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Synthesis of tris[2-(2-furyl)ethyl]phosphine, its chalcogenides and Pd^{II} complex

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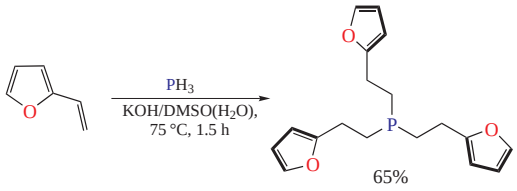
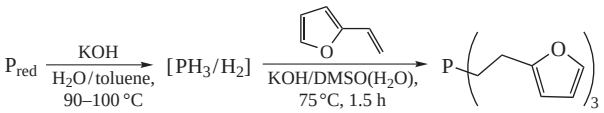
Nucleophilic addition of PH_3 to 2-vinylfuran in the KOH/DMSO(H_2O) suspension affords 65% of tris[2-(2-furyl)ethyl]-phosphine, whose treatment with H_2O_2, Se or $PdCl_2$ gives the corresponding phosphine oxide, selenide and complex of *trans*-[$Pd(L)_2Cl_2$] type in good to excellent yields.



The reaction of phosphine with unsaturated compounds is a convenient atom-economic route to various organic phosphines,[1] which are useful in-demand ligands for multi-purpose metal complexes, stabilizing agents for quantum dots as well as the reagents for organic synthesis.[2] In this line, nucleophilic addition of phosphines to the C=C and C≡C bonds in the KOH/DMSO system attracts a special attention.[3] This superbase system allows one to implement the addition of phosphine to weakly electrophilic C=C bond of substituted styrenes[4] and vinylpyridines[5] and thereby to synthesize the corresponding primary, secondary and tertiary phosphines. Also, the preparation of bis[2-(2-furyl)ethyl]-phosphine by hydrophosphination of 2-vinylfuran with PH_3 in the KOH/DMSO system containing ~70 wt% water (relative to KOH·0.5H_2O) at 60–65 °C for 2.5 h was shortly reported.[6] Note that under above conditions, tris[2-(2-furyl)ethyl]phosphine has not been obtained.[6] It should be emphasized that this phosphine was once formed from 2-vinylfuran and red phosphorus in the complex superbase system K_{met}/NH_3/THF/Bu^{t}OH in 20% yield.[7]

Here, we briefly report the elaboration of a more efficient and convenient synthesis of tris[2-(2-furyl)ethyl]phosphine **1** by nucleophilic addition of PH_3 to 2-vinylfuran in the presence of superbase suspension KOH/DMSO(H_2O).† As a phosphine source, its mixture with hydrogen generated from red phosphorus and aqueous KOH was utilized (Scheme 1). Exhaustive addition



Scheme 1

of PH_3 to 2-vinylfuran occurred under the following conditions. 2-Vinylfuran was heated at 75 °C for 1.5 h in the suspension KOH/DMSO with 20 wt% water (relative to KOH·0.5H_2O) with the steady passing of phosphine through the reaction mixture. The isolated yield of phosphine **1** reached 65% (Scheme 1). The expected intermediate primary and secondary phosphines (^{31}P NMR) in the crude product were detected in about 10 mol%.

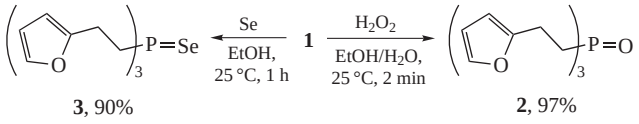
The phosphine **1** is easily oxidized by aqueous hydrogen peroxide (25 °C, 2 min) or elemental selenium (EtOH, 25 °C, 1 h) to afford the corresponding phosphine chalcogenides **2** and **3** in 97 and 90%, respectively (Scheme 2).‡

The coordination proprieties of phosphine **1** were preliminarily evaluated by the formation of its complex with $PdCl_2$ (Scheme 3). The complexation readily occurs at ambient temperature (CH_2Cl_2, 5 h) to furnish complex **4** in 72% yield.§

† ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer (at 400.13, 100.62 and 161.98 MHz) at ambient temperature and referenced to internal HDMS (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P) standards. FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer. The microanalyses were performed on a Flash EA 1112 Series analyzer. 2-Vinylfuran was synthesized by $CuSO_4$-catalyzed decarboxylation of 3-(2-furyl)acrylic acid. KOH·0.5H_2O, DMSO (1% water content) and red phosphorus (KSAN 'SIA') were employed as purchased. The PH_3 was generated as mixture with H_2 by dropwise addition of 50%-aqueous KOH solution to stirred and heated (90–100 °C) suspension of red phosphorus (10 g) in toluene (20 ml).[4(a)] All reactions were carried out under argon atmosphere.

Safety Note. Phosphine gas is toxic and explosive. It should be handled with extreme care.

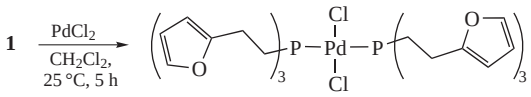
Tris[2-(2-furyl)ethyl]phosphine **1**. To a suspension of powdered KOH·0.5H_2O (20.0 g, 307 mmol), DMSO (50 ml) and water (4 ml), saturated with phosphine, a solution of 2-vinylfuran (10.0 g, 106 mmol) in DMSO (10 ml) was added dropwise for 1.5 h at 75 °C under stirring and continuous passing of phosphine. The mixture was cooled to 20–25 °C, diluted with water (100 ml) and extracted with diethyl ether (2 × 60 ml). The extract was washed with water (2 × 30 ml), dried over K_2CO_3, the solvent was removed, and the residue was fractionized *in vacuo* to give 7.28 g (65%) of phosphine **1**. Colourless oil, bp 200 °C (1.5 Torr). It should be handled under inert atmosphere to prevent its oxidation. ^{1}H NMR ($CDCl_3$) δ: 1.80–2.05 (m, 6H, CH_2P), 2.82–2.83 (m, 6H, CH_2Fur), 6.05, 6.24 and 7.28 (br.s, 9H, Fur). ^{13}C NMR ($CDCl_3$) δ: 19.1 (d, CH_2Fur, $^2J_{PC}$ 11.1 Hz), 26.5 (d, CH_2P, $^1J_{PC}$ 11.5 Hz), 105.1 (s, C-3 Fur), 109.5 (s, C-4 Fur), 140.3 (s, C-5 Fur), 154.6 (s, C-2 Fur). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: –28.96 (lit.,[7] δ_P –27.8). Found (%): C, 68.05; H, 7.12. Calc. for $C_{18}H_{21}O_3P$ (%): C, 68.34; H, 6.69.



3, 90% **2**, 97%

Scheme 2

According to X-ray diffraction analysis,¶ the Pd atom in complex **4** is located on 2-fold rotation axis and coordinated by two phosphorus atoms and by two chlorine atoms in *trans*-configuration (Figure 1). The values of the P–Pd–P and Cl–Pd–Cl



4, 72%

Scheme 3

‡ *Tris[2-(2-furyl)ethyl]phosphine oxide* **2**. To a solution of phosphine **1** (0.344 g, 1.1 mmol) in ethanol (15 ml), 35% aqueous H_2O_2 (0.5 ml, ~5.8 mmol) was added. The mixture was stirred at ambient temperature for 1–2 min, then diluted with water (30 ml) and extracted with $CHCl_3$ (2 × 20 ml). The extract was washed with water (2 × 20 ml) and dried over K_2CO_3. The solvent was removed and residue was dried *in vacuo* to give 0.350 g (97%) of **2**. Colorless powder, mp 108–109 °C. ^{1}H NMR ($CDCl_3$) δ: 1.98–2.05 (m, 6H, CH_2P), 2.89–2.86 (m, 6H, CH_2Fur), 6.04, 6.27 and 7.30 (br. s, 9H, Fur). ^{13}C NMR ($CDCl_3$) δ: 20.2 (s, CH_2Fur), 26.4 (d, CH_2P, $^1J_{PC}$ 64.2 Hz), 105.6 (s, C-3 Fur), 110.3 (s, C-4 Fur), 141.3 (s, C-5 Fur), 153.6 (d, C-2 Fur, $^3J_{PC}$ 13.7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 46.33. FT-IR (KBr, ν/cm^{-1}): 1162, 1148 ($\nu_{P=O}$), 731 (ν_{P-C}). Found (%): C, 64.88; H, 6.45. Calc. for $C_{18}H_{21}O_4P$ (%): C, 65.05; H, 6.37.

Tris[2-(2-furyl)ethyl]phosphine selenide **3**. To a solution of phosphine **1** (0.445 g, 1.4 mmol) in ethanol (15 ml), powdered gray selenium (0.111 g, 1.4 mmol) was added and the suspension was stirred at ambient temperature for 1 h. Ethanol was removed *in vacuo* and the residue was washed with hexane and dried *in vacuo* to give 0.500 g (90%) of **3**. Colorless powder, mp 78–80 °C (light petroleum). ^{1}H NMR ($CDCl_3$) δ: 2.17–2.24 (m, 6H, CH_2P), 2.92–2.99 (m, 6H, CH_2Fur), 6.05, 6.27 and 7.29 (m, 9H, Fur). ^{13}C NMR ($CDCl_3$) δ: 21.9 (s, CH_2Fur), 28.5 (d, CH_2P, $^1J_{CP}$ 43.1 Hz), 105.9 (s, C-3 Fur), 110.2 (s, C-4 Fur), 141.3 (s, C-5 Fur), 153.1 (d, C-2 Fur, $^3J_{CP}$ 14.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 38.25 (satellites: $^1J_{PC}$ 43.1 Hz, $^1J_{PSe}$ 706 Hz). FT-IR (KBr, ν/cm^{-1}): 735 (ν_{P-C}), 530 ($\nu_{P=Se}$). Found (%): C, 54.61; H, 5.56. Calc. for $C_{18}H_{21}O_3PSe$ (%): C, 54.69; H, 5.35.

§ trans-*Dichloro-bis{tris[2-(2-furyl)ethyl]phosphine}palladium(II)* **4**. To a solution of phosphine **1** (0.192 g, 0.61 mmol) in CH_2Cl_2 (7 ml), $PdCl_2$ (0.049 g, 0.28 mmol) was added. The suspension was stirred at ambient temperature for 5 h, then filtered and evaporated *in vacuo*. The residue obtained was re-crystallized from hot hexane/CH_2Cl_2 mixture and dried *in vacuo* to give 0.161 g (72%) of complex **4**. Yellow crystals, mp 112–113 °C (hexane). The X-ray quality crystals were grown by slow evaporation of CH_2Cl_2 solution of **4** (20–23 °C, several days). ^{1}H NMR ($CDCl_3$) δ: 2.15–2.25 (m, 12H, CH_2P), 2.92–3.02 (m, 12H, CH_2Fur), 6.01–6.06, 6.21–6.26 and 7.20–7.25 (m, 18H, Fur). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 12.13. Found (%): C, 53.25; H, 5.40; P, 7.65. Calc. for $C_{36}H_{42}Cl_2O_6P_2Pd$ (%): C, 53.38; H, 5.23; P, 7.37.

¶ *Crystal data for* **4**. $C_{36}H_{42}Cl_2O_6P_2Pd$, M = 809.94 g mol^{-1}, monoclinic, space group C_2/c, a = 13.1944(4), b = 18.0483(5) and c = 16.0088(5) Å, β = 91.661(1)°, V = 3810.7(2) Å^3, Z = 4, d_{calc} = 1.412 g cm^{-3}, μ = 0.753 mm^{-1}, T = 200(2) K, scanning area 2θ < 61.0°, 19825 reflections measured, 5725 unique (R_{int} = 0.0248), 4835 reflections with $I \geqslant 2\sigma(I)$, 277 refined parameters, $R_1[I \geqslant 2\sigma(I)]$ = 0.0365, wR_2 = 0.1296 (all data). Data were collected on a Bruker Apex II CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares method against all F^2 in anisotropic approximation for non-hydrogen atoms using the SHELX-97 programs set.[11] Hydrogen atoms were included at geometrically calculated positions during the refinement using the riding model.

CCDC 1447020 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

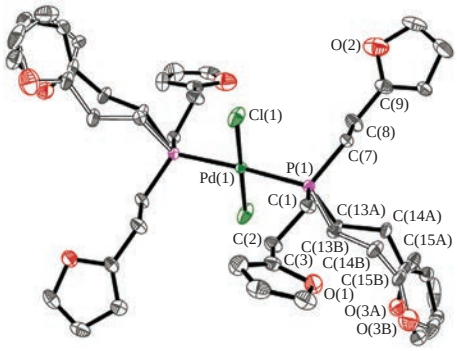


Figure 1 X-ray structure of complex **4** (the H atoms are omitted for clarity). Selected bond lengths (Å) and bond angles (°): Pd(1)–Cl(1) 2.2921(7), Pd(1)–P(1) 2.3136(6), P(1)–C 1.819(3)–1.843(6); P(1)–Pd(1)–P(1′) 176.08(3), Cl(1′)–Pd(1)–Cl(1) 179.52(6). The torsion angle Cl(1′)–Pd(1)–P(1)–C(13A) 2.8(6).

bond angles [176.08(3)° and 179.52(6)°, respectively] indicate the distorted square planar geometry of the Pd atom. The deviation of the latter from the mean PdP_2Cl_2 plane is 0.028 Å. The Pd–P and Pd–Cl distances are comparable with those in related complexes.[8] Note that the one of three 2-(2-furyl)ethyl fragments of the ligand, *viz*. C(13)–C(18), is disordered over two positions in the ratio of 0.53(1) : 0.47(1).

In summary, a novel atom-economic expedient synthesis of previously inaccessible tris[2-(2-furyl)ethyl]phosphine has been elaborated based on nucleophilic addition of phosphine to 2-vinylfuran in the KOH/DMSO(H_2O) suspension. Some basic reactions of the synthesized phosphine (oxidation with H_2O_2 or elemental selenium and complexation with $PdCl_2$) demonstrate its high reactivity and potential for diverse applications. For example, the synthesized compounds with furyl moieties can be of interest for drug-oriented products since numerous furan derivatives are important pharmaceuticals[9] and bioactive natural products.[10] Furthermore, tris[2-(2-furyl)ethyl]phosphine and its chalcogenides can be promising polydentate ligands for design of in-demand polynuclear complexes.

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