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Facile base-free *in situ* generation and palladation of mesoionic and normal *N*-heterocyclic carbenes at ambient conditions

Bemineni Sureshbabu, Venkatachalam Ramkumar and Sethuraman Sankararaman*

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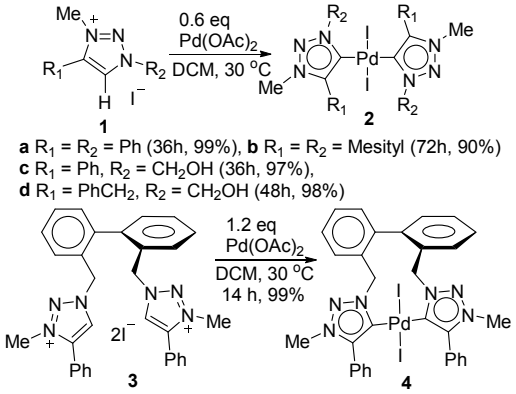
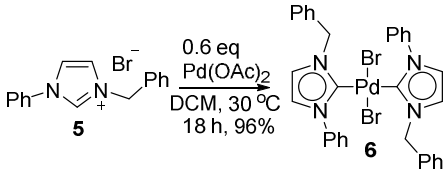
Synthesis of normal and mesoionic *N*-heterocyclic carbene Pd(II) complexes in near quantitative yields from the corresponding NHC precursor salts under base free and ambient conditions is reported. A plausible mechanism involving charge-assisted hydrogen bonded intermediates is proposed.

During the past two decades *N*-heterocyclic carbene (NHC) ligands have transformed transition metal (TM)[1] and lanthanide organometallic chemistry[2] and the associated homogeneous catalysis[3] significantly. NHC ligands have systematically replaced the conventional phosphane ligands in NHC-metal complexes due to higher thermal and oxidative stability, ease of introduction of chirality and higher catalytic activity.[4] Imidazol-2-ylidenes (normal NHC) and 1,2,3-triazol-5-ylidenes (mesoionic NHC) have dominated the scene of NHC-TM chemistry. Among the TMs Pd(II) is popular due to its use as a catalyst in many catalytic processes.[5] Therefore developing newer and efficient methods of synthesis of NHC-Pd(II) complexes and their use as homogeneous catalysts are desirable goals in this area. In the literature NHC-Pd(II) complexes are synthesized by (a) generation of NHC-Ag(I) complexes followed by transmetallation,[6] (b) generation of NHC using strong bases followed by metallation[7] and (c) thermal metallation method using $Pd(OAc)_2$ in DMSO at 120 °C.[8] The silver carbene transmetallation method is wasteful due to the generation of stoichiometric amount of silver salts. Strong bases such as LiHMDS and *t*-BuOK are used under anhydrous conditions and inert atomosphere to *in situ* generate the free carbene. One of the drawbacks of this method is the nucleophilic attack by the base resulting in the dealkylation of alkyl substituted precursor salts leading to the formation of the parent neutral heterocycles.[7a] Thermal method in DMSO at 120 °C results in poor to moderate yields of often a mixture of *cis/trans* and mono/dinuclear complexes.[9] There is an earlier report on the room temperature synthesis a palladium complex of a benzimidazolylidene ligand in THF using $Pd(OAc)_2$.[10] In the present study we have investigated the reaction of $Pd(OAc)_2$ (0.6 eq) with 3-methyl-1,4-diphenyl-1*H*-1,2,3-triazolium iodide (**1a**) (1.0 eq) in various solvents at 30 °C (ambient temperature in Chennai) for prolonged period of time (2-3 days). In DMSO, THF and 1,4-dioxane no reaction was observed and the starting materials were recovered after 48 h. However, to our pleasant surprise, the reaction carried out in DCM displayed vivid color changes.[8a] Upon mixing all the starting materials, the initial dark brown to black DCM solution changed to light brown over 24 h and finally to yellow to orange after 36 h at room temperature. Evaporation of solvent gave nearly pure **2a** in almost quantitative yield as bright yellow solid (Scheme 1). When the reaction of **1a** was carried out in the presence of 1.2 equivalents of $Pd(OAc)_2$ complex **2a** was obtained in 98% yield. Reaction of the bis(triazolium) salt **3** was complete within 14 h and gave chelated bis(triazolylidene) complex **4** in 99% yield (Scheme 1).



Scheme 1. Base free synthesis of triazolylidene-Pd(II) diiodo complexes at ambient conditions.

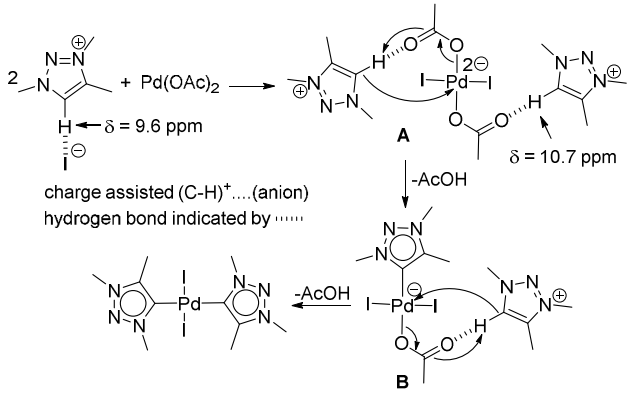


Scheme 2. Base free synthesis of imidazolylidene-Pd(II) complex at ambient conditions.

When imidazolium bromide **5** was treated with $Pd(OAc)_2$ in DCM at 30 °C the reaction proceeded in a similiar manner to afford complex **6** in 96 % yield (Scheme 2).

Instead of **1a** (iodide salt) when the corresponding tetrafluoroborate salt was used the reaction did not proceed under otherwise identical conditions. Only starting material was recovered. ^{1}H NMR spectra of these salts in $CDCl_3$ revealed that the chemical shift of the triazolium proton was 9.6 ppm for the iodide salt (**1a**) and 8.9 ppm for the corresponding tetrafluoroborate salt. This observation reflects the effect of

counter ion on the acidity of the triazolium proton.[11] In a non-polar solvent such as DCM, in addition to strong ion pairing, charge-assisted [(C-H)$^+$…(anion)] hydrogen bond (CAHB) of iodide ion to the triazolium ring proton can further enhance its acidity which is supported by the higher chemical shift value of the triazolium proton in the iodide salt in comparison to that in the tetrafluoroborate salt. A recent systematic NMR study of CAHB in imidazolium and 1,2,3-triazolium salts with various anions supports our observation.[11a] Acidity of the triazolium proton is an important factor but that alone cannot explain the reactivity pattern in various solvents. For example the chemical shift of triazolium proton in DMSO-d_6 was 9.86 ppm, about 0.26 ppm higher than that in $CDCl_3$, indicating higher acidity in DMSO. This might be due to hydrogen bonding of DMSO solvent to the triazolium ring proton. Nevertheless the reaction did not proceed in DMSO at 30 ^oC. The solvent dependent basicity of acetate ion could also play a crucial role in the success of this reaction. The pK_a of acetate in DMSO is 12.3.[12] In DMSO as solvent palladium acetate is likely to exist as $[Pd(OAc)_2(OS(CH_3)_2)_2]$ in which the basicity of acetate might be lower compared to that in DCM or $CDCl_3$. This also explains why the reaction proceeded only at higher temperatures in DMSO.[8,9] It is unlikely that free acetate ions are involved in the deprotonation reaction in DCM. Upon addition of 0.6 equivalent of $Pd(OAc)_2$ to a $CDCl_3$ solution of **2a** resulted in the complete disappearance of the signal at 9.6 ppm instantly and concomitant appearance of a signal at 10.7 ppm. The new signal is attributed to the formation of $[(triazolium)_2(Pd(I)_2(OAc)_2)]$, intermediate **A** in Scheme 3.[8a] The acetate groups form CAHB in **A** which results in further deshielding of triazolium proton to 10.7 ppm.[11a] The reactivity in DMSO is lower because of solvation of the triazolium ion as well as lack of formation of CAHB intermediates such as **A** and **B** (Scheme 3) in dipolar aprotic solvent such as DMSO. Based on the above discussions we propose a plausible mechanism for the reaction (Scheme 3).



Scheme 3. Plausible mechanism of formation of $(NHC)_2PdI_2$ complex.

Structures of complexes **2a**, **2c**, **4** and **6** have been confirmed by single crystal XRD data (Figure1). Compounds **2a**, **4** and **6** have *trans* square planar geometry whereas in **2c** has *cis* square planar geometry around Pd atom. The *cis* geometry in the hydroxylmethyl substituted derivative **2c** is consistent with our earlier report of the corresponding dichloro derivative.[13] The Pd-$C_{carbene}$ bond lengths in these complexes are in accordance with the earlier reports of structurally similar complexes.[6b,13,14]

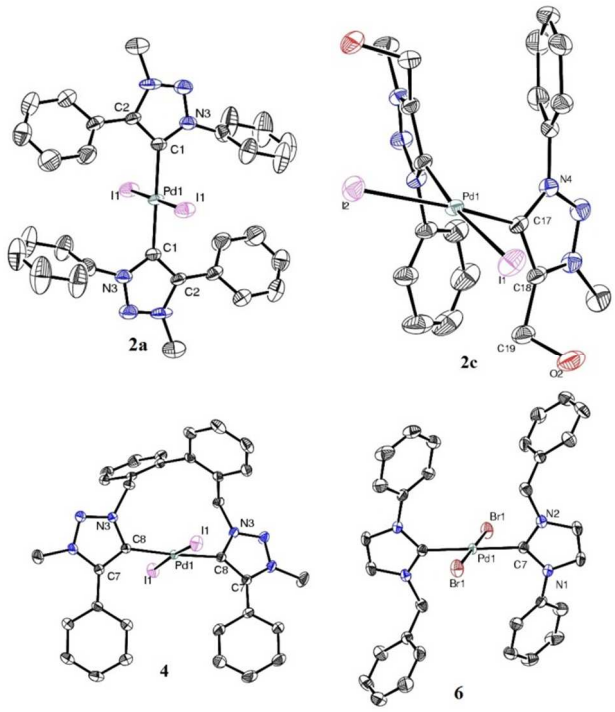


Figure 1. ORTEP diagram (30% probability) of structure of complexes **2a**, **2c**, **4** and **6** in the crystal. Hydrogen atoms and solvent molecules are omitted for clarity.

In an attempt to prepare other transition metal complexes, **1a** was reacted with anhydrous salts such as $Co(OAc)_2$, $Ni(OAc)_2$ and $Mn(OAc)_2$ in DCM and DMSO at ambient and higher temperatures. In all these cases the acetate salts were not soluble in DCM and no reaction could be observed in either solvent. Reaction of **1a** with DCM soluble salts such as $Co(acac)_2$ and $Ni(acac)_2$ also did not yield the corresponding NHC complexes.

We have developed a base-free methodology for the synthesis of NHC-Pd(II) iodo complexes using $Pd(OAc)_2$ in DCM at ambient conditions in excellent yields. The reaction could be easily followed by visual color changes. A mechanism involving charge-assisted hydrogen bonded intermediates is proposed.

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Notes and references

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India. Fax: 91 44 22570545; Tel: 91 44 22574210; E-mail: sanka@iitm.ac.in

† Electronic Supplementary Information (ESI) available: [synthesis and characterization and cif data of all the complexes. CCDC 994995, 957604, 994996, 994997 contain XRD data for complexes **2a**, **2b**, **4** and **6**, respectively]. See DOI: 10.1039/b000000x/

‡ General procedure for the synthesis of complexes: To a solution of the precursor salt (100 mg, 0.2 – 0.3 mmol) in DCM (20 mL) was added solid $Pd(OAc)_2$ (0.6 equivalent) at room temperature (30 ^oC) under N_2 atmosphere. The solution turned dark brown to black instantaneously. The reaction mixture was stirred for 14-72h during which the solution turned to orange to bright yellow. Removal of solvent followed by crystallization

of the crude product gave the complexes in >90% yield as yellow crystalline solids.

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