

New phosphazene chains and ligands in complexes and clusters

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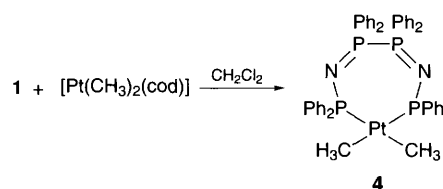
$\text{Ph}_2\text{PNP}(\text{Ph})_2\text{P}(\text{Ph})_2\text{NPPh}_2$ **1** is oxidised by S or Se to give $\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{Ph})_2\text{P}(\text{Ph})_2\text{NP}(\text{E})\text{Ph}_2$ (E = S **2**, E = Se **3**), endcapped by ClAu units or coordinated as a chelate with $(\text{CH}_3)_2\text{Pt}$; the diselenide **3** reacts with $[\text{Ru}_3(\text{CO})_{12}]$ via oxidative addition of Se^{2-} ions and expulsion of a PPh_2^- group to form a novel cluster containing the $[\text{Ph}_2\text{PNP}(\text{Ph})_2\text{NPPh}_2]^-$ ligand which is ligated by two terminal P atoms and by one N atom.

The coordination chemistry of $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^{-1-3}$ and $[\text{R}_2\text{PNP}(\text{E})\text{R}_2]^{-4,5}$ (E = O, S, Se) anions has generated great interest recently. These types of ligands are useful in selective metal complexation and have potential as hard/soft donor systems in catalysis. Both classes of anions are readily prepared via R_2PNHPR_2 . Interestingly, Braunstein *et al.*⁶ have very recently described the oxidative coupling of $\text{Li}[\text{N}(\text{PPh}_2)_2]$ using I_2 to give $\text{Ph}_2\text{PNP}(\text{Ph})_2\text{P}(\text{Ph})_2\text{NPPh}_2$ **1**. Here we describe the first examples of coordination compounds of **1** together with the synthesis and structure of an unusual Ru_3 cluster containing the $[\text{Ph}_2\text{PNP}(\text{Ph})_2\text{NPPh}_2]^-$ ligand in a new binding mode.

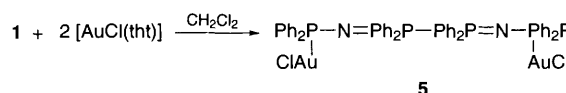
We have found that **1**‡ may be readily oxidised (without P–P bond cleavage) with sulfur or selenium in thf (Scheme 1). The products (E = S **2**, E = Se **3**) were obtained in good yield (81 and 76% respectively) and display the expected spectroscopic properties.‡ An X-ray structure§ (Fig. 1) of **3** reveals two independent half molecules with each disposed about a crystallographic centre of symmetry. The Se–P–N–P–P–N–P–Se backbone is planar with the selenium atoms being *anti* with respect to each other. The P=Se distance is typical of a double bond, whilst the P–N bond lengths show significant alternation in accord with a substantial degree of localised bonding along

the chain. **1** may also be complexed either as a chelate (Scheme 2) or as a bridging ligand (Scheme 3). Compounds **4** and **5** were characterised spectroscopically‡ and **5** displays (Fig. 2) a similar structure§ to **3** with the Au–Cl groups being *anti* and the molecule being disposed about a crystallographic centre of symmetry.

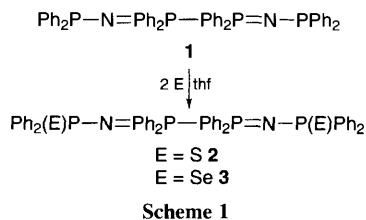
Reaction of **3** with $[\text{Ru}_3(\text{CO})_{12}]$ and the oxidative-decarbonylation reagent Me_3NO (1:1:1.1 ratio respectively) in refluxing toluene (90 min) gave, after chromatographic separation [preparative TLC, 2:1 CH_2Cl_2 –light petroleum (bp 40–60 °C)], a major green band, which after recrystallisation afforded the novel $[\text{Ru}_3(\text{CO})_6(\mu_3\text{-Se})_2(\mu\text{-PPh}_2)\text{-}\{\text{Ph}_2\text{PNP}(\text{Ph})_2\text{NPPh}_2\}]$ cluster **6** (Scheme 4) in 35% yield as an air-stable, dark green crystalline solid.¶ Cluster **6** has a complex



Scheme 2



Scheme 3



Scheme 1

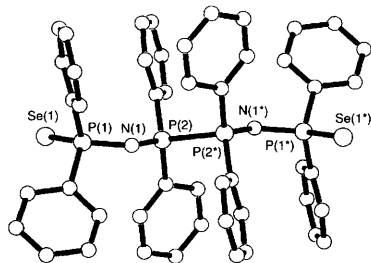


Fig. 1 The X-ray structure of **3**, showing one of the two independent molecules. Selected bond lengths (Å) and angles (°), values in square brackets are the equivalent parameter in the second molecule: P(1)–Se(1) 2.120(2) [2.122(2)], P(1)–N(1) 1.609(6) [1.618(6)], N(1)–P(2) 1.574(5) [1.559(7)], P(2)–P(2′) 2.218(4) [2.226(4)]; Se(1)–P(1)–N(1) 117.4(2) [118.2(3)], P(1)–N(1)–P(2) 135.5(4) [137.0(4)], N(1)–P(2)–P(2′) 104.6(3) [104.5(3)].

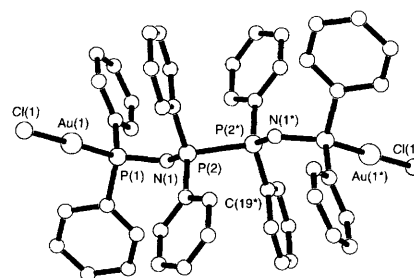
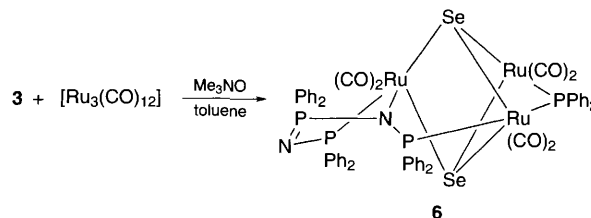


Fig. 2 The X-ray structure of **5**, selected bond lengths (Å) and angles (°): Au(1)–Cl(1) 2.299(4), Au(1)–P(1) 2.231(4), P(1)–N(1) 1.64(1), N(1)–P(2) 1.581(10), P(2)–P(2′) 2.215(7); Cl(1)–Au(1)–P(1) 178.4(2), Au(1)–P(1)–N(1) 116.7(4), P(1)–N(1)–P(2) 128.7(7), N(1)–P(2)–P(2′) 103.3(5).



Scheme 4

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum \ddagger which reveals four unique phosphorus environments with one phosphorus signal at high frequency being readily assigned as a phosphido ligand and the other three phosphorus resonances being readily assigned to the individual P centres in the $[\text{Ph}_2\text{PNP}(\text{Ph})_2\text{NPPh}_2]^-$ ligand. The X-ray structure (Fig. 3) \S of **6** enabled complete characterisation. The Ru_3 core is not symmetric [Ru(1)–Ru(2) 3.08, Ru(2)–Ru(3) 3.17, Ru(3)–Ru(1) 3.67 Å] with the largest Ru–Ru distance being associated with the bridging PPh_2 ligand. Furthermore, the PNPNP backbone of the $[\text{Ph}_2\text{PNP}(\text{Ph})_2\text{NPPh}_2]^-$ ligand is coordinated to ruthenium at each terminal phosphorus atom as well as being bonded [Ru–N 2.268(5) Å] to one nitrogen atom which results in the formation of two fused Ru_2NP and RuN_2P_2 rings. The five-membered ring is puckered with the N(1)–P(2)–N(2)–P(3) fragment approximately planar [maximum deviation 0.21 Å for N(2)] and inclined by 32° to the Ru(2)–N(1)–P(3) plane. The diphenylphosphido group is asymmetrically bonded to the ruthenium centres [Ru(1)–P(4) 2.383(2), Ru(3)–P(4) 2.261(2) Å] with the shorter distance being associated with the five-coordinate Ru(3) centre. Overall there are two six-coordinate ruthenium centres [Ru(1) and Ru(2)] and one five-coordinate centre [Ru(3)]. The Se–Se distance is 3.39 Å with the Se(1) and Se(2) being equidistant from the Ru_3 plane. The oxidative addition of the chalcogen to the ruthenium atoms results in the formation of the Ru_3Se_2 core. A similar type of reaction has been noted for $\text{CH}_2\{\text{P}(\text{SePh})_2\}_2$. 7 The use of these types of system as chalcogen donors may be generalisable.

There have previously been only two reports of the $[\text{Ph}_2\text{PNP}(\text{Ph})_2\text{NPPh}_2]^-$ anion and in both cases these were obtained 8,9 from reactions involving $\text{Li}[\text{Ph}_2\text{PNPPh}_2]$. It is not possible to compare structure parameters since the previous examples involved simple mononuclear systems rather than the cluster system seen here.

There is currently great interest in the formation of inorganic/organometallic polymers. The compounds described here represent prepolymer fragments as well as potential intermediates in polymerisation reactions. Further studies into the polymerisation of **1**, **5** and the generality of the elimination reaction used in the formation of **6** are in progress.

We are grateful to the EPSRC for funding and to Johnson Matthey for loans of precious metals.

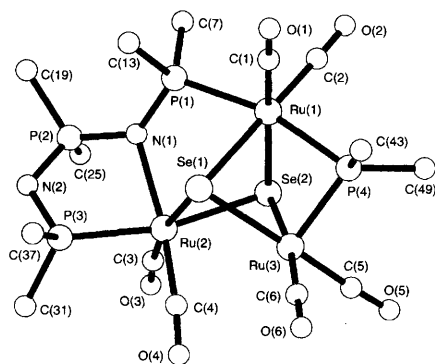


Fig. 3 The X-ray structure of **6**, only the bridgehead phenyl carbon atoms are shown for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ru(1)–P(4) 2.383(2), Ru(3)–P(4) 2.261(2), Ru(1)–P(1) 2.388(2), P(1)–N(1) 1.660(5), N(1)–P(2) 1.644(5), P(2)–N(2) 1.600(6), N(2)–P(3) 1.623(6), P(3)–Ru(2) 2.348(2), Ru(2)–N(1) 2.268(5), Ru–Se range 2.522(1)–2.600(1), Ru–C range 1.842(8)–1.894(8); Ru(1)–P(4)–Ru(3) 83.22(6), Ru(1)–P(1)–N(1) 111.0(2), P(1)–N(1)–P(2) 131.3(3), N(1)–P(2)–N(2) 111.9(3), P(2)–N(2)–P(3) 117.4(3), N(2)–P(3)–Ru(2) 107.2(2); Ru–Se–Ru range 73.74(3)–90.70(3).

Footnotes

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\S **1** was prepared as described in ref. 6. Selected spectroscopic data for complexes **2–6** (all new compounds gave satisfactory C, H, N analyses). For **2**: NMR (CDCl_3): $^{31}\text{P}\{^1\text{H}\}$ (ref. 85% H_3PO_4) δ 47.2 (P_S), 13.5 [$J(\text{PP})$ 7.2 Hz]; ^1H δ 7.83–7.49, 7.35–7.18 (arom. H); IR (KBr) 1207, 1174 (ν_{PN}); 603 (ν_{PS}) cm^{-1} . For **3**: NMR (CDCl_3): $^{31}\text{P}\{^1\text{H}\}$ δ 38.4 [$J(\text{PSe})$ 714 Hz], 14.5 [$J(\text{PP})$ 7.2 Hz]; ^1H δ 7.83–7.51, 7.35–7.18 (arom. H); IR (KBr) 1206, 1174, 1160 (ν_{PN}); 550 (ν_{PSe}) cm^{-1} . For **4**: NMR (CDCl_3): $^{31}\text{P}\{^1\text{H}\}$ δ 51.7 [$J(\text{PIP})$ 211 Hz], –0.1 [$J(\text{PP})$ 13.3 Hz]; $^{195}\text{Pt}\{^1\text{H}\}$ δ –4353.5; ^1H δ 7.43–6.97 (arom. H), 0.09 [Pt–CH $_3$, $J(\text{PtH})$ 65.7, $J(\text{PH})$ 12.7 Hz]. For **5**: NMR (CDCl_3): $^{31}\text{P}\{^1\text{H}\}$ δ 50.8 (P_{Au}), 16.6; ^1H δ 7.66–7.27 (arom. H). For **6**: NMR ($\text{CH}_2\text{Cl}_2\text{-}C_6D_6$): $^{31}\text{P}\{^1\text{H}\}$ δ 163.8 [P_4 , $J(\text{P}_4\text{P}_1)$ 362 Hz], 64.2 [P_3 , $J(\text{P}_3\text{P}_2)$ 29.8 $J(\text{P}_3\text{P}_1)$ 11.2 Hz], 46.4 [P_2 , $J(\text{P}_2\text{P}_1)$ 71.4 Hz], 45.6 (P_1); ^1H (CDCl_3) δ 8.14–8.07, 7.84–6.79 (arom. H); IR $\nu(\text{CO})$ (CH_2Cl_2) 2093w, 2037m (sh), 2022vs, 2013s (sh), 1973m, 1955m; (KBr) 2089w, 2038m (sh), 2020vs, 1973m, 1956m, 1943m cm^{-1} ; FABMS: m/z 1399, (M^+), 1371–1231, ($\text{M}-n\text{CO}$) $^+$ ($n = 1-6$).

\S Crystal data: all measurements were performed at room temperature using Cu–K α radiation, $\lambda = 1.54178$ Å, Rigaku AFC7S diffractometer and ω -scans, $2\theta_{\text{max}} 120^\circ$. For **3**: $\text{C}_{48}\text{H}_{40}\text{N}_2\text{P}_4\text{Se}_2\cdot 2\text{CHCl}_3$, $M = 1165.4$, triclinic, space group $P\bar{1}$, $a = 12.656(2)$, $b = 19.066(3)$, $c = 11.427(4)$ Å, $\alpha = 96.95(2)$, $\beta = 100.82(2)$, $\gamma = 102.26(1)^\circ$; $U = 2609$ Å 3 , $Z = 2$, $D_c = 1.48$ g cm^{-3} , $F(000) = 1172$, $\mu(\text{Cu-K}\alpha) 6.04$ mm $^{-1}$. Crystal dimensions $0.11 \times 0.13 \times 0.30$ mm. Of 8174 measured data, 7767 were unique ($R_{\text{int}} = 0.22$) and 5193 were observed [$I > 1.5\sigma(I)$]. An empirical absorption correction was applied. The structure was solved by direct methods and refined to give $R = 0.074$ and $R_w = 0.060$. For **5**: $\text{C}_{42}\text{H}_{46}\text{Au}_2\text{Cl}_2\text{N}_2\text{P}_4\cdot 3\text{H}_2\text{O}$, $M = 1287.6$, monoclinic, space group $P2_1/n$, $a = 9.910(4)$, $b = 14.544(3)$, $c = 18.604(3)$ Å, $\beta = 97.49(2)^\circ$; $U = 2658$ Å 3 , $Z = 2$, $D_c = 1.61$ g cm^{-3} , $F(000) = 1248$, $\mu(\text{Cu-K}\alpha) 12.4$ mm $^{-1}$. Crystal dimensions $0.22 \times 0.21 \times 0.31$ mm. Of 4412 measured data, 4143 were unique ($R_{\text{int}} = 0.115$) and 3119 were observed [$I > 2.0\sigma(I)$]. An empirical absorption correction was applied. The structure was solved by the heavy-atom method and refined to give $R = 0.063$ and $R_w = 0.062$. For **6**: $\text{C}_{54}\text{H}_{40}\text{N}_2\text{O}_6\text{P}_4\text{Ru}_3\text{Se}_2$, $M = 1397.9$, monoclinic, space group $P2_1/n$, $a = 14.777(2)$, $b = 18.081(2)$, $c = 20.942(2)$ Å, $\beta = 98.621(7)^\circ$; $U = 5532$ Å 3 , $Z = 4$, $D_c = 1.68$ g cm^{-3} , $F(000) = 2744$, $\mu(\text{Cu-K}\alpha) 9.56$ mm $^{-1}$. Crystal dimensions $0.18 \times 0.18 \times 0.20$ mm. Of 8906 measured data, 8534 were unique ($R_{\text{int}} = 0.028$) and 6090 were observed [$I > 2.0\sigma(I)$]. An absorption correction based on azimuthal scans was applied. The structure was solved by the heavy-atom method and refined to give $R = 0.038$ and $R_w = 0.040$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/192.

\P In addition to several other minor products which are currently under investigation.

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Received, 28th May, 1996; Com. 6/03682A