

Reactions of Di-*o*-tolyl Telluride and Selenide with Palladium Acetate: Isolation of a Novel Palladium Complex of a Tellurenic Acid Anhydride and Related Trinuclear and Tetranuclear Palladium Complexes

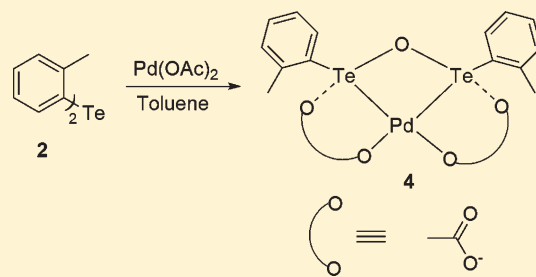
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S Supporting Information

ABSTRACT: The reaction of di-*o*-tolyl telluride with palladium acetate provided a novel palladium complex of a tellurenic acid anhydride, (*o*-tolylTe)₂OPd(OAc)₂, and a linear trinuclear complex, [Pd(*o*-tolyl){di-*o*-tolyl telluride}]₂Pd(μ -OAc)₂. The reaction of di-*o*-tolyl selenide with palladium acetate afforded a tetranuclear complex of rare geometry, [Pd(OAc)(μ -Se-*o*-tolyl)]₄.



Palladacycles are one of the most important classes of organometallic compounds which have been used as catalyst precursors for coupling reactions.¹ Herrmann and co-workers demonstrated the use of palladacycles derived from Pd(OAc)₂ and phosphines such as tri-*o*-tolylphosphine (**1a**, Chart 1) in Heck and Suzuki coupling reactions.²

These thermally stable palladacyclic catalysts showed excellent catalytic activity and have set a milestone in homogeneous catalysis. Since then, a wide variety of known and new palladacycles with PC, NC, SC, PCP, PCN, NCN, and SCS coordination modes have been successfully used in C–C coupling reactions.^{1a,b,3,4} Sulfur-based palladacycles have also been employed successfully in C–C coupling reactions.⁵

Palladacycles synthesized from ligands with phosphorus and nitrogen donor atoms are numerous. There are very few palladacycles with selenium,⁶ and none have been reported with tellurium. Use of heavier chalcogens as ligands for catalysts in the coupling reactions has high potential. Recently, Yao et al. have reported that selenium-ligated palladacycles (**1b,c**, Chart 1) act as highly active and efficient catalysts for the Heck reaction.⁶ In view of the observation that the PC-type palladacycle **1a** derived via activation of a benzylic C–H bond as well as selenium palladacycles have shown high activity in C–C coupling reactions, we set out to synthesize palladacycles based on selenium and tellurium via activation of benzylic C–H bonds. Herein we report the unexpected and interesting outcome of the reactions.

RESULTS AND DISCUSSION

The ligands di-*o*-tolyl telluride (**2**)^{7a,b} and di-*o*-tolyl selenide (**3**)⁸ were prepared by minor modification of the known

methods. Di-*o*-tolyl ditelluride prepared from the corresponding Grignard reagent was detellurated using copper^{7c} to give **2**. Monoselenide **3** was synthesized by reacting the in situ generated reagent SeCl₂ with *o*-tolyl Grignard reagent.⁸ However, the reaction could not be reproduced as a high-yield method. Instead, the use of the in situ generated reagent SeBr₂ provided **3** in much better yield.

Reaction between Di-*o*-tolyl Telluride and Palladium Acetate: Synthesis of a Palladium Complex of Tellurenic Acid Anhydride and a Linear Trinuclear Palladium Complex. The reaction between **2** and palladium acetate in toluene provided two palladium complexes (**4** and **5**). Complex **4** has a bidentate tellurenic acid anhydride ligand, (*o*-tolylTe)₂O, coordinated to a monomeric Pd(OAc)₂ fragment, and **5** is coordinated to a tolyl group and tellurium, as shown in Scheme 1. The coordination chemistry of tellurium and selenium ligands has continued to be an area of growing interest. The chemistry of metal complexes of the telluroethers,⁹ diorganoditellurides,¹⁰ and tellurolates¹¹ has been the subject of many reviews and books. However, to the best of our knowledge, there has been no report on the coordination behavior of a tellurenic acid anhydride until now. Complex **4** represents a novel palladium complex with a tellurenic acid anhydride, which results from trimeric palladium complex **5**. The source of oxygen in the ligand could be adventitious water from the atmosphere. It has been characterized by elemental analysis, NMR (¹H, ¹³C, and ¹²⁵Te) spectroscopy, and mass spectrometry.

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The complex crystallizes as a toluene solvate (*vide infra*), and the calculated value of elemental analysis of the compound is in good agreement with the observed value when half a molecule of toluene is considered as part of the formula. The reaction was also carried out in benzene, and the ^1H NMR spectrum of the product was essentially the same as that of **4**, barring the signature peaks due to the solvents toluene and benzene. The ^{125}Te NMR of the compound in CDCl_3 showed two peaks at δ 1325 and 1286 ppm. The ^{125}Te NMR chemical shifts are shifted upfield as compared with those of a related tellurenic acid anhydride, bis[(2-(phenylazo)phenyl-*C,N'*)tellurium] oxide (1535 ppm).¹² The intensity of the latter was almost one-fourth that of the former. The lower intensity peak was due to some unidentified species in solution, indicating some sort of decomposition/dissociation or scrambling in solution.

The trinuclear palladium complex **5** was obtained serendipitously as a minor product in the reaction and could not be isolated in pure form in sufficient amount for its characterization. However, a single-crystal X-ray structure (*vide infra*) of the complex could be determined. The ^1H and ^{125}Te NMR spectra of the crude product indicated its existence in solution. Several attempts were made to isolate the complex by varying reaction conditions such as temperature from 25 to 75 °C and reaction time from 2 to 30 min. However, in all the attempts the product was the more stable tellurenic acid anhydride palladium complex **4**, presumably formed via fragmentation of the less stable **5** as an intermediate, as indicated by the ^1H NMR (see the Supporting Information).

Reaction between Di-*o*-tolyl Selenide and Palladium Acetate: Synthesis of a Tetranuclear Palladium Selenolate Complex. The reaction between **3** and palladium acetate in toluene provided the tetranuclear palladium selenolate complex **6**, as shown in Scheme 2. Complex **6** represents only the second example of the $[\text{PdSeR}(\text{OAc})]_4$ framework formed via cleavage of the C–Se bond. Dehnen et al. have reported very recently a

tetranuclear palladium selenolato complex having a $[\text{PdSeR}(\text{OAc})]_4$ framework by the reaction of $(\text{PhSe})_3\text{Sn}-(\text{CH}_2)_4-\text{Sn}(\text{SePh})_3$ with palladium acetate.¹³ Transmetalation of ArSe moiety from tin to palladium has been achieved at ambient temperature. On the other hand, in our case cleavage of the C–Se bond of $(o\text{-tolyl})_2\text{Se}$ required more drastic conditions. Complex **6** has been characterized by elemental analysis, NMR (^1H , ^{13}C , ^{77}Se) spectroscopy, and mass spectrometry. The ^{77}Se NMR chemical shift appeared at δ –83 ppm, an upfield shift of 418 ppm compared to selenide **3** (δ 335 ppm).

Crystallographic Studies. The molecular structure of **4** is depicted in Figure 1a. The bidentate ligand $(o\text{-tolylTe})_2\text{O}$ is coordinated to palladium via two tellurium atoms. The other two coordination sites of palladium are satisfied by oxygen atoms of the two acetate groups. The geometry around palladium is essentially square planar. The Pd–Te bond length (Pd–Te#1 = 2.47105(15) Å) is less than the sum of their covalent radii¹⁴ and is slightly shorter than those in the palladium complexes of telluroether macrocycles.¹⁵ The bite angle Te#1–Pd–Te is 78.980(6)°. The presence of strong $\text{Te}\cdots\text{O}$ secondary bonding interactions between other two oxygen atoms of the two acetate groups with tellurium atoms is observed from the bond distances and the geometry. For example, the $\text{Te}\cdots\text{O1}$ distance, 2.4022(11) Å, is much shorter than the sum of their van der Waals radii¹⁶ and the angle $\text{O}=\text{Te}\cdots\text{O1}$ = 169.12(4)° is close to linearity. This near-planar unit is linked to

Scheme 2. Reaction between **3** and $\text{Pd}(\text{OAc})_2$

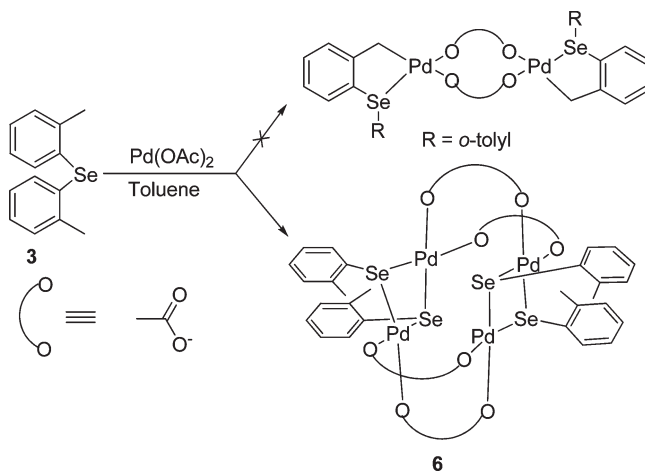
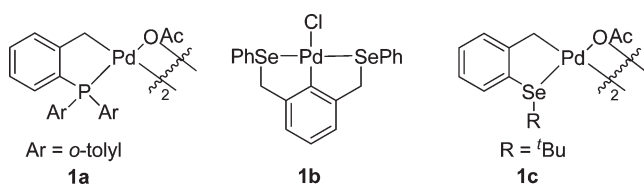
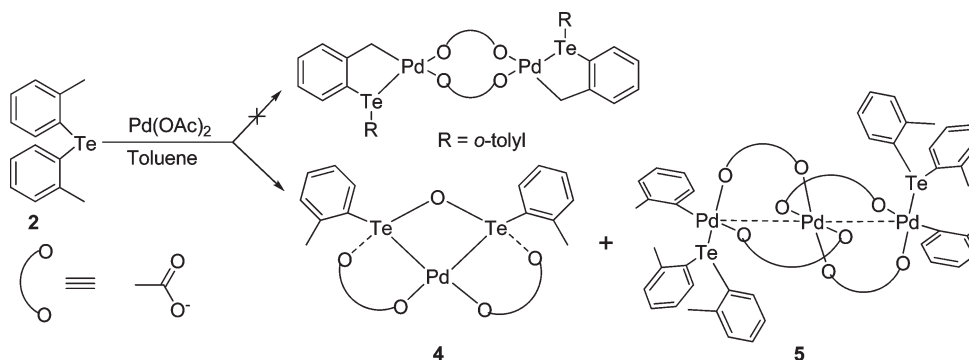


Chart 1



Scheme 1. Reaction between **2** and $\text{Pd}(\text{OAc})_2$



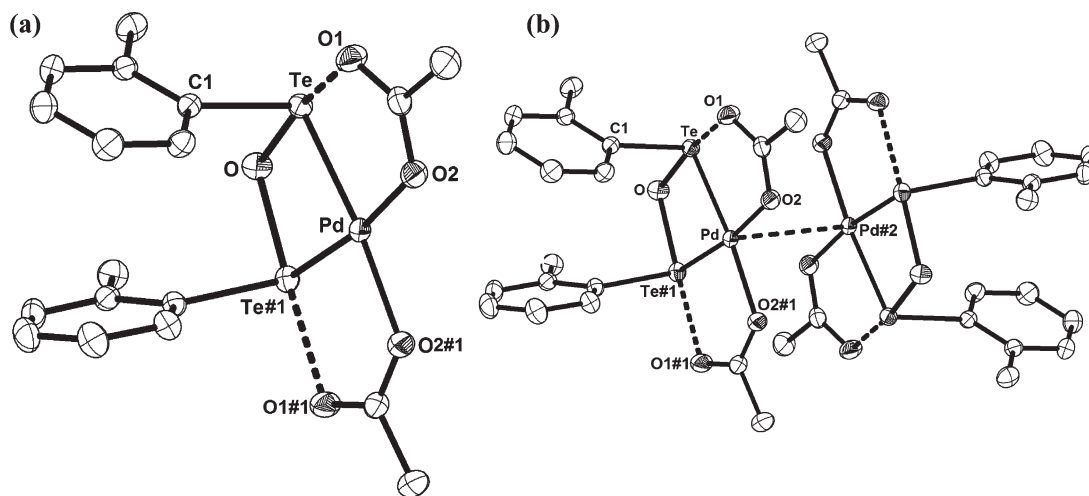


Figure 1. (a) Molecular structure of the complex 4. Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms and solvent molecules are removed for clarity. Significant bond lengths (Å) and bond angles (deg): Te–O = 2.0208(9), Te–C1 = 2.1171(14), Te···O1 = 2.4022(11), Te–Pd = 2.47106(15), Pd–O2 = 2.1096(11), Pd–O2#1 = 2.1097(11), Pd–Te#1 = 2.47105(15), Te···Te#1 = 3.1429(2) Å; O–Te–C1 = 92.75(6), O–Te–O1 = 169.12(4), C1–Te–O1 = 84.84(5), O–Te–Pd = 89.28(3), C1–Te–Pd = 101.57(4), O1–Te–Pd = 80.83(3), O–Te–Te#1 = 38.96(3), C1–Te–Te#1 = 96.21(4), O1–Te–Te#1 = 130.68(3), Pd–Te–Te#1 = 50.510(3), O2–Pd–O2#1 = 94.31(6), O2–Pd–Te#1 = 172.24(3), O2#1–Pd–Te#1 = 93.34(3), O2–Pd–Te = 93.34(3), O2#1–Pd–Te = 172.24(3), Te#1–Pd–Te = 78.980(6), O2–Pd–Pd#2 = 87.05(3), O2#1–Pd–Pd#2 = 87.05(3), Te#1–Pd–Pd#2 = 94.631(6), Te–Pd–Pd#2 = 94.630(6), Te–O–Te#1 = 102.09(7)°. (b) Pd···Pd interaction between two molecular units. Pd···Pd#2 = 3.1993(3) Å.

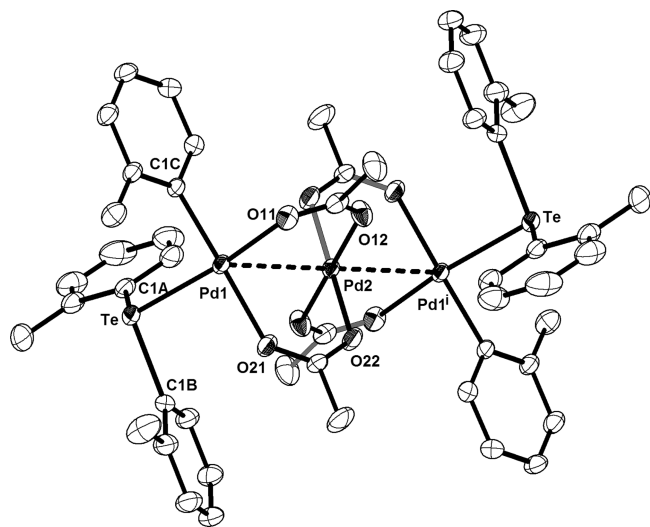


Figure 2. Molecular structure of the complex 5. Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are removed for clarity. Significant bond lengths (Å) and bond angles (deg): Pd1–C1C = 1.994(4), Pd1–O11 = 2.102(4), Pd1–O21 = 2.132(3), Pd1–Te = 2.5054(5), Pd1···Pd2 = 3.0483(4), Pd2–O22 = 1.991(4), Pd2–O12 = 1.999(4) Å; C1C–Pd1–O21 = 172.11(18), O11–Pd1–O21 = 88.64(15), C1C–Pd1–Te = 87.44(13), O11–Pd1–Te = 170.21(10), O21–Pd1–Te = 94.60(11), C1C–Pd1–O11 = 88.15(17), O22–Pd2–O22ⁱ = 180.0(2), O22–Pd2–O12ⁱ = 89.81(18), O22–Pd2–O12 = 90.19(18), O12ⁱ–Pd2–O12 = 180.0(2), Pd1–Pd2–Pd1ⁱ = 180.0.

another such planar structure in an antiparallel fashion via a weak Pd···Pd (Pd···Pd#2) interaction (Figure 1b). The distance between these two palladiums (Pd···Pd#2) is 3.1993(3) Å, which is slightly shorter than the sum of their van der Waals radii.¹⁶

The Te–O bond distance (2.0208(9) Å) is slightly shorter than the sum of the covalent radii,¹⁴ and the Te–O–Te#1 bond

angle is 102.09(7)°, which is close to that in the water molecule (104.45°). The aromatic rings of the tolyl groups are nearly parallel to each other.

Complex 5 represents a linear trinuclear palladium complex where terminal palladium ions are simultaneously coordinated to a tellurium and an aromatic carbon. The molecular structure of 5 is shown in Figure 2.

Complex 5 has a perfectly linear arrangement of metal atoms. The linear arrangement of three palladium atoms has been observed much less frequently, compared to the triangular arrangement.¹⁷ These structures contain a central Pd₃(OAc)₄ moiety. The Pd–Pd distance (3.0483(4) Å) is less than the sum of their van der Waals radii (4.10 Å)¹⁶ and indicates the presence of a metal–metal interaction. The Pd–Pd distances reported in similar complexes containing a linear array of three palladium ions fall in the range 2.933–3.075 Å.¹⁸ The molecule has three palladium ions in two different environments: (i) Pd2 is situated at the crystallographic inversion center and coordinated by the oxygen atoms of two pairs of mutually orthogonal acetate groups, i.e., the central Pd is perfectly square planar, and (ii) the terminal palladium ions, Pd1 and Pd1', are coordinated by the oxygen atoms of a pair of mutually orthogonal acetate groups, the tellurium atom of di-*o*-tolyl telluride, and the carbon atom of the tolyl group at the ortho position. The geometry around the terminal palladium ions is slightly distorted square planar with the angles around the metal ions being in the range of 88.15–(17)–94.60(11)°. The square planes generated by the coordination environment around Pd1 and Pd2 are nearly parallel to each other with a dihedral angle of ca. 8° between them (Te–Pd1–Pd2–O12ⁱ = 7.47(13)°). The Pd–C bond length (1.994(4) Å) is less than the sum of the covalent radii of palladium and sp²-hybridized carbon (1.39 + 0.73 = 2.12 Å) and fall within the range reported for these types of compounds.¹⁸ The Pd–Te bond length (2.5054(5) Å) is slightly shorter than those in the palladium complexes of tellurium-containing macrocycles,¹⁵

however, it is somewhat longer than that in $(2\text{-NH}_2\text{-5-MeC}_6\text{-H}_3\text{)Te(4-C}_2\text{H}_5\text{OC}_6\text{H}_4\text{)PdCl}_2$.¹⁸

The molecular structure of **6** is shown in Figure 3. The molecule assumes a paddle-wheel type geometry with two pairs of orthogonal acetate groups and another two pairs of orthogonal

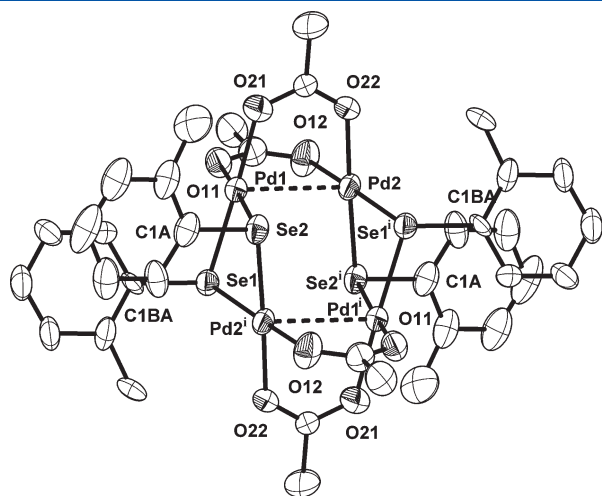


Figure 3. Molecular structure of the complex **6**. Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are removed for clarity. Significant bond lengths (Å) and bond angles (deg): Pd1–O21 = 2.079(11), Pd1–O11 = 2.080(10), Pd1–Se1 = 2.3748(16), Pd1–Se2 = 2.3868(17), Pd1–Pd2 = 2.8939(12), Pd2–O12 = 2.092(11), Pd2–O22 = 2.075(11), Pd2–Se2ⁱ = 2.3720(17), Pd2–Se1ⁱ = 2.3864(15), Se1–C1BA = 1.912(11) Å; O21–Pd1–O11 = 91.1(5), O21–Pd1–Se1 = 175.8(3), O11–Pd1–Se1 = 91.9(3), O21–Pd1–Se2 = 94.1(4), O11–Pd1–Se2 = 174.5(3), Se1–Pd1–Se2 = 83.04(5), O22–Pd2–O12 = 91.8(6), O22–Pd2–Se2ⁱ = 176.2(4), O12–Pd2–Se2ⁱ = 92.1(4), O22–Pd2–Se1ⁱ = 93.1(4), O12–Pd2–Se1ⁱ = 174.1(4), Se2ⁱ–Pd2–Se1ⁱ = 83.11(5), C1BA–Se1–Pd1 = 101.5(5).

tolylselenolate groups bridging two different pairs of palladium atoms.

The palladium atoms form a rectangular plane, each of which is coordinated to two oxygen and two selenium atoms of the acetate and tolylselenolate groups, respectively, in an essentially square-planar geometry, as observed in the isostructural complex $[\text{Pd}(\text{OAc})(\text{SePh})]_4$ (**6a**).¹³ The short Pd–Pd distance bridged by two acetate groups in the $[\text{Pd}_2(\text{OAc})_2]^{2+}$ unit is 2.8805(8) Å. This distance is less than the sum of their van der Waals radii (4.10 Å)¹⁶ and is marginally greater than the sum of their covalent radii (2.78 Å),¹⁴ hence indicating the presence of a significant metal–metal interaction. This Pd–Pd distance falls within the range reported for Pd–Pd bonds.¹⁹ The corresponding Pd–Pd distance in **6a** is 2.864(18) Å. The longer Pd···Pd contact bridged by two tolylselenolate groups is 3.438 Å, which is less than the corresponding distance in the isostructural complex **6a** (3.496(2) Å). The Pd–Se bond lengths (2.3720(17)–2.3864(15) Å) are shorter than those in the mesitylselenolato-bridged palladium complex $\text{Pd}_2(\mu\text{-SeMes})_2(\eta^3\text{-C}_3\text{H}_7)_2$ (2.4694(17)–2.4732(18) Å).²⁰

CONCLUSION

A novel palladium complex of a tellurenic acid anhydride has been isolated in good yield from the reaction of di-*o*-tolyl telluride with $\text{Pd}(\text{OAc})_2$, obtained by the cleavage of the C–Te bond. Another telluride-coordinated trinuclear palladium complex was obtained from the same reaction and could be characterized by X-ray crystallography. A tetranuclear selenolato-bridged palladium complex was isolated from the reaction of di-*o*-tolyl selenide with $\text{Pd}(\text{OAc})_2$.

EXPERIMENTAL SECTION

All reactions were carried out under nitrogen or argon using standard vacuum-line techniques. Solvents were purified and dried by standard procedures and were distilled prior to use. Melting points were recorded on a Veego VMP-I melting point apparatus in capillary tubes and were

Table 1. Crystal Data and Structure Refinement Details for **4–6**

	4 , $\frac{1}{2}\text{C}_7\text{H}_8$	5	6
empirical formula	$\text{C}_{43}\text{H}_{48}\text{O}_{10}\text{Pd}_2\text{Te}_4$	$\text{C}_{50}\text{H}_{54}\text{O}_8\text{Pd}_3\text{Te}_2$	$\text{C}_{36}\text{H}_{40}\text{O}_8\text{Pd}_4\text{Se}_4$
fw	1448.01	1357.33	1342.12
cryst syst	monoclinic	triclinic	monoclinic
space group	$I2/m$	$P\bar{1}$	$C2/c$
<i>a</i> (Å)	7.8457(2)	10.1676(2)	18.1021(12)
<i>b</i> (Å)	15.1119(4)	10.3479(3)	13.1486(9)
<i>c</i> (Å)	19.1215(4)	14.0427(3)	18.6113(12)
α (deg)	90	71.258(3)	90
β (deg)	91.798(2)	87.1053(19)	104.214(7)
γ (deg)	90	64.937(3)	90
<i>V</i> (Å ³)	2265.99(10)	1261.07(5)	4294.2(5)
<i>Z</i>	2	1	4
<i>D</i> _{calcd} (Mg m ^{−3})	2.121	1.787	2.076
temp (K)	200(2)	200(2)	293(2)
θ range (deg)	4.81–34.77	4.61–34.71	4.54–77.55
abs coeff (mm ^{−1})	3.372	2.242	17.558
final <i>R</i> (<i>F</i>) (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0214	0.0578	0.0975
<i>R</i> _w (<i>F</i> ²) indices (<i>I</i> > 2σ(<i>I</i>))	0.0294	0.0915	0.1281
no. of data/restraints/params	4740/0/164	9337/0/291	4370/15/226
goodness of fit on <i>F</i> ²	1.028	1.078	1.356

^a Definitions: $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w(F_o^2) = \{\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_c^2)^2]\}^{1/2}$.

uncorrected. ^1H (400 MHz) and ^{13}C (100.56 MHz) nuclear magnetic resonance spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer and ^{77}Se (57.22 MHz) and ^{125}Te (94.79 MHz) spectra on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to Me_4Si as internal standard (^1H , ^{13}C) and Me_2Se (^{77}Se) and Me_2Te (^{125}Te) as external standards. Elemental analyses were performed on a Carlo Erba Model 1106 elemental analyzer. The ESI mass spectra were recorded on a Q-ToF micro (YA-105) mass spectrometer.

Synthesis of 4. To a pale yellow solution of di-*o*-tolyl telluride (435 mg, 1.35 mmol) was added palladium acetate (225 mg, 1.00 mmol) in 25 mL of toluene. The mixture was heated at ca. 60 °C for 5 min. Then the reaction mixture was filtered through a short Florisil column to remove any insoluble black particles formed and concentrated under vacuum to ca. 5 mL. A greenish yellow precipitate was obtained on triturating with hexane (10 mL). The precipitate was filtered off, washed with hexane, and dissolved in warm toluene to give yellow crystals of the title compound at room temperature. Yield: 115 mg. Mp: 160–162 °C. Anal. Calcd for $\text{C}_{43}\text{H}_{48}\text{O}_{10}\text{Pd}_2\text{Te}_4$: C, 35.67; H, 3.34. Found: C, 35.62; H, 3.15. ^1H NMR (CDCl_3): δ 2.00 (s, CH_3COO , 12H), 2.36 (s, CH_3 (solvent), 3H), 2.43 (s, $\text{CH}_3\text{C}_6\text{H}_4$, 12H), 6.96–6.98 (m, 8H), 7.00–7.19 (m, 4H), 8.47–8.49 (m, 4H). ^{125}Te NMR (CDCl_3): δ 1325, 1286. ESI-MS: m/e 1254.88, 604.94.

Synthesis of 5. Complex 5 was obtained serendipitously from the filtrate of the reaction of di-*o*-tolyl telluride with palladium acetate as a minor product by following the procedure above for 4. The complex could not be isolated in good yield for characterization.

Synthesis of 6. To a pale yellow solution of di-*o*-tolyl selenide (705 mg, 1.35 mmol) was added palladium acetate (225 mg, 1.00 mmol) in 25 mL of toluene. The mixture was heated at ca. 100 °C for 90 min. The reaction was monitored by TLC. A metallic mirror was observed when the reaction was stopped. Then the reaction mixture was filtered through a short Florisil column to remove the insoluble black particles formed and concentrated under vacuum to ca. 5 mL. A gray precipitate was obtained on adding hexane (10 mL). The precipitate was filtered off, washed with hexane, and dissolved in toluene (2 mL) and this solution layered with diethyl ether to give dark red crystals of the title compound at room temperature after 2 days. Yield: 75 mg. Mp: 177–179 °C. Anal. Calcd for $\text{C}_{36}\text{H}_{40}\text{O}_8\text{Pd}_4\text{Se}_4$: C, 32.21; H, 3.00. Found: C, 31.57; H, 2.43. ^1H NMR (CDCl_3): δ 2.03 (s, CH_3COO , 12H), 2.75 (s, $\text{CH}_3\text{C}_6\text{H}_4$, 12H), 6.68–6.71 (m, 4H), 6.98 (m, 4H), 7.10–7.13 (m, 4H), 8.82 (m, 4H). ^{13}C NMR (CDCl_3): δ 23.9, 24.2, 126.4, 128.4, 128.9, 130.8, 137.8, 140.9, 181.1. ^{77}Se NMR (CDCl_3): δ –83. ESI-MS: m/e 628.99 [$\text{C}_{15}\text{H}_{12}\text{O}_4\text{Pd}_2\text{Se}_2^+$, 20%].

X-ray Crystallography. The diffraction measurements were performed on an Oxford Diffraction Gemini diffractometer. The data were corrected for Lorentz, polarization, and absorption effects. The structures were determined by routine heavy-atom methods using SHELXS 97²¹ and Fourier methods and refined by full-matrix least squares with the non-hydrogen atoms anisotropic and hydrogen with fixed isotropic thermal parameters of 0.07 Å² by means of the SHELXL 97²² program. The hydrogens were partially located from difference electron density maps, and the rest were fixed at predetermined positions. Scattering factors were from common sources.²³ Some details of the data collection and refinement are given in Table 1.

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving crystal data and figures giving spectroscopic data (^1H , ^{13}C , ^{125}Te , and ^{77}Se NMR and ESI-MS) for 4–6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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