Journal of Organometallic Chemistry 695 (2010) 955–962

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Palladium and half sandwich ruthenium(II) complexes of selenated and tellurated benzotriazoles: Synthesis, structural aspects and catalytic applications

Dipanwita Das, Pradhumn Singh, Ajai K. Singh *

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India

ARTICLE INFO

Article history:
Received 18 September 2009
Received in revised form 6 November 2009
Accepted 9 November 2009
Available online 14 November 2009

Keywords:
Chalcogenated benzotriazole derivatives
Palladium
Ruthenium
Crystal structure
C–C coupling reaction
Oxidation of alcohols

ABSTRACT

1-(Phenylselenomethyl)-1*H*-benzotriazole ($\mathbf{L^1}$) and 1-(4-methoxyphenyltelluromethyl)-1*H*-benzotriazole ($\mathbf{L^2}$) have been synthesized by reacting 1-(chloromethyl)-1H-benzotriazole with in situ generated nucleophiles $PhSe^-$ and $ArTe^-$, respectively. The complexes of $\mathbf{L^1}$ and $\mathbf{L^2}$ with Pd(II) and Ru(II)(η^6-*p*-cymene) have been synthesized. Proton, carbon-13, Se-77 and/or Te-125 NMR spectra authenticate both the ligands and their complexes. The single crystal structures of $\mathbf{L^1}$, $\mathbf{L^2}$ and [RuCl(η^6-*p*-cymene)(**L**)][PF_6] (**L** = $\mathbf{L^1}$: **3**, **L** = $\mathbf{L^2}$: **4**) have been solved. The Ru–Se and Ru–Te bond lengths have been found 2.4801(11) and 2.6183(10) Å, respectively. The palladium complexes, [$PdCl_2$(**L**)] (**L** = $\mathbf{L^1}$: **1**, **L** = $\mathbf{L^2}$: **2**) have been explored for Heck and Suzuki–Miyaura C–C coupling reactions. The TON values are upto 95,000. The Ru-complexes have been found promising for catalytic oxidation of alcohols (TON ~ 7.8–9.4 × 10^4). The complexes of telluroether ligands are as efficient catalysts as those of selenoether ones and in fact better for catalytic oxidation.

1. Introduction

In the class of heterocyclic compounds benzotriazole derivatives have an important place. In the recent past derivatives of benzotriazole have been reported as chiral C-acylating reagents [1]. They show biological activities [2,3]. Solid supported benzotriazoles have been used for combinatorial synthesis of amine libraries [4]. Their potential as UV stabilizers for polymers has also been reported [5]. Using benzotriazole ligands chiral bikitaite zeolite metal–organic frameworks have been designed recently [6]. The selenation and telluration of benzotriazoles can result in multidentate hybrid selenium and tellurium ligands. However, among various possible Se or Te donors having benzotriazole skeletons only bis(1-*H*-benzotriazolylmethyl) selenide has been explored [7,8] so far. It was therefore thought worthwhile to develop a high yield synthetic route for designing $\mathbf{L^1}$ and $\mathbf{L^2}$ and explore their ligand chemistry. In the present paper the syntheses of these ligands and their complexes with Pd(II) and Ru(II)(*p*-cymene) are described. The structures of $\mathbf{L^1}$, $\mathbf{L^2}$, [RuCl(η^6-*p*-cymene)($\mathbf{L^1}$)][PF_6] and [RuCl(η^6-*p*-cymene)($\mathbf{L^2}$)][PF_6] have been authenticated by single crystal X-ray crystallographic analyses. The complexes [$PdCl_2$(**L**)] (where **L** = $\mathbf{L^1}$: **1**, **L** = $\mathbf{L^2}$: **2**) have been found promising for Heck and Suzuki–Miyaura C–C coupling reactions and these results are part of the present paper.

There is a current interest in half sandwich complexes of Ru(II) having (η^6-benzene or -*p*-cymene) unit because some of them are known for their diverse catalytic activities [9,10]. Süss-Fink et al. have carried out hydrogenation of benzene using cluster having Ru(η^6-arene) units [11]. Arene–ruthenium complexes with salicyloxazolines are suitable as asymmetric catalysts for Diels–Alder reactions [12]. The compounds, [Ru=C=C=CR_2(**L**)(Cl)(arene)][PF_6] (**L** = PCy_3, PPr^i_3), are reported as excellent catalyst precursors for ring closing olefin metathesis by Dixneuf's group [13]. The atom transfer radical polymerization of methyl methacrylate has been catalyzed with [$RuCl_2$(η^6-*p*-cymene)(PCy_3)] [14]. Dixneuf and his co-workers have reported that in situ generated catalyst, from [$RuCl_2$(η^6-*p*-cymene)]$_2$ and a pyrimidinium or benzimidazolium salt in the presence of Cs_2CO_3, selectively promotes the diarylation of 2-pyridylbenzene with arylbromides [15]. Acetate-assisted C–H activation of 2-substituted pyridines with [$RuCl_2$(η^6-*p*-cymene)]$_2$ has been reported by Davies and co-workers [16]. A variety of neutral ruthenium–carbene complexes, [$RuCl_2$(carbene)(arene)] have been used in the catalytic synthesis of furans [17]. Kharasch additions is catalyzed with [$RuCl_2$(η^6-*p*-cymene)(PAr_3)] [18]. Demonceau et al. have recently reported the exceptional efficacy of [$RuCl_2$(η^6-*p*-cymene)(PR_3)] complexes as a catalyst precursor for the ring-opening metathesis polymerization of low-strain cyclo-olefins [19]. Chiral cationic (η^6-arene)(pyridylamino)ruthenium(II)-complexes act as enantioselective catalysts for the Diels–Alder reactions with good *exo:endo* selectivity [20]. The half sandwich compounds of Ru(II) show promising anticancer activity [21–25]. Thiolate ligand oxygenation is believed to activate

* Corresponding author. Tel.: +91 11 26591379; fax: +91 11 26581102.
E-mail addresses: ajai57@hotmail.com, aksingh@chemistry.iitd.ac.in (A.K. Singh).

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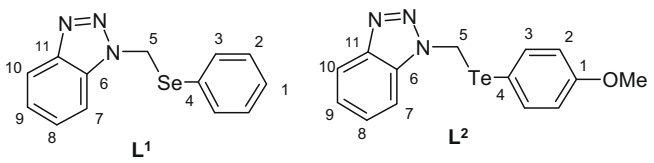
doi:10.1016/j.jorganchem.2009.11.009

cytotoxic half sandwich [Ru(η^6-arene)(en)(SR)]$^+$ complexes toward DNA binding [26]. Ru(II)–arene complexes with pyrone-derived ligands are rendered active against cancer cells by replacement of the coordinated (O,O) donor with (S,O) donor [27]. Hartinger and co-workers [28] have reported that promising cytotoxic effects of water-soluble dinuclear Ru–arene complexes in human cancer cells can be increased by increasing the spacer length between the metal centers. The interaction of [$RuCl_2(\eta^6$-*p*-cymene)(pta)] reported as an effective anticancer and antimetastatic agent, with biological nucleophiles important with respect to its mechanism of action has been studied [29]. Organometallic ruthenium(II)–arene complexes coordinated to maltol-derived ligands were prepared and their anticancer activity against human tumor cell lines was studied. [30]. Therrien and co-workers have found that water-soluble arene ruthenium complexes containing pyridinethiolato ligands show cytotoxicity towards ovarian cancer cells [31]. In vitro studies by Dyson and co-workers have revealed that (3,5,6-bicyclophosphite-α-D-glucofuranoside)(η^6-*p*-cymene)-dihalogenido-ruthenium(II) complex is the most cytotoxic compound for human cancer cell lines [32].



L¹ **L²**

The half sandwich species [RuCl(η^6-*p*-cymene)(**L**)][PF_6] (**L** = **L¹**: **3**, **L** = **L²**: **4**) have been found promising for catalytic oxidation of primary alcohols with *N*-methylmorpholine-*N*-oxide (NMO). These results are also given in the present paper.

2. Experimental

The C and H analyses were carried out with a Perkin–Elmer 2400 Series II C, H, N analyzer. The ^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H} and ^{125}Te{^{1}H}NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, 57.24 and 94.69 MHz, respectively. IR spectra in the range 4000–250 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Single crystal X-ray diffraction data for **L¹**, **L²** and [RuCl(η^6-*p*-cymene)(**L**)][PF_6] (**L** = **L¹**: **3**, **L** = **L²**: **4**) were collected with a Bruker AXS SMART Apex CCD diffractometer using Mo Kα (0.71073 Å) radiations at 298 (2) K. The SHELXTL was used for space group, structure determination and refinements [33,34]. For absorption correction (if needed) software SADABS was used [35]. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. In Table S.1 of online Supplementary material crystal data and structural refinements are summarized. The catalytic oxidation yields were determined with NUCON Engineers (New Delhi, India) gas chromatograph (with FID detector), model 5765 equipped with an Alltech (Ec^{TM-1}) column of 30 m length, 0.25 mm diameter and having liquid film of 0.25 μm thickness. The cyclic voltammetric studies were performed on BAS CV 50 W instrument at University of Delhi (Department of Chemistry), India. A three-electrode configuration composed of Pt disk working electrode (3.1 mm^2 area), Pt wire counter electrode and Ag/AgCl reference electrode was used for the measurements. Ferrocene was used as an internal standard ($E_{1/2}$ = 0.500 V vs. Ag/AgCl) and all the potentials are expressed with reference to Ag/AgCl. The [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$], were prepared according to literature method [36].

2.1. Synthesis of *L¹*

Diphenyldiselenide (0.32 g, 1 mmol) dissolved in 30 mL of EtOH was stirred under nitrogen atmosphere and treated with a solution of sodium borohydride (0.076 g, ~2 mmol) made in 5 mL of aqueous NaOH (5%) dropwise till it became colourless due to the formation of PhSeNa. 1-(Chloromethyl)-1H-benzotriazole (0.34 g, 2 mmol) dissolved in 10 mL of ethanol was added to the colourless solution with constant stirring and the mixture stirred further for 3 h. It was poured into cold water (30 mL). The **L¹** was extracted with chloroform (4 × 25 mL). The extract was washed with water (3 × 40 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated off under reduced pressure on a rotary evaporator to get a pale yellow solid. The solid on recrystallization from chloroform–hexane mixture (1:1), gave pale yellow coloured single crystals of **L¹**. Yield 0.46 g (~80%). Anal. Calc. for $C_{13}H_{11}N_3Se$: C, 54.19; H, 3.85; N, 14.58. Found: C, 53.96; H, 3.82; N, 14.46%. NMR (^{1}H, $CDCl_3$, 25 °C vs. TMS): (δ, ppm): 6.02 (s, 2H, H_5), 7.20–7.44 (m, 8H, H_1, H_2, H_3, H_7, H_8, H_9), 8.02 (d, 1H, ^3J = 8.1 Hz, H_{10}); (^{13}C{^{1}H}, $CDCl_3$, 25 °C vs. TMS): (δ, ppm): 43.1 (C_5), 110.0 (C_{10}), 120.0 (C_7), 124.1 (C_9), 127.3 (C_1), 127.4 (C_4), 128.8 (C_8), 129.3 (C_2), 132.1 (C_6), 135.2 (C_3), 146.3 (C_{11}); (^{77}Se {^{1}H}, $CDCl_3$, 25 °C vs. Me_2Se): (δ, ppm) 406.3. IR (KBr, cm^{-1}): 3732, 3004, 1435, 1219, 1064, 740, 680, 605.

2.2. Synthesis of *L²*

Bis(4-methoxyphenyl)ditelluride (0.469 g, 1 mmol) was treated with sodium borohydride (0.076 g, ~2 mmol) and 1-(chloromethyl)-1H-benzotriazole (0.34 g, 2 mmol) as described in Section 2.1 for diphenyldiselenide. The **L²** was isolated by a workup described for **L¹** and its single crystals were also obtained by a similar procedure. Yield 0.580 g (~80%). Anal. Calc. for $C_{14}H_{13}N_3OTe$: C, 45.83; H, 3.57; N, 11.45. Found: C, 45.77; H, 3.39; N, 11.38%. NMR (^{1}H, $CDCl_3$, 25 °C vs. TMS): (δ, ppm): 3.78 (s, 3H, OMe), 6.11 (s, 2H, H_5), 6.68 (d, ^3J = 9 Hz, 2H, H_2), 7.22 (t, ^3J = 8.0 Hz, 1H, H_8), 7.38 (m, 2H, H_7 + H_9), 7.54 (d, ^3J = 8.4 Hz, 2H, H_3), 8.03 (d, ^3J = 8.1 Hz, 1H, H_{10}); (^{13}C{^{1}H} $CDCl_3$, 25 °C vs. TMS): (δ, ppm): 21.0 (C_5), 55.2 (OCH_3), 100.7 (C_4), 110.7 (C_{10}), 115.4 (C_2), 120.1 (C_7), 124.0 (C_9), 127.0 (C_8), 132.2 (C_6), 142.7 (C_3), 146.3 (C_{11}), 160.7 (C_1); (^{125}Te {^{1}H}, $CDCl_3$, 25 °C vs. Me_2Te) (δ, ppm), 705.4. IR (KBr, cm^{-1}): 3007, 2947, 1484, 1239, 1058, 748, 514, 262.

2.3. Synthesis of [$PdCl_2$(*L¹*)] (*1*) and [$PdCl_2$(*L²*)] (*2*)

The solution (in 5 mL water) of $Na_2[PdCl_4]$ (0.294 g, 1 mmol) was mixed with a solution of **L¹** (0.288 g, 1 mmol) or **L²** (0.367 g, 1 mmol) made in acetone (10 mL) with vigorous stirring. An orange precipitate of **1** or **2** obtained instantaneously. The precipitate was filtered, washed with water and dried.

1: Yield ca. 0.368 g (~79%). Anal. Calc. for $C_{13}H_{11}Cl_2N_3PdSe$: C, 33.55; H, 2.38; N, 9.03. Found: C, 33.60; H, 2.09; N 9.13%. NMR (^{1}H, DMSO-d_6, 25 °C vs. TMS): (δ, ppm) 6.37 (s, 2H, CH_2), 7.18–7.28 (m, 3H, H_1 + H_2), 7.37–7.44 (m, 3H, H_3, H_8), 7.52 (t, ^3J = 9 Hz, 1H, H_9), 7.76 (d, ^3J = 8.7 Hz 1H, H_7), 8.00 (d, ^3J = 9 Hz, 1H, H_{10}); (^{13}C{^{1}H}, DMSO-d_6, 25 °C vs. TMS): (δ, ppm) 44.4 (C_5), 112.5 (C_{10}), 119.2 (C_7), 124.4 (C_9), 127.1 (C_1), 128.2 (C_4), 128.9 (C_8), 129.4 (C_2), 133.7 (C_6), 134.4 (C_3), 145.4 (C_{11}); (^{77}Se{^{1}H} DMSO-d_6, 25 °C vs. Me_2Se): (δ, ppm) 420.6. IR (KBr, cm^{-1}): 3488, 3022, 1448, 1309, 1226, 744, 305.

2:. Yield ~ 0.480 g (~90%). Anal. Calc. for $C_{14}H_{13}Cl_2N_3OTePd$: C, 30.90; H, 2.41; N, 7.72. Found: C, 29.53; H, 2.42; N, 5.81%. NMR (^{1}H, DMSO-d_6, 25 °C vs. TMS) (δ, ppm) 3.78 (s, 3H, OMe), 6.75 (s, 2H, H_5), 6.90 (d, ^3J = 9 Hz, 2H, H_2), 7.37 (t, ^3J = 9 Hz, 1H, H_8), 7.54 (t, ^3J = 9 Hz, 1H, H_9), 7.56 (d, ^3J = 8.7 Hz, 2H, H_3), 7.71 (m, 1H, H_7), 7.95 (d, ^3J = 9 Hz, 1H, H_{10}); (^{13}C{^{1}H} DMSO-d_6, 25 °C vs. TMS): (δ,

ppm) 34.3 (C_5), 55.2 (OCH_3), 106.2 (C_4), 110.9 (C_{10}), 115.0 (C_2), 119.2 (C_7), 124.9 (C_9), 127.5 (C_8), 132.6 (C_6), 138.4 (C_3), 145.1 (C_{11}), 161.1 (C_1); (^{125}Te{^{1}H}, DMSO-d_6, 25 °C vs. Me_2Te): (δ, ppm) 722.4. IR(KBr, cm^{-1}): 3454, 2953, 1580, 1489, 1251, 1177, 748, 325.

2.4. Synthesis of [RuCl(η^6-p-cymene)(**L^1**)][PF_6] (**3**) and [RuCl(η^6-p-cymene)(**L^2**)][PF_6] (**4**)

[Ru(η^6p-cymene)Cl_2]$_2$ (0.061 g, 0.1 mmol) dissolved in 10 mL of dry methanol was treated with **L^1** (0.288 g, 0.1 mmol) or **L^2** (0.367 g, 0.1 mmol) dissolved in 10 mL of dry methanol with vigorous stirring. The reaction mixture was stirred further overnight. Its volume was reduced to ~5 mL on a rotary evaporator and ammonium hexafluorophosphate (0.0163 g, 0.1 mmol) was added to get an orange precipitate of **3** or **4**. The precipitate was filtered and washed with cold methanol. The single crystals of **3** and **4** both were grown from chloroform and acetonitrile mixture (1:1).

3: Yield ~ 0.035 g (~50%); Anal. Calc. for $C_{23}H_{25}ClN_3SeRuPF_6$: C, 39.25; H, 3.58; N, 5.97. Found: C, 39.53; H, 3.42; N, 5.81%. NMR: (^{1}H, $CDCl_3$, 25 °C vs. TMS) (δ, ppm): 1.28–1.32 (m, 6H, CH_3 of *i*-Pr), 2.00 (s, 3H, CH_3 of *p*-cymene, *p* to *i*-Pr), 2.73–2.85 (m, 1H, CH of *i*-Pr), 5.44–5.67 (m, 4H, Ar–H of *p*-cymene), 5.94 (s, 2H, H_5), 7.18–7.63 (m, 6H, $H_1 + H_2 + H_8 + H_9 + H_7$), 7.70–7.71 (m, 2H, H_3), 8.17 (d, ^3J = 8.4 Hz, 1H, H_{10}. The stability of solution of **3** for recording carbon-13 NMR was inadequate. (^{77}Se{^{1}H}, $CDCl_3$, 25 °C vs. Me_2Se): (δ, ppm) 401.4. IR (KBr, cm^{-1}): 3450, 2950, 1584, 1490, 1243, 1137, 840, 738, 320.

4: Yield ~ 0.046 g (~60%); Anal. Calc. for $C_{24}H_{27}ClN_3OTeRuPF_6$: C, 36.85; H, 3.48; N, 5.37. Found: C, 36.53; H, 3.42; N, 5.81%. NMR: (^{1}H, $CDCl_3$, 25 °C vs. TMS): (δ, ppm) 1.21–1.27 (m, 6H, CH_3 of *i*-Pr), 1.96 (s, 3H, CH_3 of *p*-cymene, *p* to *i*-Pr), 2.74–2.83 (m, 1H, CH of *i*-Pr), 3.73 (s, 3H, OCH_3), 5.25 (d, ^3J = 11.4 Hz, 1H, Ar–H of *p*-cymene), 5.41 (d, ^3J = 11.1, 1H, Ar–H of *p*-cymene), 5.66 (d, ^3J = 6.0 Hz, 1H, Ar–H of *p*-cymene), 6.01–6.04 (m, 2H, H_5), 6.13 (d, ^3J = 6.3 Hz, 1H, Ar–H of *p*-cymene), 6.79 (d, ^3J = 8.7 Hz, 2H, H_2), 7.14 (d, ^3J = 8.4 Hz, 2H, H_3), 7.52–7.70 (m, 3H, $H_7 + H_8 + H_9$), 8.11 (d, ^3J = 8.4 Hz, 1H, H_{10}); (^{13}C{^{1}H}, $CDCl_3$, 25 °C vs. TMS): (δ, ppm)18.8 (*p*-cymene CH_3, *p* to *i*-Pr), 21.5, 23.0 (CH_3 of *i*-Pr of *p*-cymene), 31.8(CH of *i*-Pr of *p*-cymene), 32.1(C_5), 56.2 (OCH_3), 83.6, 85.1, 91.1, 92.2 (ArC of *p*-cymene *m* and *o* to *i*-Pr), 102.2 (C_4), 108.1, 110.3 (ArC attached to CH_3 of *p*-cymene + ArC attached to *i*-Pr of *p*-cymene), 112.4 (C_{10}), 117.0 (C_2), 120.3 (C_7), 127.8 & 131.4 (C_9 and C_8), 135.2 (C_6), 138.3 (C_3), 148.3 (C_{11}), 163.2 (C_1); (^{125}Te{^{1}H}, $CDCl_3$, 25 °C vs. Me_2Te): (δ, ppm) 700.5. IR(KBr, cm^{-1}): 3474, 2973, 1560, 1488, 1236, 1147, 835, 740, 319.

2.5. Procedure for catalytic Heck reaction

A mixture of methyl acrylate (1.5 mmol), aryl bromide (1 mmol), *n*-butylamine (0.146 g, 2.0 mmol), *p*-xylene (~3 mL) and complex **1** or **2** [10^{-4} M, 100 μL (in DMA), ~0.001 mol%] was stirred for 24 h at 100–110 °C on an oil bath. It was cooled to room temperature, treated with chloroform (40 mL) and filtered. The chloroform extract was washed with acidified (HCl) water, dried over anhydrous Na_2SO_4 and its solvent was evaporated on a rotary evaporator to obtain the product, which further was purified by flash chromatography.

2.6. Procedure for catalytic Suzuki–Miyaura reaction

A mixture of phenylboronic acid (1.5 mmol), aryl bromide (1 mmol), K_2CO_3 (3 mmol), toluene (~10 mL) and complex **1** or **2** [10^{-4} M, 100 μL (in DMA), ~0.001 mol%] was stirred for 15 h at 100–110 °C on an oil bath. It was cooled to room temperature, treated with chloroform (40 mL) and filtered. The chloroform extract was washed with acidified (HCl) water, dried over anhydrous Na_2SO_4 and the solvent was evaporated on a rotary evaporator to obtain the product which was purified by flash chromatography.

2.7. Procedure for catalytic oxidation of alcohols

A typical procedure used for catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to ketones with *N*-methylmorpholine-*N*-oxide (NMO) and complexes **3** or **4** is as follows. A solution of ruthenium complexes (0.001 mol%) in 20 cm^3 of CH_2Cl_2 was added to the solution of substrate (1 mmol) and NMO (3 mmol) made in CH_2Cl_2. The mixture was refluxed for 3 h and solvent was evaporated off under reduced pressure. The resulting reaction mixture containing the complex **3** or **4** and the oxidized product was extracted with petroleum ether (60–80 °C) (20 cm^3). The complex **3** or **4** precipitated as solid was recovered quantitatively for next catalytic cycle. The oxidized product separated in petroleum ether was analyzed by GC.

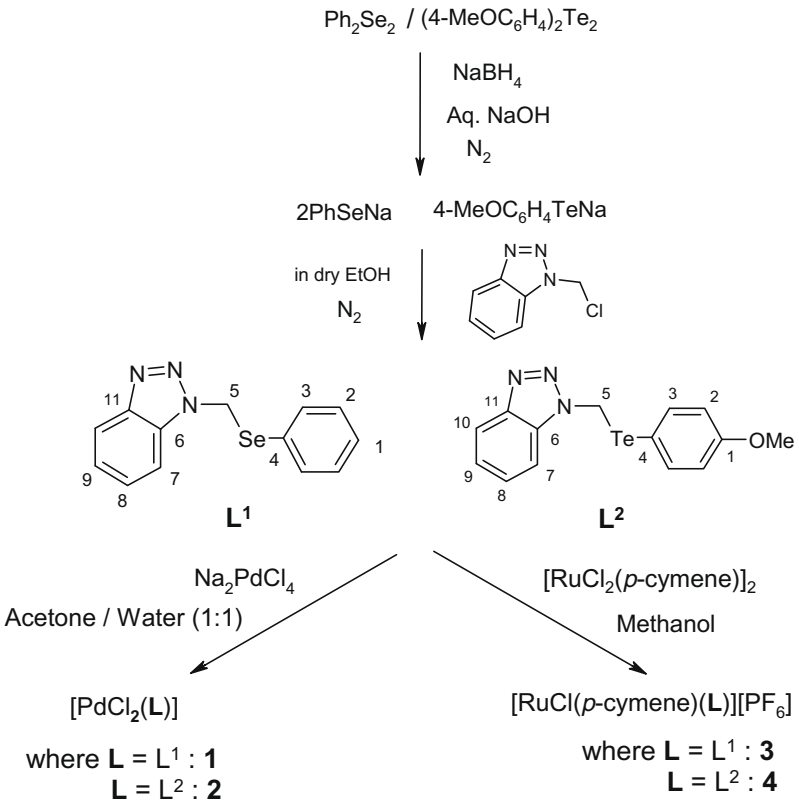
3. Results and discussion

The ligands **L^1** and **L^2** and their complexes have been synthesized by the reactions given in Scheme 1. The ligands are non-electrolytes and stable as they can be stored under ambient conditions up to 6 months. In $CHCl_3$, CH_2Cl_2, CH_3CN, CH_3OH, C_2H_5OH and acetone their solubility is good but poor in hexane. The complexes **1** and **2** are soluble in DMSO and almost insoluble in $CHCl_3$, CH_2Cl_2, CH_3CN, EtOH, MeOH, acetone and hexane. However, their solutions in DMSO on keeping for more than 12 h or exposing them to air show the sign of decomposition. The complexes **3** and **4** expected to be chiral have been isolated as racemic mixture. They are stable under ambient conditions and soluble in $CHCl_3$, CH_2Cl_2, CH_3CN, EtOH, MeOH and acetone but almost insoluble in hexane. The solutions of **3** and **4** in DMSO also show the signs of decomposition after 5–6 h.

The cyclic voltammetric (CV) experiments performed at 298 K in CH_3CN (0.01 M N(*n*-Bu)$_4ClO_4$ as supporting electrolyte) for both **3** and **4** at scan rate 100 mV s^{-1} (anodic sweep) show two metal centered voltammetric responses. A quasi-reversible oxidation (Fig. S.1) with $E_{1/2}$ values +0.588 and +0.644 V (vs. Ag/AgCl), respectively, for **3** and **4** has been observed. More details are in Table S.3 of online Supplementary material. The higher value of $E_{1/2}$ for **4** in comparison to that of **3** suggests that substitution of (N, Se) ligand with a (N, Te) at ruthenium center leads to a less thermodynamically favourable oxidation. Moreover these $E_{1/2}$ values indicate that **3** and **4** are expected to be reasonably efficient catalyst for a redox process [37].

3.1. NMR spectra

The lone signal in ^{77}Se{^{1}H}NMR spectrum of **L^1** is at lower frequency (56.3 ppm) with respect to that of precursor diphenyldiselenide, which shows a signal at 462.6 ppm. On contrary signal in ^{125}Te{^{1}H}NMR spectrum of **L^2** is at high frequency (~249 ppm) with respect to that of precursor ditelluride whose signal appears at 456.3 ppm. The ^{13}C{^{1}H} and ^{1}H NMR spectra of both **L^1** and **L^2** were found as expected. The signal of C_4 (bonded to Se) in carbon-13 spectrum of **L^1** appears at lower frequency (~3 ppm) with respect to that of precursor Ph_2Se_2 (130.5 ppm). But the signal of C_4 (bonded to Te) in the spectrum of **L^2** has been observed at higher frequency (~3 ppm) with respect to that of precursor Ar_2Te_2 (96.6 ppm). However, the signal of C_5 appears at lower frequency (~10 ppm for **L^1** and ~32 ppm for **L^2**) in ^{13}C{^{1}H}spectra of both **L^1** and **L^2** with respect to that of corresponding precursor chloro compound (53.5 ppm). In ^{1}H NMR spectra of both **L^1** and **L^2** the signals of H_5 protons were



Scheme 1.

found at lower frequency (0.31−0.56 ppm) with respect to that of precursor chloro compound (6.42 ppm) and satellites due to coupling of H_5 with Se or Te ($^2J_{Se,H}$ = 9.0 Hz; $^2J_{Te,H}$ = 18.9 Hz) observed. Palladium complexes **1** and **2**, [$PdCl_2$(**L**)] (**L** = $\mathbf{L^1}$: **1**, **L** = $\mathbf{L^2}$: **2**) show $^{77}Se\{^1H\}$/$^{125}Te\{^1H\}$/NMR spectra which support their formation. The signal in $^{77}Se\{^1H\}$ NMR spectrum of **1** is at higher frequency with respect to that of corresponding ligand by 14 ppm. Similarly in $^{125}Te\{^1H\}$NMR spectra of **2** the signal appears shifted to a higher frequency by 43.1 ppm (with respect to that of corresponding free ligand). These high frequency shifts indicate the formation of metal–chalcogen bond in the Pd-complexes **1** and **2**. This is further supported by their $^{13}C\{^1H\}$ NMR spectra as signals of C_5 and C_4 appear at higher frequency (C_5: 1.27 (**1**) and 13.25 (**2**) ppm; C_4: 0.79 (**1**) and 5.53 (**2**) ppm) with respect to those of corresponding free ligands. The signals of H_5 and H_3 are also observed at higher frequency (upto ~0.6 ppm) with respect to those of corresponding free ligands in ^1H NMR spectra of **1** and **2**, further supporting the formation of metal–chalcogen bond. The single crystal structures of complexes **3** and **4** reveal the formation of metal–chalcogen bond. However, the signals in $^{77}Se\{^1H\}$ NMR spectrum of **3** and $^{125}Te\{^1H\}$NMR spectrum of **4** appear unexpectedly at lower frequency (~5 ppm) with respect to those of corresponding free ligands. In $^{13}C\{^1H\}$ NMR spectrum of **4** signals of C_5 as well as C_4 were observed at higher frequency (C_5: 11.06 ppm and C_4: 1.51 ppm) with respect to those of free $\mathbf{L^2}$. The signals of H_3 in ^1H NMR spectrum of **3** were also found at higher frequency (0.38 ppm) with respect to those of corresponding free ligand. Thus formation of Ru–chalcogen bond in the complexes **3** and **4** is supported by their ^1H and $^{13}C\{^1H\}$ spectra.

3.2. Crystal structures

The crystal structures of $\mathbf{L^1}$, $\mathbf{L^2}$, **3** and **4** have been solved. Molecular structures of $\mathbf{L^1}$ and $\mathbf{L^2}$ are shown in Figs. 1 and 2, respectively, along with selected bond lengths and angles. All crystal data and refinement parameters are given in online Supplementary material (Table S.1). The Se–C(aryl) bond distance [1.916(4) Å] is somewhat shorter than Se–C(alkyl) distance [1.953(4) Å] in $\mathbf{L^1}$. Similarly in the case of $\mathbf{L^2}$ Te–C(aryl) bond distance [2.117(3) Å] is found shorter than Te–C(alkyl) distance [2.159(3) Å]. The bond angles C(alkyl)–Se–C(aryl) (97.39(15)°) in $\mathbf{L^1}$ and C(alkyl)–Te–C(aryl) (95.16(10)°) in $\mathbf{L^2}$ are as expected. The Table S.2 of online Supplementary material has more values of bond lengths and angles. The hydrogen atoms of CH_2 group of $\mathbf{L^1}$ are engaged in non-covalent interaction [N···H hydrogen bonding (inter and intra molecular both)] which may be the result of stacking forces. The π–π interactions between the benzotriazole rings are also present in its crystal, probably due to similar reason. In case of $\mathbf{L^2}$ also both intermolecular N···H and O···H non-covalent interactions (hydrogen bonding) probably due to stacking have been observed. Further details of these non-cova-

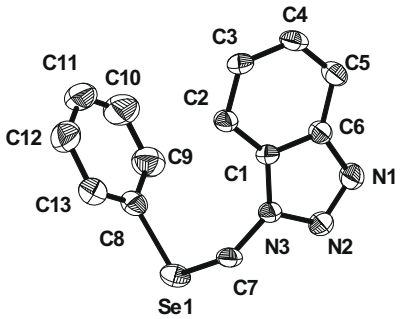


Fig. 1. ORTEP diagram of $\mathbf{L^1}$ with 30% probability ellipsoids: bond distances (Å): Se(1)–C(8) 1.916(4), Se(1)–C(7) 1.953(4), N(3)–C(6) 1.366(5); bond angles (°): C(8)–Se(1)–C(7) 97.39(15), N(1)–C(7)–Se(1) 114.5(2), N(3)–N(2)–N(1) 109.1(3).

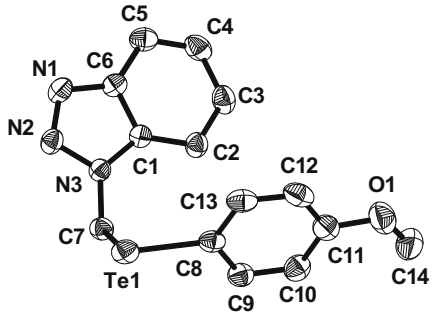


Fig. 2. ORTEP diagram of $\mathbf{L^2}$ with 30% probability ellipsoids: bond distances (Å): Te(1)–C(7) 2.159(3), Te(1)–C(8) 2.117(3), N(3)–C(7) 1.447(3); bond angles (°): N(1)–N(2)–N(3) 109.0(2), C(7)–Te(1)–C(8) 95.16(10), Te(1)–C(7)–N(3) 115.69(17).

lent interactions are given in online Supplementary material (Figs. S.3–S.5).

The ORTEP diagrams of cation of **3** and **4** are given in Figs. 3 and 4, respectively, with their some selected bond lengths and angles. Further details are given in the online Supplementary material (Table S.2). In both the cations of **3** and **4**, Ru exhibits the pseudo-octahedral half sandwich "piano-stool" disposition around Ru. The ring of *p*-cymene occupies one face of octahedron. The Ru-complexes of selenoether ligands have scantly investigated. However, Ru(II)(η^6-benzene)- and Ru(II)(η^6-*p*-cymene)-complexes of selenated pyrrolidine derivatives have been reported by our research group recently in which Ru is coordinated through Se and N forming a five membered chelate ring [38]. The **3** is another example of such Ru–selenoether complex. The Ru–C distances (2.182(7)–2.225(8) Å) in the cation of **3** are normal and consistent with the earlier reports [38–40]. In the crystal of **3**, π–π and C–H···π interactions along with intra and inter molecular non-covalent interactions (hydrogen bonds) between F and various H atoms have been observed resulting in extended structures (Figs. S.6 and S.7 in online Supplementary material). The Ru–N bond length in the cation of **3**, 2.089(6) Å is comparable to that of cation of **4** and consistent with recent literature reports (2.0511(17)–2.163(10) Å) [39,40]. It is however, shorter than 2.146(3)–2.201(5) Å reported for half sandwich complex of Ru(II) with *N*-{2-(phenylseleno)ethyl}pyrrolidine [38]. The Ru–Se bond length of the cation of **3** (2.4801(11) Å) falls within the range 2.4756(10)–2.5240(9) Å reported for Ru–Se bond lengths in clusters [$Ru_3(\mu_3\text{-}Se)(CO)_7(\mu_3\text{-}CO)(\mu\text{-}dppm)$] and [$Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}S)(CO)_7(\mu\text{-}dppm)$] [41]. For Ru(IV) complex [$RuCp^*\{\eta^2\text{-}Se_2P(i\text{-}Pr)_2\}\{\eta^2\text{-}SeP(i\text{-}Pr)_2\}][PF_6$] the Ru–Se bond lengths [42] are reported in the range 2.538(2)–2.590(2) Å, longer than that of cation of **3** due to steric crowding. The Ru–Se bond distance found in bimetallic species [$RuCp(CO)(C{\equiv}CPh)(\mu\text{-}Se)ZrCp_2$] 2.494(1) Å [43], is closer to that of cation of **3**. In [$Ru(\eta^5\text{-}C_5Me_5)(\mu_2\text{-}SeR)_3Ru(\eta^5\text{-}C_5Me_5)$]Cl (R = Tolyl) Ru–Se bond distances are in the range 2.446(4)–2.466(4) Å [44] and shorter than that of cation of **3**, because RSe^- is expected to be bonded strongly in comparison to a selenoether. In a diselenide bridged complex [$Ru(MeCp)(PPh_3)]_2(\mu\text{-}Se_2)_2(Otf)_2$, Ru–Se bond distances are 2.518(1) and 2.556(1) Å [45], somewhat longer than that of cation of **3**. In cation of complex **4**, ligand $\mathbf{L^2}$ is coordinated with Ru in a bidentate (Te, N) mode forming a five membered chelate ring. The Ru–N bond length (2.085(7) Å) is consistent with the sum of covalent radii ca. 1.95 Å and with literature reports of 2.142(3) Å for [{$RuCl(\eta^6\text{-}p\text{-}cymene)(H_2NCH_2CH_2Te\text{-}C_6H_4OMe)$}$Cl{\cdot}H_2O$] [46], 2.141(2)–2.156(2) Å for [$RuCl(\eta^6\text{-}p\text{-}cymene)(o\text{-}phenylenediamine)][PF_6$] [47], 2.0652(19)–2.0756(19) Å for Ru(II)(η^6-benzene)-complexes of bis(pyrazol-1-yl)pyridazine and Ru(II)(η^6-*p*-cymene)-complexes of 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine [48], 2.13(1)–2.14(1) Å for [$RuCl(\eta^6\text{-}p\text{-}cymene)(\kappa^2\text{-}N,O\text{-}phenylalanineamide)$] [49], 2.060(5) and 2.079(4) Å for [$RuCl(\eta^6\text{-}p\text{-}cymene)$\{2,3-bis(2-pyridyl)pyrazine\}]$\cdot BF_4$ [50] and 2.077(3)–2.113(3) Å for Ru(II)(η^6-*p*-cymene)-complexes of oxazoline-based ligands [51]. The Ru–Te bond length (2.6183(10) Å) of cation of **4** is consistent with earlier reports 2.619(8) Å for [$RuCl_2(\eta^6\text{-}p\text{-}cymene)\mathbf{L}$] where **L** is 2-(4-ethoxyphenyl telluromethyl)tetrahydro-*2H*-pyran [52] and 2.6371(4) Å for [{$RuCl(\eta^6\text{-}p\text{-}cymene)(H_2NCH_2CH_2TeC_6H_4OMe)Cl{\cdot}H_2O$] [46]. It is somewhat shorter than 2.6528(9) Å for [dichloro(η^6-*p*-cymene)-bis{2-(2-thienyl)ethyl}telluride]ruthenium(II) [53], 2.651(5) Å for [$RuCl_2(\eta^6\text{-}p\text{-}cymene)$\{bis(1,3-dioxan-2-yl)\}ethyl telluride}] [54] and 2.6559(9) Å for [$RuCl_2(\eta^6\text{-}p\text{-}cymene)$\{N-[2-(4-methoxyphenyltelluro)ethyl]-phthalimide}] [55]. The hybrid organotellurium ligands in all these complexes of Ru(II)(η^6-*p*-cymene) bind in a monodentate mode via Te and probably this may be responsible to some extent for the longer Ru–Te bond lengths observed in them. The Ru–Cl bond length of the cation of **4**, 2.412(3) Å (sum of covalent radii ca. 2.24 Å) is consistent with earlier reports 2.415(2)/2.422(2) Å for [dichloro(η^6-*p*-cymene)bis{2-(2-thienyl)-ethyl}telluride]ruthenium(II) [36], 2.417(2)–2.436(2) Å for

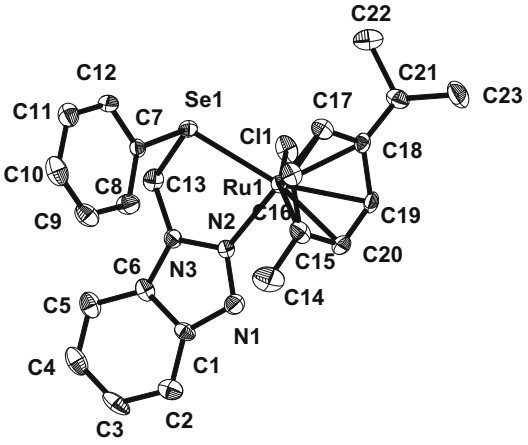


Fig. 3. ORTEP diagram of cation of **3** with 30% probability ellipsoids; bond distances (Å): Ru(1)–N(2) 2.089(6), Ru(1)–Cl(1) 2.416(2), Ru(1)–Se(1) 2.4801(11), Ru(1)–C 2.182(7)–2.225(8); bond angle (°): N(2)–Ru(1)–Cl(1) 86.92(18), N(2)–Ru(1)–Se(1) 81.41(17), Cl(1)–Ru(1)–Se(1) 80.49(6).

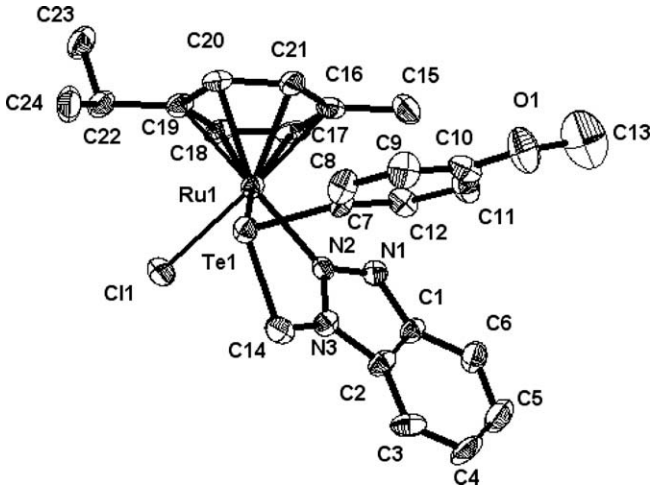


Fig. 4. ORTEP diagram of cation of **4** with 30% probability ellipsoids; bond distances (Å): Te(1)–Ru(1) 2.6183(10), Ru(1)–N(2) 2.085(7), Ru(1)–Cl(1) 2.412(3), Ru(1)–C 2.170(10)–2.231(10); bond angle (°): N(2)–Ru(1)–Cl(1) 87.6(2), N(2)–Ru(1)–Te(1) 82.6(2), Cl(1)–Ru(1)–Te(1) 79.88(8).

Table 1
Parameters for catalytic performance of **1** and **2** in Heck reactions of aryl halide with methyl acrylate.

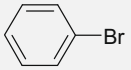
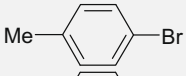
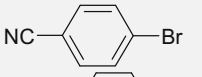
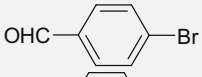
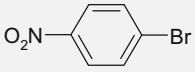
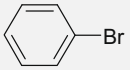
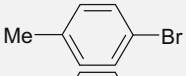
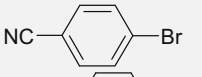
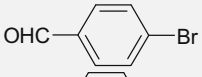
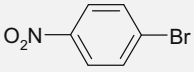
Ar–X	**1**			**2**		
	% Conversion	TON	TOF (h^{-1})	% Conversion	TON	TOF (h^{-1})
	55	55,000	2291	57	57,000	2375
	28	28,000	1166	30	30,000	1250
	90	90,000	3750	92	92,000	3833
	92	92,000	3833	94	94,000	3916
	91	91,000	3791	95	95,000	3958

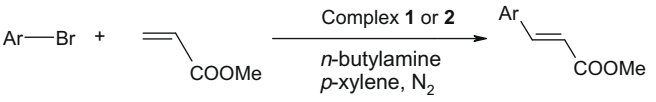
Table 2
Parameters of catalytic performance of **1** and **2** in Suzuki–Miyaura reactions of aryl bromide with phenylboronic acid.

Ar–X	**1**			**2**		
	% Conversion	TON	TOF (h^{-1})	% Conversion	TON	TOF (h^{-1})
	40	40,000	2666	41	41,000	2733
	23	23,000	1533	24	24,000	1600
	85	85,000	5666	87	87,000	5800
	89	89,000	5933	92	92,000	6133
	91	91,000	6066	90	90,000	6000

$[RuCl_2(p\text{-cymene})\mathbf{L}]$ (**L** = monodentate Te-ligand) [56–58] and $[RuCl\{\eta^2\text{-C,N-}C_6H_3(CH_2NMe_2)_2\text{-2,6}\}\{\eta^6\text{-}C_{10}H_{14}\}]$ [59]. However, Ru–Cl bond distance of the cation of **4** is somewhat longer than 2.308(2) Å reported for $[\{Ru(p\text{-cymene})Cl(H_2NCH_2CH_2TeC_6H_4O\text{-Me})\}Cl\cdot H_2O]$ [46]. The Ru–C bond distances 2.170(10)−2.231(10) Å and C–Ru–C bond angles of the cation of **4** are consistent with earlier reports on species having Ru(*p*-cymene) unit [52–58]. The bond angles at the coordinating Te and N atoms are as expected for nearly trigonal–pyramidal and tetrahedral geometries, respectively. There are non-covalent interactions (F···H) in the crystal of **4** (for details see online Supplementary material Fig. S.6) probably due to stacking forces.

3.3. Catalytic C–C coupling and oxidation of alcohols

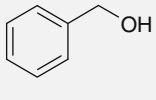
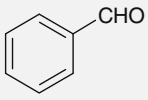
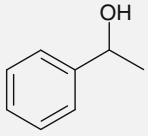
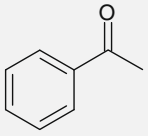
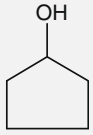
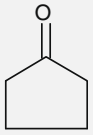
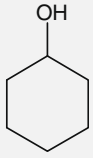
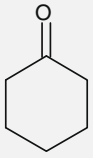
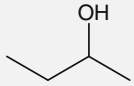
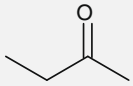
The strong donating properties of organoselenides has made Pd(II) complex of (Se, C, Se) pincer ligand an outstanding catalyst system [60] for Heck C–C coupling. This has motivated us to explore **1** and **2** as catalyst for Heck reaction at concentration 0.001 mol% using *n*-butyl amine as base. The results are given in Table 1. The TON value are high (upto ~95,000) showing the promise of both **1** and **2** as catalyst for Heck coupling. However, the TON values when Pd-complex of (Se, C, Se) pincer ligand is used, are upto 1,10,000. The performance of **1** and **2** both is much superior than that of palladium salicylaldehyde thiosemicarbazone complex, which shows TON values upto 43,000 only [61]. For aryl chlorides 1 mol% of phosphine based palladacycle is needed for high yield of the reaction [64]. The **1** and **2** for catalyzing Heck reaction are as efficient as Pd-complexes of (Se, N, Se) pincer ligand reported recently [66] (TON upto 97,000).

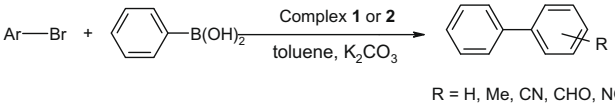


(1)

Suzuki–Miyaura reaction, is also among the most important palladium-catalyzed cross-coupling reactions of both academic and industrial interest [62–69]. In view of air and moisture sensitivity of complexes of phosphorus ligands there is an interest in phosphine-free ligands for the Suzuki–Miyaura reaction. The complexes **1** and **2** have been explored for Suzuki–Miyaura reaction (Eq. (2)). The results given in Table 2, indicate that both the complexes are promising. The results given in Tables 1 and 2 also indicate that Pd(II)-telluroether complexes are as efficient as their selenium analogues. The TON values are <10,000 when Pd-complex of a selenated Schiff bases is used as catalyst for Suzuki–Miyaura coupling. Phosphine ligand based Pd-complexes are suitable for Suzuki–Miyaura coupling of aryl chlorides but the requirements of a co-catalyst and high mol% of catalyst are stringent [64–68]. In the course of Suzuki–Miyaura coupling reaction there was a black deposit formation (Pd(0)), indicating that the mechanism of catalysis by **1** and **2** is probably Pd(II)/Pd(0) one.

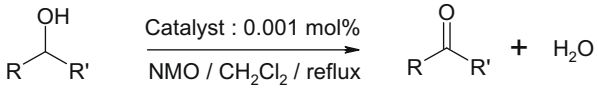
Table 3
Catalytic oxidation of alcohols to corresponding aldehydes and ketones with complexes **3** and **4** in the presence of NMO.

	Substrate	Product	TON (% conversion)	
			3	**4**
1			7.8×10^4 (78)	8.2×10^4 (82)
2			8.4×10^4 (84)	8.7×10^4 (87)
3			8.5×10^4 (85)	8.9×10^4 (89)
4			8.8×10^4 (88)	9.1×10^4 (91)
5			9.2×10^4 (92)	9.4×10^4 (94)



(2)

The catalytic oxidation (Eq. (3)) in the presence of complexes **3** and **4** was found promising as TON values were found to be upto 94,000 (Table 3). It has been observed that neither **3** or **4** nor *N*-methylmorpholine-*N*-oxide (NMO) alone causes these organic transformations under identical reaction conditions. Moreover, oxidation in aqueous medium is not smooth as neither complex **3** nor **4** is soluble in water. The **3** and **4** both effectively catalyze the oxidation of benzyl alcohol with maximum selectivity to aldehyde, importantly, with no further oxidation to carboxylic acid. It appears that probably NMO reacts with Ru-complex to yield ruthenium(IV)-oxo species, which in turn oxidizes the alcohols. The earlier reports [70–72] on the oxidation of various substrates including alcohols by oxo-ruthenium species support our proposition. It is interesting to note that the complex **4** having tellurium donor site is somewhat more efficient catalyst than **3.** The complexes **3** and **4** can be reused as catalyst but their activity diminishes nearly 10–15%. In comparison to recently reported Ru based catalytic species [73–77] for oxidation of alcohols, **3** and **4** are more efficient as they are needed in less quantity and reaction time is shorter. For example ~2 mol% of the catalyst [Ru(PPh_3)(OH)salen] is required [76] for aerobic oxidation of primary alcohols.



(3)

Catalyst: **3** or **4**

R= R'= Alkyl (or) aryl (or) H

4. Conclusion

Selenated and tellurated benzotriazole derivatives, 1-(phenylselenomethyl)-1*H*-benzotriazole (**L**^{1}) and 1-(4-methoxyphenyltellluromethyl)-1*H*-benzotriazole (**L**^{2}) have been synthesized for the first time. Their complexes [$PdCl_2$(**L**)] and [Ru(*p*-cymene)(**L**)Cl][PF_6] (where **L** = **L**^{1} or **L**^{2}) are suitable for C–C coupling reactions (Heck and Suzuki–Miyaura) and catalytic oxidation of alcohols, respectively. The TON values are high (upto 95,000 for coupling and 94,000 for oxidation) The **L**^{1}, **L**^{2}, [Ru(*p*-cymene)(**L**^{1})Cl[PF_6] and [Ru(*p*-cymene)(**L**^{2})Cl][PF_6] have been characterized by X-ray crystallography. The Ru–Se and Ru–Te bond lengths have been found 2.4801(11) and 2.6183(10) Å, respectively. It is interesting to note that the complexes of telluroether ligands are as efficient catalysts as those of selenoethers and in fact better for catalytic oxidation.

Acknowledgements

Authors thank Department of Science and Technology (India) for research Project No. SR/S1/IC-23/06 and for partial financial assistance given to establish single crystal X-ray diffraction facility at IIT Delhi, New Delhi (India) under its FIST programme. D.D. and P.S. thank University Grants Commission (India) for the award of Junior/Senior Research Fellowship.

Appendix A. Supplementary material

CCDC 747791, 709839, 747792 and 709841 contain the supplementary crystallographic data for **L1**, **L2**, **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.009.

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