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Versatile Routes to Selenoether Functionalised Tertiary Phosphines

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New selenoether functionalised tertiary phosphines, based on aryl (2a, 2b) or alkyl (3a) backbones, have been synthesised and characterised. P,Se-chelation has been achieved upon complexation to square-planar PtIV (3a) or PdIV (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 catalytic applications.4 Tertiary phosphines with an additional selenium donor centre have been very poorly developed in comparison to their lighter Group 16 counterparts.3 In contrast, numerous tertiary phosphine selenides (R3P=Se) have been documented8 and there has been much recent interest in the soft/hard donor atom combination.1

We 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-tetramethyldiamantyl 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.

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.1 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 ºC 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 [31P(Se) 139 Hz] and δ(P)≈−34.6 ppm [31P(Se) 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 phosphadiamantyl cage and selenoether group. Metric parameters are broadly as anticipated and the transannular P(1)···Se(1) separation of 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); 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 CDC13/(CH3)2SO or CH2Cl2 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) 2.356(5) for 2a; Pd(1)–Se(1) 2.365(2) for 2b] are consistent with selenoether coordination. 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 4.9º and 11.4º respectively indicating marginal folding. In the free ligand 2a, the dihedral angle is 54.1º which expands to 87.0º for 3a and 82.1º 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. 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).

**Fig. 2** Molecular structures of (a) 3a and (b) 3b. All C–H hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg) for 3a Pt(1)–P(1) 2.2094(11), Pt(1)–Se(1) 2.356(5), Pt(1)–Cl(1) 2.366(8), Pt(1)–Cl(2) 2.314(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) 2.261(4), Pd(1)–Se(1) 2.365(2), Pd(1)–Cl(1) 2.350(4), Pd(1)–Cl(2) 2.318(5); P(1)–Pd(1)–Se(1) 87.902(12), P(1)–Pd(1)–Cl(1) 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 reaction of PhP(CH2)2CH2 with PhSeH afforded solid 4 (Scheme 2) regioselectively which has been characterised (δ(P) = -15.4). Reaction of the anti-Markovnikov product 4 with PdCl2(cod) gave the five-membered chelate complex 5 displaying the expected spectroscopic and analytical properties. The significant downfield shift in the 31P{1H} NMR spectrum of 5 [δ(P) 62.3 ppm] is fully consistent with coordination of both P and Se donor atoms to a single Pd(II) metal centre.

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, C21H22O7PSe: Mr = 447.35, orthorhombic, space group P212121, 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, χ(Mo-Kα) = 0.71073 Å, 17792 data measured, 4890 unique (Rint = 0.0366), dw = 1.466 g cm−3, R = 0.0391 (for 4049 data with I > 2σ(I)), wR2 = 0.0858 (all data), and 248 parameters. CCDC xxxxxx. For 3a, C21H22O7PSe: Mr = 683.31, monoclinic, space group P21/n, a = 11.2539(7) Å, b = 13.4809(8) Å, c = 14.7665(9) Å, β = 101.0079(10)º, V = 2199.0(2) Å3, T = 150(2) K, Z = 4, χ(Mo-Kα) = 0.71073 Å, 19234 data measured, 5350 unique (Rint = 0.0357), dw = 2.064 g cm−3, R1 = 0.0276 (for 4130 data with I > 2σ(I)), wR2 = 0.0557 (all data), and 262 parameters. CCDC xxxxxx. For 3b, C21H22Cl2OPdSe2Cl2CH2Cl2: Mr = 709.58, triclinic, space group P 1, a = 11.0639(5) Å, b = 11.0640(5) Å, c = 11.7585(5) Å, α = 89.7421(7)º, β = 76.3793(7)º, γ = 68.4046(6)º, V = 1298.32(10) Å3, T = 150(2) K, Z = 2, χ(Mo-Kα) = 0.71073 Å, 11577 data measured, 6012 unique (Rint = 0.0110), dw = 1.815 g cm−3, R1 = 0.0188 (for 5490 data with I > 2σ(I)), wR2 = 0.0464 (all data) and 302 parameters. CCDC xxxxxx. All three structures were determined routinely.

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