

Selenoether ligand assisted Heck catalysis

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ABSTRACT

Selenoether ligands, 2,2'-methylenebis(selenediyl)bis(2,1-phenylene)dimethanol (**5**), (2,2'-(ethane-1,2-diylbis(selenediyl))bis(2,1-phenylene))dimethanol (**6**) and (2-(benzylselenyl)phenyl)methanol (**7**) have been synthesized by reducing di-*o*-formylphenyl diselenide and reacting the *in situ* generated selenolate with dibromomethane, 1,2-dibromoethane and benzyl chloride, respectively. The ligands, bis(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenylselenyl)methane (**8**) and 1,2-bis(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenylselenyl)ethane (**9**) have been synthesized similarly from bis[2-(4,4-dimethyl-2-oxazolyl)phenyl] diselenide using electrophiles dibromomethane and 1,2-dibromoethane, respectively. Activity of ligands **5–9** along with 2-(2-(benzylselenyl)phenyl)-4,4-dimethyl-4,5-dihydrooxazole (**10**) and 1-(2-(benzylselenyl)phenyl)-*N,N*-dimethylmethanamine (**11**) were examined for the Heck reaction of aryl halides with olefins. Bidentate Se,N ligand **11** was found to be the best one in the series and constitutes an efficient phosphine-free catalytic system with PdCl₂. The catalytic system showed moderate activity for the coupling of activated aryl chlorides in the presence of tetra-*n*-butyl ammonium bromide (TBAB). Complexes [10-PdCl₂] (**12**) and [11-PdCl₂] (**13**) have shown marginally better activity in comparison to the *in situ* generated catalysts from PdCl₂ and **10** and **11**, respectively in the coupling of 4-bromoacetophenone with *n*-butylacrylate. Ligand **9** and complex **13** have been characterized by single crystal X-ray diffraction analysis.

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1. Introduction

Palladium catalyzed arylation or vinylation of olefins, known as the Heck or the Mizoroki–Heck reaction, has evolved as a powerful tool in organic synthesis for C–C bond formation [1–14]. A conventional Heck reaction involves coupling of an aryl halide and a terminal olefin bearing an electron withdrawing group catalyzed by 1–5 mol% of a palladium catalyst in presence of a phosphine ligand and a suitable base [15–18]. However, the phosphine ligands are generally expensive and air-sensitive. A number of phosphine-free catalysts have been employed in the Heck reaction. Among them the palladacycle catalysts [19] and *N*-heterocyclic carbene (NHC) ligands [20] have shown excellent activity. Other phosphine-free catalyst systems involve nitrogen, oxygen and sulfur ligated complexes of palladium either as preformed catalysts or as *in situ* catalysts generated from an added ligand and a suitable palladium precursor. Although not much explored, these types of ligands have been shown to have interesting applications in the Heck reaction.

Among the recent examples are amino acids [21], benzothiazoles [22], imidazolines [23], phenylureas [24], pyridylpyrazoles [25], and thiazolidine-1-oxides [26].

The use of selenium containing ligands in the Heck reaction is much rarer. Recently, the use of selenium ligated palladacycles and palladium complexes in the Heck reaction has shown great potential [27]. These catalysts (**1a–1c**, Chart 1) are reported to outperform the phosphorus and sulfur ligated catalysts including the best in the business like Herrmann palladacycle [28] and Milstein's catalysts [29]. Recently, Singh and co-workers have used palladium complexes of SeNSe pincer ligands (**2a**, **2b**, Chart 2) and seleno- and telluroether ligands containing benzotriazole moiety in the Heck and Suzuki–Miyaura coupling reactions [30,31]. More recently, they have demonstrated that air and moisture stable palladacycle generated from Se,N ligand in the Suzuki–Miyaura coupling reactions show high catalytic activity [32]. We envisaged that the use of bidentate or tetradentate, heteroleptic selenoether ligands incorporating nitrogen or oxygen can show interesting catalytic properties in the Heck reaction. Herein, we report the synthesis of selenoether ligands derived from di-*o*-formylphenyl diselenide [33] and bis[2-(4,4-dimethyl-2-oxazolyl)phenyl] diselenide [34]. Utility of these ligands and other related ligands in the Heck reaction is described.

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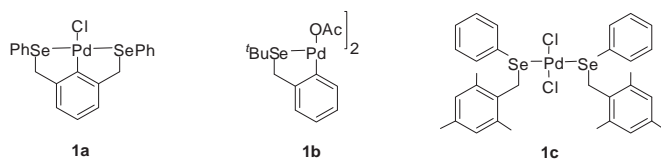


Chart 1. Selenium ligated catalysts.

2. Results and discussion

2.1. Synthesis of ligands

Selenoether ligands **5–9** were synthesized by reducing the diselenides viz. di-*o*-formylphenyl diselenide (**3**) [33] and bis[2-(4,4-dimethyl-2-oxazolanyl)phenyl] diselenide (**4**) [34] with NaBH₄ and reacting the resulting selenolates with various electrophiles shown in Scheme 1. The newly synthesized ligands were characterized by elemental analysis and NMR (¹H, ¹³C and ⁷⁷Se) spectroscopy. The ⁷⁷Se NMR spectroscopic data are given in the following table (Table 1).

The –OH peak in the ¹H NMR spectrum of **5** in CDCl₃ appeared as a broad band at δ 2.34 ppm. However, the –OH peak in the ¹H NMR spectrum of **7** appeared as a sharp triplet at δ 1.91 ppm in CDCl₃. The reason may be the presence of strong intramolecular interaction in this case. The chemical shifts in the ⁷⁷Se NMR spectra of the ligands **5–7** [δ 287 (**5**), 280 (**6**) and 320 ppm (**7**)] showed an upfield shift with respect to the parent diselenide **3** (δ 468 ppm) [33]. Similarly, the ⁷⁷Se chemical shift of the ligands **8** (δ 325) and **9** (350 ppm) showed an upfield shift with respect to the parent diselenide **4** (δ 454 ppm) [34]. Ligands **10** and **11** were prepared by reducing the corresponding diselenides with NaBH₄ and reacting the resulting selenolates with PhCH₂Cl. This represents a minor modification of the reported method for synthesis of the ligands where they were synthesized from the selenolates, generated *in situ* from the *ortho*-lithiated derivatives [35].

2.2. Synthesis of complexes

Palladium complexes **12** and **13** were synthesized as shown in Scheme 2. The complexes were obtained by stirring the ligands and metal precursor at room temperature. Any unreacted metal precursor was separated from the synthesized complexes by crystallizing from dichloromethane/hexane. The complexes were characterized by ¹H and ⁷⁷Se NMR spectroscopy and elemental analysis. The methylene protons appeared as doublets at δ 3.94 and 4.20 ppm having coupling constant 12.0 Hz in the ¹H NMR spectrum of **12** showing their diastereotopic nature. A similar splitting pattern was observed in the ¹H NMR spectrum of **13** (at δ 3.06 and 4.58 with coupling constant 12.0 Hz). The ⁷⁷Se NMR chemical shift of **12** appeared downfield by 54 ppm with respect to the free ligand **10** (δ 421 ppm). However, the ⁷⁷Se NMR signal of **13** was upfield shifted by 78 ppm with respect to the free ligand **11** (δ 321 ppm) [35].

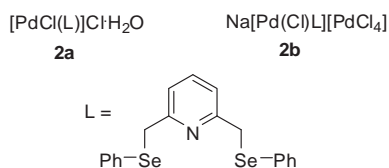
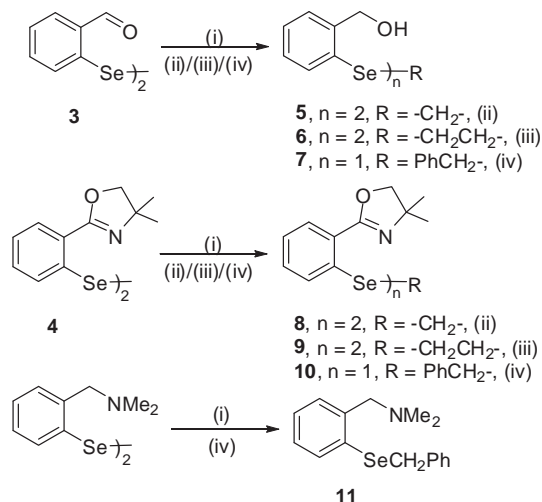


Chart 2. SeNSe pincer ligands.

Scheme 1. (i) NaBH₄, EtOH; (ii) CH₂Br₂, (iii) Br(CH₂)₂Br, (iv) PhCH₂Cl.

2.3. Crystallographic studies

2.3.1. Molecular structure of **9**

The molecular structure of **9** is shown in Fig. 1. The geometry around the two selenium atoms is V-shaped. The intramolecular Se...N distance (2.830 Å) is less than the sum of their van der Waals radii (3.40 Å) [36] showing significant secondary bonding interaction and is comparable with the Se...N distances observed in [2-(4,4-dimethyl-2-oxazolanyl)phenyl]benzyl selenide (2.798 Å) [35] and bis[2-(4,4-dimethyl-2-oxazolanyl)phenyl]diselenide (2.819 Å, 2.705 Å) [34]. Selenium–carbon(sp²) distance, Se–C1 [1.9141(18) Å] is shorter than the selenium–carbon(sp³) distance, Se–C [1.9652(17) Å] and also shorter than the corresponding distances in [2-(4,4-dimethyl-2-oxazolanyl)phenyl]benzyl selenide [1.916(3) Å] and bis[2-(4,4-dimethyl-2-oxazolanyl)phenyl]diselenide [1.946(9) Å, 1.940(9) Å]. Torsion angles, C1–Se–C–Cⁱ [172.50(15)°], C–Se–C1–C6 [174.96(13)°], C–Se–C1–C2 [–5.30(15)°] are close to 180° or 0° showing the molecule to be almost planar.

2.3.2. Molecular structure of **13**

The molecular structure is depicted in Fig. 2. The geometry around the palladium center is distorted square planar with the four coordinations being defined by selenium, nitrogen and two *cis*-chloro donors. *Trans*-angle, Cl1–Pd–Se [169.79(2) Å] deviates more than the other angle, N–Pd–Cl2 [176.53(7) Å] from linearity. The bite angle, N–Pd–Se is 95.94(7) Å. The Pd–Cl2 bond distance [2.2898(8) Å], *trans* to nitrogen is slightly longer than the Pd–Cl1 bond distance [2.2674(8) Å], *trans* to selenium. Pd–N [2.065(2) Å] and Pd–Cl [2.2674(8) Å, 2.2898(8) Å] bond lengths are comparable to the corresponding distances in the similar structures [37–44].

Table 1
⁷⁷Se NMR of ligands and complexes.

Compound	⁷⁷ Se NMR (δ)
5	287 ^a
6	280 ^a
7	320 ^a
8	325 ^b
9	350 ^b
12	367 ^b
13	399 ^b

^a In CD₃OD.^b In CDCl₃.

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