

Synthesis and coordination properties of palladium(II) and platinum(II) complexes with phosphonated triphenylphosphine derivatives

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Abstract

Two triphenylphosphine derivatives, diethyl [4-(diphenylphosphanyl)benzyl]phosphonate (**3a**) and tetraethyl {[5-(diphenylphosphanyl)-1,3-phenylene]dimethylene}bis(phosphonate) (**3b**), and also the corresponding free acids **4a** and **4b** were prepared. These ligands were characterized by ¹H, ¹³C and ³¹P NMR spectroscopy and mass spectrometry. A full set of their Pd(II) and Pt(II) complexes of the general formula [MCl₂L₂] and one dinuclear complex *trans*-[Pd₂Cl₄(**3a**)₂] were synthesized and their isomerization behaviour in solution was studied. The complexes were characterized by ¹H, ¹³C, ³¹P and ¹⁹⁵Pt NMR spectroscopy, mass spectrometry and far-IR spectroscopy. The X-ray structures of all complexes with **3a** or **3b** have usual slightly distorted square-planar geometry on the metal ion. Salts of phosphonic acids **4a** and **4b** and their complexes are freely soluble in aqueous solution; therefore, they can be potentially useful in aqueous or biphasic catalysis.

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1. Introduction

Transition metal-phosphine complexes are of great importance for both industrial- and laboratory-scale catalytic applications. Ambitions to use various “field-proven” homogeneous catalysts under aqueous and biphasic conditions made for the synthesis of a vast amount of phosphines modified by hydrophilic groups such as ammonium and phosphonium (cationic), sulfonate, phosphonate and carboxylate (anionic) or alcohol and polyether chain (neutral) [1]. Phosphines modified by phosphonate moiety [2] have been attracting attention as alternatives to well-established sulfonates [1]; several examples of their use in biphasic catalysis have been mentioned in literature [3–17] (e.g., Pd-catalysed electrochemical reduction of CO₂ [3], Rh-catalysed

carbon–carbon double bond hydrogenation or hydroformylation [4,5], Pd-catalysed benzyl halide carbonylation [6] and Suzuki coupling [7]). A great advantage (compared with other hydrophilic moieties) is the possibility to bind the phosphonated ligand to an inert oxide surface (e.g., Al₂O₃) [8], onto activated carbon surface [9] or into a layered framework, e.g., zirconium phosphonate [10,12] or zirconium phosphite/phosphonate hybrid material [13]. Such supported catalysts have been successfully tested in Rh-catalysed alkene hydroformylation [12,14], Rh-catalysed methanol carbonylation [9,15], Ru-catalysed asymmetric β-keto ester hydrogenation [4,11] or Heck reaction [13]. Several tests were also performed in organic solvents under homogeneous conditions (e.g., Pt/Sn-catalysed alkene hydroformylation [11], Rh-catalysed methanol carbonylation [16] and Rh-catalysed styrene hydroformylation [17]).

Here we present the synthesis of triphenylphosphine-based ligands bearing one or two diethyl phosphonomethyl

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groups (**3a** and **3b**) and corresponding acids (**4a** and **4b**) (Fig. 1) as well as a study of their Pd(II) and Pt(II) complexes. The ligand design promises similar coordination behaviour and catalytic activity as is known for triphenylphosphine, good solubility in water and flexible strong attachment to a solid surface. The *ortho* and *meta* isomers of **3a** and **4a** (and their disodium salts) were already reported by Liek et al. [7] having been used as catalysts in Pd-catalysed Suzuki coupling under biphasic conditions with satisfactory results. Later, also the *para* isomer has been mentioned [14] in a set of phosphanyl-phosphonates (including **4a** and its disodium salt) and experiments on Rh-catalyzed hydroformylation were performed, but no details on characterization of the complexes were mentioned and no attention to Pd(II) and Pt(II) chemistry was paid. To our knowledge, ligands **3b** and **4b** have not been reported yet.

2. Results and discussion

2.1. Ligands

2.1.1. Synthesis

Ligands **3a**, **3b** and **4a**, **4b** were synthesized according to Scheme 1. For the synthesis of iodoaryl phosphonates, standard methods of organic and organophosphorus synthesis were used (Sandmeyer reaction, radical bromination and Michaelis–Becker reaction [18]). The last reaction required at least two-fold molar excess of NaP(O)(OEt)₂ for complete substitution; the residual reagent was then removed by extraction with 2% (w/w) aqueous NaOH solution. Out of a variety of reactions introducing the phosphanyl group into the molecule [18] we chose a mild Pd-catalyzed P–C cross-coupling reaction employing the reaction conditions similar to those already used [7,19]. In this reaction diphenylphosphine is used; we have summarized the synthetic methods for its preparation [20] and proposed a simplified procedure, in which we reduced the volume of solvents, avoided unnecessary drying and deoxy-

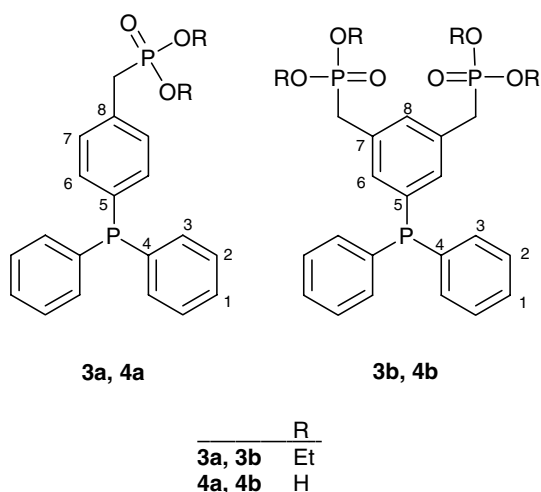


Fig. 1. Structure of **3a**, **3b**, **4a** and **4b**.

genation procedures and minimized the number of extraction and washing steps [21]. For details, see Section 4.

After several unsuccessful experiments with bromoaryl derivatives as starting materials we used more reactive aryl iodides, which were treated with diphenylphosphine in the presence of 0.2 mol% of Pd(OAc)₂ as catalyst and anhydrous KOAc as base. Under the reaction conditions used (toluene, 70–90 °C, 12–36 h), the ³¹P NMR signal of Ph₂PH disappeared and a new signal assigned to the desired product appeared. A small excess (2 mol%) of Ph₂PH was used to ensure total conversion.

After work-up of the reaction mixture, compounds **3a** and **3b** were obtained as yellowish oils well soluble in organic solvents and in strongly acidic aqueous solutions. Purity of the samples varied between 93% and 97% (³¹P NMR spectroscopy), which was acceptable for most purposes. In order to prepare samples of higher purity and also to enable the recovery of the ligands from partially oxidized samples, the standard borane protection method was employed [23]. The synthesis of borane adducts of **3a** and **3b** was performed by the reaction with excess of commercial THF·BH₃ solution and standard work-up of the reaction mixture [24]. The **3a**·BH₃ was purified by column chromatography and then obtained as colourless crystalline powder upon recrystallization from THF/hexanes (purity 98+% ³¹P NMR). We failed to crystallize **3b**·BH₃ before as well as after chromatographic purification; it was obtained with purity 96% (³¹P NMR).

The adducts were deprotected after the purification. The use of secondary amines as the deprotection agent was not

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