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Phosphorus-Selenium Heterocycles

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PHOSPHORUS-SELENIUM HETEROCYCLES

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Abstract The preparation of $(PPh)_3Se_2$ (1) from reaction of Na_2Se with $PhPCl_2$ is described. We also report the syntheses and X-Ray crystal structures of $(PMe)_4Se_3$ (2), $Pt(Se_3PPh)(dppe)$ (3), $Na_2[PPh_2Se_2]_2 \cdot thf \cdot 5H_2O$ (4), $Pt(P(O)Ph_2)_2(SeP(OH)Ph_2)_2$ (5) and $[(Pt(dppe))_3S_2][Ph_2POS]_2$ (6).

INTRODUCTION

Although there is a wide range of phosphorus-sulphur heterocycles¹ much less work has been reported on phosphorus-selenium rings and cages. We have investigated the preparation of P-Se rings by a number of routes. Here, we report on an alternative route to $(PPh)_3Se_2$ (1). The synthesis and X-Ray crystal structure of the related ring system $(PMe)_4Se_3$ (2) is also described. The preparation of the platinum complexes $Pt(Se_3PPh)(dppe)$ (3) and $Pt(P(O)Ph_2)_2(SeP(OH)Ph_2)_2$ (5) from $PhP(Se)Se_2P(Se)Ph_2$ and $Ph_2P(Se)OH$ respectively, together with the X-Ray crystal structures of $Na_2[PPh_2Se_2]_2 \cdot thf \cdot 5H_2O$ (4), and $[(Pt(dppe))_3S_2][Ph_2POS]_2$ (6) are also reported.

RESULTS AND DISCUSSION

Reaction of $(PPh)_5$ with grey selenium gives rise to a variety of compounds, including $(PPh)_3Se_2$ (1), depending on the P:Se ratio and the conditions used^{2–4}. However, the reactions are performed at elevated temperatures limiting the product distribution to the thermodynamically preferred species. In efforts to extend the range of heterocycles we have investigated the use of Na_xSe_y with $PhPCl_2$. The sodium selenide was prepared by dissolving appropriate quantities of sodium and selenium in liquid ammonia and, after evaporation of the ammonia, was reacted with $PhPCl_2$ in *thf*. Surprisingly, this strategy was not especially successful

although we were able to obtain moderate yields of (1).

We have investigated⁵ the effect changing the relatively bulky electron-withdrawing phenyl rings in the preparation of (1) for smaller, electron-donating methyl groups. The reaction of selenium with (PMe)₅ in refluxing toluene was found, by ³¹P-{¹H} nmr, to give a complex mixture whatever the P:Se ratio of the reactants. Slow diffusion of hexane into final toluene solution gave crystals of (PMe)₄Se₃ (2) (Figure 1a) in each case. The X-Ray structure of (2) reveals a folded five-membered P₄Se ring with significant intermolecular non-bonded interactions between the exocyclic selenium atoms and the 'vacant' site of the P(III) atoms.

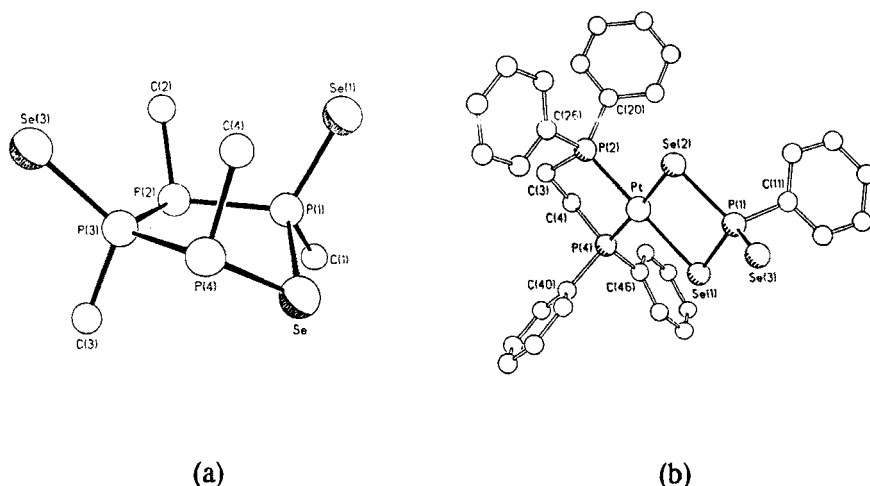
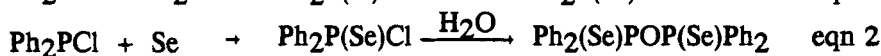
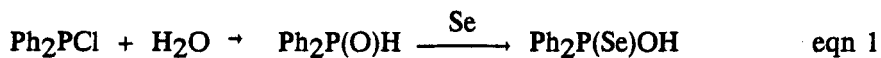


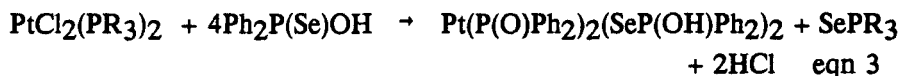
FIGURE 1 The X-Ray crystal structures of (a) (PMe)₄Se₃ (2) and (b) Pt(Se₃PPh)(dppe) (3).

We have previously reported^{6,7} on the reaction of Lawessons reagent with PtCl₂(PR₃)₂. The four-membered heterocycle Ph(Se)PSe₂P(Se)Ph behaves in a similar fashion⁸ with formation, in good yield, of Pt(Se₃PPh)(PR₃)₂. X-Ray studies on the dppe complex (3) reveal square planar coordination about platinum and a folded PtSe₂P ring (Figure 1b).

We have also investigated the synthesis of P-S and P-Se compounds containing the Ph₂P moiety. For example, it is quite straightforward to prepare Ph₂P(Se)OH and Ph₂(Se)POP(Se)Ph₂ (eqn 1 & 2). The sodium salt of Ph₂PSe₂⁻ has been isolated in compound (4) where there is an unusual polymeric structure made up of six-membered sodium-oxygen rings (Fig 2).



The reactions of $\text{Ph}_2\text{P(Se)OH}$ with $\text{PtCl}_2(\text{PR}_3)_2$ (for $\text{PR}_3 = \text{PEt}_3$, PMe_2Ph) proceeds smoothly in refluxing dichloromethane to give $\text{Pt}(\text{P(O)Ph}_2)_2(\text{SeP(OH)Ph}_2)_2$ (**5**) together with SePR_3 (eqn 3). The ^{31}P NMR



spectrum of (**5**) consists of two multiplets with platinum satellites and is surprisingly complex. Interestingly, the X-Ray crystal structure reveals a short $\text{O} \cdots \text{O}$ intramolecular contact between the oxygen atoms of the ligands. (Fig 3)

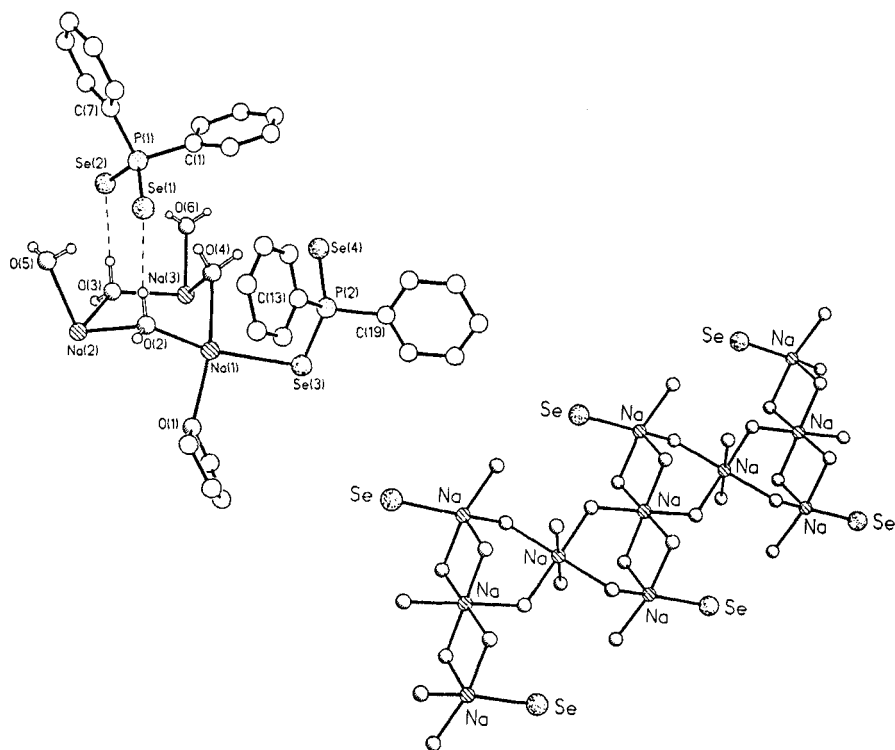


FIGURE 2 The X-Ray crystal structure of (**5**) showing the asymmetric unit and the sodium-oxygen framework.

In contrast to its selenium analogue when $\text{Ph}_2\text{P(S)OH}$ is refluxed in dichloromethane with $\text{PtCl}_2(\text{PR}_3)_2$ simple complexes are not formed, indeed the ^{31}P NMR of the reaction mixture reveals decomposition of both starting materials. However when $2\text{PR}_3 = \text{dppe}$ we have been able to isolate $[(\text{Pt}(\text{dppe}))_3\text{S}_2][\text{Ph}_2\text{POS}]_2$ (**6**) as a minor product (Fig 4).

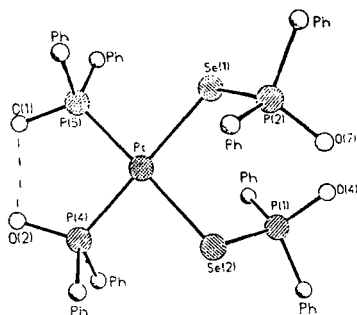


FIGURE 3 The X-Ray crystal structure of $\text{Pt}(\text{P}(\text{O})\text{Ph}_2)_2(\text{SeP}(\text{OH})\text{Ph}_2)_2$ (**5**)

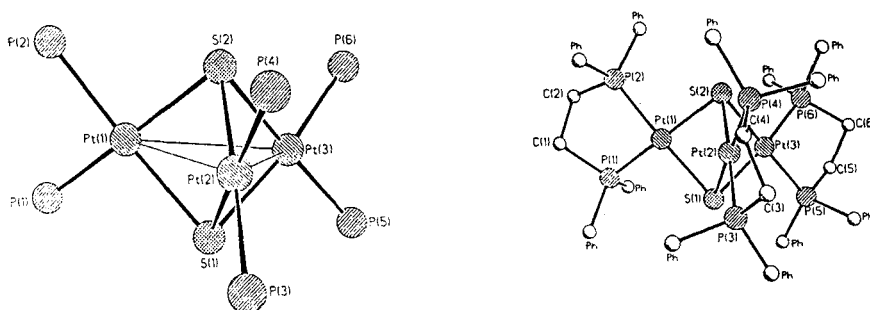


FIGURE 4 The X-Ray crystal structure of $[(\text{Pt}(\text{dppe}))_3\text{S}_2][\text{Ph}_2\text{POS}]_2$ (**6**)

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