

Versatile Routes to Selenoether Functionalised Tertiary Phosphines

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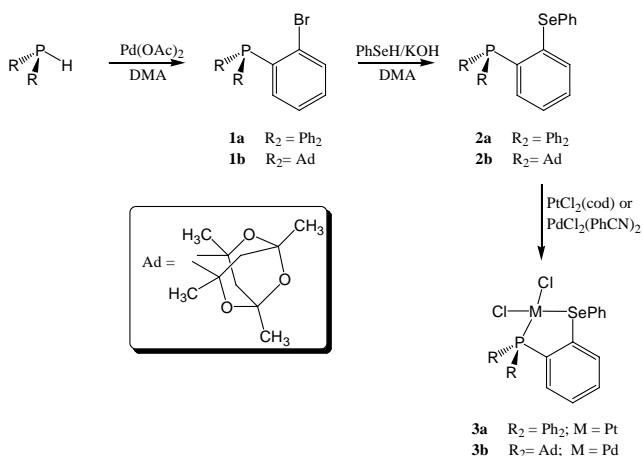
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5 New selenoether functionalised tertiary phosphines, based on aryl (2a, 2b) or alkyl (4) backbones, have been synthesised and characterised. P,Se-chelation has been achieved upon complexation to square-planar Pt^{II} (3a) or Pd^{II} (3b) metal centres. For 3a and 3b, weak non covalent M...Se contacts were established using single crystal X-ray crystallography.

Tertiary phosphines continue to remain an integral tool in the design and synthesis of new metal based complexes. Hybrid tertiary phosphines, bearing additional donor atoms such as oxygen, have frequently been described as hemilabile by virtue of the soft/hard donor atom combination.¹ Considerable recent interest has focused on mixed P,O- and P,S-ligands for their fascinating coordination chemistry,² including water-soluble macrocyclic complexes using a weak-link approach,³ and catalytic applications.⁴ Tertiary phosphines with an additional selenium donor centre have been very poorly developed in comparison to their lighter Group 16 counterparts.⁵ In contrast, numerous tertiary phosphine selenides (R₃P=Se) have been documented⁶ and there has been much recent interest in phosphorus-selenium chemistry *e.g.* Woollins' reagent.⁷

We⁸, and others⁹ have been interested in exploiting the favourable stereoelectronic, solubility and crystalline properties of the 6-phospha-2,4,8-trioxa-1,3,5,7-tetramethyladamantyl cage group in the synthesis of new phosphine ligands. Herein we describe the synthesis of a new, air-stable, selenoether phosphine containing this diamondoid group, along with two further selenoether phosphines and their square-planar dichloropalladium and platinum(II) complexes.



Scheme 1

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The synthetic procedure to the new selenoether modified phosphines **2a** and **2b** was achieved using standard methodology (Scheme 1). Following a known procedure for accessing bromophosphine **1a**,¹⁰ reaction of the parent cage phosphine, AdPH, with 1-bromo-2-iodobenzene in dimethylacetamide (DMA) under standard P–C coupling conditions afforded **1b** in good yield (55%) as an air-stable crystalline solid.[†] One noticeable difference in the preparation of **1b**, opposed to **1a**, was the considerably shorter reaction time to proceed to completion (typically 2 d for **1b**; 5 d for **1a**). In the ³¹P{¹H} NMR spectrum of **1b** a single phosphorus resonance was observed at δ(P) –29.6 ppm, some 25 ppm upfield with respect to **1a** [δ(P) –4.9 ppm]. Reaction of either **1a** or **1b** with PhSeH and KOH, in DMA, for 5 d at *ca.* 160 °C afforded **2a** or **2b** in reasonable yields (53% and 40% respectively). ³¹P{¹H} NMR spectroscopy of **2a** and **2b** showed single phosphorus resonances at δ(P) –10.0 [³J(PSe) 139 Hz] and δ(P) –34.6 ppm [³J(PSe) 201 Hz] respectively.

Crystals of **2b**, suitable for X-ray crystallography, were grown by vapour diffusion of Et₂O into a CDCl₃ solution.[‡] The molecular structure (Fig. 1) of **2b** revealed crystallisation of a single enantiomer and confirmed the *ortho* arrangement of the bulky chiral phosphadamantyl cage and selenoether group. Metric parameters are broadly as anticipated and the transannular P(1)–Se(1) separation [3.230 Å] suggests *cis*-co-ordination to metal centres should be feasible. To the best of our knowledge we believe this structure determination represents the first example of a functionalised selenoether tertiary phosphine.

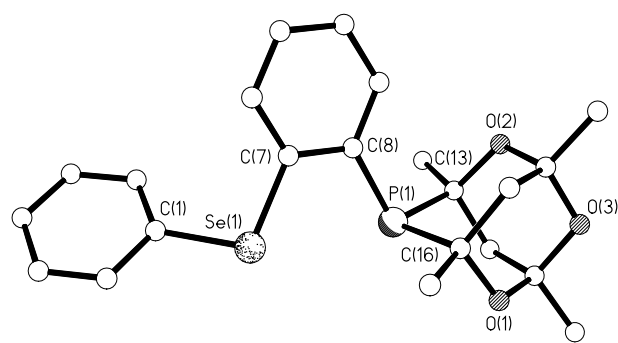


Fig. 1 Molecular structure of **2b**. All C–H hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)–Se(1) 1.919(3), Se(1)–C(7) 1.925(3), C(8)–P(1) 1.844(3); C(1)–Se(1)–C(7) 102.41(14), Se(1)–C(7)–C(8) 119.7(2), C(13)–P(1)–C(16) 92.40(14).

To demonstrate the co-ordination potential of **2a** and **2b**, reaction of 1 equiv. of each ligand with either PtCl₂(cod) (cod = cycloocta-1,5-diene) or PdCl₂(PhCN)₂ in CH₂Cl₂ at ambient temperature afforded the dichlorometal(II) complexes **3a** and **3b** in good yields. Crystals of **3a** and **3b** were grown by vapour

diffusion of diethyl ether into either a $\text{CDCl}_3/(\text{CH}_3)_2\text{SO}$ or CH_2Cl_2 solution (Fig. 2).[‡] In both cases, P,Se-chelation is clearly evident with P(1)–M(1)–Se(1) bond angles of 90.28(3) and 87.902(12)°. Furthermore the M(1)–Se(1) bond lengths [Pt(1)–Se(1) 2.3561(5) for **2a**; Pd(1)–Se(1) 2.3656(2) for **2b**] are consistent with selenoether coordination.¹¹ The M(1)–Se(1)–C(7)–C(8)–P(1) five-membered rings are essentially coplanar to within ± 0.046 Å for **3a** and ± 0.104 Å for **3b**). The interplanar angles for **3a** and **3b**, as defined by the Se(1)/C(7)/C(8)/P(1) vs. Se(1)/M(1)/P(1) planes, are 4.9° and 11.4° respectively indicating marginal folding along the P(1)⋯Se(1) vector. In addition, there is a clear change in dihedral angle between the phenyl/phenylene rings attached to Se(1) as a function of chelation. In the free ligand **2a**, the dihedral angle is 54.1° which expands to 87.0° for **3a** and 82.1° for **3b**. As a consequence, weak non covalent M(1)⋯Se(1) intermolecular contacts [Pt(1)⋯Se(1) 3.709 Å for **3a**; Pd(1)⋯Se(1) 3.787 Å for **3b**] link adjacent molecules into dimer pairs.¹² Although not shown in Fig. 2, additional Se(1)⋯Cl(1A) interactions are present (3.445 Å for **3a**; 3.679 Å for **3b**). In the case of **3a** this distance is significantly less than the sum of the van der Waals radii for Se and Cl atoms (3.65 Å).¹³

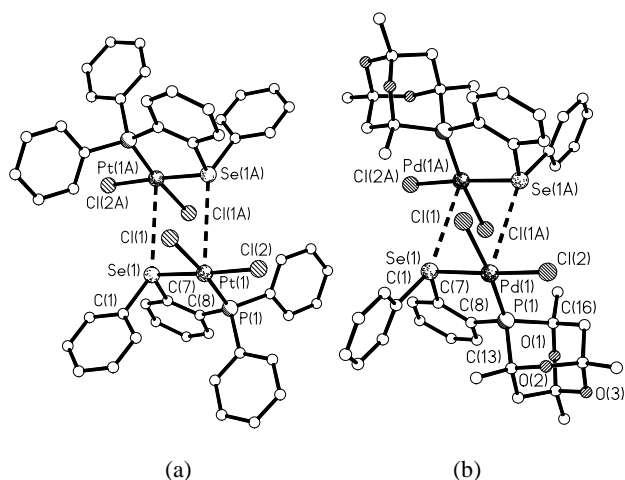
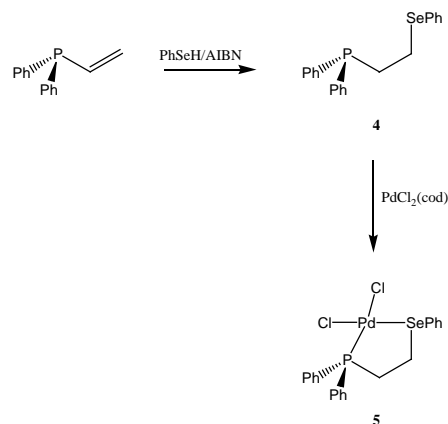


Fig. 2 Molecular structures of (a) **3a** and (b) **3b**. All C–H hydrogen atoms are omitted for clarity. For complex **3b** the CH_2Cl_2 solvate has been removed. Selected bond distances (Å) and angles (deg) for **3a** Pt(1)–P(1) 2.2094(11), Pt(1)–Se(1) 2.3561(5), Pt(1)–Cl(1) 2.3668(11), Pt(1)–Cl(2) 2.3142(11); P(1)–Pt(1)–Se(1) 90.28(3), P(1)–Pt(1)–Cl(2) 91.89(4), Se(1)–Pt(1)–Cl(1) 85.94(3), Cl(1)–Pt(1)–Cl(2) 92.04(4). For **3b**: Pd(1)–P(1) 2.2615(4), Pd(1)–Se(1) 2.3656(2), Pd(1)–Cl(1) 2.3506(4), Pd(1)–Cl(2) 2.3180(5); P(1)–Pd(1)–Se(1) 87.902(12), P(1)–Pd(1)–Cl(2) 98.800(17), Se(1)–Pd(1)–Cl(1) 84.577(14), Cl(1)–Pd(1)–Cl(2) 88.709(18).

Having successfully demonstrated the preparation of aryl based selenoether phosphines, we also found the ease by which an alkyl backboned selenoether phosphine can be readily obtained. Using an AIBN radical initiated hydroselenation,¹⁴ reaction of $\text{Ph}_2\text{PCH}=\text{CH}_2$ with PhSeH afforded solid **4** (Scheme 2) regioselectively which has been characterised [$\delta(\text{P}) -15.4$].¹⁵ Reaction of the anti-Markovnikov product **4** with $\text{PdCl}_2(\text{cod})$ gave the five-membered chelate complex **5** displaying the expected spectroscopic and analytical properties. The significant downfield shift in the $^{31}\text{P}\{\text{H}\}$ NMR spectrum of **5** [$\delta(\text{P}) 62.3$

ppm] is fully consistent with coordination of both P and Se donor atoms to a single Pd(II) metal centre.



Scheme 2

In summary, we have shown how established synthetic routes can be used to access, hitherto unknown, selenoether modified tertiary phosphines and demonstrated their ease of P,Se-chelation at soft metal centres. Further coordination studies are in progress and results from these will be reported in due course.

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Notes and References

[†] See ESI for synthetic details and characterising data for all new compounds.

[‡] *Crystal data*: For **2b**, $\text{C}_{22}\text{H}_{25}\text{O}_3\text{PSe}$: $M_r = 447.35$, orthorhombic, space group $P2_12_12_1$, $a = 8.1752(5)$ Å, $b = 10.1189(6)$ Å, $c = 24.5004(14)$ Å, $V = 2026.8(2)$ Å³, $T = 150(2)$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.71073$ Å, 17792 data measured, 4890 unique ($R_{\text{int}} = 0.0366$), $d_{\text{calc}} = 1.466$ g cm⁻³, $R1 = 0.0391$ (for 4049 data with $I > 2\sigma(I)$), $wR2 = 0.0858$ (all data), and 248 parameters. CCDC xxxxxx. For **3a**, $\text{C}_{24}\text{H}_{19}\text{Cl}_2\text{PPtSe}$: $M_r = 683.31$, monoclinic, space group $P2_1/n$, $a = 11.2539(7)$ Å, $b = 13.4809(8)$ Å, $c = 14.7665(9)$ Å, $\beta = 101.0079(10)^\circ$, $V = 2199.0(2)$ Å³, $T = 150(2)$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.71073$ Å, 19234 data measured, 5350 unique ($R_{\text{int}} = 0.0357$), $d_{\text{calc}} = 2.064$ g cm⁻³, $R1 = 0.0276$ (for 4130 data with $I > 2\sigma(I)$), $wR2 = 0.0557$ (all data), and 262 parameters. CCDC xxxxxx. For **3b**, $\text{C}_{22}\text{H}_{25}\text{Cl}_2\text{O}_3\text{PPdSe}\cdot\text{CH}_2\text{Cl}_2$: $M_r = 709.58$, triclinic, space group $P1$, $a = 11.0639(5)$ Å, $b = 11.0640(5)$ Å, $c = 11.7858(5)$ Å, $\alpha = 89.7421(7)^\circ$, $\beta = 76.3793(7)^\circ$, $\gamma = 68.4046(6)^\circ$, $V = 1298.32(10)$ Å³, $T = 150(2)$ K, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.71073$ Å, 11577 data measured, 6012 unique ($R_{\text{int}} = 0.0110$), $d_{\text{calc}} = 1.815$ g cm⁻³, $R1 = 0.0188$ (for 5490 data with $I > 2\sigma(I)$), $wR2 = 0.0464$ (all data), and 302 parameters. CCDC xxxxxx. All three structures were determined routinely.

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