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# 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 $CaH_2$ 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-$Ph_2PC_6H_4Br$ **1a** was prepared according to a previously reported procedure.[1] The metal precursors $PdCl_2(PhCN)_2$ and $MCl_2$(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. $^{1}H$ NMR and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) reported relative to external TMS or 85% $H_3PO_4$. Coupling constants (*J*) in Hz. All NMR spectra were recorded in $CDCl_3$ 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 $CH_2Cl_2/CH_3OH$ as the solvent.

**Preparation of 2-$AdPC_6H_4Br$, 1b.** To a DMA solution (70 $cm^3$) of $Pd(OAc)_2$ (10.6 $cm^3$ 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 $N_2$. AdPH (4.9 g, 26.5 mmol) in DMA (30 $cm^3$) was added dropwise over 20 min and the mixture heated to reflux for 2 d under $N_2$. The solution was cooled, distilled water (50 $cm^3$) added and the product extracted into $CH_2Cl_2$ (2 x 50 $cm^3$). The organic extracts were combined, washed with saturated KCl solution (50 $cm^3$) and dried over anhydrous $MgSO_4$. The solution was concentrated under reduced pressure to *ca.* 20 $cm^3$ and stored at 0 ºC. Solid **1b** was filtered off, washed with cold absolute ethanol (2 x 10 $cm^3$) and dried *in vacuo*. Yield: 5.3 g, 55%. Selected spectroscopic data for **1b**: $\delta_P$ (162 MHz: $CDCl_3$) −29.6 ppm. $\delta_H$ (400 MHz: $CDCl_3$): 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; $C_{16}H_{20}O_3BrP\cdot H_2O$ requires C, 49.37; H, 5.71.

**Preparation of 2-$Ph_2PC_6H_4SePh$, 2a.** Freshly ground KOH (0.284 g, 5.05 mmol) was dissolved in DMA (50 $cm^3$), PhSeH (0.579 g, 2.53 mmol) added and the orange solution purged with $N_2$. Compound **1a** (0.784 g, 2.30 mmol), dissolved in DMA (30 $cm^3$), 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 $cm^3$) added. After extraction with $CH_2Cl_2$ (2 x 50 $cm^3$), the organic extracts were combined, washed with water (50 $cm^3$), the organic layer separated and dried over anhydrous $MgSO_4$. The volume was reduced to *ca.* 5–10 $cm^3$, distilled water added to afford a white suspension that was stirred overnight. Decantation of the solvent followed by addition of cold absolute EtOH (40 $cm^3$) 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**: $\delta_P$ (162 MHz: $CDCl_3$) −10.0 ppm, $^{3}J_{PSe}$ 139 Hz. $\delta_H$ (400 MHz: $CDCl_3$): 7.46–7.12 (m, 19H, arom. H) ppm. FAB–MS 418 [$M^+$]. Found: C, 68.06; H, 4.58; $C_{24}H_{19}PSe\cdot 0.25H_2O$ requires C, 68.33; H, 4.67.

**Preparation of 2-$AdPC_6H_4SePh$, 2b.** Compound **1b** (0.373 g, 1.005 mmol), dissolved in DMA (30 $cm^3$), 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 $cm^3$). The mixture was stirred at 160 ºC for 7 d under $N_2$, cooled and water (60 $cm^3$) added to afford a light brown suspension. $CH_2Cl_2$ (2 x 60 $cm^3$) was added and the combined extracts washed with water (60 $cm^3$), separated and the organic layer dried over anhydrous $MgSO_4$.

Reduction of the solvent to *ca.* 15 cm$^3$, precipitation with water (30 cm$^3$) gave a cloudy suspension that was stirred for 12 h affording a brown solid. The solvent was decanted, cold absolute ethanol (20 cm$^3$) added and **2b** filtered and dried *in vacuo*. Yield: 0.178 g (40%). Selected spectroscopic data for **2b**: $\delta_P$ (162 MHz: $CDCl_3$) −34.6 ppm, ${}^3J_{PSe}$ 201 Hz. $\delta_H$ (400 MHz: $CDCl_3$): 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; $C_{22}H_{25}PO_3Se$ requires C 59.07, H 5.63. Suitable crystals for X-ray crystallography were obtained by vapour diffusion of diethyl ether into a $CDCl_3$ solution of **2b**.

**Preparation of $PtCl_2(2\text{-}Ph_2PC_6H_4SePh)$ 3a.** To a $CH_2Cl_2$ (10 cm$^3$) of $PtCl_2$(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 cm$^3$. Addition of diethyl ether (20 cm$^3$) 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: $CDCl_3$) 36.6 ppm, ${}^1J_{PtP}$ 3555 Hz, ${}^2J_{PSe}$ 68 Hz. $\delta_H$ (400 MHz: $CDCl_3$): 7.85–7.15 (m, 19H, arom. H) ppm. EI–MS 684 [$M^+$]. Found: C, 42.42; H, 2.97; $C_{24}H_{19}Cl_2PPtSe$ requires C, 42.18; H, 2.81. Suitable crystals for X-ray crystallography were obtained by vapour diffusion of diethyl ether into a $CDCl_3/(CH_3)_2SO$ solution of **3a**.

**Preparation of $PdCl_2(2\text{-}AdPC_6H_4SePh)$ 3b.** To a $CH_2Cl_2$ (7 cm$^3$) of $PdCl_2(PhCN)_2$ (0.031 g, 0.082 mmol) was dropwise added a $CH_2Cl_2$ (7 cm$^3$) 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 cm$^3$ and $Et_2O$ (20 cm$^3$)/petroleum ether (60–80ºC, 50 cm$^3$) 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: $CDCl_3$) 46.6, 45.9 ppm. $\delta_H$ (400 MHz: $CDCl_3$): 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, $CH_2$), 2.16–0.92 (m, 30H, PAd) ppm. EI–MS 590 [$M-Cl^+$] Found: C, 41.76; H, 3.81; $C_{22}H_{25}Cl_2PO_3PdSe$ requires C, 41.38; H, 3.97. Suitable crystals for X-ray crystallography were obtained by vapour diffusion of diethyl ether into a $CH_2Cl_2$ solution of **3b**.

**Preparation of $Ph_2P(CH_2)_2SePh$, 4.** Vinyldiphenylphosphine (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: $CDCl_3$) −15.4 ppm. $\delta_H$ (400 MHz: $CDCl_3$): 7.68–7.15 (m, 15H, arom. H), 2.99 (m, 2H, $CH_2$), 2.56 (m, 2H, $CH_2$) ppm. Found: C, 64.40; H, 5.16; $C_{20}H_{19}PSe$ requires C, 65.05; H, 5.20.

**Preparation of $PdCl_2\{Ph_2P(CH_2)_2SePh\}$, 5.** To a $CH_2Cl_2$ (10 cm$^3$) of $PdCl_2$(cod) (0.077 g, 0.27 mmol) was dropwise added a $CH_2Cl_2$ (5 cm$^3$) 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 cm$^3$ and $Et_2O$ (60 cm$^3$) 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: $CDCl_3$) 62.3 ppm. $\delta_H$ (400 MHz: $CDCl_3$): 8.00–7.35 (m, 15H, arom. H), 3.24 (m, 1H, $CH_2$), 2.84 (m, 3H, $CH_2$) ppm. Found: C, 43.62; H, 3.16; $C_{20}H_{19}Cl_2PPdSe$ requires C, 43.95; H, 3.50.

## References

1. P. Machnitzki, T. Nickel, O. Stelzer and C. Landgrafe, *Eur. J. Inorg. Chem.*, 1998, 1029.
2. D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 47
3. J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.

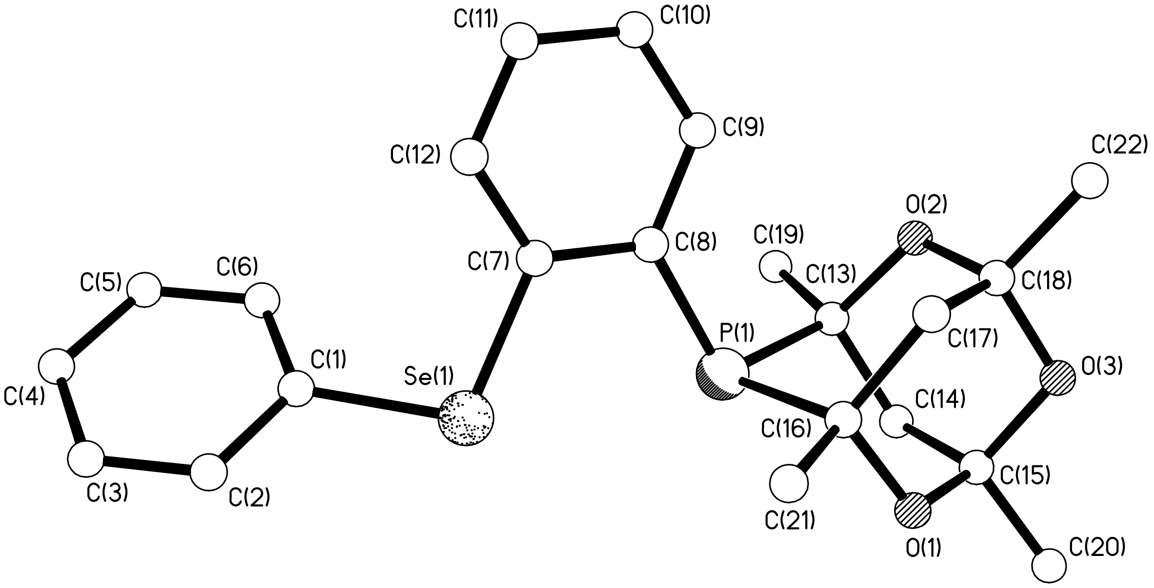
## Additional Single Crystal X-ray Figures

Further figures for all crystallographically characterised compounds reported are included.

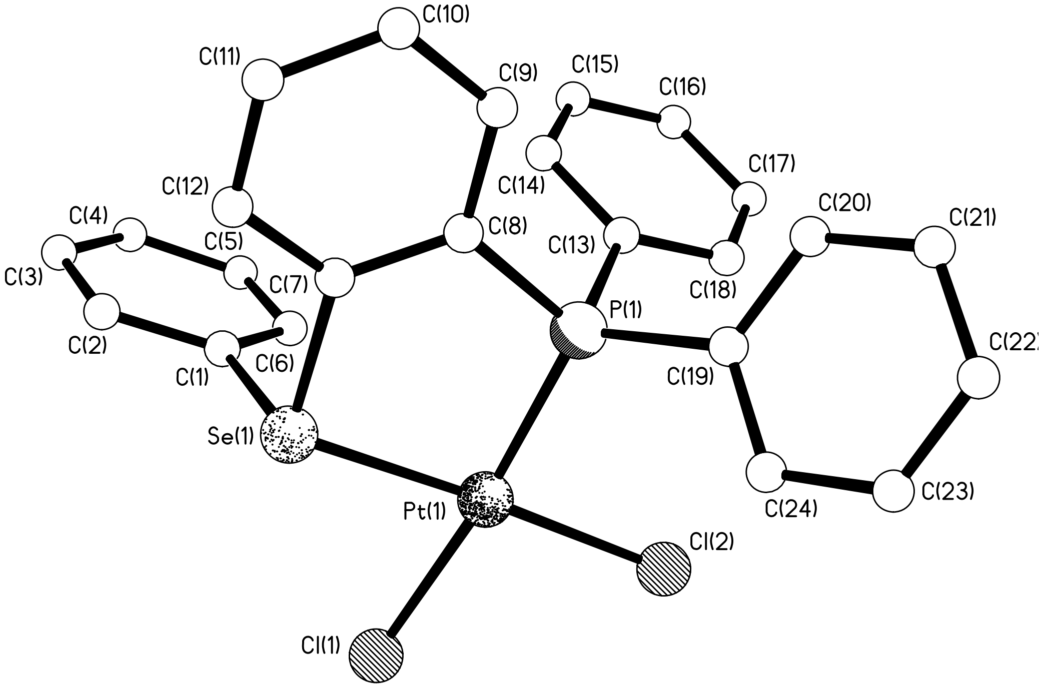
**ESIFIG1** for **2a** showing the full atom numbering scheme.
**ESIFIG2** for **3a** showing the full atom numbering scheme.
**ESIFIG2** for **3b** showing the full atom numbering scheme.

## 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.