ORGANOMETALLICS

Selenium-Containing N-Heterocyclic Carbenes and Their First Palladium(II) Complexes: Synthesis, Structure, and Pendent Alkyl Chain Length Dependent Catalytic Activity for Suzuki–Miyaura Coupling

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S Supporting Information

ABSTRACT: Three new *N*-alkyl-*N'*-(2-ethyl-1-selenophenyl)imidazolium salts, **L1–L3** (differing in the chain length of alkyl substituent of *N*), which are precursors to (Se, C_{NHC}) ligands and their N-heterocyclic carbene (NHC) complexes [Pd(L-HX)Cl₂] (1–3) [L = L1–L3, X = I/Br], have been synthesized and characterized by multinuclear NMR and HR-MS. For the synthesis of Pd complexes 1–3 from appropriate imidazolium salts (L1–L3), the route of the silver carbene transfer reaction has been adopted. Single-crystal structures of 1 and 2 have been established with X-ray diffraction. Thermally stable, moisture- and airinsensitive complexes 1–3 have been found to be efficient catalysts for Suzuki– Miyaura coupling reactions (yield up to 96% in 2 h at 80 °C). Nanoparticles (NPs) (size of 80–85% particles ~2–5 nm) formed in the beginning of these reactions (i.e., when the temperature of the reaction mixture reaches 80 °C) appear to be important for catalytic coupling, probably as dispensers of Pd(0), and contain Pd



and Se. The Pd:Se is nearly 3:2, 4:5, and 1:1 in NPs formed from 1, 2, and 3, respectively. The catalytic activity of 3, having the longest alkyl chain containing (Se C_{NHC}) ligand among the three complexes, has been found to be higher relative to those of 1 and 2. The length of the alkyl chain present in the complex molecule probably controls the catalytic activity by influencing the dispersion of NPs (containing Pd and Se) generated *in situ* during the catalytic process. The two-phase test has indicated a homogeneous nature of catalytic process, which probably occurs via leaching of Pd(0) from these NPs. This is first example where Pd–Se NPs catalyze Suzuki coupling largely via a homogeneous process, which is probably combined with oxidative addition to Pd(0) at the surface. The effect of alkyl chain length on catalytic efficiency may be useful in designing ligands/Pd complexes that efficiently catalyze Suzuki–Miyaura coupling.

INTRODUCTION

N-Heterocyclic carbenes (NHCs), which acquired importance due to the pioneering work of Wanzlick,¹ Lappert,² and Arduengo,³ have received intensive attention as ligands.⁴ They constitute a class of compounds that have contributed extensively to organometallic chemistry⁵ and homogeneous catalysis.⁶ Their medicinal applications⁷ are also important. Carbenes derived from five-membered heterocycles make up the most common class of NHCs.^{3,8} However, their four-, six-,¹⁰ and seven-membered¹¹ analogues have also been reported. In organometallic chemistry and catalytic organic transformations, NHCs have been found to bring stability to the metal center and become ligands of spectacular choice in place of costly and air-sensitive phosphines. The tunability of NHCs has made a wide variety of these ligands feasible,¹² and thus their size is comparable to the range shown by phosphines.¹³ Palladium(II)-monodentate NHC ligand complexes have remarkable activities for palladium-catalyzed C-C coupling reactions,¹⁴ and many research efforts have been devoted to the synthesis of NHC-based polydentate ligands.¹⁵ NHCs are often used as alternatives to phosphines owing to

their better stability toward oxidation and the formation of more stable metal complexes.¹⁶ Consequently NHCs have made up a class of ligands able to challenge tertiary phosphines¹³ used to design Pd complexes for cross-coupling reactions for a long time. Recently chalcogen ligands have emerged as alternatives to phosphines due to strong donor properties and the air/moisture stability of their metal complexes.¹⁷ Sulfur-containing NHCs in association with palladium(II) precursors have been extensively studied in catalysis,¹⁸ and in many research papers palladium complexes of bidentate (S, C_{NHC}) and (S, C_{NHC}, S) pincer-type ligands have been reported as efficient catalysts for cross-coupling reactions, thus establishing the effectiveness of the sulfur-NHC combination for these ligands.¹⁹ However, for catalysis of Suzuki–Miyaura C–C coupling, use of palladium(II) complexes of selenium-containing NHC ligands does not exist to our knowledge. Thus it would be worthwhile to explore Pd(II) complexes with a bidentate ligand framework constructed by a

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combination of selenium and NHC for catalysis of Suzuki-Miyaura C-C coupling. The catalytic activity of palladium species having a dendritic macromolecular structure^{20,21} increases with the generation of dendrimers,²¹ and a significant effect of alkyl chain length on catalytic efficiency for the Suzuki-Miyaura coupling reaction has been recently reported in the case of Pd(II) complexes of selenated Schiff bases.^{1/a} The effect of the length of the pendent alkyl chain of an NHC on catalytic activity of its Pd complexes has not been reported so far and therefore is worth investigating. The NHCs linked to a polymer or silica have been reported for catalyst designing.²² Thus the length of a pendent (noncoordinating) alkyl chain present on a ligand framework of a palladium complex of a selenium-containing NHC has been varied from C1 to C18 to study its influence on catalytic properties for Suzuki-Miyaura C-C cross-coupling reactions. Generally the mechanism² ³ of Suzuki-Miyaura coupling with molecular complexes of palladium(II) is believed to be through Pd(0), which may be in nanoparticle (NP), colloid, and/or soluble form. The catalytic process²⁴ has been reported to be homogeneous, heterogeneous, and a mixture of the two. However, in the case of Pd(II) complexes of a chalcogenated ligand as a catalyst^{17a,d} mostly the formation of Pd- and chalcogen-containing NPs has been observed. To understand how a catalytic process proceeds via such NPs is a very interesting part of our research program.

In the present paper we report three new seleniumcontaining imidazolium salts, differing in the alkyl chain length (longest in L3) and counteranion present (see Scheme 1),





which are precursors of the selenium-containing NHC ligands. The palladium(II) complexes have been prepared from these imidazolium salts via typical silver carbene transfer reactions.²⁵ The carbenic proton of an imidazolium salt is first deprotonated by the basic ligand of the metal precursor, Ag_2O , and thereafter Ag is abstracted in favor of Pd. The catalytic applications of these new palladium(II) complexes (two of them are structurally characterized) in Suzuki–Miyaura coupling reactions have been explored. The complexes act as dispensers of Pd- and Se-containing nanoparticles and are stable in solution as well as in solid state and probably carry out catalytic coupling again by releasing Pd(0) (largely via a homogeneous process, which is probably combined with oxidative addition to Pd(0) at the surface). The length of the

alkyl chain present on the ligand of the molecular complex appears to influence the dispersion of these Pd–Se NPs, which in turn affects the catalytic efficiency.

EXPERIMENTAL DETAILS

Physical Measurements. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 Series II C, H, N analyzer. The ¹H, ¹³C{¹H}, and ⁷⁷Se{¹H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, and 57.24 MHz, respectively. IR spectra in the range 4000-400 cm⁻¹ were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. High-resolution mass spectral (HR-MS) measurements were performed with electron spray ionization (10 eV, 180 °C source temperature) and using sodium formate as calibrant on a Bruker MIcroTOF-Q II, taking samples in CH₃CN. The diffraction data on single crystals of 1 and 2 were collected on a Bruker AXS SMART Apex CCD diffractometer using Mo K α (0.71073 Å) radiations at 298(2) K. The software SADABS²⁶ was used for absorption correction (if needed) and SHELXTL for space group, structure determination, and refinements.²⁷ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached. The least-squares refinement cycles on F^2 were performed until the model converged. High-resolution TEM characterization revealing particle sizes and shapes was performed with a Philips Tecnai F20 operated at 200 kV. Samples for high-resolution transmission electron microscopy (HR-TEM) were prepared by drying a drop of dispersion of nanocrystals in cyclohexane or ethanol on a carbon-coated copper grid. The elemental composition of NPs was studied with a Carl ZEISS EVO5O scanning electron microscope (SEM) and associated EDX system model QuanTax 200, which is based on the SDD technology and provides an energy resolution of 127 eV at Mn K α . The sample was mounted on a circular metallic sample holder with a sticky carbon tape. The melting points determined in an open capillary are reported as such. Yields refer to isolated yields of compounds, which have a purity of \geq 95%. Estimation of palladium in NPs was carried out on an AA700 series flame atomic absorption spectrometer (Lab India, New Delhi). Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer system in a flowing nitrogen atmosphere with a heating rate of 10 °C/min.

Chemicals and Reagents. Imidazole, diphenyl diselenide, sodium borohydride, palladium(II) chloride, methyl iodide, 1-bromooctane, and 1-bromooctadecane procured from Sigma-Aldrich (USA) were used as received. 1-(2-Phenylselanylethyl)-1*H*-imidazole was prepared by the method reported earlier.²⁸ All the solvents were dried and distilled before use by standard procedures.²⁹ The common reagents and chemicals available commercially within the country were used.

Synthesis of 1-Methyl-3-(2-ethyl-1-selenophenyl)-3*H*-imidazol-1-ium lodide (L1). 1-(2-Phenylselanylethyl)-1*H*-imidazole (0.251 g, 1.0 mmol) was taken in 10 mL of chloroform, and an excess of methyl iodide (1.419 g, 10.0 mmol) was added to it. The reaction mixture was stirred at room temperature for 1 day. After the completion of the reaction, the solvent was evaporated off under reduced pressure on a rotary evaporator to get L1 as an orange, viscous oil.

Yield: 0.373 g, 95%. ¹H NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 3.47 (t, ³J_{H-H} = 6.59 Hz, 2H, H₅), 3.99 (s, 3H, CH₃), 4.63 (t, ³J_{H-H} = 6.6 Hz, 2H, H₆), 7.27–7.28 (m, 3H, H₂ and H₁), 7.41 (s, 1H, H₇), 7.49–7.52 (m, 2H, H₃), 7.56 (s, 1H, H₈), 9.74 (s, 1H, H₉). ¹³C{¹H} NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 27.1 (C₅), 36.9 (C₁₀), 50.1 (C₆), 122.6 (C₈), 123.1 (C₇), 127.5 (C₄), 127.7 (C₁), 129.4 (C₂), 132.9 (C₃), 136.4 (C₉). ⁷⁷Se{¹H} NMR (CDCl₃, 25 °C vs Me₂Se): δ (ppm) 279.0. HR-MS (CH₃CN) [M – I]⁺ (*m*/*z*) = 267.0395; calculated value for [C₁₂H₁₅N₂Se]⁺ = 267.0395 (δ : 0.0 ppm). IR (KBr, cm⁻¹): 3081 (m; $\nu_{C-H \text{ aromatic}}$), 743 (m; $\nu_{C-H \text{ aromatic}}$).

Synthesis of 1-Octyl-3-(2-ethyl-1-selenophenyl)-3*H*-imidazol-1-ium Bromide (L2). 1-(2-Phenylselanyl-ethyl)-1*H*-imidazole (1.255 g, 5.0 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer, and then 1-bromooctane (0.965 g, 5.0 mmol) was added. The mixture was heated for 12 h at 85 °C under a N₂ atmosphere and then allowed to cool to room temperature. The dark orange oil so obtained was washed with dry CH₃CN (2 × 40 mL) and dried *in vacuo*.

Yield: 1.998 g, 90%. ¹H NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 0.88 (t, ³J_{H-H} = 6.9 Hz, 2H, H₁₇), 1.26–1.33 (m, 10H, H_{12–16}), 1.84– 1.89 (m, 2H, H₁₁), 3.50 (t, ³J_{H-H} = 5.1 Hz, 2H, H₅), 4.22 (t, ³J_{H-H} = 6.9 Hz, 2H, H₁₀), 4.68 (t, ³J_{H-H} = 5.1 Hz, 2H, H₆), 7.11 (s, 1H, H₈), 7.27–7.30 (m, 3H, H₂ and H₁), 7.34 (s, 1H, H₇), 7.49–7.50 (m, 2H, H₃), 10.45 (s, 1H, H₉). ¹³C{¹H} NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 13.9 (C₁₇), 22.4 (C₁₆), 26.0 (C₁₅), 27.2 (C₅), 28.7 (C₁₄), 28.8 (C₁₃), 30.0 (C₁₂), 31.5 (C₁₁), 49.8 (C₁₀), 49.9 (C₆), 121.4 (C₈), 122.7 (C₇), 127.5 (C₁), 127.7 (C₄), 129.3 (C₂), 132.8 (C₃), 136.5 (C₉). ⁷⁷Se{¹H} NMR (CDCl₃, 25 °C vs Me₂Se): δ (ppm) 276.1. HR-MS (CH₃CN) [M - Br]⁺ (m/z) = 365.1490; calculated value for [C₁₉H₂₉N₂Se]⁺ = 365.1491 (δ: 0.3 ppm). IR (KBr, cm⁻¹): 3135, 3061 (m; ν_{C-H aromatic}), 2926, 2857 (s; ν_{C-H aliphatic}), 1566 (m; ν_{C=N aromatic}), 1468 (m; ν_{C=C aromatic}), 1262 (m; ν_{C-N aliphatic}), 741 (m; ν_{C-H aromatic}).

Synthesis of 1-Octadecyl-3-(2-ethyl-1-selenophenyl)-3*H*imidazolium Bromide (L3). 1-(2-Phenylselanylethyl)-1*H*-imidazole (1.255 g, 5.0 mmol) and 1-bromooctadecane (1.665 g, 5.0 mmol) were reacted as described for L2. The dark orange oil so obtained was washed with dry CH_3CN (2 × 40 mL) and dried *in vacuo*.

Yield: 2.628 g, 90%. ¹H NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 0.89 (t, ³J_{H-H} = 6.9 Hz, 3H, H₂₇), 1.26–1.32 (m, 28H, H_{13–26}), 1.82–1.86 (m, 4H, H₁₁ and H₁₂), 3.50 (t, ³J_{H-H} = 6.0 Hz, 2H, H₅), 4.23 (t, ³J_{H-H} = 7.5 Hz, 2H, H₁₀), 4.68 (t, ³J_{H-H} = 6.0 Hz, 2H, H₆), 7.12 (s, 1H, H₈), 7.28–7.30 (m, 3H, H₂ and H₁), 7.35 (s, 1H, H₇), 7.48–7.52 (m, 2H, H₃), 10.45 (s, 1H, H₉). ¹³C{¹H} NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 14.0 (C₂₇), 22.5 (C₂₆), 26.1 (C₂₅), 27.2 (C₅), 28.8 (C₂₄), 29.2 (C₂₃), 29.2 (C₂₂), 29.35 (C₂₁), 29.43 (C₂₀), 29.47 (C_{17–19}), 29.51 (C_{13–16}), 30.1 (C₁₂), 31.7 (C₁₁), 49.8 (C₁₀), 50.0 (C₆), 121.4 (C₈), 122.8 (C₇), 127.6 (C₁), 127.7 (C₄), 129.4 (C₂), 132.9 (C₃), 136.7 (C₉). ⁷⁷Se{¹H} NMR (CDCl₃, 25 °C vs Me₂Se): δ (ppm) 275.7. HR-MS (CH₃CN) [M – Br]⁺ (*m*/*z*) = 505.3055; calculated value for [C₂₉H₄₉N₂Se]⁺ = 505.3057 (δ: 0.2 ppm). IR (KBr, cm⁻¹): 3048 (m; *ν*_{C=N aromatic}), 1468 (m; *ν*_{C=C aromatic}), 1265 (m; *ν*_{C-N aromatic}), 732 (m; *ν*_{C-H aromatic}).

 $\nu_{C-H \text{ aromatic}}$). **General Procedure for the Synthesis of [Pd(Se, C_{NHC})Cl₂] Complexes (1–3).** The imidazolium salt (L1/L2/L3) (0.196 g/0.222 g/0.292 g, 0.5 mmol) was dissolved in dry CH₂Cl₂ (50 mL), and solid Ag₂O (0.116 g, 0.5 mmol) added under nitrogen atmosphere. The reaction mixture was stirred overnight in the dark at room temperature and filtered through a Celite pad. The filtrate was concentrated to 20 mL on a rotary evaporator. Thereafter it was added to a suspension of [Pd(CH₃CN)₂Cl₂] (0.129 g,, 0.5 mmol) in CH₃CN with continuous stirring at room temperature in a N₂ atmosphere. It was stirred further for 8 h and filtered through a Celite pad. The filtrate was concentrated on a rotary evaporator to about 5 mL and mixed with diethyl ether (15 mL) to obtain 1–3 as yellow solids, which were filtered and dried *in vacuo*. The single crystals of 1 and 2 were grown by slow evaporation of their solutions in CH₃CN–Et₂O mixtures (3:1).

1. Yield: 0.181 g, 82%. Anal. Calcd for $C_{12}H_{14}Cl_2N_2PdSe: C, 32.57$; H, 3.19; N, 6.33. Found: C, 31.69; H, 2.81; N, 5.70. Mp: 190.0 °C. ¹H NMR (CD₃CN, 25 °C): δ (ppm) 2.73 (bs, 1H, H₅), 3.45 (bs, 1H, H₅), 3.96 (s, 3H, H₁₀), 4.68 (bs, 2H, H₆), 7.04 (s, 1H, H₈), 7.18 (s, 1H, H₇), 7.40–7.43 (m, 3H, H_{1 and 2}), 7.58 (bs, 2H, H₃). ¹³C{¹H} NMR (CD₃CN, 25 °C): δ (ppm) 14.6 (C₁₀), 29.5 (C₅), 50.4 (C₆), 124.4 (C_{8 and 7}), 128.2 (C₄), 129.9 (C₁), 131.9 (C₂), 134.4 (C₃). HR-MS (CH₃CN) [M – Cl]⁺ (m/z) = 406.9057; calculated value for C₁₂H₁₄ClN₂PdSe = 406.9045 (δ : –2.9 ppm). IR (KBr, cm⁻¹): 3104 (m; ν _{C=H aromatic}), 1716 (m; ν _{C=N aromatic}), 1471 (m; ν _{C=C aromatic}), 743 (m; ν _{C-H aromatic}).

2. Yield: 0.227 g, 84%. Anal. Calcd for $C_{19}H_{28}Cl_2N_2PdSe: C, 42.20;$ H, 5.22; N, 5.18. Found: C, 41.59; H, 4.46; N, 4.69. Mp: 210.0 °C. ¹H NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 0.88 (t, ³J_{H-H} = 6.6 Hz, 3H, H₁₇), 1.19 (bs, 10H, H₁₂₋₁₆), 1.81 (bs, 2H, H_{11 and 12}), 3.71 (bs, 1H, H₅), 4.02 (bs, 1H, H₅), 4.37 (bs, 2H, H₁₀), 4.87 (bs, 1H, H₆), 5.17 (bs, 1H, H₆), 6.92 (s, 1H, H₈), 7.09–7.27 (m, 4H, H₁, 2, and 7), 7.66 (bs, 2H, H₃). ¹³C{¹H} NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 14.1 (C₁₇), 22.5 (C₁₆), 26.5 (C₁₅), 28.9 (C₁₄), 29.0 (C₁₃), 29.1 (C₁₂), 30.7 (C₅), 31.6 (C₁₁), 50.9 (C₁₀), 51.5 (C₆), 122.5 (C₈), 123.7 (C₇), 128.1 (C₄), 129.5 (C₁), 130.0 (C₂), 134.8 (C₃). HR-MS (CH₃CN) [M - Cl]⁺ (m/z) = 505.0113; calculated value for [C₁₉H₂₈ClN₂PdSe]⁺ = 505.0143 (δ : 6.0 ppm). IR (KBr, cm⁻¹): 3048 (m; ν _{C=H aromatic}), 2922 (s; ν _{C-H aliphatic}), 2854 (s; ν _{C-H aliphatic}), 1625 (m; ν _{C=N aromatic}), 1468 (m; ν _{C=C aromatic}), 741 (m; ν _{C-H aromatic}).

Procedure for Suzuki–Miyaura Coupling Reaction. An ovendried flask was charged with aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), DMF (3.0 mL), H_2O (2.0 mL), and complex **1**, **2**, or **3**. The flask was fitted with a water condenser and placed on an oil bath maintained at 80 °C. The reaction mixture was stirred and the reaction monitored with TLC until maximum conversion of aryl bromide to the product occurred. Thereafter the mixture was extracted with diethyl ether (2 × 20 mL). The extract was washed with water and dried over anhydrous Na₂SO₄. The solvent of the extract was evaporated off on a rotary evaporator, and the residue was purified by a column of silica gel using CHCl₃–hexane as eluent. All coupling products were authenticated by ¹H and ¹³C{¹H} NMR spectra.

Hg Poisoning Test. An excess of Hg (Hg:Pd, 400:1) was taken in the reaction flask before the addition of reactants. Thereafter the coupling reaction of 4-bromobenzaldehyde (1.0 mmol) with phenylboronic acid (1.2 mmol) using **1**, **2**, or **3** (1.0 mol %) as catalyst was carried out in the flask under optimum conditions. A 5-10% conversion was observed after 5 h of reaction.

PPh₃ Poisoning Test. To the coupling reaction of 4bromobenzaldehyde with phenylboronic acid, PPh₃ (0.5 mol %) was added under optimal conditions before addition of catalyst (1.0 mol %). After 5 h of reaction cross-coupled products were obtained in 5– 10% yield.

Two-Phase Test. The 4-bromobenzoic acid-immobilized (as amide) silica (0.20 g) prepared by standard procedure³⁰ (details in the Supporting Information), phenylboronic acid (0.36 g, 3 mmol), 4bromoacetophenone (0.20 g, 1 mmol), and K₂CO₃ (0.56 g, 4 mmol) were taken in a mixed solvent DMF (8 mL) + water (4 mL), and the mixture was heated at 80 °C for 12 h. Thereafter it was cooled to room temperature and filtered through a G-4 crucible. The residue was washed with 20 mL of H₂O 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 ¹H 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 and extracted with dichloromethane, followed by ethyl acetate. The solvent of the combined extract was evaporated off, and the resulting residue was analyzed with ¹H NMR.

Isolation of NPs Generated from Complexes 1–3 during Suzuki–Miyaura Coupling. A mixture of Pd(II) complex 1/2/3 (0.5 mmol), phenylboronic acid (1.5 mmol), 4-bromobenzaldehyde (1.0 mmol), and K₂CO₃ (2.0 mmol) in DMF (4.0 mL) and water (4.0 mL) was heated at 100 °C for 2 h and then cooled to room

temperature. The solvent was decanted, and the black residue (NPs) was washed with a water-acetone mixture (1:3) and dried *in vacuo*. The NPs were characterized by SEM-EDX, HR-TEM, and TEM-EDX.

Procedure for Suzuki–Miyaura Coupling Catalyzed by NPs Obtained from 1–3. The coupling reactions of 4-bromobenzaldehyde, 4-bromotoluene, and 4-bromoanisole in the presence of 5 mg of NPs obtained from 1 and 3 (Pd mol %: 2.98 and 2.13, respectively) were carried out under conditions optimized for complexes 1–3. All products were authenticated by ¹H and ¹³C{¹H} NMR spectra.

RESULTS AND DISCUSSION

The preparations of carbene ligand precursors (L1, L2, and L3) and palladium(II) complexes (1, 2, and 3) are shown in Scheme 1. 1, 2, and 3 are the first examples of Pd(II) complexes of selenium-containing carbene. They were synthesized by silver carbene transfer reaction in which L1, L2, or L3 was first treated in CH2Cl2 with Ag2O in a N2 atmosphere at room temperature and in the dark, followed by addition to the resulting solution of silver complex, a suspension of [Pd- $(CH_3CN)_2Cl_2$ in CH_3CN . The yellow solids 1, 2, and 3 were found to be stable and thermally robust. The ligands L1, L2, and L3 were found to be soluble in common organic solvents. The complex 1 shows good solubility in DMF, DMSO, and CH₃CN. It has been found sparingly soluble in CH₂Cl₂ and CHCl₃, and in CH₃OH, diethyl ether, THF, and hexane negligibly soluble. On the other hand complexes 2 and 3 have been found sparingly soluble in DMF, DMSO, CH₃CN, CH₂Cl₂, CHCl₃, and CH₃OH and insoluble in diethyl ether, hexane, and CH₃OH.

The air-stable imidazolium salts (L1, L2, and L3) and Pd complexes 1-3 were characterized with ¹H, ¹³C{¹H}, and ⁷⁷Se{¹H} NMR, HR-MS, and IR spectra. The ⁷⁷Se{¹H} NMR spectra of L1, L2, and L3 are given in Figures S19-S21 of the Supporting Information. A single signal was observed at 279.0, 276.1, and 275.7 ppm respectively in the ⁷⁷Se{¹H} NMR spectra of L1, L2, and L3. The ¹H and ¹³C{¹H} NMR spectra (see Supporting Information, Figures S7-S18) of L1-L3 and their complexes 1-3 have been found to be consistent with their molecular structures (Scheme 1). In the ¹H NMR spectra protons attached to C-9 of L1, L2, and L3 have been observed at 9.74, 10.45, and 10.46 ppm, respectively, and are in the range reported for the related imidazolium halides (δ 9.0–12.0), suggesting the high acidity of these protons. In the ¹H NMR spectra of 1, 2, and 3 a signal around 9.0-11.0 ppm was found to be absent, indicating the deprotonation of C-9 and hence the coordination of NHC with Pd(II).

In the mass spectrum of imidazolium salts L1, L2, and L3 the peak appearing at 267.0395, 365.1491, and 505.3055, respectively, may be ascribed to imidazolium cations (see Supporting Information, Figures S1–S3). The mass spectra of complexes 1, 2, and 3 show peaks at 406.9057, 505.0113, and 645.1703, which may be ascribed to the $[M - Cl]^+$ cationic fragment of the corresponding complex (see Supporting Information, Figures S4–S6).

Crystal Structures. The crystal structures of complexes 1 and 2, the first examples of Pd(II) complexes of seleniumcontaining carbene, have been solved. Their crystal and refinement data are given in Table S1 of the Supporting Information. The ORTEP diagrams of 1 and 2 are shown in Figures 1 and 2 with selected bond lengths and angles (more values are given in Table S2 of the Supporting Information). In each of the two structures, the palladium center adopts a nearly square planar geometry. The ligands are coordinated with Pd in a bidentate (Se, C_{NHC}) mode, forming a six-membered chelate



Figure 1. Thermal ellipsoid diagram of 1 at the 30% probability level. Bond lengths (Å): Pd(1)-Se(1) 2.3694(7), Pd(1)-C(9) 1.945(3), Pd(1)-Cl(1) 2.3512(10), Pd(1)-Cl(2) 2.3156(11). Bond angles (deg): Cl(1)-Pd(1)-Se(1) 86.18(3), Cl(2)-Pd(1)-Se(1)170.50(3), C(9)-Pd(1)-Se(1) 89.30(10), C(9)-Pd(1)-Cl(1)171.31(11), C(9)-Pd(1)-Cl(2) 91.35(10), Cl(2)-Pd(1)-Cl(1)94.34(4).



Figure 2. Thermal ellipsoid diagram of complex 2 at the 30% probability level. Bond lengths (Å): Pd(1)-Se(1) 2.3909(15), Pd(1)-C(9) 1.957(10), Pd(1)-Cl(1) 2.395(3), Pd(1)-Cl(2) 2.378(3). Bond angles (deg): Cl(1)-Pd(1)-Se(1) 86.48(7), Cl(2)-Pd(1)-Se(1) 173.61(8), C(9)-Pd(1)-Se(1) 87.9(3), C(9)-Pd(1)-Cl(1) 167.8(3), C(9)-Pd(1)-Cl(2) 91.5(3), Cl(2)-Pd(1)-Cl(1) 95.30(9).

ring, and the imidazole ring is twisted, making an angle with the coordination plane of the metal. The twisting causes inefficient overlapping of metal d_{π} orbital with the p_z orbital of the carbenic atom and is consistent with the negligible π -accepting property of NHC ligand.

The Pd–Se bond lengths of complexes 1 and 2 are 2.3694(11) and 2.3909(15) Å, respectively, consistent with the earlier reported values³² 2.381(7)–2.385(5) Å for species [PdCl₂(Se, N)ligand] and [PdCl(N, Se, N)ligand]⁺, in which also the six-membered chelate ring is present. The Pd–C bond lengths of complexes 1 and 2 are 1.945(3) and 1.957(10) Å, respectively, consistent with reported values of 1.978(4)–1.989(4) Å for [PdCl₂(S, C_{NHC})ligand] complexes.^{19a} The Pd–Cl bond lengths [2.3156(11)–2.315(3) Å] of 1 and 2 are normal.^{19a} In the crystals of 1 and 2, due to secondary interactions (see Table S3 of the Supporting Information (SI) for interatomic distances), several interesting supramolecular structural patterns (Figures 3–5) have been observed. The inter/intramolecular Cl…H–C [2.733(11)–2.856(2) Å] and



Figure 3. Inter/intramolecular C–H…Cl and C–H… π interactions in complex 1.



Figure 4. Inter/intramolecular C-H…Cl interactions in complex 2.

C-H… π [2.733(1)-3.744(1) Å] interactions result in chain structures for complexes 1 and 2.

Application in the Suzuki-Miyaura Coupling Reaction. The catalytic potential of 1-3 for the Suzuki-Miyaura coupling reaction has been investigated. The results given in Table 1 suggest that the complexes 1-3 are efficient for Suzuki-Miyaura coupling, as good yields were obtained even with deactivated substrates such as 4-bromoanisole. With many substrates a reaction time of 2 h was sufficient for good conversion. The catalytic efficiency of 3 has been found to be highest among 1-3. Complex 1 shows a significantly lower efficiency than those of 2 and 3. As the pendent alkyl chain length is the longest in the case of complex 3, the observed difference in efficiency may be ascribed to its presence fully or partly, as such an observation has been made in the case of catalysis of Suzuki coupling by palladium(II) complexes of Schiff bases.^{17a} In the course of Suzuki reactions catalyzed with 1-3, black particles appear immediately at the start of the

reaction. Therefore, it is possible that 1-3 are precatalysts and during catalytic coupling reactions black particles that form are Pd-containing species, which have a role in the catalytic process. This implies that variations observed in catalytic efficiency with the alkyl chain length may arise due to some difference in these species generated in situ in the course of catalysis with 1-3. Thus the black precipitates obtained from 1, 2, and 3 in the course of catalysis of the coupling reaction of 4bromobenzaldehyde with PhB(OH)₂ under optimum reaction conditions have been isolated (details in the Experimental Section) and analyzed in detail so that a possible correlation among the length of the alkyl chain present on the ligand's framework, catalytic activity, and nature of the precipitate (possibly true catalysts or having a role in the catalysis) can be understood. The SEM-EDX (see SI; Figures S22-S24), TEM-EDX (see SI; Figures S25-S27), and HR-TEM (Figures 6-8) of the black precipitate suggest that it is made of nanosized particles of spherical shape. These nanosized species contain Pd



Figure 5. In	iter/intramolecular	$C-H\cdots\pi$	interactions	in	complex 2.	
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Entry	Aryl Bromides	Pa	Time	Y 1eld (%)		TON			
No.		mol %	h	1	2	3	1	2	3
1	Br-NO2	0.01	2	71	80	96	7100	8000	9600
2	Вг-СНО	0.01	2	70	81	94	7000	8100	9400
3	Br COCH3	0.01	2	70	82	96	7000	8200	9600
4	Br	0.01	2	68	80	96	6800	8000	9600
5	Br	0.1	5	70	78	96	700	780	960
6	Br-CH3	1.0	24	55	76	95	55	76	95
7	Br-OCH3	1.0	24	48	72	96	48	72	96
8	Вг-СООН	1.0	2	75	85	95	75	85	95





Figure 6. HR-TEM micrographs of NPs (50 nm scale bar) generated from complexes 1, 2, and 3 during Suzuki–Miyaura coupling.

Figure 7. HR-TEM micrographs of NPs (20 nm scale bar) generated from complexes 1, 2, and 3 during Suzuki–Miyaura coupling.



Figure 8. Size distribution of NPs generated from complexes 1, 2, and 3 during Suzuki-Miyaura coupling.

and Se. The Pd:Se ratio on the basis of EDX is nearly 3:2, 4:5, and 1:1 in NPs formed from 1, 2, and 3, respectively. They are stable in solution as well as in the solid state. The stability is imparted by Se and may be contributed by associated organic fragments (see below). The size of 80-85% of these NPs obtained from 1-3 is between 2 and 5 nm (see Figures 6–8). The Pd, C, H, and N in these nanosized species were determined (Pd by flame AAS). The results are given in Table

Table 2. Suzuki–Miyaura Coupling Catalyzed with NP1 and NP3

Entry	Aryl Bromide	Time	NP1		NP3		
No.		h	Pd mol %	Yield %	Pd mol %	Yield %	
1	BrСНО	2	2.98	55	2.13	93	
2	Br-CH3	24	2.98	45	2.13	91	
3	Br — OCH3	24	2.98	45	2.13	91	

Table 3. Data Ana	yses of	Isolated	NPs
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		analyses (%)			
nanoparticle	Pd (% wt)	С	Н	N	weight (%) loss in TGA (up to 200 °C)
NP1	63.6	4.26	1.36	2.06	9.98
NP2	54.9	6.36	1.39	1.80	14.52
NP3	45.2	7.55	1.36	1.82	16.73

3. The NPs were subjected to TGA, and weight loss up to 200 °C is also shown in Table 3. It appears that on the basis of weight loss in TGA and C, H, and N analyses results that the NPs are associated with organic matter (most likely the dissociation fragment of ligands). As the percentage of C in NPs follows the order NP3 > NP2> NP1 (obtained from 3, 2, and 1, respectively), these fragments most probably have pendent alkyl chain related species. To identify whether the reaction is heterogeneous or homogeneous, Hg-poisoning^{17a} and triphenylphosphine^{17a} tests were carried out. Both tests suggest that the catalysis is not completely proceeding heterogeneously via NPs containing Pd and Se. To answer the heterogeneous vs homogeneous question, a two-phase test³³ has been carried out, as in the absence of clear-cut

poisoning tests the possibility of involvement of surface Pd atoms of nanoparticles in oxidative addition to form soluble Pd(II) intermediate Ar-Pd-Br and driving the catalysis homogeneously thereafter also exists.³⁴ This test (called a three-phase test when the catalyst is a solid phase), developed by Rebek and co-workers,³³ is considered to be more definitive for the presence of metal species that are catalytically active homogeneously. The test involves covalent immobilization of one of the reaction partners; for example, 4-bromobenzoic acid has been immobilized on silica in the present case. If the catalyst behaves in a heterogeneous fashion, the immobilized substrate is not expected to be converted to a coupled product. When Pd is released (i.e., catalysis is homogeneous), the anchored 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. The present two-phase test made with an immobilized aryl bromide is shown in Scheme 3. 4-Bromoacetophenone and immobilized





Scheme 3. Two-Phase Test for Suzuki-Miyaura Coupling



4-bromobenzoic acid (as amide) have been reacted with phenylboronic acid under optimum reaction conditions. The soluble part has been separated by filtration and analyzed after workup with ¹H NMR. The yield of the cross-coupled product (4-acetylbiphenyl) has been found to be ~95%. The solid phase has been hydrolyzed, and the resulting products after workup have been analyzed with ¹H NMR. Of the immobilized 4-bromobenzoic acid (as amide), ~95% has been converted to the cross-coupled product (biphenyl-4-carboxylic acid). This observation suggests that the catalytically active Pd atoms leach out from the *in situ* generated NPs and are probably responsible

for carrying out catalysis homogeneously. The leaching may happen first and is followed by oxidative addition required for coupling. The surface Pd atoms of nanoparticles undergo oxidative addition to form soluble Pd(II) intermediate Ar-Pd-Br, and the catalysis is driven thereafter (homogeneously). The catalysis in the present case is thus a largely homogeneous process and is probably combined with oxidative addition to Pd(0) at the surface.

The nanoparticles, formed in the case of 3, are much more uniformly dispersed than those from 1 and 2 (see Figures 6-8). The $-CH_3$ group is present on the ligand framework of 1, and the linear $C_{18}H_{37}$ group on that of 3. The large size of the alkyl chain in the case of 3 appears to have made the nanoparticles more uniformly dispersed (Figure 7), resulting in its higher catalytic activity. The carbon analyses results discussed above suggest that ligand fragments associated with NPs appear to have the effect of the alkyl chain (full or in part) of the original ligand. This corroborates with the effect of the alkyl chain on the characteristics of NPs. The influence of alkyl chain length on the catalytic activity and nanoparticle dispersion both suggest that the real catalysts are NPs or originating from them. This is shown independently by the catalytic activity of nanoparticles for Suzuki coupling (Table 2). The isolated NPs appear to be somewhat deactivated in comparison to those generated in situ, as their amount needed (>2.13 mol % of Pd) for comparable conversions is more than those of 1 and 3. Some Pd may be leached in the reaction mixture before isolation. This may result in lowering of reactivity, which may be further reduced due to some aggregation in the course of isolation. However the isolated NPs are not recyclable. This is consistent with the inference made above that the coupling reactions catalyzed with 1-3 are largely homogeneous and probably combined with oxidative addition at the surface. Thus 1-3 are dispensers of NPs, which further generate probably homogeneous real Pd(0) catalysts. The level of catalytic activity of 3 for coupling of aryl bromides as substrates is generally good. The time required for activated aryl bromides is short, while a relatively longer time is required for deactivated aryl bromides. The effect of chain length of selenated Schiff bases ligated with Pd(II) on catalytic efficiency in Suzuki-Miyaura coupling reactions has been recently reported by our research group,^{17a} but similar effect of alkyl chain length of N in the case of NHC has been observed for the first time. Such an observation is important in the context of designing efficient catalysts for Suzuki coupling.

CONCLUSIONS

The first Pd complexes, $[Pd(L-HX)Cl_2]$ (1–3), of (Se, C_{NHC}) ligands [L = L1-L3, X = I/Br] have been synthesized from appropriate N-alkyl-N'-(2-ethyl-1-selenophenyl) imidazolium salts (L1-L3) through the route of a silver carbene transfer reaction. Single-crystal structures of 1 and 2 have been established by X-ray diffraction. Thermally stable, moistureand air-insensitive complexes 1-3 have been found to be efficient catalysts for Suzuki-Miyaura coupling reactions (yield up to 96% in 2 h at 80 °C). Nanoparticles (size of 80-85% particles $\sim 2-5$ nm) formed in the beginning of these reactions (i.e., when the temperature of the reaction mixture reaches 80 °C) contain Pd and Se (Pd:Se ratio: 3:2, 4:5, and 1:1 in for NP1, NP2, and NP3, respectively) and appear to have a role in the catalysis. The catalytic activity of complex 3, having the longest alkyl chain containing (Se C_{NHC}) ligand, has been found to be higher relative to those of 1 and 2. The length of the alkyl chain present in the complex molecule probably controls the catalytic activity by influencing the dispersion of Pd- and Se-containing NPs generated *in situ* during the catalytic process. The two-phase test has indicated the homogeneous nature of the catalytic process, which probably occurs via leaching of Pd(0) from these NPs. This is the first example where Pd–Se NPs are catalyzing Suzuki coupling largely via a homogeneous process and is probably combined with oxidative addition at the surface. These results may pave the way to design ligands/Pd complexes that catalyze Suzuki coupling more efficiently.

ASSOCIATED CONTENT

Supporting Information

Crystal and refinement data, bond lengths and angles, NMR and mass spectra TGA, and CIFs of 1 (CCDC no. 923390) and 2 (CCDC no. 923391). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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