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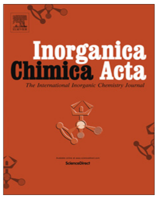

Research paper

Coordination properties of a 2-aryl-1,3,2-dioxaphospholane

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Dedicated to the memory of our friend and colleague, the late Professor K. Wade, FRS.

ABSTRACT

The coordination properties of the 2-aryl-1,3,2-dioxaphospholane 2,6-$(CF_3)_2C_6H_3P(OCH_2)_2$ **1** (L) have been investigated, by reaction with elemental selenium in solution to form the phosphorus(V) oxidation product 2,6-$(CF_3)_2C_6H_3P(Se)(OCH_2)_2$ **2**, and with metal-containing precursors to form three new complexes *trans*-[PdCl(μ-Cl)(L)]$_2$ **3**, *cis*-[$PdMe_2L_2$] **4** and [AuCl(L)] **5**. All of the metal complexes have been characterised by single-crystal X-ray structure determination.

1. Introduction

Complexes containing chiral phosphonites have been shown to act as catalysts for asymmetric hydrogenation [1–7] and asymmetric hydroformylation reactions [8,9]. Two sterically hindered 1,3,2-dioxaphospolanes (cyclic phosphonites) **6** and **8** have been described in the literature; [10] their 1: 1 coordination compounds with AuCl **7** and **9** respectively were also synthesised, and characterised crystallographically [11]. These compounds are shown schematically in Fig. 1.

Attempts at preparing platinum(II), rhodium(I) and tungsten(0) derivatives of these ligands were unsuccessful, however, and no identifiable products were obtained [11]. We had synthesised the 2-aryl-1,3,2-dioxaphospholane, 2,6-$(CF_3)_2C_6H_3P(OCH_2)_2$ **1** (Fig. 2) as a potential precursor for a metaphosphate intermediate in a pyrolysis reaction [12]. In a recent paper we reported the crystal and molecular structures of this compound, together with the synthesis of some platinum(II) complexes containing this ligand [13]. These coordination compounds were also characterised crystallographically. Because of the electron-withdrawing CF_3 groups, **1** is expected to be a comparatively electron-poor donor. We have extended our investigation into its chemistry by reaction of the dioxaphospholane **1** with elemental selenium, where the magnitude of the $^1J_{Se-P}$ coupling constant in the product **2** (Fig. 2) provides useful information about its donor properties [14–21]. We have also synthesised two new palladium(II) complexes containing this ligand, a chloro-bridged dimeric complex **3** and a monomeric derivative **4**, as well as a gold(I) chloro-complex **5** (Fig. 2). These coordination compounds have all been characterised by single-crystal X-ray diffraction. The gold(I) complex parallels **7** and **9** reported by Schmutzler et al. for the dioxaphospholanes 2,4,6-^{t}Bu$_3C_6H_2P(O_2C_6H_4)$ **6** and 2,4,6-^{t}Bu$_3C_6H_2P(O_2C_6Cl_4)$ **8**, (Fig. 1) respectively [10,11], but no comparable palladium complexes of phospholanes have been described previously.

2. Results and Discussion

As only limited amounts of ligand **1** were available, a ^{31}P NMR solution-state investigation of its reactivity towards elemental selenium and selected metal-containing precursors was planned. Hence solutions were prepared in NMR tubes and deuterated solvents (Experimental section). Potential catalytic applications would be enhanced if **1** could be shown to coordinate to palladium, so reactions were attempted with the palladium(II) species [$PdCl_2(MeCN)_2$] and [$PdMe_2$(TMEDA)]. Also chosen was AuCl, which was expected to form a complex with **1** analogous to compounds **7** and **9** described by Schmutzler et al., [11] enabling useful comparisons to be made. Our aims were only partially realised in that both palladium reactions yielded solid products, and no solution spectra could be obtained, other than weak signals from unreacted starting material. The compounds were crystalline, however, and proved to be suitable for single-crystal X-ray diffraction. In the case of the AuCl reaction, a ^{31}P NMR solution-state spectrum was recorded before the product again separated in crystalline form, suitable for X-ray study. The reactions are considered in more detail below.

*2.1. Reaction of **1** with elemental selenium*

This reaction was carried out on a qualitative basis, purely to ascertain the $^1J_{Se-P}$ value, and no attempt was made to isolate the product **2**. Reaction of 2,6-$(CF_3)_2C_6H_3P(OCH_2)_2$ **1** with a large

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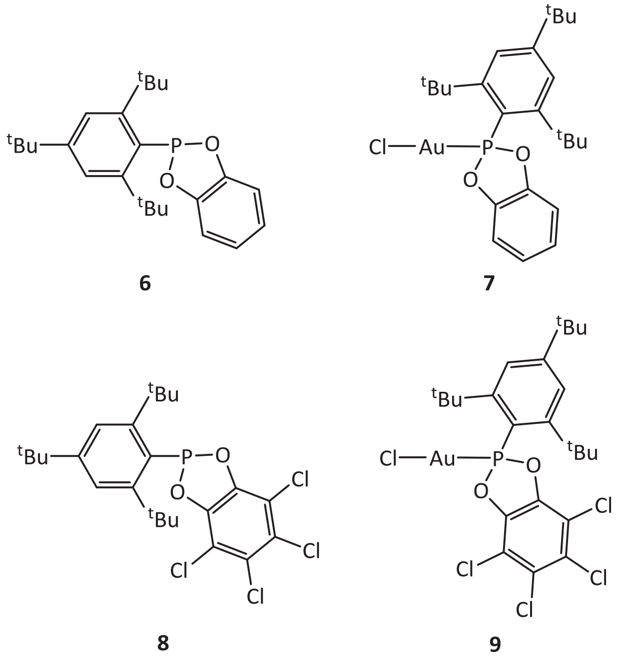


Fig. 1. Dioxaphospholanes and their AuCl complexes [10,11].

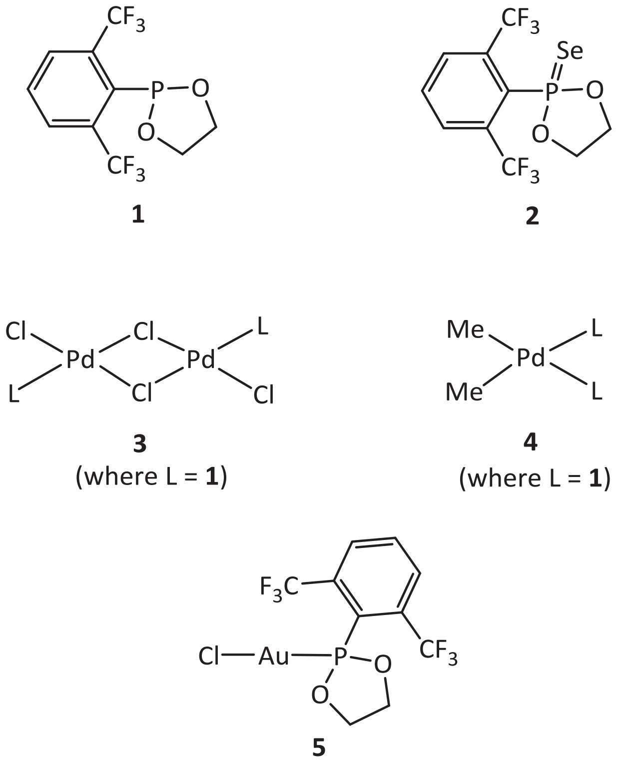
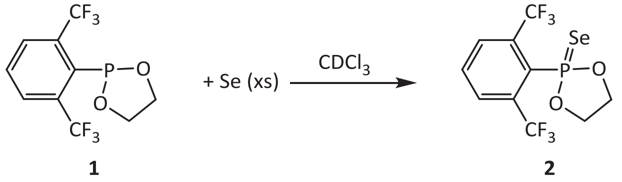


Fig. 2. Compounds in this work.



Scheme 1. Reaction of **1** with elemental selenium.

excess of grey selenium powder in $CDCl_3$ gave a single phosphorus-containing product **2**, (Scheme 1), with a ^{31}P NMR solution-state signal at 94.1 ppm (s with satellites, $^1J_{Se\text{-}P}$ 980 Hz). No $^4J_{P\text{-}F}$ coupling was resolved, unlike **1** which yielded a ^{31}P septet at 158.2 ppm, $^4J_{P\text{-}F}$ 35 Hz [13]. This observation parallels the behaviour in organo-chlorophosphanes and –chlorophosphoranes bearing aromatic groups with CF_3 substituents, where $^4J_{P\text{-}F}$ could be readily measured in the P(III) compounds, but not in their P(V) counterparts, formed by chlorination [22]. The shift to lower frequency from **1** to **2** is as expected for oxidation from P(III) to P(V), (a lower frequency shift of 64.1 ppm from **1** to **2**, compared with 79.2 ppm from $MeP(OMe)_2$ to $MeP(Se)(OMe)_2$, 61.5 ppm from $PhP(OMe)_2$ to $PhP(Se)(OMe)_2$ and 61.3 ppm from $PhP(OEt)_2$ to $PhP(Se)(OEt)_2$)) [23].

The magnitude of $^1J_{Se\text{-}P}$ is expected to reflect the donor ability of the P(III) starting material, with a larger coupling constant showing poorer donor ability [14–21]. Table 1 shows the ranges of values from the literature [14–21,24–34] for $^1J_{Se\text{-}P}$ in various structural types of compounds. In previously-studied examples of $R(R'O)_2PSe$, J values of 837 – 965 Hz were recorded. While the present value of 980 Hz is the highest yet reported for a compound of this structural type (Table 1), it is only marginally higher than that of 965 Hz for compound 4 in reference [34], which has a naphthyl substituent and no electronegative groups such as CF_3 attached. Hence **1** is not expected to be a strong donor. This Se-P coupling constant is significantly lower than in the selenium derivatives of some phosphites $(RO)_3P$, however (Table 1), with J values in the literature for $(PhO)_3PSe$ of 1027 [17] and 1086 [32] Hz. From the data these compounds may be regarded as even poorer donors than dioxaphospholane **1**.

2.2. Synthesis of metal complexes

The dimeric complex *trans*-$[PdCl(\mu\text{-}Cl)(L)]_2$ **3** was prepared by reaction between $[PdCl_2(MeCN)_2]$ and **1** in C_6D_6, (Scheme 2). The reaction mixture was heated to 50° C for 72 h, and crystals of **3** formed upon allowing it to stand. The only signal visible in the ^{31}P NMR solution-state spectrum was a weak resonance from the starting material **1**.

The complex *cis*-$[PdMe_2L_2]$ **4** was synthesised by adding **1** to a solution of $[PdMe_2(TMEDA)]$ in C_6D_6, (Scheme 3). Crystals formed in the NMR tube on standing. The ^{31}P NMR solution-state spectrum again showed a weak signal from compound **1** (δ 158.4 ppm, $^4J_{P\text{-}F}$ 34.5 Hz; lit [13]. δ 158.2 ppm, $^4J_{P\text{-}F}$ 35 Hz). The crystal and molecular structures of these complexes are considered in detail in the following section. It should be emphasised that our results from the palladium(II) reactions only identify the crystalline materials isolated as **3** and **4** respectively, and do not show that these are the sole reaction products, or indeed the major products. Nevertheless **3** and **4** clearly arise from coordination of ligand **1** to palladium(II) species derived from the precursor complexes in each case. Thus ligand **1** is undoubtedly capable of coordination to palladium(II).

The gold(I) complex [AuCl(L)] **5** was prepared by adding AuCl to a solution of **1** in $CDCl_3$ (Scheme 4), in an NMR tube. In this system, a ^{31}P NMR solution-state spectrum was successfully recorded before the onset of crystallisation. Complex **5** gave a septet spectrum, δ 154.5 ppm, $^4J_{P\text{-}F}$ 24 Hz., showing a shift to lower frequency compared with ligand **1** (δ 158.2 ppm, $^4J_{P\text{-}F}$ 35 Hz) [13]. Similar behaviour, though with larger shifts to lower frequency on complexation, has been observed for the AuCl complexes **7** and **9** of dioxaphospholanes in the literature [10,11] (**6** (L′) δ 188.7 ppm, **7** [AuCl(L′)] δ165.1 ppm; **8** (L″) δ 218.1 ppm, **9** [AuCl(L″)] δ 184.9 ppm). The shift on complexation is comparable to those observed in a series of *trans*-platinum(II) complexes of ligand **1**, with values