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# Short Communication

## Platinum and palladium complexes of the type $[M(EPh)_2(dppe)]$ ($E=O$, S, Se)

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### Abstract

The syntheses of platinum and palladium dppe (dppe = 1,2-bis(diphenylphosphino)ethane) complexes containing anionic Group 16 ligands are reported. $[Pt(OPh)_2(dppe)]$ is prepared by reaction of the chloro complex with NaOPh, but the palladium analogue is too unstable to be isolated. Complexes of the form $[M(SPh)_2(dppe)]$ (M = Pd, Pt) are obtained from $[MCl_2(dppe)]$ and PhSH in the presence of tributylamine, whereas $[M(SePh)_2(dppe)]$ species are formed by oxidative addition of $Ph_2Se_2$ to $[M(C_2H_4)(dppe)]$, generated *in situ*. Bond cleavage in $[Pt(OPh)_2(dppe)]$ occurs much more readily than in its sulfur and selenium analogues.

### Introduction

In the course of our work on photolysis reactions of the platinum oxalate complex $[Pt(C_2O_4)(dppe)]$ [1] we had occasion to carry out the photolysis of this complex in the presence of phenol. This reaction was complicated but, in order to attempt to identify the products of this reaction, we prepared $[Pt(OPh)_2(dppe)]$ and investigated its chemistry. This led us to consider the corresponding thio and seleno compounds, as well as their palladium analogues.

The phenoxo complexes $[M(OPh)_2(PPh_3)_2]$ (M = Pd, Pt) have reportedly been prepared by reaction of $[M(PPh_3)_4]$ with phenol [2], and monophenoxo complexes of palladium [3, 4] and platinum [4, 5] have also been prepared. Benzenethio complexes of the type $[M(SPh)_2L_2]$ (M = Pd, Pt) have been prepared by cleavage of the polymeric species $[M(SPh)_2]_n$ with phosphine or diphosphine ligands [6], or by treating $[MCl_2L_2]$ with $SiMe_3(SPh)$ [7], NaSPh [8], or PhSH in the presence of $Et_3N$ [9]. The molecular structure of $[Pd(SPh)_2(dppe)]$ has been reported [8]. When the cyclohexyne complex $[Pt(C_6H_8)(dppp)]$ (dppp = 1,3-bis(diphenylphosphino)propane) was treated with benzenethiol a mixture of $[Pt(SPh)_2(dppp)]$ and $[Pt(C_6H_9)(SPh)(dppp)]$ was obtained, whereas the dppb (dppb = 1,4-bis(diphenylphosphino)butane) analogue gave $[Pt(C_6H_9)(SPh)(dppb)]$ only [10]. Benzeneseleno complexes have also been prepared from $[Pd(SePh)_2]_n$ and $PPh_3$ [11], or by treatment of $[MCl_2L_2]$ (M = Pd, Pt) with NaSePh [11, 12]. Addition of excess PhSeH to $[Pt(PPh_3)_4]$ or $[Pt(PMePh_2)_4]$ has been reported to produce $[Pt(SePh)_2(PPh_3)_2]$ or $[Pt(SePh)_2(PMePh_2)_2]$ [13], whereas addition of diphenyldiselenide to $[Pt(C_2H_4)(PPh_3)_2]$, or to $[PtCl_2(dppp)]$ in the presence of $NaBH_4$, also gave products of the form $[Pt(SePh)_2L_2]$ [14].

In this work we have concentrated on compounds containing dppe ligands. The preparation of $[Pt(OMe)_2(dppe)]$ has been reported previously, and this complex reacts with CO by insertion into the Pt–O bonds [15], but $[Pt(OPh)_2(dppe)]$ is a new compound, which exhibits quite different reactivity. The complexes $[M(EPh)_2(dppe)]$ (M = Pd, Pt; E = S, Se) have been prepared previously, but here we report alternative methods for their preparation, as well as a brief study of their reactivity.

### Experimental

$^{31}P\{^1H\}$ NMR spectra were recorded for $CDCl_3$ solutions on a Varian XL-300 spectrometer and referenced to external $H_3PO_4$. Microanalyses were performed by Atlantic Microlabs, Inc., Norcross, GA.

#### *Preparation of $[Pt(OPh)_2(dppe)]$*

A methanol solution (5 ml) of NaOPh (0.11 g, 0.92 mmol) (prepared from phenol and NaOH in aqueous methanol solution) was added to a stirred slurry of $[PtCl_2(dppe)]$ (0.20 g, 0.30 mmol) in benzene (10 ml) under an argon atmosphere. After stirring overnight the mixture was evaporated to dryness. The residue was stirred vigorously with THF (40 ml). The resulting solution was filtered and evaporated to dryness, leaving the product as a white solid which was dried *in vacuo* (0.17 g, 72%). *Anal.* Found: C, 57.97; H, 4.61. Calc. for $C_{38}H_{34}O_2P_2Pt$: C, 58.53; H, 4.40%. $^{31}P\{^1H\}$ NMR: $\delta P$ 28.5, $^1J(Pt, P)$ 3595 Hz.

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### *Preparation of [Pt(SPh)$_2$(dppe)]*

[PtCl$_2$(dppe)] (0.66 g, 1.0 mmol) was suspended in CH$_2$Cl$_2$ (50 ml) and PhSH (1.0 ml) and *n*-Bu$_3$N (2.0 ml) were added. The solids dissolved immediately to give a yellow solution. After stirring for 2 h the solution was concentrated and ethanol was added. The resulting precipitate was washed with water then dried *in vacuo* to give the product as a yellow powder (0.70 g, 86%). *Anal.* Found: C, 56.26; H, 4.15. Calc. for $C_{38}H_{34}P_2PtS_2$: C, 56.22; H, 4.22%. $^{31}P\{^1H\}$ NMR: $\delta P$ 46.2, $^1J(Pt, P)$ 2877 Hz.

### *Preparation of [Pd(SPh)$_2$(dppe)]*

PhSH (0.6 ml) and *n*-Bu$_3$N (1.0 ml) were introduced to a CH$_2$Cl$_2$ suspension (50 ml) of [PdCl$_2$(dppe)] (0.57 g, 1.0 mmol), and a clear red solution was formed immediately. After 1 h the solution was reduced in volume and ethanol was added to produce a golden-yellow solid. This was dissolved in benzene and poured on to an alumina column, eluting with benzene then dichloromethane. The CH$_2$Cl$_2$ fraction was evaporated and the residue was washed with pentane then dried *in vacuo*, giving the product as an orange–red powder (0.32 g, 45%). *Anal.* Found: C, 62.97; H, 4.78. Calc. for $C_{38}H_{34}P_2PdS_2$: C, 63.11; H, 4.74%. $^{31}P\{^1H\}$ NMR: $\delta P$ 55.0.

### *Preparation of [Pt(SePh)$_2$(dppe)]*

Ethylene was bubbled through a THF suspension (50 ml) of [PtCl$_2$(dppe)] (0.80 g, 1.20 mmol), then a green THF solution of NaC$_{10}$H$_8$ (18 ml, 0.15 M) (prepared from sodium metal and naphthalene) was added over a 30 min period. The mixture was stirred for 1 h, then Ph$_2$Se$_2$ (0.37 g, 1.20 mmol) was added. After a further 1 h the solvent was evaporated and the sticky residue was dissolved in benzene. The benzene was passed down a 15 cm alumina column, eluting with more benzene. The resulting solution was evaporated and the residue was washed with pentane, leaving the product as an orange powder (0.61 g, 56%). *Anal.* Found: C, 50.53; H, 3.73. Calc. for $C_{38}H_{34}P_2PtSe_2$: C, 50.40; H, 3.78%. $^{31}P\{^1H\}$ NMR: $\delta P$ 46.9, $^1J(Pt, P)$ 2947 Hz.

### *Preparation of [Pd(SePh)$_2$(dppe)]*

Ethylene was passed through a THF suspension of [PdCl$_2$(dppe)] (0.58 g, 1.0 mmol) and a THF solution of NaC$_{10}$H$_8$ (15 ml, 0.14 M) was introduced over 30 min. A dark solution was obtained and Ph$_2$Se$_2$ (0.31 g, 1.0 mmol) was added. After a further 1 h the solvent was evaporated, and the residue was washed with pentane, water, ethanol and finally pentane. The resulting solid was dissolved in benzene and poured on to an alumina column, eluting with more benzene. Some dark material remained on the column, and the benzene solution was poured on to a second column and eluted with dichloromethane. The CH$_2$Cl$_2$ solution was evaporated and the residue was washed with pentane, giving the product as a reddish powder (0.33 g, 40%). *Anal.* Found: C, 56.44; H, 4.40. Calc. for $C_{38}H_{34}P_2PdSe_2$: C, 55.87; H, 4.20%. $^{31}P\{^1H\}$ NMR: $\delta P$ 55.0.

## Results and discussion

Treatment of a benzene suspension of [PtCl$_2$(dppe)] with excess sodium phenoxide (eqn. (1)) in methanol under an inert atmosphere yields, after workup,

$$[PtCl_2(dppe)] + 2NaOPh \longrightarrow [Pt(OPh)_2(dppe)] + 2NaCl \quad (1)$$

[Pt(OPh)$_2$(dppe)] as a white solid. The compound is stable in the solid state, and is characterized in solution by a single $^{31}P$ NMR resonance at 28.5 ppm with a one-bond Pt–P coupling constant of 3595 Hz. The latter indicates that the phenoxide ligand exerts a NMR *trans*-influence similar to that of chloride. Addition of NaOPh to a suspension of [PdCl$_2$(dppe)] results in an immediate color change from yellow to dark red–brown, and subsequent decomposition. The palladium phenoxide complex, if formed, appears to be less stable than its platinum analogue, and we have been unable to isolate it.

When carbon monoxide is bubbled through a benzene suspension of [Pt(OPh)$_2$(dppe)] the major product is the platinum(0) species [Pt(CO)$_2$(dppe)]. (The latter is also formed when a solution of [Pt(C$_2$O$_4$)(dppe)] is photolyzed in the presence of CO [1].) The fate of the phenoxide ligands is uncertain. When [Pt(OPh)$_2$(dppe)] is treated with $^{13}CO$ the dicarbonyl species is observed as a triplet in the $^{31}P\{^1H\}$ NMR spectrum, but efforts to identify the organic product(s) by $^{13}C\{^1H\}$ NMR spectroscopy have been unsuccessful. When the carbonylation reaction is performed in benzonitrile solution the dicarbonyl complex is again the major product, but in CDCl$_3$ both [Pt(CO)$_2$(dppe)] and [PtCl$_2$(dppe)] are obtained, the latter being the predominant product after longer reaction times.

The platinum and palladium complexes [M(SPh)$_2$(dppe)] may be prepared by reaction of the corresponding chloro complex with benzenethiol in the presence of tributylamine (eqn. (2)). In the platinum

$$[MCl_2(dppe)] + 2PhSH + 2n\text{-}Bu_3N \longrightarrow [M(SPh)_2(dppe)] + 2n\text{-}Bu_3NH^+Cl^- \quad (2)$$

M = Pd, Pt

case washing with water to remove tributylammonium chloride left the product as a yellow powder in good yield. With palladium the solution turns red, suggesting the formation of cluster species, and the monomeric complex is isolated by chromatographic separation as an orange–red powder in moderate yield. Each complex exhibits a single resonance in its $^{31}P\{^1H\}$ NMR spectrum, deshielded relative to $[Pt(OPh)_2(dppe)]$, and the $^1J$(Pt, P) value of 2877 Hz in the platinum case indicates that the NMR *trans*-influence of the thiolate ligand exceeds that of phenoxide.

In contrast to the phenoxide complex, and in keeping with stronger M–SPh bonds, neither complex reacts with carbon monoxide (1 atm, 25 °C). Although $Ph_2S_2$ is a stable compound, reductive elimination of the two SPh groups does not occur, addition of 1 mol equiv. of dppp also having no effect on either complex. Treatment with HCl, generated from acetyl chloride and methanol, converts each complex back to the corresponding chloride (eqn. (3)).

$$[M(SPh)_2(dppe)] + 2HCl \longrightarrow [MCl_2(dppe)] + 2PhSH \quad (3)$$

M = Pd, Pt

The benzeneseleno compounds $[M(SePh)_2(dppe)]$ may be generated via the intermediacy of the metal(0) ethylene species. $[Pt(C_2H_4)(dppe)]$ is known [16] and we have extended the synthetic method to the palladium analogue, although we have used the ethylene species *in situ*. Thus, $[PtCl_2(dppe)]$ is reduced by sodium naphthalenide in THF solution in the presence of ethylene to generate $[Pt(C_2H_4)(dppe)]$, to which is added 1 mol equiv. of $Ph_2Se_2$. The latter adds oxidatively to platinum to produce $[Pt(SePh)_2(dppe)]$ (eqn. (4)) which, after chromatographic purification, is obtained as an orange solid in moderate yield.

$$[PtCl_2(dppe)] \xrightarrow[-2NaCl]{\substack{2NaC_{10}H_8 \\ C_2H_4}} [Pt(C_2H_4)(dppe)] \xrightarrow[-C_2H_4]{Ph_2Se_2} [Pt(SePh)_2(dppe)] \quad (4)$$

The palladium complex is obtained similarly, but again the reaction is complicated by formation of dark red materials which we believe to be clusters. Following repeated chromatographic purification, however, $[Pd(SePh)_2(dppe)]$ is obtained as a reddish powder in reasonable yield. Each complex exhibits a single $^{31}P$ resonance, and the Pt–P coupling constant points to the SePh group having a marginally lower NMR *trans*-influence than SPh.

Neither complex reacts with carbon monoxide and the platinum complex does not react with dppp. $[Pt(SePh)_2(dppe)]$ cleanly produces $[PtCl_2(dppe)]$, however, when treated with excess HCl.

In summary, the palladium and platinum complexes $[M(EPh)_2(dppe)]$ (E = S, Se), once formed, appear to be quite robust. In contrast, $[Pd(OPh)_2(dppe)]$ could not be isolated, and the Pt–O bonds are readily cleaved in $[Pt(OPh)_2(dppe)]$.

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