Versatile Routes to Selenoether Functionalised Tertiary Phosphines

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Experimental Section

Materials. Reactions were carried out under aerobic conditions unless otherwise stated. Dichloromethane was previously distilled over CaH₂ and diethyl ether over sodium/benzophenone. All chemicals were obtained from commercial suppliers and used without further purification. AdPH was a kind donation from Cytec Canada Inc. The bromophosphine 2-Ph₂PC₆H₄Br 1a was prepared according to a previously reported procedure.¹ The metal precursors PdCl₂(PhCN)₂ and MCl₂(cod) (M = Pd, Pt) were synthesised according to known procedures.²,³

Instrumentation. FT–IR spectra were recorded as pressed KBr pellets over the range 4000–400 cm⁻¹ using a Perkin-Elmer system 2000 FT spectrometer. ¹H NMR and ³¹P{¹H} NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) reported relative to external TMS or 85% H₃PO₄. Coupling constants (J) in Hz. All NMR spectra were recorded in CDCl₃ solutions at ca. 298 K. Elemental analyses (Perkin-Elmer 2400 CHN or Exeter Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry. Compound 1b was analysed (JEOL SX102 instrument) by fast atom bombardment (FAB) in a positive ionization mode using a 3-nitrobenzyl alcohol (NOBA) matrix. Compounds 2a, 3a and 3b were analysed (Finnigan MAT 95XP instrument) by low-resolution EI (positive ionisation mode) using CH₂Cl₂/CH₃OH as the solvent.

Preparation of 2-AdPC₆H₄Br, 1b. To a DMA solution (70 cm³) of Pd(OAc)₂ (10.6 cm³ of a 5 x 10⁻³ mol solution, 0.05 mmol) and K(OAc) (2.07 g, 29.2 mmol) was added 1,2-bromo(iodo)benzene (7.5 g, 26.5 mmol) and thoroughly purged with N₂. AdPH (4.9 g, 26.5 mmol) in DMA (30 cm³) was added dropwise over 20 min and the mixture heated to reflux for 2 d under N₂. The solution was cooled, distilled water (50 cm³) added and the product extracted into CH₂Cl₂ (2 x 50 cm³). The organic extracts were combined, washed with saturated KCl solution (50 cm³) and dried over anhydrous MgSO₄. The solution was concentrated under reduced pressure to ca. 20 cm³ and stored at 0 ºC. Solid 1b was filtered off, washed with cold absolute ethanol (2 x 10 cm³) and dried in vacuo. Yield: 5.3 g, 55%. Selected spectroscopic data for 1b: δₚ (162 MHz: CDCl₃) −29.6 ppm. δₜ (400 MHz: CDC1₃): 8.19 (dt, 1H, arom. H), 7.55 (ddd, 1H, arom. H), 7.26 (dt, 1H, arom. H), 7.15 (dt, 1H, arom. H), 2.07–1.33 (m, 16H, PAd) ppm. FAB−MS 371 [M⁺]. Found: C, 49.34; H, 5.29; C₁₆H₂₀O₃BrP·H₂O requires C, 49.37; H, 5.71.

Preparation of 2-Ph₂PC₆H₄SePh, 2a. Freshly ground KOH (0.284 g, 5.05 mmol) was dissolved in DMA (50 cm³), PhSeH (0.579 g, 2.53 mmol) added and the orange solution purged with N₂. Compound 1a (0.784 g, 2.30 mmol), dissolved in DMA (30 cm³), was added to the stirred PhSeH solution over 5 min. After heating at 170 ºC for 3d, the solution was cooled and distilled water (80 cm³) added. After extraction with CH₂Cl₂ (2 x 50 cm³), the organic extracts were combined, washed with water (50 cm³), the organic layer separated and dried over anhydrous MgSO₄. The volume was reduced to ca. 5–10 cm³, distilled water added to afford a white suspension that was stirred overnight. Decantation of the solvent followed by addition of cold absolute EtOH (40 cm³) gave an off-white solid 2a which was collected by filtration and dried in vacuo. Yield: 0.504 g, 53%. Selected spectroscopic data for 2a: δₚ (162 MHz: CDC1₃) −10.0 ppm. δₜ (400 MHz: CDCl₃): 7.46–7.12 (m, 19H, arom. H) ppm. FAB−MS 418 [M⁺]. Found: C, 49.34; H, 5.29; C₂₄H₁₉PSe·0.25H₂O requires C, 49.37; H, 5.71.

Preparation of 2-AdPC₆H₄SePh, 2b. Compound 1b (0.373 g, 1.005 mmol), dissolved in DMA (30 cm³), was added dropwise to a solution of PhSeH (0.158 g, 1.005 mmol) and KOH (0.085 g, 1.110 mmol) in DMA (30 cm³). The mixture was stirred at 160 ºC for 7 d under N₂, cooled and water (60 cm³) added to afford a light brown suspension. CH₂Cl₂ (2 x 60 cm³) was added and the combined extracts washed with water (60 cm³), separated and the organic layer dried over anhydrous MgSO₄.
Reduction of the solvent to ca. 15 cm³, precipitation with water (30 cm³) gave a cloudy suspension that was stirred for 12 h affording a brown solid. The solvent was decanted, cold absolute ethanol (20 cm³) added and 2b filtered and dried in vacuo. Yield: 0.178 g (40%). Selected spectroscopic data for 2b: $\delta_P$ (162 MHz: CDCl₃) –34.6 ppm, $^3J_{PSe}$ 201 Hz, $\delta_H$ (400 MHz: CDCl₃): 8.10 (dt, 1H, arom. H), 7.51–7.27 (m, 5H, arom. H), 7.09 (dt, 1H, arom. H), 7.05 (dt, 1H, arom. H), 6.97 (ddd, 1H, arom. H), 2.10–1.35 (m, 16H, PAd) ppm. Found: C 58.52, H 5.65; C₂₂H₂₅PO₃Se requires C 59.07, H 5.63. Suitable crystals for X-ray crystallography were obtained by vapour diffusion of diethyl ether into a CDCl₃ solution of 2b.

Preparation of PtCl₂(2-Ph₂PC₆H₄SePh) 3a. To a CH₂Cl₂ (10 cm³) of PtCl₂(cod) (0.074 g, 0.20 mmol) was added solid 2a (0.093 g, 0.22 mmol) in one portion. The yellow solution was stirred for 35 min and the volume concentrated, under reduced pressure, to ca. 2–3 cm³. Addition of diethyl ether (20 cm³) afforded 3a which was collected by suction filtration and dried in vacuo. Yield: 0.130 g, 96%. Selected spectroscopic data for 3a: $\delta_P$ (162 MHz: CDCl₃) 36.6 ppm, $^1J_{PtP}$ 3555 Hz, $^2J_{PSe}$ 68 Hz. $\delta_H$ (400 MHz: CDCl₃): 7.85–7.15 (m, 19H, arom. H) ppm. EI−MS 684 [M⁺]. Found: C, 42.42; H, 2.97; C₂₄H₁₉Cl₂PPtSe requires C, 42.18; H, 2.81. Suitable crystals for X-ray crystallography were obtained by vapour diffusion of diethyl ether into a CDCl₃/(CH₃)₂SO solution of 3a.

Preparation of PdCl₂(2-AdPC₆H₄SePh) 3b. To a CH₂Cl₂ (7 cm³) of PdCl₂(PhCN)₂ (0.031 g, 0.082 mmol) was dropwise added a CH₂Cl₂ (7 cm³) solution of 2b (0.037 g, 0.082 mmol) over 10 min. The yellow solution was stirred for ca. 3.5 h, the volume concentrated under reduced pressure to ca. 2–3 cm³ and Et₂O (20 cm³)/petroleum ether (60–80ºC, 50 cm³) added. The solid 3b was collected by suction filtration and dried in vacuo. Yield: 0.031 g, 61%. Selected spectroscopic data for 3b: $\delta_P$ (162 MHz: CDCl₃) 46.6, 45.9 ppm. $\delta_H$ (400 MHz: CDCl₃): 8.48 (t, 1H, arom. H), 8.42 (m, 1H, arom. H), 7.88 (d, 1H, arom. H), 7.73–7.25 (m, 15H, arom. H), 4.13 (m, 2H, CH₂), 2.16–0.92 (m, 30H, PAd) ppm. EI−MS 590 [M−Cl⁺]. Found: C, 41.76; H, 3.81; C₂₂H₂₅Cl₂PO₃PdSe requires C, 41.38; H, 3.97. Suitable crystals for X-ray crystallography were obtained by vapour diffusion of diethyl ether into a CH₂Cl₂ solution of 3b.

Preparation of Ph₂P(CH₂)₂SePh, 4. Vinylidiphenylphosphine (0.30 g, 1.41 mmol) was placed in a Schlenk tube and heated to 110 ºC. Selenophenol (0.22 g, 1.40 mmol) was added and the reaction mixture stirred for 5 min. After addition of AIBN (0.05 g), the mixture was stirred at 110 ºC for 14 h. Whilst at 80 ºC the contents of the Schlenk tube were placed under vacuum for 6 h to remove any volatile side products. Solid 4 was collected, after cooling, and used directly in co-ordination studies. Selected spectroscopic data for 4: $\delta_P$ (162 MHz: CDCl₃) –15.4 ppm. $\delta_H$ (400 MHz: CDCl₃): 7.68–7.15 (m, 15H, arom. H), 2.99 (m, 2H, CH₂), 2.56 (m, 2H, CH₂) ppm. Found: C, 64.40; H, 5.16; C₂₀H₁₉PSe requires C, 65.05; H, 5.20.

Preparation of PdCl₂{Ph₂P(CH₂)₂SePh}, 5. To a CH₂Cl₂ (10 cm³) of PdCl₂(cod) (0.077 g, 0.27 mmol) was dropwise added a CH₂Cl₂ (5 cm³) of 4 (0.10 g, 0.27 mmol) over 10 min. The solution was stirred for ca. 2 h, the volume concentrated under reduced pressure to ca. 2–3 cm³ and Et₂O (60 cm³) added. The solid 5 was collected by suction filtration and dried in vacuo. Yield: 0.081 g, 55%. Selected spectroscopic data for 5: $\delta_P$ (162 MHz: CDCl₃) 62.3 ppm. $\delta_H$ (400 MHz: CDCl₃): 8.00–7.35 (m, 15H, arom. H), 3.24 (m, 1H, CH₂), 2.84 (m, 3H, CH₂) ppm. Found: C, 43.62; H, 3.16; C₂₀H₁₉Cl₂PPdSe requires C, 43.95; H, 3.50.

References
Additional Single Crystal X-ray Figures

Further figures for all crystallographically characterised compounds reported are included.

ESIFIG1 for 2a showing the full atom numbering scheme.
ESIFIG2 for 3a showing the full atom numbering scheme.
ESIFIG2 for 3b showing the full atom numbering scheme.
Additional Single Crystal X-ray Figures (for 2a, 3a and 3b)

ESIFIG1 for 2a showing the full atom numbering scheme.
ESIFIG2 for 3a showing the full atom numbering scheme.
ESIFIG3 for 3b showing the full atom numbering scheme.