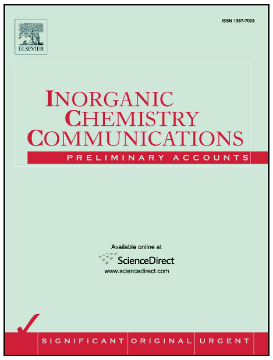

A new access to tri(1-naphthyl)phosphine and its catalytically active palladacycles and luminescent Cu(I) complex

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A new access to tri(1-naphthyl)phosphine and its catalytically active palladacycles and luminescent Cu(I) complex

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ABSTRACT

New approach to synthesis of tri(1-naphthyl)phosphine (Np_3P) and its application for design of new Pd(II) and Cu(I) complexes are reported. This phosphine has been prepared in 32% yield through exhaustive P–H arylation of PH_3 with 1-chloronaphthalene in the superbasic *t*-BuOK/DMSO system at 70 °C. The Np_3P was found to readily reacts with chloro-bridged dimers, $[(\kappa^2\text{-}C,N)Pd(\mu\text{-}Cl)]_2$ ($\kappa^2\text{-}C,N$ = $\underline{Ph}CH_2\underline{N}Me_2$ (**2a**) or $\underline{Fc}CH_2\underline{N}Me_2$ (**2b**), to give new mononuclear palladacycles $[(\kappa^2\text{-}C,N)Pd(Np_3P)Cl]$ (**3**, **4**), in which metal has a square-planar geometry. These complexes show good catalytic activity in the Sonogashira reaction under low catalyst loadings (2 mol% Pd) and relatively mild conditions. We also synthesized and characterized first Cu(I) complex with Np_3P, namely, $[Cu(phen)(Np_3P)I]$, that exhibits red emission (λ_{max} = 650 nm) at room temperature.

Tertiary phosphines are widely used as versatile ligands in coordination and organometallic chemistry [1]. They have also multiple applications in organic synthesis, catalysis and material science [2]. A special attention is currently devoted to the phosphines bearing bulky and sterically hindered substituents at the phosphorus atom [3]. Typically, these phosphines show remarkable results in metal-catalyzed reactions, in which common phosphine ligands (such as Ph_3P and related ones) are either of low efficiency or do not work at all. One of typical representatives of such ligands is tri(1-naphthyl)phosphine [4], that was firstly synthesized in 1939 [5]. Later, this phosphine has been found to be highly efficient ligand for performance of diverse metal-catalyzed reactions [4]. For example, utilizing tri(1-naphthyl)phosphine, Pd-catalyzed addition of arylboronic acids to aldehydes has been implemented, providing a variety of diarylmethanols in good to high yields [6]. The $Pd(OAc)_2/Np_3P$ combination has been used as excellent catalyst for the cross-coupling of arylboronic acids or their esters with methyl iodide [7] and α-bromoacetic acid derivatives [8]. The similar catalytic system has been exploited for Pd-catalyzed dehydroarylation of triarylmethanols [9], a cross-coupling of aldehydes and organoboronic acids [10] as well as for monofluoromethylation of arylboronic esters [11]. Np_3P ligand has been also successfully employed in Rh-catalyzed asymmetric hydrogenation [12], hydroformylation of 1-hexene [13] and vinyl acetate [14], stereoselective 1,4-hydrosilylation of α,β-unsaturated ketones [15] and several other reactions [16]. Furthermore, tri(1-naphthyl)phosphine has been used for preparation of Au(I) [17], Rh(I) [18], Pd(II) [19] complexes, Ru and Os clusters [20].

Meanwhile, despite the fact that tri(1-naphthyl)phosphine is commercial product, it remains of a limited access due to the high price. The traditional syntheses of this compound via reaction of lithiated 1-bromonaphthalene with PCl_3 are laborious and low-yielding. In 2011 [21], novel synthesis of this phosphine has been developed basing on the direct reaction of 1-bromonaphthalene with red phosphorus in the KOH/DMSO system at 47-70 °C or under microwave irradiation. However, the yields of tri(1-naphthyl)phosphine did not exceed 25% [21]. Thus, the elaboration of a higher yield synthesis of tri(1-naphthyl)phosphine is a steady challenge for progressing coordination and organometallic chemistry.

In this work, we report new approach to synthesis of tri(1-naphthyl)phosphine *via* P-H arylation of PH_3 with 1-chloronaphthalene in superbasic medium. Phosphine (PH_3) is an industrial tail gas from phosphorus chemical industry [22] and can serve as cheap source of P, therefore search for its utilization is an urgent problem. Also, to uncover some new facets of application of this phosphine, e.g. design of new catalytically active palladacycles and first Cu(I) complex with Np_3P, seems to be a timely task.

Tri(1-naphthyl)phosphine (**1**) has been synthesized by arylation of PH_3 with available and cheap 1-chloronaphthalene in the *t*-BuOK/DMSO superbasic system (Scheme 1). As a phosphine source, its mixture with H_2 generated from red phosphorus and