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# Structural Variation in $[PdX_2{RE(CH_2)_nNMe_2}]$ (E = Se, Te; X = Cl, OAc) Complexes: Experimental Results, Computational Analysis, and Catalytic Activity in Suzuki Coupling Reactions

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A series of chalcogenoether ligands  $\text{RE}(\text{CH}_2)_n\text{NMe}_2$  (1) [E = Se or Te; R = Ph, o-tol (o-tol = ortho-tolyl), Mes (Mes = 2,4,6-trimethylphenyl); n = 2 or 3] and their palladium complexes [PdX<sub>2</sub>{RE(CH<sub>2</sub>)<sub>n</sub>NMe<sub>2</sub>}]<sub>m</sub> [X = Cl (2) or OAc (3); m = 1, 2] were synthesized. Complexes [PdCl<sub>2</sub>(RECH<sub>2</sub>CH<sub>2</sub>CMe<sub>2</sub>)] [R/E = Ph/Se (2a), Mes/Se (2b), Mes/Te (2c)] were isolated as monomers. Complexes [PdCl<sub>2</sub>(RECH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CMe<sub>2</sub>)]<sub>m</sub> [R/E = Ph/Se (2d), Ph/Te (2e), o-tol/Te (2f)] exist in one monomeric and two dimeric forms in solution; their ratio depends on E

# Introduction

Among various transition-metal complexes, palladium complexes have played a pivotal role in metal-catalyzed organic transformations and have emerged as the most versatile catalytic systems.<sup>[1]</sup> They can catalyze a wide variety of reactions that range from carbon–carbon to carbon–heteroatom bond formations.<sup>[1–3]</sup> Catalyst design has remained of paramount importance for understanding various catalytic processes as well as for improving the activity of catalyst systems. Accordingly, catalysts derived from phosphane as well as non-phosphane ligands have been designed and extensively utilized for a variety of synthetic transformations. More recently, metal complexes that contain hemilabile hybrid ligands that consist of one strong (soft) donor in combination with a weak (hard) donor have shown great potential in catalytic reactions.<sup>[4]</sup> The hard donor atom in these

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and R as revealed by NMR spectroscopic data. Crystal structures of monomeric **2a**, **2b**, **3b**, **2d**, **2f**, and dimeric **2e** were established. Compounds **2a**, **2d**, **2e**, and **2f** were also investigated by means of density functional theory (DFT)-based quantum chemical calculations to understand structural variation. The complexes that contained acetate or chalcogenoether ligands with n = 3 showed higher catalytic activity than other derivatives in Suzuki C–C cross-coupling reactions.

ligands can bind weakly and reversibly to the metal center. The electronic differences, differing *trans* influence, and the variable chemical reactivity of two different donor atoms of these hybrid ligands, in addition to substituents on them, influence the overall activity and the selectivity of a reaction.<sup>[4]</sup> Accordingly palladium complexes that contain hybrid ligands derived from various combinations of donor atoms, such as (P,O),<sup>[5]</sup> (P,S),<sup>[4c,6,7]</sup> (P,N),<sup>[1a,8]</sup> (N,O),<sup>[9]</sup> (N,S),<sup>[10]</sup> (N,Se),<sup>[11]</sup> and so forth have been synthesized and several of them are effective catalysts in a number of C–C bond-formation reactions. Hemilabile ligands have an advantage as they can protect one or more coordination sites that are formed during the catalytic reaction and are also capable of stabilizing the active catalytic species/reactive intermediates.<sup>[4,12]</sup>

Palladium complexes with hemilabile phosphane ligands have been used for quite some time as catalysts in various coupling reactions,<sup>[13–16]</sup> but their air and moisture sensitivity has often posed difficulty in handling.<sup>[8a]</sup> Thus there is an enduring interest in developing phosphane-free, inexpensive, efficient catalyst systems. Sulfur-based ligands, despite their rich transition-metal chemistry, remained dormant as they are often considered catalyst poisons. Of late, palladium complexes derived from both a chalcogenolate group (RE<sup>–</sup>; E = S or Se)<sup>[4c,17]</sup> and chalcogenoether ligands<sup>[11]</sup> have been successfully used in C–C coupling reactions. Scant attention has been paid to palladium complexes with tellurium ligands in catalysis, possibly due to the lack of availability of suitable ligands and also the markedly different reactivity pattern of tellurium ligands with respect to the lighter congeners (S or Se).

To pursue our interest in the chemistry of platinumgroup metals with selenium and tellurium ligands,<sup>[18–20]</sup> we have synthesized palladium complexes with dimethylaminoalkyl chalcogenoether  $RE(CH_2)_nNMe_2$  (E = Se and Te) ligands that contain neutral donor atoms, namely, a chalcogen and nitrogen, and evaluated their catalytic activity in Suzuki C–C coupling reactions. The results of this work are reported herein.

## **Results and Discussion**

## Synthesis of Ligands

Aryl chalcogenoethers,  $RE(CH_2)_nNMe_2$ , were synthesized by a nucleophilic substitution reaction of sodium aryl chalcogenolate with freshly distilled dimethylaminoalkyl chloride (Scheme 1). Yellow selenoethers and red telluroethers were isolated as oils after silica-gel column chromatography. The selenoethers can be stored at room temperature for several months, whereas telluroethers were stored in the refrigerator at approximately 5 °C due to decomposition at room temperature.

$R_2E_2$	Me	eOH			
+			2 NaER		
2 NaBH	4 - (B <sub>2</sub>	$H_{6} + H_{2}$			
			2 1	∕le₂N	(CH <sub>2</sub> ) <sub>n</sub> Cl
ER	<u>n</u>		V		
PhSe MesSe MesTe PhSe MesSe PhTe <i>o</i> -tolTe	2 (1a) 2 (1b) 2 (1c) 3 (1d) 3 (1e) 3 (1f) 3 (1g)	2 Me <sub>2</sub> N	l(CH <sub>2</sub> ) <sub>n</sub> El 1	२ +	2 NaCl

Scheme 1. Syntheses of aryl chalcogenoether ligands.

The <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$  NMR spectra of these compounds displayed the expected resonances and peak multiplicities. The <sup>13</sup>C NMR spectra exhibited a resonance due to CH<sub>2</sub>Se and CH<sub>2</sub>Te carbon at approximately  $\delta = 25$  ppm and in the region of  $\delta = 4.7-9.2$  ppm, respectively. The resonances in telluroethers are influenced by the substituents, whereas the corresponding resonance for the selenoethers are barely influenced. These resonances were flanked by <sup>77</sup>Se/<sup>125</sup>Te couplings. The observed magnitude of  ${}^{1}J({}^{77}\text{Se},{}^{13}\text{C})$  (ca. 63 Hz) for selenoethers is in accordance with the values reported for selenoethers.<sup>[21]</sup> The <sup>77</sup>Se/<sup>125</sup>Te{<sup>1</sup>H} NMR spectra displayed single resonances that are influenced by the nature of the substituents. The <sup>77</sup>Se NMR spectroscopic resonance is deshielded by  $\delta = 15$  ppm upon increasing the alkyl chain length from  $(CH_2)_2$  to  $(CH_2)_3$  (Table S1 in the Supporting Information). Shielding of the resonances is noted on replacing the phenyl with a methyl-substituted aryl ring (otol or Mes) (o-tol = ortho-tolyl; Mes = 2,4,6-trimethylphenyl) within a series. The 125Te NMR spectroscopic signal of telluroethers is deshielded with respect to the corresponding diaryl ditelluride, whereas the converse is true for analogous selenoethers.

#### Synthesis and Spectroscopy of Palladium Complexes

Treatment of [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] or [Pd(OAc)<sub>2</sub>]<sub>3</sub> with chalcogenoethers gave complexes of the composition  $[PdX_2{RE(CH_2)_nNMe_2}]_m$  (X = Cl or OAc; E = Se or Te) (Schemes 2 and 3) as yellow to orange-red to red crystalline solids. The chloride complexes are sparingly soluble in chloroform, acetone, benzene, and ether, but moderately soluble in dichloromethane. Recrystallization from dichloromethane resulted in low yields of chloride complexes. The acetato complexes are lighter in color than the corresponding chloro derivatives. The telluroether complexes are darker in color than the analogous selenoether derivatives. The telluroether complexes 2e and 2f decompose at 325 and 305 °C, respectively; thermogravimetric analysis (TGA) suggests the formation of Pd<sub>3</sub>Te<sub>2</sub> (Figures S13 and S14 in the Supporting Information). It is worth noting that the reaction of palladium acetate trimer with mesityl chalcogenoethers MesECH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> yields a coordination complex rather than the cyclopalladated derivatives.<sup>[22]</sup> It has been demonstrated that the proton of the 2-methyl of the mesityl group forms short contacts (anagostic interaction) with the palladium atom before undergoing cyclopalladation.<sup>[22]</sup> In the present case ligands are chelated without any interactions between the aryl ring and the metal center. For instance, the mesityl ring in 3b is almost perpendicular to the metal coordination plane and there is hardly any Pd···H (methyl) interaction. As a result, metalation is not facilitated.



[a] Relative % of I, II and III based on <sup>1</sup>H NMR integrals.

[b] A product ~4 % was observed in NMR spectra.

Scheme 2. Syntheses of palladium chloride complexes.

All these complexes were characterized by elemental analyses, NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se, <sup>125</sup>Te) and UV/Vis spectroscopy, and in several cases by single-crystal X-ray diffraction analyses. The chloride complexes **2a–2c** derived

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Scheme 3. Syntheses of palladium acetato complexes.

from RECH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> ligands invariably exist as a discrete monomeric species with chelating chalcogenoether ligands. In contrast, complexes 2d-2f, which contain RECH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, exist as one monomeric and two different dimeric species in solution; however, in the solid state only one species could be obtained by crystallization.

The <sup>1</sup>H NMR spectra of **2a–2c** at room temperature showed a complex ABXY spin system for the CH<sub>2</sub> groups of the ligand (Figure S2 in the Supporting Information). The  ${}^{13}C{}^{1}H$  NMR spectra displayed a single set of peaks, except for the NMe<sub>2</sub> groups for which two singlets were observed. The <sup>77</sup>Se{<sup>1</sup>H} (Figure S3 in the Supporting Information) and <sup>125</sup>Te{<sup>1</sup>H} NMR spectra also showed sharp singlets that indicated only one isomer in solution. The complex pattern of <sup>1</sup>H spectra at room temperature can be explained by the chiral center generated at chalcogen atom after complexation. The CH<sub>2</sub> group attached to this chalcogen atom become diastereotopic (and also the NMe<sub>2</sub> groups are anisochronous) in the absence of any interconversion process. Variable-temperature NMR spectra of 2a (Figure S1) were determined in [D<sub>6</sub>]DMSO. Upon increasing the temperature, the separation between two doublet of triplets for the SeCH<sub>2</sub> group, two doublet of doublet of doublets for the NCH<sub>2</sub> group, and two singlets for the NMe<sub>2</sub> group begin decreasing and broadening. At 358 K, two peaks for NMe<sub>2</sub> groups coalesce and become a broad singlet at 368 K. The rate constant calculated for the interconversion of the two isomers is 59.5 s<sup>-1</sup>, and the activation energy barrier is 18.2 kcalmol<sup>-1</sup>.

The 2,6-methyl groups of the Mes part of  $[PdCl_2(Mes-SeCH_2CH_2NMe_2)]$  (**2b**) displayed a very broad peak in the range  $\delta = 2.9-3.2$  ppm in the <sup>1</sup>H NMR spectrum at room temperature. Upon lowering the temperature to 253 K, two broad singlets appeared at  $\delta = 3.46$  and 2.53 ppm for the two *ortho*-methyl groups of the Mes group owing to the slow rotation of Se–C(Mes) bond (Figure 1). The 3,5-aryl protons of the Mes group, which showed a sharp singlet at  $\delta = 7.04$  ppm at ambient temperature, split into two broad singlets at 243 K. In the case of analogous Te complex **2c**, a sharp singlet was observed at  $\delta = 3.03$  ppm, thus indicat-

ing a comparatively less hindered rotation of the Te–C(Mes) bond than the Se–C(Mes) bond at room temperature (Figure S4 in the Supporting Information). The longer Pd–Te bond keeps the two *ortho* methyl groups away from the vicinity of other groups in complex **2c**, hence free rotation occurs at room temperature. By contrast, in both acetato complexes [Pd(OAc)<sub>2</sub>(MesECH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] (E = Se (**3b**), Te (**3c**)), the broad singlets at  $\delta$  = 3.09 and 3.01 ppm for Se and Te derivatives, respectively, for 2,6-Me groups also indicate the hindered rotation of the E–C(Mes) bond.

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Figure 1. Variable-temperature 400 MHz  $^{1}$ H NMR spectra of [PdCl<sub>2</sub>(MesSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)]<sub>n</sub> (**2b**) in CD<sub>2</sub>Cl<sub>2</sub>.

Complexes 2d–2f, derived from RECH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> and [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] exhibited three sets of resonances (see Figures S5–S12 in the Supporting Information) in <sup>1</sup>H, <sup>13</sup>C, and <sup>77</sup>Se/ <sup>125</sup>Te NMR spectra (Figures 2 and 3), thus clearly indicating the existence of three species in solution. By comparing the <sup>1</sup>H NMR spectroscopic peaks of analogous monomers 2a–2c in which the ligands adopt a chelating mode, the sharp singlets for NMe<sub>2</sub> groups of monomers have been assigned in the deshielded range relative to the dimers of 2d–2f (see Figures S8 and S10), and the corresponding integration ratio has been used for the calculation of their relative ratio. A minor product (ca. 4%) was observed in <sup>1</sup>H and <sup>125</sup>Te ( $\delta$  = 566 ppm) NMR spectra, which might be due to the oligomeric/trimeric form of 2e.

The X-ray structural analysis of 2d and 2f revealed a chelating monomeric structure, whereas a dimeric structure was observed for the analogous 2e (see later). It is likely that both monomeric (Scheme 2, I) and dimeric structures (Scheme 2, II and III) can form in solution and their relative concentration is influenced by the nature of the ligand. The inversion at the chiral Se or Te centers in both the dimeric structures would generate invertomers that are diasteroisomers. For example, the crystallographically characterized dimer (2e) is the *meso* form (out–out) (II) in which the two aryl groups are outwardly oriented with respect to the metallo ring and away from the chloride groups. The inversion at one or two Se/Te centers of II can lead to unstable invertomers IV (DL: out–in) or V (*meso*: in–in) (see

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Figure 3.  $^{125}$ Te{ $^{1}$ H} NMR spectrum of [PdCl<sub>2</sub>(PhTeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-NMe<sub>2</sub>)]<sub>*n*</sub> (**2e**).

Scheme S1 in the Supporting Information) in which the aryl groups occupy a position inside the metallo ring and very close to the chloride groups, which is sterically unfavorable. This is justified by theoretical modeling; the gradual inversion at the Se/Te center finally leads to an unstable species before forming IV or V. The two DL forms IV and VI are identical by rotation. The pyramidal inversion at the sulfur, selenium, and tellurium center in mononuclear complexes *trans*- $[MX_2(ER_2)]$  (M = Pd, Pt; X = Cl, Br; R = Et,<sup>[23]</sup>  $CH_2SiMe_3^{[24]}$  and *trans*- $[MX_2{RE(CH_2)_3ER}]$  (X = Cl, Me;  $R = Me^{[25]} Ph^{[26]}$  has been reported to generate invertomers. For selenoether complex 2d, the monomeric form predominates, whereas for telluroether ligands, all three structural forms of 2e and 2f exist with nearly equal probability. It is clear that the complexes of the ligand that possess longer chains and larger Te atoms generate more dimeric forms than monomers in solution.

The <sup>77</sup>Se and <sup>125</sup>Te NMR spectroscopic resonances for the complexes are considerably deshielded from the respective signals for the corresponding free ligands. The deshield-ing is more pronounced in telluroether complexes than the analogous selenoether derivatives. In the case of acetato complexes **3a** and **3b**, the <sup>77</sup>Se NMR spectra displayed two

small peaks at  $\delta = 414$ , 426 and 339, 361 ppm in addition to the major peaks at  $\delta = 442$  and 345 ppm assigned to **3a** and **3b**, respectively. On the basis of the previous discussion and theoretical calculations (see below), as the ligand of two carbon spacer length RECH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> is unable to form bridged dimeric structures, the small peaks in the present case might be due to acetato-bridged oligomeric complexes of **3a** and **3b** as minor products; no attempt was made to isolate either one. Even after repeated recrystallization these minor products could not be removed. As a result the yields of these acetato complexes are low.

The absorption spectra of all the yellow to orange complexes in CH<sub>2</sub>Cl<sub>2</sub> displayed a characteristic broad and weak band at 400-409 nm in the visible region. Variation of the chalcogen center or the chain length hardly affects the wavelength at the absorption maxima, thus indicating that the highest-occupied orbitals are not formed from any significant orbital contribution from the chalcogen atom. The charge-transfer transitions from the selenolato or tellurolato centers to unoccupied orbitals that involve mainly the phosphane coligands (LLCT) for the PtII compounds and more delocalized MOs for the Pd<sup>II</sup> analogues has been observed in  $[MCl(E^{\cap}N)(PR_3)]$  (M = Pd, Pt;  $E^{\cap}N$  = 2-C<sub>5</sub>H<sub>4</sub>N,<sup>[27]</sup> ECH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub><sup>[19]</sup>). In the case of non-phosphane complexes [PdCl(SeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)]<sub>2</sub>,<sup>[28]</sup> the long-wavelength transitions have been assigned as chargetransfer transitions from the selenolato centers to unoccupied metal orbitals [ligand-to-metal charge transfer (LMCT)]. In the present case, the observed absorption is assigned to the charge-transfer transition from the bonding orbital of Pd to the antibonding  $(\pi^*)$  orbital of the phenyl ring of the ligand [metal-to-ligand charge transfer (MLCT)] and is also supported by time-dependent (TD) DFT calculations (see below).

#### X-ray Crystallography

Molecular structures of  $[PdCl_2(PhSeCH_2CH_2NMe_2)]$ · 0.5CH<sub>2</sub>Cl<sub>2</sub> (**2a**·0.5CH<sub>2</sub>Cl<sub>2</sub>),  $[PdX_2(MesSeCH_2CH_2NMe_2)]$ [X = Cl (**2b**), OAc (**3b**)],  $[PdCl_2(PhSeCH_2CH_2CH_2NMe_2)]$ (**2d**),  $[PdCl_2(PhTeCH_2CH_2CH_2NMe_2)]_2$  (**2e**), and  $[PdCl_2-(o-tolTeCH_2CH_2CH_2NMe_2)]$  (**2f**) have been established by single-crystal X-ray analyses. ORTEP drawing with atomic numbering schemes are shown in Figures 4, 5, 6, 7, and 8, as well as Figures S15 and S16 of the Supporting Information, whereas selected interatomic parameters are given in Tables 1, 2, 3, and 4.

These complexes, except for **2e**, are discrete monomers with chelating chalcogenoether ligands. The **2e** is a dimer with a bridging chalcogenoether ligand. The coordination environment around the distorted square-planar palladium atom is defined by E, N, and two anionic ligands (Cl or OAc). The latter in monomeric complexes are *cis* disposed, whereas in **2e** the chloride ligands occupy *trans* positions. There are two distinctly different Pd–Cl distances (ca. 2.30 and ca. 2.33 Å) in mononuclear complexes, with the Pd–Cl bond *trans* to the chalcogen atom being marginally longer Job/Unit: I42943

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Figure 4. Molecular structure of  $[PdCl_2(MesSeCH_2CH_2NMe_2)]$ (2b) ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.



Figure 5. Molecular structure of  $[PdCl_2(PhSeCH_2CH_2CH_2NMe_2)]$  (2d) ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.



Figure 6. Molecular structure of  $[PdCl_2(PhTeCH_2CH_2CH_2NMe_2)]_2$  (2e) ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

than the one *trans* to nitrogen. This difference is due to the difference in the *trans* influence of chalcogen and the chloride ligand. The observed distances are in good agreement with the values reported in palladium complexes.<sup>[7,22a,29]</sup> The Pd–O and Pd–N (2.067–2.121 Å) distances are com-



Figure 7. Molecular structure of  $[PdCl_2(o-tolTeCH_2CH_2CH_2-NMe_2)]$  (2f) ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.



Figure 8. Molecular structure of  $[Pd(OAc)_2(MesSeCH_2CH_2NMe_2)]$ -1.5(H<sub>2</sub>O) (**3b**·1.5H<sub>2</sub>O) ellipsoids drawn at 50% probability. Two molecules of **a** and **b** are associated through intermolecular hydrogen bonds. Hydrogen atoms in the ligands have been omitted for clarity.

Table 1. Selected interatomic parameters (bonds [Å], angles [°]) of  $[PdCl_2(RSeCH_2CH_2NMe_2)]$  (R = Ph, Mes).

	<b>2a</b> •0.5CH <sub>2</sub> Cl <sub>2</sub>	2b
Pd1–Se1	2.3611(11)	2.3914(6)
Pd1-Cl1	2.287(2)	2.3085(7)
Pd1-Cl2	2.326(2)	2.3383(7)
Pd1–N1	2.083(6)	2.0882(19)
Se1-C1	1.941(8)	1.962(2)
Se1-C5	1.945(7)	1.957(2)
N1-Pd1-Se1	89.06(19)	89.30(5)
N1-Pd1-Cl1	175.36(19)	176.91(5)
N1-Pd1-Cl2	92.95(19)	90.77(5)
Cl2-Pd1-Cl1	91.53(8)	91.13(2)
Se1-Pd1-Cl1	86.59(6)	88.55(2)
Se1-Pd1-Cl2	174.45(6)	173.583(17)
Pd1-Se1-C5	105.0(2)	113.12(6)
Pd1-Se1-C1	94.6(2)	92.60(7)
C1-Se1-C5	99.1(3)	97.73(10)

parable to complexes of the composition  $[Pd(OAc){E(CH_2)_n}-NMe_2]_m$  (n = 2 or 3; m = 3 or 2; E = S, Se, or Te).<sup>[17a,28b]</sup> The Pd–N distance in **2e**, however, is much longer (2.210 Å). This is in accordance with the distances reported in compounds that contain a nitrogen atom *trans* to strong



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Table 2. Selected interatomic parameters (bonds [Å], angles [°]) of [Pd(OAc)<sub>2</sub>(MesSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)].

	<b>3b</b> •1.	<b>3b</b> ·1.5(H <sub>2</sub> O)	
	molecule a	molecule <b>b</b>	
Pd1–Se1	2.3582(4)	2.3595(5)	2.3730(3)
Pd1–O1	2.0365(18)	2.006(2)	2.0460(13)
Pd1–O3	2.0197(19)	2.0469(19)	2.0087(14)
Pd1–N1	2.067(2)	2.067(2)	2.0714(16)
Se1-C1	1.965(3)	1.957(3)	1.972(2)
Sel-C5	1.942(3)	1.929(3)	1.9447(18)
Se1-Pd1-N1	87.97(6)	87.32(6)	88.71(5)
N1-Pd1-O1	88.47(8)	174.70(8)	89.23(6)
N1-Pd1-O3	174.44(8)	89.15(8)	174.33(6)
O1-Pd1-O3	86.18(8)	86.96(8)	85.60(6)
O3-Pd1-Se1	97.28(6)	175.82(6)	96.06(4)
Se1-Pd1-O1	175.17(5)	96.70(6)	171.40(4)
Pd1-Se1-C5	115.13(8)	114.88(8)	114.74(6)
Pd1-Se1-C1	93.61(9)	94.03(8)	94.49(6)
C1-Se1-C5	99.23(12)	103.77(11)	97.96(8)

Table 3. Selected interatomic parameters (bonds [Å], angles [°]) of  $[PdCl_2(RECH_2CH_2CH_2NMe_2)]_n$  (RE = PhSe, *o*-tolTe).

	2d	2f
Pd1–E1	2.3938(11)	2.5395(8)
Pd1-Cl1	2.298(2)	2.3161(18)
Pd1-Cl2	2.313(3)	2.353(2)
Pd1-N1	2.121(7)	2.111(5)
E1-C3	1.935(9)	2.136(7)
E1-C6	1.943(8)	2.135(7)
N1-Pd1-E1	96.2(2)	100.17(16)
N1-Pd1-Cl1	172.2(2)	176.14(18)
N1-Pd1-Cl2	91.4(3)	90.68(16)
Cl2-Pd1-Cl1	89.34(12)	88.86(8)
Cl1-Pd1-E1	83.25(8)	80.54(6)
E1-Pd1-Cl2	172.18(9)	168.62(6)
Pd1-E1-C6	101.8(2)	99.65(19)
Pd1-E1-C3	108.7(3)	104.6(2)
C3-E1-C6	101.2(4)	94.0(3)

Table 4. Selected bond lengths [Å] and angles [°] of  $[PdCl_2(PhTeCH_2CH_2CH_2NMe_2)]_2$  (2e).

Pd1–Te1 <sup><i>i</i></sup>	2.5321(15)	Pd1-Cl2	2.297(4)
Pd1-N1	2.210(13)	Te1-C3	2.144(14)
Pd1-Cl1	2.310(4)	Te1-C6	2.118(13)
Cl1-Pd1-Cl2	173.24(16)	N1–Pd1–Te1 <sup>i</sup>	176.1(4)
Cl1-Pd1-N1	93.9(4)	Pd1–Te1 <sup><i>i</i></sup> –C3 <sup><i>i</i></sup>	108.6(4)
Cl1–Pd1–Te1 <sup>i</sup>	82.27(12)	Pd1–Te1 <sup><i>i</i></sup> –C6 <sup><i>i</i></sup>	98.6(3)
Cl2-Pd1-N1	92.1(4)	C3 <sup>i</sup> -Te1 <sup>i</sup> -C6 <sup>i</sup>	93.3(5)
Cl2–Pd1–Te1 <sup>i</sup>	91.73(11)		

*trans*-influencing ligands (e.g., [PdI(SeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2)-(PPh<sub>3</sub>)] [Pd–N = 2.1958(18) Å];<sup>[30]</sup> [Pd<sub>2</sub>( $\mu$ -Sepy)<sub>2</sub>(Me<sub>2</sub>-NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*C*,*N*)<sub>2</sub>] [Pd–N = 2.189(8) Å]<sup>[31]</sup>. The Pd–Se (ca. 2.37 Å) and Pd–Te (ca. 2.53 Å) bond lengths are in conformity with the values reported for palladium chalcogenoether complexes, such as [Pd<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>{MesSeC<sub>6</sub>H<sub>2</sub>-(Me<sub>2</sub>)CH<sub>2</sub>}] [Pd–Se = 2.3438(8) Å],<sup>[22a]</sup> [PdCl<sub>4</sub>(OC<sub>6</sub>H<sub>4</sub>C(Ph)=NCH<sub>2</sub>CH<sub>2</sub>SePh}] [Pd–Se = 2.3575(6) Å],<sup>[32]</sup> [PdCl<sub>2</sub>{TeMe(C<sub>4</sub>H<sub>3</sub>O)}] [Pd–Te = 2.5068(13) Å],<sup>[33]</sup> and [Pd<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(TeMes<sub>2</sub>)<sub>2</sub>] [Pd–Te = 2.5068(13) Å],<sup>[22b]</sup> The Pd–Se bond in [PdCl<sub>2</sub>{RSe(CH<sub>2</sub>)<sub>n</sub>NMe<sub>2</sub>}] is slightly elon-

gated either by replacing a phenyl group by mesityl with n = 2 {e.g., **2a** [2.3611(11) Å] and **2b** [2.3914(6) Å]} or increasing the alkyl chain length {e.g., **2a** and **2d** [Pd–Se = 2.3938(11) Å]}. A similar elongation of the Pd–Se bond is noted for selenolato complexes [PdCl(SeCH<sub>2</sub>CH<sub>2</sub>-NMe<sub>2</sub>)]<sub>3</sub><sup>[34]</sup> and [PdCl(SeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)]<sub>2</sub>.

The binuclear complex **2e** forms a 12-membered macrocyclic ring; the two phenyl groups lie on the opposite side of the ring, thus leading to an *anti* conformation, which is actually a *meso* invertomer (**III**: out–out). The Pd–N bond [2.210(13) Å] is elongated relative to the chelated complex [PdCl<sub>2</sub>(*o*-tol–TeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] [2.111(5) Å], whereas in similar dinuclear complexes of a *trans*-"PdCl<sub>2</sub>TeN" coordination environment, comparatively shorter Pd–N distances [2.097(4), 2.101(4) Å] are observed in which the nitrogen donor atom is a part of the pyridyl group.<sup>[35]</sup> Dinuclear and trinuclear complexes [PdCl<sub>2</sub>( $\mu$ -6-MepyCH<sub>2</sub>EPh-*N*,*E*)]<sub>*n*</sub> (E = S, *n* = 3; E = Se, *n* = 2) of *trans*-"PdCl<sub>2</sub>EN" geometry have also been reported to form a macrocyclic ring.<sup>[36]</sup>

The acetato complex **3b** could be crystallized with and without a water molecule (Figure 8 and Figure S16 in the Supporting Information). There is a slight variation in various interatomic parameters in the two structures. In the hydrated molecule the Pd1–O3 bond is slightly elongated (0.011 Å), whereas the Se1–Pd1–O1 angle is opened up (3.77°) relative to the values of the structure without a water molecule. The O3 oxygen in fact is hydrogen bonded to the lattice water molecule. There are two independent molecules in the crystal lattice (Figure 8) of the hydrated complex that differ slightly in their interatomic parameters.

## **Theoretical Calculations**

To assess the factors responsible for structural variation of palladium complexes with the nature of ligand, DFT calculations were performed. Minimum-energy equilibrium structures were obtained in each of these monomers and dimers of palladium complexes with different possible input structures based on different spatial orientations of the groups. Optimization of the structures were carried out by applying the BP86 functional, which is known to work well for Pd-based complexes with mixed atomic basis functions for the metal and other atoms. The final optimized structures of monomer and dimer units are shown in Figure 9 and Figure S17 in the Supporting Information. The largest discrepancies occur for the Pd-Te and Pd-N bonds, which were calculated with distances that are too long by about 0.12 and 0.10 Å, respectively, whereas the Pd-Se bond lengths were calculated to be 0.07 Å higher than the experi-

Table 5. Comparison of DFT-calculated bond lengths with experimental data for  $[PdCl_2{RE(CH_2)_nNMe_2}]_m$ .

	2a-I (E = Se)		2d-I (E = Se)		<b>2f-I</b> (E = Te)		<b>2e-II</b> (E = Te)	
	calcd.	exp.	calcd.	exp.	calcd.	exp.	calcd.	exp.
Pd–E	2.43	2.36	2.45	2.39	2.66	2.54	2.65	2.53
Pd–N	2.18	2.08	2.19	2.12	2.17	2.12	2.22	2.21



Table 6. Stabilization energy of monomer and dimer complexes of  $PdCl_2$  with  $RE(CH_2)_nNMe_2$  (E = Se, Te) units [kcalmol<sup>-1</sup>] at the current DFT level.

	$RE(CH_2)_nNMe_2$					
	PhSe(CH <sub>2</sub> ) <sub>2</sub> NMe <sub>2</sub>	PhSe(CH <sub>2</sub> ) <sub>3</sub> NMe <sub>2</sub>	PhTe(CH <sub>2</sub> ) <sub>3</sub> NMe <sub>2</sub>	o-tolTe(CH <sub>2</sub> ) <sub>3</sub> NMe <sub>2</sub>		
Monomer Dimer	77.3 ( <b>2a-I</b> ) does not form ( <b>2a-II</b> )	79.4 ( <b>2d-I</b> ) 24.8 ( <b>2d-II</b> )	77.0 ( <b>2e-I</b> ) 31.4 ( <b>2e-II</b> ) 22.7 ( <b>2e-III</b> )	77.7 ( <b>2f-I</b> ) 28.4 ( <b>2f-II</b> ) 19.6 ( <b>2f-III</b> )		

mental values (Table 5). With the present rigid all-electron basis set applied for Pd and Te, these observed differences in bond lengths are understandable. In a good comparison, the monomer unit of the selenoether complex with three - $CH_2$ - groups (2d-I) is slightly more stable (2.1 kcal mol<sup>-1</sup>; Table 6) than the corresponding complex with two  $-CH_{2}$ groups (2a-I). The monomer units of telluroether complexes that contain phenyl and o-tolyl have comparable stability. The structure of the dimer unit of PdCl<sub>2</sub> with PhSe(CH<sub>2</sub>)<sub>2</sub>-NMe<sub>2</sub> (2a-II) could not be obtained on optimization, which might be due to the instability of the complex, thus firmly supporting the experimental data as observed in NMR spectra. All the monomers (2a-I, 2d-I, 2e-I, and 2f-I) are more stable than the corresponding dimers. The relative stability of the dimer unit of PdCl<sub>2</sub> with PhSe(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub> (2d-II) relative to the monomer unit was calculated to be 24.8 kcal mol<sup>-1</sup>.



Figure 9. Optimized structures of monomer units of  $[PdCl_2{PhSe(CH_2)_2NMe_2}]$  (2a) and monomer and dimer units of  $[PdCl_2{PhTe(CH_2)_3NMe_2}]$  (2e) calculated by applying the density functional theory and adopting all-electron basis functions.

Minimum-energy dimeric structures of symmetric as well as asymmetric telluroether complexes from the corresponding monomer units (**2e-I** and **2f-I**) are calculated (Figure 9 and Figure S17 in the Supporting Information). Symmetric dimeric structures (**2e-II** and **2f-II**) are predicted to be more stable by approximately 9 kcal mol<sup>-1</sup> over asymmetric structures (**2e-III** and **2f-III**), which is in agreement with the experimentally determined crystal structure of **2e-II**, even though **2e-II** and **2e-III** remain in a 1:1 ratio in solution as determined by NMR spectroscopic data.

Excited-state calculations were also carried out to predict UV/Vis absorption peaks of the four monomer units of Pd complexes. The optical absorption peaks of 2a, 2d, 2e, and 2f are calculated at 382, 385, 386, and 395 nm, respectively, with low oscillator strength and are in close agreement with the observed band at 400-409 nm for the complexes of various groups. To find out the origin of these electronic transition bands, calculated MOs of these complexes are also visualized. Excited-state calculations based on time-dependent density functional theory suggest that the experimental optical absorption peak at 405 nm for complex 2a-I is due to electronic transition from MO 97 (HOMO-2) to MO 100 (LUMO). Figure 10 depicts the plot of the two MOs suggesting the charge-transfer transition predominantly from metal bonding orbital  $(d_{xy})$  to antibonding  $(\pi^*)$  orbital of phenyl ring of the ligand (MLCT). The low molar extinction coefficient of only 1500 M<sup>-1</sup> cm<sup>-1</sup> points to a symmetryforbidden transition.



Figure 10. Plot of MOs 97 (HOMO–2) and 100 (LUMO) for the palladium selenoether complex **2a-I** with a contour cut off of 0.1 a.u. Plot of MO 97 indicates that the MO is contributed by metal  $d_{xy}$  orbital and lone pairs of two Cl atoms. Plot of MO 100 points out that it is constructed mainly by phenyl  $\pi^*$  orbitals.

### Suzuki C-C Coupling Reactions

To assess whether the chalcogenoether complexes of palladium can be employed as the catalyst in C–C bond formation, their suitability as a catalyst in Suzuki C–C coupling reactions was studied. The reaction conditions were initially optimized with respect to solvent and base in the coupling of 4-iodotoluene with phenylboronic acid using 0.1 mol-% of [Pd(OAc)<sub>2</sub>(MesSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] as a catalyst (Tables S4–S6 in the Supporting Information). 1,4-Dioxane was the preferred solvent among the solvents DMF, tolu-



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Table 7. Suzuki C-C cross-coupling reaction.[a]



Entry	R	Х	Base	"Pd" complex		Yield <sup>[b]</sup>	TON
no.				-	[mol-%]	[%]	
1	4-CH <sub>3</sub>	Ι	Na <sub>2</sub> CO <sub>3</sub>	[PdCl <sub>2</sub> (PhSeCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	59	590
2	$4-CH_3$	Ι	$K_2 CO_3$	[PdCl <sub>2</sub> (MesSeCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	62	620
3	$4-CH_3$	Ι	$Na_2CO_3$	[PdCl <sub>2</sub> (PhSeCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	62	620
4	$4-CH_3$	Ι	Bu <sub>4</sub> NOH	[PdCl <sub>2</sub> (PhSeCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	94	940
5	$4-CH_3$	Ι	Bu <sub>4</sub> NOH	[PdCl <sub>2</sub> (PhSeCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.01	94	9400
6	2-CHO	Br	Bu <sub>4</sub> NOH	[PdCl <sub>2</sub> (PhSeCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	80	800
7	2-CHO	Br	Bu <sub>4</sub> NOH	[PdCl <sub>2</sub> (PhSeCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.01	21	2100
8	$4-NO_2$	Br	Bu <sub>4</sub> NOH	[PdCl <sub>2</sub> (PhSeCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	95	950
9	$4-CH_3$	Ι	$Na_2CO_3$	[PdCl <sub>2</sub> (PhTeCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	88	880
10	2-CHO	Br	$K_2CO_3$	[Pd(OAc) <sub>2</sub> (PhSeCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	65	650
11	$4-CH_3$	Ι	$K_2CO_3$	[Pd(OAc) <sub>2</sub> (MesSeCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	76	760
<sup>[c]</sup> 12	$4-CH_3$	Ι	Bu₄NOH	[Pd(OAc) <sub>2</sub> (MesSeCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	94	940
<sup>[c]</sup> 13	2-CHO	Br	Bu <sub>4</sub> NOH	[Pd(OAc) <sub>2</sub> (MesSeCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )]	0.1	72	720

[a] Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.3 mmol), base (2 mmol), dioxane (2 mL). [b] Isolated yield. [c] When refluxed in methanol the yields were 88% (entry 12) and 80% (entry 13).

ene, and methanol. The use of inorganic bases K<sub>2</sub>CO<sub>3</sub> and  $Na_2CO_3$  led to the comparable yields (76%), whereas the organic base Bu<sub>4</sub>NOH gave a higher yield (94%) of biaryls. By using the optimized conditions, the catalytic activity of the complexes was evaluated in the coupling reaction of aryl halides and phenylboronic acid (Table 7). Moderate to quantitative yields of desired products were obtained within six hours in the presence of 0.1 mol-% of Pd complexes in cases of 4-iodotoluene and arylbromides activated by CHO and NO<sub>2</sub> groups. A comparative study on the complexes showed that complexes of the acetato ligand (entries 2 and 11) performed better than the corresponding chloro analogues. This is possibly due to the formation of more active catalytic species in the case of the more labile acetato ligand capable of facile ligand displacement during the catalysis reaction.<sup>[17c]</sup> Enhancement of the catalytic activity was observed on increasing the chain length from strongly chelating CH<sub>2</sub>CH<sub>2</sub> to flexible CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> in the ligand (entries 6 and 13). However, a significant improvement in activity was noted on replacing selenium by tellurium (entries 3 and 9).

## Conclusion

A series of palladium complexes with dimethylaminoalkyl chalcogenoether ligands have been isolated and characterized. The color of these complexes arises from the charge-transfer transition from the palladium  $d_{xy}$  orbital to the antibonding  $\pi^*$  orbital of the aryl ring. The complexes with the five-membered chelate ring formed by Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>ER exist exclusively in monomeric form both in the solid state and in solution. The complexes derived from ligands Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>ER, capable of forming six-membered chelates, tend to exist both as monomeric chelates and in two dimeric forms in solution and on crystallization only one form is preferentially crystallized out. DFT calculations support the existence of all the isomeric forms. The observed coordination pattern of the latter ligand, a system comparable to  $R_2PCH_2CH_2CH_2PR_2$ (dppp), is clearly distinct from chelating bis-phosphanes. The flexibility of chalcogenoether ligands aids in improving the catalytic activity in C–C Suzuki coupling reactions.

# **Experimental Section**

**General Methods:** All reactions were carried out in Schlenk flasks under a nitrogen atmosphere. The compounds Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub>Cl<sub>1</sub>HCl, Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl<sub>1</sub>HCl, arylboronic acids, aryl halides, and other reagents were procured from commercial sources. The compounds Ph<sub>2</sub>Se<sub>2</sub>, Mes<sub>2</sub>Se<sub>2</sub>, Ph<sub>2</sub>Te<sub>2</sub>, *o*-tol<sub>2</sub>Te<sub>2</sub>, Mes<sub>2</sub>Te<sub>2</sub>, and palladium precursors Na<sub>2</sub>PdCl<sub>4</sub>, [PdCl<sub>2</sub>(PhCN)<sub>2</sub>], and [Pd(OAc)<sub>2</sub>]<sub>3</sub> (see references S1, S2, and S3, respectively, in the Supporting Information) were prepared according to the literature methods.

Melting points were determined in capillary tubes and are uncorrected. Elemental analyses were carried out on a Carlo–Erba EA-1110 CHN-S instrument. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>77</sup>Se{<sup>1</sup>H}, and <sup>125</sup>Te{<sup>1</sup>H} NMR spectra were recorded on a Bruker Ascend TM-400 NMR spectrometer operating at 400, 100.61, 76.31, and 126.24 MHz, respectively. Chemical shifts are relative to the internal chloroform peak ( $\delta$  = 7.26 ppm for <sup>1</sup>H and  $\delta$  = 77.0 ppm for <sup>13</sup>C{<sup>1</sup>H}) and external Ph<sub>2</sub>Se<sub>2</sub> ( $\delta$  = 463 ppm relative to Me<sub>2</sub>Se) for <sup>77</sup>Se{<sup>1</sup>H} and Ph<sub>2</sub>Te<sub>2</sub> ( $\delta$  = 421 ppm relative to Me<sub>2</sub>Te) for <sup>125</sup>Te{<sup>1</sup>H}. TG curves were obtained at a heating rate of 10 °Cmin<sup>-1</sup> under flowing argon on a Setaram Setsys evolution-1750 instrument.

**Preparation of Ligands:** Synthesis of chalcogenoether ligands (Scheme 1) PhSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (1a),<sup>[37]</sup> MesSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (1b) (Mes = 2,4,6-trimethylphenyl), MesTeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (1c), PhSeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (1d), MesSeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (1e), PhTeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CMe<sub>2</sub> (1f), and *o*-tolTeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (1g) (*o*-tol = *ortho*-tolyl) together with their characterization data are given in the Supporting Information.



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#### Synthesis of Complexes

 $[PdCl_2(PhSeCH_2CH_2NMe_2)]$  (2a):  $[PdCl_2(PhCN)_2]$  (152 mg, 0.396 mmol) in acetone (10 mL) was added to a solution of PhSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (203 mg, 0.891 mmol) in toluene (10 mL). The red solution was stirred at room temperature for 4 h. The solvents were removed under vacuum and the residue was washed thoroughly with diethyl ether followed by hexanes. The product was extracted with dichloromethane  $(5 \times 10 \text{ mL})$ , passed through Celite, concentrated to 15 mL, which on slow evaporation at room temperature gave orange-red crystals of 2a (103 mg, 0.254 mmol, 64%), m.p. 200 °C (decomp.). C<sub>10</sub>H<sub>15</sub>Cl<sub>2</sub>NPdSe (405.50): calcd. C 29.62, H 3.73, N 3.45; found C 29.21, H 3.60, N 3.30. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\varepsilon$  in M<sup>-1</sup> cm<sup>-1</sup>) = 239 (40900), 316 (7300), 405 (1500) nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.71, 3.18 (dt, <sup>2</sup>J<sub>H,H</sub> = 13.2 Hz, <sup>3</sup>J<sub>H,H</sub> = 4 Hz, 2 H, AA'BB' pattern, SeCH<sub>2</sub>), 2.88, 2.97 (each s, 6 H, NMe<sub>2</sub>), 2.96, 3.35 (ddd,  ${}^{2}J_{H,H}$  = 13.2 Hz,  ${}^{3}J_{H,H}$  = 11.6 Hz,  ${}^{3}J_{H,H}$  = 3.6 Hz, 2 H, AA'BB' pattern, NCH<sub>2</sub>), 7.46–7.55 (m, 3 H, Ph), 8.19–8.26 (m, 2 H, Ph) ppm.  $^{77}Se\{^{1}H\}$  NMR ([D<sub>6</sub>]-DMSO):  $\delta = 474$  ppm.

[PdCl<sub>2</sub>(MesSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] (2b): Complex 2b was prepared similarly to that of 2a by using MesSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (109 mg, 0.403 mmol) and [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (141 mg, 0.377 mmol) in dichloromethane (15 mL). Recrystallization from dichloromethane yielded orange crystals of 2b (70 mg, 0.156 mmol, 43%), m.p. 195 °C (decomp.). C<sub>13</sub>H<sub>21</sub>Cl<sub>2</sub>NPdSe (447.58): calcd. C 34.88, H 4.73, N 3.13; found C 34.71, H 4.61, N 2.98. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\varepsilon$  in  $M^{-1}$  cm<sup>-1</sup>) = 405 (1100), 313 (6960), 268 (13300), 237 (27100) nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 2.30$  (s, 3 H, 4-Me, Mes), 2.68-2.75 (m), 2.89-3.29 (br. m, 10 H, SeCH<sub>2</sub>CH<sub>2</sub>, 2,6-Me of Mes), 2.88, 2.89 (each s, 6 H, NMe<sub>2</sub>), 7.00 (s, 2 H, 3,5-H, Mes) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 21.2 (s, 4-Me, Mes), 25.3 (br. s, 2,6-Me, Mes), 30.8 (s,  ${}^{1}J_{\text{Se,C}} = 47.5 \text{ Hz}$ , SeCH<sub>2</sub>), 52.1, 53.1 (each s, NMe<sub>2</sub>), 67.8 (s, NCH<sub>2</sub>), 123.5 (s, 1-C, Mes), 131.3 (s, 3,5-C, Mes), 141.5 (s, 2,6-C, Mes), 142.4 (s, 4-C, Mes) ppm. 77Se{1H} NMR  $(CD_2Cl_2): \delta = 361$  (s) ppm.

[PdCl<sub>2</sub>(MesTeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] (2c): Complex 2c was prepared in a manner similar to that of 2b by using a methanolic solution (5 mL) of MesTeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (99 mg, 0.310 mmol) and [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (108 mg, 0.282 mmol) in benzene (20 mL). Recrystallization from dichloromethane yielded orange crystals of 2c (70 mg, 0.141 mmol, 50%), m.p. 180 °C (decomp.). C<sub>13</sub>H<sub>21</sub>Cl<sub>2</sub>NPdTe (496.22): calcd. C 31.46, H 4.27, N 2.82; found C 31.88, H 4.13, N 2.60. <sup>1</sup>H NMR  $(CD_2Cl_2)$ :  $\delta = 2.34$  (s, 3 H, 4-Me, Mes), 2.48, 4.00 (ddd,  ${}^2J_{H,H} =$ 15.6,  ${}^{3}J_{H,H} = 4.4 \text{ Hz}$ , 2 H, AA'BB' pattern, TeCH<sub>2</sub>), 2.85, 3.23  $(ddd, {}^{2}J_{H,H} = 13.4 \text{ Hz}, {}^{3}J_{H,H} = 4 \text{ Hz}, 2 \text{ H}, \text{AA'BB' pattern, NCH}_{2}),$ 2.85, 2.88 (each s, 6 H, NMe2), 3.04 (s, 6 H, 2,6-Me, Mes), 7.08 (2 H, 3,5-H, Mes) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR(CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 12.1 (s, 4-Me, Mes), 20.3 (s, 2,6-Me, Mes), 28.0 (s, TeCH<sub>2</sub>), 51.2 (s, NMe<sub>2</sub>), 70.5 (s, NCH<sub>2</sub>), 129.6 (s, 3,5-C, Mes), 142.7 (s, 2,6-C, Mes) ppm. Another peak corresponds to the NMe2 group merged with the solvent peak. The peaks for 1-C and 4-C of Mes could not be detected from spectral noise. <sup>125</sup>Te{<sup>1</sup>H} NMR(CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 643 (s) ppm.

**[PdCl<sub>2</sub>(PhSeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] (2d):** Complex **2d** was prepared similarly to **2a** by using PhSeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (147 mg, 0.607 mmol) and [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (210 mg, 0.548 mmol) in dichloromethane (20 mL). Recrystallization from dichloromethane yielded orange-red crystals of **2d** (86 mg, 0.205 mmol, 37%), m.p. 140 °C (decomp.). C<sub>11</sub>H<sub>17</sub>Cl<sub>2</sub>NPdSe (419.53): calcd. C 31.49, H 4.08, N 3.34; found C 31.44, H 4.24, N 3.16. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$  in M<sup>-1</sup>cm<sup>-1</sup>) = 240 (20200), 264 (16700), 306 (8300), 400 (1900) nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.05–2.70, 2.89–3.48, 3.70–3.91 (m, 6 H, SeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.65, 2.66, 2.85, 3.01 (each s, 6 H,

NMe<sub>2</sub>), 7.38–7.55 (m, 3 H, 3,4-H, Ph), 7.85–7.92, 7.92–7.98, 8.28– 8.38 (m, 2 H, 2-H, Ph) (in 64:23:13 ratio) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 25.3, 27.2, 27.5 (s, 7:2:1 ratio, –CH<sub>2</sub>–), 30.9, 31.7, 31.8 (s, in 6:2:1 ratio, SeCH<sub>2</sub>), 52.4, 53.9 (each s), 52.5, 52.6 (each s), 52.65, 52.70 (each s) (in 12:5:3 ratio, NMe<sub>2</sub>), 64.16, 64.20, 64.93 (s, in 3:2:10 ratio, NCH<sub>2</sub>), 127.0, 127.3 (s, *i* to Se), 129.7, 129.9, 130.2 (s, in 1:2:7 ratio, *m* to Se), 130.1, 130.3, 130.6 (s, in 6:2:3 ratio, *p* to Se), 132.55, 132.62, 133.22 (s, in 1:2:5 ratio, *o* to Se) ppm. <sup>77</sup>Se{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 339, 344, 348 ppm (2:1:6 ratio).

[PdCl<sub>2</sub>(PhTeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] (2e): Complex 2e was prepared in a manner similar to that of 2a by using PhTeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (298 mg, 1.024 mmol) in benzene/acetone (5 mL; 1:1 v/v) and  $[PdCl_2(PhCN)_2]$  (350 mg, 0.912 mmol) in acetone (20 mL). Recrystallization from dichloromethane yielded red crystals of 2e (150 mg, 0.160 mmol, 35%), m.p. 120 °C (decomp.). C<sub>11</sub>H<sub>17</sub>Cl<sub>2</sub>NPdTe (468.17): calcd. C 28.21, H 3.66, N 2.99; found C 27.93, H 3.67, N 2.81. UV/Vis (MeOH):  $\lambda_{max}$  ( $\varepsilon$  in  $M^{-1}$  cm<sup>-1</sup>) = 332 (5400), 405 (1600) nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.13–2.61 (m, 2 H, -CH<sub>2</sub>-), 2.17, 2.46; 2.48, 2.57; 2.64, 2.69; 2.83, 3.04 (each s, 6 H, NMe<sub>2</sub>) (in 1:10:10:6 ratio), 2.61-3.79 (m, 4 H, TeCH<sub>2</sub>, NCH<sub>2</sub>), 7.32-7.49 (m, 3 H, 3,4-H, Ph), 7.89-7.99; 8.23-8.29 (m, 2 H, 2-H, Ph) (in 7:2 ratio) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 16.7, 17.8, 17.8 (s, in 1:2:2 ratio, -CH<sub>2</sub>-), 26.5, 27.5, 27.9 (s, in 1:2:2 ratio, TeCH<sub>2</sub>), 50.4, 50.8; 51.4, 51.9; 52.6, 54.0 (s, in 2:2:1 ratio, NMe<sub>2</sub>), 64.16, 64.25, 68.61 (s, in 2:2:1 ratio, NCH<sub>2</sub>), 115.23, 115.29, 118.48, (s, in 2:2:1 ratio, *i* to Te), 129.76, 129.88, 130.48 (s, in 2:2:1 *m* to Te), 130.29, 130.37, 130.42 (s, in 1:2:2 ratio, 1 H, p to Te), 136.6, 136.9 (s, in 5:4 ratio, 2 H, o to Te) ppm. <sup>125</sup>Te{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 607, 643, 680 (s, 1:2:2 ratio) ppm. A small peak (<5%) at  $\delta$  = 566 ppm. TG: weight loss 40% corresponds to the formation of Pd<sub>3</sub>Te<sub>2</sub> (calcd. weight loss 40.8%).

[PdCl<sub>2</sub>(o-tolTeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] (2f): Complex 2f was prepared in a way similar to complex 2e by using o-tolTeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (177 mg, 0.576 mmol) in methanol (5 mL) and [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (202 mg, 0.526 mmol) in benzene/acetone (20 mL). Red crystals (107 mg, 0.222 mmol, 42%) were obtained by recrystallization from dichloromethane, m.p. 136 °C (decomp.). C<sub>12</sub>H<sub>19</sub>Cl<sub>2</sub>NPdTe (482.19): calcd. C 29.89, H 3.97, N 2.90; found C 29.23, H 3.72, N 2.71. UV/Vis (MeOH):  $\lambda_{\text{max}}$  ( $\varepsilon$  in  $M^{-1}$  cm<sup>-1</sup>) = 328 (3800), 409 (1000) nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 2.24–2.49, 2.51–2.77, 2.83–3.12, 3.48– 3.76 (m, 6 H, TeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.50, 2.56; 2.63, 2.66; 2.91, 2.95 (s, 6 H, 6:7:8 ratio, NMe<sub>2</sub>), 2.61, 2.62, 2.63 (s, 3 H, tolCH<sub>3</sub>), 7.21-7.49 (m, 3 H, 3,4,5-H, Ph), 8.12; 8.20; 8.97 (dd,  ${}^{3}J_{H,H} = 7.6$  Hz,  ${}^{4}J_{H,H}$ = 1.2 Hz, 1 H, 7:8:9 ratio, 2-H, Ph) ppm.  ${}^{13}C{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 15.8, 17.0, 17.3$  (s, 5:2:4 ratio, TeCH<sub>2</sub>), 26.03, 26.09, 26.87 (s, 2:2:3 ratio, tolCH<sub>3</sub>), 26.09, 27.87, 28.09 (s, 5:3:3 ratio, -CH<sub>2</sub>-), 50.9, 51.1; 51.6, 51.9; 52.9, 53.9 (s, 3:3:5 ratio, NMe<sub>2</sub>), 64.6, 64.7, 69.8 (s, 4:3:5 ratio, NCH<sub>2</sub>), 118.75, 118.83. 121.90 (s, 4:4:5 ratio, *i* to Te) ppm. <sup>125</sup>Te{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 560, 572, 588 (ca. 1:1:1 ratio) ppm. TG weight loss corresponds to the formation of Pd<sub>3</sub>Te<sub>2</sub> (found 38; calcd. for Pd<sub>3</sub>Te<sub>2</sub> 39.7%).

**[Pd(OAc)<sub>2</sub>(PhSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] (3a):** A solution of  $[Pd(OAc)_{2}]_{3}$  (130 mg, 0.193 mmol) in toluene/acetone (25 mL, 3:2 v/v) was added to a solution of Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>SePh (263 mg, 1.150 mmol) in toluene (5 mL). The contents were stirred at 60 °C for 4 h. The solution was passed through a Florosil column to remove any insoluble solid particles. To the clear solution, a few drops of hexane were added whereupon the title complex was precipitated. The latter was filtered, extracted with toluene (3 × 10 mL), concentrated to 5 mL, and a few drops of diethyl ether were added and kept overnight at -5 °C. The recrystallized product was thoroughly washed with diethyl ether and hexane, and was extracted with benz-

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ene  $(3 \times 10 \text{ mL})$ , concentrated to 5 mL, and a few drops of hexane were added and on cooling gave a sticky orange-red solid (107 mg, 0.236 mmol, 32%). C14H21NO4PdSe (452.68): calcd. C 37.20, H 4.68, N 3.09; found C 37.81, H 4.98, N 2.87. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ = 1.87 (s, 3 H, OAc, trans to N), 2.11 (s, 3 H, OAc, trans to Se), 2.42 (dt,  ${}^{2}J_{H,H}$  = 13.2 Hz,  ${}^{3}J_{H,H}$  = 4 Hz, AA'BB' pattern, 2 H, SeCH<sub>2</sub>, another peak of same pattern merged in the base of NMe<sub>2</sub> peak at  $\delta$  = 2.71 ppm), 2.55, 2.67; 2.61, 2.73; (s, 6 H, 1:7 ratio, NMe<sub>2</sub>), 2.82 (ddd,  ${}^{2}J_{H,H}$  = 13.2 Hz,  ${}^{3}J_{H,H}$  = 11.8 Hz,  ${}^{3}J_{H,H}$  = 4 Hz, AA'BB' pattern, 2 H, NCH<sub>2</sub>, another peak of same pattern merged in the base of NMe<sub>2</sub> peak at  $\delta$  = 2.61 ppm) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = 21.6$  (s, COCH<sub>3</sub>, trans to N), 23.8 (s, COCH<sub>3</sub>, trans to Se), 30.8 (s,  ${}^{1}J_{Se,C}$  = 45.3 Hz, SeCH<sub>2</sub>), 31.3 (s, SeCH<sub>2</sub>) (6:1 ratio), 47.2, 49.8; 48.8, 51.1; 50.2, 52.1 (s, 1:5:34 ratio, NMe<sub>2</sub>), 64.9, 65.6 (s, 1:6 ratio, NCH<sub>2</sub>), 125.7 (s, *i* to Se), 128.6, 129.9, 130.0, 130.5, 130.9 (s, m and p to Se), 133.5, 133.9, 134.9 (s, in 37:6:1 ratio, o to Se), 177.4 (s, -COCH<sub>3</sub>), 178.2 (br. s, -COCH<sub>3</sub>) ppm. <sup>77</sup>Se{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 414, 426, 442 (each s, in ca. 5:1:28 ratio) ppm.

[Pd(OAc)<sub>2</sub>(MesSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] (3b): A solution of [Pd(OAc)<sub>2</sub>]<sub>3</sub> (140 mg, 0.208 mmol) in toluene/acetone (25 mL, 3:2 v/v) was added to a solution of MesSeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (178 mg, 0.659 mmol) in toluene (5 mL). The yellow precipitate was heated at 65 °C for 1 h. After allowing it to cool to room temperature, solvents were removed under vacuum, washed thoroughly with hexane and diethyl ether, extracted with toluene  $(8 \times 10 \text{ mL})$ , concentrated to 30 mL and which on slow evaporation at room temperature gave pale yellow crystals of **3b** (100 mg, 0.202 mmol, 32%), m.p. 165 °C (decomp.). C<sub>17</sub>H<sub>27</sub>NO<sub>4</sub>PdSe (494.76): calcd. C 41.27, H 5.50, N 2.83; found C 41.46, H 5.40, N 2.67. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε in  $M^{-1}cm^{-1}$ ) = 268 (13300), 311 (7310), 402 (1640) nm. IR (KBr):  $\tilde{v}$  = 1594, 1618 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.76$  (s, 3 H, OAc, *trans* to N), 2.09 (s, 3 H, OAc, trans to Se), 2.26 (s, 3 H, 4-Me, Mes), 2.33-2.42, 2.59-2.80 (m, 4 H, SeCH<sub>2</sub>CH<sub>2</sub>), 2.69, 2.71 (each s, 6 H, NMe<sub>2</sub>), 2.97-3.28 (br., 6 H, 2,6-Me, Mes), 6.95 (s, 2 H, 3,5-H, Mes) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 21.0 (s, 4-Me, Mes), 21.5 (s, COCH<sub>3</sub>, trans to N), 23.8 (br. s, 2,6-Me, Mes), 24.6 (s, COCH<sub>3</sub>, *trans* to Se), 29.64 (s,  ${}^{1}J_{Se,C}$  = 42.4 Hz, SeCH<sub>2</sub>), 51.4, 51.6 (each s, NMe2), 66.3 (s, NCH2), 126.4 (s, 1-C, Mes), 130.6 (s, 3,5-C, Mes), 140.1 (s, 2,6-C, Mes), 140.6 (s, 4-Me, Mes), 177.7 (s, -COCH<sub>3</sub>), 178.4 (br. s, -COCH<sub>3</sub>) ppm. <sup>77</sup>Se{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ = 339, 345, 361 (each s, in ca. 1:10:2 ratio) ppm.

**[Pd(OAc)<sub>2</sub>(MesTeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)] (3c):** Prepared similarly to that of **3a** using a solution of MesTeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (134 mg, 0.420 mmol) in toluene (5 mL) and a solution of [Pd(OAc)<sub>2</sub>]<sub>3</sub> (90 mg, 0.134 mmol) in toluene/acetone (20 mL, 2:1 v/v) and isolated as a red crystalline solid (yield 60 mg, 0.110 mmol, 28%), m.p. 140 °C (decomp.). C<sub>17</sub>H<sub>27</sub>NO<sub>4</sub>PdTe (543.40): calcd. C 37.57, H 5.01, N 2.58; found C 37.52, H 4.97, N 2.41. IR (KBr):  $\tilde{v} = 1581$ , 1619 cm<sup>-1.</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.92$  (s, 3 H, OAc, *trans* to N), 2.13 (s, 3 H, *trans* to Te), 2.28 (s, 3 H, 4-Me, Mes), 2.25–2.39 (br., 2 H, TeCH<sub>2</sub>), 2.66, 2.67 (each s, 6 H, NMe<sub>2</sub>), 2.88–3.10 (br., 8 H, NCH<sub>2</sub>, 2,6-Me, Mes), 6.99 (s, 2 H, 3,5-H, Mes) ppm.

#### **Coupling Reaction**

General Procedure for Suzuki Cross-Coupling Reaction of Aryl Halides with Arylboronic Acid: A two-necked flask was charged with dioxane (3 mL), aryl halide (1.0 mmol), arylboronic acid (1.3 mmol), base (2.0 mmol), and catalyst (0.1 mol-%). The reactants were heated at 100 °C with stirring for a specified time under a nitrogen atmosphere. After cooling the reaction mixture to room temperature, the contents were diluted with water (5 mL), neutralized with diluted HCl, and extracted with hexane (3×20 mL). The whole organic extract was washed with water (2×15 mL), brine  $(2 \times 10 \text{ mL})$ , dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The residue was characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra. In the case of a poor yield of the product or its contamination with other impurities, the product was subjected to chromatography on a silica-gel column.

DFT Calculations: Full geometry optimization of Se and Te complexes of palladium 2a, 2d, 2e, and 2f has been carried out by applying a DFT functional, namely, BP86. The BP86 is a generalized gradient approximation (GGA) functional that combines Becke's 1988 exchange functional with Perdew's 1986 correlation functional. Gaussian-type atomic basis functions, 6-31G(d,p) for H, C, N, Cl, and Se atoms were considered for all the calculations. However, for Te and Pd atoms, all-electron basis sets 3-21G were applied as more flexible all-electron basis functions are not available in the literature for these two atoms. The quasi-Newton–Raphson-based algorithm was applied to carry out geometry optimization to locate the minimum energy structure in each case. All these calculations were carried out by applying GAMESS suit of ab initio programs.<sup>[38]</sup>

CCDC-1010153 (for  $2a \cdot 0.5$ CH<sub>2</sub>Cl<sub>2</sub>), 1010154 (for 2b), 1010155 (for 2d), 1010156 (for 2e), 1010157 (for 2f), 1010158 (for  $3b \cdot 1.5$ H<sub>2</sub>O), and -1010159 (for 3b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data\_request/cif.

**Supporting Information** (see footnote on the first page of this article): It contains details of general procedures of the experiments; crystallographic and structure-refinement data of all complexes; optimization of reaction parameters of Suzuki reactions; NMR spectra; ORTEP diagrams; optimized structures calculated by applying DFT; and single-crystal X-ray diffraction studies.

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# Seleno- and Telluroether as Ligands

Structural Variation in  $[PdX_2{RE(CH_2)}_nNMe_2]$  (E = Se, Te; X = Cl, OAc) Complexes: Experimental Results, Computational Analysis, and Catalytic Activity in Suzuki Coupling Reactions

**Keywords:** Palladium / Cross-coupling / C– C coupling / Chalcogens / Density functional calculations



Complexes  $[PdX_2{RE(CH_2)_nNMe_2}]_m$  (X = Cl, OAc) exist in one monomeric and two dimeric forms in solution depending on E and *n*. Molecular structures were established by X-ray structural analyses and supported by DFT calculations. These complexes act as catalyst in Suzuki coupling reactions.