



Palladium-ADC complexes as efficient catalysts in copper-free and room temperature Sonogashira coupling



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ABSTRACT

The metal-mediated coupling between *cis*-[PdCl₂(CNR¹)₂] [R¹ = cyclohexyl (Cy) 1, *t*-Bu 2, 2,6-Me₂C₆H₃ (Xyl) 3, 2-Cl-6-MeC₆H₃ 4] and hydrazones H₂NN=CR²R³ [R², R³ = Ph 5; R², R³ = C₆H₄(OMe-4) 6; R²/R³ = 9-fluorenyl 7; R² = H, R³ = C₆H₄(OH-2) 8] provided carbene complexes *cis*-[PdCl₂{C(N(H)N=CR²R³)=N(H)R¹}(CNR¹)] (**9–24**) in good (80–85%) yields. Complexes **9–24** showed high activity [yields up to 99%, and turnover numbers (TONs) up to 3.7 × 10⁴] in the Sonogashira coupling of various aryl iodides with a range of substituted aromatic alkynes without the need of copper co-catalyst. The catalytic procedure runs at 80 °C for 1 h in EtOH using K₂CO₃ as a base. No formation of homocoupling or acetylene decomposition products was observed. Designed copper-free Sonogashira system can also run at room temperature giving target products with yields up to 87% and TONs up to 87.

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1. Introduction

In the last decades, *N*-heterocyclic carbenes (NHCs) turned out to be one of the most powerful classes of ancillary ligands [1,2–5], and corresponding NHC-based metal complexes were successfully employed as catalysts in a wide range of organic transformations [4,6–13]. In particular, outstanding accomplishments were achieved in the field of cross-coupling, e.g. in Suzuki–Miyaura and Heck reactions where palladium-NHC catalysts guaranteed some of the highest catalytic efficiencies [6–8,10].

Compared to hundreds of reports describing the use of palladium-NHCs in Suzuki–Miyaura and Heck reactions [7,8], the application of NHCs for Sonogashira coupling is limited to just a dozen of examples [7,8,14–25]. Nearly all known procedures employ high catalyst loading (typically between 1 and 3 mol%)

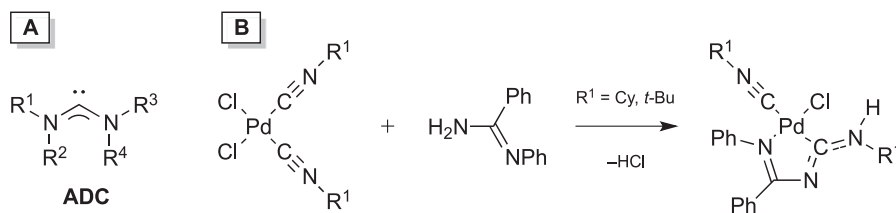
[14–25], operate in toxic organic solvents (e.g. dimethylformamide or dimethylacetamide) [14,15,18,19,21–23], frequently require copper co-catalysts [14,15,18,19,21,25], and demand further purification of the target products due to occurrence of side-reactions [8]. Taking into account the constantly growing price of palladium and tightened requirements for greener reaction conditions, the search for alternative catalysts and catalytic systems is due.

In the past years, several research groups have demonstrated that acyclic diaminocarbene ligands (ADCs, Scheme 1–A) are a promising alternative to *N*-heterocyclic species. Indeed, some of the reported ADC metal complexes catalyze cross-coupling processes with activities comparable or even higher than those of NHCs (for recent reviews and manuscripts on the topic see Refs. [26–32]). In pursuit of our own research on chemistry of acyclic diaminocarbenes [33–39], we found that palladium-ADC complexes prepared via the metal-mediated coupling of *N*-phenylbenzamidines with palladium-bound isocyanides (Scheme 1–B) work as efficient catalysts for Sonogashira coupling [36]. Despite the fact that the scope of that system is limited, it operates in EtOH (organic solvent with the lowest environmental impact) and requires lower catalyst loading (0.05 mol%) when compared to the conventional schemes [36]. Following these initial reports, we decided to evaluate the

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Scheme 1. Acyclic diaminocarbenes (A) and generation of palladium-ADC species via the addition of *N*-phenylbenzamide to palladium-bound isocyanides (B).

catalytic properties of other ADC derivatives in Sonogashira reaction. We focused our attention on previously described by some of us palladium-ADC complexes formed via the addition of hydrazones to palladium-bound isocyanides (Scheme 2) [38]. These ADC were evaluated previously as catalysts for Suzuki–Miyaura coupling showing an excellent catalytic activity [38]. However, the use of ADC complexes in Sonogashira catalysis is still rare and this field remains almost unexplored [27,28] (see also below).

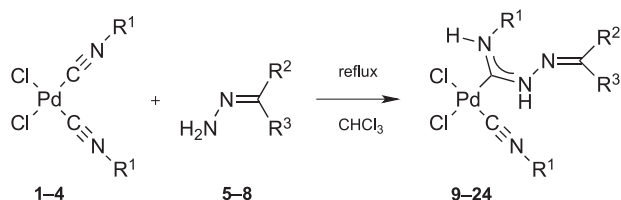
The scenario of our work was the following. Firstly, we prepared a series of palladium-diaminocarbene complexes through the addition of hydrazones to palladium-bound isocyanides. Some of these species were previously reported but we substantially extended the series by application of new hydrazones and new isocyanides. Secondly, we employed the prepared palladium-ADCs as catalysts in the Sonogashira cross-coupling and discovered that they exhibit a remarkable catalytic activity without the need of copper co-catalyst. In addition, we evaluated the efficacy of these complexes prepared in this work at room temperature Sonogashira coupling. Finally, we got some first evidence on the nature of the catalytic species in this palladium-ADC-based system. Our results are disclosed in the sections that follow.

2. Results and discussions

2.1. Synthesis and characterization of palladium-aminocarbene complexes

Previously, we reported [38] the coupling of *cis*-[PdCl₂(CNR¹)₂] [R¹ = cyclohexyl (Cy) **1**, *t*-Bu **2**, 2,6-Me₂C₆H₃ (Xyl) **3**] [35,40–42], and benzophenone hydrazone [IUPAC name: (diphenylmethylene)hydrazine] (**5**), leading to the corresponding aminocarbene complexes **9–11** (Scheme 2). In the current study, we extended the series by using the new isocyanide species *cis*-[PdCl₂{CN(2-Cl-6-MeC₆H₃)₂}₂] [35] (**4**) and three new hydrazones with different donor and sterical properties. Thus, we used 4,4-dimethoxybenzophenone hydrazone [(*bis*(4-methoxyphenyl)methylene)hydrazine] (**6**) containing donor substituents in the aromatic ring [43,44], sterically hindered 9-fluorenone hydrazone [(9H-fluoren-9-ylidene)hydrazine] (**7**), and salicylaldehyde hydrazone [2-(hydrazonomethyl)phenol] (**8**), that is derived from the corresponding aldehyde (R² = H).

Previously, we reported [38] that the reaction between equimolar amounts of **1–3** and **5** (in all combinations) proceeds in refluxing CHCl₃ for ca. 8 h. In the current study, we employed nearly



Scheme 2. Generation of aminocarbene complexes **9–24** through the reaction between **1–4** and hydrazones **5–8**.

similar conditions for the coupling of any palladium-isocyanide complex **1–4** with any of hydrazones **5–8**. Therefore, reflux of the reaction mixture in chloroform for ca. 8 h [or 12 h for the reactions of *cis*-[PdCl₂(C*n*-t-Bu)₂] (**2**)] followed by the appropriate workup, allowed the isolation of the corresponding carbene complexes *cis*-[PdCl₂{C(N(H)N=CR²R³)=N(H)R¹}(CNR¹)] (**9–24**) in good (80–85%) yields (Table 1, Scheme 2).

The authenticity of the known species **9–11** was established upon comparison of the recorded ¹H nuclear magnetic resonance spectra (¹H NMR) and IR spectra with those previously reported by some of us [38], while the new complexes **12–24** were characterized using (C, H, N) analyses, ESI⁺-MS (electrospray ionization mass-spectrometry), IR, 1D (¹H, ¹³C{¹H}) and 2D (¹H,¹H-COSY, ¹H,¹³C-HMQC/¹H,¹³C-HSQC, ¹H,¹³C-HMBC) NMR spectroscopies. In addition, the structures of **15**, **19**, and **24** were elucidated by single crystal X-ray diffraction.

Compounds **12–24** gave satisfactory C, H, and N elemental analyses, which are consistent with the proposed formulations for *cis*-[PdCl₂{C(N(H)N=CR²)=N(H)R¹}(CNR¹)]. The ESI⁺-MS mass spectra display molecular ion peaks and/or a fragmentation corresponding to the loss of Cl⁻ from the molecular ion, *viz.* [M – nCl]⁺, with the characteristic isotopic distribution. The examination of the IR spectra revealed the presence of one strong ν(C≡N) stretching vibration in the range between 2229 and 2198 cm⁻¹, that belongs to the unreacted isocyanide ligand. In the formed carbene moiety, the ν(N–H) bands emerge in the range of 3256–3210 cm⁻¹, while the corresponding very strong bands due to ν(C_{carbene}–N) stretches appear between 1570 and 1533 cm⁻¹. The medium/weak intensity bands in the range of 2980–2836 cm⁻¹ are characteristic of the ν_s(C–H) and ν_{as}(C–H) vibrations, while medium intensity bands due to δ(C–H from Ar) appear in the range of 698–783 cm⁻¹. The ¹H NMR spectra of carbene complexes **12–24** display a broad peak in the range of δ 8.83–9.94 assigned to the C_{carbene}–N(H)R proton, while the corresponding C_{carbene}–NH ¹³C signals were found to resonate in the range of 180–165 ppm, *i.e.* they are approximately 65–45 ppm downfield shifted in comparison with the ¹³C signal of the isocyanide in the starting (isocyanide)Pd^{II} complexes **1–4** (e.g. 115 ppm for C≡N in *cis*-[PdCl₂(CNCy)₂]).

The crystallographic data and processing parameters for **15**, **19**, and **24** are very similar and are listed in Table 1S of **Supplementary Data**, while corresponding plots can be found in **Figs. 1–3**, respectively. Bond lengths and angles are given in the legends to each plot.

In **15**, **19**, and **24**, the chloride ligands are mutually in *cis* position [Cl1–Pd1–Cl2 in **15**: 93.001(15), **19**: 91.73(3), Cl1–Pd1–Cl2 in **24**: 93.41(9)°]. The slightly distorted square planar environment around the metal center is completed with one unreacted isocyanide ligand, CNR¹, and one newly formed carbene ligand, C(N(H)N=CR²)=N(H)R¹.

The Pd–C_{carbene} distances [1.9805(15) in **15**, 2.006(3) in **19**, and 1.964(10) Å in **24**] are comparable to those reported for the similar palladium carbene complexes *cis*-[PdCl₂{C(N(H)N=CPh₂)=N(H)Xyl}(CNXyl)] (Pd1–C11 1.973(3) Å). [38] In all complexes, the carbene moiety is roughly planar and the angles around the carbene carbon atom range from

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