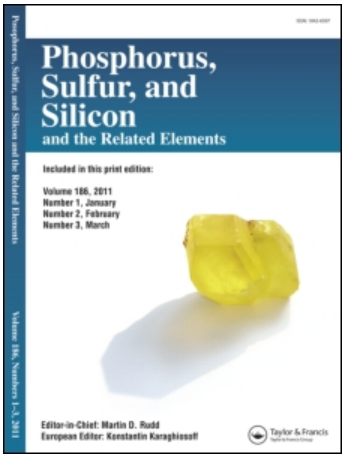

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SYNTHESIS AND CHARACTERISATION OF NEW METALLACYCLES CONTAINING $[Ph_2P(E)NP(E)Ph_2]^-$ (E = S OR Se) LIGANDS

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Abstract Reaction of $[Ph_2P(E)NP(E)Ph_2]^-$ (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 $[Ph_2P(E)NP(E)Ph_2]^-$ (E = O, S or Se) are excellent ligands for metal ion complexation.[1] One particularly attractive feature of $[Ph_2P(E)NP(E)Ph_2]^-$ is their ready synthesis from commercially available $(Ph_2P)_2NH$ and the appropriate chalcogen followed by deprotonation with base (*e.g.* $KOBu^t$). Several recent reports have described new complexes of $[Ph_2P(E)NP(E)Ph_2]^-$ (E = S or Se) with Group VIII metals such as Rh(I), Pd(II) and Pt(II).[2-4] Here we present some new examples of six-membered ME_2P_2N (E = S or Se) metallacycles with Ru(II), Rh(III), Pd(II) and Pt(II).[5] In these complexes, $[Ph_2P(E)NP(E)Ph_2]^-$ chelates to the metal centre in a bonding mode typical for this class of ligand.

RESULTS AND DISCUSSION

The potassium salts $K[Ph_2P(E)NP(E)Ph_2]$ (E = S **I**; E = Se **II**) were synthesised according to known methods.[3,6] Previous work has shown that the chloro bridges in $[\{MCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$ (M = Pd, Pt) or

[{Rh(μ-Cl)(cod)}$_2$] (cod = cycloocta-1,5-diene) are cleaved with **II** to give [MCl{Ph_2P(Se)NP(Se)Ph_2-*Se,Se'*}PMe_2Ph] or [Rh{Ph_2P(Se)N-P(Se)Ph_2-*Se,Se'*}cod] respectively.[3] 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 $^{31}P\{^1H\}$ NMR data ($CDCl_3$) indicate single phosphorus containing species present in solution with δ(P) for the sulfur analogues *ca.* 10 ppm to higher frequency than their selenium analogues. Furthermore ^1J(PSe) (typically 500 - 600 Hz) is reduced in magnitude relative to the free ligand **II** [687 Hz, $(CD_3)_2SO$].[3] The X-ray crystal structure of a representative example, [Pd($C_9H_{12}N$){Ph_2P-(Se)NP(Se)Ph_2-*Se,Se'*}] **4**, is shown in Figure 1.

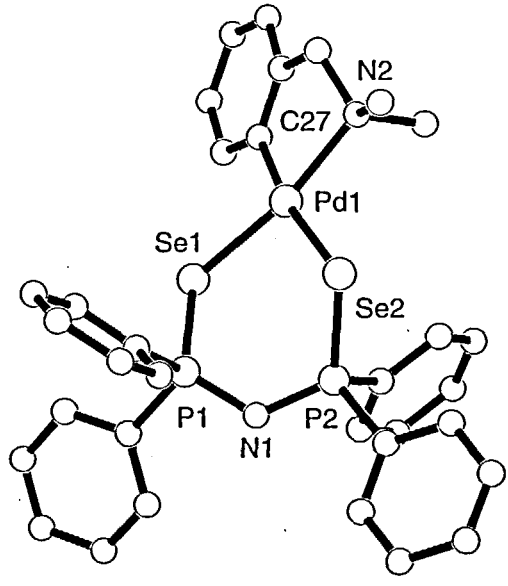
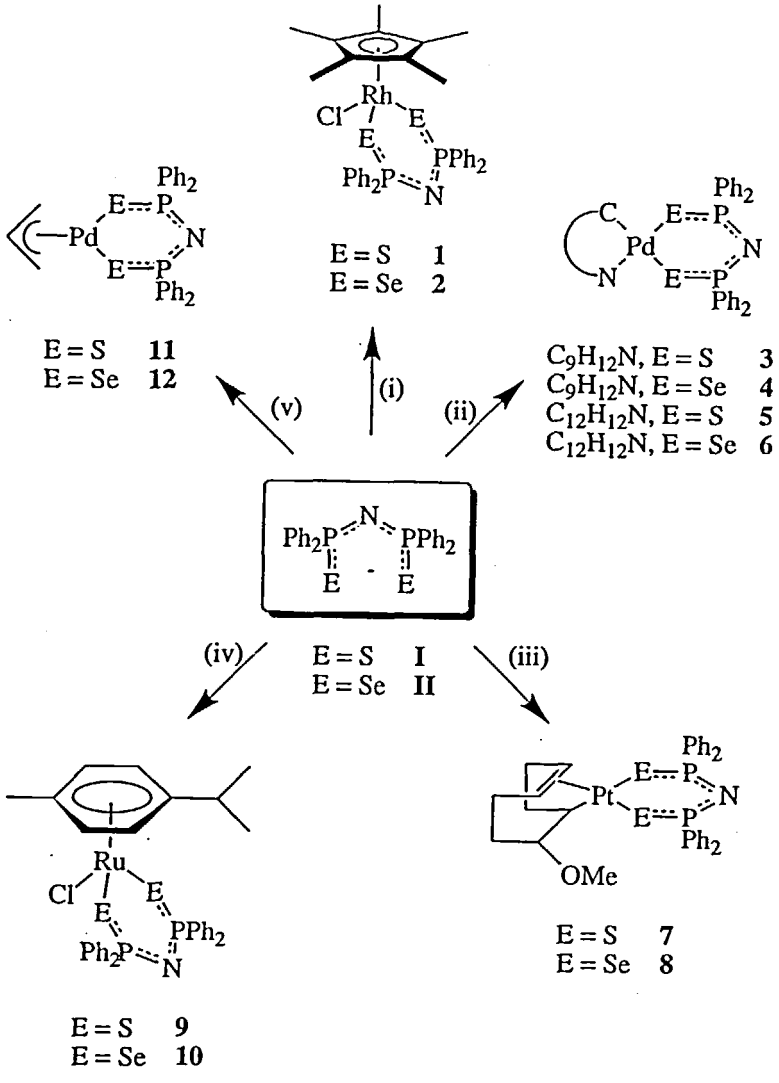


FIGURE 1 X-ray crystal structure of **4**



SCHEME 1 Synthetic routes to the complexes **1** - **12**. (i) $[\{RhCl(\mu\text{-}Cl)(C_5Me_5)\}_2]$ (ii) $[\{Pd(\mu\text{-}Cl)(C\text{-}N)\}_2]$ (C-N = $C_9H_{12}N$, $C_{12}H_{12}N$) (iii) $[\{Pt(\mu\text{-}OMe)(C_8H_{12}OMe)\}_2]$ (iv) $[\{RuCl(\mu\text{-}Cl)(C_{10}H_{14})\}_2]$ (v) $[\{Pd(\mu\text{-}Cl)(C_3H_5)\}_2]$

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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