Dalton
Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 1142

www.rsc.org/dalton

COMMUNICATION

Palladium(II)–selenoether complexes as new single source precursors: First synthesis of Pd_4Se and Pd_7Se_4 nanoparticles†

Ved Vati Singh, Gyandshwar Kumar Rao, Arun Kumar and Ajai K. Singh*

Received 4th November 2011, Accepted 22nd November 2011
DOI: 10.1039/c2dt12113a

Pd_4Se and Pd_7Se_4 nanoparticles (size 38–104 nm), protected by TOP, have been obtained for the first time using Pd(II) ligated with selenated primary and secondary amines (see 1 and 2) as single source precursors respectively. TEM, SEM, powder XRD and photoluminescence have been used to characterize them. 1 and 2 are also the first Pd(II)–selenoether complexes used for the synthesis of nanoparticles containing palladium and selenium.

Platinum group metal chalcogenides find extensive applications in catalysis,[1–3] low resistance ohmic contacts of semiconducting electronic devices,[3] light image receiving materials with silver halides,[4] and recording films in optical discs and lithographic films.[3] The search of suitable precursors for these chalcogenides, which may replace presently used volatile and/or toxic Se/Te (=E) containing species like H_2Se or R_2E_2, continues to be a challenge of great importance. The complexes of platinum group metals with chalcogenated ligands can be envisaged as a good single source precursor. The chalcogenated Schiff bases, pincer and other ligands form metal complexes which have rich structural chemistry[5–7] and relevance in catalysis[7] have also shown, in some cases, potential as molecular precursors for the synthesis of metal chalcogenides.[8] For low temperature preparation of chalcogenide materials[1–4] metal chalcogenolates[1–3] constitute the class of compounds which have mainly been explored as single-source precursors.

Palladium, an important platinum group metal forms selenides, the compositions of which have been identified as PdSe, $Pd_{17}Se_{15}$, Pd_7Se_4, $Pd_{2.5}Se$, Pd_3Se, Pd_7Se, Pd_4Se, $Pd_{4.5}Se$, Pd_8Se and $PdSe_2$. The known routes for the preparation of these phases typically involve heating of the two constituent elements in an evacuated sealed tube followed by annealing at high temperatures for several days. The formation of some of these phases has also been reported on pyrolysis of several palladium(II) complexes. The monoselenocarboxylates, benzylselenolates, β-functionalised ethyl selenolates, dimeric bridged species having Pd(II) or allylpalladium(II) generally give the $Pd_{17}Se_{15}$ phase. One of the exceptions is $[Pd_2(\mu\text{-SePh})_2(\eta^3\text{-}C_4H_7)_2]$ which leads to the formation of a Pd_4Se phase.

Nanoparticles of $PdSe_2$ and $Pd_{17}Se_{15}$ have been recently grown using bis(*N*,*N*-diethyl-*N*′-naphthoylselenoureato)palladium(II) as a single source precursor.[9] Phase-pure $Pd_{17}Se_{15}$ nanocrystals have also been synthesized by heating a solid sample of $[Pd(SeC_6H_5)_2]_\infty$ under solvothermal conditions.[10] The *in situ* formation of $Pd_{17}Se_{15}$ nanoparticles have been reported during the course of Suzuki–Miyaura C–C coupling reactions catalyzed by a selenium ligated palladacycle.[7g] These NPs have been proposed as true catalytic species for the coupling reaction.[7g] To our knowledge there is no report in the literature on the growth of nanoparticles of Pd_4Se and Pd_7Se_4. In fact nanoparticles of none of the remaining other palladium selenide phases mentioned above have been reported. In this communication we present the growth of Pd_4Se and Pd_7Se_4 nanoparticles using the Pd(II) complexes **1** and **2**. So far no complex of selenated primary or secondary amines has been used for this purpose. Furthermore no other Pd(II)–selenoether complex has ever been used as a single source precursor for the growth of nanoparticles containing palladium and selenium.

The $[PdCl_2(PhSe\text{-}CH_2CH_2CH_2\text{-}NH_2)]$ (**1**), Pd(II) complex of a primary amine has been synthesized by a slight modification in the method reported in the literature.[11]‡ However, from a secondary amine the palladacycle (**2**), $[PdCl\{C_6H_4CH(C_6H_4\text{-}2\text{-}OH)\text{-}NHCH_2CH_2CH_2\text{-}SePh\}]$ has been synthesized by following a method reported earlier.[7g]

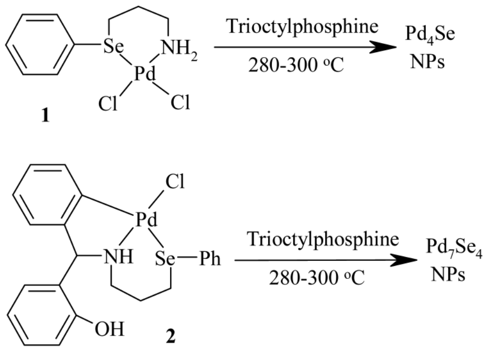
The complexes **1** and **2** give characteristic proton and carbon-13 NMR (Fig. S5.5, S5.7–S5.9, ESI†). The assignments of signals in $^{13}C\{^1H\}$ NMR of the ligand of **1** were made using HMQC experiments (Fig. S5.4, ESI†). In ^{77}Se NMR spectrum of **1** (Fig. S5.6, ESI†) the signal is deshielded (by 21 ppm) with respect to that of the free ligand (Fig. S5.3, ESI†) but in the case of **2** (Fig. S5.12, ESI†) it is shielded by 27 ppm in comparison to that of its free ligand (Fig. S5.10, ESI†). The molecular complexes **1** and **2** were used as single source precursors to synthesize nanoparticles of Pd_4Se and Pd_7Se_4 in a one-step process in moisture and oxygen-free atmosphere.

The process (Scheme 1) involves the thermolysis of an 11 : 1 mixture of tri-*n*-octylphosphine (TOP) and **1** or **2** at 280–300 °C. The composition of resulting products analyzed using powder XRD was found to be precursor dependent. The Pd_4Se was selectively obtained from precursor **1** and Pd_7Se_4 from **2** even when

---

Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016, India. E-mail: aksingh@chemistry.iitd.ac.in, ajai57@hotmail.com; Fax: +91-11-26581102; Tel: +91-11-26591379

† Electronic supplementary information (ESI) available: Synthesis and full characterization of **1** and **2**; DLS, powder XRD and SEM-EDX studies of Pd_4Se and Pd_7Se_4 nanoparticles; ^1H, $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra of known compounds ($PhSe\text{-}CH_2CH_2CH_2\text{-}NH_2$, $PhSe\text{-}CH_2CH_2CH_2\text{-}NH\text{-}CH(Ph)\text{-}C_6H_4\text{-}2\text{-}OH$, and Pd(II) complexes **1** and **2**. See DOI: 10.1039/c2dt12113a



Scheme 1 Methodology for syntheses of palladium selenide NPs.

similar thermolytic conditions were used. Each of the powder XRD patterns of both types of nanoparticles was found matching with that of the corresponding known standard phase of the same composition (Fig. S4, ESI†). The sharp nature of the powder XRD patterns (Fig. 1 and Fig. 2) indicates high crystallinity and the possibility of the presence of somewhat large sized nanoparticles. Powder XRD patterns also suggest that the Pd_4Se phase has a tetragonal structure whereas Pd_7Se_4 is orthorhombic.

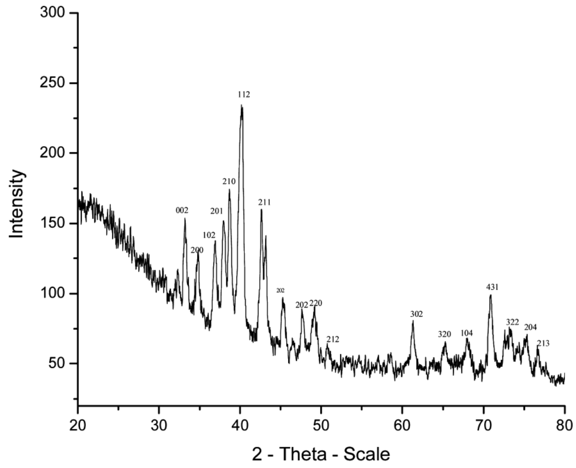


Fig. 1 Powder XRD pattern of Pd_4Se.

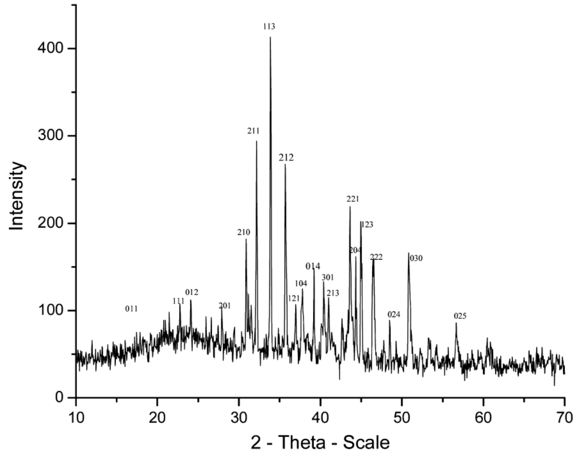


Fig. 2 Powder XRD pattern of Pd_7Se_4 nanoparticles.

The morphology of these nanoparticles as revealed by SEM is shown in Fig. 4. The results of SEM-EDX show that they are capped with TOP (Fig. S4.1–S4.4, ESI†). HRTEM images of TOP capped nanoparticles obtained from **1** show their particle size in the range 38–43 nm, while in case of those obtained from **2** the size was found in the range 62–104 nm. Nanoparticles of Pd_4Se are cubic (Fig. 3) and those of Pd_7Se_4 are spherical (Fig. 3) in shape. In the absorption spectra of both Pd_4Se and Pd_7Se_4 nanoparticles in visible region there is no excitonic peak corresponding to band edges at 385 nm (3.22 eV) and 384 nm (3.22 eV) respectively (Fig. 5). Both Pd_4Se and Pd_7Se_4 show broad peaks in their luminescence spectra. The emission maxima of Pd_4Se (489 nm) as well as Pd_7Se_4 (522 nm) are red shifted in relation to these band edges (Fig. 6 and 7). In these nanoparticles the broad shape of the emission spectra is not characteristic of band edge luminescence previously observed in the case of CdSe.[12] This could be due to a broad size distribution of the particles or inefficient passivation of the surface traps by TOP. However the particle size distribution as determined by DLS analysis (Fig. S3.1, S3.2, ESI†) is narrow in the case of Pd_7Se_4 nanoparticles relative to that of Pd_4Se nanoparticles. Therefore the broad emission spectrum could be due to recombination from shallow traps, present on the surface, which have not been passivated by TOP.

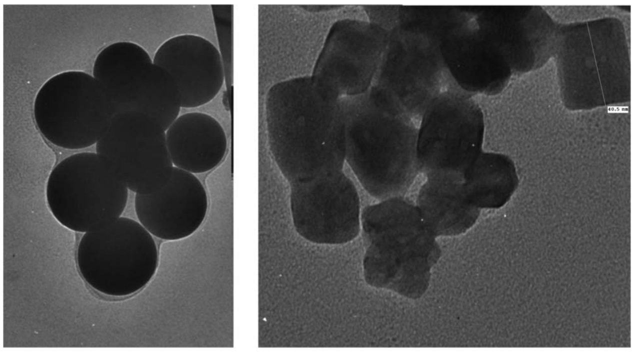


Fig. 3 HTEM images of NPs of Pd_7Se_4 and Pd_4Se respectively.

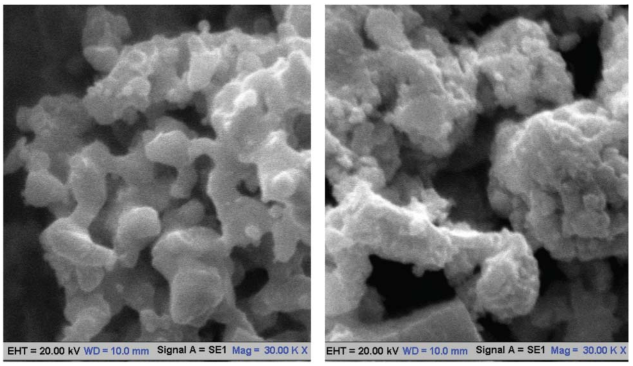


Fig. 4 SEM images of NPs of Pd_7Se_4 and Pd_4Se respectively.

In conclusion, good quality TOP capped nanoparticles of compositions Pd_4Se (38–43 nm) and Pd_7Se_4 (62–104 nm) in good yield have been prepared from one pot synthesis for the first time by thermolysis in TOP of $[PdCl_2(PhSe\text{-}CH_2CH_2CH_2\text{-}NH_2)]$

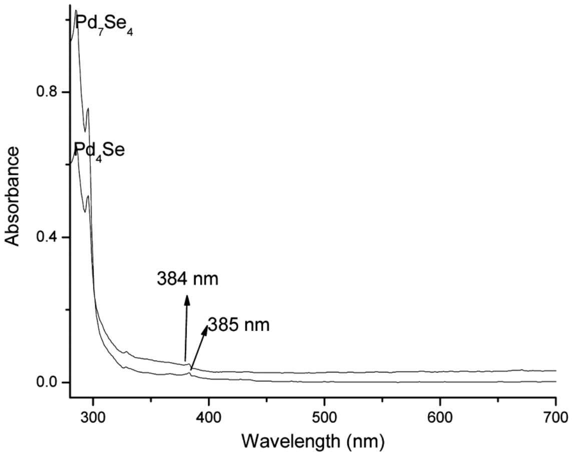


Fig. 5 UV-VIS spectra of Pd_4Se and Pd_7Se_4.

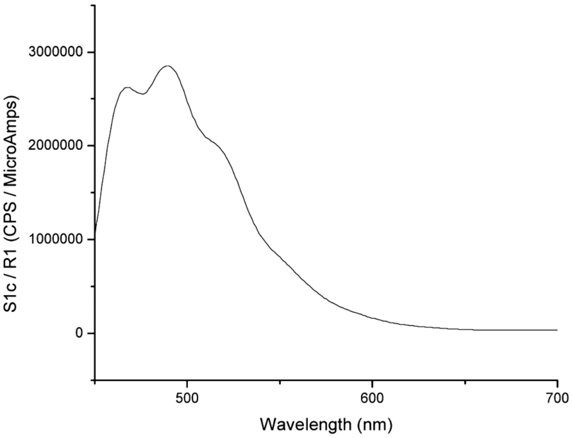


Fig. 6 Photoluminescence spectrum of Pd_4Se.

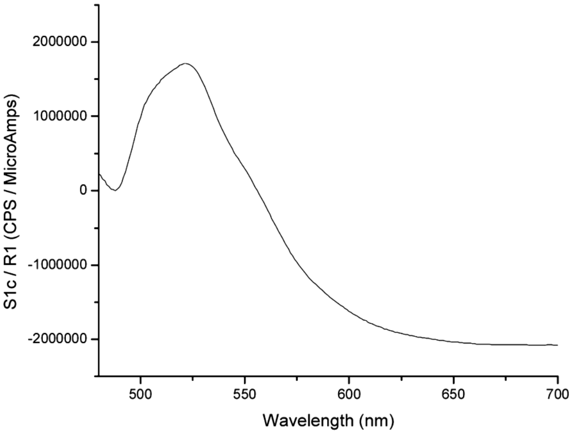


Fig. 7 Photoluminescence spectrum of Pd_7Se_4.

and [PdCl{$C_6H_4CH(C_6H_4$-2-OH)-$NHCH_2CH_2CH_2$-SePh}] respectively. Pd(II)-selenoether complexes **1** and **2** are first used single molecule precursors of this type, which are stable, air/moisture insensitive and are easy to synthesize by room temperature reactions of selenoether type ligands with Na_2PdCl_4.

This work (SR/WOS–A/CS–22/2009) was supported by the Department of Science and Technology, New Delhi-110016 (India) and the Council of Scientific and Industrial Research (India). The authors also thanks the NSIT (DST) funded HRTEM central facility installed at IIT Delhi.

Notes and references

‡ All the reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. All chemicals were bought from Sigma-Aldrich. NMR spectra were obtained using $CDCl_3$ as solvent on a Bruker Spectrospin DPX300 NMR instrument. H_2N-$(CH_2)_3$-SePh and C_6H_5-CH(-C_6H_4-2-OH)-HN-$(CH_2)_3$-SePh: the preparation of the primary amine was carried out by a slight modification of the method reported in the literature.[11] Instead of alkaline ethanolic solution of $NaBH_4$ we used an alkaline aqueous solution of $NaBH_4$ for reduction of the diphenyl diselenide. Yield, 70%; elemental analysis (found: C, 50.52; H, 6.09; N, 6.49%, calc: C, 50.47; H, 6.12; N, 6.54%) IR: 3256 ν(N–H), 1208 ν(C–N), 495 ν(Se–C). ^{1}HNMR ($CDCl_3$, 300 MHz, TMS): 1.822 (quintet, 2H, –C_{alkyl}–CH_2–C_{alkyl}), 1.972 (broad s, 2H, –NH_2), 2.772 (t, 2H, –NCH_2), 2.932 (t, 2H, –$SeCH_2$), 7.223–7.28 (m, 3H, ArH), 7.467–7.492 (m, 2H, ArH); ^{13}C{^{1}H}NMR ($CDCl_3$, 300 MHz, TMS), 24.81 (–$SeCH_2$), 33.37 (–C_{alkyl}–CH_2–C_{alkyl}), 41.55 (–NCH_2), 126.58, 128.84, 130.04, 132.30; ^{77}Se{^{1}H}NMR ($CDCl_3$, 300 MHz, Me_2Se): 289.49 ppm. [$PdCl_2$(PhSe–$CH_2CH_2CH_2$–NH_2)] (**1**). The preparation of the palladium complex of the primary amine (**1**) was also carried out by a modification of the method reported in the literature.[11] A solution of compound H_2N-$(CH_2)_3$-Se-C_6H_5 (1 mmol) in acetone (10 cm^3) was added dropwise with stirring to a solution of sodium tetrachloropalladate (0.294 g, 1 mmol) in water (15 cm^3). A yellow precipitate separated after about 15 min but the mixture was stirred for another 2 h and the solid then filtered off, washed with cold methanol, and dried *in vacuo*. Repeated attempts to get good quality crystals of the palladium complex of primary amine were unsuccessful. yield 70%, elemental analysis (found: C, 27.61; H, 3.57; N, 3.63%), calculated: C 27.54, H 3.60, N 3.57%. IR: 3235 ν(N–H), 1158 ν(C–N), 479 ν(Se–C), 330, 304 ν(Pd–Cl) cm^{-1}. ^{1}HNMR ($CDCl_3$, 300 MHz): 1.59–2.28 (m, 4H, NH_2 + C_{alkyl}–CH_2–C_{alkyl}), 2.27–3.01 (m, 4H, $SeCH_2$ + NCH_2), 7.28–7.51 (m, 3H, *meta* to Se + *para* to Se), 8.21 (d, 2H, *ortho* to Se); ^{77}Se{^{1}H} NMR ($CDCl_3$, 300 MHz): 310.36 ppm. Synthesis of palladium selenide nanoparticles: A mixture of 5.0 mL (11.0 mmol) of tri-*n*-octylphosphine (TOP) and precursor (**2**: 0.537 g, 1.0 mmol; **1**: 0.391 g, 1.0 mmol) was heated to 280–300 °C under nitrogen atmosphere in a three neck flask for 2 h with continuous stirring. The colour of the mixture changed from yellowish to red–brown within 40 min and brown–black precipitate started appearing after two hours. The reaction mixture was cooled to room temperature and 20 mL of acetone was added into the flask to obtain a brown–black precipitate which was separated by centrifugation. The obtained precipitate was washed three times with methanol (20 mL) and dried.

1 L. Y. Chiang, J. W. Sioirczeweki, R. Kastrup, C. S. Hsu and R. B. Upasani, *J. Am. Chem. Soc.*, 1991, **113**, 6574.
2 S. Eijsbouts, V. H. J. DeBeer and R. Prins, *J. Catal.*, 1988, **109**, 217.
3 S. Dey and V. K. Jain, *Platinum Met. Rev.*, 2004, **48**, 16.
4 H. Kyama and T. Iwata, *Japanese Patent* 08/095, 209, Mitsubishi Paper Mills Ltd, 1996; O. Tanabe, *U.S. Patent* 5,030,545, Fuji Photo Film Co Ltd, 1991.
5 (*a*) I. G. Dance, *Polyhedron*, 1986, **5**, 1037; (*b*) P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121; (*c*) M. A. Ansari and J. A. Ibers, *Coord. Chem. Rev.*, 1990, **100**, 223; (*d*) J. Arnold, *Prog. Inorg. Chem.*, 1995, **43**, 353; (*e*) J. R. Dilworth and N. Wheatley, *Coord. Chem. Rev.*, 2000, **199**, 89.
6 A. Panda, S. Panda, K. Srivastava and H. B. Singh, *Inorg. Chim. Acta*, 2011, **372**, 17.
7 (*a*) Q. Yao, E. P. Kinney and C. Zheng, *Org. Lett.*, 2004, **6**, 2997; (*b*) A. Kumar, M. Agarwal and A. K. Singh, *Polyhedron*, 2008, **27**, 485; (*c*) A. Kumar, M. Agarwal and A. K. Singh, *J. Organomet. Chem.*, 2008, **693**, 3533; (*d*) A. Kumar, M. Agarwal and A. K. Singh, *Inorg. Chim. Acta*, 2009, **362**, 3208; (*e*) D. Das, G. K. Rao and A. K. Singh, *Organometallics*, 2009, **28**, 6054; (*f*) D. Das, P. Singh, M. Singh and A. K. Singh, *Dalton Trans.*, 2010, **39**, 10876; (*g*) G. K. Rao, A. Kumar, J. Ahmed and A. K. Singh, *Chem. Commun.*, 2010, **46**, 5954.

8 (*a*) A. Singhal, V. K. Jain, R. Mishra and B. Varghese, *J. Mater. Chem.*, 2000, **10**, 1121; (*b*) L. B. Kumbhare, V. K. Jain, P. P. Phadnis and M. Nethaji, *J. Organomet. Chem.*, 2007, **692**, 1546; (*c*) S. Dey, V. K. Jain and B. Varghese, *J. Organomet. Chem.*, 2001, **623**, 48; (*d*) S. Dey, V. K. Jain, S. Chaudhury, A. Knoedler, F. Lissner and W. Kaim, *J. Chem. Soc., Dalton Trans.*, 2001, 723; (*e*) L. B. Kumbhare, V. K. Jain and B. Varghese, *Inorg. Chim. Acta*, 2006, **359**, 409; (*f*) L. B. Kumbhare, A. P. Wadawale, V. K. Jain, S. Kolay and M. Nethaji, *J. Organomet. Chem.*, 2009, **694**, 3892.

9 J. Akhtar, R. F. Mehmood, M. A. Malik, N. Iqbal, P. O'Brien and J. Raftery, *Chem. Commun.*, 2011, **47**, 1899.

10 S. S.-Y. Chui, K.-H. Low, J. Lu, V. A. L. Roy, S. L.-F. Chan and C.-M. Che, *Chem.–Asian J.*, 2010, **5**, 2062.

11 A. Khanna, A. Bala and B. L. Khandelwal, *J. Organomet. Chem.*, 1995, **494**, 199.

12 B. Ludolph, M. A. Malik, N. Revaprasadu and P. O'Brien, *Chem. Commun.*, 1998, 1849.