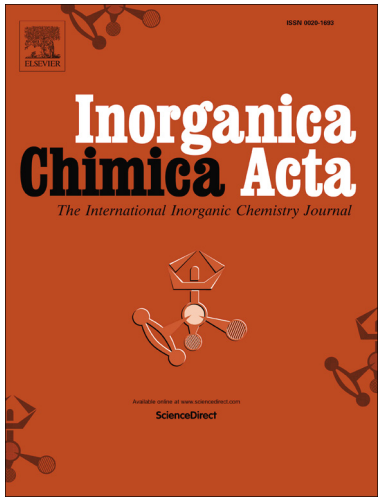

Research paper

Reactivity of hemilabile pyridyl- and methyl-substituted pyrimidylselenolates with [MCl_2(dppf)] (M = Pd, Pt; dppf = bis(diphenylphisphino)ferrocene)

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Reactivity of hemilabile pyridyl- and methyl-substituted pyrimidylselenolates with [MCl_2(dppf)] (M = Pd, Pt; dppf = bis(diphenylphisphino)ferrocene)

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Abstract:

The bis(diphenylphisphino)ferrocene (dppf) derived palladium analogue of [$PdCl_2$(dppf)] on reaction with the sodium salt of pyridyl/pyrimidyl selenolate yielded mononuclear *cis* configured complex [Pd($SeAr)_2$(dppf)] (Ar = C_5H_4N, $C_4H(4,6\text{-}Me)_2N_2$), as did the platinum precursor [$PtCl_2$(dppf)] with methyl substituted pyrimidyl salt giving [Pt{$SeC_4H(4,6\text{-}Me)_2N_2$}$_2$(dppf)]. In contrast, the reaction of platinum precursor with the sodium salt of pyridylselenolate gave two different complexes [$Pt_2(\mu\text{-}SeC_5H_4N)_2(dppf)_2]^{2+}$ and [Pt(Cl)(SeC_5H_4N)(dppf)] depending in the reaction solvent. These complexes were characterized by elemental analysis and NMR (^1H, ^{31}P) spectroscopy. The molecular structure of [Pt{$SeC_4H(4,6\text{-}Me)_2N_2$}$_2$(dppf)] was established by single crystal X-ray diffraction analysis.

Keywords: Selenolate, NMR, X-ray, dppf.

1. Introduction

The ferrocenylphosphine ligand has been extensively used as an efficient auxiliary ligand mainly due to its rich coordination chemistry without tormenting the intrinsic property of derived complex [1-3]. This inherent characteristic makes it an efficient materials and catalyst for the alkene hydroformylation, alkoxycarbonylation and heck coupling reactions [1, 4]. Even though ferrocenyl phosphine ligand was reported more than three decades ago but its chemical reactivity and application were not been unearthed until recently [1, 5-7].

The reaction of $[MCl_2(dppf)]$ (M = Pd, Pt) with Na_2S has afforded a binuclear product $[M_2(\mu\text{-}S)_2(dppf)_2]$ which transformed to $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Cl)(dppf)_2]$ and terminal thio alkyl complex $[Pt(SCH_2Cl)_2(dppf)]$ in chlorinated solvents [8]. The latter mononuclear product has also been reported by an oxidative reaction between $[Pt(dppf)_2]$ and bis(chloromethyl)disulfide [9-11]. The sulfurized dppf on reaction with $[PdCl_2(PhCN)_2]$ yielded a mononuclear complex of composition $[PdCl_2(L)]$ (L = $Fe(C_5H_4P(S)Ph_2)(C_5H_4PPh_2)$) [4]. However the reaction of other chelating phosphine precursors $[M(P\cap P)_2]$ (M= Pd, Pt; P∩P = dppe, dppp) with Ar_2E_2 (Ar = C_5H_4N, $C_5H_3N_2$; E = Se, Te) yielded a mononuclear compound $[M(EAr)_2(P\cap P)]$ as well as the binuclear product $[M_2(\mu\text{-}TeAr)_2(P\cap P)_2]$ (M = Pd, Pt; P∩P = dppe; Ar = C_5H_4N) [12-14] which decomposes to high nuclearity complex along with unidentified product in chlorinated solvents [15-17]. The facile transformation of bridging chalcogenolates to terminal one is predominantly due to high nucleophilicity of the complex which makes them highly susceptible towards attack on chlorinated solvent [8, 16, 18, 19].

In this report, we describe the synthesis and characterization of various ferrocenyl phosphine based palladium and platinum(II) selenolate complexes derived from pyridyl and methyl substituted pyrimidyl selenolate ligand and studies their reactivity in chlorinated solvent.

2. Experimental:

All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk technique. Solvents used in the reactions were degassed with nitrogen and distilled using standard procedures. The precursor complex $[PtCl_2(PhCN)_2]$ [20] and the ligands $(SeC_5H_4N)_2$, [21] and $\{SeC_4H(4,6\text{-}Me)_2N_2\}_2$ [17] were prepared by literature methods. The metal precursors $PdCl_2$, and dppf were procured from Strem chemicals. The ^1H, and $^{31}P\{^1H\}$NMR spectra were recorded on a Bruker Avance-II spectrometer operating at 500, 202.40 MHz, respectively and referenced for the solvent peak of chloroform at δ 7.26 for ^1H and externally to 85% H_3PO_4 (0.00 ppm) for ^{31}P NMR. Elemental analyses were carried out on a Thermo Fischer Flash EA1112 CHNS analyzer.

$[Pt\{SeC_4H(4,6\text{-}Me)_2N_2\}_2(dppf)].0.5C_6H_6$ (**1a**) were collected at 173K on using a Rigaku FR-XUltrahigh Brilliance Microfocus RA generator/confocal optics and XtaLAB P200 diffractometer, Mo-K_α radiation (λ = 0.71075 Å). Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. A multi-scan absorption correction was applied by using Crystal Clear [22]. The structures were solved by heavy-atom Patterson methods [23], expanded using Fourier techniques and least-squares refinement [23] was on F^2 using data converged with unweighted and weighted agreement factors. The non-hydrogen atoms were refined anisotropically and riding a model was used for hydrogen atoms. Molecular structures were drawn using ORTEP [24]. Crystallographic and structural determination data are listed in Table 1.

2.1 Synthesis of complexes

2.1.1 Preparation of [Pd{2-Se-$C_4H(4,6\text{-}Me)_2N_2$}$_2$(dppf)] (**1a**):

To a benzene-methanolic solution (10 cm^3) of $NaSeC_4H(4,6\text{-}Me)_2N_2$ [freshly prepared from 45 mg, 0.12 mmol of $(SeC_4H(4,6\text{-}Me)_2N_2)_2$, methanol (5$cm^3$) and $NaBH_4$ (10 mg, 0.26 mmol)] a solution (10 cm^3) of [$PdCl_2$(dppf)] (98 mg, 0.12 mmol) was added in the same solvents with stirring, which continued for 4 hours at room temperature. The wine red solution was concentrated to 5 cm^3 under reduced pressure. A reddish brown precipitate was formed which was washed thoroughly with hexane and diethyl ether. The residue was recrystallized from dichloromethane and few drops of hexane to afford reddish brown powder. (yield: 54 mg, 48%; m.p.:151 °C). Anal. Calcd for $C_{46}H_{42}FeN_4P_2PdSe_2$: C, 53.49; H, 4.10; N, 5.42%. Found: C, 53.88; H, 3.94; N, 5.39%. UV-Vis: 270 nm (br), 405 nm (sh). ^{1}H NMR ($CDCl_3$) δ : 1.25 (s, 6H, Me), 1.74 (s, 6H, Me), 4.31 (br, 4H, C_5H_4), 4.69 (br, 4H, C_5H_4), 6.86 (d, 4.8Hz, 2H, Ph), 7.49 -7.56 (m, 8H, Ph), 7.60-7.64 (td, 2.6Hz, 4H, Ph), 7.66-7.72 (m, 6H, Ph), 7.80 (d, 4.8Hz, 2H, $C_4H(4,6\text{-}Me)_2N_2$); ^{31}P{^{1}H}NMR ($CDCl_3$) δ : 28.6 ppm.

2.1.2 Preparation of [Pd($SeC_5H_4N)_2$(dppf)] (***1b***):

Prepared in a similar manner to complex **1a** using [$PdCl_2$(dppf)] (65 mg, 0.08 mmol) and $(SeC_5H_4N)_2$ (25 mg, 0.08 mmol) as the ligand precursor and recrystallized from dichloromethane-hexane to give a brown powder. (yield 67 mg, 92%; m.p.:110 °C). Anal. Calcd. for $C_{44}H_{36}N_2P_2FePdSe_2$: C, 54.21; H, 3.72; N, 2.87%. Found: C, 54.61; H, 3.67; N, 2.47%. UV-Vis (λ_{max}) : 278 nm (sh), 328 nm (br) . ^{1}H NMR ($CDCl_3$) δ : 4.26 (t, 1.5 Hz, 4H, C_5H_4), 4.70 (t, 1.8 Hz, 4H, C_5H_4), 6.41 (d, 3.2 Hz, 2H, C_5H_4N), 7.34-7.41 (m, 8H, Ph), 7.58-7.64 (m, 4H, Ph),

7.68-7.73(m, 10H, o-Ph+ C_5H_4N) 7.80 (d, 4.5 Hz, 2H, C_5H_4N), 8.2(d, 4.8 Hz, 2H, C_5H_4N); $^{31}P\{^1H\}$NMR ($CDCl_3$) δ : 28.3 ppm.

2.1.3 Preparation of [Pt{2-Se-$C_4H(4,6\text{-}Me)_2N_2$}$_2$(dppf)] (**2a**):

Prepared in a similar manner to complex **1a**, using [$PtCl_2$(dppf)] (99 mg, 0.12 mmol) and Na{2-Se-$C_4H(4,6\text{-}Me)_2N_2$} [freshly prepared from {2-Se-$C_4H(4,6\text{-}Me)_2N_2$}$_2$ (45 mg, 0.12 mmol) in benzene and $NaBH_4$ (10 mg, 0.26 mmol) in methanol]and recrystallized from benzene-acetone to afford yellow cryatals in 72% yield (80 mg), m.p.: 176 °C (dec.). Anal. Calcd for $C_{46}H_{42}FeN_4P_2PtSe_2$: C, 49.26; H, 3.77; N, 4.99%. Found: C, 49.68; H, 3.52; N, 4.74%. UV-Vis (λ_{max}) : 348 nm (br), 435 nm (sh). ^1H NMR ($CDCl_3$) δ : 1.26 (s, 6H, Me), 1.74 (s, 6H,Me), 4.19 (br, 4H, C_5H_4), 4.38 (br, 4H, C_5H_4), 7.28-7.35 (m, 4H, Ph), 7.38-7.48 (m, 8H, Ph), 7.67 (d, 4.5Hz, 2H, C_5HN_2), 7.82-7.87 (m, 8H, Ph) ; $^{31}P\{^1H\}$NMR ($CDCl_3$) δ : 12.6 [^1J(Pt-P) = 3183 Hz] ppm.

2.1.4 Preparation of [$Pt_2(\mu\text{-}SeC_5H_4N)_2(dppf)_2]Cl_2$ (**3**):

To a benzene solution (15 cm^3) of [$PtCl_2$(dppf)] (110 mg, 0.14 mmol), a methanolic solution (8 cm^3) of Na(SeC_5H_4N) [freshly prepared from $(C_5H_4N)_2Se_2$ (42 mg, 0.14 mmol) and $NaBH_4$ (11 mg, 0.29 mmol)] was added and the mixture was stirred for 4 hours. The solvents were evaporated under vacuum and the residue was extracted with benzene and passed through celite. The ensuing solution on slow evaporation afforded a yellow powder (Yield 54 mg, 43%) m.p.: 118°C (dec.). Anal. Calcd. for $C_{78}H_{64}N_2Cl_2P_4Fe_2Pt_2Se_2$: C, 55.47; H, 3.82; N, 1.66%. Found: C, 55.78; H, 4.14; N, 1.88%. UV-Vis (λ_{max}) : 435 nm (br), 509 nm (br). ^1H NMR (CD_3OH) δ: 4.32 (br, 4H, C_5H_4), 4.67 (br, 4H, C_5H_4), 6.38 (d, 2.8 Hz, 2H, C_5H_4N), 7.32-7.42 (m, 8H, Ph), 7.56-7.66 (m, 4H, Ph+C_5H_4N), 7.81-7.88 (m, 8H, Ph+C_5H_4N), 8.48 (d, 5.0Hz, 2H,

C_5H_4N); $^{31}P\{^1H\}$NMR (CD_3OH) δ : 12.3 [^1J(Pt-P) = 3169Hz] ppm. On recording the NMR of titled complex **3** in $CDCl_3$ Solution; ^1H NMR ($CDCl_3$) δ: 4.14 (br, 4H, C_5H_4), 4.32 (br, 4H, C_5H_4), 7.08-7.13 (m, 4H, Ph), 7.33-7.39 (m, 9H, Ph+C_5H_4N), 7.66-7.73 (m, 9H, Ph+C_5H_4N), 8.48 (d, 4.1Hz, 1H, C_5H_4N); $^{31}P\{^1H\}$NMR ($CDCl_3$) δ : 9.9 [^1J(Pt−P) = 3762Hz], 14.9 [^1J(Pt−P) = 3149Hz] ppm.

2.1.5 Preparation of [Pt(Cl)(SeC_5H_4N)(dppf)] (**4**):

To a dichlormethane solution (15 cm^3) of [$PtCl_2$(dppf)] (165 mg, 0.21 mmol) a methanolic solution (8 cm^3) of Na(SeC_5H_4N) [freshly prepared from $(C_5H_4N)_2Se_2$ (65 mg, 0.21 mmol) and $NaBH_4$ (16 mg, 0.42 mmol)] was added and the mixture was stirred for 4 hour. The solvents were reduced *in vacuo* and the residue was extracted with dichloromethane which on slow evaporation afforded a yellow powder (Yield 139 mg, 73%) m.p. 161 °C (dec.). Anal. Calcd. for $C_{39}H_{32}NClP_2FePtSe$: C, 49.73; H, 3.42; N, 1.49%. Found: C, 49.48; H, 3.59; N, 1.58%. UV-Vis (λ_{max}) : 277 nm (sh), 307 nm (br). ^1H NMR ($CDCl_3$) δ: 4.21 (br, 4H, C_5H_4), 4.34 (br, 4H, C_5H_4), 7.11-7.16 (m, 4H, Ph), 7.31-7.36 (m, 9H, Ph+C_5H_4N), 7.68-7.73 (m, Ph+C_5H_4N), 8.41 (d, 4.4Hz, 4H, C_5H_4N); $^{31}P\{^1H\}$NMR ($CDCl_3$) δ : 10.1 [^1J(Pt−P) = 3766Hz], 14.6 [^1J(Pt−P) = 3143Hz] ppm.

3. Results and Discussion:

Treatment of [$PdCl_2$(dppf)] with two equivalents of sodium aryl selenolate NaSeAr (Ar = C_5H_4N, $C_4H(4,6\text{-}Me)_2N_2$) prepared by the reductive cleavage of the Se−Se bond of diselenide by $NaBH_4$ in methanol, afforded an orange mononuclear product of composition [$Pd(SeAr)_2$(dppf)] (Ar = $C_4H(4,6\text{-}Me)_2N_2$: **1a**,C_5H_4N: **1b**, scheme 1). The ^{31}P NMR of both of the complexes showed one resonance at ~28 ppm. It is noteworthy that an oxidative reaction of [$Pd(dppe)_2$]

with dipyridyldiselenides resulted the similar mononuclear product [Pd{SeC_5H_3(3-R)N}$_2$(dppe)] (R = H, Me) [16]. Similarly, reaction of platinum precursor with the sodium salt of methyl substituted pyrimidylselenolate in a benzene-methanol mixture gave rise to a yellow powder of composition [Pt{2-Se-C_4H(4,6-$Me)_2N_2$}$_2$(dppf)] (**2a**, Scheme 1). The observed coupling constant 3183 Hz is in good agreement with reported value for the mononuclear complexes [17, 25, 26].

The molecular structures of [Pt{2-Se-C_4H(4,6-$Me)_2N_2$}$_2$(dppf)]. 0.5C_6H_6 (**1a**) has been established by X-ray diffraction (Figures 2). Selected interatomic parameters for **1a**.0.5C_6H_6 are summarized in Tables 2. The complex **1a**, adopts the expected distorted square planner geometry around the platinum atom, defined by the coordination of two phosphorus and two selenium atoms. The Pt−Se distances [2.4578(10) and 2.4595(11)Å] fall in the middle of the range of reported Pt–Se distance for both complexes of the type [Pt$(SeR)_2$(dppf)] (Pt–Se range 2.453–2.477 Å) [27-30] and [Pt$(SeAr)_2$(P∩P)] (Pt–Se range 2.418–2.511 Å) [27, 31-34]. The Pt−P distances [2.295(2) and 2.301(2)Å] are slighly longer than other reported Pt–P bonds for compounds of the type values for [Pt$(SeAr)_2$(P∩P)] (2.238–2.274 Å) [31-34]; however, when comparing against Pt(dppf) complexes with any selenolate ligands, [Pt$(SeR)_2$(dppf)], the Pt–Se bond distances in **3a** fall into the known range (2.279–2.306 Å) [27, 32-34]. The Se−Pt−Se angle is acute [84.38(3)°] as a result of the bond angle imposed by the wide bite-angle of dppf [P–Pt–P 101.83(8)°]. These angles are similar to those found in [Pt($SeC{\equiv}C(CH_2)_4Me)_2$(dppf)]·$C_6H_6$(Se–Pt–Se 85.08°, P–Pt–P 97.98°) [29].

The reaction of [$PtCl_2$(dppf)] with two equivalents of sodium 2-pyridylselenolate in a benzene-methanol mixture yielded a binuclear product of composition [Pt_2(μ-$SeC_5H_4N)_2$(dppf)$_2$]Cl_2 (**3**). In contrast, a similar reaction in a dichloromethane-methanol mixture afforded exclusively a product of the type [Pt(Cl)(SeC_5H_4N)(dppf)] (**4**) (scheme 2). The ^{31}P

NMR of complex **4** displayed two resonances at 14.6 and 10.1 ppm with ^{1}J(Pt−P) values of 3143 and 3766Hz, respectively. These two resonances, with different Pt-P coupling constants arise, due to the differing chemical environments of each phosphorus; one being *trans* to the selenolate, the other *trans* to the chloride [15, 35]. In an attempt to substitute both the chloride, the reaction has been performed between [$PtCl_2$(dppf)] and [$Pb(SeC_5H_4N)$] which also has resulted similar composition of complex **4**. It is noteworthy that similarly an oxidative addition reaction of [$Pd(PPh_3)_4$] with dipyridyl ditellurides gave an expected oxidative addition product [$Pd\{2\text{-}TeC_5H_3(3\text{-}R)N\}_2(PPh_3)_2$] (R = H, Me) which on keeping in $CDCl_3$ solution resulted derivative [$PdCl\{2\text{-}Te(Cl)_2C_5H_3(3\text{-}Me)(PPh_3)$] [16]. Even the reaction of [$Pd_2Cl_2(\mu\text{-}Cl_2)(PPh_3)_2$] with sodium salt of pyridyl tellurolate afforded complex [$PdCl\{2\text{-}TeC_5H_3(3\text{-}Me)(PPh_3)$] [35]. The complex $[Pt_2(\mu\text{-}SeC_5H_4N)_2(dppf)_2]^{2+}$ (**3**) in $CDCl_3$ solution also exhibited similarly two phosphorus peaks corroborated with platinum satellites as discussed above for the complex **4** (scheme 2). The ^{31}P NMR of complex **3** in CD_3OH exhibited a single resonance at 12.6 ppm with a ^{1}J(Pt–P) coupling of 3169Hz, corresponding to a symmetrical phosphorus environment, with a selenolate ligand *trans* to the phosphine ligand [15, 26, 35, 36]. In contrast, in $CDCl_3$ solution, complex **3** exhibited two phosphorus peaks with almost identical chemical shifts and coupling to platinum as seen for complex **4**. This suggests, that in $CDCl_3$ solution, the cationic binuclear complex **3** converts to the mononuclear complex **4** (Scheme 2). The four membered ring of $\{Pt_2Se_2\}$ in complex **3** has been stabilized due to π bonding effect [8, 37]. The chlorination of seleno bridge, has been anticipated due to perturbation of π cloud in presence of electron-withdrawing group to weaken the Pt-Se bond and open up the four membered ring [38]. An ionic nature of complex **3** has also been monitored by molar conductivity measurement where complex $[Pt_2(\mu\text{-}SeC_5H_4N)_2(dppf)_2]^{2+}$ (**3**) showed a non electrolyte nature in $CHCl_3$ (1.8 μS

$cm^2\ mole^{-1}$) however, it is 1:2 electrolyte in methanol (133.2 μS $cm^2\ mole^{-1}$). This indicates the existence of neutral species in dichloromethane, while in polar solvent like CH_3OH complex adopts ionic structure. A similar reactivity pattern has been reported for the complex like $[Pt_2(\mu\text{-}S)_2(dppf)_2]^{2+}$ [8], $[Pt_2(\mu\text{-}SeCH_2CH_2NMe_2)_2(dppe)_2]^{2+}$ [35, 36], and $[Pt_2(\mu{-}TeC_5H_3(3\text{-}Me)_2(dppe)_2]^{2+}$ (dppe=1,2-bis(diphenylphosphino)ethane) [15]. The rapid conversion of binuclear complex to mononuclear compound is well documented in literatures [8, 15, 18, 19]. The possibilty of the formation of a mononuclear species is expected to be due to the strong trans effect of phosphine ligand which weaken the bridging chalcogenolate linkage and results the formation of the mononuclear mixed halide/chalcogenolates complexes.

All complexes are colored and show absorption bands in visible range of electronic spectra. The bands are red-shifted with respect to the diselenide ligands. The highest occupied molecular orbital (HOMO) is located on the selenolate ligands, whereas the lowest unoccupied molecular orbital (LUMO) is probably delocalised over phosphine ligand [35].

4. Conclusion:

The substitution reaction of pyridyl/pyrimidyl selenolate with palladium and platinum(II) metal precursors $[MCl_2(dppf)]$ (M = Pd, Pt) afforded mono or binuclear products. The pyrimidyl derived selenolate gave rise solely to mononuclear complexes with both platinum and palladium, and the pyridylselenolate gave rise to equivalent complexes with palladium. In contrast, on reaction with platinum, the pyridyl derived selenolate yielded either binuclear, $[Pt_2(\mu\text{-}SeC_5H_4N)_2(dppf)_2]Cl_2$, or mononuclear $[Pt(Cl)(SeC_5H_4N)(dppf)]$ products. The isolation of these mononuclear $[M(SeAr)_2(dppf)]$ (M = Pd, Pt; Ar = C_5H_4N, $C_4H(2,6\text{-}Me)N_2$) and ionic compounds depend upon substituent present on phenyl ring and solvent involved during the course of reaction. The instant conversion of binuclear to mono-nuclear species is mainly

aroused due to nucleophilic attack of chlorinated solvent on selenolate bridged binuclear complex.

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Supporting Information

CCDC-Nos. 1574352-1574354 for $[PdCl_2(dppf)].CH_2Cl_2$, $[PtCl_2(dppf)].0.5CH_2Cl_2$ and $[Pt\{2\text{-}Se\text{-}C_4H(4,6\text{-}Me)_2N_2\}_2(dppf)].0.5C_6H_6$, respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 1. Crystallographic and structural determination data for [Pt{2-Se-C_4H(4,6-Me)$_2N_2$}$_2$(dppf)]. 0.5C_6H_6 (**1a**)

Complex	**1a**
Chemical formula	$C_{49}H_{45}FeN_4P_2PtSe_2$
Formula wt.	1160.73
Crystal size (mm^3)	0.09 x 0.03 x 0.01
Crystal system	Triclinic
Space group	$P\bar{1}_{-1}$
Unit cell dimensions	
a (Å)	11.3463(18)
b (Å)	15.7103(15)
c (Å)	15.896(2)
α (°)	117.826(7)
β (°)	101.96(2)
γ (°)	93.179(15)
Volume ($Å^3$)	2413.3(7)
ρ_{cacld}, g cm^{-3}	1.597
Z	2
μ (mm^{-1})/F(000)	4.795/1138
Limiting indices	-13≤h≤13
	-18≤k≤18
	-17≤l≤19
θ for data collection(°)	1.864-25.388
No of reflections collected	29339
No of independent reflection (R_{int})	8733 (0.0749)
Data/restraints/parameters	8733/36/551
Final R_1, wR_2 indices ($I>2\sigma I$)	0.0487, 0.1081
R_1, wR_2 (all data)	0.0881, 0.1200
Goodness of fit on F^2	0.933

Table 2: Selected bond lengths (Å) and angles (°) of [Pt{2-Se-$C_4H(4,6\text{-}Me)_2N_2$}$_2$(dppf)] **1a**·0.5C_6H_6

Pt(1)-P(1)	2.301(2)	Pt(1)-P(2)	2.295(2)
Pt(1)-Se(1)	2.4595(11)	Pt(1)-Se(2)	2.4578(10)
Se(1)-C(35)	1.901(10)	Se(2)-C(43)	1.922(10)
P(2)-Pt(1)-P(1)	101.83(8)	Se(1)-Pt(1)-Se(2)	84.38(3)
P(1)-Pt(1)-Se(1)	85.52(6)	P(2)-Pt(1)-Se(2)	88.84(6)
P(1)-Pt(1)-Se(2)	167.23(6)	P(2)-Pt(1)-Se(1)	171.66(6)

Figure captions

Figure 1: ORTEP diagram of [Pt{2-Se-$C_4H(4,6\text{-}Me)_2N_2$}$_2$(dppf)].0.5C_6H_6 (**1a.**0.5C_6H_6) with atomic numbering scheme. The ellipsoids were drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

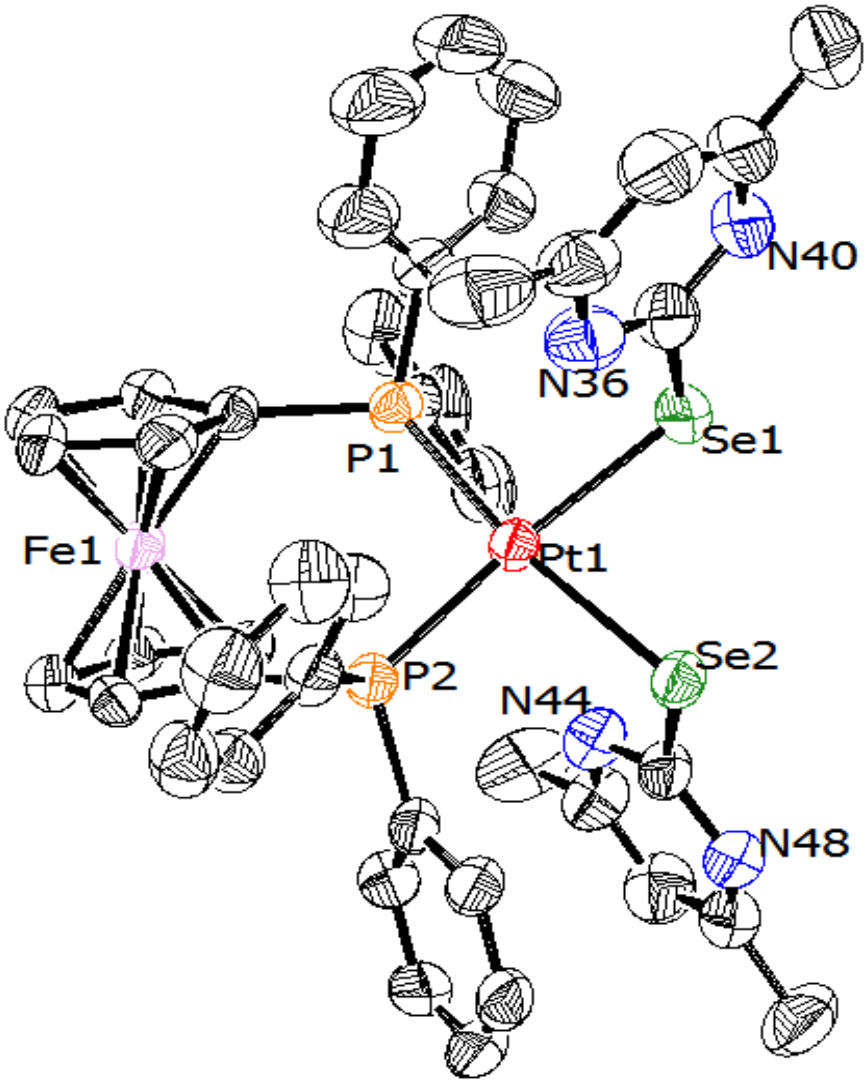
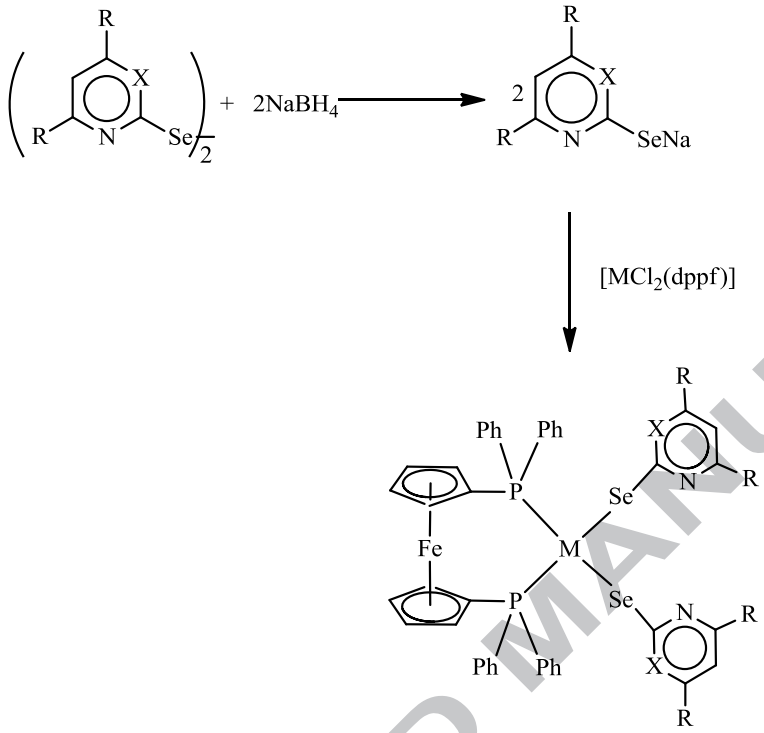
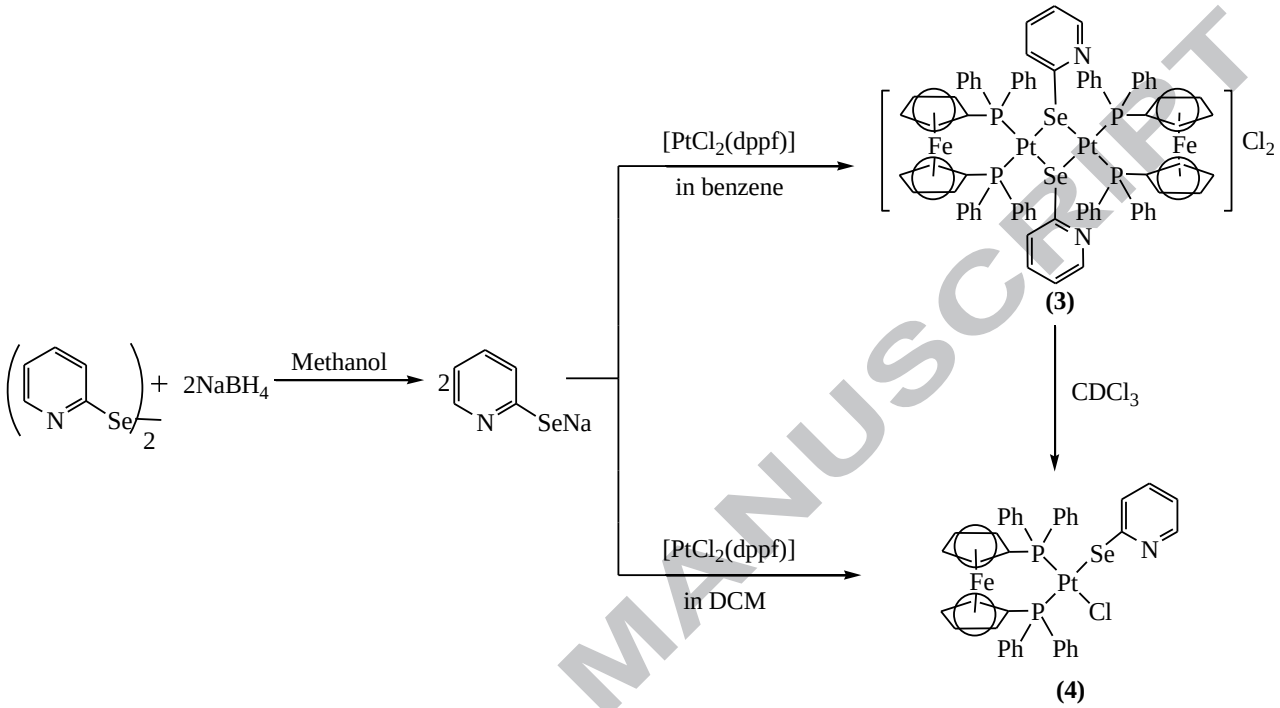


Figure 1: ORTEP diagram of [Pt{2-Se-$C_4H(4,6\text{-}Me)_2N_2$}$_2$(dppf)].0.5C_6H_6 (**1a**) with atomic numbering scheme. The ellipsoids were drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

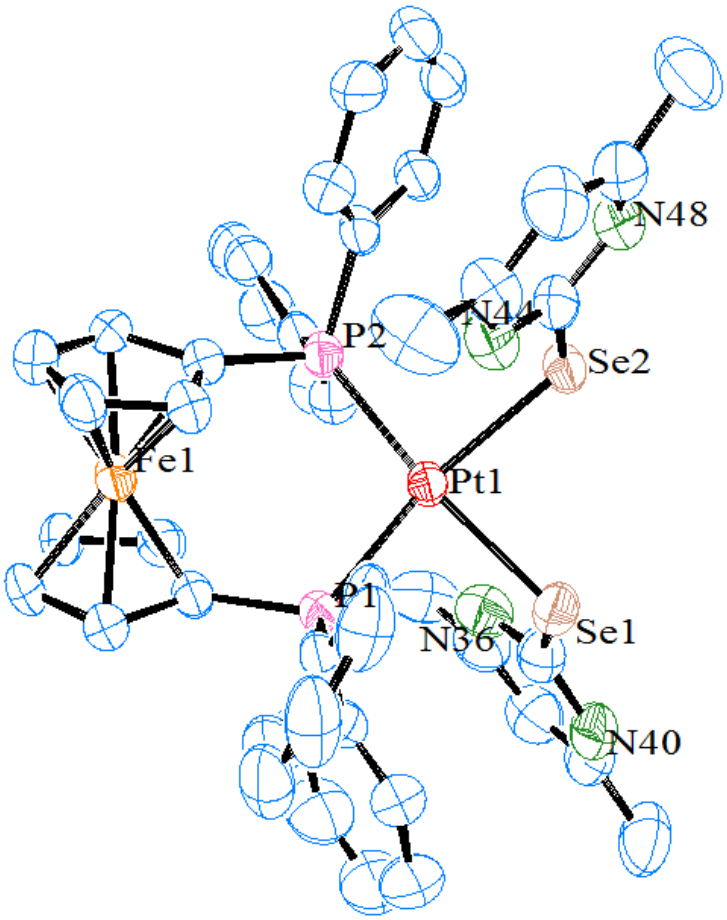


M	X	R	
Pd	N	Me	**1a**
Pd	C	H	**1b**
Pt	N	Me	**2a**

Scheme 1



Scheme 2



The bis(diphenylphisphino)ferrocene (dppf) derived palladium analogue of $[PdCl_2(dppf)]$ on reaction with the sodium salt of pyridyl/pyrimidyl selenolate yielded mononuclear *cis* configured complex $[Pd(SeAr)_2(dppf)]$ (Ar = C_5H_4N, $C_4H(4,6\text{-}Me)_2N_2$), as did the platinum precursor $[PtCl_2(dppf)]$ with methyl substituted pyrimidyl salt giving $[Pt\{SeC_4H(4,6\text{-}Me)_2N_2\}_2(dppf)]$. In contrast, the reaction of platinum precursor with the sodium salt of pyridylselenolate gave two different complexes $[Pt_2(\mu\text{-}SeC_5H_4N)_2(dppf)_2]^{2+}$ and $[Pt(Cl)(SeC_5H_4N)(dppf)]$ depending in the reaction solvent.

Highlights

- Studied the reaction of [$PdCl_2$(dppf)] with the sodium salt of pyridyl/pyrimidyl selenolate.
- Reaction of [$PtCl_2$(dppf)] with sodoim salt of pyridyl selenolate ligands.
- Isolation of binuclear and mononuclear products depending upon the solvent.