Facile Chalcogenide Elimination Reactions: The Crystal Structures of $[Pt\{(Ph_2PO)_2H\}\{(Ph_2PSeO)_2H\}]\cdot1.25CHCl_3$ and $[Pt_3(Ph_2PCH_2CH_2PPh_2)_3S_2][(Ph_2PSO)_2H][OH]\cdot0.5CH_2Cl_2$

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Reaction of Ph_2PSeOH with $[PtCl_2(PR_3)_2]$ (PR_3 = PEt_3 or PMe_2Ph) gives $[Pt\{(Ph_2PO)_2H\}\{(Ph_2PSeO)_2H\}]$ **1**, whereas the analogous sulfur compound Ph_2PSOH with $[PtCl_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) gives the bipyramidal Pt_3S_2 containing cluster $[Pt_3(dppe)_3S_2]^{2+}$.

The co-ordination chemistry of R_2PE^- (E = O, S or Se) and $R_2PE_2^-$ is well established[1-4] whereas that of mixed-donor ligands has been little investigated. We have recently reported[5] the heterobimetallic compound $[(Me_2PhP)_2Pt\{SP(OPr^i)_2O\}_2ZnCl_2]$ which makes use of the hard oxygen and soft sulfur atoms of the thiophosphate ligand to co-ordinate to zinc and platinum respectively. Here, we report that the related free acids Ph_2PSeOH and Ph_2PSOH react with $[PtCl_2(PR_3)_2]$ with elimination of selenium and sulfur to form $[Pt\{(Ph_2PO)_2H\}\{(Ph_2PSeO)_2H\}]$ **1** and the *triangulo* cluster $[Pt_3(dppe)_3S_2]^{2+}$ (dppe = $Ph_2PCH_2CH_2PPh_2$) respectively.

Reaction of *cis*-$[PtCl_2(PR_3)_2]$ (*ca.* 0.25 mmol) with Ph_2PSeOH (1 mmol) in refluxing toluene proceeds as described in equation (1) (typical yield 63% for PR_3 = PEt_3) with

$$[PtCl_2(PR_3)_2] + 4Ph_2PSeOH \longrightarrow [Pt\{(Ph_2PO)_2H\}\{(Ph_2PSeO)_2H\}] + 2HCl + 2SePR_3 \quad (1)$$

elimination of $Se{=}PR_3$ providing a new route to co-ordinated phosphinite.

The X-ray crystal structure analysis of **1**† shows (Fig. 1) the molecule to have non-crystallographic C_2 symmetry about an axis passing through the platinum atom and bisecting the Se–Pt–Se angle. The platinum is square planar with a maximum deviation from planarity for the co-ordination shell of 0.02 Å (for Pt); O(3) and O(4) lie 0.15 and 0.11 Å above and below this plane. The Pt–Se distances [2.530(2) and 2.513(2) Å] are noticeably larger than those in $[Pt(Se_3PPh)(dppe)]$ **2**[7] [2.465(1) and 2.471(1) Å], whereas the P–Se distances in **1** are shortened [2.177(5) and 2.188(4), *cf.* 2.215(3) and 2.239(3) Å in **2**]. The P–O bonds in the selenophosphinate are both marginally shorter (0.02 Å) than those in the phosphinite ligands, possibly reflecting the difference in formal oxidation number of the phosphorus atoms.

There are two very strong intramolecular O···H···O

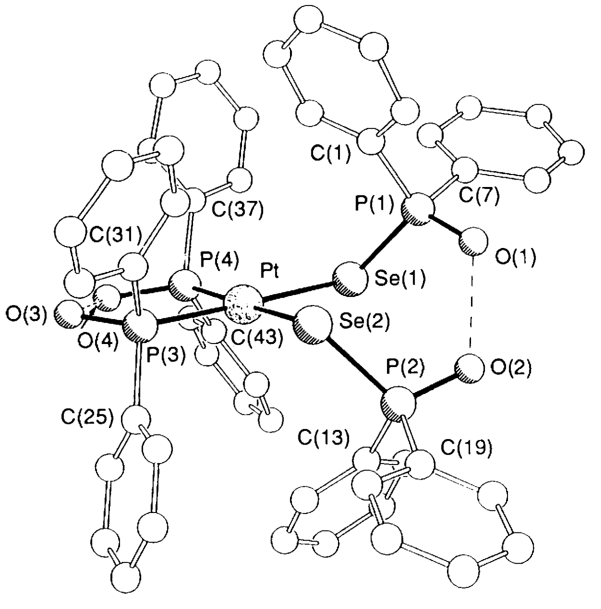

Fig. 1 The crystal structure of compound **1**. Selected distances (Å) and angles (°): Pt–Se(1) 2.530(2), Pt–Se(2) 2.513(2), Pt–P(3) 2.271(4), Pt–P(4) 2.255(4), Se(1)–P(1) 2.178(5), Se(2)–P(2) 2.187(4), P(1)–O(1) 1.533(13), P(2)–O(2) 1.529(10), P(3)–O(3) 1.553(12), P(4)–O(4) 1.550(11), O(1)···O(2) 2.42 and O(3)···O(4) 2.39; Se(1)–Pt–Se(2) 94.4(1), P(3)–Pt–P(4) 92.8(1), Pt–P(3)–O(3) 116.3(5), Pt–P(4)–O(4) 116.0(5), Pt–Se(1)–P(1) 107.4(1), Pt–Se(2)–P(2) 104.4(1), Se(1)–P(1)–O(1) 115.7(5), Se(2)–P(2)–O(2) 114.6(4), P(1)–O(1)···O(2) and P(2)–O(2)···O(1) mean 120, P(3)–O(3)···O(4) and P(4)–O(4)···O(3) mean 106

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† *Crystal data.* **1**, $C_{48}H_{42}O_4P_4PtSe_2\cdot1.25CHCl_3$, M = 1308.9, monoclinic, space group $C2/c$, a = 24.884(11), b = 12.003(4), c = 37.211(14) Å, β = 99.03(3)°, U = 10 977(7) Å^3, Z = 8, D_c = 1.584 g cm^{-3}, λ = 1.541 78 Å, μ(Cu-Kα) = 94.0 cm^{-1}, $F(000)$ = 5124. Data were measured on a Nicolet R3m diffractometer with graphite-monochromated Cu-Kα radiation using ω scans, crystal dimensions 0.17 × 0.23 × 0.24 mm. The structure was solved by the heavy-atom method and refined anisotropically using absorption-corrected data to give R = 0.064, R' = 0.064 for 5652 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leqslant 116°$], $w^{-1} = \sigma^2(F) + 0.0005\,F^2$.

3, $C_{102}H_{94}O_3P_8S_4Pt_3\cdot0.5CH_2Cl_2$, M = 2371.5, triclinic, space group $P\bar{1}$, a = 13.589(10), b = 16.782(13), c = 24.13(2) Å, α = 79.46(6), β = 89.35(6), γ = 68.55(6)°, U = 5026(3) Å^3, Z = 2, D_c = 1.567 g cm^{-3}, λ = 1.541 78 Å, μ(Cu-Kα) = 102.5 cm^{-1}, $F(000)$ = 2338. Data were measured as above using a crystal of dimensions 0.30 × 0.30 × 0.42 mm. The structure was solved by direct methods and refined anisotropically using absorption-corrected data to give R = 0.070, R' = 0.068 for 9054 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leqslant 100°$] $w^{-1} = \sigma^2(F) + 0.0003F^2$. Computations of both structures were carried out on an IBM PS70 386 computer using the SHELXTL PC program.[6] For both structures, atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

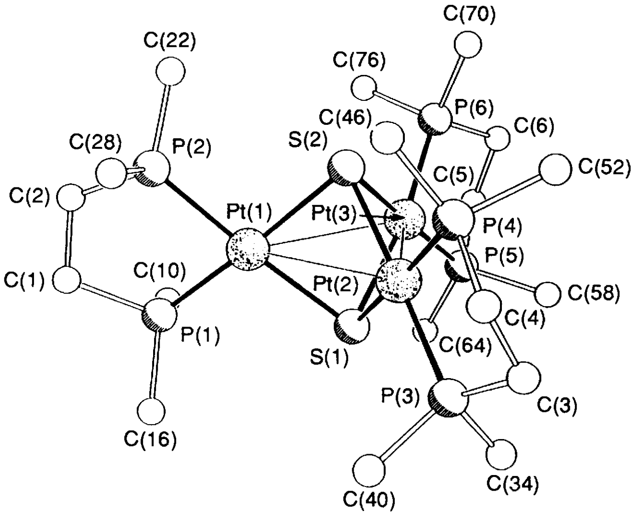

Fig. 2 The crystal structure of the cation in **3**, phenyl rings have been omitted for clarity. Selected bond lengths and non-bonding distances (Å) and angles (°): Pt(1) ··· Pt(2) 3.132(3), Pt(2) ··· Pt(3) 3.093(3), Pt(1) ··· Pt(3) 3.140(3), Pt(1)–S(1) 2.378(5), Pt(2)–S(1) 2.363(4), Pt(3)–S(1) 2.370(4), Pt(1)–S(2) 2.355(5), Pt(2)–S(2) 2.356(5), Pt(3)–S(2) 2.375(4) and mean Pt–P 2.25; S(1)–Pt(1)–S(2) 80.7(2), S(1)–Pt(2)–S(2) 81.0(1), S(1)–Pt(3)–S(2) 80.5(1), P(1)–Pt(1)–P(2) 85.6(2), P(3)–Pt(2)–P(4) 86.4(2) and P(5)–Pt(3)–P(6) 84.4(2)

hydrogen bonds, O(1) ··· O(2) 2.42 and O(3) ··· O(4) 2.39 Å. The positions of the hydrogen atoms could not be unambiguously determined from the X-ray data but the shortness of each of these O ··· O interactions is indicative of a symmetric single-minimum proton potential, *i.e.* each pair of ligands is singly protonated. There is an additional intermolecular C–H ··· O hydrogen bond (3.1 Å) from one of the partial occupancy $CHCl_3$ solvate molecules to O(3).

In contrast to reaction (1), reactions with thiophosphate did not occur for monodentate phosphines but when $2PR_3$ = dppe they resulted in Ph_2PSOH acting as a source of sulfide with formation of $[Pt_3(dppe)_3S_2][(Ph_2PSO)_2H][OH]$ **3**. A compound formulated as $[\{Pt(PMe_2Ph)_2\}_3S_2]X_2$ (X = Cl, ClO_4 or BF_4) was reported[8] in 1970 from the reaction of Na_2S with $[PtCl_2(PMe_2Ph)_2]$ in ethanol. The X-ray crystal structure of the cation in **3** is shown in Fig. 2 The cation has molecular D_3 symmetry being comprised of three fused, slightly distorted square-planar (dppe)PtS_2 units. Each platinum co-ordination shell displays a twist (3–10°), in the same sense, of each PtP_2 plane with respect to its associated PtS_2 plane. The Pt–P distances are normal and in the range 2.238(5) [for Pt(2)–P(3)]–2.259(6) Å [for Pt(1)–P(2)]. The central Pt_3S_2 core is a nearly regular trigonal bipyramid with Pt ··· Pt distances in the range 3.093(3)–3.140(3) Å and an average Pt–S distance of 2.37 Å. Atoms S(1) and S(2) lie equidistant above and below the Pt_3 plane, the S(1) ··· S(2) distance being 3.07 Å. The two Ph_2PSO^- anions exhibit a very short approach of their oxygen atoms (2.34 Å) analogous to those seen in **1**. This indicates the presence of an O ··· H ··· O hydrogen bond. Two 50% occupancy oxygen atoms were located in the difference electron-density map. Thus the overall charge balance for **3** is satisfied if these are regarded as being two 50% occupancy OH^- groups.

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