



Novel triphenylarsinyl-functionalized *N*-heterocyclic carbene ligands in palladium-catalyzed C–C coupling reactions [☆]

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ABSTRACT

Synthesis of novel triphenylarsinyl-functionalized *N*-heterocyclic carbene pre-ligands starting from *N,N*-dimethylbenzylamine, chlorodiphenylarsine and different 1-substituted imidazoles and their characterization by NMR and X-ray analysis is reported. Furthermore, these precursors are applied to different palladium-catalyzed reactions such as Heck-, hydro-Heck, π , σ domino-Heck and Suzuki reactions to give the C–C coupling products in good to excellent isolated yields.

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1. Introduction

Since Arduengo succeeded in the generation of stable imidazol-2-ylidenes [1], cyclic, electron-rich carbenes have gained increasing importance as ligands in homogenous catalysis [2] with transition metals such as Ni [3], Cu [4] or Pd [5]. In comparison to standard phosphines carbenes as ligands in transition metal complexes often show higher stability towards oxygen and temperature and less sensitivity to moisture [2]. Additionally, a ligand excess is not required [2]. Carbene palladium complexes have already been applied to Heck and Suzuki reactions [6], successfully. Several bridged bis-imidazolium salts are known as chelating carbene pre-ligands in Heck reactions (see Scheme 1).

Herrmann [7] et al. were able to generate palladium complexes **1** and to identify the chelating ligand by X-ray analysis as well as the Douthwaite [8] group. Danopoulos [9a,b], Lee [10] and Zhou [11] went a step further. They combined the properties of carbenes with the ones of phosphines and synthesized chelating carbene phosphine pre-ligands of the types shown in Scheme 2.

X-ray analyses of type **2** salts have been published by Labande and Poli [9c]. In all cases generation of the carbene was achieved by deprotonation of the corresponding salts. Lee [10] trapped the free carbene of type **2** as a palladium complex and reported its

X-ray structure. Neither X-ray analyses of the salts of type **3** nor their Pd-complexes have been reported yet, though.

The use of arsine ligands has proved especially advantageous [12] in Pd-catalyzed C–C coupling reactions, due to their high reactivity and selectivity as well as their high stability towards air in comparison to the structurally analogous phosphines [13]. Therefore, we decided to substitute phosphorus by arsenic in chelating carbene complexes of type **3**.

2. Results and discussion

2.1. X-ray analysis of 3-(2-(diphenyl-phosphinyl)benzyl)-1-phenyl-1*H*-imidazol-3-ium chloride (**3a**)

For homogenous catalysis it appeared desirable to learn to know and compare the geometric parameters of mixed carbene phosphine and arsine ligands of type **3** by means of X-ray analyses. Therefore, we first synthesized salt **3a** (Ar = Ph) by the procedure published by Zhou [11]. Recrystallisation from a mixture of acetonitrile and dichloromethane gave single crystals suitable for X-ray crystallography.

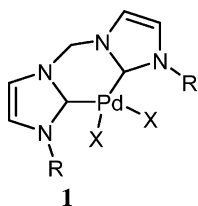
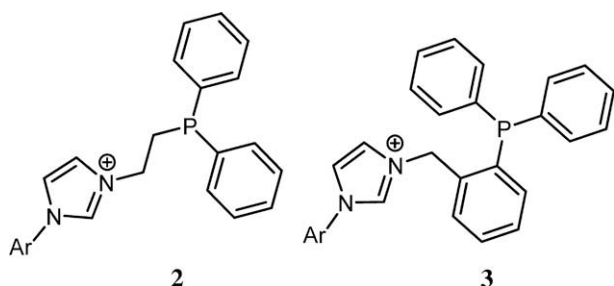
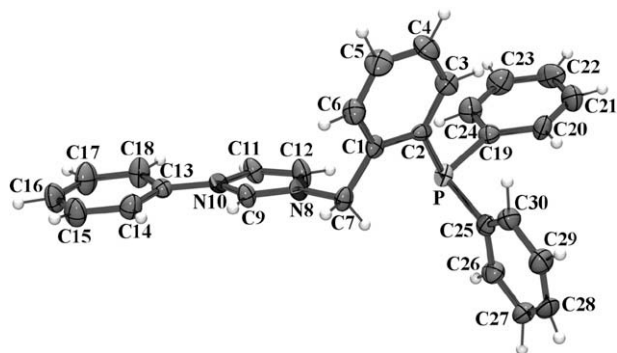
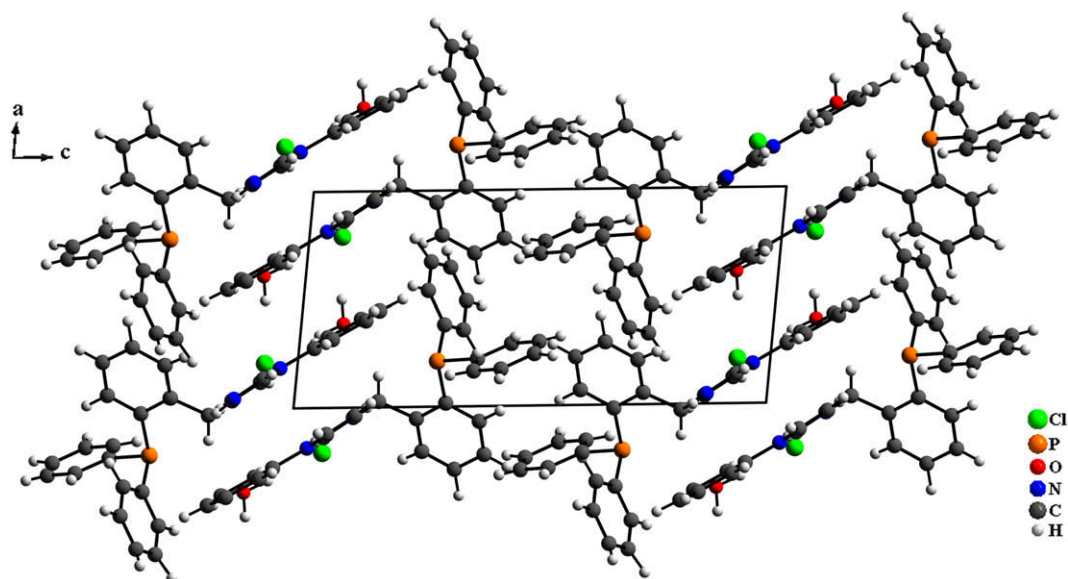
Compound **3a** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with two formula units in the unit cell. The crystal structure is characterized by discrete 3-(2-(diphenyl-phosphinyl)benzyl)-1-phenyl-1*H*-imidazol-3-ium cations, chloride anions and water molecules, which are involved in hydrogen bonds (Fig. 2).

A view of the cation is shown in Fig. 1, the relevant bond lengths and angles are listed in Table 2. The three aromatic rings are

[☆] Palladium-catalyzed reactions part 6; For part 5 see Ref. [12a].

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Scheme 1. Palladium-carbene-complexes **1**.Scheme 2. Imidazolium salts **2** and **3** of mixed carbene phosphine ligands.Fig. 1. X-ray crystal structure of **3a**.Fig. 2. Packing of unit cell of **3a** along axis *b*.

attached to the phosphorus atom in a propeller-like conformation. The $\text{P}(\text{C}_6\text{H}_5)_3$ moiety of this cation exhibits a C_3 symmetry with torsion angles $\text{C}(1)\text{--}\text{C}(2)\text{--}\text{P}\text{--}\text{C}(25)$ $86.32(2)^\circ$, $\text{C}(20)\text{--}\text{C}(19)\text{--}\text{P}\text{--}\text{C}(2)$ $99.79(3)^\circ$ and $\text{C}(30)\text{--}\text{C}(25)\text{--}\text{P}\text{--}\text{C}(19)$ $88.41(1)^\circ$. The P–C bond lengths range from 181.8(1) to 183.9(1) pm, and C–P–C angles from 102.43(1) to 104.30(2) $^\circ$ (Table 2). Each Cl^- anion is connected via hydrogen bonds to water molecules. The intermolecular $\text{O}\cdots\text{Cl}$ distances between the oxygen atoms of water molecules and the chloride anions range from 321.2(1) to 3.300(1) pm and the $\text{O}\cdots\text{Cl}$ angles from 169.1(1) to 174.6(1) $^\circ$.

The distance between the carbene precursor carbon and the phosphorus atom is 5.119 Å. The packing of the unit cell is dominated by the π -stacking of the aromatic rings on the one hand and on the other hand by the alteration of layered imidazolium units including their counterion chloride.

2.2. Synthesis of three novel triphenyl-arsinyl-functionalized imidazolium salts

The starting material chlorodiphenylarsine, unlike its phosphine analog, is commercially not available. But it can be synthesized in a safety-apparatus following a procedure by Kauffmann [14] et al. Arsenic oxide is used as arsenic source. This oxide is easily converted into arsenic acid by addition of water. Under catalytic reduction conditions arsenic acid can react with phenylhydrazine in the presence of copper(I) oxide to give after addition of hydrochloric acid the desired chlorodiphenylarsine **4** (see Scheme 3).

After *ortho*-lithiation of *N,N*-dimethylbenzylamine (**5**) molecule **4** is added to give *o*-(diphenylarsinyl)-*N,N*-dimethylbenzylamine (**6**) in 77% isolated yield. This novel amine **6** is converted under reflux conditions in the presence of chloroethyl formate into the key intermediate *o*-(diphenylarsinyl)benzyl chloride (**7**) in 76% yield (see Scheme 4).

This key intermediate **7** is converted into 3-(2-(diphenylarsinyl)benzyl)-1-phenyl-1*H*-imidazol-3-ium chloride (**11**), 3-(2-(diphenylarsinyl)benzyl)-1-mesityl-1*H*-imidazol-3-ium chloride (**12**) and 1-*tert*-butyl-3-(2-(diphenylarsinyl)benzyl)-1*H*-imidazol-3-ium chloride (**13**) by adding the commercially available 1-phenylimidazole (**8**) or 1-mesitylimidazole (**9**) and *t*-butylimidazole (**10**) under reflux conditions in ethanol. The latter are synthesized

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