

Synthesis of the first imidazolyl-triphosphines containing a *Triphos* unit

Jacques Andrieu ^{*}, Michèle Azouri

Laboratoire de Synthèse et Electrosynthèse Organométalliques, UMR 5188 CNRS, Université de Bourgogne, 9 avenue Alain Savary, 21000 Dijon, France

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Abstract

Since biphasic liquid–liquid continuous-flow catalytic processes often require the use of cationic phosphine ligands for the metal sequestration in the polar phase, we have prepared the first imidazolyl triphosphines, named *Triphosim* and *Triphosmim*. These ligands contain the *Triphos* unit [-P(CH₂CH₂PPh₂)] which is linked to the imidazole fragment and have been obtained in three steps from imidazole (or 2-methylimidazole), diethylvinylphosphonate and diphenylvinylphosphine with global yields of 42–48%. The *Triphosim* ligand adopts a tridentate P-coordination mode in a palladium dichloride complex and the reaction of the dangling imidazole function with alkyl halides leads to a new kind of imidazolium-phosphine complexes.

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1. Introduction

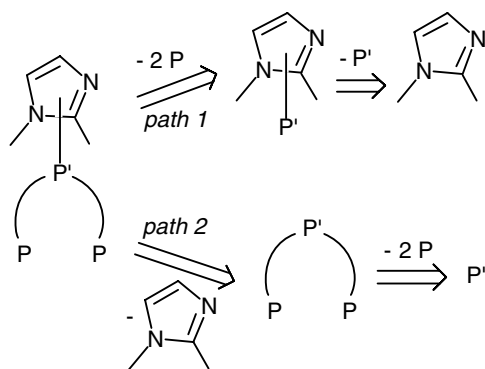
The development of efficient continuous-flow catalytic systems represents a major challenge in modern homogeneous catalysis. However, it requires a perfect immobilisation, or sequestration, of the catalytic species in one liquid phase while the organic products are continuously extracted from the catalytic medium by a mobile phase [1,2]. For example, the association of a nonvolatile solvent has given very good results in Rh catalysed olefins hydroformylation [3,4] or in Ni catalysed styrene hydrovinylation in continuous-flow conditions [5]. Nevertheless, the efficiency of the catalytic processes can still be increased by introduction of a cationic imidazolium fragment on the coordinated phosphines, which strongly decreases the metal-phosphine leaching in the mobile phase [6]. For example, imidazolium monophosphines salts obtained from the neutral bis(1-imidazolylethyl)phosphines were

employed in hydroformylation of 1-octene and no Rh catalyst leaching from the [BMIM](PF₆) ionic phase to the organic layer was observed [7]. In the same manner, the presence of an imidazolium fragment on a chiral 1,4-diphosphine has allowed the rhodium leaching in asymmetric hydrogenation of N-acetylphenylethanamine to decrease from 2% to less than 1 ppm [6]. On the other hand, chelating polydentate phosphines, especially the *Triphos* ligand [PhP(CH₂CH₂PPh₂)₂], offer advantages over mono or diphosphines in homogeneous catalysis. Indeed, the higher nucleophilic character of the metal centre due to the presence of three coordinated phosphorus atoms (i) favours the C–H bond oxidative addition and subsequently increases the catalytic activity of rhenium catalysts in cyclooctane dehydrogenation [8] or of rhodium catalysts in aldehydes decarbonylation [9] or (ii) increases the reactivity of the metal-hydride bond towards the weak polar carbonyl function of an ester [10].

Imidazolyl- or imidazolium-triphosphines are thus very appealing to perform the above catalyses in continuous-flow conditions and we decided to investigate the elaboration of a synthetic method allowing the open access to such unprecedentedly described ligands, see Scheme 1.

^{*} Corresponding author.

E-mail address: Jacques.Andrieu@u-bourgogne.fr (J. Andrieu).



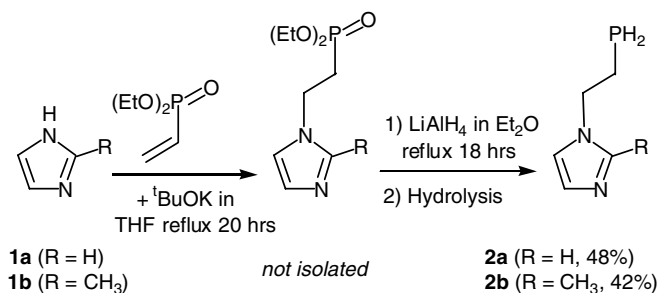
Scheme 1.

2. Results and discussion

Scheme 1 shows two possible pathways for the preparation of triphosphines bearing an imidazole moiety (or an imidazolium group, omitted for the sake of clarity). In contrast to the di- or tri-phosphines which are rather difficult to functionalise [11–13], many syntheses of polyphosphines from monophosphines ligands are well known and some examples are given below. Besides, in the last years, different preparations of imidazolyl or imidazolium mono- [7,14,15] and di-phosphines [7,15–17] have been described. This literature examination drove us to choose path 1 (Scheme 1) to elaborate the first triphosphine imidazole ligands.

The vinylphosphonate esters are interesting building blocks in the synthesis of polyphosphines ligands since the vinyl function can react with P–H bonds of primary (or secondary) phosphines under specific conditions. Moreover, their phosphonate function can easily be reduced to primary or secondary phosphines with LiAlH_4 [18]. By analogy with the Michael type addition, we wished to extend the reactivity from the P–H bond to the N–H bond of imidazoles. We have thus applied the procedure described for the preparation of $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PH}_2$ (from Ph_2PH and $\text{CH}_2=\text{CHP}(\text{=O})(\text{OEt})_2$ [18]) to imidazole **1a** and 2-methylimidazole **1b** (see Scheme 2). Both ligands **2a** and **2b** are obtained in good yields. The presence of the PH_2 group is confirmed by the existence of a triplet at -136.17 and -137.60 ppm with a $J(\text{P},\text{H}) = 193$ Hz, respectively, for **2a** and **2b** in their phosphorus-proton coupled NMR spectra.

The above functional primary phosphines **2a** and **2b** are excellent starting materials in the construction of polyphosphines ligands. Indeed, it was reported that the P–H bond from aryl primary (or secondary) phosphines leads to the $\text{PCH}_2\text{CH}_2\text{P}$ unit by a base-catalysed addition to the $\text{C}=\text{C}$ double bond of vinylphosphines, phenyllithium and the more efficient ${}^t\text{BuOK}$ [19] being the most common catalysts to perform this reaction. It is also interesting to note that a less basic organic catalyst like NEt_3 can also be efficient in this addition reaction, provided that the P–H bond is previously activated by a platinum coordination, although the

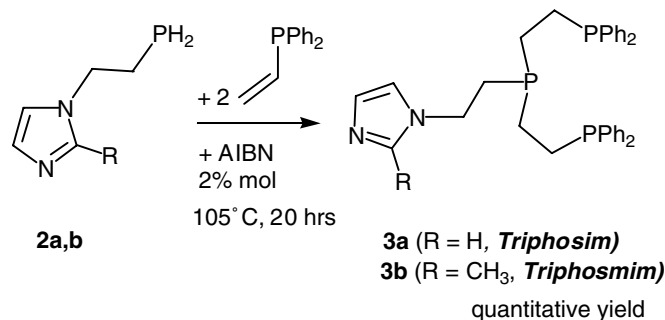


Scheme 2.

reaction does not lead then to free triphosphine ligand [20]. We thus applied a similar procedure to the primary phosphine **2b** in the presence of diphenylvinylphosphine and a catalytic amount of ${}^t\text{BuOK}$ (10 mol%) and heating under THF or toluene reflux for 20 h. The ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the crude product in C_6D_6 reveals the expected ligand **3b** with an unsatisfying conversion of 60%. Thus, an alternate synthetic method has been attempted, based on the anti-Markovnikov radical addition of primary phosphines to vinyl derivatives. Indeed, the addition of phenylphosphine to terminal fluoros olefins can be catalysed by AIBN at about 80°C to lead to the corresponding dialkyl-phenylphosphine in good to excellent yields [21]. We used similar conditions to achieve our transformation of ligand **2** into **3** with only 2 mol% of AIBN per mol of diphenylvinylphosphine, see Scheme 3.

The analysis of NMR phosphorus spectra of the crude products obtained from **2a** and **2b** after reaction at 105°C for 20 h shows a complete and selective conversion to the corresponding imidazolyl- and methylimidazolyl-triphosphine ligands **3a** and **3b**, which have been named, respectively, *Triphosim* and *Triphosmim* (see Scheme 3) due to their very close analogy with the *Triphos* ligand [$\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$]. Their ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra confirm unambiguously the formation of the two $\text{PCH}_2\text{CH}_2\text{P}$ units by the presence of a doublet at $\delta = -0.11$ ppm for the terminal P in both **3a** and **3b** and a triplet at $\delta = -12.63$ ppm and -12.83 ppm for the internal P of **3a** and **3b**, respectively, with a ${}^2J(\text{P},\text{P})$ coupling constant of 27 Hz.

The further addition of an equimolar amount of ligand **3a** to $[\text{PdCl}_2(\text{NCPH}_2)_2]$ leads to the air stable complex **4a**



Scheme 3.

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