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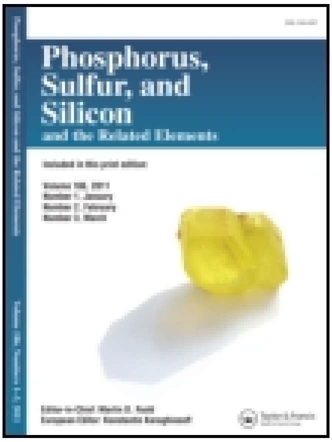

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Binuclear Orthometalated N,N-Dimethylbenzylamine Complexes of Palladium(II): Synthesis, Structures and Thermal Behavior

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Binuclear Orthometalated N,N-Dimethylbenzylamine Complexes of Palladium(II): Synthesis, Structures and Thermal Behavior

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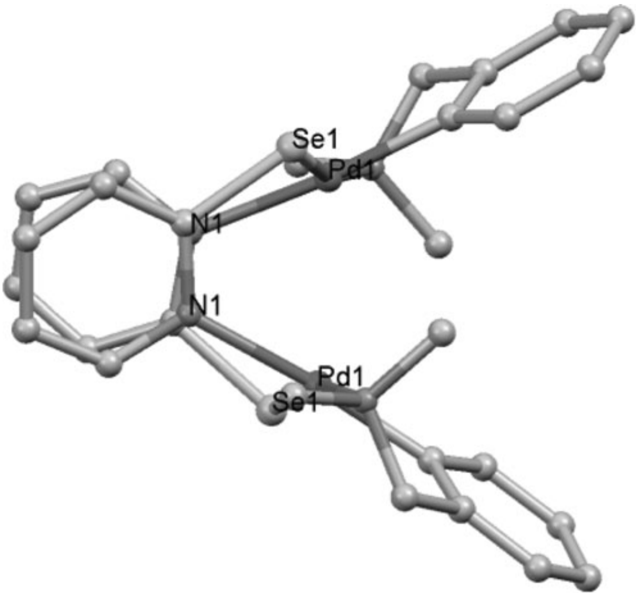
GRAPHICAL ABSTRACT



Abstract *Organochalcogenolate-bridged cyclometalated palladium(II) complexes of the formulae, $[Pd_2(\mu\text{-}Epy)_2(Me_2NCH_2C_6H_4\text{-}C,N)_2]$ (**2**) (E = S (**2a**), Se (**2b**)), $[Pd_2(\mu\text{-}SAr)(\mu\text{-}Cl)(Me_2NCH_2C_6H_4\text{-}C,N)_2]$ (**3**) (Ar = Ph (**3a**), Mes (Mes = 2,4,6-$Me_3C_6H_2$) (**3b**)) and $[Pd_2(\mu\text{-}SeAr)_2(Me_2NCH_2C_6H_4\text{-}C,N)_2]$ (**4**) (Ar = Ph (**4a**), Mes (**4b**)), have been synthesized by the reactions of $[Pd_2(\mu\text{-}Cl)_2(Me_2NCH_2C_6H_4\text{-}C,N)_2]$ with lead or sodium salts of the chalcogenolate ligand. These complexes have been characterized by elemental analysis, mass spectral data, and NMR (^1H and $^{77}Se\{^1H\}$) spectroscopy. The molecular structure of **2**, determined by single crystal X-ray diffraction analysis, revealed a Epy-bridged head-to-tail arrangement in*

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which the eight-membered "(PdECN)$_2$" ring adopts a distorted twist boat conformation. The Pd····Pd separation in ***2a*** *is within the van-der-Waals interaction but in* ***2b*** *it is too large to support the presence of any metal–metal interaction. The thermal behavior of these complexes has been studied by thermogravimetric analysis.*

Supplementary materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *for the following free supplemental files:* Additional figures.

Keywords Cyclometaled complexes; palladium; chalcogen ligands; x-ray structure, NMR, TGA

INTRODUCTION

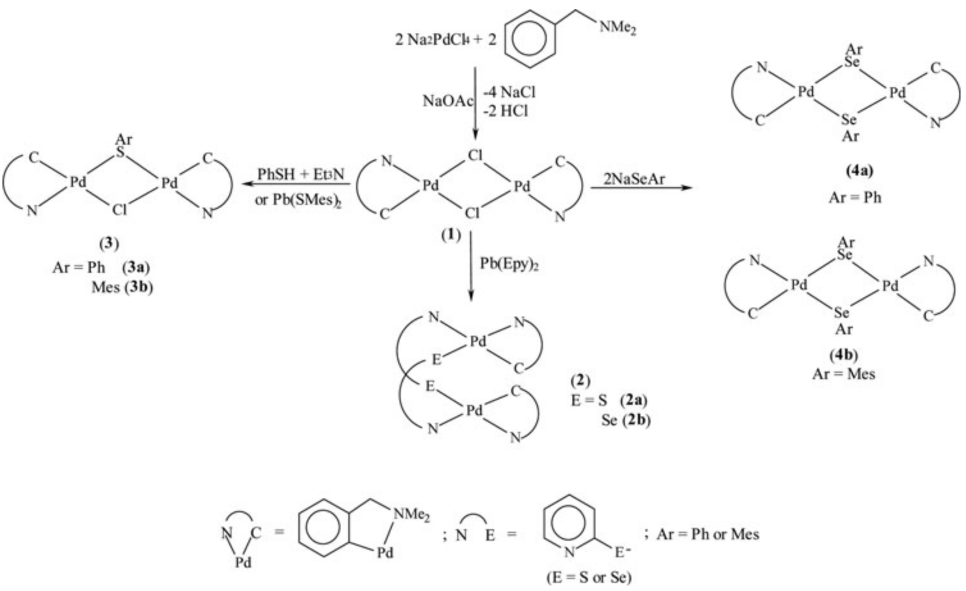
Cyclometalated platinum group metal complexes have been of considerable interest[1–3] since early studies by Cope and Siekman in the mid 1960s. Recently we have isolated cyclometalated palladium and platinum complexes derived from metalated ligand differing in the metalocyclic ring size and the nature of neutral donor group as well as a variety of anionic auxiliary ligands.[4–7] It is worth noting that simple thiolate ligands invariably gave chloro/thiolato-bridged derivatives of palladium, $[Pd_2(\mu\text{-Cl})(\mu\text{-SR})(C^\wedge N)_2]$ under different experimental conditions.[4] In contrast, similar reactions with selenolate ligands afforded bis-selenolato-bridged derivatives.[4] Such reactions employing platinum precursors and both thiolate and selenolate ligands yielded the expected products, $[Pt_2(\mu\text{-ER})_2(X^\cap C)_2]$ (E = S or Se; X = N or P).[5,6] Interestingly, reaction involving platinum precursors with internally functionalized ligands, e.g., Spy, $Me_2NCH_2CH_2E^-$ (E = S or Se) afforded several products varying from cleavage of metalated ligands, cleavage of the Pt-C bond, mono-, bi- and tetranuclear platinum(II) complexes to a platinum(III) derivative $[Pt_2Cl_2(\mu\text{-Spy})_2(ppy)_2]$.[5–7] The 2-mercaptopyridine bridged platinum complex with metalated 2-phenylpyridine show a facial redox ($Pt^{II}\cdots Pt^{III}$) behavior[8] and exhibit red luminescence from metal to metal ligand charge transfer (MMLCT) arising from short Pt····Pt (2.849(1) Å) interaction.[8,9] Similarly, other Spy-bridged binuclear complexes of palladium(II) and platinum(II) with short M····M (M = Pd or Pt) interactions, e.g., $[Pd_2(\mu\text{-Spy})_2(C^\wedge N)_2]$,[10] $[Pt_2(\mu\text{-Spy})_2(bipy)_2][PF_6]_2$,[11] have been shown to be luminescent.[10–12] Deeming and coworkers[13] reported Spy and SpyMe (6-methylpyridine-2-thiolate) bridged binuclear palladium complexes derived from metalated N,N-dimethylbenzylamine, $[Pd_2(\mu\text{-SAr})_2(Me_2NCH_2C_6H_4\text{-C,N})_2]$ (Ar = py or C_5H_3(6-Me)N) and described the structural aspects based on ^1H NMR spectral data.

In the light of the above we have now examined palladium(II) complexes containing N,N-dimethylbenzylamine as a metalated ligand and pyridine-2-chalcogenolate ions as a bridging ligand. For comparison purpose complexes with non-hemilabile chalcogenolate ligands bearing bulky (Mes = 2,4,6-$Me_3C_6H_2$-) and simple (Ph) aryl groups have also been synthesized. Results of this work are described herein.

RESULTS AND DISCUSSION

Synthesis and Spectroscopy

The reaction of $[Pd_2(\mu\text{-Cl})_2(Me_2NCH_2C_6H_4{-}C,N)_2]$ (**1**) with lead salt of 2-mercapto or selenopyridine in dichloromethane afforded 2-chalcogenopyridine-bridged binuclear palladium complexes, $[Pd_2(\mu\text{-Epy})_2(Me_2NCH_2C_6H_4\text{-C,N})_2]$ (**2**) (E = S (**2a**) or Se (**2b**)) in fairly good yield (Scheme 1). Interestingly, a similar reaction with simple arylthiolate groups gave mixed chloro/mercapto-bridged derivatives, $[Pd_2(\mu\text{-Cl})(\mu\text{-SAr})(Me_2NCH_2C_6H_4{-}C,N)_2]$ (**3**) (Ar = Ph (**3a**) or Mes (**3b**)). Contrary to this, the analogous arylselenolate ligand yielded the expected bis selenolato-bridged complexes, $[Pd_2(\mu\text{-SeAr})_2(Me_2NCH_2C_6H_4\text{-}C,N)_2]$ (**4**) (Ar = Ph (**4a**) or Mes (**4b**)).



Scheme 1

The mass spectra of **2** did not show a molecular ion peak, instead a peak due to M-Epy fragment with the expected isotopic pattern was observed. The mass spectra of **3** and **4** displayed molecular ion peaks. The ^{1}H NMR spectral data for **2a** are consistent with the one reported earlier.[13] Deeming described temperature independent ^{1}H NMR spectra of **2a** while the analogous complex $[Pd_2(\mu\text{-SC}_5H_3(Me\text{-}6)N)_2(Me_2NCH_2C_6H_4\text{-}C,N)_2]$ is fluxional at room temperature.[13] Unlike **2a**, the ^{1}H NMR spectrum of **2b** showed broad resonances indicative of fluxional nature of the complex in solution. The spectrum displayed a singlet for NMe_2 protons and two separate resonances for CH_2 protons, i.e., a singlet at 2.97 ppm and a broad AB pattern in the region 3.13– 3.37 ppm in the ratio of 1:1.6 at room temperature. On lowering the temperature, two separate signals for NMe_2 protons appeared. At –30 °C, the spectrum showed two separate signals for NMe_2 at 2.49 and 2.52 ppm while the NCH_2 protons showed a singlet at 2.97 ppm and an AB pattern in the region 3.05-3.14 ppm in the ratio of 1:8.8. The singlet at 2.97 ppm may be attributed to the sym-cis isomeric form. The spectra of **3** and **4** exhibited singlets for NMe_2 and CH_2 protons at ~2.75 and ~3.85 ppm, respectively, indicating magnetic equivalence of protons of methyl and methylene groups. This suggests that these groups of both the metalated ligands are trans to the similar bridging ligands. Recent X−ray analysis of $[Pd_2(\mu\text{-Cl})(\mu{-}SMes)(Me_2NC_{10}H_6{-}C,N)_2]$[4] and $[Pd_2(\mu\text{-Cl})(\mu{-}SBu^n)\{(Bu^nO)C_6H_3CH{=}NC_6H_4(OBu^n{-}4)\}_2]$[14] have shown a sym-cis configuration with the nitrogen atom of the metalated ligands trans to the bridging thiolate group. The ^{1}H NMR spectra of **3** can be interpreted in terms of sym-cis configuration. The ^{77}Se NMR spectrum of **4a** showed a singlet at 181 ppm indicating that both the bridging selenolates are magnetically equivalent as is expected for sym-trans configuration. However, for **4b** ^{77}Se NMR spectrum displayed two resonances at –10 and 30 ppm indicating the existence of sym-cis configuration. This configuration has been reported for the complex $[Pd_2(\mu\text{-}SePh)_2(Me_2NC_{10}H_6{-}C,N)_2]$ both in the solid state (X–ray crystallography) and in solution (^{77}Se NMR data).[4]

Crystal Structures of $[Pd_2(\mu\text{–}Epy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ (E = S or Se)

Molecular structures of $[Pd_2(\mu\text{–}Epy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ (E = S or Se), established by X–ray diffraction analysis, are shown in Figures 1 and 2, while the selected inter-atomic parameters are given in Tables 1 and 2. The coordination around each palladium atom, defined by C, N, E, N, donor set, is nearly planar. The sulfur or selenium atoms in the two bridging pyridine-chalcogenolate ligands occupy the trans position to the N atoms of the metalated ligands resulting in an *anti* configuration (head-to-tail arrangement) which is usually observed for this type of complexes.[10,11,15]

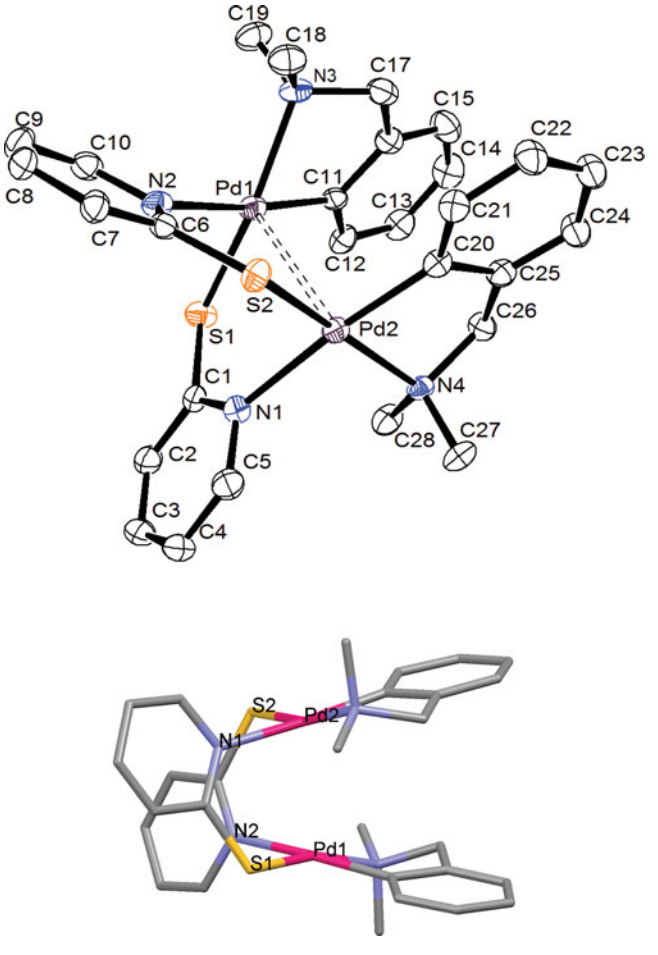


Figure 1 Crystal structure of $[Pd_2(\mu\text{-}Spy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ with 25% ellipsoid probability (H atoms are excluded for clarity) (Color figure available online).

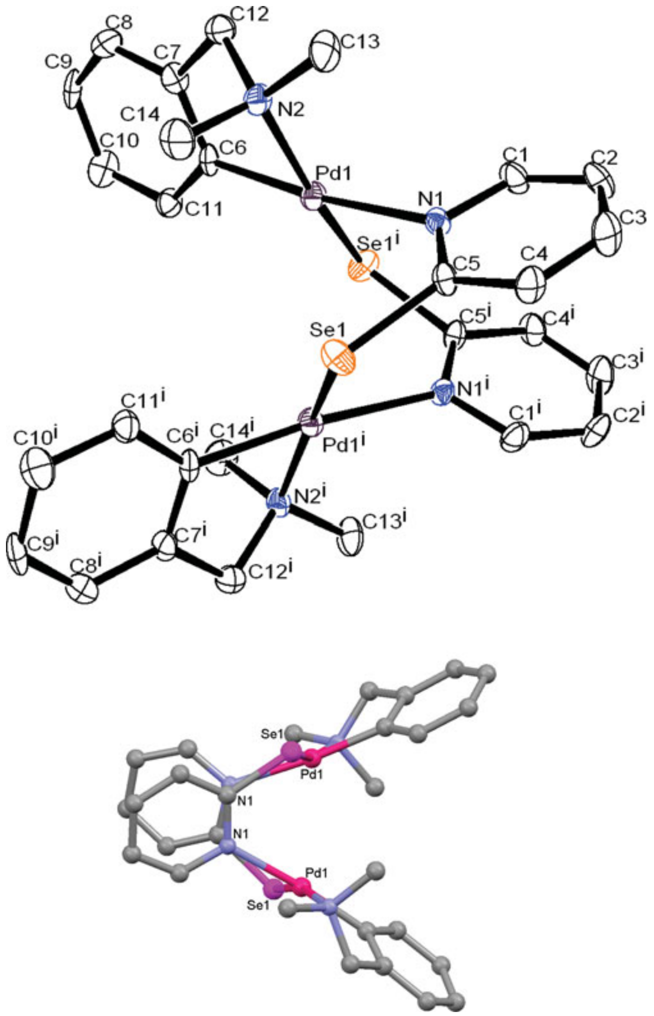


Figure 2 Crystal structure of $[Pd_2(\mu\text{-}Sepy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ with 25% ellipsoid probability (H atoms are excluded for clarity) (Color figure available online).

The eight-membered ring adopts a distorted twist-boat conformation. The methyl groups of NMe_2 of the metalated rings are mutually *anti* but differ in their conformation in two complexes. In case of the Spy bridged complex, they are *exo* with resepect to the eight-membered boat configuration while in the case of Sepy-bridged complex they adopt an *endo* configuration. The Pd–C and Pd–$N_{(\text{metalated})}$ are well in agreement with those reported for $[Pd_3(\mu\text{–}Spy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_3][BF_4]$[13] and other related cyclometalated palladium complexes.[14] The two Pd–S distances are essentially similar and can be compared with those reported in $[Pd_3(\mu\text{–}Spy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_3][BF_4]$,[13] $[Pd_2(\mu\text{–}Spy)_2(Bzq)_2]$,[10] and $[Pd_2(\mu\text{–}Spy)_2(4,4'\text{–}Bu^t{}_2bipy)_2][ClO_4]_2$.[12] The Pd–Se distance (2.410Å) is as expected and can be compared with the one trans to nitrogen atom as observed in $[Pd_2(\mu\text{–}SePh)_2(C_{10}H_6NMe_2\text{–}C,N)_2]$.[4]

Table 1 Selected bond lengths (Å) and angles (°) for [$Pd_2(\mu\text{-}Spy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_2$]

Pd1-C11	2.028(8)	Pd2-C20	2.004(8)
Pd1-N2	2.184(7)	Pd2-N1	2.157(7)
Pd1-N3	2.143(6)	Pd2-N4	2.163(6)
Pd1-S1	2.295(2)	Pd2-S2	2.305(2)
S1-C1	1.728(9)	S2-C6	1.732(8)
		Pd1-Pd2	2.976(2)
N2-Pd1-N3	92.7(2)	N1-Pd2-N4	93.4(2)
N2-Pd1-S1	92.81(18)	N1-Pd2-S2	91.37(18)
N2-Pd1-C11	174.0(3)	N1-Pd2-C20	174.7(3)
N3-Pd1-C11	81.6(3)	N4-Pd2-C20	82.1(3)
N3-Pd1-S1	166.84(19)	N4-Pd2-S2	167.55(17)
C11-Pd1-S1	92.2(2)	C20-Pd2-S2	92.5(2)
N1-C6-S2	122.2(6)	N1-C1-S1	122.4(6)
C11-Pd1-Pd2	98.6(2)	C20-Pd2-Pd1	98.5(2)

The Pd–Pd distance in Spy-bridged complex (2.976(2) Å) is significantly longer than those reported in [$Pd_2(Spy)_4$] (2.677(1) Å),[16] [$Pd_2(\mu\text{–}Spy)_2(4,4'\text{–}Bu^t{}_2bipy)_2$][$ClO_4$]$_2$ (2.891(4)Å),[12] [$Pt_2(Spy)_2(ppy)_2$] (2.8491(4) Å),[8] but only marginally longer than the one reported in [$Pd_2(\mu\text{–}Spy)_2(Bzq)_2$] (2.941(4) Å).[10] However, it is shorter than the sum of van der Waals radii of Pd atoms (3.26Å) and is within the acceptable value for a Pd···Pd intramolecular interaction. The Pd···Pd separation in the corresponding Sepy bridged complex (3.420Å) is much longer than the analogous thio derivative and is also longer than the sum of van der Waals radii of Pd atoms indicative of absence of Pd···Pd interaction.

Thermal studies

Palladium chalcogenolate complexes have been employed as molecular precursors for moderately low temperature synthesis of palladium chalcogenides[4,17,18] which find numerous applications.[19,20] These are also believed to be formed during several catalytic processes involving palladium chalcogenolate complexes.[21,22] Depending on auxiliary ligands on palladium and the nature of R group on chalcogenolate ligand, a variety of palladium chalcogenides are formed. To understand decomposition pattern of these complexes thermogravimetric analysis (TGA) were carried out and the TG residues were characterized by powder XRD. Some of these complexes were also heated in a furnace under different heating conditions and the final residues were characterized by powder XRD analysis. The TG-DTG curves (Supplementary Material) revealed that these complexes undergo a multistep decomposition in the temperature range 200–300 °C leading to the formation of palladium

Table 2 Selected bond lengths (Å) and angles (°) for [$Pd_2(\mu\text{-}Sepy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_2$]

Pd1-C6	1.994(9)	Pd1-Se1^i	2.410(2)
Pd1-N1	2.189(8)	Se1-C5	1.906(10)
Pd1-N2	2.140(8)	Pd1-Pd1^i	3.420
N1-Pd1-N2	94.3(3)	N2-Pd1-C6	81.4(4)
N1-Pd1-Se1^i	94.7(2)	N2-Pd1-Se1^i	165.2(2)
N1-Pd1-C6	173.6(4)	C6-Pd1-Se1^i	88.5(3)
		N1-C5-Se1	118.3(7)

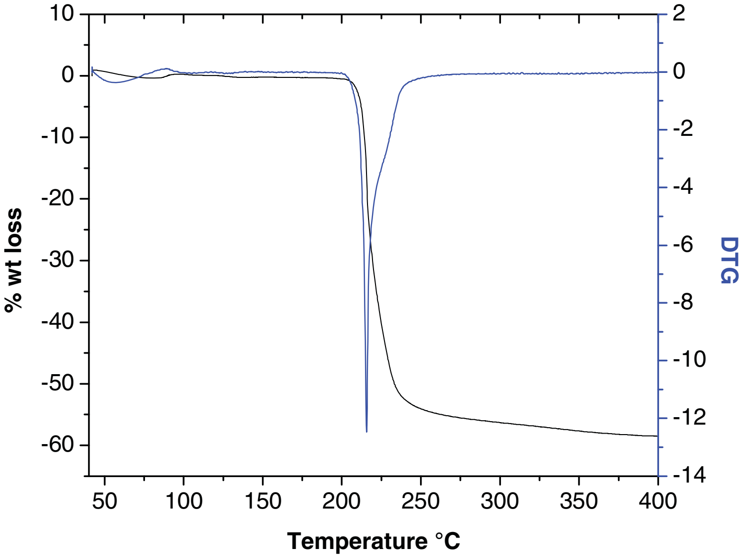


Figure 3 TG-DTG curve of $[Pd_2(\mu\text{-}Spy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ (Color figure available online).

chalcogenides. The thiolato-bridged complexes decomposed to single phase Pd_4S (JCPD file No 73-1387). The TG curve (Figure 3) of $[Pd_2(\mu\text{-}Spy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ appears to be a single-step decomposition but the DTG clearly shows overlapping of closely spaced two-step decomposition (weight loss 30, 28%) at ~215 °C with the formation of Pd_4S (from XRD pattern, Figure 4). This complex can be converted into single phasic Pd_4S

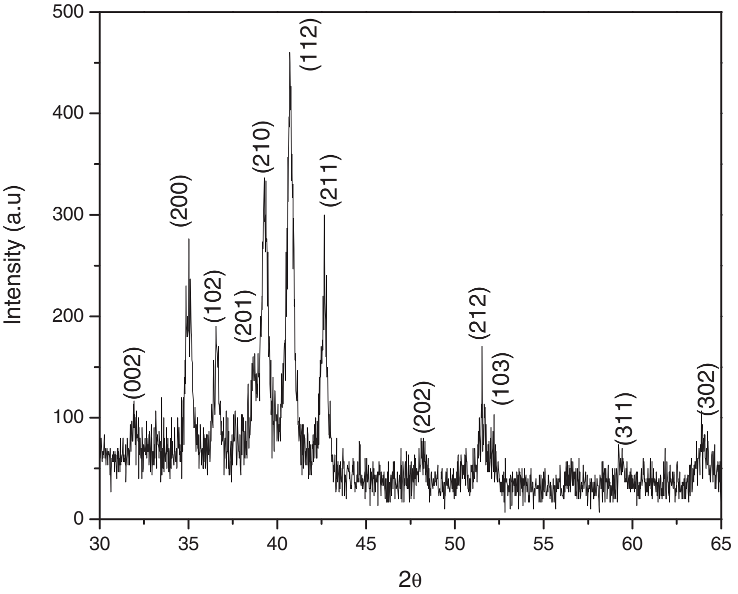


Figure 4 XRD pattern of Pd_4S obtained from $[Pd_2(\mu\text{-}Spy)_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$.

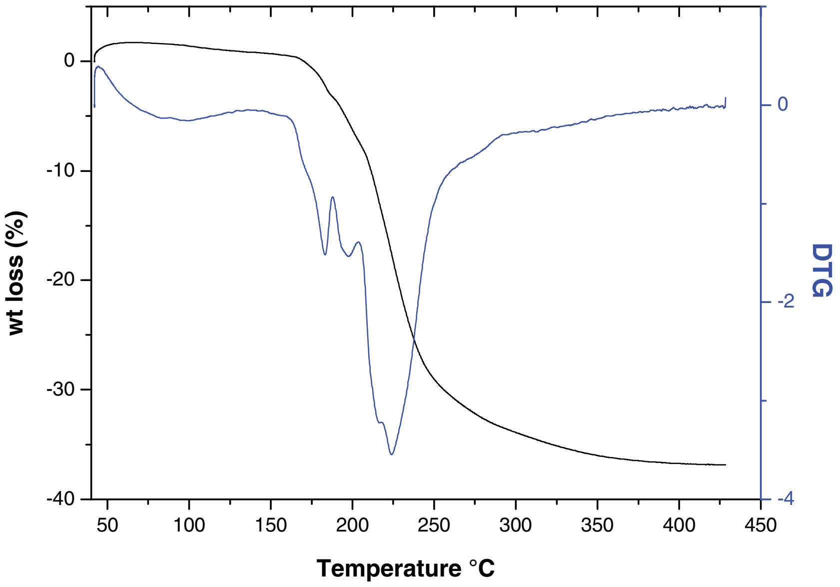


Figure 5 TG-DTG curve of $[Pd_2(\mu\text{-Sepy})_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ (Color figure available online).

even at low temperature (210 °C) as seen during the conventional furnace heating under dynamic argon flow condition.

The selenolato-bridged complexes in general gave a mixture of palladium selenides on decomposition. The TG curve of $[Pd_2(\mu\text{-SePh})_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ showed that the complex decomposed at ~290 °C into single phasic Pd_7Se_4 (confirmed from the XRD pattern JCPDS 44-0875). We have also tried to identify the low temperature decomposition product by carrying out the decomposition of the complex at 200 °C in a furnace under flowing argon, air, and H_2 atmospheres. However, in every case, Pd_4Se was the major product together with Pd_7Se_4 as confirmed from their powder XRD patterns. Similarly, $[Pd_2(\mu\text{-SeMes})_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ decomposed into a biphasic mixture of $Pd_{34}Se_{11}$ (JCPDS file No: 79-0140) and Pd_4Se_7 (JCPDS file No: 31-0939) at ~350 °C. The complex $[Pd_2(\mu\text{-Sepy})_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ undergoes a multi-step decomposition (Figure 5) at 225 °C to yield $Pd_{17}Se_{15}$ as confirmed by the XRD pattern (Figure 6) (JCPDS file No 73-1424). Figures S2–S12 (Supplemental Materials) provide additional characterization spectra for TG-DTG and XRD of the products.

EXPERIMENTAL

Materials and Methods

Solvents were dried and distilled under a nitrogen atmosphere prior to use according to literature method.[23] All reactions were carried out in Schlenk flask under a nitrogen atmosphere. N,N-Dimethylbenzylamine, PhSH, MesSH (Mes = 2,4,6-$Me_3C_6H_2$), Ph_2Se_2, pySH, and other reagents were obtained from commercial sources and were used without further purification. Palladium precursor $[Pd(\mu\text{-Cl})(C^\frown N)]_2$ (**1**) ($C^\frown NH$ = N,N-dimethylbenzylamine),[24] Mes_2S_2,[25] Mes_2Se_2,[26] py_2Se_2,[27] $Pb(SMes)_2$,[18] and $Pb(Spy)_2$ [7] were prepared according to literature methods. Elemental analyses were carried out on a

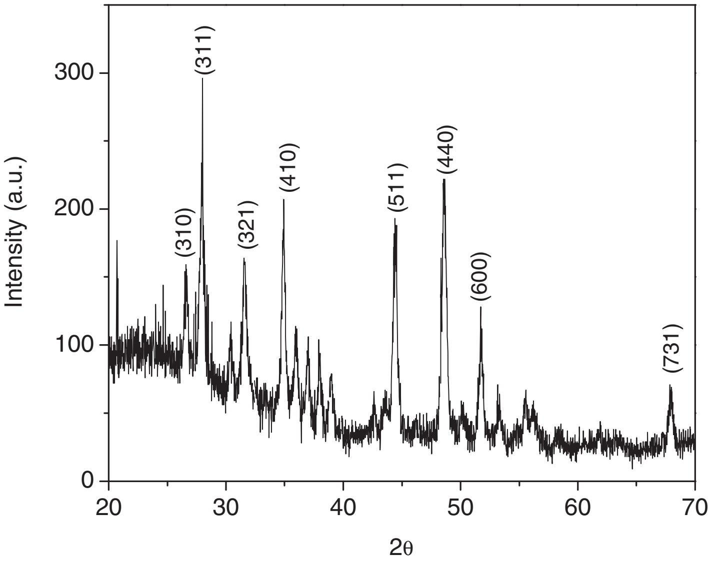


Figure 6 XRD pattern of $Pd_{17}Se_{15}$ obtained from $[Pd_2(\mu\text{-Sepy})_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$.

Thermo Fisher Flash CHN-S instrument. Melting points were determined in capillary tubes and are uncorrected. UV-vis spectra were recorded on a Chemito Spectroscan UV-2600 double beam UV-vis spectrophotometer. ^1H and $^{77}Se\{^1H\}$ NMR spectra were recorded on a Bruker Avance II-300 NMR spectrometer operating at 300 and 57.24 MHz, respectively. Chemical shifts are relative to internal chloroform peak (δ 7.26 for ^1H) and external Me_2Se for $^{77}Se\{^1H\}$ (secondary reference Ph_2Se_2 in $CDCl_3$, δ 463 ppm). TG curves were recorded on a Setsys Evolution 1750 instrument at a heating rate of 5ºC/min under flowing argon atmosphere. Mass spectra were recorded in an MS-500 Ion Trap (IT) Varian mass spectrometer at Sophisticated Analytical Instrumentation Facility (SAIF), Indian Institute of Technology-Bombay, Mumbai. Powder XRD patterns were recorded on a Philips PW1820 using Cu-K_α radiation.

Single crystal X-ray data of $[Pd_2(\mu\text{-Epy})_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$ (E = S or Se) were collected on a Rigaku AFC 75 diffractometer using graphite monochromated Mo- Kα ($\lambda = 0.71069$ Å) radiation so that $\theta_{max} = 27.5$ °. Crystallographic data, together with data collection and refinement details are given in Table 3. All the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods[28] and expanded using Fourier technique.[29] The nonhydrogen atoms were refined anisotropically and fitted with hydrogen atoms in their calculated positions. All calculations were performed using crystal structure crystallographic software package.[30,31] Molecular structures were drawn using ORTEP.[32]

Synthesis

Synthesis of $[Pd_2(\mu\text{-Spy})_2(Me_2NCH_2C_6H_4\text{–}C,N)_2]$(2a). The complex was prepared by a method different from the one reported by Deeming[13]. To a dichloromethane solution (15 mL) of $[Pd(\mu\text{-Cl})(Me_2NCH_2C_6H_4\text{–}C,N)]_2$ (208 mg, 0.38 mmol), solid $[Pb(Spy)_2]$ (167 mg, 0.39 mmol) was added and the reactants were stirred for 24 h. The contents were

Table 3 Crystal data and structure refinement details for [$Pd_2(\mu\text{-Spy})_2(Me_2NCH_2C_6H_4\text{–C,N})_2$] and [$Pd_2(\mu\text{-Sepy})_2(Me_2NCH_2C_6H_4\text{–C,N})_2$]

	[$Pd_2(\mu\text{-Spy})_2$ $(Me_2NCH_2C_6H_4\text{–C,N})_2$]	[$Pd_2(\mu\text{-Sepy})_2$ $(Me_2NCH_2C_6H_4\text{–C,N})_2$]
Empirical formula	$C_{28}H_{32}N_4Pd_2S_2$	$C_{28}H_{32}N_4Pd_2Se_2$
Formula weight	701.56	795.30
Crystal size (mm)	0.20 × 0.20 × 0.20	0.40 × 0.20 × 0.05
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	C2/c
Unit cell dimensions		
a (Å)	10.333(3)	16.131(9)
b (Å)	11.294(10)	9.812(8)
c (Å)	13.794(6)	18.867(11)
α (°)	70.62(5)	—
β (°)	72.560(17)	110.03(5)
γ (°)	79.50(5)	—
Volume (Å^3)	1442.6(14)	2806(3)
D_{calc} (g cm^{--1})	1.615	1.883
Z	2	4
μ (mm^{-1}) / F(000)	1.415 / 704	3.901 / 1552
θ range of data collection(°)	2.51–27.61	2.53–27.50
Index ranges	$-13 \leq h \leq 7$	$-11 \leq h \leq 20$
	$-14 \leq k \leq 14$	$-12 \leq k \leq 7$
	$-17 \leq l \leq 17$	$-24 \leq l \leq 23$
Reflection collected / unique	6583 / 3231	3217 / 1291
Data/restraints/parameters	6583 / 0 / 323	3217 / 0 / 165
Final R_1, ωR_2 indices	0.0551, 0.1081	0.0600, 0.1002
R_1, ωR_2 (all data)	0.1760, 0.1455	0.2326, 0.1407
Goodness of fit on F^2	0.973	0.929
Largest difference in peak and hole (e A $^{\circ\text{-}3}$)	0.957, −0.957	0.844, −1.555

passed through a Celite column. The clear filtrate was concentrated. To this hexane was added, whereupon a yellow precipitate was formed, which was washed with diethyl ether and recrystallized from dichloromethane containing few drops of hexane at 0–5 °C as yellow crystals (yield 176 mg; (66%), m.p.: >195 °C (dec). Anal. Calcd. for $C_{28}H_{32}N_4Pd_2S_2$: C, 47.9; H, 4.6; N, 8.0; S, 9.1. Found: C, 48.0; H, 4.7; N, 7.9; S, 8.9 %. Mass: m/z: 591 (M$^{\cdot+}$-Spy,). UV-Vis at λ_{max}: 276, 337 nm. ^{1}H NMR ($CDCl_3$) δ: 2.39, 2.55 (each s, NMe_2); 2.84–3.10 (AB pattern CH_2N); 6.65–6.69 (m), 6.91 (br, C_6H_4); 6.99 (t, J = 6.6 Hz, CH–5), 7.30 (d, 7.5Hz, CH–4), 7.66 (d, J = 7.5 Hz, CH–3), 8.60 (d, J = 6Hz, CH–6) (Spy).

Synthesis of [$Pd_2(\mu\text{-Sepy})_2(Me_2NCH_2C_6H_4\text{–C,N})_2$](2b). To a toluene solution (20 mL) of NaSepy, prepared in situ by reduction of py_2Se_2 (115 mg, 0.37 mmol) with methanolic $NaBH_4$ (0.03 g, 0.79 mmol), [$Pd(\mu\text{-Cl})(Me_2NCH_2C_6H_4\text{–C,N})$]$_2$ (200 mg, 0.36 mmol) dissolved in toluene (10 mL) was added and the reaction mixture was stirred for 2 h. The reaction mixture was evaporated under vacuum. The complex was extracted with toluene and the solution was passed through Celite. The clear filtrate was concentrated under reduced pressure. The residue was washed with diethyl ether and recrystallized from dichloromethane-hexane mixture to give yellowish brown crystals (yield 225 mg; 78%), m.p.: 193 °C (dec.). Anal. Calcd. for $C_{28}H_{32}N_4Pd_2Se_2$: C, 42.3; H, 4.0; N, 7.0. Found: C, 42.2; H, 4.1; N, 7.2. Mass: m/z: 638 (M$^+$ - Sepy); 504 (M$^+$ - (N,N-dimethylbenzylamine

+ Sepy)). UV-Vis at λ_{max}: 275, 287, 330 nm. ^{1}H NMR (500 MHz) ($CDCl_3$) δ: (at room temperature) 2.53 (s, NMe_2), 2.97 (s), 3.13-3.37 (AB pattern) (NCH_2), 6.68 (br) 6.76 (t, J = 6 Hz), 6.87 (m), 6.94 (m), 7. 45 (d, 8 Hz), 7.69 (br), 8.73 (d, J = 5 Hz); (at −30 °C): 2.49, 2.52 (each s, NMe_2), 2.97 (s) 3.05–3.14 (AB pattern) (NCH_2), 6.68 (t, 1H, C_6H_4), 6.81 (t, 6.5 Hz,1H, C_5H_4N), 6.89 (t, 4.5 Hz, 2H, C_6H_4), 6.98 (t,7 Hz, 1H, C_5H_4N), 7.46 (d, 8 Hz, 1H, C_5H_4N), 7.75 (t,5 Hz, 1H, C_6H_4), 8.73 (d, 5Hz, 1H, C_5H_4N); ^{77}Se{^{1}H} NMR ($CDCl_3$) δ: 311 ppm.

Synthesis of [Pd_2(μ-Cl)(μ-SPh)($Me_2NCH_2C_6H_4$–C,N)$_2$] (3a). To a toluene solution (20 mL) of [Pd(μ-Cl)($Me_2NCH_2C_6H_4$–C,N)]$_2$ (300 mg, 0.54 mmol), PhSH (120 mg, 1.09 mmol) in toluene (5 mL) was added. After stirring for 5 min, Et_3N (151 μL, 1.0 mmol) was added and the whole reaction mixture was further stirred for 2 h. The contents were passed through a Celite column and the clear filtrate was shaken first with distilled water (1 × 10 mL) and then with aqueous NaCl solution (2 × 5 mL) in a separating funnel and, in both the cases, organic fraction was collected. The organic fraction was stored over anhydrous Na_2SO_4. The clear solution was decanted and passed through Celite. The filtrate was concentrated to 5 mL and the title complex was precipitated by adding hexane, which was filtered and washed with diethyl ether and dried under vacuum. The complex was recrystallized as a yellow crystalline solid from dichloromethane containing few drops of hexane at 0–5 °C. Yield: 253 mg (74 %), m.p. 185 °C (dec.). Anal. Calcd. for $C_{24}H_{29}ClN_2Pd_2S$: C, 46.0; H, 4.7; N, 4.5; S, 5.1. Found: C, 45.9; H, 4.6; N, 4.6; S, 4.9 %. Mass: m/z: 626 (M^+); 590 (M - Cl$^-$). UV-Vis : λ_{max}: 282, 339 nm. ^{1}H NMR ($CDCl_3$) δ: 2.77 (s, 12H, NMe_2); 3.89 (s, 4H, $-CH_2-$); 6.94–6.97 (m), 7.13 (m) (SPh); 7.60–7.63 (m),8.15–8.18 (m) (C_6H_4).

Synthesis of [Pd_2(μ-Cl)(μ-SMes)($Me_2NCH_2C_6H_4$–C,N)$_2$] (3b). To a dichloromethane solution (15 mL) of [Pd(μ-Cl)($Me_2NCH_2C_6H_4$–C,N)]$_2$ (260 mg, 0.47 mmol), solid [Pb(SMes)$_2$] (240 mg, 0.47 mmol) was added with stirring. The yellow solution turned orange with appearance of a white precipitate. The reaction mixture was stirred for 2 h and the solution was passed through a Celite column. The clear filtrate was concentrated and the complex was precipitated by adding hexane. The precipitate was washed with diethyl ether until the color of the washings became colorless. The complex was crystallized from dichloromethane containing few drops of hexane at 0–5 °C whereupon orange crystals were separated (yield 187 mg; 59%), m.p.: 166 °C (dec). Anal. Calcd. for $C_{27}H_{35}ClN_2Pd_2S$: C, 48.5; H, 5.3; N, 4.2; S, 4.8. Found: C, 48.7; H, 5.2; N, 4.3; S, 4.5%. Mass: m/z: 668 (M^+); 632 (M^+-Cl) ; 517 (M^+- SMes). UV-Vis at λ_{max}: 279, 341 nm. ^{1}H NMR ($CDCl_3$) δ: 2.16 (s, 3H, 4-Me); 2.71 (s, 12H, NMe_2); 3.14 (s, 6H ,2,6-Me); 3.85 (s, 4H, -CH_2-); 6.44(s); 6.47 (s) ($C_6H_2Me_3$); 6.54–6.60 (m); 6.79–6.82 (m) (C_6H_4).

Synthesis of [Pd_2(μ-SePh)$_2$($Me_2NCH_2C_6H_4$–C,N)$_2$] (4a). To a toluene solution (20 mL) of NaSePh, prepared in situ by reduction of Ph_2Se_2 (113 mg, 0.36 mmol) with methanolic $NaBH_4$ (30 mg, 0.79 mmol), [Pd(μ-Cl)($Me_2NCH_2C_6H_4$–C,N)]$_2$ (200 mg, 0.36 mmol) dissolved in 20 mL toluene was added and stirred for 2 h. The solvents were evaporated under reduced pressure and the residue was extracted with benzene. The solution was passed through Celite, concentrated and precipitated by adding hexane. The precipitate was washed with diethyl ether and recrystallized from benzene/hexane mixture as red crystals, (yield: 174 mg (61%), m.p. 158 °C (dec)). Anal. Calcd. for $C_{30}H_{34}N_2Pd_2Se_2$: C, 45.4; H, 4.3; N, 3.5. Found: C, 45.1; H, 4.3; N, 3.2%. Mass: m/z: 793 (M^+), 659 (M^+-N,N-dimethylbenzylamine), 637 (M^+-SePh). UV-Vis : λ_{max} : 276, 335 nm. ^{1}H NMR ($CDCl_3$) δ: 2.76 (s, 12H, NMe_2); 3.91 (s, 4H, -CH_2—); 6.89–6.97 (m), 7.12–7.15 (m), 7.63 (d, J = 6.6 Hz); 8.81 (d, d, 1.8, 7.8 Hz) (Ph + C_6H_4). ^{77}Se {^{1}H} NMR ($CDCl_3$) δ: 181 ppm.

Synthesis of $[Pd_2(\mu\text{-SeMes})_2(Me_2NCH_2C_6H_4\text{–C,N})_2]$ (4b). Prepared similar to reported method.[4] (Characterization details are given in supplementary information). Figure S13 shows the ^{77}Se NMR spectrum of 4b.

SUPPLEMENTARY DATA

The full crystallographic data were deposited in the form of CIF files at the Cambridge Structural Database (CCDC-Nos. 870373 and 870374 for $[Pd_2(\mu\text{-Sepy})_2(Me_2NCH_2C_6H_4\text{–C,N})_2]$(**2b**) and $[Pd_2(\mu\text{-Spy})_2(Me_2NCH_2C_6H_4\text{–C,N})_2]$(**2a**), respectively) and are available freely on request citing the deposition number from the website: www.ccdc.cam.ac.uk/conts/retrieving.html.

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