Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 4306

COMMUNICATION

Didocosyl selenide stabilized recyclable Pd(0) nanoparticles and coordinated palladium(II) as efficient catalysts for Suzuki–Miyaura coupling[†]

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Received 25th November 2011, Accepted 2nd February 2012 DOI: 10.1039/c2dt12256a

First selenium ligand stabilized Pd(0) nanoparticles (~3–5 nm) catalyze Suzuki–Miyaura C–C coupling in short time and are recyclable (up to 94% yield after 5 reuses). The air stable compound $[PdCl_2(L1)_2]$ shows high catalytic efficiency for this coupling as its 3×10^{-5} mol% is sufficient for activated ArBr.

Metal nanoparticles (NPs), more active than their particulate counterparts due to large surface area, are among the promising species for efficient catalysis under mild and environmentally benign conditions. Generally dendrimers, organic/organofluorous ligands, polymers, ionic liquids and surfactants are used to stabilize such NPs¹⁻⁴ for efficient catalytic organic synthesis. In the absence of a stabilizing agent they generally tend to aggregate or precipitate losing their catalytic activities. Palladium(0) NPs stabilized by several agents have been used directly in olefin hydrogenation³ and various C–C coupling reactions^{3,4} including Suzuki–Miyaura coupling.²⁻⁴ This is because palladium complexes^{4c,5,6} of a large number of phosphorus, carbene, oxime and other ligands are known efficient catalysts for Suzuki–Miyaura coupling, and in many instances the formation of nano-sized species^{4c,6} has been recognized as the pathway.

The stabilizing ligands determine the dispersion of the NPs to a great extent and also affect their catalytic efficiency recyclability, composition, solubility and size. They function via ligating with them. The ligands having strongly coordinating groups stabilize metal NPs well but may render them catalytically inactive due to strong chemisorptions. For example functional groups like thiol, amine, carbonyl or hydroxyl, if present in the stabilizer, limit the activity 2a,7 of NPs. The sterically demanding P(n-octyl)₃ also stabilizes⁸ NPs of palladium well. Thus to get NPs suitable^{2a,c,9} for multiple reaction cycles, the ligand should be strong enough to stabilize NPs but should readily allow access of the reactant to its surface. No ideal stabilizer for Pd NPs which does not deactivate them at all is known. Therefore, search of new stabilizers which improve stabilization with minimal surface deactivation is of current interest. For this purpose selenium ligands may be good candidates. Such type of

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 L1 and 1–4; general procedures for the Suzuki reactions. See DOI: 10.1039/c2dt12256a ligands have been reported in the recent past as important building blocks for catalysts.^{6*a*,10} The strong electron-donating ability of selenium, has made it attractive for designing catalyst frameworks.^{6*a*,10} Organic selenides having large alkyl groups may have the combination of electronic and steric properties which can make them favorable ligands for stabilization of Pd NPs as well as designing of Pd(II) catalysts. However, they have been so far unexplored. The large alkyl group as in didocosyl selenide (**L1**) is envisaged to minimize the surface deactivation of Pd NPs by preventing the strong sorption of ligands onto the surface.

In this communication we present Suzuki reactions catalyzed with recyclable Pd(0) NPs, stabilized with $(C_{22}H_{45})_2$ Se (L1) and highly efficient Pd(1) complex, [PdCl₂(L1)₂].

The syntheses of L1, its air stable Pd(π)-complex 1 and L1stabilized Pd(0) NPs 2–4 have been summarized in Scheme 1. The centrifugation at 6000 rpm of NPs 2–4 in chloroform does not result in any aggregation (ESI: Fig. S20†). The ¹H, ¹³C{¹H} and ⁷⁷Se{¹H} NMR spectra (ESI: S2, Fig. S7–S12†) of L1 and diamagnetic complex 1 are consistent with their structures depicted in Scheme 1. The Pd(0) NPs 2–4 were characterized by powder XRD, ⁷⁷Se{¹H}NMR spectroscopy (Fig. 1), HRTEM (Fig. 2), TEM-EDX (ESI: Fig. S1–S3†) and SEM (ESI: Fig. S4– S6†). The size of the NPs is ~3 nm in the case of 2 whereas ~5 nm in the case of 3 and 4.

The coordination of the ligand **L1** *via* Se with Pd(II) and Pd(0) NPs was supported by 77 Se{¹H} NMR spectroscopy. The signal in 77 Se NMR spectrum of **1** appears at 257.2 ppm, deshielded by ~94 ppm with respect to that of free **L1** (163.8 ppm). Two



Scheme 1 Synthesis of L1, its Pd(II) complex 1 and NPs 2-4.



3: Pd NPs (Pd:Ligand = 1:1)

Pd NPs obtained from 2 after 5th

reaction cycle

2: Pd NPs (Pd:Ligand = 1:4)

4: Pd NPs (Pd:Ligand = 4:1)

Fig. 2 HRTEM images at 10 nm, 20 nm, 50 nm and 100 nm scale bar.

signals (Fig. 1) are present in the 77 Se{¹H} NMR spectra of 2 and **3** (δ , ppm; **2**: 160.2, 257.5 and **3**: 160.8, 257.5 ppm). The deshielded ones around 257 ppm indicate that some ligand molecules are as strongly coordinated with NPs as with Pd(II) in complex 1. The signals at ~ 160 ppm in the case of 2 and 3 are due to L1 interacting weakly (or free) with Pd NPs. In the spectra of 2-4 (Fig. 1) the intensities of the signals reveal that the ratio of weakly and strongly coordinated L1 is higher for 2 than that of 3. Probably this results in uniformity and dispersion of NPs in the case of 2. The 77 Se{¹H} NMR spectrum of 4 (Pd: L1 ratio 4:1) suggests that almost all L1 molecules are strongly coordinated to NPs. The peaks at $d \sim 2.24$ (*hkl*: 111) and 1.96 (hkl: 200) observed in their powder XRD (ESI: Fig. S17-S19† (JCPDS \neq 88–2335)) support the presence of palladium(0) with face-centered cubic structure. The 1 and Pd(0) NPs 2-4 have been explored as catalysts for Suzuki-Miyaura C-C coupling reactions of several aryl halides (Tables 1 and 2).

The most appropriate base for the functioning of catalyst 1 was found to be K_2CO_3/Cs_2CO_3 (Table 1: entries 8–11). For alternatives viz. NEt₃, NaOAc or Na₂CO₃ a longer reaction time was required for reasonable conversions. Further a DMF and water mixture was found to be the best solvent system for the reaction. Compound 1 showed catalytic activity for ArCl in the

Table 1 Suzuki-Miyaura C-C coupling reactions catalyzed by Pd(II) complex 1^c

$Ar-X + PhB(OH)_2 \rightarrow Ar-Ph (Ar = aryl/heteroaryl; X = Cl/Br)$									
Entry	Aryl/heteroaryl halide	Mol% Pd	<i>t</i> (h)	Yield ^b					
1^c	1-Chloro-4-nitrobenzene	2	20	100					
2	1-Chloro-4-nitrobenzene	5	17	92					
3	4-Chlorobenzaldehyde	5	12	95					
4	4-Chloroacetophenone	5	40	85					
5	Chlorobenzene	5	24	89					
6	4-Chlorotoluene	5	22	89					
7	4-Chloroanisole	5	28	83					
$8^{d,e}$	1-Bromo-4-nitrobenzene	3×10^{-5}	20	100					
9^d	1-Bromo-4-nitrobenzene	10^{-3}	16	94					
$10^{d,f}$	4-Bromobenzaldehyde	3×10^{-5}	40	86					
$11^{d,f}$	4-Bromobenzaldehyde	10^{-4}	36	100					
12	4-Bromobenzaldehyde	10^{-3}	24	92					
13	4-Bromoacetophenone	0.1	10	87					
14	Bromobenzene	0.1	15	94					
15	4-Bromotoluene	0.1	15	84					
16	4-Bromoanisole	0.1	16	85					
17	4-Bromoaniline	1	16	80					
18	2-Bromothiophene	0.1	16	91					
19	2-Bromopyridine	0.1	20	87					
20	3-Bromoquinoline	0.1	15	90					

^a Reaction conditions: aryl/heteroaryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), K_2CO_3 (2.0 equivs.), aq. DMF (3 mL), 100 °C. ^b Isolated yield after column chromatography. ^c Conversion (57 ; 43 ratio of cross coupled product and N,N-dimethylaminated product). ^dCs₂CO₃ as base. ^e Conversion (50: 50 ratio of cross coupled product and N,Ndimethylaminated product). ^fNMR % conversion.

Table 2 Suzuki-Miyaura C-C coupling reactions catalyzed by Pd(0) NPs

 $Ar-X + PhB(OH)_2 \rightarrow Ar-Ph (X = Cl or Br)$

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				Conversion ^b		
Entry	Aryl halide	t (min)	Cycle	2	3	4
1	4-BrC ₆ H₄-OMe	90	1	100	100	100
2	0 4	90	2	100	98	97
3		120	3	90 (79)	85	91
4		120	4	86 (70)	90	89
5		150	5^c	82 (55)	80	82
5	4-BrC ₆ H ₄ -CH ₃	60	1	100	100	95
7		120	2	98 (83)	100	97
8		120	3	84 (71)	95	82
9		180	4	93 (58)	94	88
10		180	5^c	87 (43)	89	82
11	4-BrC ₆ H ₄ -CHO	20	1	100	100	100
12		30	2	100 (96)	98	100
13		45	3	100 (84)	98	98
14		60	4	98 (79)	96	95
15		60	5^c	94 (72)	87	88
$16^{c,d}$	4-ClC ₆ H ₄ -CHO	24 h	—	32	17	_

^a Reaction conditions: aryl halide (5.0 mmol), phenylboronic acid (6.0 mmol), K₂CO₃ (8.0 mmol), aq. DMF (12 mL), 100 °C, amount of 2, 3 or 4 equivalent to 0.5, 1.0 and 1.5 mol% of palladium respectively. ^bNMR % conversion to coupled product with reference to substrate. ^c Isolated yield after column chromatography (lower to NMR yield by \sim 3–5%). ^d Amount of **2**, **3** or **4** equivalent to 5.0 mol% of palladium. The NMR yields given in parentheses in the case of 2 correspond to the time used for first cycle.

presence of its 2–5 mol%. For aryl bromides 1 showed high catalytic activity as its 3×10^{-5} to 0.1 mol% was sufficient for good conversions (Table 1).

In the coupling reaction of 1-chloro-4-nitrobenzene at 2 mol% loading of catalyst **1**, cross coupled product, 4-nitrobiphenyl, along with *N*,*N*-dimethylaminated product (ratio = 57:43, Table 1: entry 1) was obtained. However, at 5 mol% of catalyst loading, only 4-nitrobiphenyl was obtained in 92% yield (Table 1: entry 2). The coupling reaction of 1-bromo-4-nitrobenzene at 3×10^{-5} mol% loading of **1** and in the presence of Cs₂CO₃ resulted in the formation of cross-coupled and *N*,*N*-dimethylaminated products in equimolar ratio (Table 1: entry 8) whereas for loading of 10^{-3} mol% of catalyst (1) only cross coupled product 4-nitrobiphenyl in 92% yield (Table 1: entry 9) was obtained. 4-Bromobenzaldehyde was successfully converted to biphenyl-4-carboxyaldehyde (yield 86%, Table 1: entry 10) at 3×10^{-5} mol% loading of catalyst **1** in the presence of Cs₂CO₃.

The results of NPs 2-4 assisted Suzuki coupling (see ESI: S3.2[†]) are given in Table 2. The distinct feature of these coupling reactions is the time for maximum conversion which is found significantly short (20 min to 3 h). The efficiency of 2 was found better than those of 3 and 4 as it was able to catalyze the reactions to give comparable conversions at lower loading. It appears that greater shielding of NPs by weakly associated ligand molecules is favorable for higher catalytic efficiency. The order of reactivity of NPs towards 4-chlorobenzaldehyde was 2 >3 (yields of biphenyl-4-carboxaldehyde: 32 and 17% respectively) at 5 mol% loading of catalyst. The conversion of the substrate was almost negligible when 4 was used as a catalyst at similar loading. The higher ligand to Pd ratio in 2 makes better dispersion of NPs which probably results in its higher activity. The recyclability (ESI: S3.2[†]) of Pd(0) NPs (2-4) was studied for coupling of 4-bromoanisole, 4-bromotoluene and 4-bromobenzaldehyde. The conversions were lowered when reaction time was kept same for each higher cycle but with prolonged reaction time these remained reasonably intact even for fifth cycle (Table 2). The NPs of palladium stabilized with L1 are needed in more amounts than that of 1 for getting comparable conversion in Suzuki coupling.

Generally molecular complexes have been found to be more efficient in comparison to NPs (except *in situ* generated ones) but recyclability of NPs is a distinct advantage as observed presently. The TEM image of nano-particles obtained after using **2** for five times is shown in Fig. 2. Their size (\sim 5 nm) and dispersion both suggest that aggregation of nano-particles is not extensive which probably results in their recyclability.

To understand further the catalysis by Pd(0) NPs hot filtration experiments¹¹ were carried out with **3** (1 mol%). When the reaction mixture was filtered hot, after 60% conversion (occurred in 10 min), the reaction continued in filtrate at a lower rate (ESI: S4.1†) indicating that some palladium was leached from the NPs during catalysis. The amount of leached palladium estimated by flame AAS was found to be 0.5% of the initial catalyst loading. A mercury poisoning test¹¹ was performed (ESI: S4.2†) on a representative coupling reaction of 4-bromoanisol with phenylboronic acid using **1** (0.1 mol%) and **3** (1 mol%) as catalyst under optimal conditions. The biaryl product was obtained in 100% yield when **1** was used as catalyst even in the presence of an excess of Hg and with **3** only traces of product were obtained.

Thus in the case of **1** it is unlikely that catalysis is *via* Pd nanoparticles as active catalyst. The quenching of the catalytic reaction in the case of **3** is as expected for NPs. Triphenyphosphine¹¹ (ESI: S4.3†) also quenched the catalysis by **3** supporting the results of the Hg test.

Some Pd(0) NPs stabilized² by other ligands are reported to show somewhat better activity than 2-4 but their preparation usually includes a series of steps and separations that commonly result in their low yields. The synthesis of L1 is a simple one step with good yield, which is a distinct advantage. Various analogues of L1 may be developed, which may constitute a family of easily accessible ligands suitable for stabilizing various metal NPs.

In summary newly synthesized $[PdCl_2(n-C_{22}H_{45}-Se-n-C_{22}H_{45})_2]$ has been found air stable and highly efficient for Suzuki coupling as its 3×10^{-5} mol% is enough for some ArBr. The catalytic properties for Suzuki coupling of Pd(0) NPs (no aggregation on centrifugation even at 6000 rpm in chloroform) stabilized for the first time with a selenium ligand (didocosyl selenide, L1) vary with Pd : L1 ratio and the NPs are recyclable. The short reaction time is a distinct feature of 2–4 catalyzed Suzuki coupling.

The Council of Scientific and Industrial Research, India supported the work through the award of SRF/RA and project 01 (2421)10/EMR-II. The authors thank Professor A. K. Ganguli of IIT Delhi for providing HRTEM as well as powder XRD facility.

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