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Allylpalladium (II) complexes with dichalcogenoimidodiphosphinate ligands: Synthesis, structure, spectroscopy and their transformation into palladium chalcogenides

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Abstract

The synthesis, characterization and thermal behavior of new monomeric allylpalladium (II) complexes with dichalcogenoamidodiphosphinate anions are reported. The complexes $[Pd(\eta^3\text{-}CH_2C(R)CH_2)\{R'_2P(E)NP(E)R'_2\text{-}E,E'\}]$ [R = H, R′ = Pr^i, E = S (**1a**); R = H, R′ = Pr^i, E = Se (**1b**); R = H, R′ = Ph, E = S (**1c**); R = H, R′ = Ph, E = Se (**1d**); R = Me, R′ = Pr^i, E = S (**2a**); R = Me, R′ = Pr^i, E = Se (**2b**); R = Me, R′ = Ph, E = S (**2c**); R = Me, R′ = Ph, E = Se (**2d**)] have been prepared by room temperature reaction of $[Pd(\eta^3\text{-}CH_2C(R)CH_2)(acac)]$ (acac = acetylacetonate) with dichalcogenoimidodiphosphinic acids in acetonitrile solution. The complexes have been characterized by multinuclear NMR (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{77}Se{^{1}H}), FT-IR and elemental analyses. The crystal structures of complexes **1a**, **1d** and **2d** have been reported and they consist of a six-membered PdE_2P_2N ring (E = S for **1a** and Se for **1d** and **2d**) and an allyl group, C_3H_4R(R = H for **1a** and **1d** and Me for **2d**). Thermogravimetric studies have been carried out for few representative complexes. The complexes thermally decompose in argon atmosphere to leave a residue of palladium chalcogenides, which have been characterized by PXRD, SEM and EDS.

Keywords: η^3-Allylpalladium complexes; Dichalcogenoamidodiphosphinate ligands; Multinuclear NMR spectroscopy; X-ray crystal structure; Thermogravimetric studies; Scanning electron microscopy

1. Introduction

Platinum group metal chalcogenolates have been important in view of their rich reaction chemistry [1–4], structural diversity and relevance in catalysis [5–8]. Of late, they have also gained much attention due to their possible role as single source molecular precursors for metal chalcogenides [9–12], which find extensive applications in catalysis [13–17] and material science [18–20]. Examples of the latter include manufacture of semiconductor and solar cells [18], lithographic films/plates with high resolution [19], optical disc recording films [20], etc. The continuing drive for scaling down of the dimensions of these devices has motivated research into the design and development of molecular "single source" precursors for solid state materials. Single source precursors have several potential advantages over conventional MOCVD which uses dual-sources. The major advantages include limited pre-reactions, as there is only a single molecule in the supply stream and good quality films [21]. Furthermore, in single molecule precursors it should be possible to have a control over decomposition temperature by varying the design of precursor molecule and consequently, low growth temperatures should be accessible. Thus, there has been considerable interest in developing

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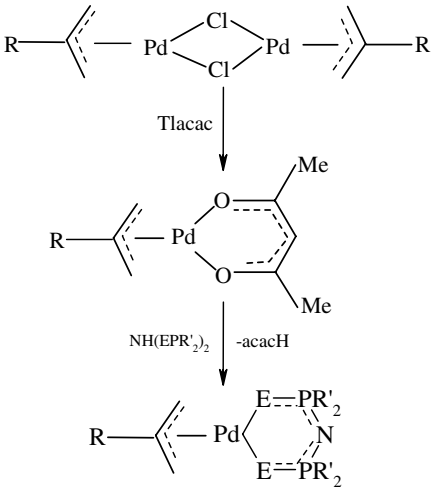
suitable precursor molecules which afford metal chalcogenides with cleaner depositions at low decomposition temperatures.

Dichalcogenoimidodiphosphinato anions $[R_2P(E)NP(E)R_2]^-$ (R = alkyl/aryl; E = S, Se) are versatile ligands [22], and their coordination chemistry has been the focus of substantial research over the last few years [23–27]. This is mainly due to the flexibility of the EPNPE system and large E···E bite (ca 4 Å), which results in various chelate ring conformations (planar, boat, chair, etc.). They are readily prepared and their properties can be finely tuned by varying the chalcogen and the substituents at phosphorus. The anion $[R_2P(E)NP(E)R_2]^-$, closely related to acetylacetone ($acac^-$), forms many complexes with various metal ions and metal complexes incorporating such ligands have demonstrated improved thermal and chemical stability over traditional organic based ligands such as β-diketonate complexes [28] (which are susceptible to oxidation, polymerization and hydration) and thus are excellent candidates as single source precursors for CVD and quantum dot synthesis [29–34]. We are interested in developing cleaner form of single source precursors having low decomposition temperatures for the preparation of platinum group metal chalcogenide materials. Earlier, we have reported organochalcogenide bridged allylpalladium (II) complexes which showed interesting thermal behavior and gave metal rich chalcogenides at moderately low temperatures [10]. The present investigation was undertaken in order to test the suitability of allyllpalladium (II) dichalcogenodiphosphinato complexes as single source precursors for the preparation of palladium chalcogenides. The only previously known allylpalladium (II) complexes with dichalcogenoimidodiphosphinato anions $[R_2P(E)NP(E)R_2]^-$ (R = alkyl/aryl; E = S, Se) are **1c** and **1d** reported by Bhattacharyya et al. [35] and obtained by reacting chloro-bridged allylpalladium dimers with potassium salt of ligands. In this work, we report a different way to synthesize **1c**, **1d** and other complexes with dichalcogenoimidodiphosphinato ligands, their characterization and thermal behaviour. We also report, for the first time, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR data for the ligands.

2. Results and discussion

2.1. Synthesis and characterization

The complexes $[Pd(\eta^3\text{-}CH_2C(R)CH_2)\{R'_2P(E)NP(E)R'_2\text{-}E,E'\}]$ (R = H or CH_3; R′ = Pr^i or Ph; E = S or Se) have been prepared by the reaction between appropriate dichalcogenoimidodiphosphinato ligand with the complex $[Pd(acac)(\eta^3\text{-}CH_2C(R)CH_2)]$ (generated in situ by the reaction between the chloro-bridged allylpalladium dimer and thallium(I) acetylacetonate) (Scheme 1). The reactions are complete within *ca.* 30 min and all complexes can be obtained in high yields as crystalline solids via crystallization from CH_3CN–diethylether mixtures. There are many literature reports on use of acetylacetonato gold (I) complexes as synthetic intermediates to prepare several other coordination and organometallic gold (I) complexes by Vicente et al. [36,37], but none on use of acetylacetonato palladium (II) complexes to the best of our knowledge. We have successfully used $[Pd(acac)(\eta^3\text{-allyl})]$ complexes to synthesize several other dimeric allylpalladium (II) complexes [38] and now monomeric allylpalladium (II) complexes with $[(R_2PE)_2N]^-$ ligands.



	1a	1b	1c	1d	2a	2b	2c	2d
R	H	H	H	H	Me	Me	Me	Me
R'	Pr^i	Pr^i	Ph	Ph	Pr^i	Pr^i	Ph	Ph
E	S	Se	S	Se	S	Se	S	Se

Scheme 1.

The only previously known allylpalladium (II) complexes with dichalcogenoimidodiphosphinato anions $[R_2P(E)NP(E)R_2]^-$ (R = alkyl/aryl; E = S, Se) are **1c** and **1d**, obtained by reacting $[Pd(\mu\text{-}Cl)(\eta^3\text{-}CH_2CHCH_2)]_2$ with $K[Ph_2P(E)NP(E)Ph_2]$(E = S or Se) [35]. Most of the complexes are stable towards air and moisture both in solid state and in solution but **1b** and **2b** decompose slowly in solution. The complexes have been characterized by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR and by FTIR spectroscopy. In addition, X-ray crystal structure determinations have been carried out for **1a**, **1d** and **2d** and are described below.

The ligands behave like typical E, E′ chelates and the complexes are monomeric. The spectroscopic and analytical data for the complexes are in good accord with the proposed structures (see Section 4). The ^1H NMR spectra of the complexes are straightforward showing correct proton ratios for both the ligands. For allylpalldium complexes (**1a**–**1d**), a doublet is observed each for *syn* and *anti* protons of the allyl group and a multiplet appears for the proton bound to central carbon atom of the allyl ligand along with expected resonances for dichalcogenoimidodiphosphinato anions. For methallyl complexes (**2a**–**2d**), singlets each for methyl group, *syn* and

anti protons are observed. The $^{31}P\{^{1}H\}$ NMR spectra of the complexes, **1b**, **1d**, **2b** and **2d**, at room temperature consist of singlet flanked by ^{77}Se satellites ($^{1}J(^{31}P–^{77}Se) = 546–554$ Hz), indicating equivalence of the phosphorus centers in solution. The phosphorus resonances (~54 ppm for **1b** and **2b**; ~26.6 for **1d** and **2d**) are shielded with respect to the free dichalcogenoimidodiphosphinato ligand [$(NH(SePPr^{i}_{2})_2$ $\delta_P = 91.2$ ppm; $NH(SePPh_2)_2$, $\delta_P = 53.4$ ppm]. The $^{1}J(^{31}P–^{77}Se)$ couplings in the complexes are lower in magnitude than in the free ligands suggesting a reduction in P–Se bond order. The corresponding sulfur analogues, **1a**, **1c**, **2a**, **2c** show single ^{31}P peaks due to the distinct absence of coupling between phosphorus and non-NMR active sulfur nuclei. The ^{31}P resonances also show chalcogen dependence with shielding as S is replaced by Se. $^{77}Se\{^{1}H\}$ NMR spectra for **1b**, **1d**, **2b** and **2d** show doublets due to coupling with phosphorus nucleus and are deshielded with respect to the signals for free ligands (See Section 4). In the IR spectra, $\nu(P_2N)$ bands for the complexes appear in the range 1210–1225 cm^{-1}, ν(P–S) band appear in the range 550–574 cm^{-1} and ν(P–Se) band appear in the range 475–540 cm^{-1}. These frequency shifts are consistent with an increase in P–N bond order and decrease in P–S/Se bond order associated with the formation of $[R_2PE)_2N]^-$ ion in complexes [39].

2.2. Crystal structures of *1a, 1d, 2d*

The molecular structures of **1a**, **1d** and **2d** (Figs. 1–3, respectively) consist of a six-membered PdE_2P_2N ring (E = S for **1a** and Se for **1d** and **2d**) and an allyl group, C_3H_4R (R = H for **1a** and **1d** and Me for **2d**). Key bond lengths and bond angles for **1a**, **1d** and **2d** are given in Tables 1–3, respectively. The Pd–S distances in **1a** (Table 1) (2.3579 (16) and 2.3705 (15) Å) are close to those reported for $[Pd(\eta^3\text{-}C_3H_5)\{Ph_2P(S)NP(S)Ph_2\text{-}S,S'\}]$ (2.3769(9) and 2.3654(9) Å) [35]. The Pd–Se distances in **1d** (Table 2) (2.4711(10) and 2.4799(11) Å) and **2d** (Table 3) (2.4645(6) and 2.4766(6) Å) are longer than the Pd–Se distances in the pseudo square-planar complex $[Pd(C_9H_{12}N)\{Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se'\}]$ (2.4069(9) and 2.560(1) Å) but similar to the average Pd–Se bond distance in the dimeric $[\{Pd(\eta^3\text{-}C_3H_5)\{Ph_2P(O)NP(Se)Ph_2\text{-}Se\}_2] \cdot 2CHCl_3$. There is a general lengthening of the P–E bonds and a shortening of the P–N bonds in **1a**, **1d** and **2d** with respect to known

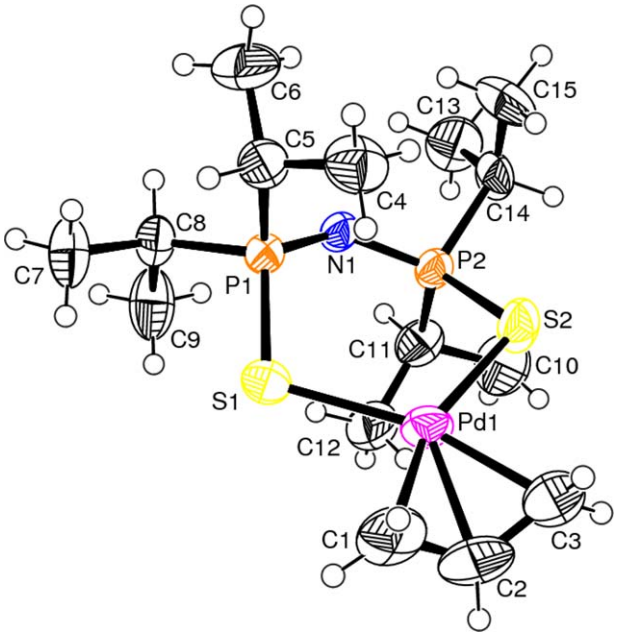


Fig. 1. The molecular structure of $[Pd(\eta^3\text{-}CH_2CHCH_2)\{Pr^{i}_{2}P(S)NP(S)Pr^{i}_{2}\text{-}S,S'\}]$ (**1a**) showing atomic numbering scheme.

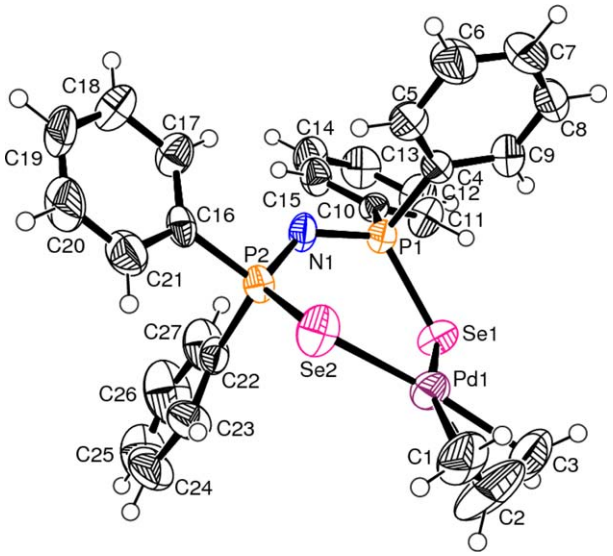


Fig. 2. The molecular structure of $[Pd(\eta^3\text{-}CH_2CHCH_2)\{PhP(Se)NP(Se)Ph\text{-}Se,Se'\}]$ (**1d**) showing atomic numbering scheme.

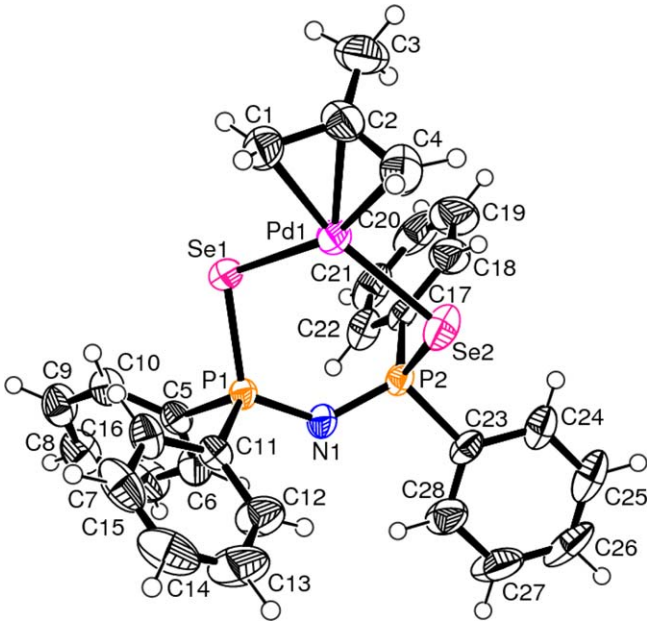


Fig. 3. The molecular structure of $[Pd(\eta^3\text{-}CH_2C(CH_3)CH_2)\{PhP(Se)NP(Se)Ph\text{-}Se,Se'\}]$ (**2d**) showing atomic numbering scheme.

Table 1
Selected bond length and bond angles for **1a**

Pd(1)–C(2)	2.105(6)	P(1)–S(1)	2.0218(19)
Pd(1)–C(1)	2.130(6)	P(2)–S(2)	2.0197(19)
Pd(1)–C(3)	2.134(6)	P(1)–N(1)	1.583(4)
Pd(1)–S(2)	2.3579(16)	P(2)–N(1)	1.590(4)
Pd(1)–S(1)	2.3705(15)		
C(2)–Pd(1)–S(2)	124.5(3)	S(2)–Pd(1)–S(1)	108.99(5)
C(1)–Pd(1)–S(2)	158.3(2)	P(1)–S(1)–Pd(1)	108.61(7)
C(3)–Pd(1)–S(2)	90.89(19)	P(2)–S(2)–Pd(1)	107.02(7)
C(2)–Pd(1)–S(1)	125.0(3)	N(1)–P(1)–S(1)	118.40(16)
C(1)–Pd(1)–S(1)	91.7(2)	N(1)–P(2)–S(2)	118.74(17)
C(3)–Pd(1)–S(1)	159.6(2)	P(1)–N(1)–P(2)	136.6(3)

Table 2
Selected bond length and bond angles for **1d**

Pd(1)–C(2)	2.103(9)	Se(1)–P(1)	2.1656(19)
Pd(1)–C(3)	2.128(9)	Se(2)–P(2)	2.1638(19)
Pd(1)–C(1)	2.147(8)	P(1)–N(1)	1.576(5)
Pd(1)–Se(1)	2.4711(10)	P(2)–N(1)	1.598(6)
Pd(1)–Se(2)	2.4799(11)		
C(2)–Pd(1)–Se(1)	124.6(4)	Se(1)–Pd(1)–Se(2)	108.65(3)
C(3)–Pd(1)–Se(1)	91.8(3)	P(1)–Se(1)–Pd(1)	103.62(6)
C(1)–Pd(1)–Se(1)	159.3(3)	P(2)–Se(2)–Pd(1)	102.93(6)
C(2)–Pd(1)–Se(2)	125.1(4)	N(1)–P(1)–Se(1)	119.7(2)
C(3)–Pd(1)–Se(2)	159.3(3)	N(1)–P(2)–Se(2)	118.8(2)
C(1)–Pd(1)–Se(2)	91.9(3)	P(1)–N(1)–P(2)	131.3(4)

Table 3
Selected bond length and bond angles for **2d**

Pd(1)–C(4)	2.133(5)	Se(1)–P(1)	2.1652(11)
Pd(1)–C(2)	2.136(4)	Se(2)–P(2)	2.1700(12)
Pd(1)–C(1)	2.141(5)	N(1)–P(1)	1.594(3)
Pd(1)–Se(1)	2.4645(6)	N(1)–P(2)	1.589(4)
Pd(1)–Se(2)	2.4746(6)		
C(4)–Pd(1)–Se(1)	158.63(15)	Se(1)–Pd(1)–Se(2)	107.68(2)
C(2)–Pd(1)–Se(1)	122.22(14)	P(1)–Se(1)–Pd(1)	104.08(3)
C(1)–Pd(1)–Se(1)	91.51(14)	P(2)–Se(2)–Pd(1)	102.28(3)
C(4)–Pd(1)–Se(2)	93.68(15)	P(1)–N(1)–P(2)	128.4(2)
C(2)–Pd(1)–Se(2)	126.95(14)	N(1)–P(1)–Se(1)	119.38(14)
C(1)–Pd(1)–Se(2)	160.04(15)	N(1)–P(2)–Se(2)	118.83(14)

P=E double bond distances and the P–N single bond distances (e.g. in $\{E{=}P(Ph)_2\}_2NH$, E = S, 1.950(1) and 1.936(1) Å [40], P=Se, 2.085(1) and 2.101(1) Å [41], P–N, 1.671(2) and 1.684(2) Å [42]), indicative of some delocalization of the metallacycle. A similar effect has been observed earlier in the structure of the related molecules, $[Pd(C_9H_{12}N)\{Ph_2P(Se)NP(Se)Ph_2\text{-}Se,Se'\}]$, $[Pt(C_8H_{12}OMe)\{Ph_2P(S)NP(S)Ph_2\text{-}S,S'\}]$ and $[Pd(\eta^3\text{-}C_3H_5)\{Ph_2P(S)NP(S)Ph_2\text{-}S,S'\}]$ [43].

3. Thermal studies

Thermogravimetric analyses of **2a**, **2b** and **2d** have been carried out in flowing argon atmosphere and the results are summarized in Table 4. From TG analysis it is found that the complexes decompose in two steps. For **2d**, the mass loss in the first step corresponds to the loss of allyl moiety and in the second step corresponds to the loss of $[(R_2P)_2N]$ (R = Ph) moiety leaving the residue $PdSe_2$. A further loss of selenium is observed upto 650 °C (although not a distinct step is observed) leaving a residue of non-stoichiometric palladium selenide, $Pd_{17}Se_{15}$ corresponding to total weight loss of 73.8%. This has been confirmed by bulk thermolysis of **2d** in furnace at 500 °C under an argon atmosphere. However, the complexes, **2a** and **2b** containing $[N(EPPr^i_2)_2]^-$ (E = S(**2a**) or Se(**2b**)) partly evaporate and partly decompose leaving a small amount of PdS_2 and $Pd_{17}Se_{15}$, respectively. The typical TG traces for two representative complexes are shown in Fig. 4.

Table 4
TGA data for $[Pd(\eta^3\text{-}CH_2C(R)CH_2)\{R_2P(E)NP(E)R_2\text{-}E,E'\}]$

Compound	Step I		Step II	
	Temperature range (°C)	wt% Loss[a]	Temperature range (°C)	wt% Loss[a]
2a	169–246	14.2 (11.6)	273–355	49.5 (52.4)
2b	156–215	14.4 (9.7)	290–318	70.7 (57.6)
2d	170–212	8.2 (7.8)	348–436	55.5 (54.6)

[a] The values in parentheses correspond to expected weight loss.

3.1. Thermal decomposition of the complexes

Thermolyses of the complex **2b** at 300 °C and of **2d** at 500 °C at a rate of 5 °C min^{-1} in a furnace under an argon atmosphere were carried out and palladium selenide with the composition $Pd_{17}Se_{15}$ was obtained in each case. X-ray diffraction patterns of the products obtained compared well with the pattern reported for palladium selenide $Pd_{17}Se_{15}$ and indexing of lattice parameter patterns of XRD indicate the formation of cubic phases [43]. Fig. 5 shows the XRD spectrum of the powder obtained from thermolysis of **2b**. The average crystallite size of 45 nm was estimated with the Scherrer equation for the particles derived from complex **2b**. The surface morphology of the particles obtained has been studied by SEM technique. The scanning electron micrographs of $Pd_{17}Se_{15}$ (Fig. 6) taken at different resolutions showed aggregates of microcrystals. The aggregates are spherical in shape and their size varied between 120 and 200 nm (Fig. 6). The chemical composition of the products has been verified by energy dispersive X-ray spectroscopy (expected wt% for $Pd_{17}Se_{15}$: Pd, 60.43; Se, 39.56, observed wt%: Pd, 59.00; Se, 40.19:).

4. Experimental

4.1. General experimental details

All the reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. The chloro-bridged allylpalladium

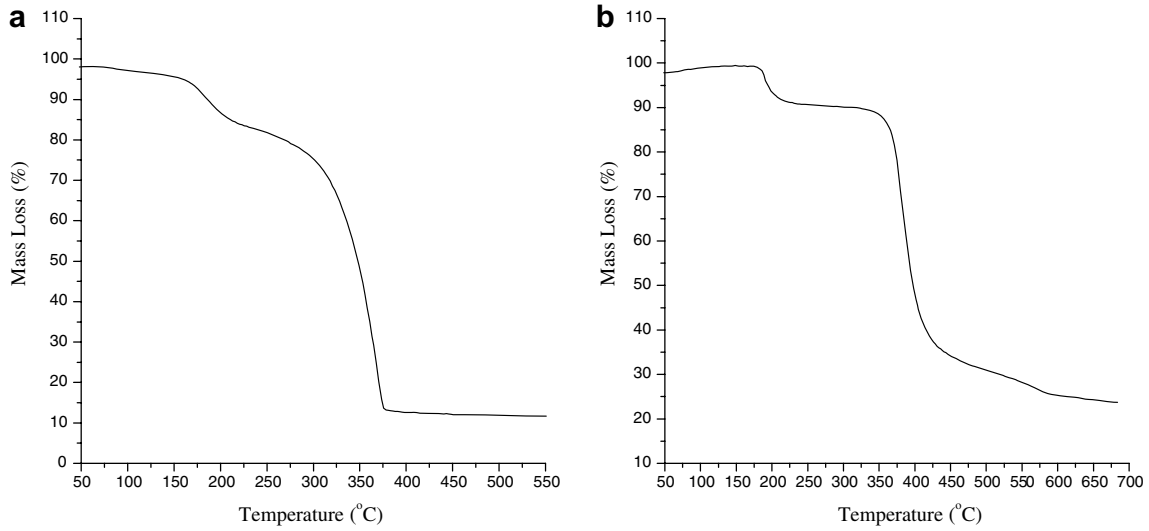


Fig. 4. TGA traces for: (a) [Pd(η^3-$CH_2C(CH_3)CH_2$){$Pr^i_2P(Se)NP(Se)Pr^i_2$-Se,Se′}] (**2b**) (initial weight: 5.00 mg) which decomposed in two steps leaving a 13% residue and (b) [Pd(η^3-$CH_2C(CH_3)CH_2$){PhP(Se)NP(Se)Ph-Se,Se′}] (**2d**) (initial weight: 4.9 mg) which decomposed in two steps leaving a 26.3% residue.

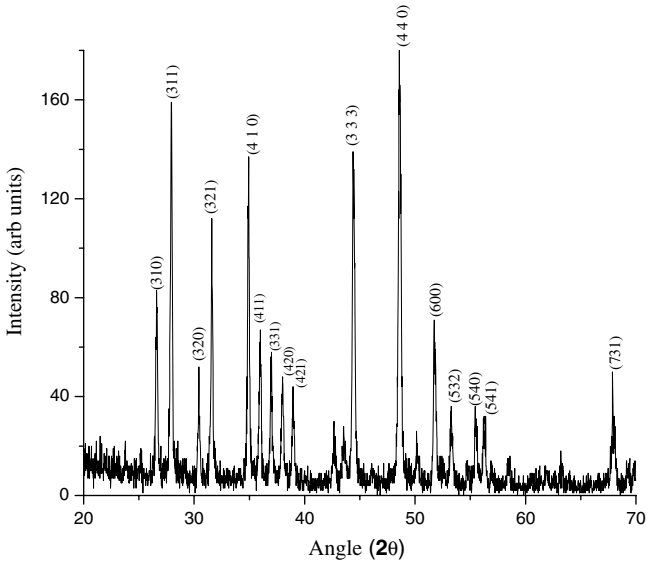


Fig. 5. XRD diffraction pattern for the product obtained after thermolysis of [Pd(η^3 – $CH_2C(CH_3)CH_2$){$Pr^i_2P(Se)NP(Se)Pr^i_2$-Se,Se′}] (**2b**). The pattern has been indexed and peaks with the following observed d (Å) values (hkl): 3.19 (311), 2.83 (321), 2.57 (410), 2.04 (333), 1.87 (440), 1.76 (600), 1.72 (532), 1.65 (540), 1.63 (541) correspond to cubic phase of palladium selenide.

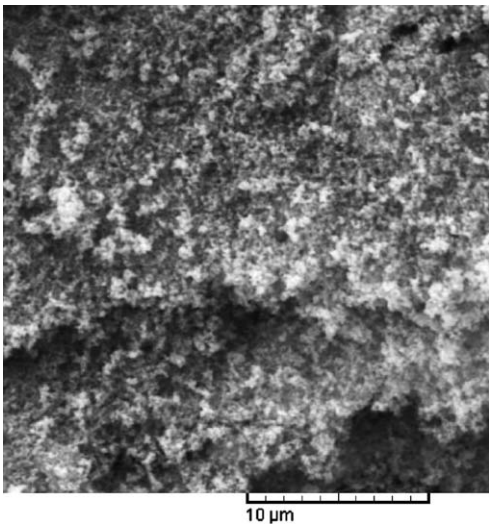


Fig. 6. Scanning electron micrograph of the $Pd_{17}Se_{15}$ obtained from thermolysis of [Pd(η^3-$CH_2C(CH_3)CH_2$){$Pr^i_2P(Se)NP(Se)Pr^i_2$-Se,Se′}] (**2b**).

dimers, [$Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_4R)_2$] [44], Tl(acac) [45] $NH(SPPr^i_2)_2$ [46], $NH(SePPr^i_2)_2$ [47], $NH(SPPh_2)_2$ [48] and $NH(SePPh_2)_2$ [49] were prepared by following the literature procedures. Melting points were determined in sealed capillaries with an electro thermal melting point apparatus and are uncorrected. C, H, N analyses were carried out with a Thermo Finnigan Flash 1112 series elemental analyser. Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Bomem MB-102 FT-IR spectrophotometer as nujol mulls between polythene sheets. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ spectra were recorded on a Bruker DPX 300 spectrometer operating at 300, 75, 121, and 57 MHz, respectively. Chemical shifts are referenced to the internal chloroform peak (^1H and ^{13}C), external 85% H_3PO_4 (^{31}P) and to Ph_2Se_2 ($CDCl_3$, δ 463 ppm) (^{77}Se). Thermogravimetric analyses (TGA) were carried out using NETZSCH STA 409 PC/PG instrument. The TG curves were recorded at a heating rate of 5 °C min^{-1} under a flow of nitrogen gas. X-ray powder diffraction data were collected on a Philips X-ray diffractometer (Model PW 1729) using Cu Kα radiation (λ 1.54060 Å) at 30 kV and 20 mA. SEM micrographs of the samples were obtained using a Vega MV2300t/40 scanning electron microscope. EDS (energy dispersive spectroscopy) analyses

were carried out using a Inca Energy 250 instrument coupled to Vega MV2300t/40 scanning electron microscope.

4.2. Synthesis of complexes

The same general method was used to synthesize all the complexes, **1a**–**1d** and **2a**–**2d**. It consists of the reaction between allyl(acetylacetonato) palladium (II) complex and dichalcogenoimidodiphosphinic acids as illustrated by one specific example.

4.3. Synthesis of [Pd(η³-$CH_2C(CH_3)CH_2$)-{$Pr^i_2P(Se)NP(Se)Pr^i_2$-Se,Se′}]

Solid Tl(acac) (0.840 g, 2.76 mmol) was added to a degassed acetonitrile (50 ml) solution of [Pd(μ-Cl)(η³-$CH_2C(CH_3)CH_2$)]$_2$ (0.54 g, 1.37 mmol) at 0 °C. After it was stirred for 30 min at 0 °C, an acetonitrile (10 ml) solution of $NH(SePPr^i_2)_2$ (1.10, 2.70 mmol) was added to it. The resulting mixture was stirred at room temperature for 0.5 h and then filtered through a small Celite pad. The filtrate was evaporated to dryness under reduced pressure and the residue was recrystallised from acetonitile–ether mixture at −10 °C to obtain complex **2b** as reddish-brown solid. The product was collected by suction filtration. Yield: 0.74 g, 95%.

4.4. NMR data for the ligands

4.4.1. $NH(SPPr^i_2)_2$

^{1}H NMR ($CDCl_3$): 1.21–1.34 (m, 24H, C*H*$_3$ Pr^i), 2.49–2.62 (m, 4H, C*H* of Pr^i), 2.82 (br, 1H, N*H*). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): 17.23 (d, 22 Hz, *C*H$_3$ Pr^i), 31.68, 32.07, 32.48 (*C*H Pr^i). ^{31}P{^{1}H} (121 MHz, $CDCl_3$): δ 91.22 (s).

4.4.2. $NH(SePPr^i_2)_2$

^{1}H NMR ($CDCl_3$): δ 1.16–1.38 (m, 24H, C*H*$_3$ Pr^i), 2.66–2.72 (m, br, 4H, C*H* of Pr^i), 3.01 (br, 1H, N*H*). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 17.61, 18.03 (*C*H$_3$ Pr^i); 32.00, 32.33, 32.65 (*C*H Pr^i). ^{31}P{^{1}H} (121 MHz, $CDCl_3$): δ 90.69 (s, ^1J(P–Se) = 796 Hz). ^{77}Se{^{1}H} (57 MHz, $CDCl_3$): −368.92 (d, ^1J(P–Se) = 792 Hz).

4.4.3. *NH(SPPh$_2$)$_2$*

^{1}H NMR ($CDCl_3$): δ 4.42 (s, 1H, N*H*), 7.30–7.45 (m, 12H, Ph), 7.80–7.93 (m, 8H, Ph). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): 128.12 (br, *o-C*), 131.83 (s, *p-C*), 132.09 (br, *m-C*), 133.42 (d, 106 Hz, *ipso-C*). ^{31}P{^{1}H} (121 MHz, $CDCl_3$): δ 57.60 (s).

4.4.4. *NH(SePPh$_2$)$_2$*

^{1}H NMR ($CDCl_3$): δ: δ 4.48 (s, 1H, N*H*), 7.31–7.43 (m, 12H, Ph), 7.87–7.94 (m, 8H, Ph). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): 128.13 (br, *o-C*); 131.98 (s, *p-C*); 132.45 (br, *m-C*). ^{31}P{^{1}H} (121 MHz, $CDCl_3$): δ 53.26 (s, ^1J(P–Se) = 792 Hz). ^{77}Se{^{1}H} (57 MHz, $CDCl_3$): −163.57(d, ^1J(P–Se) = 792 Hz).

4.4.5. [Pd(η³-CH_2CHCH_2){$Pr^i_2P(S)NP(S)Pr^i_2$-S,S′}] (*1a*)

Yield: 86%; m.p.: 111 °C. Anal. Calc. for $C_{15}H_{33}NP_2S_2Pd$: C, 39.17; H, 7.23; N, 3.05; S, 13.94. Found: C, 39.47; H, 7.12; N, 2.89; S, 13.82. IR (cm^{-1}): *v*(P_2N), 1215 (s), *v*(P–S): 553(s). ^{1}H NMR ($CDCl_3$): δ 1.14–1.31 (m, 24H, C*H*$_3$ of Pr^i), 2.02–2.11 (m, 4H, C*H* of Pr^i), 2.95 (d, 12.3 Hz, 2H, *anti H*, allyl C*H*$_2$), 3.97 (d, 6.8 Hz, 2H, *syn H*, allyl C*H*$_2$), 5.25 (h, 6.8 Hz, 1H, allyl C*H*). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 17.20 (br, *C*H$_3$ of Pr^i ligand), 31.52, 32.02, 32.50 (*C*H of Pr^i), 64.58 (s, allyl *C*H$_2$), 110.70 (s, allyl *C*H). ^{31}P{^{1}H} (121 MHz, $CDCl_3$): δ 62.04 (s).

4.4.6. [Pd(η³-CH_2CHCH_2){$Pr^i_2P(Se)NP(Se)Pr^i_2$-Se,Se′}] (*1b*)

Yield: 82%; m.p.: 84–85 °C. Anal. Calc. for $C_{15}H_{33}NP_2Se_2Pd$: C, 32.54; H, 6.00; N, 2.53. Found: C, 31.64; H, 5.80; N, 2.53. IR (cm^{-1}): *v*(P_2N), 1225 (s), *v*(P–Se): 475(s). ^{1}H NMR (C_6D_6): δ 1.18–1.29 (m, 24H, C*H*$_3$ of Pr^i); 2.02 (h, 7.1 Hz, 4H, C*H* of Pr^i); 2.64 (d, 12.3 Hz, 2H, *anti H*, allyl C*H*$_2$); 3.79 (d, 6.8 Hz, 2H, *syn H*, allyl C*H*$_2$) 4.61 (h, 6.7 Hz, 1H, allyl C*H*). ^{13}C{^{1}H}NMR (75 MHz, C_6D_6): δ 17.71 (d, ^2J(C–P) = 26 Hz, *C*H$_3$ of Pr^i), 32.42, 32.86, 33.28 (*C*H of Pr^i); 63.26 (s, allyl *C*H$_2$); 109.10 (s, allyl *C*H). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 54.13 (s); ^1J(P–Se) 546 Hz. ^{77}Se{1H} NMR (57 MHz, C_6D_6) δ −297.85 (d), ^1J(P–Se) 547 Hz.

4.4.7. *[Pd(η³-CH_2CHCH_2){$Ph_2P(S)NP(S)Ph_2$-S,S′}]* (*1c*)

Yield: 94%. Dec. pt. 188–190 °C. Anal. Calc. for $C_{27}H_{25}NP_2S_2Pd$: C, 54.41; H, 4.23; N, 2.35; S, 10.76. Found: C, 54.79; H, 4.52; N, 2.18 S, 10.77 IR (cm^{-1}): *v*(P_2N), 1212 (s), *v*(P–S), 574(s). ^{1}H NMR: δ 2.87 (d, 12.5 Hz, 2H, *anti* H, allyl C*H*$_2$); 4.04 (d, 6.8 Hz, 2H, *syn* H, allyl C*H*$_2$); 5.14 (h, 6.8 Hz, 1H, allyl C*H*), 7.37 (br, 12H, Ph), 7.96 (br, 8H, Ph). ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$): δ 65.50 (s, allyl *C*H$_2$), 111.71 (s, allyl *C*H), 127.97 (br, *o-C*), 130.45 (s, *p-C*), 130.93 (br, *m-C*), 139.51(d, ^1J(C–P) = 110 Hz, *ipso-C*) ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 38.45 (s).

4.4.8. *[Pd(η³-CH_2CHCH_2){$Ph_2P(Se)NP(Se)Ph_2$-Se,Se′}]* (*1d*)

Yield: 92%. Dec.pt. 178–182 °C. Anal. Calc. for $C_{27}H_{25}NP_2Se_2Pd$: C, 47.04; H, 3.65; N, 2.03. Found: C, 47.00; H, 3.90; N, 1.72. IR (cm^{-1}): *v*(P_2N), 1226 (s), *v*(P–Se), 541(s). ^{1}H NMR ($CDCl_3$): δ 2.81 (d, 12.5 Hz, 2H, *anti* H, allyl C*H*$_2$), 4.08 (d, 6.9 Hz, 2H, *syn* H, allyl C*H*$_2$), 4.96–5.10 (h, 6.9 Hz, 1H, allyl C*H*), 7.37 (br, 12H, Ph), 7.89–7.99 (m, 8H, Ph). ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$): δ 64.72 (s, allyl *C*H$_2$), 110.26 (allyl *C*H), 127.95 (d, ^2J(C–P) = 13 Hz, *o-C*), 130.58 (s, *p-C*), 131.20 (d, ^3J(C–P) = 11 Hz, *m-C*), 138.76 (d, ^1J(C–P) = 106 Hz, *ipso*-C). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 26.61(s); ^1J(P–Se) = 551 Hz. ^{77}Se{1H} NMR (57 MHz, C_6D_6): −142.82 (d, ^1J(P–Se) = 557 Hz).

4.4.9. [Pd(η^3-$CH_2C(CH_3)CH_2$){$Pr^i{}_2P(S)NP(S)$- $Pr^i{}_2$-S,S′}] (***2a***)

Yield: 88%; m.p.: 78 °C. Anal. Calc. for $C_{16}H_{35}NP_2S_2Pd$: C, 39.17; H, 7.23; N, 3.05; S, 13.94. Found: C, 41.48; H, 7.21; N, 2.84; S, 12.80. IR (cm^{-1}): $\nu(P_2N)$, 1219 (s), ν(P–S): 553(s). ^1H NMR ($CDCl_3$): δ 1.15–1.34 (m, 24H, CH_3 of Pr^i); 1.94 (s, 3H, CH_3 of 2-methylallyl ligand); 2.03–2.14 (m, 4H, C*H* of Pr^i); 2.83 (s, 2H, allyl CH_2); 3.78 (s, 2H, allyl CH_2). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 17.11 (br, *C*H_3 of Pr^i), 23.12 (s, *C*H_3 of 2-methylallyl ligand), 31.50, 31.99, 32.48 (H*C* of Pr^i); 64.36 (s, allyl *C*H_2); 125.84 (s, *C*–CH_3, 2-methylallyl ligand). $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 62.17 (s).

4.4.10. [Pd(η^3-$CH_2C(CH_3)CH_2$){$Pr^i{}_2P(Se)NP(Se)Pr^i{}_2$-Se,Se′}] (***2b***)

Yield: 95%; m.p.: 71 °C. Anal. Calc. for $C_{16}H_{35}NP_2Se_2Pd$: C, 33.85; H, 6.21; N, 2.46. Found: C, 32.64; H, 5.91; N, 1.97. IR (cm^{-1}): $\nu(P_2N)$, 1218 (s), ν(P–Se): 478(s). ^1H NMR (C_6D_6): δ 1.17–1.30 (m, 24H, CH_3 of Pr^i), 1.49 (s, 3H, CH_3 of 2-methylallyl ligand), 1.97–2.11 (m, 4H, C*H* of Pr^i group), 2.61 (s, 2H, allyl CH_2); 3.69 (s, 2H, allyl CH_2). $^{13}C\{^1H\}$ (75 MHz, C_6D_6): 17.71 (d, 26 Hz, *C*H_3 of Pr^i), 23.01 (s, *C*H_3 of 2-methylallyl ligand); 32.39, 32.83, 33.26 (*C*H of Pr^i); 63.44 (s, allyl *C*H_2); 123.92 (s, *C*–CH_3, 2-methylallyl ligand). $^{31}P\{^1H\}$ (121 MHz, C_6D_6): δ 54.20(s), ^1J(P–Se) = 550 Hz. $^{77}Se\{1H\}$ NMR (57 MHz, C_6D_6): δ −309.5 (d, ^1J(P–Se) = 548 Hz).

*4.4.11. [Pd(η^3-$CH_2C(CH_3)CH_2$){$Ph_2P(S)NP(S)Ph_2$-S,S′}] (**2c**)*

Yield: 94%; m.p.: 168 °C. Anal. Calc. for $C_{28}H_{27}NP_2S_2Pd$: C, 55.13; H, 4.46; N, 2.29; S, 10.51. Found: C, 54.82; H, 4.58; N, 2.05; S, 9.84. IR (cm^{-1}): $\nu(P_2N)$, 1186 (s), ν(P–S), 554(s). ^1H NMR ($CDCl_3$): δ 1.69 (s, 3H, CH_3 of 2-methylallyl ligand), 2.79 (s, 2H, allyl CH_2), 3.81 (s, 2H, allyl CH_2), 7.36 (br, 12H, Ph), 7.91–8.03 (m, 8H, Ph). $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 22.71 (s, *C*H_3 of 2-methylallyl ligand), 65.17 (s, allyl *C*H_2), 126.97 (s, *C*–CH_3 allyl), 127.94 (br, *o-C*), 130.37 (s, *p-C*); 131.07 (br, *m-C*); 139.70 (br, d, ^1J = 110 Hz, *ipso-C*) $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 38.45 (s).

*4.4.12. [Pd(η^3-$CH_2C(CH_3)CH_2$){$Ph_2P(Se)NP(Se)Ph_2$-Se,Se′}] (**2d**)*

Yield: 96%; m.p.: 181–182 °C. *Anal.* Calc. for $C_{28}H_{27}NP_2Se_2Pd$: C, 47.78; H, 3.86; N, 1.99. Found: C, 48.09; H, 4.02; N, 1.84. IR (cm^{-1}): $\nu(P_2N)$, 1211 (s), ν(P–Se),

Table 5
Details of X-ray data collection and refinement for compounds **1a**, **1d** and **2d**

Identification code	**1a**	**1d**	**2d**
Empirical formula	$C_{15}H_{33}NP_2PdS_2$	$C_{27}H_{25}NP_2PdSe_2$	$C_{28}H_{27}N\ P_2PdSe_2$
Formula weight	459.88	689.74	703.77
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, *P* 21/*n*	Monoclinic, *P* 21/*n*	Triclinic, $P\bar{1}$
Unit cell parameter			
a (Å)	9.8330(18)	9.0776(7)	8.9590(9)
b (Å)	16.4310(7)	23.3510(7)	11.7896(8)
c (Å)	13.3290(13)	12.8202(10)	13.6365(15)
α (°)	90	90	95.410(7)
β (°)	97.137(11)	97.869(7)	95.243(8)
γ (°)	90	90	102.284(7)
Volume ($Å^3$)	2136.8(5)	2691.9(3)	1391.9(2)
Z, D_{calc} ($Mg\ m^{-3}$)	4, 1.430	4, 1.702	2, 1.679
μ (mm^{-1})	1.209	3.528	3.414
F(000)	952	1352	692
Crystal size (mm)	0.35 × 0.20 × 0.15	0.25 × 0.25 × 0.20	0.35 × 0.30 × 0.20
θ Range for data collection	1.98–24.99°	1.74–24.97°	1.51–25.38°
Index ranges	$0 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 19$, $-15 \leqslant l \leqslant 15$	$-10 \leqslant h \leqslant 10$, $-27 \leqslant k \leqslant 0$, $-15 \leqslant l \leqslant 0$	$-10 \leqslant h \leqslant 10$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 11$
Reflections collected/ unique (R_{int})	3999/3769 (0.0285)	4932/4716 (0.0336)	8490/5118 (0.0299)
Maximum and minimum transmission	0.8395 and 0.6770	0.5388 and 0.4724	0.5484 and 0.3812
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3769/0/198	4716/0/298	5118/0/307
Goodness-of-fit on F^2	1.025	1.01	1.015
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0426$, $wR_2 = 0.0843$	$R_1 = 0.0503$, $wR_2 = 0.1185$	$R_1 = 0.0360$, $wR_2 = 0.0897$
R indices (all data)	$R_1 = 0.1097$, $wR_2 = 0.1019$	$R_1 = 0.1241$, $wR_2 = 0.1429$	$R_1 = 0.0593$, $wR_2 = 0.0985$
Largest difference in peak and hole ($e\ Å^{-3}$)	0.560 and −0.582	0.839 and −1.145	0.868 and −1.203

543(s). ^{1}H NMR: δ 1.67 (s, 3H, CH_3 of 2-methylallyl ligand); 2.73 (s, 2H, allyl CH_2); 3.86 (s, 2H, allyl CH_2); 7.37 (br, 12H, Ph), 7.96 (br, 8H, Ph). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 22.93 (s, *C*H_3); 64.60 (s, allyl *C*H_2); 125.30 (s, central *C*–CH_3, 2-methylallyl ligand); 127.92 (d, ^{2}J(C–P) 12.8 Hz, *o-C*); 130.50 (s, *p-C*); 131.07 (d, ^{3}J(C–P) 10 Hz, *m-C*); 139.03 (br, d, ^{1}J(C–P) = 98 Hz, *ipso-C*). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 26.75(s), ^{1}J(P–Se) = 554 Hz. ^{77}Se{1H} NMR (57 MHz, C_6D_6): δ −153.04 (d, ^{1}J(P–Se) = 560 Hz).

4.5. X-ray structure determinations

Crystals of the complexes **1a**, **1d** and **2d** suitable for X-ray study were obtained by slow evaporation of their acetonitrile solutions. X-ray crystallographic data were collected from single-crystal samples of **1a** ($0.35 \times 0.20 \times 0.15$ mm^3), **1d** ($0.25 \times 0.25 \times 0.20$ mm^3) and **2d** ($0.35 \times 0.30 \times 0.20$ mm^3) at 293 K on a Nonius MACH 3 diffractometer employing Mo Kα radiation (0.71073 Å). The unit cell parameters for **1a**, **1d** and **2d** were obtained using 25 centered reflections in the θ range 5.4800–13.0400 (**1a**), 11.2500–14.1200 (**1d**), 11.2700–14.0600 (**2d**). Relevant crystallographic data and structure refinements details are given in Table 5. The intensity data were collected by $\omega - 2\theta$ scan mode, and corrected by Lorentz Polarization and absorption effects using Psi-Scan (ψ- scan). The structure was solved by direct methods (SHELXS) and refined by full-matrix least squares against F^2 using SHELXS-97 software [50]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

4.6. Thermolysis procedure

Bulk thermolyses of **2b** and **2d** were performed at 300 °C and 500 °C, respectively, by heating 0.4 g of each in a quartz boat at a rate of 5 °C min^{-1} from 25 to 300/500 °C under high purity argon. Once at the required temperature (300 °C for **2a** and 500 °C for **2d**), an isotherm was maintained for 2 h before allowing the sample to cool to room temperature. The products for both **2b** and **2d** were dull black materials which formed coarse black shiny powders upon grinding. The typical yields obtained were 60% (**2b**) and 89% (**2d**), respectively.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 608125 (**1a**), 608126 (**1d**) and 608127 (**2d**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033; e-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk.

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