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Palladium selenolates via oxidative addition of organylselenenyl halides to palladium(0) precursor and via cleavage reaction of diselenides: Synthesis, structure and spectroscopic investigation

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ABSTRACT

Oxidative addition of bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] diselenide to $Pd(PPh_3)_4$ provided two different mononuclear palladium selenolato complexes, $Pd(Se\cap N)(PPh_3)Cl$ (**4**) [$Se\cap N$ = chelating 2-(4,4-dimethyl-2-oxazolinyl)phenylselenolate] and $Pd(Se\cap N)(Se\cap N^*)(PPh_3)$ (**5**) [$Se\cap N$ = chelating, $Se\cap N^*$ = non-chelating 2-(4,4-dimethyl-2-oxazolinyl)phenylselenolato ligand] in dicholoromethane and toluene respectively. Complex **4** has also been synthesized by the oxidative addition of 2-(4,4-dimethyl-2-oxazolinyl)phenylselenenyl chloride to $Pd(PPh_3)_4$. The bromo and iodo analogs of **4** (**9** and **10**) were similarly synthesized by the oxidative addition of 2-(4,4-dimethyl-2-oxazolinyl)phenylselenenyl bromide and iodide, respectively to $Pd(PPh_3)_4$. The oxidative addition of 2-(*N*,*N*-dimethylaminomethyl)phenylselenenyl bromide and iodide to $Pd(PPh_3)_4$ afforded mononuclear palladium selenolate complexes, $Pd(Se\cap N)(PPh_3)X$ (**13** and **14**) [$Se\cap N$ = chelating 2-(*N*,*N*-dimethylaminomethyl)phenylselenolate, X = Br: **13**, X = I: **14**]. The reactions of bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] diselenide and bis[2-(*N*,*N*-dimethylaminomethyl)phenyl] diselenide with $Pd(COD)Cl_2$ provided dinuclear selenolato-bridged complexes $[PdCl(Se\cap N)]_2$ (**15**) [$Se\cap N$ = chelating 2-(4,4-dimethyl-2-oxazolinyl)phenylselenolate] and $[PdCl(Se\cap N)]_2$ (**19**) [$Se\cap N$ = chelating 2-(*N*,*N*-dimethylaminomethyl)phenylselenolate] respectively. The complexes were characterized by elemental analysis and NMR (^1H and ^{77}Se) spectroscopy. Complexes **4** and **5** were also characterized by mass spectrometry. Molecular structures of **4**, **5**, **9**, **14** and **15** have been established by single crystal X-ray diffraction analysis. Complexes **4** and **9** are isomorphous and crystallize in the space group $P2_1/c$ of the monoclinic system where the selenolato and halo ligands are *trans* to each other. Complex **5** crystallizes in the space group $P2_1/n$ of the monoclinic system where one chelating and one non-chelating selenolato ligands are *trans* to each other. Mononuclear complex **14** and binuclear centrosymmetric complex **15** crystallize in the $P\bar{1}$ space group of the triclinic system.

1. Introduction

The coordination chemistry of the heavier organochalcogen ligands with transition metals, particularly Group 10, is a rapidly developing area of organometallic chemistry [1–5]. The interest in this area arises from the realization that the complexes may serve as single-source precursors for binary transition metal selenides and tellurides which find applications in material science [6–10]. The area is of current interest also because of the potential applications in homogeneous catalysis [11–13].

The oxidative addition of E–E bonds (E = S, Se, Te etc) to low-valent transition metal complexes is among one of the basic processes of organometallic chemistry and provides a mild and simple way to synthesize chalcogenolato complexes via the cleavage of the E–E bond. However, in some instances the bond remains intact [14–16]. On the other hand the reaction of ditellurides with M(0) (M = Ni, Pd, Pt) may also result in the cleavage of the C–E bond [17–20]. In 1978, McWhinnie and Chia reported the reaction of bis(2-dithienyl) ditelluride with $Pd(PPh_3)_4$, where formation of a dinuclear palladium complex $[Pd(TeTh)_2(PPh_3)]_2$ (Th = 2-thienyl) with two terminal and two bridging tellurolate ligands was suggested [21]. Furukawa et al. [22] also reported an analogous complex from the reaction of Ph_2Se_2 with $Pd(PPh_3)_4$. There was no structural characterization in either of the reports. Laitinen and co-workers have reported, in a series of papers, their

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work on the oxidative addition of bis(2-thienyl) diselenide and ditelluride (Th_2Se_2 and Th_2Te_2), diphenyl diselenide and ditelluride to palladium(0) and platinum(0) [23–25]. Recently, they have reported on the oxidative addition of a cyclic ditelluride to platinum(0) and have isolated two mononuclear and a dinuclear tellurolate complexes of platinum [26]. Morley and co-workers have also reported on the oxidative addition of Ph_2Se_2 and Fc_2Se_2 [Fc = ferrocenyl] to palladium(0) and platinum(0) [27]. Very recently, oxidative addition of bis(2-pyridyl)ditellurides to platinum(0) has been reported where in addition to the expected product of oxidative addition, an all-tellurium-donor tridentate ligand coordinated platinum complexes have been obtained [28]. It has been observed that the use of simple diselenides in oxidative addition to palladium(0) generally leads to the formation of dinuclear complexes [23–25]. We thought of utilizing chelating diselenides to isolate mononuclear complexes. Although the oxidative addition of Se–Se bond to palladium(0) is common, there is no report, to our knowledge, on the oxidative addition reactions of Se–X (X = Cl, Br and I) bonds to palladium(0).

In contrast to the oxidative addition reactions of diorgano dichalcogenides [R_2E_2, E = Se, Te] to palladium(0)/platinum(0) [23–26,29], there are very few examples of the cleavage reactions of R_2E_2 by palladium(II) [30]. Jain and co-workers have explored the reactions of chelating alkyl selenolates and tellurolates, generated *in situ* from the corresponding diselenides and ditellurides, as well as of alkyl diselenides and ditellurides with palladium(II) and platinum(II) [30]. For instance, diselenide $(Me_2NCH_2CH_2Se)_2$ afforded a trinuclear complex, $[PdCl(SeCH_2CH_2NMe_2)]_3$, on reaction with $Na_2[PdCl_4]$ [31]. On the other hand, selenolate $NaSeCH_2CH_2NMe_2$, prepared from the corresponding diselenide by reduction with $NaBH_4$, provided a mononuclear complex, $[Pd(SeCH_2CH_2NMe_2)_2(PPh_3)_2]$ on reaction with $PdCl_2(PPh_3)_2$. Again, selenolate $NaSeCH_2CH_2NMe_2$, provided a dinuclear complex $[Pd_2Cl_3(SeCH_2CH_2NMe_2)(PPh_3)_2]$ when reacted with $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ [31]. Very recently, Singh and co-workers have reported the cleavage reactions of a series of a related chiral and achiral multidentate selenium and tellurium ligands (**1a**–**c**: Chart 1) with palladium(II) precursor [32]. Diselenide **1b** provided a selenolate bridged dinuclear complex **2a** on reaction with $Pd(COD)Cl_2$. Ditelluride **1c** underwent cleavage of the Te–Te bond on reaction with $Pd(COD)Cl_2$ and a similar tellurolate bridged dinuclear complex **2b** was obtained. In addition to that, a dimeric chloro-bridged organyl tellurenyl chloride [$(RTeCl)_2$, R = 2-$CH_2NMe_2C_6H_4$] was isolated and characterized. It was shown that the R_2E_2 ligands (**1a**–**c**) underwent a formal self–redox reaction on treatment with $Pd(COD)Cl_2$ (Scheme 1). Ghavale et al. have also suggested that the reaction between diselenides with Pd(II) proceeds via Pd(IV) intermediate which undergo reductive elimination to afford palladium selenolate complexes along with selenenyl halides as formal reduced and oxidized product respectively [33]. Thus this reaction provides a general way to synthesize dinuclear chalcogenolato palladium complexes.

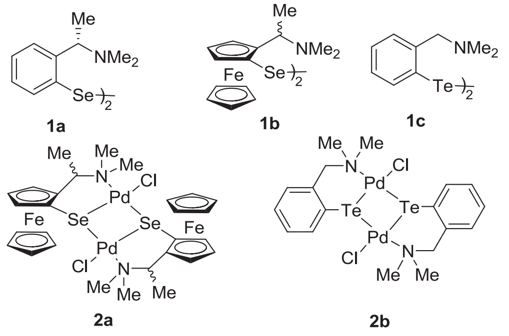


Chart 1.

$$R_2E_2^{+I} \xrightarrow{Pd(COD)Cl_2} [RE^{-I}PdCl]_2 + RE^{+II}Cl/[RE^{+II}Cl]_2$$

E = Se/Te

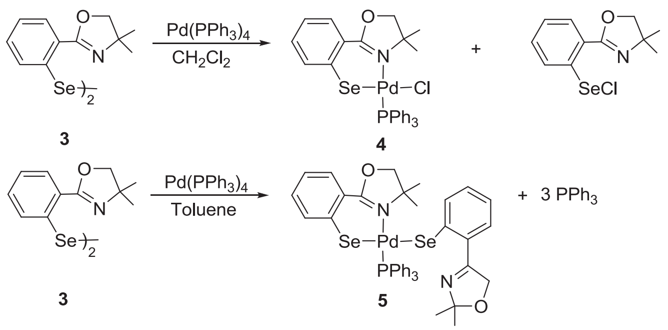
Scheme 1. Formal self–redox reaction.

Herein we report the synthesis and characterization of a few mononuclear palladium selenolato complexes by a hitherto unutilized method of oxidative addition of organylselenenyl halides to palladium(0). Also the synthesis and characterization of a few dinuclear palladium chalcogenolato complexes by the cleavage of diorgano dichalcogenides with palladium(II) is described to substantiate our earlier observation.

2. Results and discussion

2.1. Palladium selenolate complexes by oxidative addition to palladium(0)

The reaction between bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] diselenide (**3**) [34] and tetrakis(triphenylphosphine) palladium(0) in dichloromethane and toluene provided two different mononuclear palladium complexes **4** and **5** respectively (Scheme 2). Complex **4** was recrystallized from chloroform/hexane mixture (1:1) on keeping at room temperature for a week, whereas complex **5** was recrystallized from toluene/diethyl ether (10:1) on keeping at room temperature for 10 min. The source of the chloro ligand in complex **4** is, presumably, the chlorinated solvent chloroform or dichloromethane, as these solvents are reported to be cleaved by palladium(0) complexes [35]. Also slow dissociative processes of palladium(II) complexes have been observed in $CDCl_3$ [36]. Such types of dissociative processes of palladium complexes in solution have been observed earlier [23–25,37]. In view of this observation, we thought of synthesizing complex **4** by a different route. The oxidative addition of 2-(4,4-dimethyl-2-oxazolinyl)phenylselenenyl chloride (**6**) [38] to tetrakis(triphenylphosphine) palladium(0) in toluene at room temperature provided complex **4**. Complexes **9** and **10** were synthesized analogously by the oxidative addition of 2-(4,4-dimethyl-2-oxazolinyl)phenylselenenyl bromide (**7**) [38] and iodide (**8**) [38], respectively to the palladium(0) precursor. Similarly the oxidative addition of 2-(*N*,*N*-dimethylaminomethyl)phenylselenenyl bromide (**11**) [39] and iodide (**12**) [39] to $Pd(PPh_3)_4$ provided mononuclear palladium selenolate complexes **13** and **14** respectively (Scheme 3). However, the reaction of **19a** with $Pd(PPh_3)_4$ was unsuccessful. It is worth noting that for complexes **4**, **5**, **9**, **10**, **13** and **14**, only one stereoisomer was isolated as the major product. This is presumably predominantly a steric effect imposed by the relatively large PPh_3 ligand, rather than an electronic one. Complexes were soluble in most of the common organic solvents except diethyl ether and nonpolar solvents like hexane and pentane. To purify the complexes from



Scheme 2. Synthesis of mononuclear palladium selenolate complexes **4** and **5**.