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Structural and spectroscopic trends in mononuclear arylchalcogenolato-palladium(II) and -platinum(II) complexes: Crystal structures of [M(TeAr)$_2$(dppe)] {M = palladium, platinum; Ar = phenyl, 2-thienyl; dppe = 1,2-bis(diphenylphosphino)ethane}

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Abstract

A series of mononuclear [M(EAr)$_2$(dppe)] [M = Pd, Pt; E = Se, Te; Ar = phenyl, 2-thienyl; dppe = 1,2-bis(diphenylphosphino)ethane] complexes has been prepared in good yields by the reactions of [MCl$_2$(dppe)] and corresponding ArE$^-$ with a special emphasis on the aryltellurolatopalladium and -platinum complexes for which the existing structural information is virtually non-existent. The complexes have crystallized in five isomorphic groups: (1) [Pd(SePh)$_2$(dppe)] and [Pt(SePh)$_2$(dppe)], (2) [Pd(TePh)$_2$(dppe)] and [Pt(TePh)$_2$(dppe)], (3) [Pd(SeTh)$_2$(dppe)], (4) [Pt(SeTh)$_2$(dppe)] and [Pd(TeTh)$_2$(dppe)], and (5) [Pt(TePh)$_2$(dppe)]. In addition, solvated [Pd(TePh)$_2$(dppe)] · CH$_3$OH and [Pd(TeTh)$_2$(dppe)] · 1/2CH$_2$Cl$_2$ could be isolated and structurally characterized. The metal atom in each complex exhibits an approximate square-planar coordination. The Pd–Se, Pt–Se, Pd–Te, and Pt–Te bonds span a range of 2.4350(7)–2.4828(7) Å, 2.442(1)–2.511(1) Å, 2.5871(7)–2.6704(8) Å, and 2.6053(6)–2.6594(9) Å, respectively, and the respective Pd–P and Pt–P bond distances are 2.265(2)–2.295(2) Å and 2.247(2)–2.270(2) Å. The orientation of the arylchalcogenolato ligands with respect to the M(E$_2$)(P$_2$) plane has been found to depend on the E–M–E bond angle. The NMR spectroscopic information indicates the formation of only *cis*-[M(EAr)$_2$(dppe)] complexes in solution. The trends in the ^{31}P, ^{77}Se, ^{125}Te, and ^{195}Pt chemical shifts expectedly depend on the nature of metal, chalcogen, and aryl group. Each trend can be considered independently of other factors. The ^{77}Se or ^{125}Te resonances appear as second-order multiplets in case of palladium and platinum complexes, respectively. Spectral simulation has yielded all relevant coupling constants.

Keywords: Organotellurium ligands; Organoselenium ligands; Palladium complexes; Platinum complexes; X-ray crystallography; NMR spectroscopy

1. Introduction

The role of chalcogenolato complexes of palladium and platinum in the Pd(0) and Pt(0) catalyzed reactions of Ar$_2$S$_2$ and Ar$_2$Se$_2$ with alkynes has recently been discussed [1–6]. In case of the Pd(0) catalyst, the S–S or Se–Se bond addition to alkynes involves a dinuclear palladium intermediate [Pd$_2$(EAr)$_4$L$_2$] (E = S, Se; L = phosphine or a related ligand) [1–6]. Such complexes have been isolated after the oxidative addition of Ar$_2$E$_2$ to [PdL$_4$] or substitution reaction of the chloride ligands in [PdCl$_2$L$_2$] by ArE$^-$ [7–10]. The reaction utilizing the Pt(0) catalyst seems to proceed with a different mechanism, since platinum does not show as good propensity for the formation of polynuclear complexes as palladium [2]. It has been suggested that

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mononuclear *cis*-[Pt(EAr)$_2$L$_2$] complexes are catalytically active, but the catalyst degrades with time because of the formation of the *trans*-isomer [2].

We have recently investigated the ligand substitution reactions of different arylselenolates with *trans*-[PdCl$_2$(PPh$_3$)$_2$] and *cis*-[PtCl$_2$(PPh$_3$)$_2$]. Whereas the reactions involving palladium afforded solely dinuclear [Pd$_2$(SeAr)$_4$(PPh$_3$)$_2$] [11–13], those involving *cis*-[PtCl$_2$(PPh$_3$)$_2$] initially produced *cis*-[Pt(SeAr)$_2$(PPh$_3$)$_2$] that subsequently underwent facile isomerization from *cis* to *trans* form in solution [14,15]. The DFT calculations of model [Pt(SeAr)$_2$(PH$_3$)$_2$] (Ar = Ph, 2-thienyl, 2-furyl) isomers indicated that the *cis*-isomers indeed lie at higher energy than the *trans*-isomers [15] providing a rationale for the *cis–trans* interconversion.

Similar product distributions and equally facile isomerization have been observed in the reactions of [Pd(PPh$_3$)$_4$] and [Pt(PPh$_3$)$_4$] with Ar$_2$Se$_2$ [2,7,16]. It has also been reported that the oxidative addition of Ar$_2$Te$_2$ to [Pd(PPh$_3$)$_2$] affords a dinuclear complex [17,18], though the reaction has also been shown to produce hexanuclear complexes [16].

Interestingly, the *cis–trans* isomerization of mononuclear selenolato complexes seems to be dependent on the electron-withdrawing power of the organic substituent bonded to selenium, since the related *cis*-[Pt(SeR)$_2$(PPh$_3$)$_2$] (R = ^{n}Bu, ^{t}Bu) do not seem to undergo isomerization [19], though the DFT calculations of model [Pt(SeR)$_2$(PH$_3$)$_2$] isomers indicate that the *cis*-isomers lie at higher relative energy than the *trans*-isomers even in the alkylselenolato complexes [15]. Evidently, the solvent also plays a role. Isomerization of *cis*-[Pt(SeCF$_3$)$_2$(PPh$_3$)$_2$] with electronegative trifluoromethylselenolato ligands to the *trans*-form takes place rapidly in dichloromethane, but the process in acetonitrile is much slower [20]. While the investigations of the analogous tellurolato complexes are sparse [20,21], it has been reported that, contrary to the analogous selenolato complex, there was no evidence of the isomerization of *cis*-[Pt(TeCF$_3$)$_2$(PPh$_3$)$_2$] to the *trans* form [20].

The formation of dinuclear palladium complexes is avoided by using a chelating phosphine ligand [22–25] and it also forces the formation of only the *cis*-isomer. It has been reported that [M(SAr)$_2$(dppe)] and [M(SeAr)$_2$(dppe)] [M = Pd, Pt; Ar = Ph; dppe = 1,2-bis(diphenylphosphino)ethane] are virtually catalytically inactive for the addition of Ar$_2$E$_2$ to alkynes [2], but it is an open question, whether the replacement of sulfur or selenium by tellurium would lead to improved catalytic properties of the complexes.

In order to further explore the chemistry of chalcogenolato complexes of palladium and platinum, we report here a study of the synthesis, NMR spectroscopic properties, and crystal structures of a series of [M(EAr)$_2$(dppe)] (M = Pd, Pt; E = Se, Te; Ar = Ph, 2-thienyl). While the preparations of [M(EPh)$_2$(dppe)] (M = Pd, Pt; E = Se, Te) have been reported previously {E = Se [22–24], Te [22]} the only crystal structure of the series determined to date is that of [Pd(SePh)$_2$(dppe)] · C$_6$H$_6$ [24].

2. Experimental

2.1. General

All reactions and manipulations of air- and moisture-sensitive reagents were carried out under an inert atmosphere by using a standard glovebox or Schlenk techniques. [PdCl$_2$(dppe)] (Aldrich), Ph$_2$Se$_2$ (Aldrich), Ph$_2$Te$_2$ (Aldrich), *n*-butyl lithium (2.5 M in hexanes, Aldrich), tellurium (Aldrich), and selenium (Merck) were used as supplied. [PtCl$_2$(dppe)] was prepared by the method of Appleton et al. [26]. Thiophene (Aldrich) was purified by distillation and purged with argon before use. Methanol was dried on molecular sieves and degassed with argon. Toluene and *n*-hexane were dried by distillation over Na/benzophenone and CH$_2$Cl$_2$ was dried over P$_4$O$_{10}$ under an argon atmosphere prior to use.

2.2. Synthesis of [M(EAr)$_2$(dppe)] (**1**)–(**8**)

2.2.1. [Pd(SePh)$_2$(dppe)] (**1**)

0.089 g (0.285 mmol) of Ph$_2$Se$_2$ in 5 ml of methanol was treated with NaBH$_4$ until the solution became transparent. The resulting solution was added to a suspension of 0.149 g (0.260 mmol) of [PdCl$_2$(dppe)] in 10 ml toluene. The reaction mixture was stirred overnight at room temperature. Volatile materials were removed under dynamic vacuum. The red solid residue was dissolved in dichloromethane (10 ml), filtered, and concentrated by partial evaporation of the solvent. [Pd(SePh)$_2$(dppe)] was precipitated by adding *n*-hexane into the solution. The orange solid product was filtered off, washed with hexane and dried. Isolated yield 0.131 g (62%). Anal. Calc. for C$_{38}$H$_{34}$P$_2$Se$_2$Pd: C, 55.86; H, 4.20. Found: C, 54.65; H, 4.30%.

Complexes **2**–**4** were prepared in a similar fashion to **1**.

2.2.2. [Pt(SePh)$_2$(dppe)] (**2**)

0.172 g (0.260 mmol) of [PtCl$_2$(dppe)] and 0.089 g (0.285 mmol) of Ph$_2$Se$_2$. Yield 0.130 g (55%). Yellow solid. Anal. Calc. for C$_{38}$H$_{34}$P$_2$Se$_2$Pt: C, 50.39; H, 3.78. Found: C, 50.11; H, 3.64%.

2.2.3. [Pd(TePh)$_2$(dppe)] (**3**)

0.251 g (0.436 mmol) [PdCl$_2$(dppe)] and 0.200 g (0.489 mmol) Ph$_2$Te$_2$. Yield 0.249 g (63%). Reddish brown solid. Anal. Calc. for C$_{38}$H$_{34}$P$_2$Te$_2$Pd: C, 49.92; H, 3.75. Found: C, 49.08; H 3.63%.

2.2.4. [Pt(TePh)$_2$(dppe)] (**4**)

0.131 g (0.197 mmol) [PtCl$_2$(dppe)] and 0.089 g (0.217 mmol) Ph$_2$Te$_2$. Stirred for 2 h. Yield 0.084 g (42%).