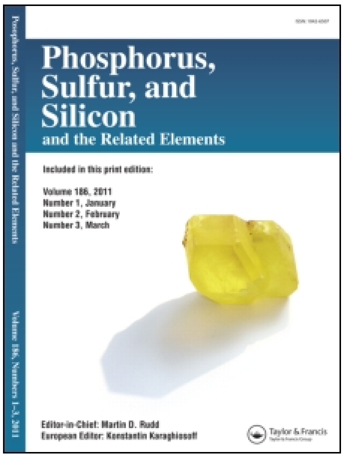

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NEW PALLADIUM(II) COMPLEXES OF $[Ph_2P(O)NP(E)Ph_2]^-$ (E = S OR Se)

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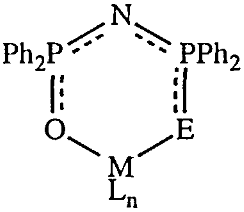
Abstract Several new palladium(II) complexes of $[Ph_2P(O)NP(E)Ph_2]^-$ (E = S or Se) have been prepared in which a variety of ligating modes (*O,E*-chelating, *E*-bridging and *E*-monodentate) are observed.

INTRODUCTION

Whereas the co-ordination chemistry of $[Ph_2P(E)NP(E)Ph_2]^-$ (E = O, S or Se) has flourished rapidly in recent years,[1] very few reports on the unsymmetrical ligands $[Ph_2P(O)NP(E)Ph_2]^-$ (E = S or Se) have been documented.[2,3] This class of ligand combines both 'hard' and 'soft' donor atoms and is reminiscent to the mixed P(V)/P(III) compound $Ph_2P(O)NHPPh_2$.[4] Since very few metal complexes of $[Ph_2P(O)N\text{-}P(E)Ph_2]^-$ (E = S or Se) are known we wished to explore the reactivity of these ligands and present here some preliminary work with Pd(II).[5] We recently reported a homoleptic palladium(II) complex *cis*-$[Pd\{Ph_2P(O)NP(Se)Ph_2\text{-}O,Se\}_2]$ in which the two Pd-O-P-N-P-Se six-membered rings adopt distinctly different conformations (X-ray evidence).[2]

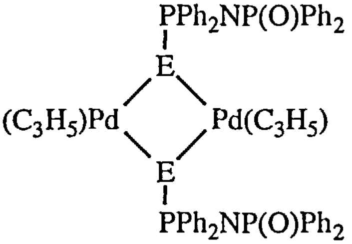
RESULTS AND DISCUSSION

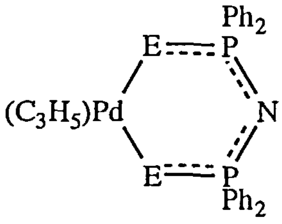
The potassium salts $K[Ph_2P(O)NP(E)Ph_2]$ (E = S **I**; E = Se **II**) were synthesised from $Ph_2P(O)NHPPh_2$, chalcogen and base according to a known procedure.[2] Reaction of **I** (or **II**) and either $[\{PdCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$, $[PdCl_2(dppp)]$ [dppp = 1,3-bis(diphenylphosphino)propane] or [$PdCl_2$(bipy)] (bipy = 2,2'-bipyridine) in a L:M ratio of 1:1 gave the palladacycles **1** - **6** respectively. The cationic complexes **3** - **6** were all isolated as their hexafluorophosphate salts. The X-ray structure of **2** confirms that the PMe_2Ph ligand is *trans* to O.



E = S, L_n = PMe_2Ph, Cl **1**; E = Se, L_n = PMe_2Ph, Cl **2**
E = S, L_n = dppp **3**; E = Se, L_n = dppp **4**
E = S, L_n = bipy **5**; E = Se, L_n = bipy **6**

In contrast reaction of **I** (or **II**) with [{Pd(μ-Cl)(C_3H_5)}$_2$] in thf gave the dimeric compounds [{Pd(C_3H_5){Ph_2P(E)NP(O)Ph_2-*E*}}$_2$] (E = S **7**; E = Se **8**). The X-ray structure of **8** (Figure 1) reveals a Pd_2Se_2 core and two non co-ordinated -P(O)Ph_2 moieties. However reaction of K[Ph_2P(E)NP(E)Ph_2] (E = S or Se) with [{Pd(μ-Cl)(C_3H_5)}$_2$] gave the monomeric complexes [Pd(C_3H_5){Ph_2P(E)NP(E)Ph_2-*E,E'*}] (E = S **9**; E = Se **10**). The difference in reactivity of these ligands towards [{Pd(μ-Cl)(C_3H_5)}$_2$] is not clear.





E = S **7**; E = Se **8**

E = S **9**; E = Se **10**

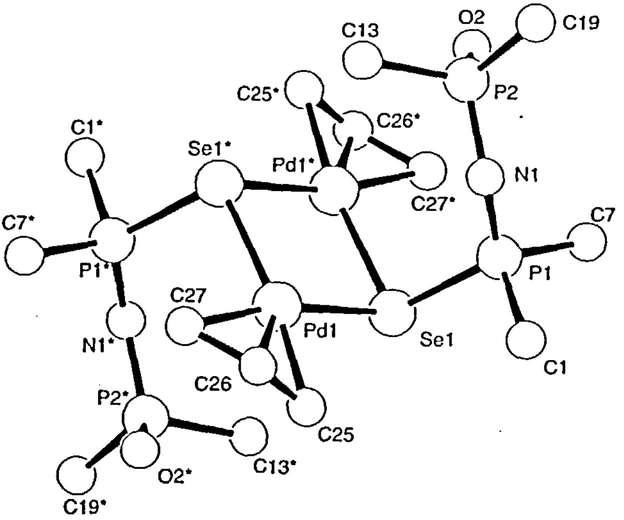
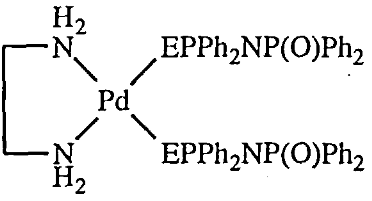
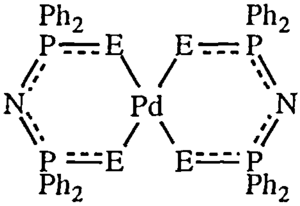


FIGURE 1 X-ray crystal structure of **8**

Metathesis of $[PdCl_2(en)]$ (en = ethane-1,2-diamine) with two equivalents of **I** (or **II**) in MeOH gave $[Pd\{Ph_2P(E)NP(O)Ph_2\text{-}E\}_2en]$ [E = S **11**; E = Se **12** (X-ray evidence)] whereas the *bis* chelate complexes $[Pd\{Ph_2P(E)NP(E)Ph_2\text{-}E,E'\}_2]$ (E = S **13**; E = Se **14**) were formed under similar conditions using $K[Ph_2P(E)NP(E)Ph_2]$ (E = S or Se).



E = S **11**; E = Se **12**



E = S **13**; E = Se **14**

Selected $^{31}P\{^{1}H\}$ NMR data ($CDCl_3$) for the potassium salt **II**, **2**, **8** and **12** are given in Table 1. In particular $^{1}J(PSe)$ for the palladium(II) complexes are reduced by *ca.* 150 Hz with respect to **II**.

Compound	II[2]	2	8	12
$\delta(P_O)$	12.9	30.7	26.7	15.6
$\delta(P_{Se})$ / $^{1}J(PSe)$	23.6 (664)	15.2 (484)	19.0 (520)	14.2 (515)

TABLE 1 $^{31}P\{^{1}H\}$ NMR data for **II**, **2**, **8** and **12**.

In conclusion we have shown that reaction of **I** (or **II**) with several Pd(II) starting materials affords a range of new complexes which have been characterised by the usual analytical / spectroscopic techniques. Full details of syntheses / characterisation will be reported elsewhere.

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