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Reactivity of dipyrimidyldiselenides with $[M(PPh_3)_4]$ and 2-pyrimidylchalcogenolates with $[MCl_2(diphosphine)]$ (M = Pd or Pt)

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ABSTRACT

Oxidative addition reactions of $\{SeC_4H(4,6\text{-}R)_2N_2\}_2$ with $[M(PPh_3)_4]$ (M = Pt or Pd) in benzene afforded complexes of composition, $[Pt\{SeC_4H(4,6\text{-}R)_2N_2\}_2(PPh_3)_2]$ (**1**) and $[Pd\{\eta^2\text{-}SeC_4H(4,6\text{-}R)_2N_2\}\{SeC_4H(4,6\text{-}R)_2N_2\}(PPh_3)]$ (**3**) (R = H or Me). The former when left in solution dissociated to $[Pt\{\eta^2\text{-}SeC_4H(4,6\text{-}R)_2N_2\}\{SeC_4H(4,6\text{-}R)_2N_2\}(PPh_3)]$ (**2**) and PPh_3. Treatment of $[PtCl_2(P^{\cap}P)]$ ($P^{\cap}P$ = dppe or dppp) and $NaEC_4H(4,6\text{-}R)_2N_2$ (for E/R = Se/H/Me or Te/Me) gave mononuclear complexes $[Pt\{EC_4H(4,6\text{-}R)_2N_2\}_2(P^{\cap}P)]$ (**4** and **6**) (R = H or Me, $P^{\cap}P$ = dppe or dppp) which on leaving for recrystallization in dichloromethane/$CDCl_3$ solution resulted in trinuclear chalcogenido-bridged complexes $[Pt_3(\mu\text{-}E)_2(P^{\cap}P)_3]\cdot 2Cl$ (E = Se or Te) (**6**). The latter were also formed when $[PtCl_2(P^{\cap}P)]$ ($P^{\cap}P$ = dppe or dppp) was treated with sodium 2-pyrimidyltellurolate. The substitution reactions between $[PdCl_2(P^{\cap}P)]$ ($P^{\cap}P$ = dppe or dppp) and $NaEC_4H(4,6\text{-}R)_2N_2$ (E = Se or Te; R = H or Me) afforded chalcogenido-bridged trinuclear complexes, $[Pd_3(\mu\text{-}E)_2(P^{\cap}P)_3]2Cl$ (**7**) ($P^{\cap}P$ = dppe or dppp). These complexes were characterized by elemental analyses and NMR (^1H, ^{31}P, ^{77}Se, ^{125}Te, ^{195}Pt) spectroscopy. The molecular structures of $[Pt(SeC_4H_3N_2)_2(PPh_3)_2]$ (**1a**) and $[Pd\{\eta^2\text{-}SeC_4H_3N_2\}\{SeC_4H_3N_2\}(PPh_3)]$ (**3a**) were established by single crystal X-ray diffraction analyses. Metal atom in these complexes acquires a distorted squareplanar configuration.

1. Introduction

The chemistry of platinum group chalcogenolate complexes continues to be an active area of considerable research owing to several obvious reasons. These include their use as molecular tectons for the synthesis of high nuclearity of complexes [1–3], precursors for low temperature synthesis of metal chalcogenides [4–6] and their relevance in catalysis [7–10]. Palladium catalyzed addition of E–E bond to alkyne has emerged an important strategy to prepare vinylsulfides/selenides [9] which find numerous applications in organic synthesis, coordination chemistry and electronics [11–14]. The catalytic reaction proceeds with excellent stereoselectivity and is believed to involve mononuclear *cis*-$[Pd(EAr)_2(PR_3)_2]$ (E = S or Se) complexes [15], although binuclear complexes, $[Pd_2(EAr)_2(\mu\text{-}EAr)_2(PR_3)_2]$ are generally isolated when $[Pd(PR_3)_4]$ is treated with ArEEAr (E = S or Se) [16–19]. Such reactions with diaryl ditellurides, in contrast, yield several products due to competitive cleavage of Te–Te and Te–C bonds [20–22].

Recently we have investigated reactions of hemilabile pyridylchalcogenolate ligands, $(RC_5H_3N\text{–}E)$ (E = Se or Te), with M^0 and M^{II} phosphine complexes in view to isolate and characterize metastable complexes stabilized through $E^{\cap}N$ bonding [23–25]. Indeed we could isolate, besides expected products, several serendipitous products like $[Pt(2\text{-}TeC_5H_4N)_2(Te)(PPh_3)]$ contain Te^0 as a ligand [23], and $[Pt\{PPh_2C(TeC_5H_3(3\text{-}R)N)PPh_2\}_2]$ (R = H or Me) [24] as well as metastable species like $[Pd(2\text{-}TeC_5H_4N)_2(dppp)]$ which in chlorinated hydrocarbon solvents solution slowly transformed to a trinuclear product $[Pd_3(\mu\text{-}Te)_2(dppp)_3]^{2+}$ via other intermediate complexes [25]. These reactions have prompted us to examine chemistry of ligand systems where chalcogen carbon is indirectly linked to two heteroatoms, e.g. 2-pyrimidyl group, so as to enhance both denticity of the ligand and basicity of

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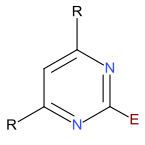
the heterocyclic ring. Accordingly we have synthesized 2-chalcogenopyrimidyl ligands (**I**) and studied their reactions with M^0 and M^{II} (M = Pd or Pt) phosphine complexes. The results for this work are reported herein.



(R = H or Me; E = Se or Te)

(I)

2. Experimental

Elemental selenium (99.99%), tellurium (99.99%), sodium borohydride and tertiary phosphines were obtained from commercial sources (Aldrich/Strem). The compounds, 2-bromopyrimidine, 2-chloro-4,6-dimethylpyrimidine [26], $[M(PPh_3)_4]$, (M = Pd [27], Pt [28]), $[MCl_2(P^{\cap}P)]$ [$P^{\cap}P$ = dppm (bis(diphenylphosphino) methane), dppe (1,2-bis(diphenylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)propane)] [29,30] and the ligands $(SeC_4H_3N_2)_2$ [31], $\{SeC_4H(4,6\text{-}Me)_2N_2\}_2$ and $\{TeC_4H(4,6\text{-}R)_2N_2\}_2$ were prepared by literature methods. All syntheses were carried out under a nitrogen atmosphere in dry solvents. Organo-selenium and -tellurium compounds were purified by column chromatography on silica gel (60/120 mesh size) using solvent mixtures as eluents and the purity was evaluated by NMR spectroscopy.

The ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$, $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker Avance-II spectrometer operating at 300, 75.47, 121.49, 57.23, 94.77 and 64.52 MHz, respectively. Chemical shifts are relative to internal chloroform peak for ^1H, $^{13}C\{^1H\}$ NMR spectra and external 85% H_3PO_4 for ^{31}P NMR, external Ph_2Se_2 (δ 463 ppm relative to Me_2Se) in $CDCl_3$ for $^{77}Se\{^1H\}$ NMR, external $[Te(dtc)_2]$ in $CDCl_3$ (δ = 440 ppm relative to Me_2Te; dtc = *N*,*N*-diethyldithiocarbamate) for $^{125}Te\{^1H\}$ NMR spectra and Na_2PtCl_6 in D_2O for ^{195}Pt NMR. Elemental analyses were carried out on a Thermo Fischer Flash EA1112 CHNS analyzer.

Intensity data for $[Pt(SeC_4H_3N_2)_2(PPh_3)_2]$ (**1a**) and $[Pd\{\eta^2\text{-}SeC_4H_3N_2\}\{SeC_4H_3N_2\}(PPh_3)]$ (**3a**) were collected on a Rigaku MM007 RA equipped with a Mercury CCD diffractometer using MoK_α radiation at 93(2) K so that $\theta_{max} = 27.5°$. The structures were solved by direct methods [32] and refinement was on F^2 using data that had been corrected for absorption effects with an empirical procedure [33]. Non-hydrogen atoms were modelled with anisotropic displacement parameters, hydrogen atoms in their calculated positions. Molecular structures were drawn using ORTEP [34]. Crystallographic and structural determination data are listed in Table 1.

2.1. Syntheses of complexes

2.1.1. Preparation of $[Pt(SeC_4H_3N_2)_2(PPh_3)_2]$ (**1a**)

To a benzene solution (15 cm^3) of $(SeC_4H_3N_2)_2$ (38 mg, 0.12 mmol) a solution (30 cm^3) of $[Pt(PPh_3)_4]$ (140 mg, 0.11 mmol) in the same solvent was added with stirring and the contents were stirred for 5 h at room temperature. The solvent was evaporated in *vacuo* and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated phosphine. The residue was extracted with dichloromethane, filtered and passed through a Florisil column. The ensuing solution on refrigeration at −5 °C afforded yellow crystals of the title complex (yield 82 mg, 70% m.p., 192 °C (dec.)). Anal. calcd. for $C_{44}H_{36}N_4P_2PtSe_2$: C, 51.02; H, 3.50, N; 5.41%. Found: C, 50.85; H, 3.36; N; 5.52%. ^1H NMR ($CDCl_3$) δ: 6.80 (br, $C_4H_3N_2$), 7.33–7.67 (m, Ph), 8.25 (br, $C_4H_3N_2$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 20.3 [(^1J(Pt–P) = 2792 Hz)], $^{195}Pt\{^1H\}$ NMR ($CDCl_3$) δ: −5120 [(^1J(Pt–P) = 2778 Hz)]; on prolonged standing in solution gave $[Pt\{\eta^2\text{-}SeC_4H_3N_2\}\{SeC_4H_3N_2\}(PPh_3)]$ (**2a**): $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 7.4 [(^1J(Pt–P) = 3873 Hz)], 29.2 ($OPPh_3$), $^{195}Pt\{^1H\}$ NMR ($CDCl_3$) δ: −4409 (d, ^1J(Pt–P) = 3886 Hz)].

2.1.2. Preparation of $[Pt\{SeC_4H(4,6\text{-}Me)_2N_2\}_2(PPh_3)_2]$ (**1b**)

Prepared in a similar fashion adopting above method (Section 2.1.1) for the synthesis of **1a**, and recrystallized from dichloromethane–hexane mixture as yellow crystals (yield 103 mg, 74%; mp: 208 °C (dec.)). Anal. calcd. for $C_{48}H_{44}N_4P_2PtSe_2$: C, 52.80; H, 4.06, N; 5.13%. Found: C, 52.31; H, 4.21; N; 5.28%. ^1H NMR ($CDCl_3$) δ: 2.18 (s, Me), 6.32 (s, C*H*-5), 7.29 (br, Ph), 7.86 (br, C_4HN_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 21.8 [(^1J(Pt–P) = 2831 Hz)]; on prolonged standing in solution gave $[Pt\{\eta^2\text{-}SeC_4H(4,6\text{-}Me)_2N_2\}\{SeC_4H(4,6\text{-}Me)_2N_2\}(PPh_3)]$ (**2b**) $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 5.5 [(^1J(Pt–P) = 4064 Hz)], 29.2 ($OPPh_3$), −5.5 ppm (PPh_3).

2.1.3. Preparation of $[Pd\{\eta^2\text{-}SeC_4H_3N_2\}\{SeC_4H_3N_2\}(PPh_3)]$ (**3a**)

To a benzene solution (10 cm^3) of $(SeC_4H_3N_2)_2$ (48 mg, 0.15 mmol), a solution (30 cm^3) of $[Pd(PPh_3)_4]$ (168 mg, 0.15 mmol) in the same solvent was added with continuous stirring for 4 h at room temperature. The solvent was evaporated under vacuum and the residue was washed thoroughly with diethyl ether to remove liberated triphenylphosphine and was recrystallized from dichloromethane to afford red crystals of the title complex (yield 75 mg, 75%, m.p. 169 °C). Anal. calcd. for $C_{26}H_{21}N_4PPdSe_2$: C, 45.60; H, 3.09, N; 8.18%. Found: C, 45.73; H, 3.30; N; 7.89%. ^1H NMR ($CDCl_3$) δ: 6.73 (t, 4.8 Hz, $C_4H_3N_2$), 7.37 (br, PPh_3), 8.20 (d, 4.8 Hz, $C_4H_3N_2$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 32.9 ppm.

Table 1
Crystallographic and structural determination data for $[Pt(SeC_4H_3N_2)_2(PPh_3)_2]\cdot 2CH_2Cl_2$ (**1a**·$2CH_2Cl_2$) and $[Pd\{\eta^2\text{-}SeC_4H_3N_2\}\{SeC_4H_3N_2\}(PPh_3)].CH_2Cl_2$ (**3a**·CH_2Cl_2).

Complex	**1a**·$2CH_2Cl_2$	**3a**·CH_2Cl_2
Chemical formula	$C_{44}H_{36}N_4P_2PtSe_2\cdot 2CH_2Cl_2$	$C_{26}H_{21}N_4PPdSe_2\cdot CH_2Cl_2$
Formula wt.	1205.57	769.68
Crystal size (mm^3)	0.11 × 0.04 × 0.03	0.15 × 0.10 × 0.10
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1/c}$	$P2_{1/n}$
Unit cell dimensions		
a (Å)	11.546(4)	14.726(4)
b (Å)	13.308(5)	10.539(3)
c (Å)	15.224(6)	19.055(6)
β (°)	107.359(8)	107.142(8)
Volume ($Å^3$)	2232.6(14)	2825.9(14)
ρ_{calcd}, g cm^{-3}	1.793	1.809
Z	2	4
μ (mm^{-1})/*F*(000)	5.123/1176	3.503/1504
Limiting indices	$-11 \le h \le 13$	$-17 \le h \le 17$
	$-11 \le k \le 16$	$-12 \le k \le 12$
	$-18 \le l \le 15$	$-17 \le l \le 22$
θ for data collection (°)	2.40–25.34	1.55–25.36
No of reflections collected	4049	5090
No of independent reflection	3092	4336
Data/restraints/parameters	4049/0/268	5090/6/334
Final R_1, wR_2 indices	0.0504/0.0985	0.0372/0.0816
R_1, wR_2 (all data)	0.0736/0.1125	0.0476/0.0955
Goodness of fit on F^2	1.091	1.089

*2.1.4. Preparation of [Pd{η²-SeC₄H(4,6-Me)₂N₂}{SeC₄H(4,6-Me)₂N₂}(PPh₃)] (**3b**)*

Prepared similar to **3a** and recrystallized from dichloromethane gave red crystals (yield 65 mg, 68%, m.p. 182 °C). Anal. calcd. for $C_{30}H_{29}N_4PPdSe_2$: C, 48.63; H, 3.94, N; 7.56%. Found: C, 48.28; H, 3.78; N; 7.63%. ^{1}H NMR ($CDCl_3$) δ: 2.23 (s, Me), 6.41 (s, C_4HN_2), 7.28 (d, Ph), 7.61 (br, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 32.7 ppm; $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ: 210 ppm.

*2.1.5. Preparation of [Pt{SeC₄H₃N₂}₂(dppe)] (**4a**)*

To a benzene suspension (10 cm^3) of [$PtCl_2$(dppe)] (90 mg, 0.13 mmol) was added a methanol–benzene solution (10 cm^3) of $NaSeC_4H_3N_2$ [freshly prepared from $(SeC_4H_3N_2)_2$ (50 mg, 0.16 mmol) in benzene and $NaBH_4$ (12 mg, 0.32 mmol) in methanol]. The reactants were stirred for 5 h at room temperature to give a yellow solution. The solvents were removed under vacuum and the residue was washed with diethyl ether and dried under reduced pressure. The product was extracted with dichloromethane, filtered and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum which on slow evaporation at room temperature gave a yellow powder (yield 79 mg, 64%, mp: 129 °C). Anal. calcd. for $C_{34}H_{30}N_4P_2PtSe_2$: C, 44.89; H, 3.32; N, 6.16%. Found: C, 45.34; H, 3.23; N, 5.89%. ^{1}H NMR ($CDCl_3$) δ: 2.13–2.37 (br, −PCH_2), 6.45 (br, $C_4H_3N_2$), 7.67–7.85 (m, Ph), 8.54 (br, pym); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 46.1 [^1J(Pt–P) = 3090 Hz] ppm. The latter in $CDCl_3$ solution on prolonged period afforded yellow crystals of a trinuclear complex of the composition, $[Pt_3Se_2(dppe)_3]Cl_2$ (**6a**) (mp: 268 °C (dec)). Anal. calcd. for $C_{78}H_{72}Cl_2P_6Pt_3Se_2$: C, 46.62; H, 3.61%. Found: C, 47.12; H, 3.79%. ^{1}H NMR ($CDCl_3$) δ: 7.22–7.70 (m, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 38.7 [^1J(Pt–P) = 3244 Hz].

*2.1.6. Preparation of [Pt{SeC₄H₃N₂}₂(dppp)] (**4b**)*

Prepared similar to **4a** and recrystallized from dichloromethane as a yellow powder (yield 87 mg, 70%, mp: 183 °C(dec.)). Anal. calcd. for $C_{35}H_{32}N_4P_2PtSe_2$: C, 45.51; H, 3.49; N, 6.06%. Found: C, 45.67; H, 3.55; N, 5.98%. ^{1}H NMR ($CDCl_3$) δ: 1.95 (br), 2.51 (br)(CH_2), 6.79–8.48 (br, m, C_4H_3 and Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −5.9 [^1J(Pt–P) = 2886 Hz] ppm.

*2.1.7. Preparation of [Pt{TeC₄H(4,6-Me)₂N₂}₂(dppm)] (**5a**)*

To a benzene suspension (10 cm^3) of [$PtCl_2$(dppm)] (120 mg, 0.18 mmol) was added a methanol–benzene solution (10 cm^3) of $NaTeC_4H(4,6\text{-}Me)_2N_2$ [freshly prepared from $\{TeC_4H(4,6\text{-}Me)_2N_2\}_2$ (90 mg, 0.19 mmol) in benzene and $NaBH_4$ (15 mg, 0.40 mmol) in methanol]. The mixture was stirred for 6 h whereupon a turbid orange solution was formed. The solvents were decanted and the precipitate was washed thoroughly with diethyl ether and extracted with dichloromethane, filtered, and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum and hexane (0.5 cm^3) was added which on refrigeration at −5 °C afforded orange crystals (yield 139 mg, 72%, mp: 129 °C (dec)). Anal. calcd. for $C_{37}H_{36}N_4P_2PtTe_2$: C, 42.36; H, 3.46; N, 5.34%. Found: C, 42.28; H, 3.43; N, 5.21%. ^{1}H NMR ($CDCl_3$) δ: 2.35 (s, Me), 4.38 (t, ^2J(P–H) = 10.2 Hz, ^3J(Pt–H) = 55 Hz, −PCH_2), 6.21 (s, C_4HN_2), 7.16–7.31 (m, Ph), 7.86 (br, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −50.1 [^1J(Pt–P) = 2512 Hz]; $^{125}Te\{^1H\}$ NMR ($CDCl_3$) δ: −32 [^1J(Pt–Te) = 1034 Hz] ppm.

*2.1.8. Preparation of [Pt{SeC₄H(4,6-Me)₂N₂}₂(dppe)] (**5b**)*

Prepared similar to **4a** using [$PtCl_2$(dppe)] (96 mg, 0.14 mmol) and $NaSeC_4H(4,6\text{-}Me)_2N_2$ [freshly prepared from $\{SeC_4H(4,6\text{-}Me)_2N_2\}_2$ (53 mg, 0.14 mmol) in benzene and $NaBH_4$ (12 mg, 0.32 mmol) in methanol] in yield 67% (93 mg), mp: 176 °C (dec). Anal. calcd. for $C_{38}H_{38}N_4P_2PtSe_2$: C, 47.26; H, 3.97, N; 5.80%. Found: C, 46.91; H, 3.78; N; 5.72%. ^{1}H NMR ($CDCl_3$) δ: 1.97 (s, Me), 2.13–2.20 (m, −PCH_2), 6.22 (s, C_4HN_2), 7.32 (br) 7.87 (m, PPh_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 45.7 [(^1J(Pt–P) = 3039 Hz)].

*2.1.9. Preparation of [Pt{TeC₄H(4,6-Me)₂N₂}₂(dppe)] (**5c**)*

Prepared and recrystallized similar to above method as a yellow powder (yield 106 mg, 68%, mp: 163 °C (dec)). Anal. calcd. for $C_{38}H_{38}N_4P_2PtTe_2$: C, 42.94; H, 3.60; N, 5.27%. Found: C, 43.12; H, 3.48; N, 5.51%. ^{1}H NMR ($CDCl_3$) δ: 2.16 (m, −PCH_2), 2.42 (s, Me), 6.22 (s, C_4HN_2), 7.31(br), 7.88 (br)(Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 45.8 [^1J(Pt–P) = 2978 Hz] ppm.

*2.1.10. Preparation of [Pt{SeC₄H(4,6-Me)₂N₂}₂(dppp)] (**5d**)*

Prepared in a similar fashion to **5a** and recrystallized from dichloromethane as yellow powder (yield 85 mg, 64%, mp: 121 °C(dec.)). Anal. calcd. for $C_{39}H_{40}N_4P_2PtSe_2$: C, 47.81; H, 4.12; N, 5.72%. Found: C, 47.69; H, 4.28; N, 5.95%. ^{1}H NMR ($CDCl_3$) δ: 1.89(br), 2.49(br)(CH_2), 2.40 (s, Me), 6.33 (s, C_4HN_2), 7.33 (br), 7.83 (br) (Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −5.0 [^1J(Pt–P) = 2887 Hz].

*2.1.11. Preparation of [Pt{TeC₄H(4,6-Me)₂N₂}₂(dppp)] (**5e**)*

Prepared and recrystallized in a similar fashion to **5a**, brown powder (yield 101 mg, 65%, mp: 174 °C (dec)). Anal. calcd. for $C_{39}H_{40}N_4P_2PtTe_2$: C, 43.49; H, 3.74; N, 5.20%. Found: C, 43.92; H, 3.89; N, 4.89%. ^{1}H NMR ($CDCl_3$) δ: 1.96 (br), 2.57 (br) (CH_2), 2.43 (s, Me), 6.40 (s, C_4HN_2), 7.32(br), 7.89 (br) (Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −6.3 [^1J(Pt–P) = 2825 Hz] ppm. When a $CDCl_3$ solution of the complex was left for more than 24 h, red crystals of **6c** (^{31}P NMR = −13.5 ppm) were formed, analysis and NMR data were consistent with other preparations.

*2.1.12. Preparation of [Pt₃(μ-Te)₂(dppe)₃]Cl₂ (**6b**)*

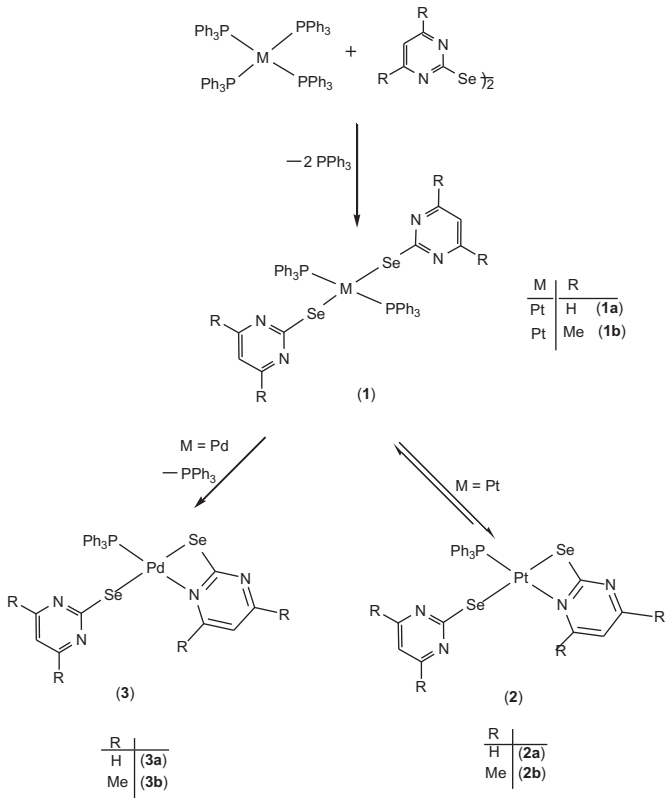
To a benzene suspension (14 cm^3) of [$PtCl_2$(dppe)] (120 mg, 0.18 mmol) was added a methanol–benzene solution (10 cm^3) of $NaTeC_4H_3N_2$ [freshly prepared from $(TeC_4H_3N_2)_2$ (75 mg, 0.18 mmol) in benzene and $NaBH_4$ (14 mg, 0.37 mmol) in methanol]. The mixture was stirred for 5 h whereupon an orange solution was obtained. The solvents were removed under reduced pressure. The residue was washed thoroughly with diethyl ether and dried under vacuum. The product was extracted with dichloromethane, filtered and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum and hexane (0.5 cm^3) was added which on refrigeration at −5 °C afforded an orange powder (yield 75 mg, 59%, mp: 167 °C (dec)). Anal. calcd. for $C_{78}H_{72}Cl_2P_6Pt_3Te_2$: C, 44.47; H, 3.44%. Found: C, 44.10; H, 3.63%. ^{1}H NMR ($CDCl_3$) δ: 2.47 (m, −PCH_2), 6.98–7.45 (m, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 40.8 [^1J(Pt–P) = 3144 Hz] ppm.

*2.1.13. Preparation of [Pt₃(μ-Te)₂(dppp)₃]Cl₂ (**6c**)*

Prepared similar to **6b** and recrystallized from dichloromethane–diethyl ether mixture as red crystals (yield 64 mg, 62%, mp: 182 °C (dec)). Anal. calcd. for $C_{81}H_{78}Cl_2P_6Pt_3Te_2$: C, 45.28; H, 3.66%. Found: C, 45.44; H, 3.42%. ^{1}H NMR ($CDCl_3$) δ: 2.51 (br, −PCH_2), 2.95 (br, CH_2), 7.13–7.21 (m, Ph), 7.40–744 (m, Ph), 7.78 (br, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −13.0 [^1J(Pt–P) = 2980 Hz] ppm.

*2.1.14. Preparation of [Pd₃(μ-Se)₂(dppe)₃]Cl₂ (**7a**)*

Prepared similar to **6b** using [$PdCl_2$(dppe)] (96 mg, 0.17 mmol) and either $NaSeC_4H(4,6\text{-}Me)_2N_2$ [prepared from $\{SeC_4H(4,6\text{-}Me)_2N_2\}_2$ (62 mg, 0.17 mmol) in benzene and $NaBH_4$ (14 mg, 0.37 mmol) in methanol] or $NaSeC_4H_3N_2$ [prepared from $(SeC_4H_3N_2)_2$ (54 mg, 0.17 mmol) in benzene and $NaBH_4$ (13.3 mg, 0.35 mmol) in methanol] and extracted with dichloromethane which on slow evaporation gave an orange crystalline solid in 52–56% yield (m.p. 293 °C (dec.)). Microanalysis and NMR data for



Scheme 1. Oxidative addition reactions of $[M(PPh_3)_4]$ (M = Pd or Pt) with 2-selenopyrimidines.

the samples isolated from these preparations were similar. Anal. calcd. for $C_{78}H_{72}Cl_2P_6Pd_3Se_2$: C, 53.74, H, 4.16%. Found: C, 54.01; H, 4.39%. ^{1}H NMR ($CDCl_3$) 2.64 (br, $-PCH_2$), 7.10 (t, 1.2 Hz, Ph), 7.38–7.47 (m, Ph), 7.48–7.55 (m, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 50.3 ppm.

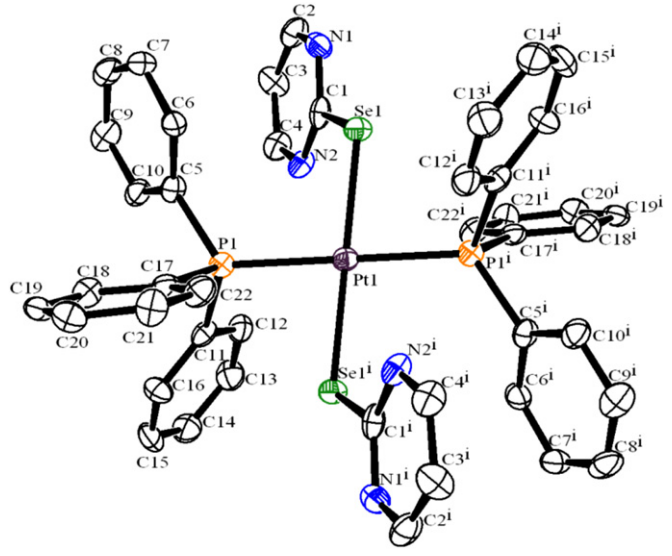


Fig. 1. ORTEP diagram of $[Pt(SeC_4H_3N_2)_2(PPh_3)_2]\cdot 2CH_2Cl_2$ (**1a**·$2CH_2Cl_2$) with atomic number scheme. The ellipsoids were drawn at 50% probability level. The solvent molecules are omitted.

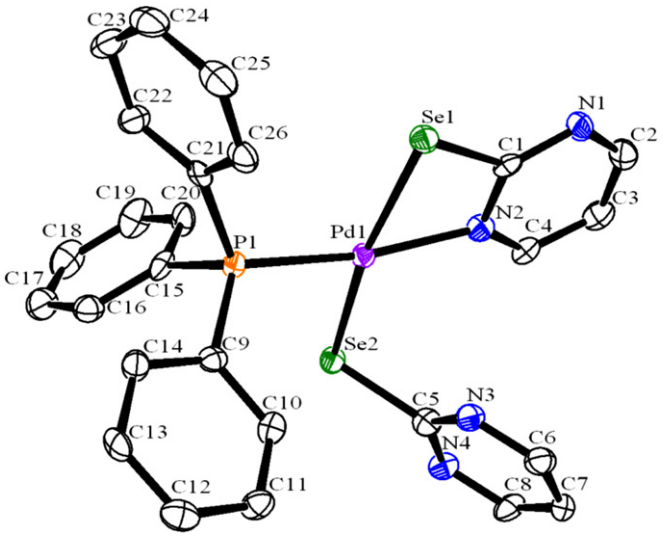


Fig. 2. ORTEP diagram of $[Pd\{\eta^2\text{-}SeC_4H_3N_2\}\{SeC_4H_3N_2\}(PPh_3)]\cdot CH_2Cl_2$ (**3a**·CH_2Cl_2) with atomic number scheme. The ellipsoids were drawn at 50% probability level. The solvent molecule is omitted.

2.1.15. *[Pd$_3$(μ-Se)$_2$(dppp)$_3$]Cl$_2$ (**7b**)*

Prepared, extracted with dichloromethane and recrystallized in a similar fashion to **7a** using $[PdCl_2(dppp)]$ and $NaSeC_4H_3N_2$ or $NaSeC_4H(4,6\text{-}Me)_2N_2$ as yellow crystalline solid in 70% yield (mp: 275 °C (dec)). Anal. calcd. for $C_{81}H_{78}Cl_2P_6Pd_3Se_2$: C, 54.49, H, 4.40%. Found: C, 54.71; H, 4.73%. ^{1}H NMR ($CDCl_3$) 2.85 (br, $-PCH_2$), 3.2 (br, $-CH_2$), 6.38–7.16 (m, Ph), 7.47–7.59 (br, Ph), 7.77–7.84 (m, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −3.0 ppm.

2.1.16. *[Pd$_3$(μ-Te)$_2$(dppe)$_3$]Cl$_2$ (**7c**)*

Prepared in a similar fashion as **7a** adopting method (i) in 61% yield as a red crystal. m.p. 193 °C (dec.). Anal. calcd. for $C_{78}H_{72}Cl_2P_6Pd_3Te_2$: C, 50.89; H, 3.94%. Found: C, 50.63; H, 3.79%. ^{1}H NMR ($CDCl_3$) 2.40 (m, $-PCH_2$), 7.40 (br), 7.79 (br) (Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 46.3 ppm. Similarly, prepared in a manner to **7a** method (ii) using reaction of $[PdCl_2(dppe)]$ (101 mg, 0.18 mmol) with $NaTeC_5H_3N_2$ [prepared from $(TeC_5H_3N_2)_2$ (75 mg, 0.18 mmol) in benzene and $NaBH_4$ (14 mg, 0.37 mmole) in methanol] gave red crystals in 63% (68 mg) yield (m.p. 193 °C (dec.)). Anal. calcd. for $C_{78}H_{72}Cl_2P_6Pd_3Te_2$: C, 50.89; H, 3.94%. Found: C, 51.13; H, 3.67%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 46.0 ppm.

2.1.17. *[Pd$_3$(μ-Te)$_2$(dppp)$_3$]Cl$_2$ (**7d**)*

Prepared in a similar fashion as **7a** adopting method (i) in 72% yield as red crystals. m.p. 212 °C (dec.). Anal. calcd. for $C_{81}H_{78}Cl_2P_6Pd_3Te_2$: C, 51.67; H, 4.18%. Found: C, 51.39; H, 4.23%. ^{1}H NMR ($CDCl_3$) 2.95 (br, $-PCH_2$), 2.51(br, $-CH_2$), 7.14–7.77 (m, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −11.0 ppm. Similarly, prepared in a manner to **7a** method (ii) using reaction of $[PdCl_2(dppp)]$ (108 mg, 0.18 mmol)

Table 2
Selected bond lengths (Å) and angles (°) of $[Pt(SeC_4H_3N_2)_2(PPh_3)_2]\cdot 2CH_2Cl_2$ (**1a**·$2CH_2Cl_2$).

Pt1–P1	2.3128(19)	Pt1–P1	2.313(2)
Pt1–Se1	2.4491(11)	Pt1–Se1	2.4491
Se1–C1	1.900(7)		
P1–Pt1–P1	179.999(1)	Se1–Pt1–Se1	179.998(11)
P1–Pt1–Se1	97.26(5)	P1–Pt1–Se1	82.74(5)
P1–Pt1–Se1	82.74(5)	P1–Pt1–Se1	97.26(5)
C1–Se1–Pt1	106.9(3)		

Table 3
Selected bond lengths (Å) and angles (°) of [Pd{η^2-$SeC_4H_3N_2$}{$SeC_4H_3N_2$}(PPh_3)].CH_2Cl_2 (**3a**·CH_2Cl_2).

Pd1–P1	2.2310(13)	Se1–C1	1.891(4)
Pd1–Se1	2.4394(7)	Se2–C5	1.917(5)
Pd1–Se2	2.4341(7)	N2–C1	1.349(6)
Pd1–N2	2.118(4)		
N2–Pd1–P1	170.76(11)	C1–Se1–Pd1	77.47(14)
P1–Pd1–Se1	100.66(4)	C1–N2–Pd1	102.3(3)
P1–Pd1–Se2	90.90(4)	C5–Se2–Pd1	96.38(14)
N2–Pd1–Se1	71.01(10)	N1–C1–Se1	125.5(3)
Se2–Pd1–Se1	168.37(2)	N2–C1–Se1	109.2(3)
N2–Pd1–Se2	97.37(10)	N1–C1–N2	125.3(4)

with $NaTeC_5H_3N_2$ [prepared from $(TeC_5H_3N_2)_2$ (77 mg, 0.19 mmol) in benzene and $NaBH_4$ (15 mg, 0.39 mmol) in methanol] gave red crystals in 69% (79 mg) yield (m.p. 212 °C (dec.)). Anal. calcd. for $C_{81}H_{78}Cl_2P_6Pd_3Te_2$: C, 51.67; H, 4.18%. Found: C, 51.54; H, 4.04%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −11.0 ppm.

3. Results and discussion

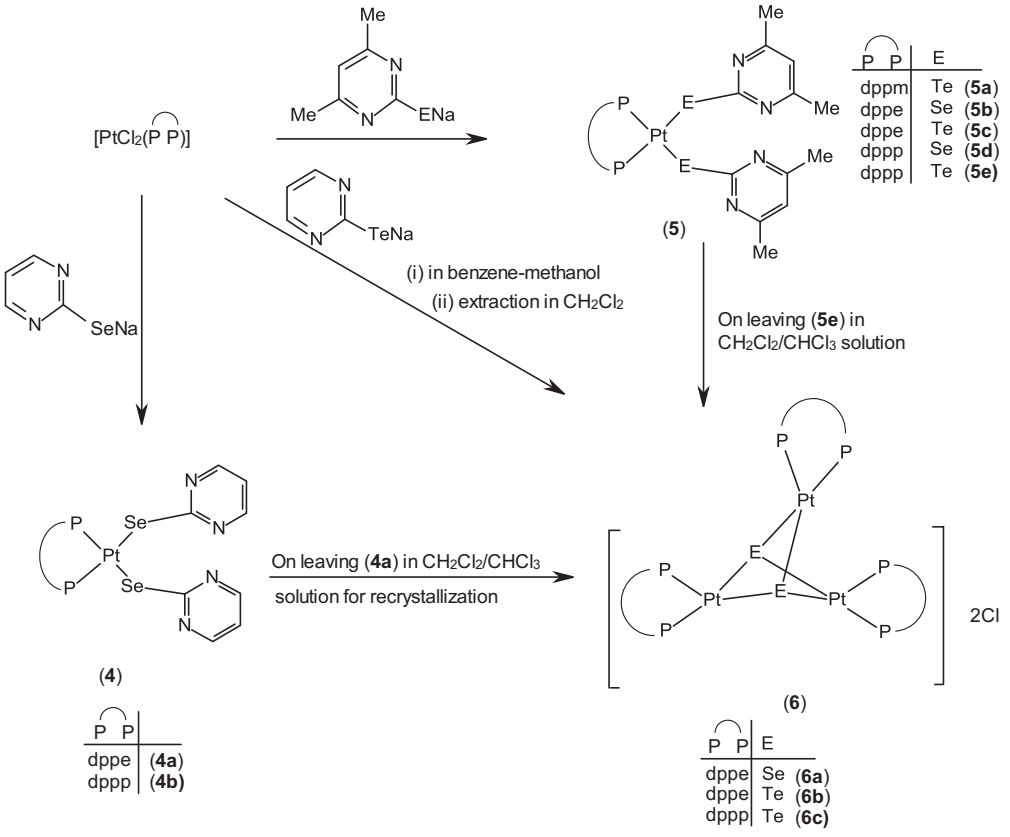
3.1. Synthesis of ligands

Treatment of 2-chloropyrimidine with Na_2E_2 (E = Se, Te) in water–ethanol mixture afforded not only a reddish diselenide but also yellow crystals of monoselenide whereas in case of tellurium only dark red (R = H) or blue crystals (R = Me) of ditellurides were obtained exclusively.

The ^1H NMR spectra of all the ligands displayed expected resonances and peak multiplicities. The ^{13}C NMR spectra of diselenides and ditellurides displayed peaks due to pyimidyl carbon in the range of 117.2–167.5 ppm. The signal due to C-4,6 carbons is significantly deshielded (~167 ppm) in dimethyl substituted dichalcogenides as compared to its position in unsubstituted derivatives (~158 ppm). The C-2 (or C–E) carbon signal in diselenided (~166 ppm) is considerably deshielded with respect to the corresponding ditellurides (~150 ppm) owing to the difference in their electronegativity and polarizability.

3.2. Reactions of $[M(PPh_3)_4]$ with di(2-pyrimidyl)diselenides

The oxidative addition reactions of $[M(PPh_3)_4]$ with dipyrimidyldiselenides proceed smoothly to afford complexes of the type *trans*-[Pt{$SeC_4H(4,6\text{-}R)_2N_2$}$_2$($PPh_3$)$_2$] (**1**) (when M = Pt) and [Pd{η^2-$SeC_4H(4,6\text{-}R)_2N_2$}{$SeC_4H(4,6\text{-}R)_2N_2$}($PPh_3$)] (**3**) (when M = Pd) (Scheme 1). Both theoretical [35] and experimental [36,37] investigations on oxidative addition reactions of $[Pt(PR_3)_4]$ with diorgano diselenides have shown that initially a *cis*-$[Pt(SeAr)_2(PPh_3)_2]$ is formed which is subsequently isomerised to a thermodynamically stable *trans* product. Isolation of **1** as a *trans* isomer in the present study indicates that the isomerisation of *cis* form to *trans* is facile. The oxidative addition reactions of $[Pd(PPh_3)_4]$ with diorgano diselenides are known to yield binuclear complexes, $[Pd_2(SeAr)_2(\mu\text{-}SeAr)_2(PPh_3)_2]$ exclusively [17–19]. However, in the present case, internal functionalization of the selenolate aids in chelation of the ligand. Based on the earlier work [17–19] and from this study it can be inferred that the oxidative addition reaction of R'_2E_2 (E = S or Se) on $[Pd(PR_3)_4]$ also yields initially a mononuclear complex, $Pd(ER')_2(PR_3)_2$, which dissociates in solution to PR_3 and a three-coordinate palladium species, "$Pd(ER')_2(PR_3)$". The latter species depending on the nature of R′ group on chalcogenolate ligand either dimerizes, when R′ is simple alkyl or aryl group, or gives a monomeric chelate complex when R′



Scheme 2. Reactions of $[PtCl_2(P^{\cap}P)]$ ($P^{\cap}P$ = dppe or dppp) with sodium pyrimidyl chalcogenolate.

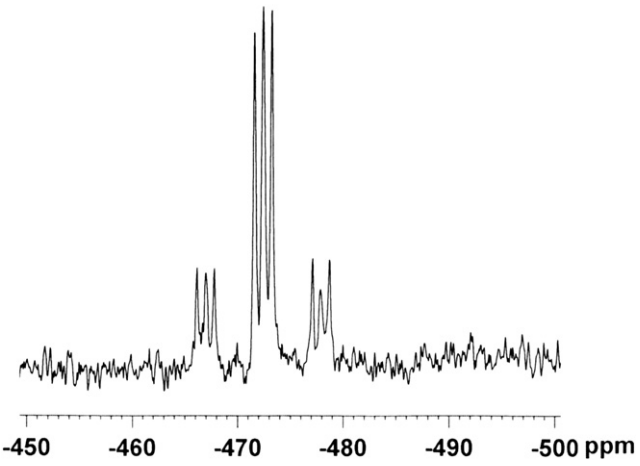


Fig. 3. $^{125}Te\{^{1}H\}$ NMR spectrum of $[Pt\{TeC_4H(4,6\text{-}Me)_2N_2\}_2(dppm)]$ (**5a**).

contains an additional donor atom like nitrogen. Formation of such a three coordinate palladium species may have implication during palladium catalyzed addition of Ar_2E_2 to alkenes [15] and can be substantiated by the fact that the palladium complexes derived from chelated phosphines are inactive in these reactions [10] because of their inability to give three coordinate palladium complex.

The ^{31}P NMR spectra of **1** and **3** exhibited a singlet while resonances for the former were flanked by ^{195}Pt satellites. The magnitude of $^{1}J(Pt-P)$ (~2800 Hz) is in conformity with *trans* configuration of the complexes [17,18,35]. The ^{195}Pt NMR spectrum of **1a** showed a triplet at −5120 ppm due to coupling with two equivalent ^{31}P nuclei. The **1** dissociated to platinum analogue (**2**) of **3** and triphenylphosphine in solution when left for a few hours. The ^{31}P NMR spectra of **2** were considerably shielded and the magnitude of $^{1}J(Pt-P)$ was also increased (~3900 Hz) with respect to **1**. The ^{195}Pt NMR spectrum of **2a** displayed a doublet due to coupling with a ^{31}P nucleus. The magnitude of $^{1}J(Pt-P)$ indicates that the phosphine ligand is *trans* to the nitrogen atom of the chelating selenolate ligand [38].

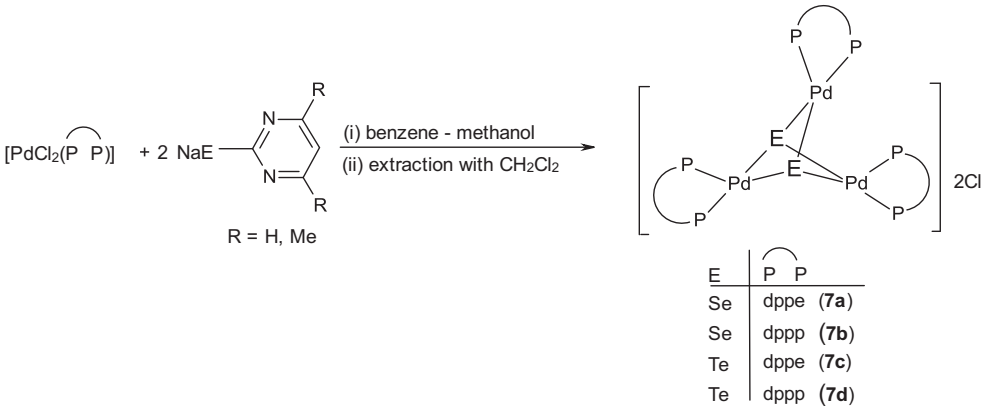
The molecular structures of $[Pt(SeC_4H_3N_2)_2(PPh_3)_2]\cdot 2CH_2Cl_2$ (**1a**·$2CH_2Cl_2$) (Fig. 1) and $[Pd\{\eta^2\text{-}SeC_4H_3N_2\}\{SeC_4H_3N_2\}(PPh_3)]\cdot CH_2Cl_2$ (**3a**·CH_2Cl_2) (Fig. 2) were established by X-ray diffraction analyses. Both the complexes crystallized with solvent molecule(s) (CH_2Cl_2). Selected interatomic parameters are given in Tables 2 and 3. The **1a** comprises of a distorted square planar central platinum atom. The *trans*-P_2Se_2 donor set defines the coordination environment around the platinum atom. The two selenolate groups adopt an *anti* configuration. The Pt–Se distances (2.4491(11) Å) are similar to those reported for the known $[Pt(SeR')_2(PR_3)_2]$; *trans*-$[Pt(SePh)_2(PPh_3)_2]$ (2.417(3), 2.419(3) Å) [36], *trans*-$[Pt(SeTh)_2(PPh_3)_2]$ (2.4629(1) Å and 2.465(1) Å) [17] and *trans*-$[Pt(SePh)_2(PR_3)_2]$ (2.461(1) Å for R = Et and 2.463(3) Å for R = Bu) [18]. The Pt–P distances are in good agreement with those reported for $[Pt(SeR')_2(PR_3)_2]$ complexes [17,18,35]. The two acute (82.74(5)°) and obtuse (97.26(5)°) P–Pt–Se angles can be compared with *trans*-$[Pt(SeTh)_2(PPh_3)_2]$ (~83 and ~96°), but differ from phenylselenolate derivatives, *trans*-$[Pt(SePh)_2(PR_3)_2]$ (R = Et, Bu, Ph) (~86 and ~94°) [18,35,37].

The palladium atom in **3a** acquires distorted square planar geometry defined by P, N, Se_2 donor atoms, the neutral donor atoms (P and N) being trans. One of the selenolate ligand forms a four-membered chelate ring while the other selenolate is bound to palladium in a monodentate fashion. The four-membered chelate ring and the pyrimidyl ring are nearly co-planar. The two Pd–Se distances are similar and are in agreement with those reported in literature, e.g. $[Pd_2(SeTh)_4(PPh_3)_2]$ (Pd–Se = 2.465(av) Å) [17]. The Pd–N and Pd–P distances are as expected, e.g. $[PdCl(TeC_5H_3(Me)N)(PPh_3)]$ (Pd–P = 2.2420(15) and Pd–N = 2.085(4) Å) [38].

3.3. Reactions of $[MCl_2(P^{\cap}P)]$ with sodium 2-pyrimidyl chalcogenolate

Treatment of $[PtCl_2(P^{\cap}P)]$ with $NaSeC_4H_3N_2$ or $NaEC_4H(4,6\text{-}Me)_2N_2$ (E = Se or Te) in benzene–methanol mixture afforded mononuclear complexes of composition, $[Pt\{EC_4H(4,6\text{-}R)_2N_2\}_2(P^{\cap}P)]$ (**4** and **5**) (Scheme 2). The similar reaction with $NaTeC_4H_3N_2$ gave an orange powder which after extraction with dichloromethane afforded tellurido-bridged trinuclear complexes, $[Pt_3(\mu\text{-}Te)_2(P^{\cap}P)_3]\cdot 2Cl$ (**6**) ($P^{\cap}P$ = dppe (**6b**) and dppp (**6c**)). When the mononuclear complexes **4a** and **5e** were left in halogenated solvents ($CDCl_3$ or CH_2Cl_2) for several hours, crystals of **6** were isolated. The ^{31}P NMR chemical shifts and $^{1}J(Pt-P)$ values for **6** are in conformity with the reported values [39,40]. The formation of telluride-bridged complex **6** either from **5e** in $CDCl_3$ or in the reaction between $PtCl_2(dppe)$ and $NaTeC_4H_3N_2$ takes place via a facile Te–C bond cleavage.

The ^{31}P NMR spectra of **4** and **5** displayed single resonances flanked by ^{195}Pt satellites. The observed $^{1}J(Pt-P)$ values are consistent with the values reported for $[Pt(EAr)_2(P^{\cap}P)]$ complexes [2,38,41,42]. The $^{125}Te\{^{1}H\}$ NMR spectrum (Fig. 3) of $[Pt\{TeC_4H(4,6\text{-}Me)_2N_2\}_2(dppm)]$ displayed a three lines centred at −32 ppm with



Scheme 3. Reactions of $[PdCl_2(P^{\cap}P)]$ ($P^{\cap}P$ = dppe or dppp) with sodium 2-pyrimidyl chalcogenolates.

platinum satellites (^1J(Pt–Te) = 1034 Hz). The observed pattern is in fact a second order spectrum originating due to coupling with *cis* and *trans* phosphorus nuclei.

The reactions between [$PdCl_2(P^{\cap}P)$] and $NaEC_4H(4,6\text{-}R_2)N_2$ (E = Se or Te; R = H or Me) in benzene–methanol mixture followed by extraction with dichloromethane invariably gave trinuclear chalcogenido-bridged palladium complexes, [$Pd_3(\mu\text{-}E)_2(P^{\cap}P)_3$]2Cl (**7**) (E = Se or Te; $P^{\cap}P$ = dppe or dppp) in 52–72% yield (Scheme 3). The ^{1}H NMR spectra were devoid of any $EC_4H(4,6\text{-}R_2)N_2$ proton resonances as expected. The ^{31}P NMR chemical shifts for **7** are in accordance with BPh_4/PF_6 salts of $[Pd_3(\mu\text{-}E)_2(P^{\cap}P)_3]^{2+}$ cations reported earlier [39,43,44]. These complexes have been isolated in low yields by a reaction between [$PdCl_2(P^{\cap}P)$] and NaEH (E = Se or Te) in the presence of $NaBPh_4$ or $NaPF_6$ [39,43]. The selenido-bridged complexes have been isolated in fairly good yield through unprecedented cleavage of C–Se bond of selenocarboxylate during the reaction of [$Pd(SeCOAr)_2(P^{\cap}P)$] with [$PdCl_2(P^{\cap}P)$] in the presence of $NaBPh_4$ in CH_2Cl_2–MeOH solvent mixture [44]. In an alternative route **7a** has been prepared in 52% yield by Morley et al. by the reaction of [$Pd(dppe)_2$] with selenium powder in CH_2Cl_2 [40].

4. Conclusions

Oxidative addition reactions of bis(2-pyrimidyl)diselenides with $M(PPh_3)_4$ afforded [$Pt\{SeC_4H(4,6\text{-}R)_2N_2\}_2(PPh_3)_2$] in the case of platinum and [$Pd\{SeC_4H(4,6\text{-}R)_2N_2\}\{\eta^2\text{-}SeC_4H(4,6\text{-}R)_2N_2\}(PPh_3)$] when M = Pd. Substitution reactions between [$PtCl_2(P^{\cap}P)$] and 2-pyrimidylchalcogenolate yielded mononuclear complexes, [$Pt\{EC_4H(4,6\text{-}R_2)N_2\}_2(P^{\cap}P)$] which are converted in to trinuclear complexes, [$Pt_3(\mu\text{-}E)_2(P^{\cap}P)_3$]·2Cl when left in $CDCl_3/CH_2Cl_2$ solution for a long time. Similar reactions with [$PdCl_2(P^{\cap}P)$], after dissolution in CH_2Cl_2, invariably afforded [$Pd_3(\mu\text{-}E)_2(P^{\cap}P)_3$]·2Cl.

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Appendix A. Supplementary material

CCDC 877824 and 877825 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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