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Alexandra M. Z. Slawin; Martin B. Smith; J. Derek Woollins

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NEW PALLADIUM(II) COMPLEXES OF [Ph₂P(O)NP(E)Ph₂][−] (E = S OR Se)

ALEXANDRA M. Z. SLAWIN, MARTIN B. SMITH AND J. DEREK WOOLLINS*

Department of Chemistry, Loughborough University, Loughborough, Leics, UK, LE11 3TU

Abstract Several new palladium(II) complexes of [Ph₂P(O)NP(E)Ph₂][−] (E = S or Se) have been prepared in which a variety of ligating modes (*O,E*-chelating, *E*-bridging and *E*-monodentate) are observed.

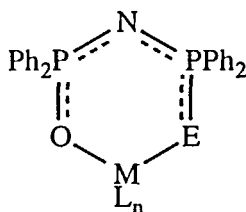
INTRODUCTION

Whereas the co-ordination chemistry of [Ph₂P(E)NP(E)Ph₂][−] (E = O, S or Se) has flourished rapidly in recent years,¹ very few reports on the unsymmetrical ligands [Ph₂P(O)NP(E)Ph₂][−] (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 Ph₂P(O)NHPPH₂.⁴ Since very few metal complexes of [Ph₂P(O)NP(E)Ph₂][−] (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{Ph₂P(O)NP(Se)Ph₂-*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[Ph₂P(O)NP(E)Ph₂] (E = S **I**; E = Se **II**) were synthesised from Ph₂P(O)NHPPH₂, chalcogen and base according to a known procedure.² Reaction of **I** (or **II**) and either [{PdCl(μ-Cl)-(PMe₂Ph)}₂], [PdCl₂(dppp)] [dppp = 1,3-bis(diphenylphosphino)pro-

pane] or $[\text{PdCl}_2(\text{bipy})]$ ($\text{bipy} = 2,2'$ -bipyridine) in a $\text{L}:\text{M}$ 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.

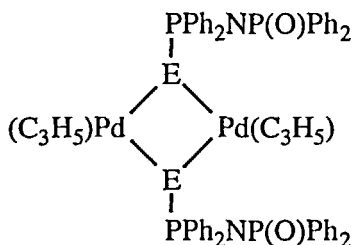


$\text{E} = \text{S}, \text{L}_n = \text{PMe}_2\text{Ph}$, **Cl 1**; $\text{E} = \text{Se}, \text{L}_n = \text{PMe}_2\text{Ph}$, **Cl 2**

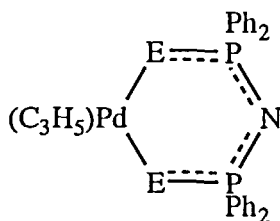
$\text{E} = \text{S}, \text{L}_n = \text{dppp}$ **3**; $\text{E} = \text{Se}, \text{L}_n = \text{dppp}$ **4**

$\text{E} = \text{S}, \text{L}_n = \text{bipy}$ **5**; $\text{E} = \text{Se}, \text{L}_n = \text{bipy}$ **6**

In contrast reaction of **I** (or **II**) with $[\{\text{Pd}(\mu\text{-Cl})(\text{C}_3\text{H}_5)\}_2]$ in thf gave the dimeric compounds $[\{\text{Pd}(\text{C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{O})\text{Ph}_2\text{-E}\}\}_2]$ ($\text{E} = \text{S}$ **7**; $\text{E} = \text{Se}$ **8**). The X-ray structure of **8** (Figure 1) reveals a Pd_2Se_2 core and two non co-ordinated $-\text{P}(\text{O})\text{Ph}_2$ moieties. However reaction of $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$ ($\text{E} = \text{S}$ or Se) with $[\{\text{Pd}(\mu\text{-Cl})(\text{C}_3\text{H}_5)\}_2]$ gave the monomeric complexes $[\text{Pd}(\text{C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-E,E'}\}]$ ($\text{E} = \text{S}$ **9**; $\text{E} = \text{Se}$ **10**). The difference in reactivity of these ligands towards $[\{\text{Pd}(\mu\text{-Cl})(\text{C}_3\text{H}_5)\}_2]$ is not clear.



$\text{E} = \text{S}$ **7**; $\text{E} = \text{Se}$ **8**



$\text{E} = \text{S}$ **9**; $\text{E} = \text{Se}$ **10**

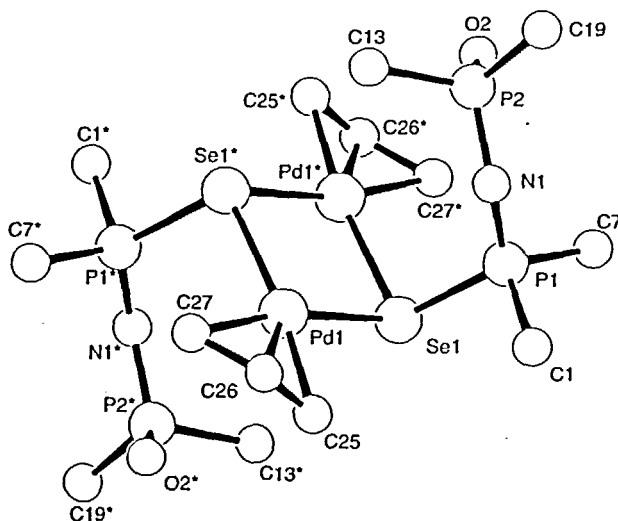
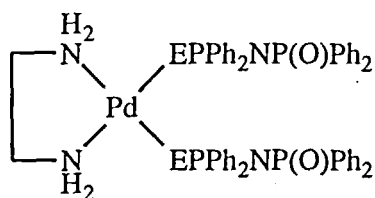
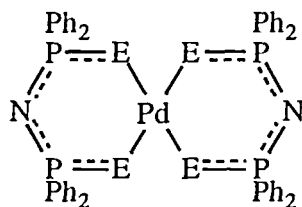


FIGURE 1 X-ray crystal structure of 8

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

 $\text{E} = \text{S}$ **11**; $\text{E} = \text{Se}$ **12** $\text{E} = \text{S}$ **13**; $\text{E} = \text{Se}$ **14**

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

Compound	II ²	2	8	12
$\delta(\text{P}_\text{O})$	12.9	30.7	26.7	15.6
$\delta(\text{P}_\text{Se}) / ^1J(\text{PSe})$	23.6 (664)	15.2 (484)	19.0 (520)	14.2 (515)

TABLE 1 $^{31}\text{P}\{^1\text{H}\}$ 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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REFERENCES

1. J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2893 (1996) and refs. therein.
2. A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 3659 (1996).
3. R. Rösler, J. E. Drake, C. Silvestru, J. Yang and I. Haiduc, *J. Chem. Soc., Dalton Trans.*, 391 (1996).
4. P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Inorg. Chem.*, **35**, 3675 (1996).
5. A. M. Z. Slawin, M. B. Smith and J. D. Woollins, manuscript in preparation.