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A mild and efficient method for the synthesis of structurally diverse 1,2,3-triazolylidene palladium(II) diiodo complexes. Comparison of catalytic activities for Suzuki–Miyaura coupling

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ABSTRACT

Synthesis of mononuclear and PEPPSI type palladium diiodo complexes of 1,4-diphenyl-3-methyl-1,2,3-triazol-5-ylidene without the use of strong bases and silver salts and at ambient conditions using $Pd(OAc)_2$ is reported. Using stoichiometric amounts of bidendate ligands such as pyrazine, 4,4′-bipyridine and DABCO bridged binuclear palladium diiodo complexes were obtained in excellent yields. By simple variation of reagents and their stoichiometry, one can control the reactions towards the selective formation of mononuclear $[(Tz)_2Pd(I)_2]$ complexes, iodo bridged binuclear complexes $[(Tz)Pd(I)(\mu\text{-}I)_2Pd(I)(Tz)]$, mononuclear PEPPSI type complexes $[(Tz)Pd(I)_2(Py)]$, bridged binuclear PEPPSI type complexes $[(Tz)Pd(I)_2$-(bridge biPy)-$(I)_2Pd(Tz)]$. The catalytic activities of these three structurally different types of complexes are compared for Suzuki–Miyaura coupling reaction.

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1. Introduction

N-Heterocyclic carbene (NHC) ligands have dominated the scene in transition metal organometallic chemistry during the past two decades due to their ease of synthesis, extraordinary stability and functional group tolerance and excellent catalytic activities [1]. Among the transition metals palladium, iridium and rhodium have led the development in view of their importance in homogeneous catalysis, palladium in cross-coupling reactions [2] and iridium and rhodium in C–H activation [3] and hydrogenation reactions [4]. Among the NHCs imidazol-2-ylidenes (normal NHC) [5] and 1,2,3-triazol-5-ylidenes (mesoionic NHC) [6] are very popular. Palladium complexes of both of these NHC ligands have served as pre-catalysts in a wide range of coupling reactions with unprecedented catalytic activities [7]. One such complex is NHC-PdX_2-Py (X = halogen, Py = pyridine), commonly known as the PEPPSI (Pyridine-Enhanced Precatalyst, Preparation, Stabilization and Initiation) complex, introduced by Organ in 2006 [8]. Since then tremendous progress has been made in the chemistry and catalysis involving Im-PdX_2-Py (Im = imidazol-2-ylidene) type complexes [9]. A few reports have appeared on the synthesis and catalytic activities of Tz-PdX_2-Py (Tz = 1,2,3-triazol-5-ylidene) type complexes [10]. Instead of pyridine whenever bidendate ligands such as 4,4′-bipyridne (bipy), pyrazine (Pz) and 1,4-diazabicyclooctane (DABCO) are used the corresponding bridged binuclear complexes, Im-PdX_2-bidendatePy-PdX_2-Im, were formed [11]. Recently we have reported a new method for the synthesis of normal and mesoionic $(NHC)_2$–PdI_2 complexes [12]. This methodology does not use strong bases [13] or silver salts [14] and more importantly the reactions were carried out at ambient temperature [15]. Herein we describe the utilization of this method for the synthesis of mononuclear PEPPSI type complexes and bridged binuclear complexes using 1,4-diphenyl-3-methyl-1,2,3-triazol-5-ylidene as the mesoionic NHC ligand. We also report an improved version of this method wherein the reaction duration is considerably shortened. In the improved version we used $(n\text{-}Bu)_4NI$ along with triazolium iodide and $Pd(OAc)_2$ in CH_2Cl_2. Under these conditions the reactions were accelerated and went to completion faster than reported earlier and gave the desired palladium diiodo complexes in excellent yields.

2. Results and discussion

2.1. Synthesis of NHC–Pd complexes

We have reported earlier that the reaction of triazolium iodide **1**

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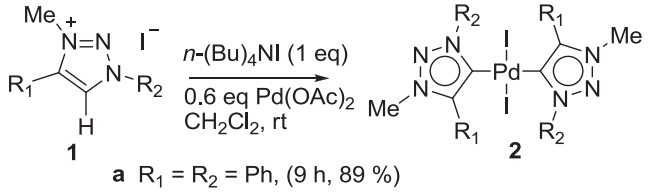
with $Pd(OAc)_2$ in CH_2Cl_2 at room temperature yielded complex **2** in near quantitative yields [12]. The reaction did not depend on the amount of $Pd(OAc)_2$, both 0.6 equivalents and 1.2 equivalents with respect to **1** gave the same result. However, triazolium iodide **(1a–c)** as the iodide source, the reactions were very slow and took several days to go to completion. In order to improve the rates of these reactions we used $(n\text{-Bu})_4NI$ along with the triazolium iodide and $Pd(OAc)_2$. Stoichiometric amounts of $(n\text{-Bu})_4NI$ on reaction with $Pd(OAc)_2$ gave dark black colour solution presumably due to the formation of palladate $[(n\text{-Bu}_4N)_2PdI_2(OAc)_2]$ as an intermediate. Evidence for the formation of the palladate complex is derived from ^1H NMR studies and detailed mechanism of formation of the NHC–Pd complex under base free conditions wherein acetate acts as the base is reported earlier from our group [12]. Further addition of triazolium salts **(1a–c)** yielded the corresponding mono nuclear palladium NHC complexes **(2a–c)** in good yields (Scheme 1). Triazolium iodide as the source of iodide ion the reactions took much longer to attain completion (**1a** and **1b** in 36 h and 1c in 48 h). The reactions were considerably faster with $(n\text{-Bu})_4NI$. Complexes **2a–c** were characterized by comparison of the spectroscopic data with authentic samples prepared in the laboratory (SI) [12] ^1H NMR spectra of **2a–b** (see SI) clearly indicated the presence of *syn* and *anti* rotomers for complex **2** [16]. We then explored the possibility of synthesizing $(Tz)_2PdCl_2$ derivatives using $(n\text{-Bu})_4NCl$ instead of the iodide salt. Triazolium salt **1a** was treated with $(n\text{-Bu})_4NCl$ in CH_2Cl_2 and stirred at room temperature for 2 h then $Pd(OAc)_2$ was added and allowed to stir at rt for 4 d. But, the same mononuclear palladium(II) diiodo compound **2a** was isolated in 66% of yield instead of the corresponding palladium(II) dichloro NHC complex. We also investigated the reaction of **1a** with 1.2 equivalents of $Pd(OAc)_2$ in the presence of excess KI which yielded very cleanly the corresponding bridged binuclear complex **3** in 95% yield as a bright yellow solid (Scheme 2). The ^1H and ^{13}C NMR spectra (in DMSO-d_6) of the product obtained in this reaction were identical to **3** reported earlier by Albrecht [15].

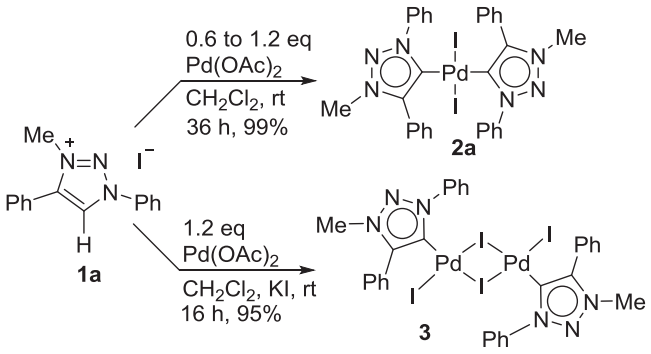
In an attempt to synthesize PEPPSI type complexes initially we investigated the reaction of triazolium iodide **1a** with 1.0 equivalent of $Pd(OAc)_2$ in the presence of excess KI and pyridine in CH_2Cl_2 as solvent at room temperature. The reaction invariably yielded the PEPPSI complex **5** along with $(Py)_2PdI_2$**(4)** as a mixture in 2:1 ratio, respectively (Scheme 3). Despite several attempts, the mixture could neither be separated by fractional crystallization nor by column chromatography. Authentic sample of **4** was prepared as a bright orange solid by the reaction of $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 in the presence of KI and pyridine and it was identified by ^1H and ^{13}C NMR spectroscopic methods.

Hong [10c] has reported the synthesis of 1,2,3-triazol-5-ylidene based PEPPSI type complexes from the corresponding chloro bridged binuclear palladium complex by treatment with pyridine in CH_2Cl_2 at room temperature. Hong's method involved the intermediate silver carbene complex. In the present study treatment of complex **3** with 2.0 equivalents of pyridine gave complex **5** in

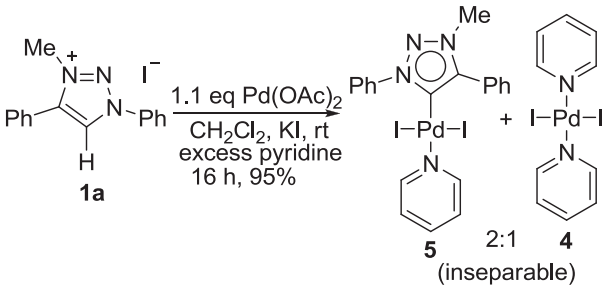


a $R_1 = R_2$ = Ph, (9 h, 89 %)
b R_1 = Ph, $R_2 = CH_2OH$, (12 h, 82 %)
c $R_1 = CH_2OH$, $R_2 = CH_2Ph$ (8h, 86 %)

Scheme 1. Synthesis of mononuclear palladium NHC complexes.



Scheme 2. Synthesis of mononuclear and iodo bridged binuclear complexes.

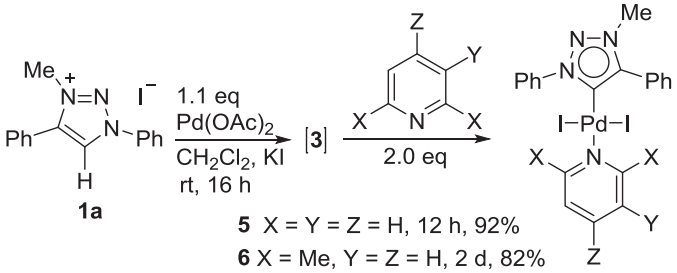


Scheme 3. Initial attempt towards the synthesis of PEPPSI type complexes.

near quantitative yield. A simple one pot procedure has been developed in which complex **3** was prepared *in situ* as shown in Scheme 2 and further treated with 2.0 equivalents of pyridine to obtain **5** without any contamination of complex **4** (Scheme 4).

There are several advantages of this method compared to the existing ones. First of all the present method, unlike the earlier reports, [9,10] does not involve the use of any strong base or silver salts. The reactions required only stoichiometric amounts of pyridine derivatives. The reactions were carried out at ambient conditions. No side products were observed in these reactions and hence the PEPPSI type complexes **(5–8)** were easily obtained in pure form (Scheme 4).

Under similar conditions used for the synthesis of **3** as in Scheme 2, we attempted the synthesis of the corresponding chloro bridged complex from the reaction of triazolium salt **1a**, $Pd(OAc)_2$ (1.2 equiv) in the presence of excess KCl. To our surprise it gave the corresponding acetate bridged palladocycle complex **9** in 68% yield as greenish yellow solid (Scheme 5) [16] The ^1H and ^{13}C NMR spectra of the product **9** obtained in this reaction were identical to that of the literature [16a]. Although the role of KCl in the formation



5 X = Y = Z = H, 12 h, 92%
6 X = Me, Y = Z = H, 2 d, 82%
7 X = Y = H, Z = Me, 12 h, 89%
8 X = Z = H, Y = Cl, 12 h, 91%

Scheme 4. Synthesis of 1,2,3-triazol-5-ylidene based PEPPSI type complexes.

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