

## Nucleophilic addition of phosphine to 1-(*tert*-butyl)-4-vinylbenzene: a short-cut to bulky secondary and tertiary phosphines and their chalcogenides

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### *Selected spectral data*

The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{77}\text{Se}$  NMR spectra were measured on a Bruker DPX 400 (400.13, 100.61, 161.98 and 76.31 MHz, respectively) spectrometer. IR spectra were recorded on a Bruker IFS-25 spectrometer in films.

*Bis*[4-(*tert*-butyl)phenethyl]phosphine (**2**): IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3090, 3050, 3012 [=CH(Ar)]; 2939, 2895, 2855 (CH); 2260 (PH); 1500 [C=C(Ar)]; 1463, 1439, 1420 ( $\delta_{\text{CH}_2}$ ); 1399, 1360, 1330, 1270, 1196 ( $\delta_{\text{CH}}$ ); 1130, 1100, 1010, 977, 923 ( $\delta_{\text{CH(Ar)}}$ ); 835, 817 ( $\delta_{\text{CH}_2}$ ); 716, 559 (P-C).

*Tris*[4-(*tert*-butyl)phenethyl]phosphine (**3**): IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3133, 3092, 3054, 3022 [=CH(Ar)]; 2960 2933, 2903, 2866 (CH); 1517 [C=C(Ar)]; 1464, 1446 ( $\delta_{\text{CH}_2}$ ); 1363, 1268 ( $\delta_{\text{CH}_3}$ ); 807 ( $\delta_{\text{CH(Ar)}}$ ); 561 (P-C).

*Bis*[4-(*tert*-butyl)phenethyl]phosphine oxide (**4a**): yield 93%; colorless powder, mp 132-134 °C (hexane).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ : 1.28 (s, 18H, Me), 2.03-2.10 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.86-2.93 (m, 4H,  $\text{CH}_2\text{Ar}$ ), 6.87 (d, 1H, PH,  $^1J_{\text{PH}}$  454.6 Hz), 7.10-7.28 (m, 8H,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ : 27.26 ( $\text{CH}_2\text{Ar}$ ), 29.96 (d,  $\text{CH}_2\text{P}$ ,  $^1J_{\text{PC}}$  63.4 Hz), 31.37 (Me), 34.43 (CMe), 125.65 ( $\text{C}_{o\text{-Ar}}$ ), 127.85 ( $\text{C}_{m\text{-Ar}}$ ), 137.04 (d,  $\text{C}_{i\text{-Ar}}$ ,  $^3J_{\text{PC}}$  12.8 Hz), 149.60 ( $\text{C}_{p\text{-Ar}}$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 33.13 (d,  $^1J_{\text{PH}}$  454.6 Hz). IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2957, 2918, 2849 (CH); 2292 (PH); 1517 [C=C(Ar)]; 1473, 1463, 1449 ( $\delta_{\text{CH}_2}$ ); 1393, 1376, 1363, 1229 ( $\delta_{\text{CH}}$ ); 1165 (P=O); 1140, 1107, 1034, 1013, 968, 889 ( $\delta_{\text{CH(Ar)}}$ ); 857, 838, 813 ( $\delta_{\text{CH}_2}$ ); 785, 562 (P-C). Found (%): C, 77.67; H, 9.13; P, 7.93. Calc. for  $\text{C}_{24}\text{H}_{35}\text{OP}$  (%): C, 77.80; H, 9.52; P, 8.36.

*Bis*[4-(*tert*-butyl)phenethyl]phosphine selenide (**4b**): yield 91%; colorless powder, mp 93-95 °C (hexane).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.28 (s, 18H, Me), 2.19-2.40 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.85-3.05 (m, 4H,  $\text{CH}_2\text{Ar}$ ), 6.02 (d, 1H, PH,  $^1J_{\text{PH}}$  433.1 Hz), 7.11-7.13 and 7.29-7.31 (m, 8H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 29.17 ( $\text{CH}_2\text{Ar}$ ), 30.24 (d,  $\text{CH}_2\text{P}$ ,  $^1J_{\text{PC}}$  43.9 Hz), 31.34 (Me), 34.44 (CMe), 125.66 ( $\text{C}_{o\text{-Ar}}$ ), 128.02 ( $\text{C}_{m\text{-Ar}}$ ), 136.51 (d,  $\text{C}_{i\text{-Ar}}$ ,  $^3J_{\text{PC}}$  12.5 Hz), 149.70 ( $\text{C}_{p\text{-Ar}}$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.37 (d,  $^1J_{\text{PH}}$  433.1 Hz).

$^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -417.76 (d,  $^1J_{\text{PSe}}$  706.9 Hz). IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3133, 3091, 3055, 3022 [=CH(Ar)]; 2999, 2959, 2903, 2865 (CH); 2329 (PH); 1608, 1569, 1516 [C=C(Ar)]; 1463, 1439 ( $\delta_{\text{CH}_2}$ ); 1363, 1268, 1203 ( $\delta_{\text{CH}}$ ); 1108, 836, 812 ( $\delta_{\text{CH(Ar)}}$ ); 481, 463 (P=Se). Found (%): C, 66.56; H, 8.19; P, 7.17; Se, 17.98. Calc. for  $\text{C}_{24}\text{H}_{35}\text{PSe}$  (%): C, 66.50; H, 8.14; P, 7.15; Se, 18.22.

*Tris[4-(tert-butyl)phenethyl]phosphine oxide (5a)*: yield 98%; colorless powder, mp 145-146 °C (benzene).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.31 (s, 27H, Me), 2.03-2.04 (m, 6H,  $\text{CH}_2\text{P}$ ), 2.89-2.91 (m, 6H,  $\text{CH}_2\text{Ar}$ ), 7.11-7.34 (m, 12H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 27.31 ( $\text{CH}_2\text{Ar}$ ), 30.15 (d,  $\text{CH}_2\text{P}$ ,  $^1J_{\text{PC}}$  62.3 Hz), 31.40 (Me), 34.46 (CMe), 125.66 ( $\text{C}_{o\text{-Ar}}$ ), 127.80 ( $\text{C}_{m\text{-Ar}}$ ), 137.86 (d,  $\text{C}_{i\text{-Ar}}$ ,  $^3J_{\text{PC}}$  12.7 Hz), 149.48 ( $\text{C}_{p\text{-Ar}}$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 47.21. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3090, 3050, 3012 [=CH(Ar)]; 2949, 2900, 2855 (CH); 1510 [C=C(Ar)]; 1463, 1390 ( $\delta_{\text{CH}_2}$ ); 1360, 1270, 1220 ( $\delta_{\text{CH}}$ ); 1150 (P-H); 1100, 1010, 990, 930, 910 ( $\delta_{\text{CH(Ar)}}$ ); 835, 817, 800 ( $\delta_{\text{CH}_2}$ ); 770, 726, 559 (P-C). Found (%): C, 81.57; H, 9.73; P, 5.81%. Calc. for  $\text{C}_{36}\text{H}_{51}\text{OP}$  (%): C, 81.46; H, 9.69; P, 5.84.

*Tris[4-(tert-butyl)phenethyl]phosphine sulfide (5b)*: yield 83%; colorless powder, mp 144-146 °C (hexane).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.31 (s, 27H, Me), 2.12-2.14 (m, 6H,  $\text{CH}_2\text{P}$ ), 2.92-2.94 (m, 6H,  $\text{CH}_2\text{Ar}$ ), 7.15 and 7.33 (m, 12H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 28.12 ( $\text{CH}_2\text{Ar}$ ), 31.40 (Me), 32.82 (d,  $\text{CH}_2\text{P}$ ,  $^1J_{\text{PC}}$  47.6 Hz), 34.46 (CMe), 125.63 ( $\text{C}_{o\text{-Ar}}$ ), 127.96 ( $\text{C}_{m\text{-Ar}}$ ), 137.53 (d,  $\text{C}_{i\text{-Ar}}$ ,  $^3J_{\text{PC}}$  13.6 Hz), 149.48 ( $\text{C}_{p\text{-Ar}}$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 48.69. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3091, 3056, 3024 [=CH(Ar)]; 2961, 2930, 2094, 2866 (CH); 1516 [C=C(Ar)]; 1463, 1448 ( $\delta_{\text{CH}_2}$ ); 1395, 1363 ( $\delta_{\text{CH}_3}$ ); 815 ( $\delta_{\text{CH(Ar)}}$ ); 563 ( $\delta_{\text{PC}}$ ); 589, 550 (P=S). Found (%): C, 79.27; H, 9.23; P, 5.41%; S, 5.84. Calc. for  $\text{C}_{36}\text{H}_{51}\text{PS}$  (%): C, 79.07; H, 9.40; P, 5.66; S, 5.86.

*Tris[4-(tert-butyl)phenethyl]phosphine selenide (5c)*: yield 83%; colorless powder, mp 144-146 °C (hexane).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.33 (s, 27H, Me), 2.23-2.38 (m, 6H,  $\text{CH}_2\text{P}$ ), 2.92-2.93 (m, 6H,  $\text{CH}_2\text{Ar}$ ), 7.15 and 7.32 (m, 12H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 28.85 ( $\text{CH}_2\text{Ar}$ ), 31.52 (Me), 32.37 (d,  $\text{CH}_2\text{P}$ ,  $^1J_{\text{PC}}$  40.8 Hz), 34.46 (CMe), 125.64 ( $\text{C}_{o\text{-Ar}}$ ), 127.99 ( $\text{C}_{m\text{-Ar}}$ ), 137.28 (d,  $\text{C}_{i\text{-Ar}}$ ,  $^3J_{\text{PC}}$  14.0 Hz), 149.57 ( $\text{C}_{p\text{-Ar}}$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 36.79. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3094, 3056, 3024 [=CH(Ar)]; 2961, 2933, 2903, 2865 (CH); 1517 [C=C(Ar)]; 1463, 1447 ( $\delta_{\text{CH}_2}$ ); 1363, 1269 ( $\delta_{\text{CH}_3}$ ); 815 ( $\delta_{\text{CH(Ar)}}$ ); 563 ( $\delta_{\text{PC}}$ ); 467 (P=Se). Found (%): C, 72.63; H, 8.89; P, 5.25; Se, 13.45. Calc. for  $\text{C}_{36}\text{H}_{51}\text{PSe}$  (%): C, 72.83; H, 8.66; P, 5.22; Se, 13.30.