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Chalcogen-Dependent Palladation at the Benzyl Carbon of 2,3-Bis[(phenylchalcogeno)methyl]quinoxaline: Palladium Complexes Catalyzing Suzuki–Miyaura Coupling via Palladium–Chalcogen Nanoparticles

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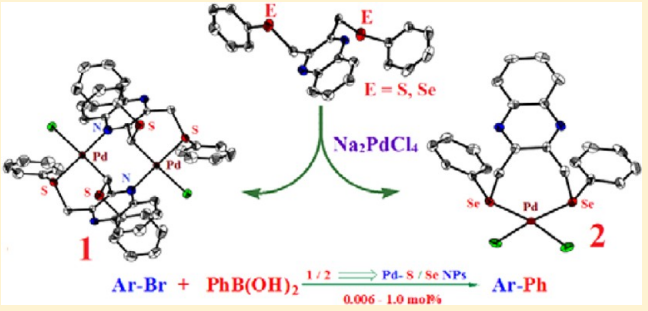
Supporting Information

ABSTRACT: The reaction of PhS^-/$PhSe^-$ with 2,3-bis(bromomethyl)quinoxaline has resulted in 2,3-bis[(phenylthio/-seleno)methyl]quinoxaline (**L1**/**L2**). They react with Na_2PdCl_4, resulting in $[Pd_2(\mathbf{L1}-H)_2Cl_2]$ (**1**)/$[Pd\mathbf{L2}Cl_2]$ (**2**). External base-free activation of the benzyl group's $C(sp^3)$–H results in palladation of **L1**, forming palladacycle **1**, whereas **L2** forms a seven-membered chelate ring with Pd(II), resulting in **2**. **L1**, **L2**, **1**, and **2** have been characterized by IR, multinuclear NMR, mass spectrometry, and single-crystal X-ray diffraction. In the case of **1** bond lengths (Å) are Pd–C = 2.001(9), Pd–N = 2.048(8), and Pd–S = 2.259(2) Å. The Pd–Se bond length in complex **2** is 2.3924(15)–2.3991(15) Å. Complexes **1**/**2** were explored in the catalyzed Suzuki–Miyaura coupling reactions of several aryl bromides (including deactivated ones). The palladacycle **1** shows better catalytic efficiency than complex **2**, as its lower reaction time and catalyst loading (up to 0.006 mol %) are sufficient for significantly good conversions. The catalysis appears to be occurring via *in situ* generated nanoparticles (size <2 nm) composed of palladium and sulfur or selenium and protected by **L1** or **L2**, as nanoparticles after isolation also show catalytic activity. The results of a two-phase test suggest that the catalysis is cocktail type (i.e., homogeneous and heterogeneous in parts).



INTRODUCTION

The quinoxaline ring is present in dyes,[1] pharmaceuticals,[2,3] and electrical/photochemical materials.[4−9] It is also present in various antibiotics such as echinomycin, levomycin, and actinoleutin.[10,11] The quinoxaline-based ligands have not been explored so far for the designing of Pd complexes catalytically active for C–C coupling reactions such as Suzuki–Miyaura coupling, which is one of the most widely used processes for the synthesis of biaryls, important intermediates in organic synthesis, and recurring functional groups in natural products.[12] Phosphorus ligand based Pd-catalysts commonly used for such reactions are often air/moisture sensitive, and therefore, catalysis under phosphine-free conditions is of high importance currently. The palladacycles of organochalcogen ligands, Pd(II) complexes of chalcogenated Schiff bases and some other S- or Se-containing ligands, have emerged[13−16] as a family of air-stable, moisture-insensitive, and efficient catalysts, which can carry out phosphine-free Suzuki–Miyaura coupling. Chalcogenated half-pincer and pincer ligands are particularly attractive for designing catalysts for phosphine-free Heck or Suzuki–Miyaura coupling. Some important ones among them have been synthesized from 2-(chloromethyl)pyridine,[17] 2,6-bis(bromomethyl)benzene,[15e,18] and 2,6-bis(chloromethyl)pyridine.[19] Considering the immense potential of chalcogenated nitrogen heterocycles as building blocks of phosphine-free Pd catalysts, an attempt to design chalcogenated quinoxaline-based palladium(II) catalysts for C–C coupling has been envisaged worth exploring. The chalcogenation of 2,3-bis(bromomethyl)quinoxaline can give ligands that may be competitive with chalogenated pyridines and related systems for designing Pd(II) catalysts. In this paper we report seleno- and thio-ether type ligands (**L1** and **L2**), synthesized from 2,3-bis(bromomethyl)quinoxaline (Scheme 1). The resulting multidentate ligands with four potential coordination sites (two N and two S/Se) may offer some additional advantages, because it is known for transition-metal complexes that an additional donor site in the ligand can act as a stabilizing group during the course of a metal-mediated reaction, which in turn may improve the catalytic efficiency of the complex.[20] Except silver(I)[21] and copper(I)[22] complexes of some quinoxaline derivatives analogous to **L1** (having different substituents in place of Ph on S) nothing else is known about ligation of chalcogeneted quinoxaline-based ligands and their applications. It was therefore thought worthwhile to explore the chemistry of **L1** and **L2**. Palladium(II) forms a seven-membered chelate ring

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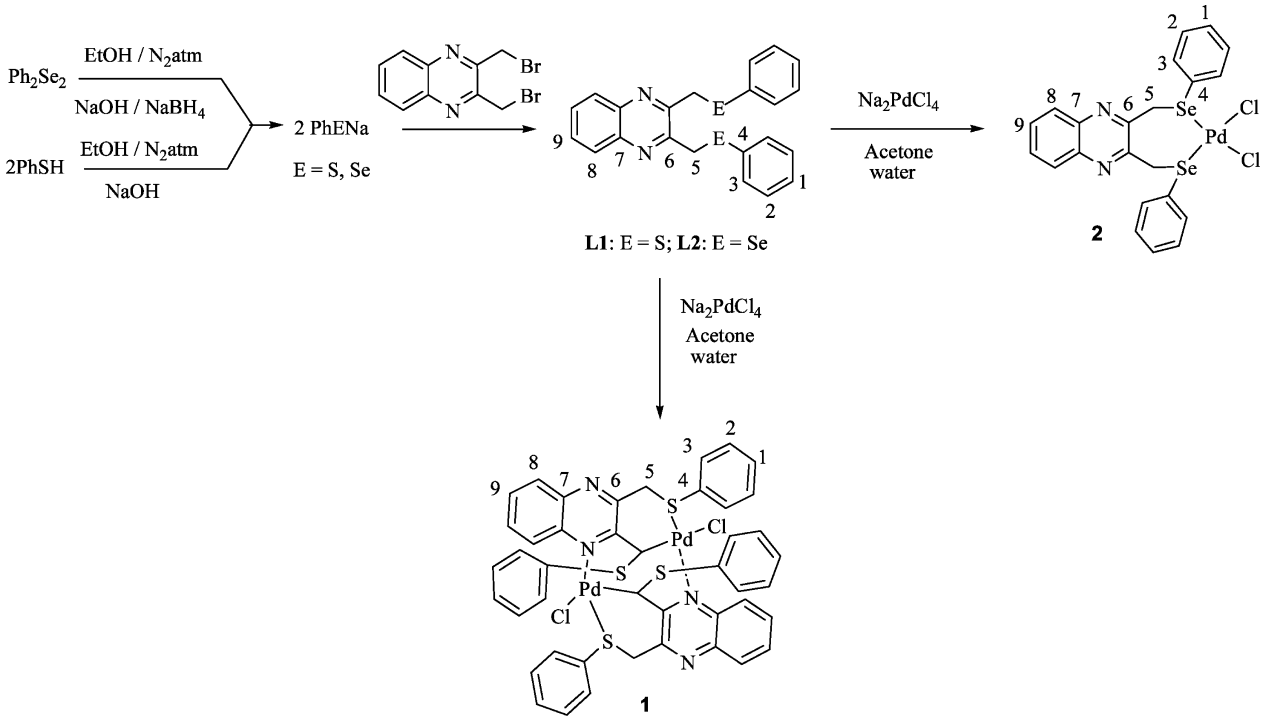
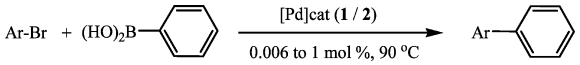
Scheme 1. Synthesis of Ligands and Pd(II) Complexes



with a selenated derivative of quinoxaline (**L2**). Palladacycle **1** is formed via an external base-free deprotonation of the $C_{(sp3)}$–H bond of the benzyl group of **L1**. Only a limited number of stable palladacycles having a Pd(II)–$C_{(sp3)}$ bond[23,24] are known, but none of them have been synthesized using Na_2PdCl_4 as a source of Pd and without using an external base. The applications of these Pd(II) complexes (**1** and **2**) in the Suzuki–Miyaura coupling (Scheme 2) have been explored

Scheme 2. Suzuki–Miyaura Coupling Reaction



and found promising. It appears that catalysis with **1** and **2** takes place via formation of nanoparticles (NPs) made of palladium and sulfur or selenium and protected by **L1**/**L2**. The role of NPs in a few Suzuki–Miyaura reactions catalyzed with palladium(II) complexes of chalogenated ligands has been reported recently.[13f,h,14g] The present results are thus important, as they would further strengthen the understanding of Suzuki–Miyaura coupling catalyzed with palladium–organochalcogen ligand complexes, such as the role of palladium–chalcogen NPs. All these results are reported in the present paper.

EXPERIMENTAL SECTION

Physical Measurements. The ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, and 57.24 MHz, respectively, with chemical shifts reported in ppm relative to normal standards. Yields refer to isolated yields of compounds that have a purity of ≥95%. All reactions were carried out in glassware dried in an oven under ambient conditions, except the synthesis of **L1** and **L2**. Commercial nitrogen gas was used after passing it successively through traps containing solutions of alkaline anthraquinone, sodium dithionite, alkaline pyrogallol, concentrated H_2SO_4, and KOH pellets. A nitrogen atmosphere, if required, was created using Schlenk techniques. Single-crystal structure data were collected with a Bruker AXS SMART-APEX CCD diffractometer using Mo Kα radiation (0.71073 Å) at 298(2) K. The software SADABS was used for absorption correction (if needed) and SHELXTL for space group, structure determination, and refinements.[25,26] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in idealized positions, and a riding model was used for the refinement. The least-squares refinement cycles on F^2 were performed until the model converged. The melting points were determined in an open capillary and reported as such. IR spectra in the range 4000–400 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out with a Perkin-Elmer 2400 Series II C, H, N analyzer. High-resolution mass spectral (HR-MS) measurements were performed with electron spray ionization (10 eV, 180 °C source temperature) and using sodium formate as a calibrant on a Bruker MIcroTOF-Q II, taking samples in CH_3CN.

TEM studies were carried out with a Technai G^2 20 electron microscope operated at 200 kV. The specimens for TEM were prepared by dispersing the powdered sample in chloroform by ultrasonic treatment, dropping the slurry onto a porous carbon film supported on a copper grid, and then drying it in air. The phase morphologies of the samples were observed by using a Carl Zeiss EVO5O scanning electron microscope (SEM). Samples were mounted on a circular metallic sample holder with a sticky carbon tape. Elemental compositions of nanoparticles on SEM were analyzed by an EDX system, model Quan Tax 200, which is based on the SDD technology and provides an energy resolution of 127 eV at Mn Kα. The samples were scanned in different regions in order to minimize the error in the analysis for evaluating the morphological parameters.

Chemicals and Reagents. Thiophenol, diphenyldiselenide, sodium borohydride, 2,3-bis(bromomethyl)quinoxaline, disodium tetrachloropalladate, and all other aryl bromides procured from Sigma-Aldrich (USA) were used as received. All the solvents were dried and distilled before use by known standard procedures.[27]

Synthesis of Ligand L1. Thiophenol (0.20 mL, 2.0 mmol) was added to a refluxing solution of sodium hydroxide (0.16 g, 4.0 mmol) made in 30 mL of EtOH under a nitrogen atmosphere, and the mixture was refluxed further for 1 h. 2,3-Bis(bromomethyl)quinoxaline (0.32 g, 1.0 mmol) dissolved in 20 mL of EtOH was added, and the

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reaction mixture refluxed again for 3 h. Thereafter the reaction mixture was stirred overnight at room temperature. It was poured into water (30 mL). The ligand **L1** was extracted with chloroform (4 × 25 mL). The extract was washed with water (3 × 40 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated off under reduced pressure on a rotary evaporator to get an off-white product, which on recrystallization from an EtOH and dichloromethane mixture (1:1) gave light yellow colored single crystals of **L1**. Yield: 0.33 g (88%); mp 110 °C. Anal. Found: C, 70.52; H, 4.91; N, 7.46. Calcd for $C_{22}H_{18}N_2S_2$: C, 70.55; H, 4.84; N, 7.48. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ (ppm), 4.57 (s, 4H, H_5), 7.17−7.26 (m, 6H, H_1, H_2), 7.36−7.38 (m, 4H, H_3), 7.67−7.70 (m, 2H, H_9), 7.92−7.96 (m, 2H, H_8). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ (ppm), 39.0 (C_5), 127.1 (C_1), 128.6 (C_2), 128.9 (C_9), 129.7 (C_3), 130.9 (C_8), 134.7 (C_4), 140.9 (C_6), 151.5 (C_7). IR (cm^{-1}): 474 (m), 687 (s), 739 [s; C−H (aromatic) bending], 768 (s), 1087 (m), 1358 (m), 1390 (m), 1478 [s; $\nu_{C-C\ (aromatic)}$], 1575 [m; $\nu_{C=N}$], 2936, 2979 [s; $\nu_{C-H\ (aliphatic)}$], 3057 [m; $\nu_{C-H\ (aromatic)}$]. HR-MS $[M + H]^+$ (m/z): 375.0970; calcd value for $C_{22}H_{18}N_2S_2H$ 375.0984 (δ 3.8 ppm).

Synthesis of Ligand L2. Diphenyldiselenide (0.62 g, 2.0 mmol) dissolved in 30 mL of EtOH was refluxed with stirring under a nitrogen atmosphere and treated with a saturated solution of sodium borohydride made in 5 mL of aqueous NaOH (5%) dropwise until it became colorless due to the formation of PhSeNa. 2,3-Bis-(bromomethyl)quinoxaline (0.63 g, 2.0 mmol) dissolved in 10 mL of EtOH was added to the colorless solution with constant stirring, and the mixture refluxed further with stirring for 3 h. Thereafter the reaction mixture was stirred overnight at room temperature. It was poured into water (30 mL). **L2** was extracted with chloroform (4 × 25 mL). The extract was washed with water (3 × 40 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated off under reduced pressure on a rotary evaporator to get a light yellow solid, which on recrystallization with an EtOH and dichloromethane mixture (1:1), gave pale yellow colored single crystals of **L2**. Yield: 0.75 g (80%); mp 105 °C. Anal. Found: C, 56.40; H, 3.89; N, 5.94. Calcd for $C_{22}H_{18}N_2Se_2$: C, 56.42; H, 3.87; N, 5.98. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ (ppm), 4.44 (s, 4H, H_5), 7.15−7.25 (m, 6H, H_1, H_2), 7.42−7.45 (m, 4H, H_3), 7.62−7.66 (m, 2H, H_9), 7.84−7.88 (m, 2H, H_8). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ (ppm), 31.3 (C_5), 127.8 (C_1), 128.4 (C_2), 129.0 (C_9), 129.5 (C_3), 134.2 (C_4, C_8), 140.8 (C_6), 152.5 (C_7). ^{77}Se{^{1}H} NMR ($CDCl_3$, 25 °C, Me_2Se): δ (ppm), 354.0. IR (cm^{-1}): 463 (s), 607 (m), 687 (s), 733 [s; C−H (aromatic) bending], 764 (s), 803 (m), 1013 (m), 1065 (m), 1127 (m), 1173 (m), 1317 (m), 1355 (m), 1435 (s), 1475 [s; $\nu_{C-C\ (aromatic)}$], 1565 [m; $\nu_{C=N}$], 2943 (m), 2993 [s; $\nu_{C-H\ (aliphatic)}$], 3056 [m; $\nu_{C-H\ (aromatic)}$]. HR-MS $[M + Na]^+$ (m/z): 492.9707; calcd value for $C_{22}H_{18}N_2Se_2Na$ 492.9696 (δ 2.1 ppm).

Synthesis of Palladium Complexes 1 and 2. A solution of Na_2PdCl_4 (0.029 g, 0.1 mmol) made in 5 mL of water was mixed with **L1** (0.037 g, 0.1 mmol) or **L2** (0.047 g, 0.1 mmol) dissolved in acetone (10 mL) with vigorous stirring. An orange precipitate was obtained instantaneously, which was filtered, washed with water, and dried. Single crystals were grown from a 1:1 mixture of chloroform and hexane.

1: Yield: 0.044 g (84%); mp 200 °C (dec). Anal. Found: C, 51.21; H, 3.35; N, 5.40. Calcd for $C_{44}H_{34}Cl_2N_4Pd_2S_4$: C, 51.27; H, 3.32; N, 5.44. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ (ppm), 4.06 (s, 2H, H_5, CH), 4.16−4.27 (m, 4H, H_5, CH_2), 7.28−7.40 (m, 12H, H_1, H_2), 7.90 (d, $^3J_{H-H}$ = 9 Hz 4H, H_8), 8.10−8.27 (m, 2H, H_3), 8.17 (m, 4H, H_9). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ (ppm), 41.1 (CH_2, C_5), 60.5 (CH, C_5), 128.3 (C_1, C_2), 129.3 (C_9), 130.2 (C_3), 130.8 (C_8), 140.9 (C_6), 142.1 (C_4), 151.0 (C_7). IR (cm^{-1}): 476 (b), 689 (s), 748 [s; $\nu_{C-H\ (aromatic)}$], 1022 (b), 1124 (m), 1226 (m), 1330 (s), 1438 [s; $\nu_{C-C\ (aromatic)}$], 1477 (s), 1625 [m; $\nu_{C=N}$], 2924 [s, $\nu_{C-H\ (aliphatic)}$], 3056 [m; $\nu_{C-H\ (aromatic)}$]. HR-MS [M − Cl] (m/z) 992.9451; calcd value for $C_{44}H_{34}N_4S_4Pd_2Cl$ 992.9429 (δ 2.5 ppm).

2: Yield: 0.056 g (87%); mp 165 °C (dec). Anal. Found: C, 40.90; H, 2.88; N, 4.30. Calcd for $C_{22}H_{18}Cl_2N_2PdSe_2$: C, 40.93; H, 2.81; N, 4.34. ^{1}H NMR (DMSO-d_6, 25 °C, TMS): δ (ppm), 4.64 (s, 4H, H_5), 7.25 (s, 6H, H_1, H_2), 7.50 (s, 4H, H_3), 7.76−7.86 (m, 2H, H_9), 7.95 (m, 2H, H_8). ^{13}C{^{1}H} NMR (DMSO-d_6, 25 °C, TMS): δ (ppm), 30.5 (C_5), 127.4 (C_1), 128.1 (C_9), 129.2 (C_2), 129.5 (C_4), 129.9 (C_8), 132.8 (C_3), 140.0 (C_6), 152.7 (C_7). ^{77}Se{^{1}H} NMR (DMSO-d_6, 25 °C, Me_2Se): δ (ppm), 334.3. IR (cm^{-1}): 464 (m), 687 (s), 743 (s), 1003 (b), 1127 (b), 1220 (b), 1327 (m), 1437 (s), 1478 [s; $\nu_{C-C\ (aromatic)}$], 1569 (b), 1651 [b; $\nu_{C=N}$], 2925 [b; $\nu_{C-H\ (aliphatic)}$], 3056 [m; $\nu_{C-H\ (aromatic)}$]. HR-MS: M = [(**L2**)$_2$Pd] (m/z) 1045.8598, calcd value for $C_{44}H_{36}N_4PdSe_4$ 1045.8664 (δ 5.4 ppm).

Procedure for the Suzuki−Miyaura Coupling Reaction. An oven-dried flask was charged with aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), DMF/H_2O (3.0/2.0 mL), and catalyst **1** (1.0 to 0.006 mol %) or **2** (1 mol %). The flask was placed on an oil bath at 90 °C under aerobic conditions, and the reaction mixture was stirred. The reaction monitored by TLC was carried out until maximum conversion of aryl bromide to product occurred. The mixture was extracted with diethyl ether, washed with water, and dried over anhydrous Na_2SO_4. The solvent of the extract was removed with a rotary evaporator to obtain the product, which was purified by column chromatography on silica gel. The products were authenticated with ^{1}H and ^{13}C{^{1}H} NMR spectra.

Isolation of Nanoparticles Generated from 1 and 2. A mixture of Pd(II) complex **1**/**2** (0.5 mmol), phenylboronic acid (1.5 mmol), 4-bromobenzonitrile (1.0 mmol), and K_2CO_3 (2.0 mmol) in DMF (4.0 mL) and water (4.0 mL) was heated at 100 °C for 1.5 h and then cooled to room temperature. The solvent was decanted, and the black residue (NPs) was thoroughly washed with a water/acetone mixture (1:3) and dried *in vacuo*. Yield: **1**, 0.23 g; **2**, 0.14 g. The NPs were characterized by SEM, SEM-EDX, TEM, and TEM-EDX.

Procedure for the Suzuki−Miyaura Coupling Reaction Catalyzed by NPs Generated from 1 and 2. This was similar to the one used for complexes **1** and **2** except that the reaction time was 3 h and NPs (10 and 50 mg of those obtained from **1** and **2**, respectively) generated from each complex were used in their place.

Hg Poisoning Test. An excess of Hg (Hg:Pd, 500:1) was taken in the reaction flask, and thereafter the coupling reactions were carried out in the same flask. For catalyst **1** coupling of 4-bromoanisole was carried out under optimum conditions, whereas in the case of **2** the substrate taken was 4-bromobenzaldehyde. The coupling products were not obtained after 3 h.

PPh_3 Test. This was carried in a manner similar to that of the Hg poisoning test using identical substrates except the amount of PPh_3 was taken as 1 mmol. Even after 3 h of reaction no cross-coupled product was obtained.

Two-Phase Test. A mixture of 4-bromoacetophenone-immobilized silica (0.20 g) prepared by standard procedure[28] (details in the Supporting Information), phenylboronic acid (0.36 g, 3 mmol), 4-bromoacetophenone (0.20 g, 1 mmol), and K_2CO_3 (0.56 g, 4 mmol) was heated at 90 °C for 12 h in a DMF/water (8 mL/4 mL) mixture. The resulting mixture was cooled and filtered through a G-4 crucible. The residue was washed with 20 mL of H_2O followed by diethyl ether (50 mL). The filtrate and washings were collected together and mixed with 50 mL of water. The resulting mixture was extracted with diethyl ether (50 mL). The solvent of the extract was evaporated off on a rotary evaporator, and the residue subjected to ^{1}H NMR. The solid residue was hydrolyzed with KOH (1.68 g dissolved in 10 mL of EtOH + 5 mL of H_2O) at 90 °C for 3 days. The resulting solution was neutralized with aqueous 20% (v/v) HCl, extracted with dichloromethane followed by ethyl acetate. The solvent of the combined extract was evaporated off, and the resulting residue was analyzed with ^{1}H NMR.

RESULTS AND DISCUSSIONS

The syntheses of **L1** and **L2** and their complexes **1** and **2** are summarized in Scheme 1. They are stable under ambient conditions and can be stored for several months. The solubility of both ligands was found to be good in common organic solvents, viz., chloroform, methanol, dichloromethane, and acetone. The complexes **1** and **2** have good solubility in chloroform and dichloromethane but moderate only in

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acetonitrile. **L1**, **L2**, and **2** have good solubility in DMSO. Complex **1** is moderately soluble in DMSO, and the stability of the solution is poor. Complex **1** is formed via deprotonation of the benzyl (sp^3) group, which results in Pd−C bond formation. The examples of palladation via activation of the C(sp^3)−H bond of the benzyl group without externally added base are few. The source of Pd is $Pd(OOCCH_3)_2$ in those cases reported[23] so far. There is no example to our knowledge in which such palladation has been carried out by $PdCl_2$ or Na_2PdCl_4 in the absence of any external base.[24] Thus this is the first example of activation of C(sp^3)−H by Na_2PdCl_4, in which the nitrogen of quinoxaline acts as an internal base. This is consistent with the interaction between nitrogen and benzylic hydrogen in the structure of **1** (Figure 5). Further the reaction mixture was not

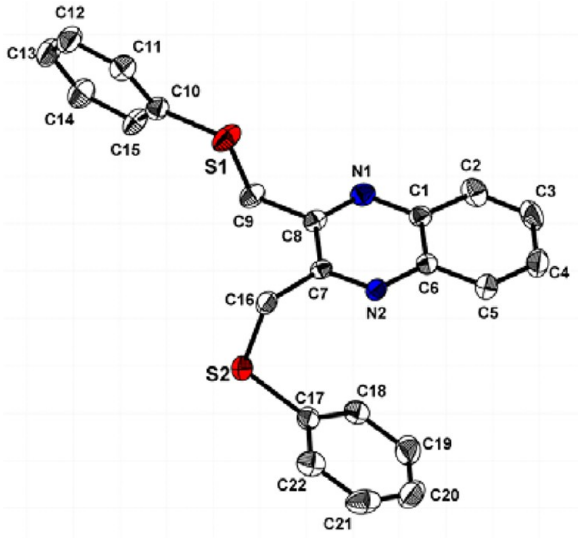

Figure 1. ORTEP diagram of **L1** with 30% probability ellipsoids; H atoms are omitted for clarity. Bond lengths (Å): S(1)−C(10) 1.757(4); S(1)−C(9) 1.802(4); S(2)−C(17) 1.774(4); S(2)−C(16) 1.823(4). Bond angles (deg): C(10)−S(1)−C(9) 103.5(2); C(17)−S(2)−C(16) 100.65(18).

found to be basic, ruling out the possibility of base effect by any component of the reaction mixture also. This kind of activation in **L2** does not occur, and due to the large size of Se, the seven-membered chelate is easily stabilized, as observed earlier also.[29]

NMR Spectra. The ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectra of **L1** and **L2** as well as their complexes **1** and **2** were found to be in agreement with their molecular structures depicted in Scheme 1. They are given in the Supporting Information (Figures S1−S10). In the ^1H NMR spectra of **L1** and **L2**, signals of H_5 ($-SCH_2/-SeCH_2$) appearing at 4.57 and 4.44 ppm, respectively, are at 0.4 ppm lower frequency with respect to those of 2,3-bis(bromomethyl)quinoxaline. The signal in the $^{77}Se\{^1H\}$ NMR spectrum of **L2** (at 354 ppm) is at 108 ppm lower frequency with respect to that of diphenyldiselenide (462 ppm). Further there is one signal in the $^{77}Se\{^1H\}$ NMR spectrum of each **L2** and **2**, implying the equivalence of two Se atoms in solution. The ^1H NMR spectrum of **1** has two benzyl CH_2 signals at 4.06 and 4.16−4.27 ppm, as expected. Both of them are at lower frequency relative to that of free **L1**. This may be due to the influence of the 4d-electron cloud of palladium on hydrogen. In the $^{13}C\{^1H\}$ NMR spectrum of **1** two benzyl signals at 41.14 and 60.50 ppm have been observed. The one at higher frequency

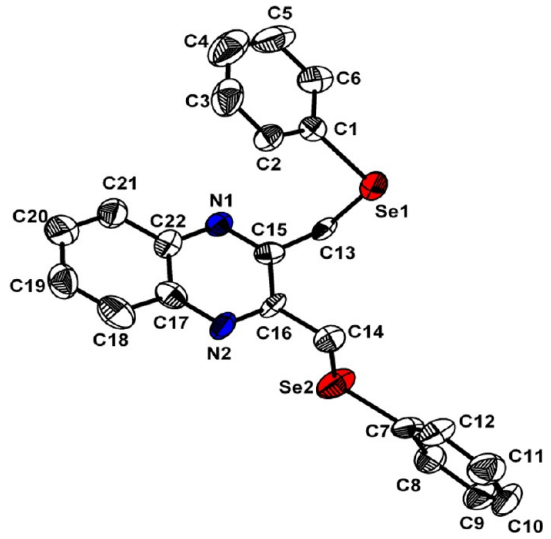

Figure 2. ORTEP diagram of **L2** with 30% thermal probability ellipsoids; H atoms are omitted for clarity. Bond lengths (Å): Se(1)−C(1) 1.926(8); Se(1)−C(13) 1.982(7); Se(2)−C(7) 1.896(8); Se(2)−C(14) 1.948(8). Bond angles (deg): C(1)−Se(1)−C(13) 97.6(3); C(7)−Se(2)−C(14) 102.0(3).

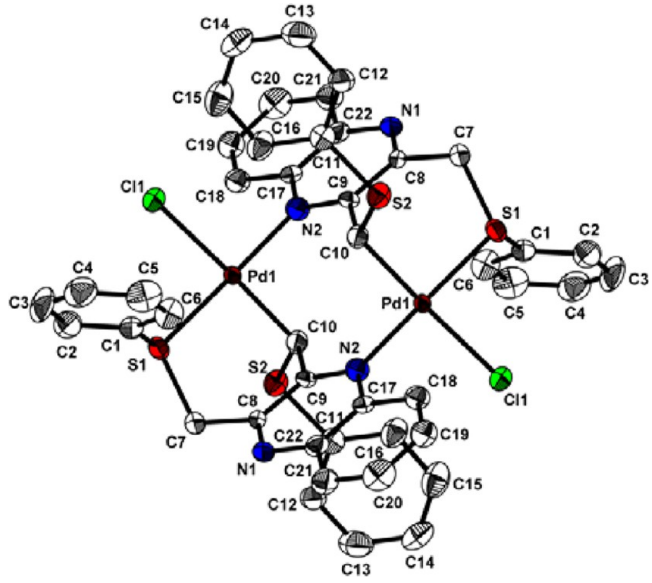

Figure 3. ORTEP diagram of **1** with 30% thermal probability ellipsoids; H atoms and $CHCl_3$ are omitted for clarity. Bond lengths (Å): C(10)−Pd(1) 2.001(9); Pd(1)−S(1) 2.259(2); N(2)−Pd(1) 2.048(8); Cl(1)−Pd(1) 2.350(3) C(1)−S(1) 1.758(11); C(11)−S(2) 1.740(10); C(7)−S(1) 1.802(9); C(10)−S(2) 1.780(10). Bond angles (deg): C(10)−Pd(1)−N(2) 89.3(3); C(10)−Pd(1)−S(1) 91.3(3); N(2)−Pd(1)−S(1) 177.4(2); C(10)−Pd(1)−Cl(1) 1178.0(3); N(2)−Pd(1)−Cl(1) 92.7(2); S(1)−Pd(1)−Cl(1) 86.70(9).

arises from the carbon bonded to palladium. These observations imply that in the solution structure also the Pd−C bond exists as observed in the single crystal of **1**. NMR spectra of crude and single crystals of **1** are not different, implying that **1** is not formed from [Pd**L1**Cl_2] during crystallization. There is only one signal in the $^{77}Se\{^1H\}$ NMR spectrum of **2**, and it is at lower frequency (19.7 ppm) with respect to that of free **L2**. This is consistent with earlier report that on formation of a six-membered chelate ring by a Se ligand such a signal may show a shift of small magnitude to lower as

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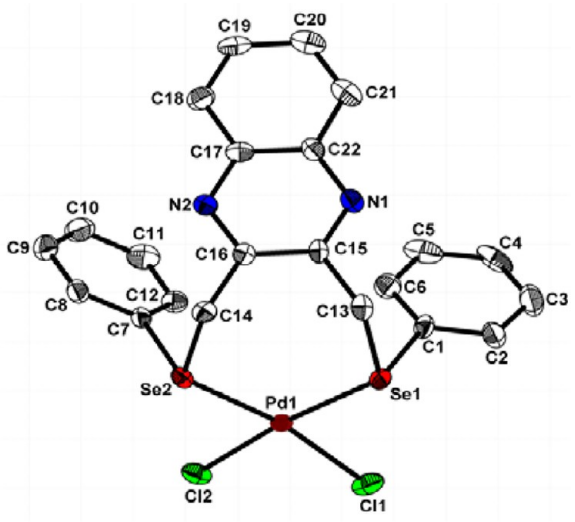

Figure 4. ORTEP diagram of **2** with 30% thermal probability ellipsoids; H atoms are omitted for clarity. Bond lengths (Å): Cl(1)−Pd(1) 2.318(3); Cl(2)−Pd(1) 2.317(3); Pd(1)−Se(1) 2.3924(15); Pd(1)−Se(2) 2.3991(15); C(1)−Se(1) 1.919(12); C(7)−Se(2) 1.938(11); C(13)−Se(1) 1.986(11); C(14)−Se(2) 1.981(11). Bond angles (deg): Cl(2)−Pd(1)−Cl(1) 90.81(14); Cl(2)−Pd(1)−Se(1) 172.25(10); Cl(1)−Pd(1)−Se(1) 81.46(11); Cl(2)−Pd(1)−Se(2) 82.66(10); Cl(1)−Pd(1)−Se(2) 169.95(10); Se(1)−Pd(1)−Se(2) 105.08(5).

well as higher frequency.[14f] The crystal structure of **2** indicates that both Se donor sites of **L2** are engaged in coordination with Pd in an almost equivalent manner, supporting the occurrence of a single signal in the $^{77}Se\{^{1}H\}$ NMR. In the case of **2** the chelate ring is seven membered, and therefore shifting to lower frequency of the signal is not surprising. The signal of C_5 in the $^{13}C\{^{1}H\}$ NMR spectrum of **2** appears somewhat shifted to lower frequency relative to that of free **L2**. However the small higher frequency shift in the H_5 signal in the ^{1}H NMR spectrum is consistent with the formation of a Pd−Se bond in **2**, as shown by the single-crystal structure. The signal of C_4(Se) in the $^{13}C\{^{1}H\}$ NMR spectrum of **2** also appears at a lower frequency (4.6 ppm) in comparison to that of free **L2**.

The high-resolution mass spectra of both the ligands and complex **1** authenticate them. The spectrum of complex **2** has one peak at $m/z \approx 1046$ (Supporting Information; Figures S15 and S16), which may correspond to $[Pd(\mathbf{L2})_2]^{+\bullet}$. Thus complex $[Pd(\mathbf{L2})_2](ClO_4)_2$ was prepared and authenticated by NMR. In its $^{77}Se\{^{1}H\}$ (Supporting Information; Figure S11), only one signal, at 324.2 ppm, appears. It is shielded nearly 10 ppm with respect to that of **2**. In the mass spectrum of complex $[Pd(\mathbf{L2})_2](ClO_4)_2$, two peaks, at $m/z \approx 1046$ and 574, have been observed (Supporting Information; Figure S17). The first one probably arises from $[Pd(\mathbf{L2})_2]^{+\bullet}$ and the second one from $[Pd\mathbf{L2}]^{+\bullet}$, formed by the fragmentation of the first. Thus $[Pd(\mathbf{L2})_2]^{2+}$ and $[Pd(\mathbf{L2})]^{2+}$ are easily converted into each other in the mass spectrometer. Further the MS/MS experiment (Supporting Information; Figures S18 and S19) on the peak at $m/z \approx 1046$ of **2** gives a peak at $m/z \approx 574$, supporting the above inference and formulation of complex **2**.

Crystal Structures. The crystal structures of **L1**, **L2**, **1**, and **2** have been solved. The crystal data and refinement parameters are given in the Supporting Information (Table S1). The ORTEP diagrams of **L1**, **L2**, **1**, and **2** are given in Figures 1 to 4 with selected bond lengths and angles. More bond angles and lengths are given in the Supporting Information (Tables S2−S5). In **L1** the S−C (aryl) bond [1.757(4) Å] is somewhat shorter than the S−C (alkyl) bond [1.802(4) Å]. The Se−C (aryl) bond [1.896(8) Å] in **L2** is also shorter than the Se−C (alkyl) bond [1.948(8) Å]. However all these bond lengths are consistent with the reported values.[14d,29] In **1** the Pd−C and Pd−S bond lengths of 2.001(9) and 2.259(2) Å, respectively, are consistent with the values 2.190(9)[24a] and 2.2644(11) Å,[14d] respectively, reported earlier. The Pd−Cl bond length in **1**, 2.350(3) Å, is also not much different from the earlier reported value of 2.3091(11) Å.[14d] Similarly the Pd−N bond length of 2.048(8) Å is consistent with the value of ∼2.0 Å reported for Pd complexes of tridentate selenated Schiff bases.[14d−g]

In complex **2** the Se−C (aryl) and Se−C (alkyl) bond lengths of 1.938(11) and 1.981(11) Å, respectively, are longer than the corresponding bond lengths of **L2**. This may be due to coordination of the Se atom with Pd. The two Pd−Se bond lengths, 2.3924(15) and 2.3991(15) Å, of **2** are similar but differ from the values 2.4567(15) and 2.4627(14) Å reported for the Pd(II) complex of the bis-pincer ligand 1,2,4,5-tetrakis[(phenyseleno)methyl]benzene,[29] which also has a seven-membered chelate ring. The Pd−Cl bond length of 2.318(3) Å in **2** is consistent with the value, 2.325(16) Å, reported in the case of a selenated palladacycle.[13h] The crystals of complexes **1** and **2** have N(1)···H(7A)−C(7) (2.742 Å) and Cl···H(3)−C(3) (aromatic) (2.797 Å) secondary interactions,

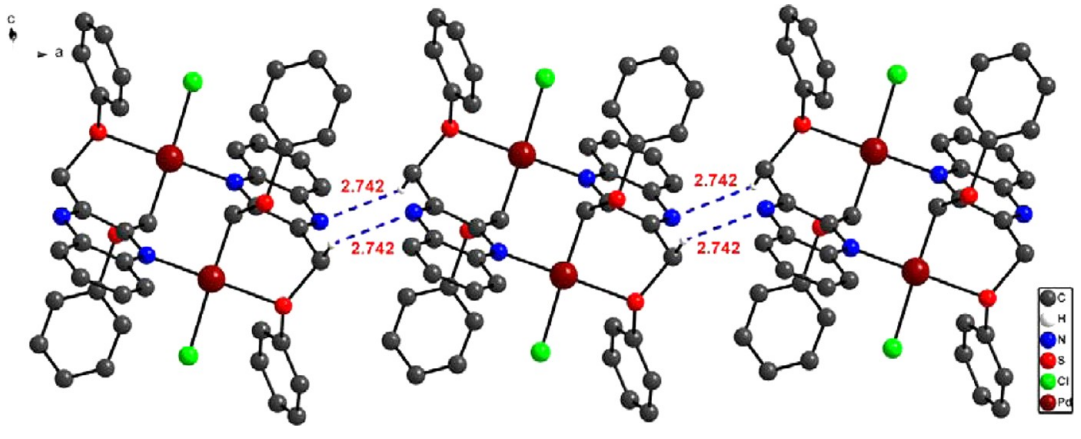

Figure 5. C(7)−H(7A)···N(1) interactions in **1**.

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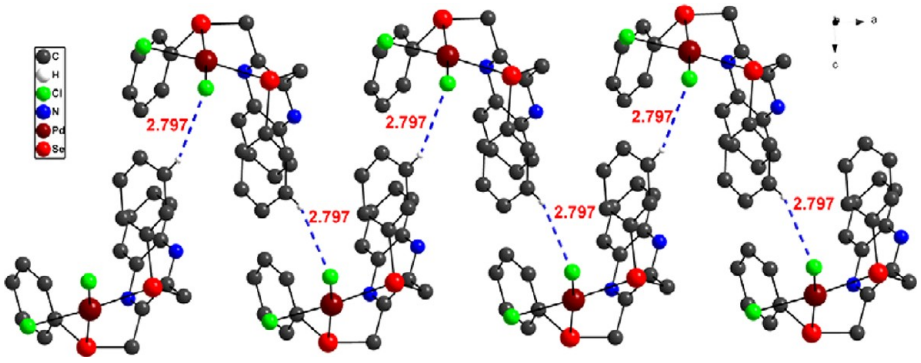

Figure 6. Helical chain of **2** arising by an (aromatic) C(3)−H(3)···Cl(1) interaction.

as shown in Figures 5 and 6, which result in the formation of a helical chain in the case of **2**.

Suzuki−Miyaura Coupling Reaction Catalyzed by 1 and 2. The complexes **1** and **2** have been explored as catalysts for the Suzuki−Miyaura C−C coupling reactions of several aryl bromides. To optimize the reaction conditions, the coupling reaction of 4-bromoanisole with phenylboronic acid in the presence of **1** was studied. K_2CO_3 has been found to be a better base for the coupling reaction than cesium carbonate, sodium acetate, or sodium methoxide, as lower yields were obtained with them under similar reaction conditions (Table 1). Further

Table 1. Effect of Base on the Suzuki−Miyaura Coupling[a,b]

entry no.	base	yield[c] (%)
1	K_2CO_3	88
2	Cs_2CO_3	47
3	CH_3COONa	28
4	CH_3ONa	16

[a]Reaction conditions: 1.0 equiv of ArBr, 1.5 equiv of phenylboronic acid, and 2 equiv of base, catalyst **1**; 1 mol %, solvent aqueous DMF, and bath temperature 90 °C. [b]Reaction time 3 h. [c]NMR (%) yields.

for the reaction, a solvent mixture of DMF and water was found to give the best result. No product was obtained when THF or an ethanol−water mixture was used as solvent system.

The results of investigations on catalytic activities of complexes **1** and **2** for Suzuki−Miyaura coupling are given in Table 2. The efficiency of palladacycle **1** appears to be better than that of **2**, in which **L2** has formed a seven-membered chelate ring with palladium. The coupling of 4-bromoanisole was negligible when 1 mol % of **2** was used as a catalyst. On increasing the reaction time the amount of catalyst **1** required was reduced (Table 2). The 4-bromobenzaldehyde in 12 h is coupled nearly quantitatively even at 0.006 mol % loading of catalyst. The performance of **1** is comparable with or better than many well-known Pd-based catalysts for Suzuki−Miyaura coupling, for example, palladium complexes of tridentate (S, N, O$^-$),[14a] (S/Se/Te, N, O$^-$),[14c,e−g] bidentate (S, N),[14b] (SNS)[15c,f]/(SCS)[15d,e] pincer, and (P, N) donor.[30] In the course of the Suzuki−Miyaura coupling reaction, black particles appear, which suggest that catalysts **1** and **2** are probably precatalysts and dispense real catalyst during the reaction. Such species obtained from **1** and **2** during the course of catalysis of the coupling reaction of 4-bromobenzonitrile with phenylboronic acid under optimum reaction conditions were isolated and analyzed to understand their nature. The black particles were subjected to SEM (Supporting Information; Figures S20

Table 2. Suzuki−Miyaura Coupling Reaction Catalyzed by Catalysts 1[a] and 2[a]

		catalyst **1**			catalyst **2**	
entry no.	aryl bromide	mol %	t (h)	yield	t (h)	yield[b]
1	4-bromobenzaldehyde	1	3	95[b]	3	90
		0.1	3	100[c]		
		0.02	3	100[c]		
		0.006	12	100[c]		
2	4-bromotoluene	1	4	75[b]	12	33
		0.1	12	83[c]		
3	4-bromobenzonitrile	1	3	94[c]	3	93
		0.01	12	66[c]		
4	4-bromoanisole	1	3	88[b]		
		0.1	4	85[c]	24	
		0.02	4	83[c]		
5	4-bromonitrobenzene	1	3	96[b]	3	93
		0.01	12	50[c]		
6	4-bromobenzoic acid	0.2	3	91[b]		
7	4-bromoacetophenone	0.2	3	95[b]		

[a]Reaction conditions: 1.0 equiv of ArBr, 1.5 equiv of phenylboronic acid, and 2 equiv of base (K_2CO_3), solvent aqueous DMF and bath temperature 90 °C. [b]Isolated yield after column chromatography, [c]NMR % yields.

and S22), SEM-EDX, and HR-TEM. They are of nanosize and spherical in shape. The size of those obtained from complex **1** is ∼1−2 nm, whereas **2** gives nanoparticles of size ∼1 nm (Figure 7). The EDX (SEM as well as TEM) has revealed that they are composed of palladium and chalcogen. The Pd:S ratio in nanoparticles generated from **1** is 43:57, while in **2**, the Pd:Se ratio is 38:62 (Supporting Information; Figure S21 and Figures S23−S25). The mercury poisoning test[31] and triphenylphosphine test[31] were performed on representative reactions of 4-bromoanisole (**1**: 0.1 mol %) and 4-bromobenzaldehyde (**2**: 1 mol %). A 500 equivalent amount of Hg with respect to that of catalyst was added at the initial stage of the reaction. After 3 h no significant conversion to product was obtained. The PPh_3 test was also positive. As these two poison tests are not enough to fully affirm the heterogeneous nature of catalyst and the possibility of involvement of surface atoms of heterogeneous nanoparticles of Pd in oxidative addition to form soluble Pd(II) intermediate[32] Ar−Pd−Br exists, a two-phase test (Scheme 3) was performed to understand the nature of the reaction (heterogeneous vs homogeneous) further.[33,34] This test (called a three-phase test when the catalyst is a solid phase), developed by Rebek and co-workers, is considered more definitive for establishing whether the nature of catalytically active metal

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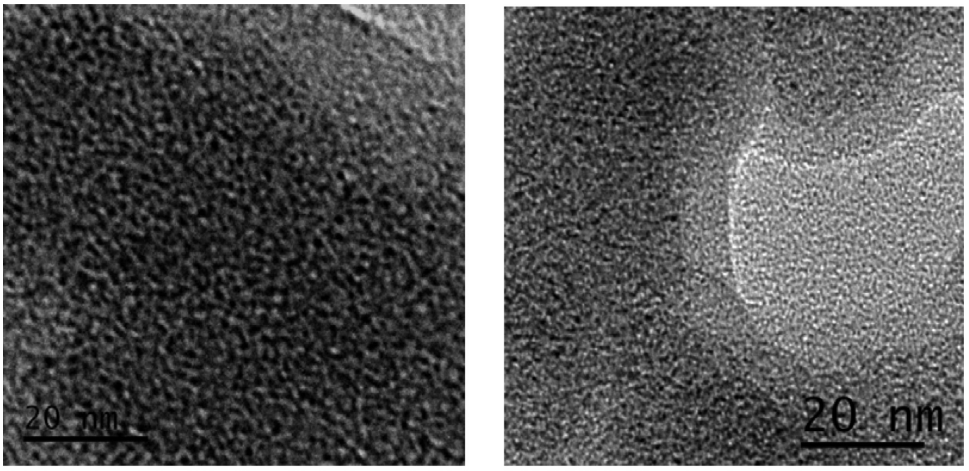
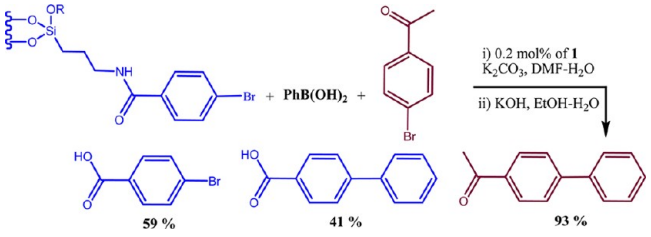


(a) (b)

Figure 7. TEM image of Pd NPs obtained from complexes **1** (a) and **2** (b) during Suzuki–Miyaura coupling.

Scheme 3. Two-Phase Test on Suzuki–Miyaura Coupling with Catalyst 1



species is homogeneous or heterogeneous.[33] If the catalyst behaves in a heterogeneous fashion, the supported aryl halide is not expected to be converted to a coupled product. When Pd is released (i.e., catalysis is homogeneous), the supported substrate can be converted to product. The addition of a soluble aryl halide to the reaction mixture ensures the presence of a catalytic process and its real active species. A two-phase test made with an immobilized aryl bromide is shown in Scheme 3. 4-Bromoacetophenone and immobilized 4-bromobenzoic acid (as amide) were reacted with phenylboronic acid under optimum reaction conditions. The soluble part was separated by filtration and analyzed after workup with ^{1}H NMR. The yield of the cross-coupled product (4-acetylbiphenyl) has been found to be ∼93%. The solid phase was hydrolyzed, and resulting products after workup were analyzed with ^{1}H NMR. Of the immobilized 4-bromobenzoic acid (as amide), ∼41% was converted to the cross-coupled product (biphenyl-4-carboxylic acid), whereas ∼59% remains unreacted (Supporting Information; Figure S27). This observation suggests that the catalytically active Pd leachs from the *in situ* generated nanoparticles and is responsible for homogeneous catalysis. Thus, it appears that in the case of **1** and **2** coupling is catalyzed with nanosized Pd species homogeneously as well as heterogeneously. Recently such a possibility has been described as "cocktail"-like mixtures of the catalysts.[35]

The ^{1}H and ^{77}Se{^{1}H} NMR spectral studies on these NPs show that they are protected by **L1** or **L2**. In the ^{77}Se{^{1}H} NMR spectrum of the NPs obtained from **2** the signals at 348.3, 353.9, and 416.3 ppm have been observed. The first two seem to originate from **L2** and third one from Se_2^{2-} species. The TGA of NPs obtained in the case of **1** shows 60% weight loss in the temperature range 110–400 °C, whereas NPs obtained from **2** show a weight loss of 58% in the temperature range 150–400 °C (Supporting Information; Figures S28 and S29). All these observations are consistent with the protection of these NPs with ligands. These NPs appear to be real catalysts. This is supported by the fact that even after isolation they continue to catalyze Suzuki–Miyaura coupling, of course with lower efficiency than those generated *in situ*, which is not unexpected. For catalytic activity of these NPs, the Suzuki–Miyaura coupling reaction was carried out under optimum conditions (Table 3). 4-Bromobenzaldehyde and 4-bromonitrobenzene react smoothly with $PhB(OH)_2$ in aqueous DMF in the presence of these NPs. The NPs obtained from **1** considerably convert 4-bromoanisole to coupled product, whereas in the presence of NPs generated from **2** no cross-coupled product has been obtained.

Table 3. Suzuki–Miyaura Coupling Reaction Catalyzed by NPs Obtained from Complexes 1[a] and 2[a]

		yield (%)[b]	
entry no.	aryl bromide	NPs obtained from complex **1**[c]	NPs obtained from complex **2**[d]
1	4-bromobenzaldehyde	94	89
2	4-bromonitrobenzene	91	85
3	4-bromoanisole	75	

[a]Reaction conditions: 1.0 equiv of ArBr, 1.5 equiv of phenylboronic acid, and 2 equiv of base (K_2CO_3), solvent aqueous DMF and bath temperature 90 °C, reaction time 3 h. [b]Isolated yield after column chromatography. [c]10 mg of NPs was used, [d]50 mg of NPs was used.

CONCLUSION

Two potentially tetradentate ligands, 2,3-bis[(phenylthio)-methyl]quinoxaline (**L1**) and 2,3-bis[(phenylseleno)methyl]-quinoxaline (**L2**), and their Pd(II) complexes (**1** and **2**) have been synthesized and characterized. Complex **1** is a palladacycle formed by unexpected palladation of the benzyl group of **L1** with Na_2PdCl_4 in the absence of external base. On the contrary **L2** behaves in **2** as a bidentate ligand via formation of a seven-membered chelate ring with a Pd(II) center. The mass spectrometric investigation on $[Pd(\mathbf{L2})_2](ClO_4)_2$ prepared separately has suggested that **2** can be an easy source of

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$[Pd(L2)_2]^{+\bullet}$, a transient species in the mass spectrum. The catalytic activity of complexes **1** and **2** for Suzuki–Miyaura coupling reactions has been studied. It was found that the palladacycle **1** shows promising catalytic activity, which is also much better than that of complex **2**. On the basis of two-phase tests the catalysis of Suzuki–Miyaura coupling with **1** and **2** via palladium–sulfur or –selenium nanoparticles (size <2 nm) protected by corresponding ligands appears to be of cocktail type (i.e., homogeneous and heterogeneous in parts). Few examples have been established so far where palladium–chalcogen NPs have been recognized as a real catalyst for Suzuki–Miyaura coupling. The present results further add a new dimension to it.

■ ASSOCIATED CONTENT

Supporting Information

NMR data, mass spectral data of ligands and complexes, SEM image, SEM-EDX, and TEM-EDX of nanoparticles obtained from complexes **1** and **2**, crystal and structural refinement data, bond lengths and bond angles for ligands and complexes, and CIFs are included. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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