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# SYNTHESIS AND CHARACTERISATION OF NEW METALLACYCLES CONTAINING $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$ (E = S OR Se) LIGANDS

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**Abstract** Reaction of  $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$  (E = S or Se) with a series of late transition-metal dimers, in thf or MeOH, leads to facile bridge cleavage and formation of new mononuclear compounds.

## INTRODUCTION

The monoanions  $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$  (E = O, S or Se) are excellent ligands for metal ion complexation.<sup>1</sup> One particularly attractive feature of  $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$  is their ready synthesis from commercially available  $(\text{Ph}_2\text{P})_2\text{NH}$  and the appropriate chalcogen followed by deprotonation with base (*e.g.*  $\text{KOBU}^t$ ). Several recent reports have described new complexes of  $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$  (E = S or Se) with Group VIII metals such as Rh(I), Pd(II) and Pt(II).<sup>2-4</sup> Here we present some new examples of six-membered  $\text{ME}_2\text{P}_2\text{N}$  (E = S or Se) metallacycles with Ru(II), Rh(III), Pd(II) and Pt(II).<sup>5</sup> In these complexes,  $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$  chelates to the metal centre in a bonding mode typical for this class of ligand.

## RESULTS AND DISCUSSION

The potassium salts  $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$  (E = S I; E = Se II) were synthesised according to known methods.<sup>3,6</sup> Previous work has shown that the chloro bridges in  $[\{\text{MCl}(\mu\text{-Cl})(\text{PMe}_2\text{Ph})\}_2]$  (M = Pd, Pt) or

$[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$  (cod = cycloocta-1,5-diene) are cleaved with **II** to give  $[\text{MCl}\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-Se,Se'}\}\text{PMe}_2\text{Ph}]$  or  $[\text{Rh}\{\text{Ph}_2\text{P}(\text{Se})\text{N-P}(\text{Se})\text{Ph}_2\text{-Se,Se'}\}\text{cod}]$  respectively.<sup>3</sup> In a similar manner the new neutral complexes **1** - **12** were prepared as depicted in Scheme 1. All compounds were isolated in good to excellent yields (64 - 97%), are air stable in the solid state and in solution and display the expected analytical and spectroscopic data. The  $^{31}\text{P}\{^1\text{H}\}$  NMR data ( $\text{CDCl}_3$ ) indicate single phosphorus containing species present in solution with  $\delta(\text{P})$  for the sulfur analogues *ca.* 10 ppm to higher frequency than their selenium analogues. Furthermore  $^1\text{J}(\text{PSe})$  (typically 500 - 600 Hz) is reduced in magnitude relative to the free ligand **II** [687 Hz,  $(\text{CD}_3)_2\text{SO}$ ].<sup>3</sup> The X-ray crystal structure of a representative example,  $[\text{Pd}(\text{C}_9\text{H}_{12}\text{N})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-Se,Se'}\}]$  **4**, is shown in Figure 1.

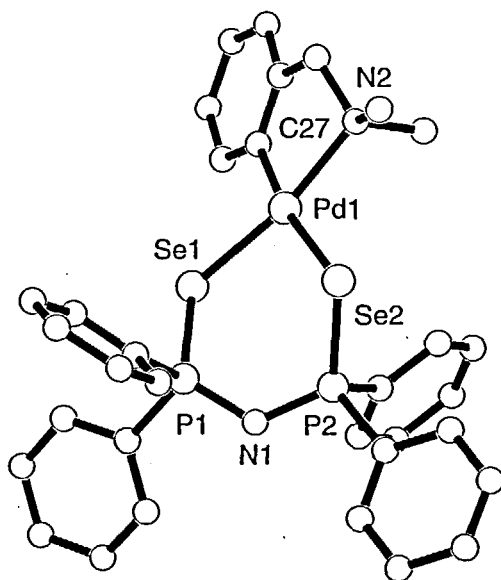
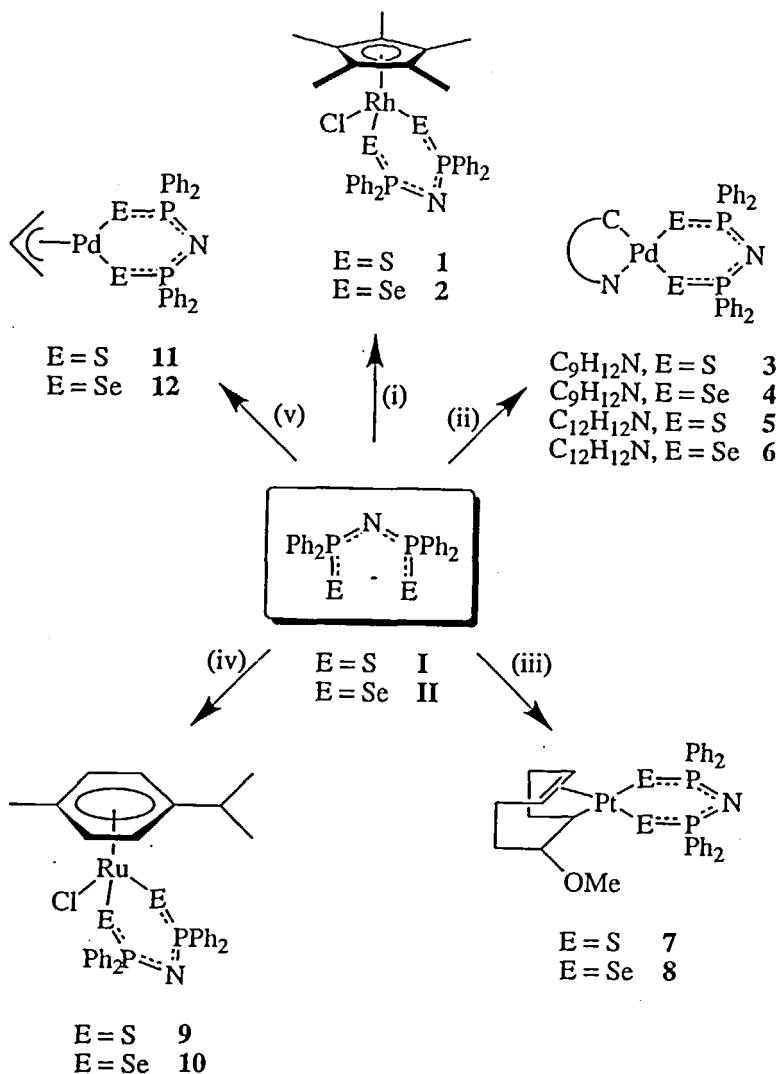


FIGURE 1 X-ray crystal structure of **4**



SCHEME 1 Synthetic routes to the complexes 1 - 12. (i)  $[\{\text{RhCl}(\mu\text{-Cl})(\text{C}_5\text{Me}_5)\}_2]$  (ii)  $[\{\text{Pd}(\mu\text{-Cl})(\text{C-N})\}_2]$  ( $\text{C-N} = \text{C}_9\text{H}_{12}\text{N}$ ,  $\text{C}_{12}\text{H}_{12}\text{N}$ ) (iii)  $[\{\text{Pt}(\mu\text{-OMe})(\text{C}_8\text{H}_{12}\text{OMe})\}_2]$  (iv)  $[\{\text{RuCl}(\mu\text{-Cl})(\text{C}_{10}\text{H}_{14})\}_2]$  (v)  $[\{\text{Pd}(\mu\text{-Cl})(\text{C}_3\text{H}_5)\}_2]$

In conclusion we have shown that reaction of I (or II) with several transition-metal reagents affords new M-E-P-N-P-E metallacycles (E = S or Se). The co-ordinated ligand adopts a familiar chelating mode of bonding. Full details of syntheses / characterisation will be reported elsewhere.

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