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Synthesis and Characterization of Chalcogenolato-Bridged Allyl Palladium Complexes: Versatile Precursors for Palladium Chalcogenides

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The complexes $[Pd(\mu\text{-}ER)(\eta^3\text{-allyl})]_2$ (ER = EMes; E = S, Se; allyl = C_3H_5, C_4H_7) have been isolated by the reaction of $[Pb(ER)_2]_n$ with $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$. Similar reactions with $[Pb(SeCH_2CH_2NMe_2)_2]_n$ resulted in the formation of a trinuclear complex $[Pd_3Cl_2(\kappa^2\text{-Se,N-}SeCH_2CH_2NMe_2)(\eta^3\text{-allyl})_3]$. Treatment of $[Pd(\mu\text{-}SR)(\eta^3\text{-}C_4H_7)]_2$ with $[Pd(SMes)_2]_n$ in 1:1 ratio yielded $[Pd_3(\mu\text{-}SMes)_4(\eta^3\text{-}C_4H_7)_2]$. These complexes were characterized by elemental analyses and mass, UV−vis, and NMR spectroscopy. The structures of $[Pd_2(\mu\text{-}EMes)_2(\eta^3\text{-}C_4H_7)_2]$ (E = S, Se) were established by single-crystal X-ray diffraction analysis, which revealed a *syn* configuration. Two new structural motifs for $[Pd_3Cl_2(\kappa^2\text{-Se,N-}SeCH_2CH_2NMe_2)(\eta^3\text{-}C_3H_5)_3]$ and $[Pd_3(\mu\text{-}SMes)_4(\eta^3\text{-}C_4H_7)_2]$ have also been identified. Pyrolysis of $[Pd(\mu\text{-}ER)(\eta^3\text{-}C_4H_7)]_2$ yielded palladium chalcogenides, which were characterized by powder XRD and EDAX.

Introduction

The chemistry of η^3-allylpalladium complexes has been a subject area of extensive research for the past several decades.[1] There are several obvious reasons for this sustained interest. These include their diverse reactivity and utility in palladium-catalyzed organic transformations[2,3] and more recently in materials science.[4] The allylpalladium complexes are usually isolated as mono- and binuclear derivatives with a few examples of tri-[5] and high-nuclearity complexes.[6]

The lability of the allyl group has made these complexes, such as $[Pd(\eta^3\text{-allyl})_2]$ (allyl = C_3H_5 or C_4H_7),[7] $[Pd(Cp)(\eta^3\text{-}C_3H_5)_2]$,[7] $[Pd(\eta^3\text{-allyl})(\beta\text{-diketonate})]$,[8] and $[Pd(\eta^3\text{-allyl})(\beta\text{-ketoiminato})]$,[9] attractive precursors for deposition of high-quality palladium films under mild conditions. Similarly the binuclear complex $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ has been used for the preparation of palladium nanoparticles.[10] The lability of the allyl group has also led to the development of single-source precursors for palladium sulfides.[4,11]

Palladium forms a range of palladium chalcogenides differing in stoichiometry and structures, and several of them are semiconducting materials (e.g., PdS: E_g = ~2.0 eV).[12] The utility of palladium sulfides has been demonstrated in a wide range of catalytic reactions[13–15] such as dehydrosulfurization of thiophenes[13] and dehydrogenation.[14] Besides the reactions of palladium salts with H_2S or Na_2S for the preparation of PdS,[16,17] classical complexes $[Pd(S_2COPr^i)_2]$[18] and $[Pd(S_2CNMeHex)_2]$[19] have been used for the deposition of thin films of PdS. The allylpalladium complexes $[Pd_2(\mu\text{-}SR)_2(\eta^3\text{-}C_4H_7)_2]$[4] and $[Pd(\eta^3\text{-}C_3H_5)(S_2CNMeHex)]$,[11] in contrast, yield palladium-rich sulfides, Pd_4S and $Pd_{2.8}S$, respectively. The allyl thiolate complexes are formed by the reactions of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ with the alkali metal thiolate salts. Thus, the reactions of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ with 1,1-dithiolates give $[Pd(\eta^3\text{-allyl})(S^\frown S)]$ complexes,[1] while with simple thiols binuclear derivatives are formed.[4] Studies of heavier chalcogenolate complexes are rather scanty.[4] In the above perspective the present investigation on allylpalladium complexes containing both bulkier and internally functionalized chalcogenolate ligands has been undertaken.

Results and Discussion

Synthesis and Spectroscopy. Reactions of chloro-bridged allylpalladium complexes with lead salts of organochalcogenolate ligands gave bi- and trinuclear chalcogenolato-bridged allylpalladium complexes (Scheme 1). With mesityl chalcogenolate, binuclear complexes $[Pd_2(\mu\text{-}EMes)_2(\eta^3\text{-allyl})_2]$ (**1**−**4**) are formed as yellow-orange crystalline solids, whereas with internally functionalized chalcogenolate ligand, $Me_2NCH_2CH_2Se^-$, trinuclear complexes $[Pd_3Cl_2(\kappa^2\text{-Se,N-}SeCH_2CH_2NMe_2)(\eta^3\text{-allyl})_3]$ (**6**, **7**) are isolated, in which selenolate selenium atom

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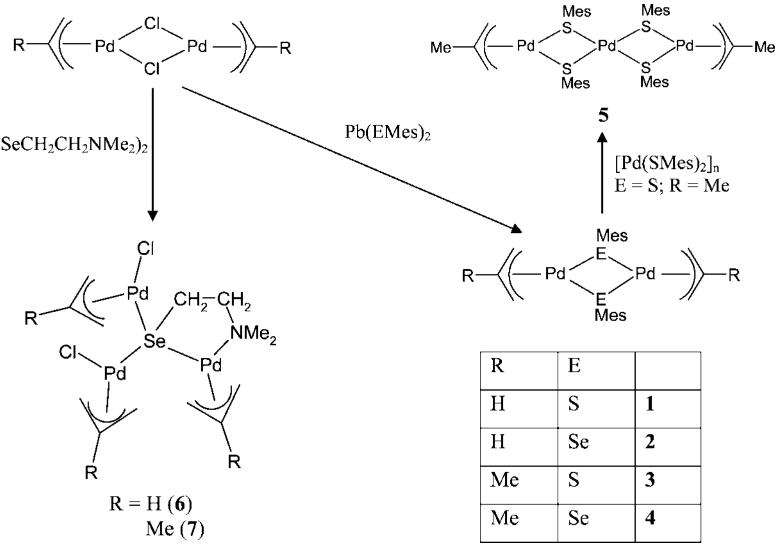
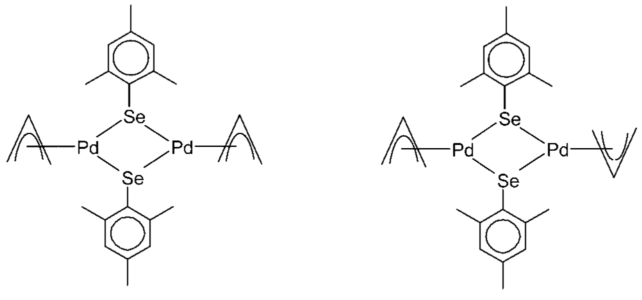
Scheme 1



R	E	
H	S	**1**
H	Se	**2**
Me	S	**3**
Me	Se	**4**

Scheme 2



A *Syn*

B *Anti*

is triply bridging. When a dichloromethane solution of **3** is left in open air for several days for recrystallization, growth of some red crystals, identified as the trimeric complex **5**, in addition to yellow-orange crystals of **3** was observed. The formation of **5** from **3** in open air seems to take place via a reaction between **3** and $[Pd(SMes)_2]_n$. The formation of **5** from **3** and $[Pd(SMes)_2]_n$ has been ascertained by carrying out a reaction between them in refluxing dichloromethane. The $[Pd(SMes)_2]_n$ appears to be formed by the nucleophilic attack of thiolate ligand on an allyl group. Cleavage of the allyl group in allylpalladium complexes by thiolate ligands has been reported earlier.[11,20,21]

The chalcogenolato-bridged allylpalladium complexes have been characterized by mass, NMR, and single-crystal X-ray diffraction analyses. The mass spectra of **3** and **6** exhibited molecular ion peaks, while for **5** a molecular ion peak was not observed. The highest ion peak (m/z = 661) in the mass spectrum of **5** has been attributed to the $[Pd_2(SMes)_3]^+$ fragment. In the case of **6**, a peak attributable to a high molecular weight species, $[PdCl(SeCH_2CH_2NMe_2)]_3$-Cl, was also observed.

The ^1H NMR spectra displayed expected peaks and integration. The complexes **1**−**4** exist into *syn* and *anti* forms depending on mutual disposition of the allyl groups (Scheme 2). Thus, the ^1H NMR spectrum of $[Pd_2(\mu\text{-SeMes})_2(\eta^3\text{-}C_3H_5)_2]$ (**2**) at 500 MHz displayed two doublets (δ 3.43, 3.56 each d 5 Hz) for *syn* protons, two closely spaced multiplets (5.09, 5.12 ppm) for the central carbon proton, and two doublets (δ 2.68, 2.84, each 11 Hz) for *anti* protons of the allyl group at room temperature.

The ^1H NMR spectrum of $[Pd_3Cl_2(\kappa^2\text{-Se,N-SeCH}_2CH_2NMe_2)(\eta^3\text{-}C_3H_5)_3]$ (**6**) displayed broad resonances at room temperature, indicating fluxional behavior of the molecule. The spectrum at −40 ^{o}C however showed separate resonances for the allyl groups and selenolate ligand. Due to the complexity of the spectrum, a 2D COSY experiment at −40 ^{o}C was performed (Supporting Information S3), and various assignments [2.78, 2.82 (each s, NMe_2); 2.90 (m, $SeCH_2$); 3.35 (m, NCH_2) (selenolate ligand); 2.45 (m, *anti*); 3.45 (br, *syn*); 5.22 (br, central CH) (chelated Pd1 allyl); 4.12 (*syn*); 3.00 (*anti*) (Pd2 allyl); 4.42 (*syn*); 3.05 (*anti*) (Pd3 allyl); 5.35 (central CH) (nonchelated Pd2 and Pd3 allyls)] were made by establishing correlations.

X-ray Structures. Solid-state structures of $[Pd_2(\mu\text{-EMes})_2(\eta^3\text{-}C_4H_7)_2]$ (E = S (**3**); Se (**4**)), $[Pd_3(\mu\text{-SMes})_4(\eta^3\text{-}C_4H_7)_2]$ (**5**), and $[Pd_3Cl_2(\kappa^2\text{-Se,N-SeCH}_2CH_2NMe_2)_2(\eta^3\text{-}C_3H_5)_3]$ (**6**) were established by single-crystal X-ray diffraction analyses. Complexes **4** and **5** crystallized out with a benzene and three water molecules, respectively. In the latter O1 and O1′ have half-occupancy in the molecule. The ORTEP plots with atomic numbering schemes are shown in Figures 1–4, and selected bond lengths and angles are given in Tables 1–3.[22]

The molecular structures of **3** and **4** are isomorphous. The dimeric molecules have two distorted square-planar palladium atoms bridged together by two EMes groups, forming a nonplanar four-membered Pd_2E_2 ring. The sterically crowded mesityl and 2-methylallyl groups are all mutually *syn*, and the former are oriented in an *endo*-cyclic configuration. The point group of the molecule is C_{2v}; the C_2 axis passes through the mid point of the nonplanar Pd_2E_2 ring. Both of the phenyl rings of the mesityl group lie on one σ_v plane. The Se(1)···Se(2) (3.252 Å) and Pd(1)···Pd(2) (3.356 Å) distances are slightly shorter than the reported binuclear complex having a similar Pd_2Se_2 core, as in $[\{Pd(\eta^3\text{-}C_3H_5)[Ph_2P(O)NP(Se)Ph_2\text{-}Se]\}_2]$ (Se···Se 3.46 Å, Pd···Pd 3.54 Å).[23] The Pd−S and Pd···Pd distances in sulfur complex **3** closely resemble those in another allyl palladium complex, $[Pd_2(\mu\text{-SBu}^t)_2(\eta^3\text{-}C_4H_7)_2]$.[4] The bond

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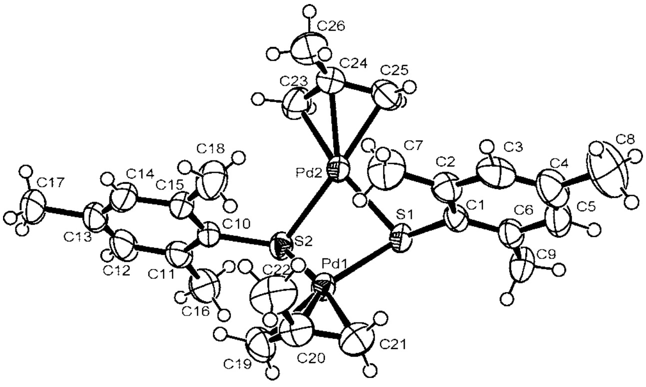

Figure 1. Molecular structure of $[Pd_2(\mu\text{-SMes})_2(\eta^3\text{-}C_4H_7)_2]$ (**3**).

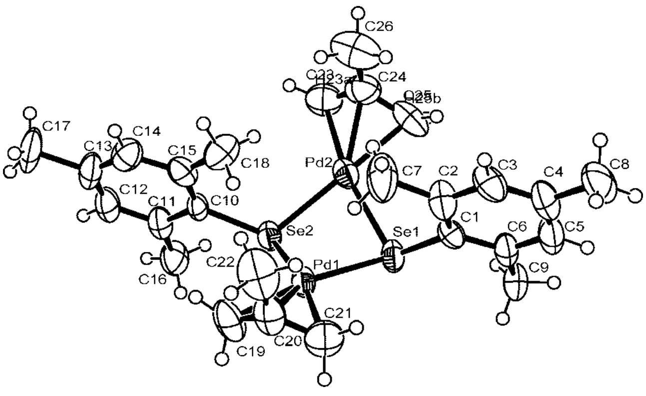

Figure 2. Molecular structure of $[Pd_2(\mu\text{-SeMes})_2(\eta^3\text{-}C_4H_7)_2]$ (**4**).

angles and average C−C (1.42 Å), Pd−C (2.14 Å), and Pd−S (2.36 Å) distances compare well with those found in other allyl palladium complexes.[4,24]

Although the overall quality of diffraction data for **5** was rather low due to poor quality of crystals, the overall chemical structure could be determined unambiguously. The trimeric complex $[Pd_3(\mu\text{-SMes})_4(\eta^3\text{-}C_4H_7)_2]$ (**5**) comprises palladium atoms arranged in a linear chain fashion and are held together by four bridging thiolate groups. The three palladium coordination spheres are almost planar. The central palladium atom is coordinated by an S_4 core, while the coordination environment around peripheral palladium atoms is defined by a $\eta^3\text{-}C_4H_7$ group and two bridging thiolate groups. The molecule **5**, with C_{2h} symmetry, has a horizontal plane σ_h that passes through the three Pd atoms and the Pd−C bond connecting to the central carbon atom of the allyl ligand. The central Pd(1) atom is the inversion center. The two mesitylthiolato ligands and the allyl group attached to the terminal palladium atoms are all mutually *syn*; however, these groups of Pd(2) and Pd(2′) adopt an *anti* configuration (see inset in Figure 3). Both of the terminal palladium square planes are parallel to each other and tilted from the central palladium square plane by 46.9°, giving a zigzag shape to the molecule.

All the Pd−S distances are essentially similar (av 2.39 Å) and are within the expected range reported for palladium thiolate complexes.[4,25] Various S−Pd−S angles around palladium atoms are within the range reported for several thiolato-bridged bi- ($[Pd_2Cl_2(\mu\text{-SR})_2(PR_3)_2]$)[1,26] and trinuclear ($[Pd_3Cl_2(\mu\text{-ScHx})_4(PMe_3)_2]$[26]) complexes. The three allyl carbons are equidistant from the palladium atom. The C−C distances of the allyl group are intermediate between single and double bond distances.

The molecular structure of $[Pd_3Cl_2(\kappa^2\text{-Se,N-SeCH}_2CH_2NMe_2)(\eta^3\text{-}C_3H_5)_3]$ (**6**) is unique and represents the first example of a triply bridging selenolato ligand, and is also an example where three square planes of palladium are sharing a corner. The coordination around Pd(1) is defined by a η^3-bonded allyl group and a chelating *N*,*N*-dimethylaminoethylselenolate ligand, while the Pd(2) and Pd(3) are each coordinated to a η^3-bonded allyl group, a chloride ligand, and a Se atom. The Pd−Se distance with Pd(1), having a chelated selenolate ligand, is slightly shorter than the Pd−Se distances with Pd(2) and Pd(3), although three distances are within the range reported for several palladium−selenolate complexes.[27,28] The Pd−Cl and Pd−C distances are all normal. The five-membered chelate ring is puckered, as reported for a number of mononuclear complexes of the type $[MCl(PR_3)(SeCH_2CH_2NMe_2)]$ (M = Pd or Pt).[29,30] The coordination planes of Pd(2) and Pd(3) lie with the square plane of Pd(1) at 50.61° and 75.71°, respectively.

Recently we have demonstrated the use of $[MCl(PR_3)(ECH_2CH_2NMe_2)]$ (E = S, Se, Te) as a metallo-ligand in constructing bi- and trinuclear complexes[28,31] in which a chelating chalcogenolate ligand is singly bonded to another metal atom, leaving one lone pair of electrons on the chalcogen atom uncoordinated. In the present case all the lone pairs of electrons on selenium are utilized in coordination to the metal atom.

Thermal Studies. Palladium-rich chalcogenides are semiconducting materials and are used in the electronic industry.[12] To assess the suitability of these complexes as molecular precursors for palladium chalcogenides, thermal studies were carried out (Supporting Information S6−S9). Thermolysis of **3** in HDA at 175 °C gave Pd_4S, as revealed by the XRD pattern. Similarly, when **4** was pyrolyzed in a furnace at 160 °C, Pd_4Se was formed. The pyrolysis of **3** in the temperature range 300−350 °C in a furnace, however, resulted in the formation of a mixture of palladium sulfides, $Pd_{16}S_7$ and $Pd_{2.8}S$.

Conclusion

Bi- and trinuclear allylpalladium complexes stabilized by bridging chalcogenolate ligands have been isolated. A new trinuclear palladium complex (**6**) was formed, in which a corner from each square plane of three palladium atoms is connected by a triply bridging selenolate ligand. The binuclear complexes have been shown to be versatile precursors for the preparation of palladium-rich chalcogenides.

Experimental Section

General Procedures. Solvents were dried by standard methods with subsequent distillation under nitrogen. All reactions were

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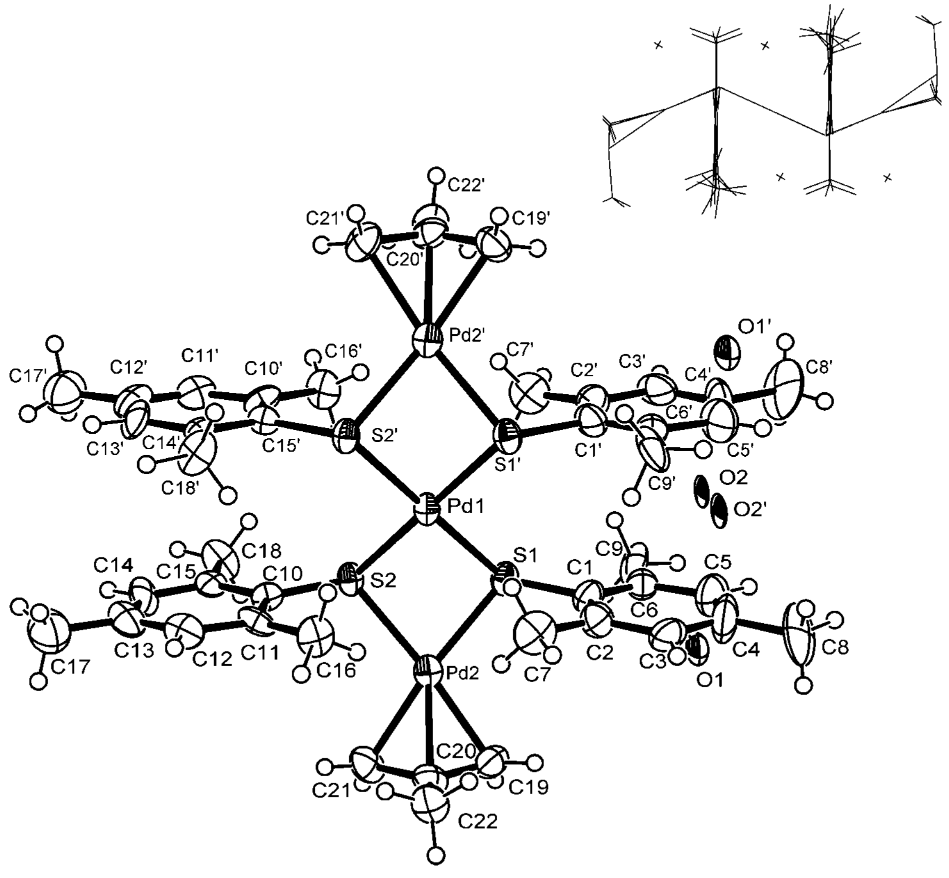

Figure 3. Molecular structure of $[Pd_3(\mu\text{-SMes})_4(\eta^3\text{-}C_4H_7)_2]\cdot 3H_2O$ (**5**).

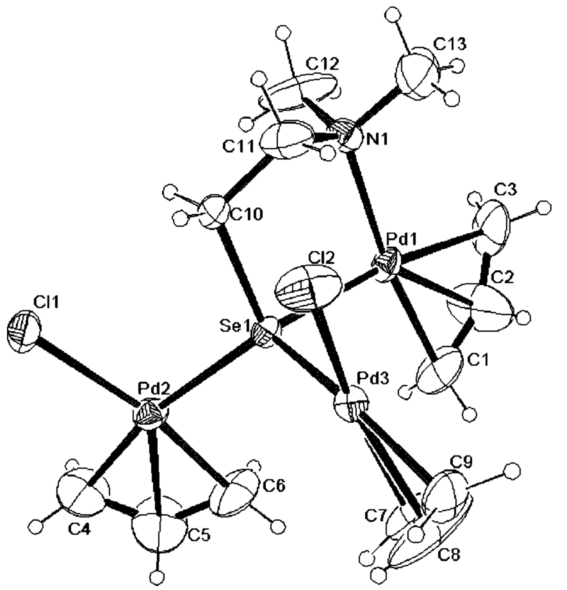

Figure 4. Molecular structure of $[Pd_3Cl_2(\kappa^2\text{-Se,N-SeCH}_2CH_2NMe_2)(\eta^3\text{-}C_3H_5)_3]$ (**6**).

carried out in a Schlenk flask under a nitrogen atmosphere. $PdCl_2$, MesSH, $Me_2NCH_2CH_2SH\cdot HCl$, and other reagents were obtained from commercial sources and were used without further purification. The compounds $[Pd_2(\mu\text{-Cl})_2(\eta^3\text{-}C_3H_5)_2]$, $[Pd_2(\mu\text{-Cl})_2(\eta^3\text{-}C_4H_7)_2]$,[32] $(MesSe)_2$,[33] and $(Me_2NCH_2CH_2Se)_2$[29] were prepared according to literature methods. Synthesis and analytical data for lead chalcogenolates used in this study are given in the Supporting Information. Elemental analyses were carried out on a Carlo-Erba EA-1110 CHN-O instrument. Melting points were determined in capillary tubes and are uncorrected. ^1H NMR spectra were recorded on a Bruker DPX-200 NMR spectrometer operating at 200 MHz. Chemical shifts are relative to an internal chloroform peak at δ 7.26. Variable-temperature ^1H NMR and 2D COSY experiments at −40 °C were performed on a Bruker Avance 500 MHz NMR instrument. Mass spectra were recorded on a Waters Q-TOF micro (YA-105) time-of-flight mass spectrometer. UV−vis absorption spectra were recorded on a Chemito Spectrascan UV 2600 spectrophotometer. TG curves were obtained at a heating rate of 10 °C min^{-1} under flowing argon on a Setaram 92-16-18 instrument. EDAX measurements were carried out with a Tescan Vega 2300T/40 instrument. Powder XRD patterns were recorded on a Philips PW1820 using Cu Kα radiation.

$[Pd_2(\mu\text{-SMes})_2(\eta^3\text{-}C_3H_5)_2]$ (1). To a benzene solution (20 mL) of $[Pd_2(\mu\text{-Cl})_2(\eta^3\text{-}C_3H_5)_2]$ (170 mg, 0.46 mmol) was added solid $Pb(SMes)_2$ (240 mg, 0.47 mmol). The yellow solution was stirred for 3 h at room temperature, whereupon $PbCl_2$ precipitated out. The solvent was evaporated *in vacuo*, and the yellow residue was extracted with dichloromethane (3 × 10 mL). The volume of extract was reduced to 5 mL, and a few drops of hexane were added to yield yellow crystals (193 mg, 64%), mp 160 °C (dec). UV−vis (CH_2Cl_2) λ_{max} in nm: 304 (14 023). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ 2.24 (s, 4-Me); 2.62 (d, 12.6 Hz, *anti* CH); 2.71, 2.74 (s,

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for [$Pd_2(\mu$-$EMes)_2(\eta^3$-$C_4H_7)_2$] (E = S (3), Se (4))

	S (**3**)	Se (**4**)		S (**3**)	Se (**4**)
C(19)−C(20)	1.383(8)	1.44(2)	C(23)−C(24)	1.385(8)	1.361(15)
C(20)−C(21)	1.404(8)	1.40(2)	C(24)−C(25)	1.410(8)	1.391(15)
Pd(1)−C(19)	2.127(6)	2.139(14)	Pd(2)−C(23)	2.126(6)	2.142(15)
Pd(1)−C(20)	2.157(5)	2.180(14)	Pd(2)−C(24)	2.153(6)	2.135(15)
Pd(1)−C(21)	2.129(6)	2.123(14)	Pd(2)−C(25)	2.140(5)	2.113(14)
E(1)−Pd(1)	2.3654(15)	2.4694(17)	E(1)−Pd(2)	2.3582(15)	2.468(2)
E(2)−Pd(1)	2.3725(15)	2.4732(18)	E(2)−Pd(2)	2.3750(14)	2.4730(18)
C(1)−E(1)	1.786(5)	1.946(11)	C(10)−E(2)	1.791(5)	1.938(11)
Pd(1)⋯Pd(2)	3.265	3.356	E(1)⋯E(2)	3.072	3.252
C(19)−Pd(1)−C(20)	37.7(2)	38.9(6)	C(23)−Pd(2)−C(24)	37.8(2)	37.1(4)
C(19)−Pd(1)−C(21)	67.4(2)	67.9(6)	C(23)−Pd(2)−C(25)	67.3(2)	67.2(6)
C(20)−Pd(1)−C(21)	38.2(2)	38.0(6)	C(24)−Pd(2)−C(25)	38.3(2)	38.2(4)
Pd(1)−C(19)−C(20)	72.4(3)	72.1(8)	Pd(2)−C(23)−C(24)	72.2(3)	71.2(9)
Pd(1)−C(20)−C(19)	70.0(3)	69.1(8)	Pd(2)−C(24)−C(23)	70.1(3)	71.7(9)
Pd(1)−C(20)−C(21)	69.8(3)	68.8(8)	Pd(2)−C(24)−C(25)	70.4(3)	70.0(9)
Pd(1)−C(21)−C(20)	71.9(3)	73.1(9)	Pd(2)−C(25)−C(24)	71.3(3)	71.7(9)
Pd(1)−C(20)−C(22)	121.1(4)	120.3 (12)	Pd(2)−C(24)−C(26)	121.2(5)	121.3(11)
C(19)−C(20)−C(21)	115.9(5)	113.9(6)	C(23)−C(24)−C(25)	115.6(6)	117.6(16)
E(1)−Pd(1)−E(2)	80.88(5)	82.29(6)	Pd(1)−E(1)−C(1)	115.12(17)	114.1(3)
E(1)−Pd(2)−E(2)	80.98(5)	82.33(6)	Pd(2)−E(1)−C(1)	116.15(17)	107.4(4)
Pd(1)−E(1)−Pd(2)	87.45(5)	85.63(6)	Pd(1)−E(2)−C(10)	116.08(18)	110.5(3)
Pd(1)−E(2)−Pd(2)	86.92(5)	85.44(6)	Pd(2)−E(2)−C(10)	116.25(18)	116.7(3)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [$Pd_3(\mu$-$SMes)_4(\eta^3$-$C_4H_7)_2$]·$3H_2O$ (5)

Pd(2^i)−C(19^i)	2.159(14)	Pd(1^i)−S(1^i)	2.344(3)
Pd(2^i)−C(20^i)	2.155(11)	Pd(1^i)−S(2^i)	2.35(3)
Pd(2^i)−C(21^i)	2.174(14)	Pd(2^i)−S(1^i)	2.345(4)
C(19^i)−C(20^i)	1.422(18)	Pd(2^i)−S(2^i)	2.355(3)
C(20^i)−C(21^i)	1.421(17)	C(1^i)−S(1^i)	1.795(12)
C(20^i)−C(22^i)	1.517(14)	C(10^i)−S(2^i)	1.782(12)
S(1^i)−Pd(1^i)−S(1^{ii})	100.03(18)	Pd(1^i)−S(1^i)−Pd(2^i)	89.97(11)
S(1^i)−Pd(1^i)−S(2^{ii})	179.43(14)	Pd(1^i)−S(2^i)−Pd(2^i)	89.57(11)
S(1^i)−Pd(1^i)−S(2^i)	79.44 (10)	Pd(1^i)−S(1^i)−C(1^i)	117.4(5)
S(1^{ii})−Pd(1^i)−S(2^i)	179.43(15)	Pd(1^i)−S(2^i)−C(10^i)	116.4(4)
S(2^i)−Pd(1^i)−S(2^{ii})	101.09(17)	Pd(2^i)−S(1^i)−C(1^i)	113.2(5)
S(1^{ii})−Pd(1^i)−S(2^{ii})	79.44(10)	Pd(2^i)−S(2^i)−C(10^i)	113.3(4)
Pd(2^i)−C(19^i)−C(20^i)	70.6(7)	C(19^i)−C(20^i)−C(21^i)	116.5(10)
Pd(2^i)−C(20^i)−C(19^i)	70.9(7)	C(19^i)−Pd(2^i)−S(1^i)	105.6(4)
Pd(2^i)−C(20^i)−C(21^i)	71.6(7)	C(20^i)−Pd(2^i)−S(1^i)	137.8(4)
Pd(2^i)−C(20^i)−C(22^i)	120.4(8)	C(21^i)−Pd(2^i)−S(1^i)	172.3(4)
Pd(2^i)−C(21^i)−C(20^i)	70.1(7)	C(19^i)−Pd(2^i)−S(2^i)	171.7(4)
C(19^i)−Pd(2^i)−C(20^i)	38.5(5)	C(20^i)−Pd(2^i)−S(2^i)	139.7(4)
C(19^i)−Pd(2^i)−C(21^i)	67.8(5)	C(21^i)−Pd(2^i)−S(2^i)	106.8(4)
C(20^i)−Pd(2^i)−C(21^i)	38.3(5)	S(1^i)−Pd(2^i)−S(2^i)	79.33(10)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [$Pd_3Cl_2(\kappa^2$-Se,N-$SeCH_2CH_2NMe_2)(\eta^3$-$C_3H_5)_3$] (6)

Pd(1)−C(1)	2.144(11)	Pd(2)−C(4)	2.131(12)
Pd(1)−C(2)	2.105(13)	Pd(2)−C(5)	2.123(14)
Pd(1)−C(3)	2.180(12)	Pd(2)−C(6)	2.154(12)
Pd(1)−N(1)	2.178(7)	Pd(3)−C(7)	2.158(12)
Pd(1)−Se(1)	2.4255(11)	Pd(3)−C(8)	2.107(14)
Se(1)−C(10)	2.007(8)	Pd(3)−C(9)	2.135(10)
Pd(2)−Cl(1)	2.380(3)	Pd(3)−Cl(2)	2.399(3)
Pd(2)−Se(1)	2.4968(11)	Pd(3)−Se(1)	2.4846(11)
Pd(1)−C(1)−C(2)	70.5(8)	C(5)−Pd(2)−C(6)	35.0(6)
Pd(1)−C(2)−C(3)	75.6(9)	C(4)−Pd(2)−Se(1)	167.1(5)
C(1)−Pd(1)−C(2)	35.8(3)	C(5)−Pd(2)−Se(1)	131.7(6)
C(1)−Pd(1)−C(3)	70.8(5)	C(4)−Pd(2)−Cl(1)	96.3(5)
N(1)−Pd(1)−C(1)	170.5(4)	C(5)−Pd(2)−Cl(1)	131.1(6)
N(1)−Pd(1)−C(2)	135.2(5)	C(6)−Pd(2)−Cl(1)	163.3(4)
N(1)−Pd(1)−Se(1)	87.28(19)	Cl(1)−Pd(2)−Se(1)	96.47(7)
Pd(1)−Se(1)−Pd(2)	119.90(4)	Pd(2)−Se(1)−Pd(3)	121.71(4)
Pd(1)−Se(1)−Pd(3)	101.71(4)	Pd(3)−C(7)−C(8)	74.3(8)
Pd(1)−Se(1)−C(10)	94.5(2)	Pd(3)−C(9)−C(8)	70.9(8)
Pd(1)−N(1)−C(11)	111.7(6)	C(7)−Pd(3)−C(8)	35.6(3)
Se(1)−Pd(1)−C(1)	101.8(4)	C(7)−Pd(3)−Se(1)	96.1(4)
Pd(2)−C(4)−C(5)	71.7(8)	C(8)−Pd(3)−Se(1)	130.5(4)
Pd(2)−C(5)−C(6)	73.8(8)	C(7)−Pd(3)−Cl(2)	164.1(4)
C(4)−Pd(2)−C(6)	67.9(6)	Cl(2)−Pd(3)−Se(1)	99.76(8)

2, 6-Me); 3.19 (d, 6.8 Hz), 3.28 (d, 6.6 Hz) (*syn* CH); 5.21 (m, CH); 6.83 (s, Mes) ppm. Anal. Calcd for $C_{24}H_{32}S_2Pd_2$ (%): C, 48.2; H, 5.3; S, 10.7. Found: C, 48.4; H, 5.5; S, 10.6.

The complexes [$Pd_2(\mu$-$SeMes)_2(\eta^3$-$C_3H_5)_2$] (**2**) and [$Pd_2(\mu$-$SMes)_2(\eta^3$-$C_4H_7)_2$] (E = S (**3**); Se (**4**)) were prepared analogously and are reported in the Supporting Information (S12).

[$Pd_3(\mu$-$SMes)_4(\eta^3$-$C_4H_7)_2$] (5). After separating the yellow crystals of **3**, the supernatant when left in air for 2 days gave red crystals in low yield (~5%), which were characterized as **5**. This has been conveniently prepared by the following reaction. To a dichloromethane solution (25 mL) of [$Pd_2(\mu$-$SMes)_2(\eta^3$-$C_4H_7)_2$] (96 mg, 0.15 mmol) was added solid [$Pd(SMes)_2$] (62 mg, 0.15 mmol), and the reaction mixture was refluxed for 2 h and then stirred for 72 h. The solution was filtered through G-3 sintered bed, and the maroon residue on the bed was extracted with hot dichloromethane (3 × 8 mL). The filtrate and extract were combined and concentrated to 8 mL, and a few milliliters of acetone was added to yield a red solid at −5 °C (74 mg, 47%), mp 148 °C (dec). UV−vis (CH_2Cl_2) λ_{max} in nm: 326 (28 666); 370 (26 733); 419 (15 800). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): 1.73, 1.78; 2.19; 2.24; 2.30; 2.39; 2.45; 2.61; 2.66; 2.73; 2.77; 6.48, 6.72, 6.82. MS: 312 [$Pd(SMes)(\eta^3$-$C_4H_7)]^+$ (12%), 463 [$Pd(SMes)_2(\eta^3$-$C_4H_7)]^+$ (35%), 559 [$Pd(SMes)_3]^+$ (8%), 661 [$Pd_2(SMes)_3]^+$ (100%). Anal. Calcd for $C_{44}H_{58}S_4Pd_3$ (%): C, 51.0; H, 5.7; S, 12.4. Found: C, 51.0; H, 5.5; S, 12.8.

[$Pd_3Cl_2(\kappa^2$-Se,N-$SeCH_2CH_2NMe_2)(\eta^3$-$C_3H_5)_3$] (6). To a benzene (20 mL) solution of [$Pd_2(\mu$-$Cl)_2(\eta^3$-$C_3H_5)_2$] (206 mg, 0.56 mmol) was added solid $Pb(SeCH_2CH_2NMe_2)_2$ (287 mg, 0.56 mmol), and the mixture was stirred for 2 h, whereupon a white precipitate of $PbCl_2$ was separated out. The solvent was evaporated under vacuum, and the residue was washed with hexane and extracted with acetone (3 × 8 mL). The extract was concentrated to 5 mL, and a few drops of benzene were added to yield yellow crystals (187 mg, 50%), mp 155 °C (dec). MS: 847 [$PdCl(SeCH_2CH_2NMe_2)]_3$ − Cl (10%), 665 $[M]^+$ (70%), 557 [M − (2Cl + $C_3H_5]^+$ (100%), 507 [M − ($3C_3H_5$) + Cl)]$^+$ (15%). Anal. Calcd for $C_{13}H_{25}NCl_2SePd_3$ (%): C, 23.5; H, 3.8; N, 2.1. Found: C, 24.0; H, 4.0; N, 2.4.

[$Pd_3Cl_2(\kappa^2$-Se,N-$SeCH_2CH_2NMe_2)(\eta^3$-$C_4H_7)_3$] (**7**) was prepared analogously and is reported in the Supporting Information (S13).

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Supporting Information Available: Mass spectra, COSY NMR spectra of **6**, details of thermal studies (TG curves, XRD pattern, and EDAX), and synthesis of lead chalcogenolates and complexes **2**, **3**, **4**, and **7**, and crystallographic experimental data and refinement of complexes **3**, **4**, **5**, and **6**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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