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# One-pot synthesis of ultra-branched mixed tetradentate tripodal phosphines and phosphine chalcogenides

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ABSTRACT

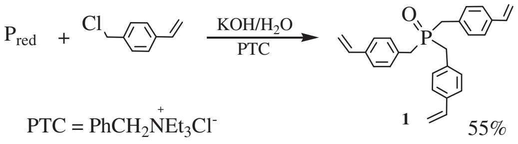
Ultra-branched mixed tetradentate tripodal phosphines and phosphine chalcogenides have been synthesized by the exhaustive regioselective addition of secondary phosphines, phosphine sulfides and phosphine selenides to available tris(4-vinylbenzyl)phosphine oxide under free-radical conditions (UV irradiation or AIBN) in good to excellent yields.

## 1. Introduction

Tetradentate tripodal ligands containing phosphine moieties are widely used for design of multi-purpose metal complexes.[1,2] For instance, complexes of Cr(III),[1] Fe(II, III),[1,3] Co(II),[1,4] Ni(II),[5] Mo(III),[1,6] Ru(II),[1,2,7] Rh(II),[1,4,8] Pd(II),[9,10] W(III),[2a,6] Os(II),[1,7b,c] Ir(II),[1] Pt(II),[1,9] Hg(II),[11] and polynuclear complexes[12] with tris[(2-diphenylphosphano)ethyl]phosphine, $(Ph_2PCH_2CH_2)_3P$ ($PP_3$), which is now one of the most thoroughly studied tetradentate tripodal ligands, act as catalysts for a variety of organic transformations.[1,3d,g,13,14] Complexes of $PP_3$ with Ru are applied for preparation of diagnostic radiopharmaceutical imaging agents[15] and complexes of this ligand with Ag and Au display intense luminescent emission at room and low temperatures.[16] In recent years, mixed chalcogene derivatives of $PP_3$ ($PP_3X_n$, X=O, S, Se; $n$=1–4) are also employed for the design of organometallic catalysts[17] and useful materials.[18] For example, rhodium complexes of $PP_3X_4$ catalyze the carbonylation of methanol to acetic acid and its ester.[17e] The readily regenerative and air-stable Pd complex, $[Pd(PP_3S_4)(dba)]$, has been used as a C–C coupling catalyst.[17b–e]

One of the limitations in the controlled design of such complexes is inaccessibility of tetradentate tripodal phosphines ligands and their derivatives, especially their polyphosphine chalcogenides. The conventional syntheses of these ligands are laborious and multistep. The known protocols utilize moisture- and air-sensitive phosphorus halides and organometallic compounds often accompanied by side-reactions.[2b,19] Besides, the reported $PP_3$ is limited by the representatives with just a few substituents (Me, Et, Cy, Ph) at the phosphorus atom. Therefore, the development of new more straightforward phosphorus halide-free approaches to various tetraphosphines and tetraphosphine chalcogenides is of standing synthetic importance.

A promising approach to the synthesis of novel tetradentate tripodal ligands could be the reaction of radical addition of secondary phosphines and phosphine chalcogenides to trialkenylphosphines or their chalcogenides. This stimulated us to pay attention to the readily available tris(4-vinylbenzyl)phosphine oxide (**1**) as a possible parent starting compound capable of adding the diverse phosphines and phosphine chalcogenides across its three double bonds. Phosphine oxide **1** is now easily prepared in a one-pot procedure by direct phosphorylation of commercially available 4-vinylbenzylchloride with red phosphorus (Scheme 1).[19]



**Scheme 1.** Synthesis of tris(4-vinylbenzyl)phosphine oxide.

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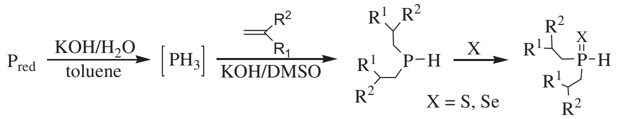
In this work, for the addition to phosphine oxide **1**, we have used accessible secondary phosphines **2**–**4** and phosphine chalcogenides **8**–**16**, which are readily synthesized from aryl- and hetarylalkenes and red phosphorus in superbasic system KOH/DMSO (Scheme 2).[20a,21]



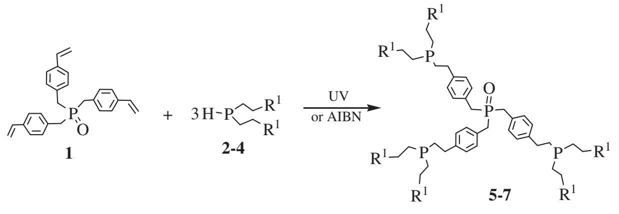
**Scheme 2.** Synthesis of secondary phosphines and phosphine chalcogenides.

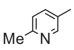
## 2. Results and discussion

The presence of three vinyl groups in phosphine oxide **1** assumes the formation of mono- and diadducts as well as products of polymerization of both initial compound **1** and intermediate adducts. Therefore, this study is aimed at the search for appropriate conditions for chemoselective synthesis of tetradentate tripodal phosphines and phosphine chalcogenides.

As our experiments have shown, under free-radical initiations, phosphine oxide **1** adds phosphines **2**–**4** regioselectively to give anti-Markovnikov adducts **5**–**7** in 60–80% yield (Table 1). The target exhaustive addition reactions have been realized using the 1:3 reactant molar ratio, respectively, UV irradiation in benzene (method *A*) or AIBN at 65–70 °C in 1,4-dioxane (method *B*), all experiments being carried out under argon.

**Table 1**
Exhaustive addition of secondary phosphines **2**–**4** to phosphine oxide **1**



| Entry | Secondary phosphine | R$^1$ | Method[a]/time (h) | Product[b] | Yield[c] (%) |
|---|---|---|---|---|---|
| 1 | **2** | Et | B/7.5 | **5** | 48 (70) |
| 2 | **3** | Ph | A/7.5 | **6** | 80 (96)[d] |
| 3 | | | B/10 | | 60 (70)[e] |
| 4 | **4** |  | A/15 | **7** | 63 (85) |

[a] Standard reaction conditions: molar ratio **1**/**2**–**4**=1:3, argon. Method *A*: UV, 25–30 °C (heating resulted from irradiation), benzene. Method *B*: AIBN (1.5–2 wt % of the reactants' mass), 65–70 °C, 1,4-dioxane.

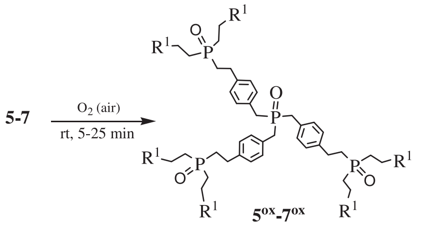
[b] Triphosphines **5**, **7** were isolated as tetraoxides **5**$^{ox}$, **7**$^{ox}$, the corresponding phosphines **5**, **7** were identified in the reaction mixture by $^{31}$P NMR.

[c] Isolated yield ($^{31}$P NMR yield was given in parentheses).

[d] Triphosphine **6** was isolated.

[e] Triphosphine oxide **6**$^{ox}$ was prepared.

The reaction has been monitored by $^{31}$P NMR spectroscopy to follow the disappearance of the signals of the initial secondary phosphines **2**–**4** at $-71\div-68$ ppm and appearance of the signals of the forming triadducts **5**–**7** at $-30\div-23$ ppm. Under the above conditions, the reaction is highly regio- and chemoselective to give almost exclusively anti-Markovnikov triadducts ($^1$H, $^{13}$C, $^{31}$P NMR): mono- and diadducts were discernible in the reaction mixtures only in trace amounts. As anticipated, triphosphines **5**–**7** are easily oxidized by air during the isolation and characterization to give the corresponding tetraphosphine oxides **5**$^{ox}$–**7**$^{ox}$ (Scheme 3).



**Scheme 3.** Oxidation of triphosphines **5**–**7**.

Using phosphine **3** as an example, we have shown that under UV irradiation (benzene, 25–30 °C), phosphination of phosphine oxide **1** proceeds more effectively and selectively than in the presence of AIBN (1,4-dioxane, 65–70 °C): yield of triadduct **6** reaches 80% (method *A*) versus 60% (method *B*), Table 1, cf. entries 2 and 3. In the latter case noticeable amounts of insoluble polymer are formed, likely due to the polymerization of the initial phosphine oxide **1** and/or intermediate mono- and diadducts.

Under similar free-radical initiation, secondary phosphine sulfides **8**–**12** and phosphine selenides **13**–**16** undergo ready addition to phosphine oxide **1** (the reactant molar ratio 3:1, respectively) to afford, in the case of UV irradiation (benzene, 25–30 °C), corresponding anti-Markovnikov triadducts **17**–**25**, tetradentate tripodal phosphine chalcogenides, in high yields (Table 2).

As with the secondary phosphines (Table 1), the UV-initiated reaction of phosphine oxide **1** with phosphine chalcogenides **8**–**16** (method *A*) is preferred over AIBN-promoted one (method *B*): the yield of triadduct **17** is by 1.5 times higher and the reaction time is significantly shorter (Table 2, entry 1). Noteworthy, the nature of the solvent substantially influences the efficacy of the reaction studied. In the example of phosphine sulfide **8**, it has been demonstrated that UV irradiation of the reactants in 1,4-dioxane (instead of benzene) leads to a cross-linked polymer in almost quantitative yield. The structure and composition of this polymer was similar to that of the phosphine oxide **1** homopolymer, prepared and characterized previously.[22]

As seen from Tables 1 and 2, diverse secondary phosphines and phosphine chalcogenides containing Bu, Ph(CH$_2$)$_2$, PhCH(Me)CH$_2$, 4-$^t$BuC$_6$H$_4$(CH$_2$)$_2$, 4-MeOC$_6$H$_4$(CH$_2$)$_2$, 2-Fur(CH$_2$)$_2$, and 6-Me-3-Py(CH$_2$)$_2$ substituents at phosphorus atom react easily with phosphine oxide **1** that supports the generality of this process.

As exemplified by triadduct **17**, triphosphine sulfides can be readily reduced with metal sodium (reflux toluene) to the corresponding triphosphines (Scheme 4).

Note that secondary phosphine oxides do not react with phosphine oxide **1** under the above free-radical conditions. So, the UV irradiation (20–35 °C, 6 h, benzene) of the mixture of bis(2-phenethyl)phosphine oxide and phosphine oxide **1** gives only polymer of phosphine oxide **1** and the unreacted initial secondary phosphine oxide. This is consistent with the known data about low reactivity of secondary phosphine oxides in the radically induced addition reactions.[23] However, tetraphosphine oxides **5**$^{ox}$–**7**$^{ox}$ can be easily prepared by the oxidation of the corresponding phosphines (Scheme 2).

The results obtained show (Tables 1 and 2) that the reactivity of the PH-addends used in the reaction with phosphine oxide **1** falls in the order: secondary phosphine selenides>secondary phosphine