



Pd(II)-complexes of telluro-substituted Schiff base ligands: Effect of the pendant alkyl group on Suzuki and Heck coupling through in situ generated palladium nanoparticles

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ABSTRACT

Two telluro-substituted Schiff bases **L1/L2** having different pendant carbon chains (–Me in **L1** and –C₁₀H₂₁ in **L2**) and their corresponding square planar Pd(II)-complexes (**1/2**) have been synthesized and their structural characterization has been carried out using multinuclear NMR and elemental analysis. The ligand **L2** showed a Smectic liquid crystalline phase and melts at 81 °C into isotropic liquid whereas **L1** and complexes (**1/2**) did not show any liquid crystalline property. The square planar Pd(II)-complexes (**1/2**) have been formed through the coordination of ligands (**L1/L2**) respectively in mono-anionic tridentate mode (Te,N,O[−]) and the fourth coordination sphere at the palladium center is occupied with chloride ion. Both complexes **1/2** (1 to 2 mol%) have been examined as a catalyst for Suzuki and Heck coupling reactions and their activity depends significantly on the length pendant alkyl chain. The results obtained from Hg-/PPh₃-poisoning and three phase test on Suzuki-Miyaura coupling indicate the participation of both homogeneous as well as heterogeneous palladium species protected with the ligand or its fragment.

1. Introduction

The element “tellurium”, belongs to the chalcogen family, is a metalloid and molecules containing tellurium can behave as Lewis acid/base [1,2]. The ligand chemistry of tellurium has evolved very slowly due to the perception that these ligands were harmful, smell bad and are sensitive to air. However, the coordination chemistry of organotellurium ligands has gained considerable attention in the last 30 years. Many research groups were fascinated by the organo-tellurium compounds due to their utilization in material chemistry [3–7], biochemistry [8–13], ligand chemistry [1,2,14–19] and supramolecular structure developments [20–22]. The organo-tellurium ligand chemistry has been intensified since their complexes were found suitable as single-source precursors for the synthesis of metal-telluride semiconductors through chemical vapor deposition (CVD) [23]. Various palladium and platinum chalcogenides [24–35] specifically tellurides have been utilized in the electronic industry [24] as well as in many organic reactions as a catalyst [36–38].

In addition to metal tellurides, several metal complexes of organo-chalcogen ligands including their palladium ones have been reported and utilized as catalysts [39–58]. Although, the data on the understanding of the association of tellurium ligands with metal, their potential use in the formation of catalysts and their application in catalysis are limited [25]. The stability of reactive organotellurium compounds can be improved via intra-molecular coordination by incorporating additional hard donor atoms for instance oxygen or nitrogen along with soft donor tellurium. This led to the possibility of the formation of a highly stable complex with the tuning of the stereo-electronic environment at the metal center [51].

Recently, Pd-complexes of (Se, N, O[−]) donor ligands having different pendant alkyl chains have been utilized as catalysts for the Suzuki-Miyaura coupling (SMC) and the alkyl chain have found to govern their efficiency through the generation of nanoparticles (NPs) said to be “the real” catalytic species [51–56]. Several other complexes have also been explored for various carbon-carbon coupling reactions and the relationship between the length of a ligand’s pendent/non-coordinating

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arm and catalytic efficiency has been evaluated [52–55]. Thus, the Pd (II)-complexes [Pd(L1/L2 – H)Cl] (1/2) of tellurated Schiff base ligands (L1/L2) having different lengths of alkyl chain in the pendant arm have been synthesized and characterized. These complexes have been utilized for Suzuki and Heck coupling reactions and complex 2 having a large alkyl chain showed higher efficiency as compared to complex 1 which has a –Me group in its pendant arm. The findings such as in situ generation of NPs from both complexes having different morphologies as well as the nature of real catalytic species have also been discussed in this paper.

2. Experimental section

2.1. General

The chemicals such as 3-chloropropylamine hydrochloride, sodium borohydride, 2,4-dihydroxyl benzaldehyde (DHB), 4-hydroxybenzoic acid, dicyclohexylcarbodiimide (DCC), 4-*N,N*-dimethyl aminopyridine (DMAP), sodium tetrachloropalladate (Na₂PdCl₄), acrylic acid, dimethylformamide (DMF), phenylboronic acid PhB(OH)₂, potassium carbonate (K₂CO₃) and the aryl halides such as methyl iodide, bromodecane, bromobenzene, 4-bromobenzonitrile, 4-bromonitrobenzene, 4-bromobenzaldehyde, 4-bromobenzoic acid, 4-bromoanisole, 4-bromotoluene and 2-bromopyridine were obtained from Merck chemicals (USA) and utilized as such. Other easily accessible reagents obtained from Spectrochem or Finar and were used as such without additional purification. The solvents like methanol, chloroform, ethanol, DMF, etc. were dehydrated using conventional techniques.

NMR spectra such as ¹H, ¹³C{¹H}, and ¹²⁵Te{¹H} of compounds were collected at 300.13, 75.47, and 94.75 MHz on a Bruker Spectrospin DPX 300 NMR spectrometer, respectively. Perkin-Elmer 2400 Series II C, H, N analyzer has been utilized for element analysis. The progress of all reactions was monitored with a silica gel TLC plate using different mixtures of solvents. The spots were either visualized using iodine or a UV chamber. Column chromatography was used to purify the ligand precursor as well as products of the SMC using 60–120 mesh silica gel. *n*-Hexane with different combinations of chloroform/ethyl acetate has been used as a mobile phase. The Schlenk procedure had been used to produce a nitrogen atmosphere, if necessary. The commercial nitrogen gas was further purified by passing through the traps containing alkaline anthraquinone-sodium dithionite solutions, conc. H₂SO₄, 1,2,3-trihydroxybenzene, and KOH respectively.

2.2. Synthesis of 3-aminopropyl(4-methoxyphenyl)telluride

The precursor amine, 3-aminopropyl(4-methoxyphenyl)telluride, H₂N(CH₂)₃TePh-4-OMe, has been synthesized using a reported method as given in Scheme 1 [56].

2.3. Synthesis of benzoate ester of 2,4-dihydroxy benzaldehyde

The precursor aldehydes required for the designing of ligands L1/L2 have been synthesized by the reaction of iodomethane (CH₃I) (1 mmol, 0.142 g)/bromodecane (C₁₀H₂₁Br) (1 mmol, 0.221 g) with 4-hydroxybenzoic acid (1 mmol, 0.138 g) in DMF at 25 °C in the presence of NaOH for 15 h [51,57]. This results in the formation of 4-

methoxybenzoic acid/4-decloxybenzoic acid. 4-Methoxybenzoic acid (1 mmol, 0.152 g)/4-decloxybenzoic acid (1 mmol, 0.278 g) was then subjected to coupling with DBH (1 mmol, 0.138 g) in the presence of DCC (1 mmol, 0.206 g) and DMAP (0.010 g) as a catalyst in DCM which results in the formation of benzoate ester of DBH. These esters were purified using column chromatography taking a 20% chloroform-hexane mixture.

2.4. Synthesis of ligands L1 and L2

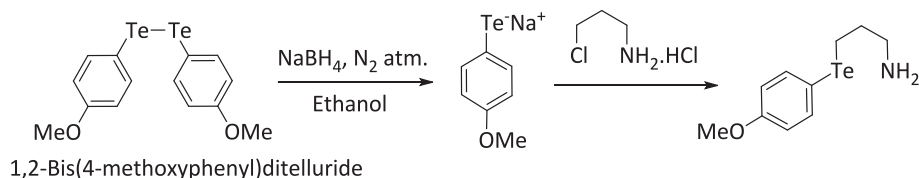
The ligands were synthesized by utilizing the condensation of aldehydes and amine. A solution of 3-aminopropyl(4-methoxyphenyl)telluride (0.293 g, 1.0 mmol) in 5 mL of dry ethanol was added drop-wise to the solution of the 4-methoxybenzoate ester of DBH (0.272 g, 1.0 mmol)/4-decloxybenzoate ester of DBH (0.398 g, 1.0 mmol) in dry ethanol. The resultant mixture was allowed to stir for another 6 h at room temperature. The precipitate was isolated, washed with cold ethanol, and dehydrated in a vacuum to obtain L1/L2 as a light yellow colored precipitate.

L1: Yield; 0.966 g (88%). Anal. Found: C, 54.93; H, 4.54; N, 2.69%. Calc. for C₂₅H₂₅NO₅Te: C, 54.89; H, 4.61; N, 2.56%. ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 2.14 (p, 2H, H₆, *J* = 6.9 Hz), 2.85 (t, 2H, H₅, *J* = 7.5 Hz), 3.63 (t, 2H, H₇, *J* = 6.3 Hz), 3.79 (s, 3H, H₁, –OMe), 3.89 (s, 3H, H₂₀), 6.71–6.79 (m, 4H, H₂, H₁₃, H₁₄), 6.98 (d, 2H, H₁₈, *J* = 8.7 Hz), 7.21 (d, 1H, H₁₁, *J* = 8.4 Hz), 7.69 (d, 2H, H₃, *J* = 8.4 Hz), 8.14 (d, *J* = 8.7 Hz, 2H, H₁₇), 8.20 (s, 1H, H₈), 13.81 (bs, 1H, –OH). ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ (ppm): 5.6 (C₆), 32.4 (C₅), 55.1 (C of –OMe), 55.5 (C₂₀), 60.1 (C₇), 100.1 (C₄), 110.4 (C₁₄), 112.3 (C₁₃), 113.8 (C₂), 115.2 (C₁₈), 116.5 (C₉), 121.5 (C₁₆), 132.1 (C₁₁), 132.3 (C₁₇), 141.0 (C₃), 154.1 (C₁₀), 159.8 (C₁₂), 163.0 (C₁₉), 163.9 (C₁₅), 164.4 (C₁), 164.6 (C₈). ¹²⁵Te{¹H} (95 MHz, CDCl₃, 25 °C, Me₂Te): δ (ppm): 444.9.

L2: Yield; 1.107 g (82%). Anal. Found: C, 60.58; H, 6.39; N, 2.13%. Calc. for C₃₄H₄₃NO₅Te: C, 60.65; H, 6.44; N, 2.08%. NMR: ¹H (300 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 0.89 (t, *J* = 6.9 Hz, 3H, H₂₉), 1.48–1.90 (m, 14H, H_{22–28}), 1.82 (p, *J* = 7.5 Hz, 2H, H₂₁), 2.15 (p, *J* = 6.9 Hz, 2H, H₆), 2.86 (t, *J* = 7.2 Hz, 2H, H₅), 3.64 (t, *J* = 6.3 Hz, 2H, H₇), 3.80 (s, 3H, –OMe), 4.04 (t, *J* = 6.6 Hz, 2H, H₂₀), 6.72–6.79 (m, 4H, H₂, H₁₃, H₁₄), 6.95 (d, *J* = 8.7 Hz, 2H, H₁₈), 7.21 (d, *J* = 8.4 Hz, 1H, H₁₁), 7.69 (d, *J* = 8.4 Hz, 2H, H₃), 8.12 (d, *J* = 9 Hz, 2H, H₁₇), 8.21 (s, 1H, H₈), 13.81 (bs, 1H, –OH). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ (ppm): 9.1 (C₆), 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.6 (C_{21–28}), 31.9 (C₅), 55.2 (C of –OMe), 60.5 (C₇), 68.4 (C₂₀), 99.8 (C₄), 110.5 (C₁₄), 112.5 (C₁₃), 114.3 (C₂), 115.3 (C₁₈), 116.5 (C₉), 121.3 (C₁₆), 132.2 (C₁₁), 132.3 (C₁₇), 141.4 (C₃), 154.2 (C₁₀), 160.0 (C₁₂), 162.9 (C₁₉), 163.7 (C₁₅), 164.4 (C₁), 164.5 (C₈). ¹²⁵Te{¹H} (95 MHz, CDCl₃, 25 °C, Me₂Te): δ (ppm): 444.5.

2.5. Synthesis of Pd(II)-complexes 1 and 2

A ligand L1 (0.549 g, 1.0 mmol)/L2 (0.643 g, 1.0 mmol) solution made in 10 mL of acetone has been added to the Na₂PdCl₄ solution in water (0.294 g, 1.0 mmol) drop-wise and the mixture was stirred for 3 h. The complexes 1/2 were extracted by using chloroform (2 × 10 mL). The residual water present in chloroform was removed using anhydrous Na₂SO₄. The chloroform was concentrated to ~ 5 mL and an excess of hexane (50 mL) was added which results in a yellow precipitate that was dehydrated to obtain the complex 1/2.



Scheme 1. Synthesis of (4-methoxyphenyl)telluropropylamine.

1: Yield; 0.632 g (92%). Anal. Found: C, 43.68; H, 3.87; N, 2.08%. Calc. for $C_{25}H_{24}ClNO_5PdTe$: C, 43.65; H, 3.92; N, 2.04%. 1H (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 2.07–2.17 (m, 1H, H_6), 2.40–2.44 (m, 1H, H_5), 2.85–3.07 (m, 2H, H_5 , H_6), 3.40–3.48 (m, 1H, H_7), 3.82 (s, 3H, H_{20}), 3.90 (s, 3H, –OMe), 4.10–4.21 (m, 1H, H_7), 6.20 (dd, $J = 8.7$ & 2.1 Hz, 1H, H_{13}), 6.65 (d, $J = 2.1$ Hz, 1H, H_{11}), 6.79 (d, $J = 8.7$ Hz, 1H, H_{14}), 6.90 (d, $J = 9.0$ Hz, 2H, H_3), 6.99 (d, $J = 8.7$ Hz, 2H, H_{18}), 7.19 (s, 1H, H_8), 8.15 (dd, $J = 7.2$ & 2.1 Hz, 2H, H_{17}), 8.21 (d, $J = 8.7$ Hz, 2H, H_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm): 22.6 (C_6), 31.9 (C_5), 55.3 (C of –OMe), 57.1 (C_7), 68.3 (C_{20}), 101.6 (C_4), 110.3 (C_{13}), 112.7 (C_{11}), 114.3 (C_2), 116.2 (C_{18}), 121.1 (C_{16}), 132.3 (C_{17}), 132.9 (C_{14}), 139.3 (C_3), 154.4 (C_9), 156.8 (C_{10}), 161.4 (C_1), 162.4 (C_8), 163.6 (C_{12}), 164.3 (C_{19}), 166.2 (C_{15}). $^{125}Te\{^1H\}$ (95 MHz, $CDCl_3$, 25 °C, Me_2Te): δ (ppm): 760.0.

2: Yield; 0.708 g (87%). Anal. Found: C, 50.19; H, 5.24; N, 1.75%. Calc. for $C_{34}H_{42}ClNO_5PdTe$: C, 50.16; H, 5.20; N, 1.72%. 1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 0.88 (t, $J = 6.9$ Hz, 3H, H_{22}), 1.27–1.59 (m, 14H, H_{21-28}), 1.61–1.73 (m, 2H, H_5 & H_6), 1.79–1.89 (m, 2H, H_{21}), 2.49–2.58 (m, 1H, H_6), 3.58–3.72 (m, 1H, H_5), 3.83 (s, 3H, –OMe), 3.93–3.98 (m, 1H, H_7), 4.06 (t, $J = 6.6$ Hz, 2H, H_{20}), 5.40–5.46 (m, 1H, H_7), 6.33 (dd, $J = 8.7$ & 1.8 Hz, 1H, H_{13}), 6.72 (d, $J = 1.8$ Hz, 1H, H_{11}), 6.85 (d, $J = 8.7$ Hz, 1H, H_{14}), 6.90 (d, $J = 8.7$ Hz, 2H, H_3), 6.98 (d, $J = 8.7$ Hz, 2H, H_{18}), 7.05 (s, 1H, H_8), 8.05 (d, $J = 8.7$ Hz, 1H, H_{17}), 8.12 (d, $J = 9.0$ Hz, 2H, H_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm): 14.2 (C_{22}), 15.8 (C_{21-28}), 22.7 (C_{21-28}), 26 (C_{21-28}), 29.1 (C_6), 29.8–29.5 (C_{21-28}), 31.9 (C_5), 55.4 (C of –OMe), 68.4 (C_7), 68.7 (C_{20}), 104.9 (C_4), 109.5 (C_{13}), 111.9 (C_{11}), 114.4 (C_{18}), 115.8 (C_2), 118.5 (C_9), 121.3 (C_{16}), 132.3 (C_{17}), 137.3 (C_3), 138.8 (C_{14}), 156.9 (C_{10}), 160.8 (C_1), 161.3 (C_8), 163.7 (C_{12}), 164.5 (C_{19}), 165.2 (C_{15}). $^{125}Te\{^1H\}$ (95 MHz, $CDCl_3$, 25 °C, Me_2Te): δ (ppm): 760.9.

2.6. Procedure for SMC reaction

Aryl halide (0.5 mmol), K_2CO_3 (1.0 mmol, 0.138 g), $PhB(OH)_2$ (0.6 mmol, 0.075 g), DMF (2.0 mL), and H_2O (1.0 mL) was added to a round bottom flask. The complex **1/2** (1 mol%) made in DMF (1 mL) was added and heated for 15 hr at 100 °C. Diethyl ether (2 × 5 mL) was used to extract the organic mixture from water using a separating funnel. The organic layer was dehydrated and the solvent was evaporated to give the crude product which was purified, if required, using column chromatography having a suitable mixture of $CHCl_3/CH_3COOC_2H_5$ with *n*-hexane.

2.7. General procedure for the Heck coupling reaction

Aryl halide (2.0 mmol), acrylic acid (2.20 mmol, 0.168 g), K_2CO_3 (4.0 mmol, 0.552 g), and DMF (5.0 mL) were taken in a flask. A stock solution of complex **1/2** (2 mol%) made in DMF was added and it was heated at 110 °C for 48 h. The reaction was cooled and then 10 mL H_2O was added to it. NaOH (10 mM) was added to the RB and pH was brought to ~7. The obtained precipitate was washed with 5 mL cold ethanol to give the pure products.

2.8. Hg poisoning test on the SMC

Hg (Hg: Pd::100:1) and **2** (1 mol%) were stirred for 30 min in DMF- H_2O (2 + 1 mL) mixture. Afterward, 4-bromonitrobenzene (0.5 mmol, 0.101 g), $PhB(OH)_2$ (0.6 mmol, 0.075 g) and K_2CO_3 (1 mmol, 0.138 g) were added and stirred at 100 °C for 15 h. The product, 4-nitrobiphenyl was obtained in 83% yield in the presence of catalyst **2**.

2.9. PPh_3 poisoning test on the SMC

Catalyst (**2**; 1 mol%), PPh_3 (1 mmol, 0.262 g), 4-bromonitrobenzene (0.5 mmol, 0.101 g), $PhB(OH)_2$ (0.6 mmol, 0.075 g) and K_2CO_3 (1 mmol, 0.138 g) were stirred under optimum reaction conditions. The cross-coupled product, 4-nitrobiphenyl was obtained 80% yield.

2.10. Separation of NPs generated in situ from **1/2** during SMC

A mixture of either of Pd(II)-complex **1/2** (0.10 mmol), 4-bromonitrobenzene (0.5 mmol, 0.101 g), $PhB(OH)_2$ (0.6 mmol, 0.075 g) and K_2CO_3 (1 mmol, 0.138 g) was stirred under optimum reaction condition. After cooling, water (10 mL) was added, and the resulting solution was centrifuged and washed three times with the water–acetone (1:3) mixture and finely with 5 mL acetone. The black residue was dehydrated and subjected to various characterizations.

2.11. Procedure for the SMC with isolated NPs

The procedure for SMC was similar to those mentioned for complexes using 4-bromonitrobenzene as substrate. In place of metal complexes, NPs (10 mg) were used and the reaction was carried out under optimum reaction conditions.

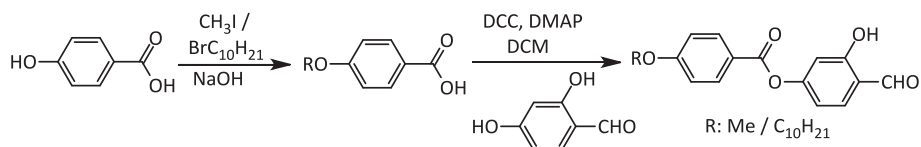
2.12. Three phase test on SMC

4-Bromoacetophenone (1 mmol, 0.199 g), $PhB(OH)_2$ (3 mmol, 0.363 g), K_2CO_3 (4 mmol, 0.552 g) and 4-bromo-*N*-propylbenzamide functionalized on silica (0.200 g) have taken in DMF-water mixture (5 + 3 mL) and stirred at 100 °C in the presence of 1 mol% of **2** for 15 h. The reaction mixture was cooled, filtered and the solid was washed with water (50 mL). The aqueous layer was extracted with diethyl ether (2 × 25 mL) for organic content, dehydrated, and subjected to 1H NMR. The solid leftover was hydrolyzed in the ethanol–water mixture (10 + 5 mL) using KOH (1.68 g) at 100 °C for three days. The solution was cooled and the pH was adjusted to ~7 using 20% (v/v) HCl. The aqueous layer was extracted with DCM (2 × 15 mL) followed by ethyl acetate (2 × 15 mL). The organic layers were mixed and dehydrated over Na_2SO_4 . The solvent was removed and subjected to 1H NMR.

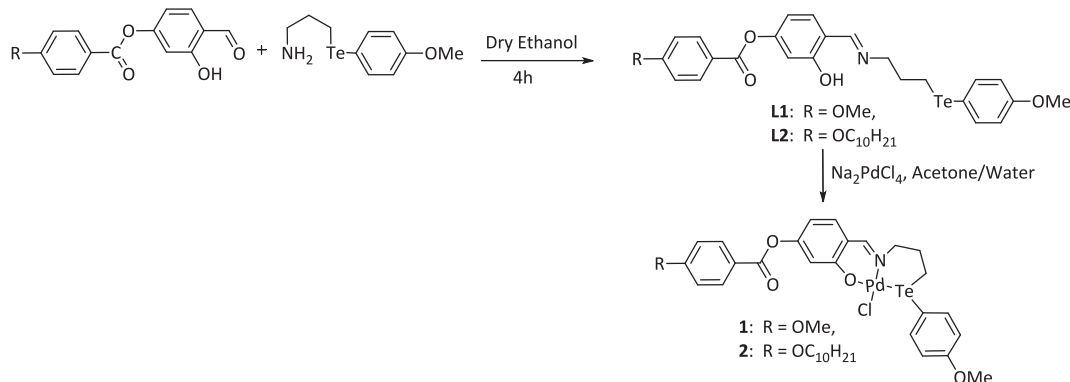
3. Results and discussion

The aldehydes and amine required to synthesize **L1/L2** have been prepared using the known literature procedure (Schemes 1 & 2) [54,56,57]. The Schiff base condensation reaction of tellurated amine with the corresponding aldehyde in ethanol for 4 hrs led to the formation of **L1/L2** (Scheme 3).

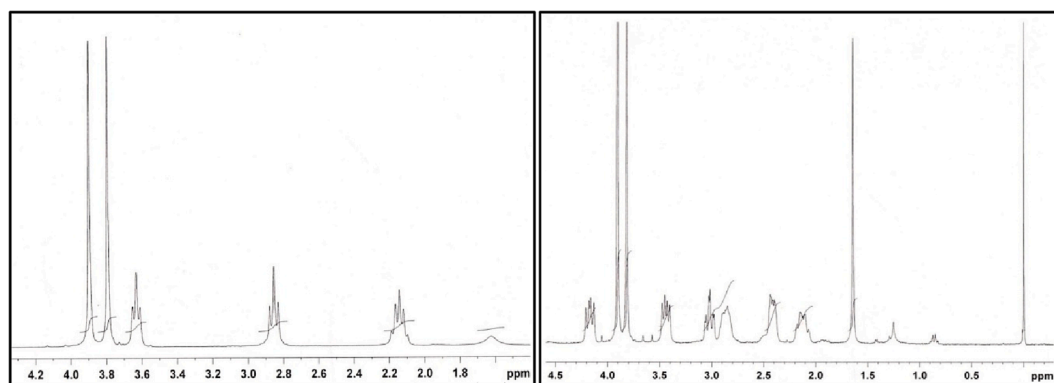
The ligands **L1/L2** (dissolved in acetone) on treatment with Na_2PdCl_4 (dissolved in water) result in the formation of their corresponding complexes (**1/2**). The ligands and their Pd(II) complexes have been found stable and can be stored under laboratory conditions for at least six months. The ligands and their Pd(II) complexes are slightly soluble in nonpolar solvents such as hexane and toluene, however, good solubility was observed in polar solvents like $CHCl_3$, DCM, DMF, and DMSO. Attempt to crystallize either ligands or their metal complexes were unsuccessful. However, the structures of **L1/L2** and their complexes **1/2** are well supported by elemental analysis and NMR spectroscopy (Fig. 1, Figs. S1–S22 in Supplementary Information) and their NMRs were well-matched with their structures as depicted in Scheme 3. The proton-carbon correlation (HMQC) has been done in order to correct assignment of the carbon associated with the proton (Fig. S11 in Supplementary Information). The NH_2 peaks of tellurium amine in the proton NMR spectrum appeared at 1.3 ppm which was dismissed after the formation of **L1/L2**. Similarly, the CH proton of –CHO group showed a singlet at ~11.3 ppm in the proton NMR spectrum which shifted 3.1 ppm upfield and appeared at ~8.2 ppm after the formation of **L1/L2**. A similar observation has been observed in the $^{13}C\{^1H\}$ NMR of amine and aldehydes. The NCH_2 peaks of amine appeared at ~54.4 ppm which after ligands (**L1/L2**) formation shifted to downfield value and appeared at ~60.4 ppm. Similarly, in the $^{13}C\{^1H\}$ NMR of aldehydes, the –CHO peak which appeared at ~196.5 ppm, shifted upfield and appeared at ~164.5 ppm (corresponding to C of –HC=NH) after the ligand (**L1/L2**) formation. The $^{125}Te\{^1H\}$ NMR spectra of tellurium



Scheme 2. Methodology for the synthesis of precursor aldehydes.



Scheme 3. The procedure used for the synthesis of L1/L2 and 1/2.

Fig. 1. ^1H NMR spectra of the aliphatic region of ligand L1 and complex 1.

amine showed a peak at 461.8 ppm [57] which has been appeared at 444.9 and 445.5 in the case of L1 and L2 respectively. The presence of a single peak around ~ 444 ppm in $^{125}\text{Te}\{^1\text{H}\}$ spectra of both ligands (L1/L2) showed the presence of a single type of Te in each case (Figs. S5 & S10 in Supplementary Information). On the formation of complexes 1 and 2, this peak disappeared and new signals appeared at ~ 760 ppm which is deshielded by ~ 316 ppm with respect to the corresponding ligand (Figs. S16 & S22 in Supplementary Information). This showed the coordination of tellurium with palladium in both complexes. In the case of both ligands, $-\text{OH}$ proton signals appeared ~ 13.8 ppm. The appearance of these protons at such a higher value is due to the hydrogen bonding of $-\text{OH}$ proton with the lone pair of imine nitrogen (Figs. S1 & S6 in Supplementary Information). This signal disappeared in the case of both the complexes which indicates the involvement of oxygen with palladium. The CH proton of the $\text{CH}=\text{N}$ bond appeared at ~ 8.2 ppm in the ^1H NMR of both the ligands which shifted to the upfield region by 1.1 ppm upon the formation of complexes 1/2 (Fig. 1; Figs. S1, S6, S12 & 17 in Supplementary Information). Furthermore, the $-\text{NCH}_2$ and $-\text{TeCH}_2$ signals of L1/L2 in their proton NMR spectra appeared as a triplet at ~ 2.85 and ~ 3.63 ppm respectively (Figs. S1 & S6 in Supplementary Information). The aliphatic CH_2 protons lie between $-\text{NCH}_2$ and $-\text{TeCH}_2$ appeared as a pentate at ~ 2.14 ppm in the case of both L1 and L2 (Figs. S1 & S6 in Supplementary Information). All six aliphatic

$-\text{CH}_2$ protons ($-\text{NCH}_2$, $-\text{TeCH}_2$, and $-\text{CH}_2$ protons lie between $-\text{NCH}_2$ and $-\text{TeCH}_2$) in case of complexes 1/2 appeared between 2.0–4.0 ppm as multiples and their pattern indicates their diastereotopic nature (Fig. 1; Figs. 12 & 17 in Supplementary Information). This supports the coordination of both nitrogen as well as tellurium with palladium in both complexes. The $^{13}\text{C}\{^1\text{H}\}$ NMR of ligands showed signals at ~ 168 and ~ 154 ppm which correspond to C_8 and C_{10} respectively and shifted to ~ 161 and ~ 157 ppm upon complexation (Figs. S4, S9, S15 & S21 in Supplementary Information). Thus, the data obtained from ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{125}\text{Te}\{^1\text{H}\}$ NMR suggest the coordination of oxygen, nitrogen and tellurium with palladium in both the complexes. The fourth coordination position of Pd is completed with chloride which lies trans to nitrogen resulting in the formation of square planar geometry having two six-membered chelate rings (Scheme 2) [51]. The Se-ligated analogous complexes have been reported to have a similar kind of binding mode [51].

The ligands L1/L2 and their complexes 1/2 have been examined for their liquid crystalline properties using polarized optical microscopy (Table 1). The ligand L1 as well as complexes 1/2 does not show any liquid crystalline property. However, the L2 appears to melt to a Smectic phase at the comparatively low temperature of 49°C which converted into isotropic liquid at 81°C (Table 1, Fig. 2) [54].

The catalytic potential of complexes 1/2 has been studied for Suzuki

Table 1
Phase transitions data of L2.

Crystal	T (°C)	Mesophase type	T (°C)	Isotropic liquid
	49	Smectic	81	

The dots symbolize temperature areas which are beyond phase-transition points.

and Heck carbon–carbon coupling reactions (Tables 2–4). The optimization of reaction conditions has been carried out on a representative reaction 4-bromonitrobenzene with PhB(OH)₂ in the presence of complex 1 using different solvents and bases. It was found that the optimum concentration of complex 1 for catalysis was 1 mol%. The maximum yield of cross-coupled product was obtained when K₂CO₃ was used as a base and DMF-water mixture as a solvent (Table 2; Entry 5) among all the bases and solvents examined. For appropriate conversions, a larger reaction time (15 h) was generally required (Table 2; Entry 6). However, in the case of other solvents and base combinations, the yields of coupled products were low or no formation of the product was observed (Table 2). The yield of cross couple product, 4-nitrobiphenyl, however, was higher (89%) in the presence of catalyst 2, under optimum reaction conditions (Table 3; Entry 4). Furthermore, several other aryl halides have been tested for cross-coupling under the optimum conditions using 1/2 as a catalyst (Table 3). In the case of aryl chlorides, 1-chloro-4-nitrobenzene, the cross-coupled product was not observed with any of the catalyst under optimum reaction conditions (Table 3; Entry 9). The effect of electron-withdrawing and electron-donating groups on aryl halide does not significantly affect the yield of cross-coupled products with either of the catalysts (Table 3). The cross-coupled product of 4-bromoanisole has been produced in 25 and 86% yield in the presence of 1 mol% of 1 and 2 respectively under optimum reaction conditions (Table 3; Entry 2). Heteroaryl halide such as 2-bromopyridine has been successfully coupled to produce 2-phenylpyridine in 22 and 90% yield in the presence of 1 and 2 respectively (Table 3; Entry 8). The highest yield (95%) has been produced for the coupling of 4-bromobenzonitrile in the presence of 1 mol% of 2 (Table 3; Entry 6). The C–Cl bond of aryl chloride possess higher bond energy than C–Br in aryl bromide. Thus, the oxidative addition of C–Cl at Pd(0) center, the first step of Suzuki coupling, is much complex, which probably results in 0% product yield in case 1-chloro-4-nitrobenzene (Table 3; Entry 9). It is important to mention that both complexes have the same donor groups i.e. (Te, N, O[−]), only the difference is the length of the pendant alkyl chain. Catalyst 2 has a larger alkyl chain (10 carbon) was found more efficient for the coupling reactions as comparison to complex 1 (having only one carbon chain in the pendant arm).

Furthermore, the catalytic activity of complexes 1/2 has also been tested for the Heck coupling reaction with various aryl halides with acrylic acid under standard reaction conditions (Table 4). Similar to Suzuki coupling, the most suitable base was found to be K₂CO₃ and DMF as solvent. However, longer reaction time (48 h) and higher catalyst loading (1/2: 2 mol%) are required to produce similar yields (Table 4). Aryl halides having electron-donating as well as electron-withdrawing groups have been successfully converted to cross-coupled products (Table 4; Entry 1–5) under optimum reaction conditions. The highest yield was obtained when 4-bromobenzaldehyde was used as a coupling

partner in the presence of 2 mol% of catalyst 2 (Table 4; Entry 5). However, the coupling of aryl chloride was unsuccessful either with the complexes which have been also observed in Suzuki coupling. Another important observation is that catalyst 2 having a large pendant alkyl chain showed much higher catalytic activity for both coupling reactions as compared to complex 1. Such observation has also been made with Pd (II)-complexes of (Se, N, O[−]) donor ligands having different lengths of pendant alkyl chain [51]. It is relevant to mention that such complexes are the reservoirs of the Pd-NPs (true catalytic species) protected with the ligand or its framework. The alkyl chain has been found to govern the size of NPs and their dispersion which turns their catalytic properties [51,53]. The larger alkyl chain on ligands has been found to in-situ generate highly uniform NPs which results in higher catalytic activity [51]. Thus, it was thought worthwhile to look at the real catalytic species produce during the catalytic process. During the reactions, the formation of black particles has been observed which enhances the probability that 1/2 acts as pre-catalysts and provides the nano-sized particles during the reaction. To examine the relationship between nature, the alkyl chain's length, and the catalytic activity of the black particles, these black species were isolated and examined using PXRD and TEM. The PXRD of both isolated NPs does not show any peaks indicating their amorphous nature. The TEM images of the NPs display that the NPs obtained in the case of complex 2 are more evenly dispersed as compared to those obtained from complex 1 (Fig. 3).

To compare the catalytic efficiency of complex 2 and NPs obtained from 2, the progress of the reaction was monitored with time by reacting 4-bromonitrobenzene with PhB(OH)₂ under optimum reaction conditions. Both complex 2, as well as NPs isolated from complex 2, showed almost similar conversions with the time (Fig. 4).

To determine the true catalytic species and the nature of catalysis, several tests including Hg-/PPh₃-poisoning and a three-phase test were performed [54,55,58]. Hg-/PPh₃-poisoning tests were conducted on the SMC of 4-bromonitrobenzene with PhB(OH)₂ using catalyst 2 (1 mol%) under optimum reaction conditions by taking Hg:2/PPh₃:2 ratios of 100:1. The product obtained in 83 and 80% conversion for Hg and PPh₃ test respectively under optimum reaction condition. These tests indicate the existence of catalytically active Pd(0) particles protected with the ligand or its fragment in the solution. However, these tests could not determine whether the catalytic procedure was homogeneous or

Table 2
Reaction conditions standardization^a.

S. No.	Solvent	Base	(%)Yield ^b
1	DMF	K ₂ CO ₃	12
2	DMSO	K ₂ CO ₃	8
3 ^c	THF	K ₂ CO ₃	7
4	Toluene	K ₂ CO ₃	9
5	DMF-Water	K ₂ CO ₃	16
6 ^d	DMF-Water	K ₂ CO ₃	21
7	DMF-Water	Cs ₂ CO ₃	20
8	DMF-Water	CH ₃ COONa	8
9	DMF-Water	NEt ₃	Traces

^a Reaction conditions: 4-Bromonitrobenzene (0.5 mmol), PhB(OH)₂ (0.6 mM), base (1 mmol), catalyst 1 (1 mol%), temperature (100 °C), reaction time 15 h, DMF: water (2:1). ^bNMR %yield. ^cTemperature (70 °C). ^dReaction time (10 h).

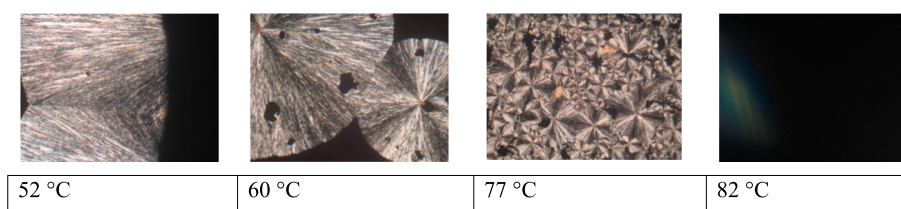


Fig. 2. Polarized micrographs were observed for L2 at different temperatures.

Table 3
SMC catalyzed by complexes 1–2^a.

S.N.	Aryl halide	Yield (%) ^b	
		1	2
1	4-Bromotoluene	25	92
2	4-Bromoanisole	25	86
3	Bromobenzene	24	88
4	4-Bromonitrobenzene	18	89
5	4-Bromobenzaldehyde	23	93
6	4-Bromobenzonitrile	28	95
7	4-Bromobenzoic acid	21	91
8	2-Bromopyridine	22	90
9	4-Chloronitrobenzene	0	0

^a Reaction conditions: Aryl halide (0.5 mmol), PhB(OH)₂ (0.6 mmol), catalyst 1/2 (1 mol%), base (K₂CO₃; 1 mmol), solvent (DMF-water, 3 + 2 mL), temperature (100 °C), reaction time 15 h. ^bIsolated yield.

Table 4
Palladium complexes 1/2 catalyzed Heck coupling ^a.

S. No.	Aryl halide	Yield (%) ^b	
		1	2
1	4-Bromotoluene	18	83
2	4-Bromoanisole	18	80
3	Bromobenzene	20	78
4	4-Bromonitrobenzene	24	86
5	4-Bromobenzaldehyde	24	89
6	4-Chloronitrobenzene	0	0

^a Reaction conditions: Aryl halide (2.2 mmol), acrylic acid (2 mmol), base (K₂CO₃; 2 mmol), catalyst 1/2 (2.0 mol%), solvent (DMF; 5 mL), temperature (110 °C), reaction time 48 h. ^bIsolated yield after workup.

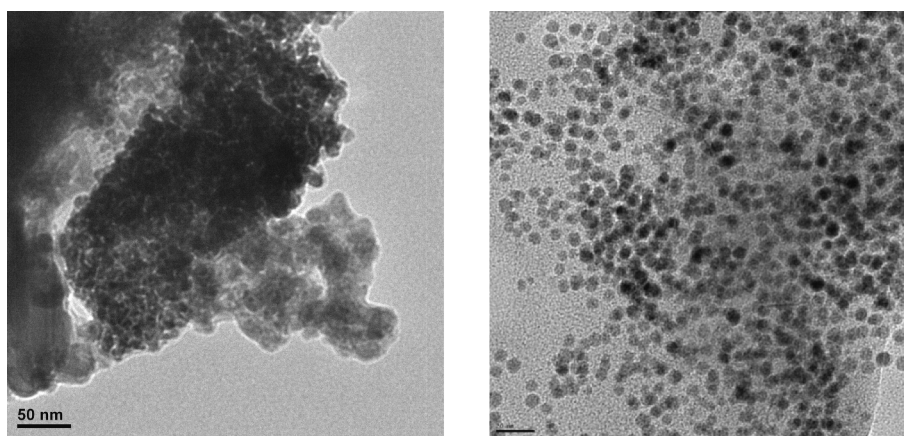


Fig. 3. TEM of NPs obtained from complex (a) 1 (scale bar: 50 nm) and (b) 2 (scale bar: 20 nm) respectively.

heterogeneous, as the leaching of surface Pd-atoms of heterogeneous NPs in solution (result in Pd(II) complex, Ar–Pd–Br by oxidative addition) could cause homogeneous catalysis. To have a better understanding of catalytic processes, a three-phase test was performed (Scheme 4), though, the colloidal or molecular nature of the catalyst cannot be specified by this test [52–56,59]. The 4-bromoacetophenone functionalized on silica gel must not convert into a coupled product if the reaction operates through a heterogeneous process. However, the conversion of the supported substrate to the product indicates homogeneous activity due to the leaching of Pd in the solution. This test was

carried out under optimal reaction conditions by using 4-bromoacetophenone, immobilized 4-bromobenzoic acid and PhB(OH)₂. The soluble part was isolated by extraction and analyzed using ¹H NMR which showed the formation of a cross-coupled product, 4-acetylbiphenyl, in 78% conversion leaving 22% reagent (4-bromoacetophenone). Furthermore, the hydrolysis of silica-functionalized with 4-bromobenzoic acid after coupling produce the product biphenyl-4-carboxylic acid in 44% conversion. Thus, the results obtained from three phase test revealed that the homogeneous palladium species (molecular or colloidal) have a remarkable contribution to the catalysis. However, the

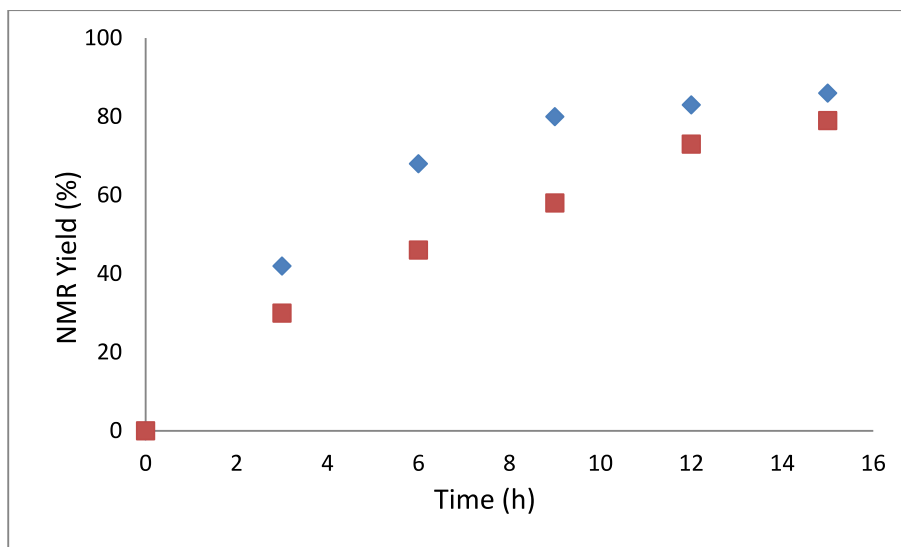
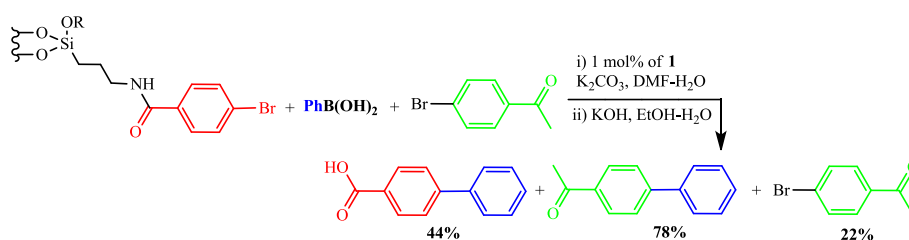


Fig. 4. Time profile activity of complex 2 and NPs obtained from complex 2.



Scheme 4. Three-phase test on Suzuki-Miyaura coupling with catalyst 2.

contribution of heterogeneous process cannot be ignored. Thus, the both coupling reactions seem to operate through the involvement of both homogeneous as well as heterogeneous processes.

4. Conclusions

The Schiff base (Te,N,O^-) ligands (**L1/L2**) and their Pd(II)-complexes $[\text{Pd}(\text{L1/L2-H})\text{Cl}]$ (**1/2**) have been synthesized and characterized using ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{125}\text{Te}\{^1\text{H}\}$ NMR spectroscopy. Additionally, the ligand **L2** showed liquid crystalline properties, melts at 81°C into isotropic liquid, and showed a Smectic liquid crystalline phase. Complexes (**1/2**) have been examined as a catalyst for Suzuki-Miyaura and Heck C—C coupling reactions. Complex **2** having a larger alkyl chain has been found to show higher catalytic activity than complex **1** having one carbon alkyl chain in the pendant arm. The higher catalytic efficiency of complex **2** is attributed to highly uniform in-situ generated NPs of palladium. However, the formation of aggregates was observed when **1** was used as a catalyst. The results obtained from PPh_3/Hg -poisoning and three-phase tests suggest the involvement of both homogeneous as well as heterogeneous catalytic processes where Pd-NPs were protected with ligands or its fragments.

CRediT authorship contribution statement

Poonam Kaswan: Validation, Investigation, Writing – original draft. **Nisha Yadav:** Validation, Writing – original draft. **Divya Choudhary:** Writing – original draft. **Chandra Mohan Srivastava:** . **Bharat Kumar:** Investigation, Writing – review & editing. **Jahangeer Ahmed:** Investigation, Writing – review & editing. **Gyandshwar Kumar Rao:** Conceptualization, Methodology, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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