Inorganic Chemistry Communications 15 (2012) 163–166

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Palladiumd(II) complexes of *N*-{2-(aryltelluro)ethyl}morpholine/piperidine: Synthesis, structure, application in Heck coupling and unprecedented conversion into nano-sized PdTe

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A R T I C L E I N F O

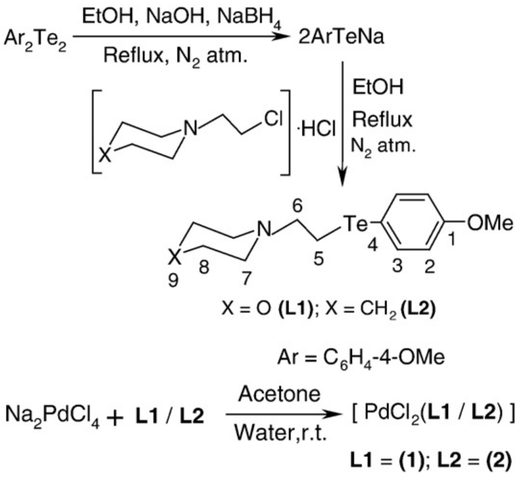
Article history:
Received 10 September 2011
Accepted 17 October 2011
Available online 25 October 2011

Keywords:
Palladium
Tellurium ligand
Synthesis
Structure
Nano-particle
Heck coupling

A B S T R A C T

The complexes, [$PdCl_2$(**L**)] (**1**–**2**) (**L** = *N*-{2-(arylteluro)ethyl}morpholine/piperidine) have been synthesized and characterized by multi-nuclei NMR and single crystal X-ray crystallography. They on reaction with aryl chloride/bromide and morpholine/piperidine give ~5 nm size nano-particles of PdTe. The 0.005 mol% of **2** is suitable for Heck coupling (conversion up to 93%).

Palladium(II) complexes of organotellurium ligands have been investigated more as academic curiosities[1], while palladium(II) complexes of many other ligands are known as catalysts or pre-catalysts for various carbon–carbon [2] and carbon–heteroatom coupling reactions (C–S [3], C–P [4], C–O [5] and C–N [6]). Among these couplings, C–N bond formation is of special interest because the resulting products are the rudiments in various compounds of relevance to biological, pharmaceutical and material sciences [7]. Consequently several new efficient palladium catalytic systems for C–N cross-coupling reactions between aryl and heteroaryl halides and amines have been reported recently [6f–h]. The complexes of palladium with some organochalcogen ligands have been found promising for C–C coupling reactions [8–10] such as Heck coupling and Suzuki–Miyaura coupling. However, they need to be extensively explored for catalytic reactions as their potential is scantly known, particularly of organotellurium ligands about which virtually nothing is reported. Further we are unaware of any report in which palladium complex of any organochalcogen ligand is explored for carbon–heteroatom coupling reaction, particularly C–N one. It was therefore thought worthwhile to design palladium complexes (**1**–**2**) of *N*-{2-(arylteluro)ethyl} morpholine/piperidine/ligands (Scheme 1) and explore their potential for C–C and C–N cross-coupling reactions. Bidentate organotellurium ligands have been envisaged suitable for this purpose in view of desired stability as well as accessibility of Pd in complexes. Thus ligands given in Scheme 1 and their Pd(II) complexes have been synthesized, characterized and explored for their potential for C–N coupling and Heck C\C Coupling. The conversions were found up to 92% when 0.005 mol% of **2** was used for Heck coupling. However, unprecedented formation of nano-size (~5 nm) particles of composition PdTe occurs while attempting C–N reactions. The resulting Pd–Te quantum dots have been characterized. These results are described in this communication.



Scheme 1. Synthesis of **L1–L2** and their Pd-complexes **1**–**2**.

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doi:10.1016/j.inoche.2011.10.015

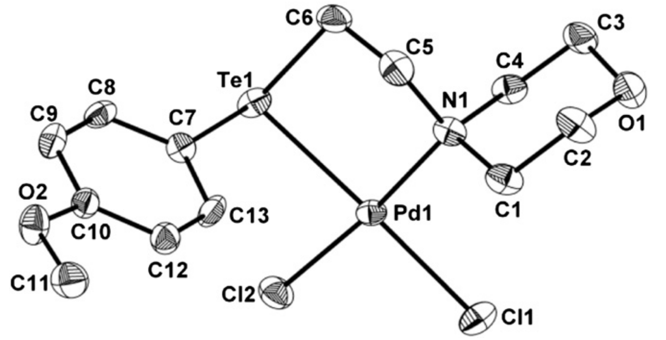


Fig. 1. ORTEP diagram of **1** with 30% probability ellipsoids; bond length(Å): Pd(1)–Te(1) 2.5054(6), Pd(1)–N(1) 2.119(5), Pd(1)–Cl(1) 2.3574(15), Pd(1)–Cl(2) 2.2880(16); bond angle (°): Cl(1)–Pd(1)–Te(1)172.44(4), Cl(2)–Pd(1)–Te(1) 84.55(4), N(1)–Pd(1)–Te(1) 90.26(13), N(1)–Pd(1)–Cl(1) 95.17(14), N(1)–Pd(1)–Cl(2) 174.59(14), Cl(2)–Pd(1)–Cl(1) 90.14(6).

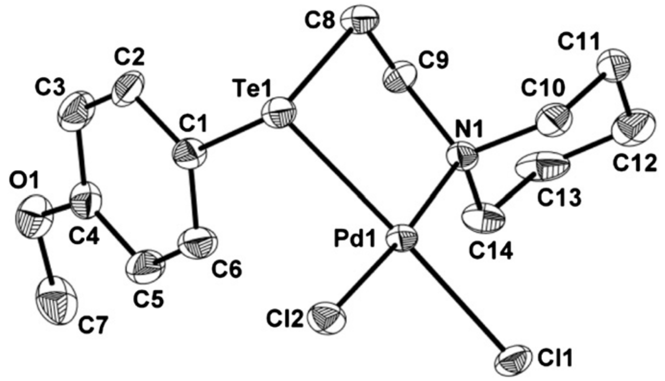


Fig. 2. ORTEP diagram of **2** with 50% probability ellipsoids; bond length(Å): Pd(1)–Te(1) 2.5145(6), Pd(1)–N(1) 2.126(5), Pd(1)–Cl(1) 2.3609(16), Pd(1)–Cl(2) 2.3099(17); bond angle (°): Cl(1)–Pd(1)–Te(1)175.96(5), Cl(2)–Pd(1)–Te(1) 85.42(5), N(1)–Pd(1)–Te(1) 90.20(14), N(1)–Pd(1)–Cl(1) 93.79(14), N(1)–Pd(1)–Cl(2) 175.56(14), Cl(2)–Pd(1)–Cl(1) 90.66(6).

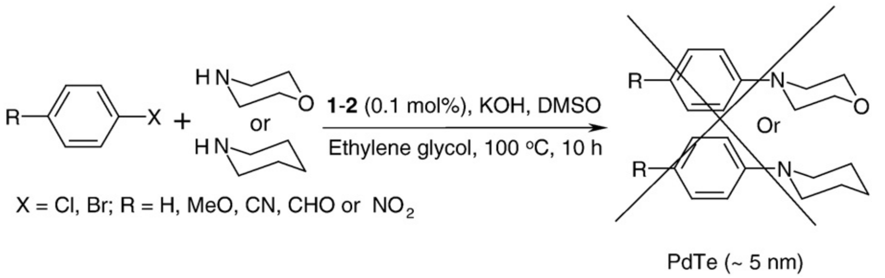
The **L1** has been reported earlier [11] while **L2** prepared for the first time. The **1** and **2** were synthesized by reaction of Na_2PdCl_4 with **L1** and **L2** respectively. The detailed procedures are given in Supplementary Material. The signals in ^{125}Te{^{1}H} NMR spectra [12] of **1** and **2** appear at higher frequency (222 and 244 ppm respectively) than those of free **L1** and **L2** (Supplementary Material), as Te donor sites are coordinated to the Pd centre. In ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** and **2** signals of all protons and carbon atoms respectively appear at higher frequency[11] relative to those of free ligands (See Supplementary Material) which coordinate with Pd in a bidentate mode. The magnitude of shifting to higher frequency is up to ~5 ppm for C5 and ~46 ppm for C7 in ^{13}C{^{1}H} NMR spectra. In ^{1}H NMR spectra also protons attached to these carbon atoms appear shifted (up to 1 ppm) to higher frequency.

The **1** and **2** have been characterized by X-ray crystallography and their ORTEP diagrams are given in Figs. 1 and 2 with some bond lengths and angles (more values are given in Table S1 and S2 of Supplementary Material) respectively. The geometry around Pd in **1** and **2** is nearly square planar and the ligands are coordinated with Pd in a bidentate (Te, N) mode forming five membered ring. This is also supported by NMR spectroscopy. The Pd–Te bond lengths of **1**, 2.5054(6) and **2**, 2.5145(6) Å are similar but shorter than the sum of their covalent radii 2.64 Å. They are consistent with the reported values [1,13] 2.5007(6)-2.5158(5) Å for [PdCl(O$^-$, N, Te)ligand] and [$PdCl_2$(N, Te)ligand]. They are also not significantly longer than the value 2.4781(3) Å reported for [$PdCl_2$(*N*-{2-(4-methoxyphenyltelluro)ethyl}pyrrolidine)] [14] but in comparison to values 2.5865(2)-2.6052(2) Å reported for [$PdCl_2$(*N*-{2-(4-methoxyphenyltelluro)ethyl}morpholine)$_2$] [15] they appear to be somewhat shorter. This difference is easily understandable in terms of minor steric factor in first case and monodentate nature of (Te, N) ligand in the other complex. The Pd – N bond lengths of **1**–**2** [2.119(5) to 2.126(5) Å] are consistent with the sum of their covalent radii 2.03 Å. The Pd – Cl bond lengths in 1 and 2 are normal (2.2880(16) to 2.3609(16) Å). The bond angles at Te and N atoms are as expected for nearly trigonal-pyramidal and tetrahedral geometries, respectively.

The reactions between morpholine or piperidine and aryl chloride or bromide (having substituent: – MeO, – CN, – CHO, – NO_2) and complexes **1** and **2** in the presence of KOH as a base, at 100 °C carried out with a motive of C – N coupling (Scheme 2) resulted in PdTe nano-particles (for detailed procedure see, Supplementary Material) due to decomposition of **1** and **2.**

The resulting nano-sized product was separated (See S4 in Supplementary material). To characterize it was converted from amorphous phase to crystalline phase by annealing at 550 °C in argon atmosphere for 5 h. Thereafter SEM-EDX (Supplementary Material: Figure S5.2–S5.3) powder X-ray diffraction (see S5 and Figure S5.1 in Supplementary Material), HR-TEM (Fig. 3 and Figure S5.4) and TEM-EDX (Figure S5.5 in Supplementary Material) were used for its characterization. These studies revealed that spherical shaped nano-particles of average size ~5 nm formulated as PdTe (composition established on the basis of matching of its powder XRD pattern with that of a known standard phase of the same composition; S5 in Supplementary Material) were formed (Fig. S5.1 in Supplementary Material).

These nano-particles were explored for C – N coupling but found catalytically inactive even immediately after formation. This appears to be contributed by steric effects of large size Te and protective ligation effect of morpholine or piperidine present in the reaction mixture [16–17], which probably coordinates strongly with palladium present on the surface of these nano-particles. The filtrates from which nano-particles were separated were extremely complex mixture of organic compounds and therefore presence of C – N coupled products could not be unequivocally established. However, the present results provide a novel low temperature (100 °C) synthetic route for preparations of PdTe quantum dots. The mechanism of formation of these quantum dots appears to be highly complicated, in



Scheme 2. C–N coupling (unsuccessful).

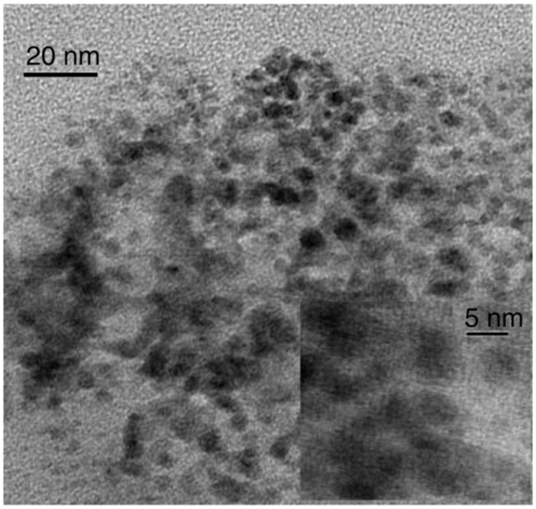
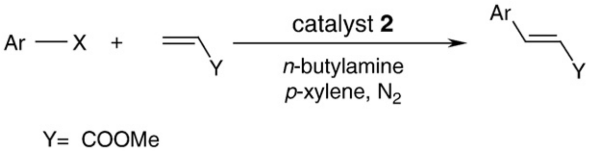


Fig. 3. HR-TEM image of PdTe obtained from **1**and **2.**



Scheme 3. Heck coupling.

view of complexity of filtrate but weak nature of C – Te bond may be a contributing factor in their formation.

To explore the possibility of catalyzing Heck coupling reaction by a Pd(II) complex of organotellurium ligand the complex was **2** explored. For this purpose 1 mmol of aryl bromide was reacted with 1.5 mmol methyl acrylate for 24 h at 100–110 °C in the presence of **2** (0.005 mol%) and *n*-butyl amine (2 mmol) as base using *p*-xylene (3 ml) as a solvent (Scheme 3). The conversions were monitored by ^{1}H NMR and results are shown in Table 1. This indicates that Pd(II) complexes of bidentate organotellurium ligands of (Te, N) type are worth exploring for Heck coupling as such examples are scantly investigated.

In summary new complexes of (Te, N) type ligand, [$PdCl_2$(**L**)] (**1**–**2**) (**L** = *N*-{2-(aryltelluro)ethyl}morpholine/piperidine) have been synthesized and their structures are solved. Attempts with **1** and **2** of catalyzing C – N cross-coupling reactions of aryl bromides and chlorides result in the formation of PdTe nano-particles of size ~5 nm unexpectedly. These nanoparticles are inactive for C – N coupling but the procedure in which they are formed is a novel low temperature route to prepare quantum dots of PdTe. The **2** has potential for Heck coupling as its 0.005 mol% gives conversions more than 90% in some cases.

Acknowledgement

Authors thank Council of Scientific and Industrial Research (India) award of project 01(2421)10/EMR-II and University Grants Commission (India) for JRF/SRF. Authors thank Professor A. K. Ganguli of IIT Delhi for HRTEM facility.

Appendix A. Supplementary material

Experimental details, crystal data and refinements table, bond lengths and angles for complex **1**–**2**. ^{125}Te{^{1}H} NMR spectra of **L1**, **L2**, **1** and **2**. Powder XRD data, SEM, TEM and EDX of Pd – Te NPs. CCDC nos. 778778 (**1**) and 709838 (**2**) have full crystallographic data.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.10.015.

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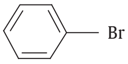
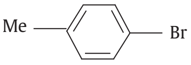
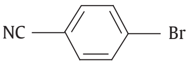
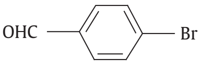
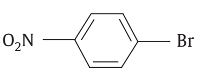
Table 1
Heck reaction catalyzed by **2.**

S.N.	Ar–Br	% Conversion	TON	TOF (h^{-1}
1		40	8000	333
2		32	6400	266
3		90	18000	750
4		93	18600	775
5		92	18400	766

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[12] **1**: Yield: (0.044 g, 80%). m.p 167.0 °C. (Found C, 29.68; H, 3.67; N, 2.68%; calc. for $C_{13}H_{19}Cl_2NO_2PdTe$: C, 29.67; H, 3.64; N, 2.66%). Molecular conductance (Λ_M) 6.5 S cm^2 mol^{-1}. δ_H(300.13 MHz; 25 °C; CD_3CN; Me_4Si) 2.82–3.02 (4 H, m, C8-H), 3.36–3.70 (4 H, m, C7-H), 3.84 (3 H, s, OCH_3), 3.89–4.38 (2 H, m, C5-H), 4.66–5.00 (2 H, m, C6-H), 7.05 (2 H, d, $J_{H\text{-}H}$ 6.9 Hz, C2-H), 8.08 (2 H, d, $J_{H\text{-}H}$ 6.9 Hz, C3-H); δ_C(75.47 MHz; 25 °C; CD_3CN; Me_4Si) 29.8 (C8), 53.7 (C7), 56.2 (OCH_3), 61.1 (C5), 64.9 (C6), 127.8 (C1), 129.9 (C2), 131.9 (C3), 134.4 (C4); δ_{Te} (94.72 MHz; 25 °C; CD_3CN; Me_2Te) 653.6. IR (KBr, cm^{-1}): 3043 (m; $\nu_{C\text{–}H\ (aromatic)}$), 2993, 2860 (s; $\nu_{C\text{–}H\ (aliphatic)}$), 1630 (m; $\nu_{C\text{–}C\ (aromatic)}$), 1193, 1116 (w; $\nu_{C\text{–}N}$), 746 (m; $\nu_{C\text{–}H\ (aromatic)}$). **2**: Yield: (0.042 g, 80%). m.p 158.0 °C. (Found: C, 32.05; H, 4.02; N, 2.67%; calc. for $C_{14}H_{21}Cl_2NOPdTe$: C, 32.08; H, 4.04; N, 2.67%). Molecular conductance (Λ_M): 6.4 S cm^2 mol^{-1}. δ_H(300.13 MHz; 25 °C; CD_3CN; Me_4Si) 1.45–1.53 (2 H, m, C9-H), 1.59–1.81 (4 H, m, C8-H), 2.58–3.05 (4 H, m, C7-H), 3.29–3.54 (2 H, m, C5-H), 3.83 (3 H, s, OCH_3), 4.02–4.52 (2 H, m, C6-H), 7.01 (2 H, d, $J_{H\text{-}H}$ 9.1 Hz, C2-H), 8.09 (2 H, d, $J_{H\text{-}H}$ 8.9 Hz, C3-H); δ_C(75.47 MHz; 25 °C; CD_3CN; Me_4Si) 14.3 (C9), 30.3 (C8), 32.9 (C7), 55.8 (C5), 56.3 (C6), 59.9 (OCH_3), 115.1 (C1), 128.4 (C2), 140.6 (C3), 159.7 (C4); δ_{Te}(94.72 MHz; 25 °C; CD_3CN; Me_2Te) 670.8. IR (KBr, cm^{-1}): 3120 (m; $\nu_{C\text{–}H\ (aromatic)}$), 2899 (s; $\nu_{C\text{–}H\ (aliphatic)}$), 1638(m; $\nu_{C\text{–}C\ (aromatic)}$), 1177, 1118 (w, $\nu_{C\text{–}N}$), 740 (m, $\nu_{C\text{–}H\ (aromatic)}$).

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