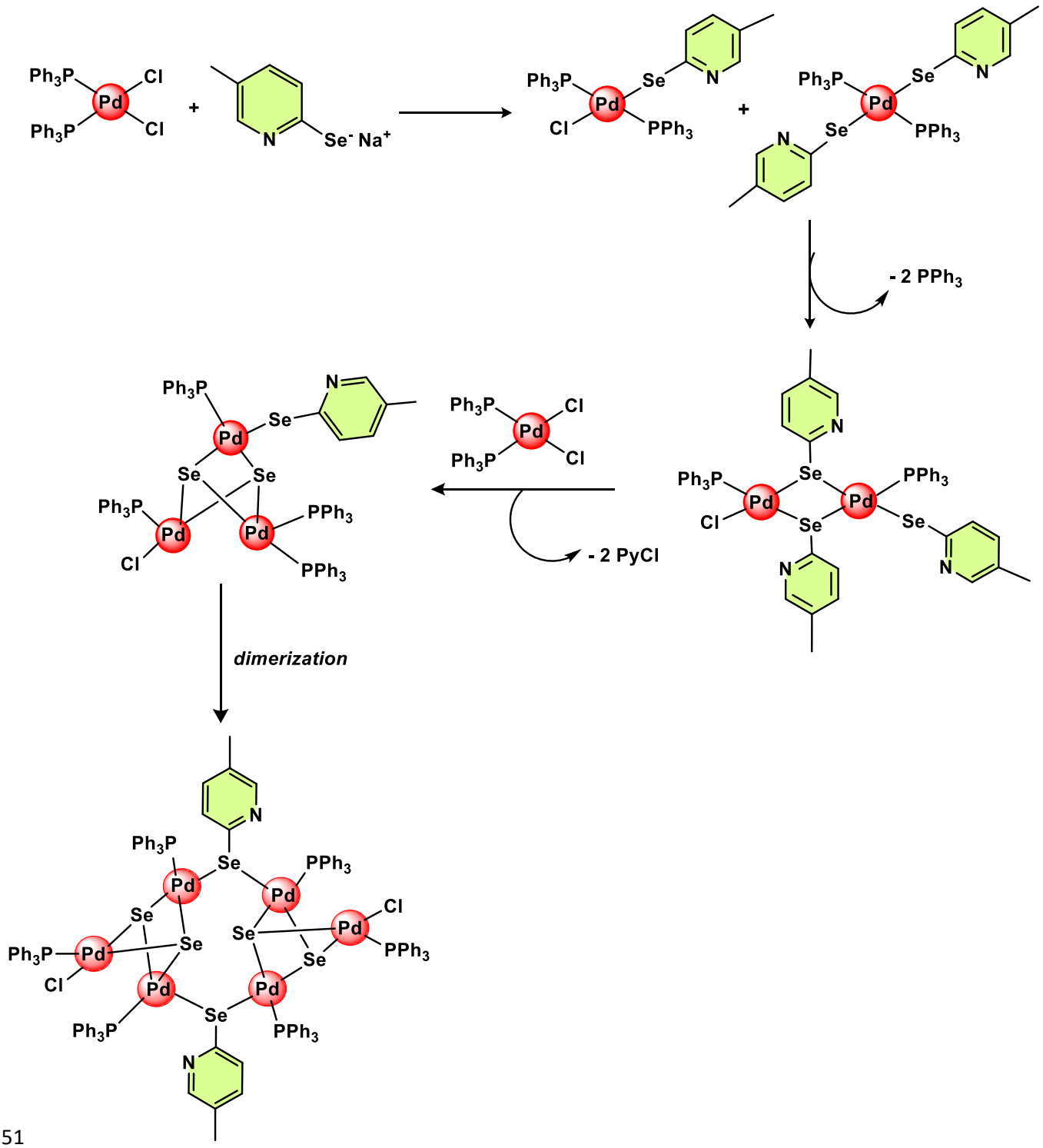
226 **Scheme 2:** Reactions of $[MCl_2(P\cap P)_2]$ (M = Pd, Pt) [(P∩P) = dppm, dppe, dppp] with sodium

227 salt of 5-methyl-2-pyridylselenolate

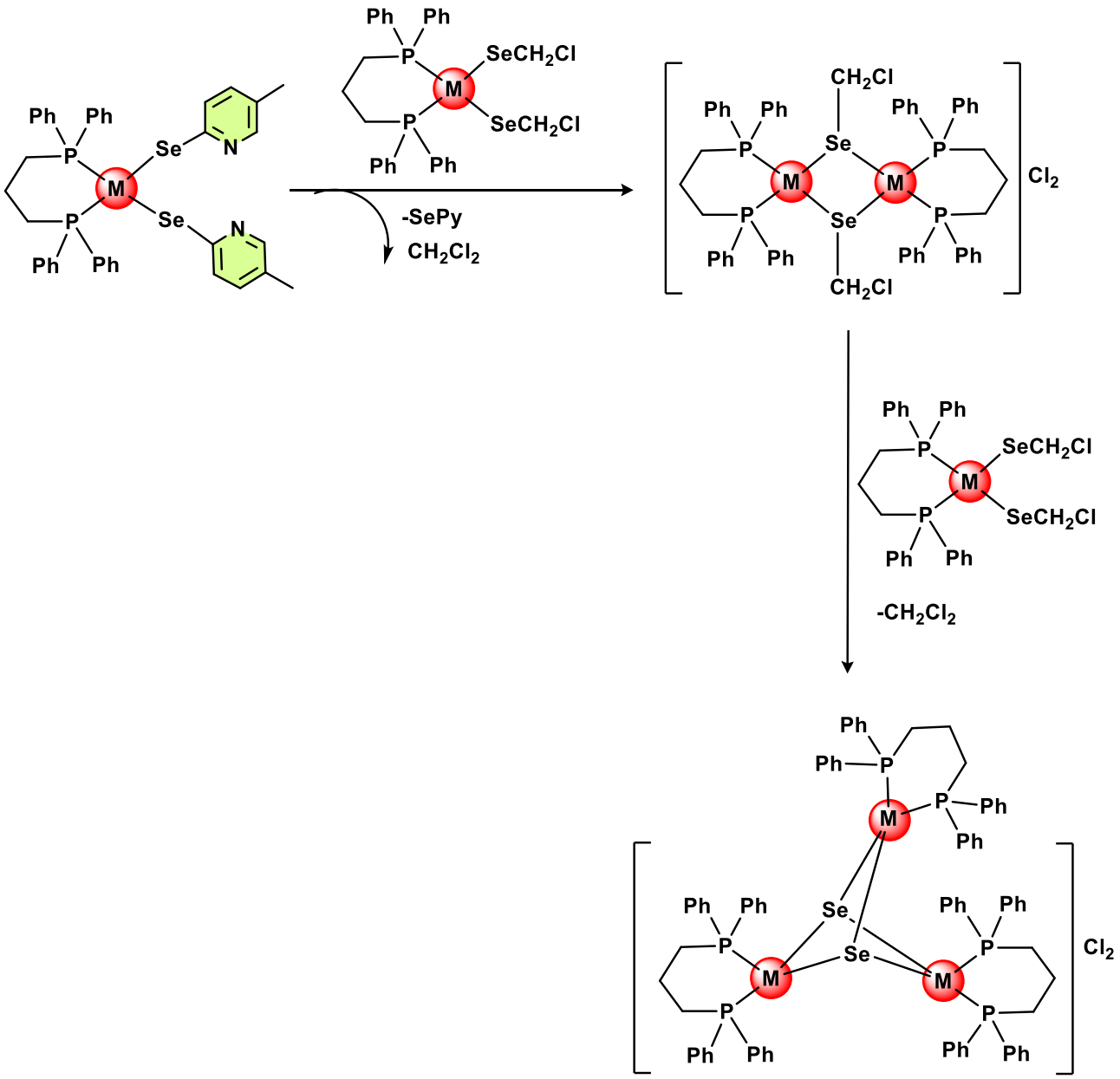
228 *Mechanistic reaction pathway*

An isolable product from the reaction between $[PdCl_2(PPh_3)_2]$ and SeC_5H_3(5-Me) is the hexanuclear complex **1a**. In this case, a mononuclear metal selenolate complex formed initially as transient species which dimerizes through corner sharing to result in binuclear moieties. The latter dimerized product on combination with $[PdCl_2(PPh_3)_2]$ assisted in forming a trinuclear product. This conceivably dimerizes with edge sharing to afford the Pd_6Se_6 core of the hexanuclear coordination cluster. Brennan et al., proposed similar mechanistic prospects in isolating homoleptic hexanuclear complex $[Pd_6Te_6(PEt_3)_8]$. Various combinations of mononuclear derivatives on condensation, yielded dinuclear complexes which on reacting with the mononuclear unit $[PdCl_2(PPh_3)_2]$ resulted in trinuclear product. Dimerization of this trinuclear specie afforded a hexanuclear complex $[Pd_6Cl_2\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**Scheme 3**).

The formation of the trinuclear coordination cluster $[M_3(\mu\text{-}Se)_2(dppp)_3]^{2+}$ (M = Pd, Pt) is quite interesting. Probably, *cis* configured mononuclear complex combines with another same mononuclear molecule to result in a nucleophilic binuclear transient species $[M_2(\mu\text{-}SeAr)_2(dppp)_2]^{2+}$ (M = Pd, Pt). An existence of such isostructural moieties $[Pt_2(\mu\text{-}S)_2(P\cap P)_2]$ (P∩P = dppe, dppp) of nucleophilic behaviour are highly susceptible towards chlorinated solvents which is well proposed in literature [27]. It seems in our case, binuclear species $[M_2(\mu\text{-}SeAr)_2(dppp)_2]^{2+}$ (M = Pd, Pt) disintegrates in chlorinated solvent to facilitate the cleavage of the Se–C bond resulting in a trinuclear complex. Moreover, strain free six membered ring projected by chelating phosphine "dppp" leads metallophilic core $\{M_2Se_2\}$ more widen up for nucleophilic attack on solvent [28]. (**Scheme 4**)



Scheme 3: Plausible mechanism for the formation of hexanuclear cluster **1a**



Scheme 4: Plausible mechanism for the formation of trinuclear complexes $[M_3(\mu\text{-}Se)_2(dppp)_3]Cl_2$ (M = Pd, Pt)

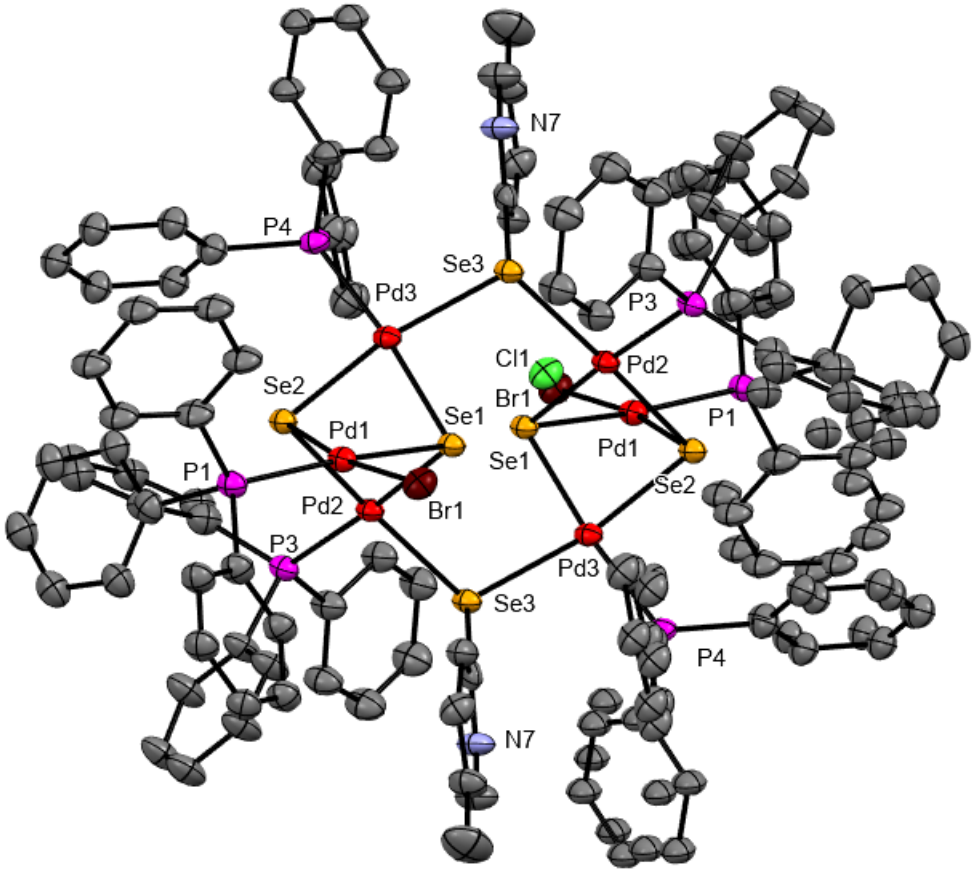
X-ray crystallography

The molecular structures of complexes $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**1a**) and $[Pt\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppm)].C_6H_5CH_3$ (**2a**) were established by X-ray diffraction analyses as shown in **Figure 1** and **2**. Selected interatomic parameters are summarized in **Tables 2** and **3**.

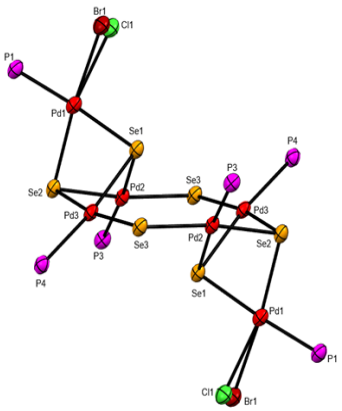
The cluster $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**1a**) crystallized out in monoclinic space group, in which the two Pd_3Se_2 fragments are consolidated via two $[\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2]$ bridging ligands to frame a cyclic hexanuclear moiety. The later framework seems to provide an inherent structure comprising of six distorted square planar Pd atoms. 8 of the 12 Pd and Se atoms are configured into essential planar parallelogram. The structure is comprised of two Pd_3Se_2 core atoms having convergent evolution from the structure of the trinuclear $[M_3E_2(P\cap P)_3]$ (M = Ni, Pd, Pt; P∩P = dppe) [14, 29] and pentanuclear $[M'\{[M(P\cap P)]_2(\mu_3\text{-}Se)_2\}_2]^{2+}$ (M' = M = Pd; M' = Pt, M = Pd Pt; E = Se, Te; P∩P = dppe) compounds [30-32]. Considering the bonding patterns around the Pd atoms, the hexanuclear species have two different coordination environments via, (a) one PPh_3, two selenium and one chlorine, (b) three bridged selenium and one PPh_3.

The $Pd\text{-}Se_{bridge}$ bond lengths [2.406(2) − 2.454(2) Å] [$Pd\text{-}(\mu_3\text{-}Se)_{avg}$ = 2.434 Å] is comparable with $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)]$ [$Pd\text{-}(\mu_3\text{-}Se)_{avg}$ = 2.4311 Å] [21] and pentanuclear fragment $[Pd'\{[Pd(dppe)]_2(\mu_3\text{-}Se)_2\}_2]^{2+}$ [$Pd\text{-}(\mu_3\text{-}Se)_{avg}$ = 2.457(7) Å] [32] while shorter with respect to high congeners of cluster $[Pd_6Cl_2Te_4(TePh)_2(PPh_3)_6$ [$Pd\text{-}(\mu_3\text{-}Te)_{avg}$ = 2.592(1) Å] [33], $[Pd_6Cl_2Te_4(TeTh)_2(PPh_3)_6$ [$Pd\text{-}(\mu_3\text{-}Te)_{avg}$ = 2.5931 Å][34]. Promising observation in complex **1a** is Pd-Se bond involving $[2\text{-}SeC_5H_3(5\text{-}Me)N]$ as bridging ligands [Pd(2)−Se(2) = 2.479 Å] is shorter than in $[Pd_6Te_6(PEt_3)_8]$ [Pd(2)-Te(2) = 2.636(14) - 2.630(14) Å] [35]. The Se−C bond length involved in bridging with $[\{2\text{-}SeC_5H_3(5\text{-}Me)N\}]$ is 1.95 Å is in the expected range when compared to $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)]$ (1.927 Å) but shorter than $[Pd_6Te_4(TeTh)_4(PPh_3)_6]$ (2.113(8) Å). The Pd-P distances (range = from 2.260(5) to 2.321(5)] while, the Pd(1)-Cl(1) bond length is 2.47(1) Å. The three isosceles triangles formed within the Pd_3Se_2 core i.e. Se(1)−Pd(1)−Se(2), Pd(3)−Se(1)−Pd(2) and Pd(3)−Se(2)−Pd(2) are 78.53º, 79.86º and 80.75º, respectively which are quite acute in nature as a consequence bond angle Se(2)−Pd(2)−Se(3) is 172.38º which is quite obtuse.

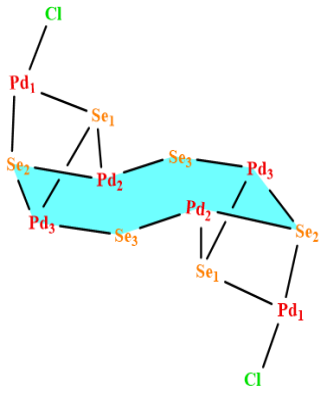
The Pd(1)····Pd(2)/Pd(2)····Pd(3)/Pd(1)····Pd(3) are 3.260(17)/3.141(16)/3.393(16) which are well within the range of Van der waal radii shows weak metallophilic interactions [36], whereas, the separation between two palladium atoms Pd(2)−Pd(3) present in the parallelogram moiety are 4.062 Å apart which is higher than the interaction range. There are close Se(1)····Se(2)/Se(1)····Se(3)/Se(1)····Se(3) contacts having distances 3.076/3.510/3.649 Å which are well within the Van der waal radii [37, 38].



(a)



(b)



(c)

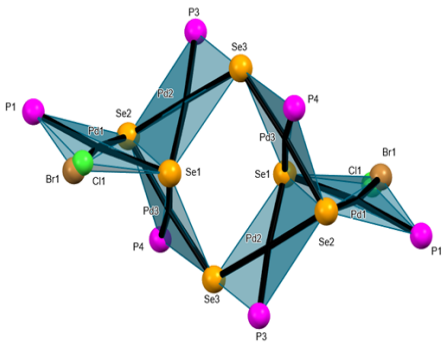
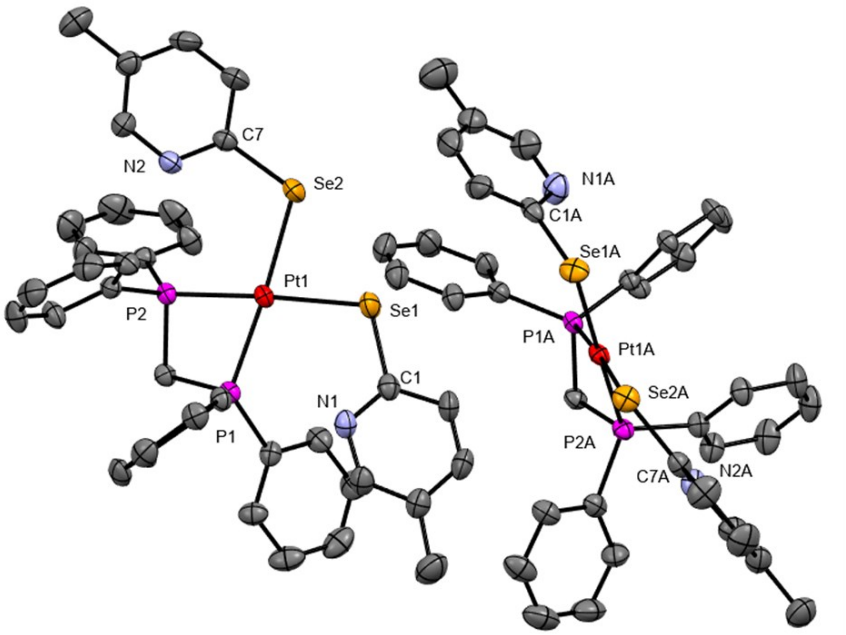


Figure 1: ORTEP diagram of $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ (**1a**) with atomic number scheme. The ellipsoids were drawn at the 25% probability level.

The crystal lattice of complex $[Pt\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppm)].C_6H_5CH_3$ (**2a**) contains two independent molecules that are slightly different from one another in terms of bond lengths and bond angles. The structures comprise of a distorted square planar central platinum atom defined by two selenolate ligands and one chelating dppm ligand in a *cis* configuration. The two pyridyl rings adopt an *anti*-conformation in both the structures. Each molecule has marginally different Pt−Se bond distances that are shorter than the complex of tellurium analogue $[Pt(TeMes)_2(dppp)].3C_6H_6$ but in good agreement with the reported compound $[Pt(SeC_4H_3N_2(PPh_3)_2]. 2CH_2Cl_2$ [23]. The Pt−P bond lengths are slightly smaller than those in $[Pt(Cl_{0.5}I_{0.5})\{C_5H_3(3\text{-}CONHPh)N\}(PPh_3)_2].HCl$ (2.3221(7), 2.3057(7) Å) [39] but in range with $[Pt(4\text{-}TeC_5H_4N)_2(dppe)]$ [40] (2.265(7), 2.262(7) Å), $[Pt(SeC_4H_3N_2)_2(dppm)]$ (2.2642(10) Å), $[Pt\{SeC_5H(4,6\text{-}Me)N_2\}_2(dppm)].CH_2Cl_2$ (2.2550(12), 2.2523(13) Å) [41]. The Se−Pt−Se angles (79.98(2), 80.23(2)) in the molecules (a) and (b) are largely deviated from the ideal value of 90º, also distinctly smaller than in $[Pt(Se_2C_8H_{12})(dppm)]$ (88.79º(4)) [42]. The observed P−Pt−P (72.74º(5) 72.92º(5)), bond angles can be compared with the complex $[Pt(SePh)_2(dppm)]$ (73.68º(8))[43] $[Pt(S\text{-}C_4H_3SN_2)_2(dppm)]$ (73.68 º(4)) [24].



(a) **(b)**

312

313 **Figure 2:** ORTEP diagram of [Pt{2-SeC$_5$H$_3$(5-Me)N}$_2$(dppm)] (**2a**) with atomic number

314 scheme. The ellipsoids were drawn at the 25% probability level. Solvent molecule was

315 omitted for clarity.

316 **Table 2:** Selected bond lengths (Å) and bond angles (º) for [Pd$_6$Br$_{0.87}$Cl$_{1.13}${2-SeC$_5$H$_3$(5-

317 Me)}$_2$(PPh$_3$)$_6$] (**1a**)

Pd(1)-Cl(1)	2.47(1)	Pd(1)-P(1)	2.321(5)
Pd(1)-Se(1)	2.454(2)	Pd(1)-Se(2)	2.406(2)
Pd(2)-Se(1)	2.451(2)	Pd(2)-Se(3)	2.479(2)
Pd(2)-Se(2)	2.435(2)	Pd(2)-P(3)	2.308(5)
Pd(3)-Se(1)	2.443(2)	Pd(3)-P(4)	2.260(5)
Pd(3)-Se(2)	2.415(2)	Pd(3)-Se(3)	2.482(2)
P(1)-Pd(1)-Cl(1)	96.6(10)	Cl(1)-Pd(1)-Se(1)	88.2(9)
Se(1)-Pd(1)-Se(2)	78.53(7)	Se(2)-Pd(1)-P(1)	96.40(14)

Cl(1)-Pd(1)-Se(2)	166.7(9)	P(1)-Pd(1)-Se(1)	171.71(14)
Se(1)-Pd(2)-Se(3)	95.50(8)	Se(3)-Pd(2)-P(3)	89.29(13)
P(3)-Pd(2)-Se(2)	97.03(13)	Se(2)-Pd(2)-Se(1)	78.02(7)
Se(1)-Pd(2)-P(3)	174.65(13)	Se(2)-Pd(2)-Se(3)	172.38(9)
Se(1)-Pd(3)-Se(3)#1	90.90(7)	Se(3)#1-Pd(3)-P(4)	95.59(14)
P(4)-Pd(3)-Se(2)	95.01(14)	Se(2)-Pd(3)-Se(1)	78.57(7)
Se(1)-Pd(3)-P(4)	172.28(14)	Se(2)-Pd(3)-Se(3)#1	169.39(8)
Pd(1)-Se(1)-Pd(2)	82.99(7)	Pd(1)-Se(1)-Pd(3)	87.73(7)
Pd(1)-Se(2)-Pd(2)	84.33(7)	Pd(1)-Se(2)-Pd(3)	89.47(8)
Pd(2)-Se(1)-Pd(3)	79.86(7)	Pd(2)-Se(2)-Pd(3)	80.75(7)
Pd(2)-Se(3)-Pd(3)#1	109.54		

318

319 **Table 3:** Selected bond lengths (Å) and bond angles (º) for [Pt{2-SeC_5H_3(5-

320 Me)N}$_2$(dppm)].$C_6H_5CH_3$ (**2a**)

	Molecule (a)			Molecule (b)			
Pt1-P1	2.2602(14)	Pt1-P2	2.2671(14)	Pt1A-P1A	2.2637(14)	Pt1A-P2A	2.2595(14)
Pt1-Se1	2.4382(7)	Pt1-Se2	2.4392(7)	Pt1A-Se1A	2.4356(6)	Pt1A-Se2A	2.4472(7)
Se1-C1	1.906(7)	Se2-C7	1.897(6)	Se1A-C1A	1.899(7)	Se2A-C7A	1.905(6)
P1-Pt1-P2	72.74(5)	Se1-Pt1-Se2	79.98(2)	P1A-Pt1A-P2A	72.92(5)	Se1A-Pt1A-Se2A	80.23(2)
P1-Pt1-Se1	104.12(4)	P2-Pt1-Se2	103.14(4)	P1A-Pt1A-Se1A	104.51(4)	P2A-Pt1A-Se2A	102.40(4)
P1-Pt1-Se2	175.85(4)	P2-Pt1-Se1	176.02(4)	P1A-Pt1A-Se2A	174.78(4)	P2A-Pt1A-Se1A	177.02(4)

4. Conclusions

The substitution reactions of $[MCl_2(P\cap P)]$ (M = Pd, Pt) [(P∩P) = 2 PPh_3, dppm, dppe, dppp] with 2-pyridyl-5-methyl pyridine selenolates afforded various complexes, ranging from chelated, trinuclear and hexanuclear nature of these products is depend upon the nature of phosphines and available binding modes in hybrid ligand. These ligands exhibit encouraging potential for building multinuclear complexes. Diversified structures and rich coordination of such complexes facilitate to evolve the further research and explore their reactivity in material chemistry.

Competing Interests

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

Appendix A. Supplementary data

CCDC 2326944, 2294251 for complexes $[Pd_6Br_{0.87}Cl_{1.13}\{2\text{-}SeC_5H_3(5\text{-}Me)\}_2(PPh_3)_6]$ and $[Pt\{2\text{-}SeC_5H_3(5\text{-}Me)N\}_2(dppm)]$ respectively contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, 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

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Declarations

Ethical approval: Not applicable.

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Availability of data and materials: The authors confirm that the data supporting the findings of this study are available in electronic supplementary information.

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