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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 (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 catalytic applications. 4 Tertiary phosphines with an additional 20 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,6 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 [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 phosphadaadamantyl 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) 102.4(1), Se(1)–C(7)–C(8) 119.7(2), C(13)–P(1)–C(16) 92.4(1). 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

Scheme 1

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† Electronic Supplementary Information (ESI) available: [Experimental procedures, spectroscopic data and additional X-ray figures]. See DOI: 10.1039/b000000x/
diffusion of diethyl ether into either a CDCl$_3$/(CH$_3$)$_2$SO or CH$_2$Cl$_2$ 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. 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.

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


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