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Application of palladium complexes bearing acyclic amino(hydrazido)carbene ligands as catalysts for copper-free Sonogashira cross-coupling

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ABSTRACT

Metal-mediated coupling of one isocyanide in *cis*-[$PdCl_2(CNR^1)_2$] (R^1 = C_6H_{11} (Cy) **1**, *t*Bu **2**, 2,6-$Me_2C_6H_3$ (Xyl) **3**, 2-Cl-6-MeC_6H_3 **4**) and various carbohydrazides $R^2CONHNH_2$ [R^2 = Ph **5**, 4-ClC_6H_4 **6**, 3-$NO_2C_6H_4$ **7**, 4-$NO_2C_6H_4$ **8**, 4-$CH_3C_6H_4$ **9**, 3,4-$(MeO)_2C_6H_3$ **10**, naphth-1-yl **11**, fur-2-yl **12**, 4-$NO_2C_6H_4CH_2$ **13**, Cy **14**, 1-(4-fluorophenyl)-5-oxopyrrolidine-3-yl **15**, (pyrrolidin-1-yl)C(O) **16**, 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propane-1-yl **17**, EtNHC(O) **18**] or sulfohydrazides $R^3SO_2NHNH_2$ [R^3 = Ph **19**, 4-MeC_6H_4 **20**] led to a series of (hydrazido)(amino)carbene complexes *cis*-[$PdCl_2$\{C(NHNHX)=N(H)R^1\}(CNR^1)]; X = COR^2, SO_2R^3 (**21**–**48**, isolated yields 60–96%). All prepared species were characterized by elemental analyses (C, H, N), HR ESI^+-MS, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and by a single-crystal X-ray diffraction for **38**. Complexes **21**–**48** demonstrated excellent activity as catalysts in copper-free Sonogashira coupling of aryl iodides and a variety of aromatic terminal alkynes. Catalytic system runs in environmentally benign EtOH ensuring product yields of up to 75–96% and TONs of up to 10^4. Mechanism of the copper-free Sonogashira catalytic cycle involving **21**–**48** as catalysts was proposed upon identification of key intermediates using HRESI-mass.

1. Introduction

In the last decade, complexes bearing acyclic diaminocarbene (ADC) ligands [1,2] attracted attention as intriguing alternative to complexes with *N*-heterocyclic species (NHCs) in the place of catalysts in several cross-coupling processes [3,4]. Thus, palladium complexes with ADC ligands were successfully employed in Suzuki–Miyaura [5–7], Heck [3,4,7], Buchwald–Hartwig [3,4], and Sonogashira reactions [3,4,7–11]. Among them, Sonogashira coupling is typically performed in the presence of a copper co-catalyst (that improves reaction efficiency but brings about the generation of undesired by-products) [12–17], although a few copper-free systems, that are free from above disadvantages, are also known. Those include pioneering reports by Dhudshia and Thadani [7] (catalyst loading: 1.5 mol%; product yields up to 91%; TONs up to 60), and by Luzyanin and Boyarskiy [10,11] (catalyst loading: 0.1 mol%; product yields up to 99%; TONs up to 3.7×10^4).

While application of palladium-ADCs as catalysts for copper-free Sonogashira reaction is recognized, to the best of our knowledge the mechanism of their action and the details of the corresponding catalytic cycle remain unclear. Indeed, in one of our recent works [11], we were able to establish for the first time the identity of the real catalytic species, derived from palladium-ADCs as precatalysts. However, we were unable to establish the mechanism of the catalytic process employing palladium-ADC catalysts, and no other data regarding the mechanism of their action emerged up to date.

Recently, we reported that palladium complexes bearing amino(hydrazido)carbene ligands (Fig. 1) act as excellent catalysts of Suzuki–Miayura reaction performed in aqueous or organic medium (yields up to 94%, TONs up to 9.4×10^4) [6]. Motivated

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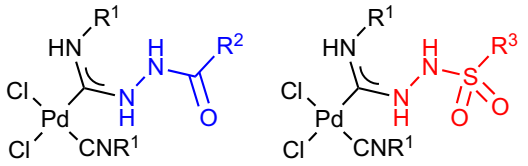


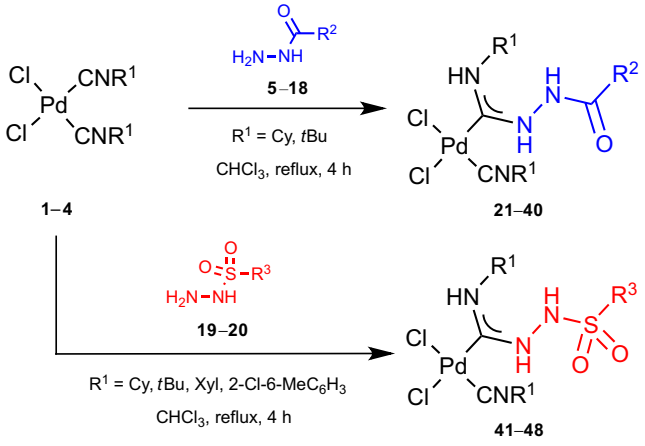
Fig. 1. Palladium complexes bearing acyclic amino(hydrazido)carbene ligands.

by an outstanding catalytic efficiency of these compounds in Suzuki–Miyaura cross-coupling, we decided to evaluate their catalytic properties in related Sonogashira reaction. To our satisfaction, application of these compounds allowed not only to perform Sonogashira coupling under mild and copper-free conditions, but also to get closer to the understanding of the mechanism of this catalytic process.

Our studies are partitioned in three parts. In the first, we expand the series of palladium complexes with amino(hydrazido)-carbene ligands as unexplored type of palladium-ADC species. In the second, we evaluate catalytic properties of these complexes in Sonogashira reaction, and finally, we attempt to identify catalytic intermediates and to shed light on mechanism of the Sonogashira process involving catalysts of this type. Our results are disclosed below.

2. Results and discussion

In the previous study, a series of known [6] palladium-(hydrazido)(amino)carbene complexes *cis*-[$PdCl_2${C(NHNHY)=N(H)R^1}(CNR^1)]; Y = COR^2, SO_2R^2 (**21**–**32**, **35**–**38**, and **41**–**44**; 60–96% isolated yields) were prepared via the metal-mediated coupling of one isocyanide ligand in *cis*-[$PdCl_2(CNR^1)_2$] [R^1 = C_6H_{11} (Cy) **1**, *t*Bu **2**, 2,6-$Me_2C_6H_3$ (Xyl) **3**, 2-Cl-6-MeC_6H_3 **4**] and various carbohydrazides $R^2CONHNH_2$ [R^2 = Ph **5**, 4-ClC_6H_4 **6**, 3-$NO_2C_6H_4$ **7**, 4-$NO_2C_6H_4$ **8**, 4-$CH_3C_6H_4$ **9**, 3,4-$(MeO)_2C_6H_3$ **10**, naphth-1-yl **11**, fur-2-yl **12**, 4-$NO_2C_6H_4CH_2$ **13**; Cy **14**, 1-(4-fluorophenyl)-5-oxopyrrolidine-3-yl **15**, (pyrrolidin-1-yl)C(O) **16**)] or sulfohydrazide $PhSO_2NHNH_2$ (**19**) (Scheme 1 and Table 1) [6]. We have now extended this synthetic procedure by employing new carbohydrazides [R^2 = 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propane-1-yl **17,** EtNHC(O) **18**] and one sulfohydrazide [R^3 = 4-MeC_6H_4 **20**] as reactants. Thus, we observed that the reaction between equimolar amounts of **1** or **2** and carbohydrazides **17** and **18** proceeds in refluxing $CHCl_3$ for *ca.* 4 h. The subsequent workup provided the aminocarbene species *cis*-[$PdCl_2${C(NHNHC(O)R^2)=N(H)R^1}(CNR^1)]



Scheme 1. Synthesis of the amino(hydrazido)carbene-palladium complexes.

Table 1
Numbering scheme for palladium-ADC complexes derived from the addition of carbo – (**21**–**40**) and sulfohydrazides (**41**–**48**) to isocyanides in *cis*-[$PdCl_2(CNR^1)_2$] (**1**–**4**).

R^1	R^2		R^2	
Cy	Ph	**21**	fur-2-yl	**28**
	4-ClC_6H_4	**22**	Cy	**29**
	3-$(NO_2)C_6H_4$	**23**	4-$(NO_2)C_6H_4CH_2$	**30**
	4-$(NO_2)C_6H_4$	**24**	1-(4-fluorophenyl)-5-oxopyrrolidine-3-yl	**31**
	4-MeC_6H_4	**25**	(pyrrolidin-1-yl)C(O)	**32**
	3,4-$(MeO)_2C_6H_3$	**26**	3-(3,5-di-tert-butyl-4-hydroxyphenyl)propane-1-yl	**33**
	naphth-1-yl	**27**	EtNHC(O)	**34**
*t*Bu	4-ClC_6H_4	**35**	Cy	**38**
	3-$(NO_2)C_6H_4$	**36**	3-(3,5-di-tert-butyl-4-hydroxyphenyl)propane-1-yl	**39**
	3,4-$(MeO)_2C_6H_3$	**37**	EtNHC(O)	**40**
Cy	Ph	**41**	4-MeC_6H_4	**45**
*t*Bu	Ph	**42**	4-MeC_6H_4	**46**
Xyl	Ph	**43**	4-MeC_6H_4	**47**
2-Cl-6-MeC_6H_3	Ph	**44**	4-MeC_6H_4	**48**

(**33**, **34**, **39**, and **40**) in good to excellent (86–96%) isolated yields. Furthermore, the coupling of equimolar amounts of any of one **1**–**4** and 4-$MeC_6H_4SO_2NHNH_2$ (**20**) occurs under similar conditions and affords the aminocarbenes *cis*-[$PdCl_2${C(NHNHSO$_2R^3$)=N(H)R^1}(CNR^1)] (**45**–**48**; 84–91%).

*Characterization of **21**–**48***. The authenticity of known species **21**–**32**, **35**–**38**, and **41**–**44** was established upon comparison of their ^{1}H NMR spectra with those previously reported by some of us [6], whereas new complexes **33**, **34**, **39**, **40**, and **45**–**48** were characterized by elemental analyses (C, H, N), high resolution ESI$^+$-MS, IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopies. In addition, the structure of one species (**38**) was elucidated by a single-crystal X-ray diffraction (Fig. 2).

The HR-ESI$^+$ mass spectra of **33**, **34**, **39**, **40**, and **45**–**48** display an ion due to $[M+H]^+$ and/or a fragmentation corresponding to the loss of HCls from the molecular ion, *viz.* $[M-Cl]^+$ and $[M-2Cl-H]^+$, with the characteristic isotopic distribution. The IR spectra exhibit from one to three weak to medium intensity broad bands in the 3282–3042 cm^{-1} region that correspond to the NH stretches. The medium/weak intensity bands in the range of 2983–2833 cm^{-1} are characteristic of ν_s(C—H) and ν_{as}(C—H) vibrations. The examination of the IR spectra revealed the presence of one strong stretching vibration in the range between 2229 and 2224 cm^{-1} (R^1 = Cy, *t*-Bu) or 2210 and 2204 cm^{-1} (R^1 = Xyl, 2-Cl-6-MeC_6H_3) from ν(C≡N) of unreacted isocyanide ligands. One strong band between 1590 and 1565 cm^{-1} was attributed to $\nu(C_{carbene}—N)$ in the newly formed ADC-moiety.

The ^{1}H NMR spectra of **33**, **34**, **39**, **40**, and **45**–**48** display a peak in the range of δ 7.6–10.3 assigned to the Pd—$C_{carbene}$=N(*H*)R^1 proton. In addition, ^{1}H NMR spectra exhibit two broad peaks from Pd—$C_{carbene}$=N(*H*)N(*H*)Y protons in the range of δ 8.8–11.0. Addition of **5**–**21** to **1**–**4** in all possible combinations is accompanied by a pronounced downfield δ ^{13}C shift of one of the isocyanide quaternary C atom to the range specific for ADC Pd—$C_{carbene}$ (δ 160–224 ppm) [5,6,18–25]. The $C_{carbene}$=NH ^{13}C signals in **34**–**35**, **40**–**41**, and **46**–**49** were found to resonate at *ca.* δ 180 ppm, that is *ca.* 65 ppm downfield shifted *vs.* **1** (e.g. 115 ppm for C≡N in *cis*-[$PdCl_2(CyNC)_2$]). These are the typical patterns observed for the related complexes with amino(hydrazido)carbene ligands [6].

The crystallographic data and processing parameters for **38** are listed in Table S1 (see Supporting Information), the plot for the

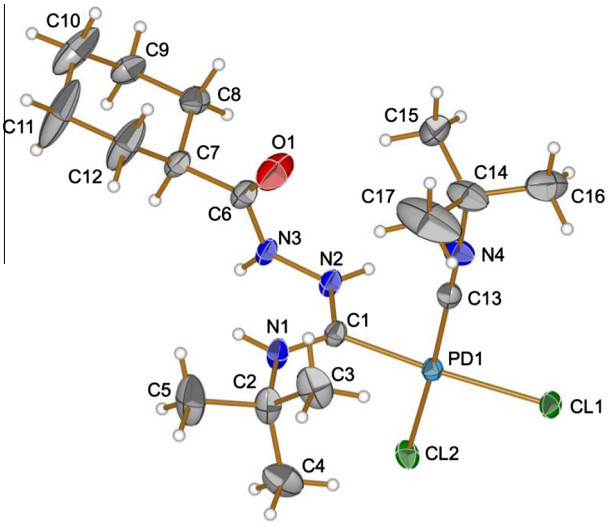


Fig. 2. View of **38** with the atomic numbering schemes. Thermal ellipsoids are drawn with the 50% probability level. Hydrogen labels are omitted for simplicity. Selected bond lengths (Å) and angles (°): Pd1—C13 1.942(4); Pd1—C1 1.978(3); Pd1—Cl2 2.3234(8); Pd1—Cl1 2.3520(8); O1—C6 1.209(4); N1—C1 1.313(4); N1—C(2) 1.503(4); N2—C1 1.340(4); N2—N3 1.389(4); N3—C6 1.353(4); N4—C13 1.140(4); N4—C14 1.464(4); C6—C7 1.510(5); C13—Pd1—C1 88.6813; C13—Pd1—Cl2 177.04(10); C1—Pd1—Cl2 88.49(9); Cl2—Pd1—Cl1 92.10(3); C1—N1—C(2) 129.3(3); C1—N2—N3 122.0(2); C6—N3—N2 120.6(3); C13—N4—C14 177.3(4); N1—C1—N2 117.6(3); N1—C1—Pd1 129.3(2); N2—C1—Pd1 113.1(2); O1—C6—N3 122.2(3); O1—C6—C7 124.9(3); N3—C6—C7 112.8(3).

structure can be found in Fig. 2, and bond lengths and angles are given in the figure legend.

In **38**, the chlorides are mutually in the *cis* position [Cl2—Pd1—Cl1 92.10(3)°] and a slightly distorted square planar environments around the metal center are completed with one unreacted isocyanide ligand and one carbene ligand, *viz.* C(NHNHCOC$_6$H$_{11}$)=NHR[1]. The Pd—C$_{carbene}$ bond lengths [Pd1—C1 1.978(3) Å] are nearly similar to those in related Pd—NHC complexes (typically 1.99–2.00 Å) [26] suggesting comparable binding strength of the ligand to the metal. The Pd—C$_{carbene}$ bond lengths are comparable to those reported for the related palladium aminocarbene complexes *cis*-[PdCl$_2$\{C(N(H)N=CPh$_2$)=N(H)Xyl\}(CNXyl)] (1.924(3) Å) [5], *cis*-[PdCl\{C(N=C(C$_6$R^{2}R^{3}R^{4}R^{5}CON))=N(H)Cy\}(CNCy)] (2.001(3) Å) [27], and *cis*-[PdCl\{C(N=C(C$_6$H$_4$CNHN))=N(H)Xyl\}(CNXyl)] (2.015(9) Å) [28]. In **38**, the carbene moiety is roughly planar and the angles around the carbene C1 atoms range from 113.1° to 129.3° therefore sustaining the *sp*^{2} hybridization of this atom. The two C$_{carbene}$—N bond lengths of the carbene fragment are slightly different [N1—C1 1.313(4), N2—C1 1.340(4) Å]. This observation indicates substantial p_π–p_π interactions within the N1—C1—N2 fragments, as detected in the abovementioned palladium-aminocarbene complexes [5,27,28]. In the isocyanide ligand, the C≡N triple bond (N4—C13 1.140(4) Å) has a normal value for the typical triple CN bond (1.136–1.144 Å) and is coherent with that observed in the related isocyanide palladium complexes, e.g. *cis*-[PdCl$_2$(CNR)$_2$] [R = Cy (1.128–1.142 Å), *t*Bu (1.108–1.149 Å), Xyl (1.145–1.156 Å)] [29–31].

*Application of **21–48** as catalysts for Sonogashira cross-coupling.* Taking into consideration our previous reports on application of the palladium-ADCs in a copper-free Sonogashira reaction [11], we evaluated catalytic properties of **21–48** in this process. The reaction of 4-iodoanisole with phenylacetylene accomplishing 1-methoxy-4-(phenylethynyl)benzene has been chosen as a model system for the copper-free Sonogashira coupling. We employed EtOH as an environmentally benign solvent and K_2CO_3 in the place of a base. Under these conditions, we observed that the conversion of 4-iodoanisole is essentially complete after *ca.* 1 h. No visible catalyst decomposition was observed.

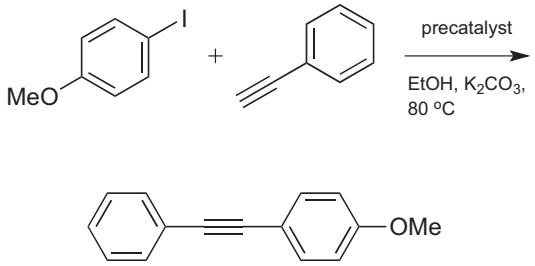
Comparison of the catalytic activity of complexes **21–48** in the model Sonogashira reaction shows that all of them exhibit elevated and comparable efficiencies (Table 2 contains results for the most active catalysts; for the full data set see Table 2S of Supporting Information). The discrepancy in observed activity between **21** and **48** is lower than a medium value of 89 ± 5% with an exception of precatalysts **21**, **27**, **30**, and **39**. Slightly lower activity of these species can be at least partially explained by their lower solubility in ethanol even at 80 °C.

Indeed, with the majority of **21–48**, the coupling product was obtained in 75–96% yields (catalyst loading of 0.01 mol%). Complexes **22** (entry 1, Table 2, product yield 94%), **28** (entry 3, 92%), **38** (entry 7, 93%), and **44** (entry 7, 92%) as the most active were tested at lower catalyst loading (0.001 mol% instead of 0.01 mol%). Moderate catalytic activity was observed, and the product yield was 26–34% (entries 2, 4, 6 and 8, Table 2), with the maximum yield of 33% for complex **38**. No product formation was observed upon further decreasing the catalyst loading to 10^{-10} mol (0.0001 mol%).

As the next step, we examined the scope of our catalytic system using representative catalysts **28**, **38**, and **44**. Aryl iodides and aromatic terminal alkynes containing both electron-donating and electron-withdrawing substituents can be successfully transformed into the target products in good to excellent yields (Table 3 and 3S). No formation of undesired homocoupling products were detected in any of these trials. Attempts to employ aryl bromides as substrates, e.g. 4-bromoanisol and 1-bromo-4-nitrobenzene under studied conditions were unsuccessful, however, we were able to transform those species under more drastic conditions (see Supporting Information for more details). Thus, moderate to good yields of the corresponding products were obtained starting from 4-bromoanisol (58%) and 1-bromo-4-nitrobenzene (95%) at 130 °C for 24 h of reaction using 1 mol% of precatalyst.

All prepared palladium complexes **21–48** were evaluated as catalysts for Sonogashira coupling of aryl iodides and aromatic terminal alkynes containing both electron-donating and electron-withdrawing substituents showing excellent activity (products yields up to 75–96%, TONs up to 10^4).

Table 2
Comparison of the catalytic activity of **21–48**.

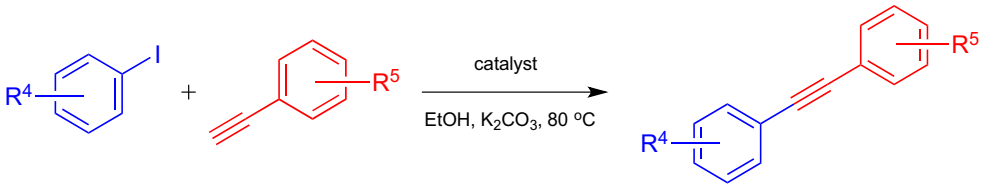


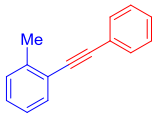
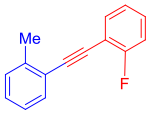
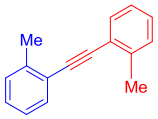
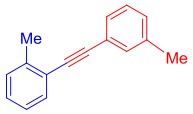
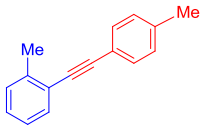
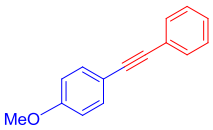
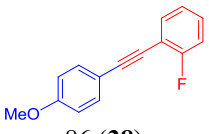
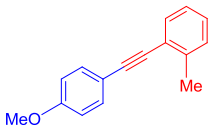
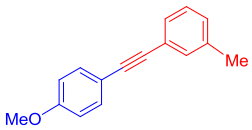
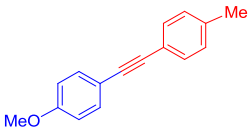
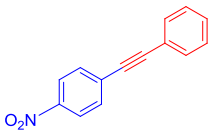
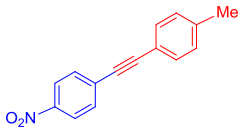
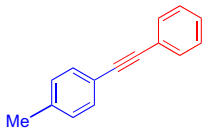
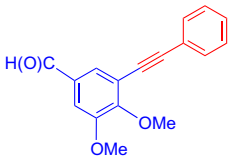
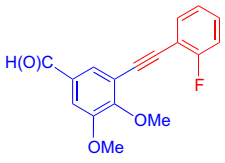
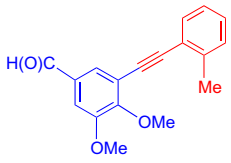
Entry	Cat	Yield, % (TON)
1–2	**22**	94 (9.4×10^3); 34 (3.4×10^4)[a]
3–4	**28**	92 (9.3×10^3); 26 (2.6×10^4)[a]
5–6	**38**	93 (9.3×10^3); 33 (3.3×10^4)[a]
7–8	**44**	92 (9.2×10^3); 31 (3.3×10^4)[a]

K_2CO_3 (2.5×10^{-4} mol, 2.5 equiv), 4-iodoanisole (1.0×10^{-4} mol, 1.0 equiv), phenylacetylene (1.5×10^{-4} mol, 1.5 equiv); selected catalyst (1×10^{-8} mol); EtOH (1 mL), 80 °C, 1 h.

[a] Yields at catalyst loading 0.001 mol% (reaction time increased to 5.5 h).

Table 3
Product scope for the copper-free Sonogashira system employing **21**–**48**.



Products and yields, % with the selected (**catalyst**)			
 97 (**28**)	 86 (**44**)	 75 (**38**)	 89 (**38**)
 92 (**44**)	 93 (**38**)	 86 (**38**)	 79 (**44**)
 74 (**28**)	 83 (**38**)	 99 (**38**, **44**)	 98 (**38**, **44**)
 98 (**28**)	 74 (**38**)	 99 (**28**, **38**)	 86 (**44**)

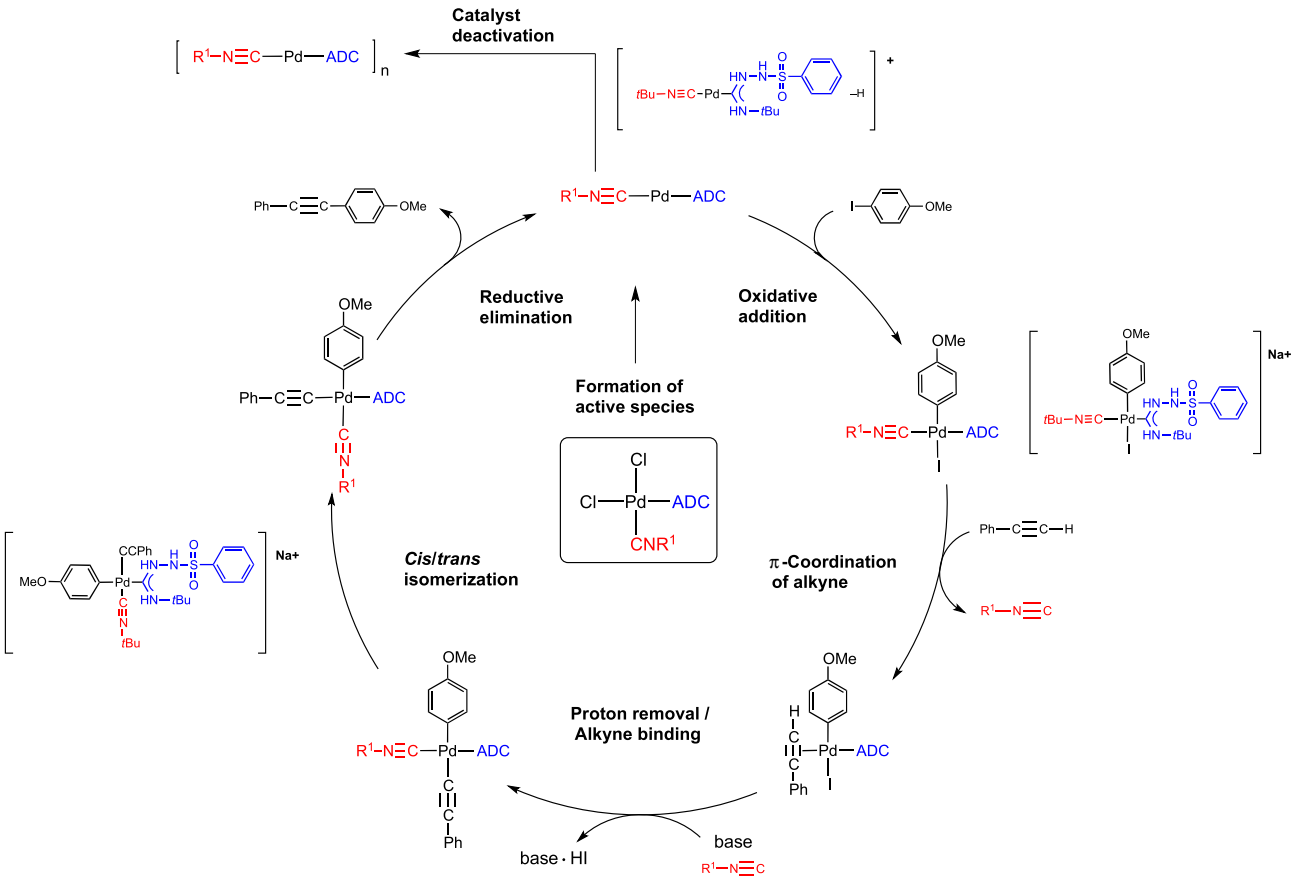
Base K_2CO_3 (2.5×10^{-4} mol, 2.5 equiv), aryl iodide (1.0×10^{-4} mol, 1 equiv), alkyne (1.5×10^{-4} mol, 1.5 equiv); selected catalyst (1×10^{-8}mol); EtOH (1 mL), 80 °C, 1 h.

Comparison of our results with those previously reported by Dhudshia and Thadani [7] indicates that Pd-ADC catalysts from this study are significantly more efficient than former, although they are only slightly better than the system based on the related palladium complexes with amino(hydrazido)carbene ligands reported previously by some of us [11].

Approaches to identification of catalytic species. Despite the fact that Sonogashira coupling is one of the most extensively explored cross-coupling reactions, its mechanism remains unclear even in case of an apparently more transparent copper-free process [32]. Furthermore, the replacement of the catalyst with one of a different type alters dramatically and unpredictably the nature of the catalytic intermediates. While application of popular palladium-NHC species in Sonogashira reaction is well documented [32–34], only limited evidence on the nature of the catalytically active species and mechanism were obtained, and the key step of the process involves the π-coordination of an alkyne to a unsaturated palladium-NHC center followed by proton removal from alkyne upon action of base that occurs directly at the metal. In case of palladium-ADC species, in our previous work we got some first evidence on the nature of the catalytic species formed from the palladium-ADC precatalysts. Indeed, we established that the [M(carbene)] fragment is responsible for the catalytic action and that the mechanism is homogeneous. We were, however, unable to identify other intermediates of the catalytic cycle (e.g. products of the oxidative addition or alkyne binding to the palladium center) and to confirm the proposed catalytic cycle.

In pursuit of this study, we resumed our previous attempts of identification of catalytic species that are formed throughout the catalytic cycle. In the first set of experiment, we performed several catalytic runs of the model system in the presence of metallic Hg (the mercury drop test [35]) using five representative precatalysts **22**, **28**, **38**, **42**, and **44**. Similar reaction rates for the corresponding processes both in the absence and in the presence of metallic Hg for any combination of substrates were detected. Furthermore, using representative precatalysts time-dependent reaction profiles for a model reaction system were acquired (see Supporting Information). On basis of those, no induction period in the system was detected, and the accumulation of the product in the initial period followed nearly linear time-dependence. Both observations suggest that no formation of palladium nanoparticles occurs during the reaction and that the catalytic system operates under typically homogeneous conditions.

In the second set of experiments, HRESI-MS monitoring (see Figs. 1S–4S, Supporting Information) of the reaction mixture for the model catalytic system [data with representative precatalyst **42**, *viz*. *cis*-[$PdCl_2${C(NHNHS(O)$_2$Ph)=N(H)*t*Bu}(CN*t*Bu)]; $C_{16}H_{26}N_4Cl_2O_2PdS$, M = 514.0183 g/mol] allowed the identification of intermediates formed in the course of our palladium-ADC-catalyzed process (Scheme 2).



Scheme 2. Proposed mechanism for the copper-free Sonogashira coupling catalyzed by **21**–**48** based upon the identification of catalytic intermediates.

Indeed, we initiated our reaction by addition of K_2CO_3 to the model reaction mixture at RT. Immediately after the addition, the signal corresponding to the [M(carbene)(CNR)]$^{2+}$ species [in the MS-spectra: [M−2Cl−H]$^+$, *m/z*: 443.0764 (found), 443.0728 (calcd.)] was detected in the spectrum. This species is formed upon removal of the chlorides from the starting **42** (Fig. 1S), and contains palladium(II) center; its reduction to palladium(0) derivatives does not proceed at RT.

Upon heating of the mixture several new peaks emerged in the HRESI-MS spectra. Indeed, the first group of signals with *m/z* of 701.0287 [M−2Cl+MeOC$_6$H$_4$I+Na]$^+$ (*m/z*: 701.0245, calcd.) matches to the product of oxidative addition of MeOC$_6$H$_4$I to the pre-formed [M(carbene)(CNR)]^0 (Fig. 2S; Oxidative addition step from Scheme 2). Unfortunately, the latter species was not evident in the spectra at any stage of the catalytic process, hence, we believe that [M(carbene)(CNR)]^0, being coordinatively unsaturated, reacts promptly with the MeOC$_6$H$_4$I substrate. The signal due to the oxidative addition remains present until full disappearance of the substrates and we believe in this case, it represents the catalyst resting state.

Second set of the signals with *m/z* of 675.1680 detected in the model catalytic reaction corresponds to the product of the alkyne binding to the metal center with subsequent coordination of the isocyanide [M−2Cl+MeOC$_6$H$_4$+CCPh+Na]$^+$ (*m/z*: 675.1592, calcd.) (Proton removal/Alkyne binding step, Fig. 3S).

To bring additional evidence on the mechanism of the process, step-by-step formation of the catalytic intermediates, was explored. Thus, the HRESI-MS spectra of the reaction mixture in the absence of phenyl acetylene (addition of MeOC$_6$H$_4$I and K_2CO_3 to the solution of **42** in EtOH followed by heating of the resulting mixture) brought about the emergence of similar signal due to oxidative addition in HRESI-MS (*m/z* of 701.0287 [M−2Cl+MeOC$_6$H$_4$I+Na]$^+$; *m/z*: 701.0245, calcd.). Subsequent addition of phenylacetylene to this solution and heating led to appearance of the signal with *m/z* of 675.1680 (product of the alkyne binding to the metal center with subsequent coordination of the isocyanide [M−2Cl+MeOC$_6$H$_4$+CCPh+Na]$^+$; *m/z*: 675.1592, calcd.). Summarizing our data with the previously reported mechanistic studies on Sonogashira catalysis [32,36,37], we propose the full catalytic cycle employing palladium-ADC precatalysts (Scheme 2).

Throughout the catalytic run, we detected the gradual deceleration of the process. After 1 h (typical time for one catalytic experiment), the addition of the fresh substrates and the base to the system does not lead to generation of a new portion of product. In the HRESI-MS spectra taken at this time (Fig. 4S), we detected the disappearance of the signals from [M(carbene)(CNR)]$^{2+}$ and oxidation addition product [M−2Cl+MeOC$_6$H$_4$I+Na]$^+$ along with the accumulation of the palladium clusters containing several palladium atoms. Despite the previous reports on catalytic activity of small palladium clusters (see Ref. [38] and references therein), in our case these compounds are apparently not catalytically competent. Indeed, we consider their formation as one of the plausible catalyst deactivation pathways. It was previously reported [39] that the generation of the catalytically active clusters from the corresponding complexes is inhibited in the presence of the carbene ligands presumably due to their strong binding to the metal core.

3. Conclusions and final remarks

In pursuit of the studies, we prepared several new amino (hydrazido)carbene-palladium complexes via the metal-mediated

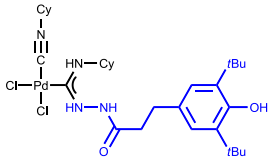
addition of carbo- and sulfohydrazides to one of the coordinated isocyanides in *cis*-[$PdCl_2(CNR^1)_2$]. Evaluation of the catalytic properties of prepared palladium-ADC species in Sonogashira coupling indicated that all of them exhibit high catalytic activity. Indeed, with catalyst loading as low as 0.01 mol%, catalytic system that runs in environmental benign EtOH under copper-free conditions afforded the target internal alkynes in 75–96% yields and with TONs up to 10^4. We were also able to propose the full catalytic cycle for this copper-free Sonogashira protocols upon identification of key intermediates, including catalytically active [M(carbene)(CNR)] species, and intermediates formed upon oxidative addition of aryl halide and alkyne binding. Catalyst deactivation in this system is accompanied by the generation of small Pd clusters that are not catalytically competent.

4. Experimental section

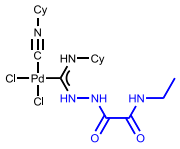
Materials and instrumentation

Solvents, $PdCl_2$, and all organic compounds were obtained from commercial sources and used as received, apart from chloroform, which was purified by the conventional distillation over calcium chloride. The complexes *cis*-[$PdCl_2(CNR^1)_2$] (**1**–**4**) [15,16] and **22**–**33**, **36**–**39**, and **42**–**45** [6] were prepared by the reported procedures. C, H, and N elemental analyses were carried out on a Euro EA 3028 HT CHNSO analyzer. Mass spectra were acquired on Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source, MeOH was used as the solvent. The instrument was operated at positive ion modes using *m/z* range of 50–3000. The capillary voltage of the ion source was set at −4500 V (ESI^+) and the capillary exit at +(70–150) V. The nebulizer gas pressure was 0.4 bar and drying gas flow was 4.0 L/min. The most intensive peak in the isotopic pattern is reported. Infrared spectra were recorded on a Shimadzu FTIR 8400S instrument (4000–400 cm^{-1}) in KBr pellets. ^1H, $^{13}C\{^1H\}$, and DEPT NMR spectra were acquired on a Bruker 400 MHz Avance spectrometer at ambient temperature.

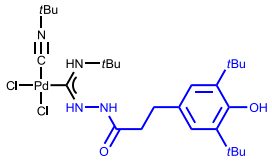
X-ray Structure Determination. The crystal of **38** was immersed in cryo-oil, mounted in a MiTeGen loop, and measured at a temperature of 123 K. The X-ray diffraction data were collected on an Agilent Technologies Supernova diffractometer using Cu Kα radiation (λ = 1.54184 Å). The *CrysAlisPro* [40] program package was used for cell refinements and data reductions. The structure was solved by charge flipping method using the *SUPERFLIP* [41] program. An analytical absorption correction (*CrysAlisPro*) [40,42] was applied to the data. Structural refinement was carried out using *SHELXL-97* [43] with the *Olex2* [44] and *SHELXLE* [45] graphical user interfaces. Solvents of crystallization ($CHCl_3$, iPr_2O, CH_2Cl_2) were severely disordered and partially lost. Only one $CHCl_3$ molecule could be located from the difference Fourier map. However, even that was partially lost and therefore refined with occupancy of 0.25. Other solvent molecules could not be located. The contribution of solvent to the calculated structure factors was taken into account by using a SQUEEZE routine of PLATON [46]. The crystal under investigation was weakly diffracting and the cyclohexyl and *tert*-butyl groups were slightly disordered. However, no disorder model was applied in the final refinement. Therefore, the U_{eq} for one of the cyclohexyl carbon (C11) remained high. Also, the poor diffraction power was the reason for missing of some reflections. The hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.98–1.00 Å, N—H = 0.88 Å, and U_{iso} = 1.2–1.5 U_{eq}(parent atom). The crystallographic details are summarized in Table S2.



33. Yield 86%. Anal. Calcd for $C_{31}H_{50}N_4Cl_2O_2Pd$: C, 54.11; H, 7.32; N, 8.14. Found: C, 54.14; H, 7.31; N, 8.13. HR-MS (ESI^+, 70 V, MeOH), *m/z*: calc 687.2418 for $C_{31}H_{51}N_4Cl_2O_2Pd^+$, found 687.2421 $[M+H]^+$, calc 651.2652 for $C_{31}H_{50}N_4ClO_2Pd^+$ found 651.2658 $[M-Cl]^+$. IR (KBr, selected bands, cm^{-1}): ν(O—H) 3642 (s), ν(N—H) 3240 (m), ν(C—H) 2962–2870 (m), ν(C≡N) 2227 (s), ν(C=O) 1708 (s), ν($C_{carbene}$—N) 1565 (s). ^1H NMR ($CDCl_3$, δ): 1.14–3.00 (m, 42H, CH_2, CH_3), 3.84–4.00 (m, 1H, *CH*NC), 4.38–4.57 (m, 1H, NHC*H*), 7.04 (s, 2H, aryls), 7.69 (s, broad, 1H, $C_{carbene}$—N*H*—Cy), 8.88 (s, broad, 1H, $C_{carbene}$—N*H*—NH), 9.36 (s, broad, 1H, $C_{carbene}$—NH—N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.2 (2C, CH_2), 24.6 (CH_2), 24.8 (2C, CH_2), 24.9 (CH_2), 30.4 (6C, CH_3), 31.0 (CH_2), 31.7 (2C, CH_2), 34.3 (2C, $C(CH_3)$), 36.1 (CH_2), 42.6 (*CH*), 55.7 (*CH*), 59.1 (*CH*), 118.6 (*C*≡N), 125.2 (*CH*, aryls), 131.1 (*C*, aryls), 135.5 (*C*, aryls), 151.9 (*C*, aryls), 169.7 (*CO*), 177.9 ($C_{carbene}$).

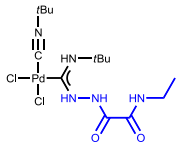


34. Yield 91%. Anal Calcd for $C_{18}H_{31}N_5Cl_2O_2Pd$: C, 41.04; H, 5.93; N, 13.29. Found: C, 41.18; H, 5.92; N, 13.25. HR-MS (ESI^+, 70 V, MeOH), *m/z*: calc 490.1196 for $C_{18}H_{31}N_5ClO_2Pd^+$, found 599.2344 $[M-Cl]^+$, calc 454.1429 for $C_{18}H_{30}N_5O_2Pd^+$, found 454.1435 $[M-2Cl-H]^+$. IR (KBr, selected bands, cm^{-1}): ν(N—H) 3245–3063 (m), ν(C—H) 2962–2853 (m), ν(C≡N) 2229 (s), ν(C=O) 1680 (s), ν($C_{carbene}$—N) 1580 (s). ^1H NMR (DMSO-d_6, δ): 0.96–2.20 (m, 23H, CH_2 + CH_3), 3.06–3.27 (m, 2H, CH_2), 4.08–4.20 (m, 1H, *CH*NC), 4.28–4.45 (m, 1H, NHC*H*), 7.80 (d, $^3J_{H,H}$ = 8.9 Hz, 1H, $C_{carbene}$—N*H*—Cy), 8.73 (t, $^3J_{H,H}$ = 5.9 Hz, 1H, N*H*Et), 10.26 (s, broad, 1H, $C_{carbene}$—N*H*—NH), 10.77 (s, broad, 1H, $C_{carbene}$—NH—N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 14.8 (CH_3), 22.3 (3C, CH_2), 24.8 (CH_2), 25.4 (4C, CH_2), 31.5 (2C, CH_2), 34.1 (2C, CH_2), 54.6 (*CH*), 59.8 (*CH*), 159.0 (*CO*), 159.3 (*CO*), 176.4 ($C_{carbene}$), C≡N were not detected.

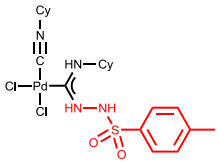


39. Yield 96%. Anal. Calcd for $C_{27}H_{46}N_4Cl_2O_2Pd$: C, 50.99; H, 7.29; N, 8.81. Found: C, 51.07; H, 7.28; N, 8.77. HR-MS (ESI^+, 70 V, MeOH), *m/z*: calc 599.2339 for $C_{27}H_{46}N_4ClO_2Pd^+$, found 599.2344 $[M-Cl]^+$, calc 563.2572 for $C_{27}H_{45}N_4O_2Pd^+$, found 563.2579 $[M-2Cl-H]^+$. IR (KBr, selected bands, cm^{-1}): ν(O—H) 3641 (s), ν(N—H) 3242 (m), ν(C—H) 2957–2871 (m), ν(C≡N) 2227 (s), ν(C=O) 1707 (s), ν($C_{carbene}$—N) 1566 (s). ^1H NMR ($CDCl_3$, δ): 1.41 (s, 18H, CH_3), 1.54 (s, 9H, CH_3), 1.68 (s, 9H, CH_3), 2.34–3.10 (m, 4H, CH_2), 7.10 (s, 2H, aryls), 7.77 (s, broad, 1H, $C_{carbene}$—N*H*—*t*Bu), 8.88 (s, broad, 1H,

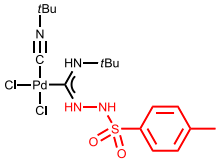
$C_{carbene}$—N*H*—NH), 9.55 (s, broad, 1H, $C_{carbene}$—NH—N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 29.8 (*C*H_3), 30.4 (*C*H_3), 31.3 (*C*H_2), 31.4 (*C*H_3), 34.3 (*C*), 36.3 (*C*H_2), 55.2 (*C*), 59.5 (*C*), 118.3 (*C*≡N), 125.4 (*C*H, aryls), 131.4 (*C*, aryls), 135.4 (*C*, aryls), 151.9 (*C*, aryls), 174.2 (*C*O), 177.4 ($C_{carbene}$).



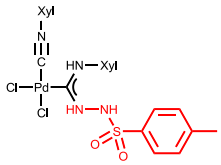
40. Yield 90%. Anal. Calcd for $C_{14}H_{27}N_5Cl_2O_2Pd$: C, 35.42; H, 5.73; N, 14.75. Found: C, 35.47; H, 5.78; N, 14.68. HR-MS (ESI^+, 70 V, MeOH), *m/z*: calc 438.0883 for $C_{14}H_{27}N_5ClO_2Pd^+$, found 438.0890 $[M-Cl]^+$. IR (KBr, selected bands, cm^{-1}): ν(N—H) 3241–3042 (m), ν(C—H) 2983–2833 (m), ν(C≡N) 2224 (s), ν(C=O) 1680 (s), ν($C_{carbene}$—N) 1576 (s). ^1H NMR (DMSO-d_6, δ): 1.08 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, *C*H_3), 1.49 (s, 9H, *C*H_3), 1.60 (s, 9H, *C*H_3), 3.09–3.27 (m, 2H, *C*H_2), 7.66 (s, 1H, $C_{carbene}$—N*H*—*t*Bu), 8.74 (t, $^3J_{H,H}$ = 5.9 Hz, 1H, N*H*Et), 10.40 (s, broad, 1H, $C_{carbene}$—N*H*—NH), 10.72 (s, broad, 1H, $C_{carbene}$—NH—N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 14.8 (*C*H_3), 29.7 (*C*H_3), 31.3 (*C*H_3), 34.1 (*C*H_2), 55.0 (*C*), 59.3 (*C*), 159.0 (*C*O), 159.5 (*C*O), 176.0 ($C_{carbene}$), C≡N were not detected.



45. Yield 86%. Anal. Calcd for $C_{21}H_{32}N_4Cl_2O_2PdS$: C, 43.35; H, 5.54; N, 9.63. Found: C, 43.38; H, 5.57; N, 9.61. HR-MS (ESI^+, 70 V, MeOH), *m/z*: calc 581.0731 for $C_{21}H_{33}N_4Cl_2O_2SPd^+$ found 581.0736 $[M+H]^+$, calc 545.0964 for $C_{21}H_{32}N_4ClO_2PdS^+$, found 545.0970 $[M-Cl]^+$. IR (KBr, selected bands, cm^{-1}): ν(N—H) 3272–3124 (m), ν(C—H) 2933–2856 (m), ν(C≡N) 2225 (s), ν($C_{carbene}$—N) 1590 (s), $\nu_{as}(SO_2)$ 1345 (s), $\nu_s(SO_2)$ 1169 (s). ^1H NMR (DMSO-d_6, δ): 1.00–1.97 (m, 20H, *C*H_2), 2.43 (s, 3H, *C*H_3), 4.17–4.42 (m, 2H, *C*H), 7.45 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, aryls), 7.74 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, aryls), 8.36 (d, $^3J_{H,H}$ = 9.4 Hz, 1H, $C_{carbene}$—N*H*—Cy), 10.03 (s, 1H, $C_{carbene}$—NH—N*H*), 10.42 (s, 1H, $C_{carbene}$—N*H*—NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 21.5 (C, *C*H_3), 22.1 (3C, *C*H_2), 24.8 (*C*H_2), 25.2 (3C, *C*H_2), 31.5 (3C, *C*H_2), 54.7 (*C*H), 59.8 (*C*H), 128.5 (2C, *C*H, aryls), 130.0 (2C, *C*H, aryls), 135.2 (*C*, aryls), 144.3 (*C*, aryls), 178.8 ($C_{carbene}$), *C*≡N were not detected.



46. Yield 91%. Anal. Calcd for $C_{17}H_{28}N_4Cl_2O_2PdS$: C, 38.54; H, 5.33; N, 10.57. Found: C, 38.62; H, 5.37; N, 10.55. HR-MS (ESI^+, 70 V, a mixture of MeOH and DMSO), *m/z*: calc 493.0651 for $C_{17}H_{28}N_4ClO_2PdS^+$, found 493.0651 $[M-Cl]^+$. IR (KBr, selected bands, cm^{-1}): ν(N—H) 3282–3128 (m), ν(C—H) 2950–2830 (m), ν(C≡N) 2227 (s), ν($C_{carbene}$—N) 1580 (s), $\nu_{as}(SO_2)$ 1345 (s), $\nu_s(SO_2)$ 1168 (s), δ(C—H from Ar) 730 (m). ^1H NMR (DMSO-d_6, δ): 1.48 (s, 9H, *C*H_3), 1.56 (s, 9H, *C*H_3), 2.44 (s, 3H, *C*H_3), 7.47 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, aryls), 7.69 (s, 1H, $C_{carbene}$—N*H*—*t*Bu), 7.76 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, aryls), 10.13 (s, 1H, N*H*), 10.69 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 21.5 (*C*H_3), 29.7 (3C, *C*H_3), 31.0 (3C, *C*H_3), 54.7 (*C*), 61.0 (*C*), 128.5 (2C, *C*H, aryls), 130.1 (2C, *C*H, aryls), 135.0 (*C*, aryls), 144.6 (*C*, aryls), 178.9 ($C_{carbene}$), C≡N were not detected.



47. Yield 84%. Anal. Calcd for $C_{25}H_{28}N_4Cl_2O_2PdS$: C, 47.97; H, 4.51; N, 8.95. Found: C, 48.06; H, 4.53; N, 8.91. HR-MS (ESI^+, 70 V, a mixture of MeOH and DMSO), *m/z*: calc 589.0651 for $C_{25}H_{28}N_4ClO_2PdS^+$, found 589.0655 $[M-Cl]^+$. IR (KBr, selected bands, cm^{-1}): ν(N—H) 3270–3154 (m), ν(C≡N) 2210 (s), ν($C_{carbene}$—N) 1565 (s), $\nu_{as}(SO_2)$ 1334 (s), $\nu_s(SO_2)$ 1170 (s). ^1H NMR (DMSO-d_6, δ): 2.23 (s, 6H, *C*H_3), 2.33 (s, 6H, *C*H_3), 2.40 (s, 3H, *C*H_3), 7.06–7.44 (m, 8H, aryls), 7.74 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, aryls), 10.20 (s, 1H, N*H*), 10.38 (s, 1H, N*H*), 10.89 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 18.5 (2C, *C*H_3), 19.3 (2C, *C*H_3), 21.6 (C, *C*H_3), 125.6 (C≡N), 128.2 (*C*H, aryls), 128.5 (*C*H, aryls), 128.6 (*C*H, aryls), 128.8 (*C*H, aryls), 129.9 (*C*H, aryls), 131.0 (*C*H, aryls), 135.3 (*C*, aryls), 135.9 (*C*, aryls), 136.0 (*C*, aryls), 136.7 (*C*, aryls), 137.9 (*C*, aryls), 144.3 (*C*, aryls), 182.9 ($C_{carbene}$).

48. Yield 88%. Anal. Calcd for $C_{23}H_{22}N_4Cl_4O_2PdS$: C, 41.43; H, 3.33; N, 8.40. Found: C, 43.46; H, 3.31; N, 8.37. HR-MS (ESI^+, 70 V, MeOH), *m/z*: calc 628.9558 for $C_{23}H_{22}N_4Cl_3O_2PdS^+$, found 628.9562 $[M-Cl]^+$. IR (KBr, selected bands, cm^{-1}): ν(N—H) 3240–3064 (m), ν(C≡N) 2204 (s), ν($C_{carbene}$—N) 1565 (s), $\nu_{as}(SO_2)$ 1340 (s), $\nu_s(SO_2)$ 1170 (s), δ(C—H from Ar) 775 (m). ^1H NMR (DMSO-d_6, δ): 2.36 (s, 3H, *C*H_3), 2.37 (s, 3H, *C*H_3), 2.40 (s, 3H, *C*H_3), 7.26–7.36 (m, 5H, aryls), 7.46–7.59 (m, 3H, aryls), 7.81 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, aryls), 10.32 (s 1H, $C_{carbene}$—N*H*—Ar), 10.36(s, 1H, $C_{carbene}$—N*H*—NH), 11.05 (s, 1H, $C_{carbene}$—NH—N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 18.9 (2C, *C*H_3), 19.8 (2C, *C*H_3), 21.6 (C, *C*H_3), 124.5 (C≡N), 127.5 (*C*H, aryls), 128.2 (*C*H, aryls), 128.8 (*C*H, aryls), 129.7 (*C*H, aryls), 130.0 (*C*H, aryls), 130.1 (*C*H, aryls), 132.2 (*C*, aryls), 132.6 (*C*, aryls), 135.1 (*C*, aryls), 136.4 (*C*, aryls), 137.9 (*C*, aryls), 139.0 (*C*, aryls), 140.7 (*C*, aryls), 144.4 (*C*, aryls), 183.7 ($C_{carbene}$).

General procedure for the catalytic Sonogashira cross-coupling. K_2CO_3 (2.5×10^{-4} mol, 2.5 equiv), aryl iodide (1.0×10^{-4} mol, 1.0 equiv), and alkyne (1.5×10^{-4} mol, 1.5 equiv) were mixed in a 10-mL vial, followed by addition of a solution of the selected catalyst (1×10^{-8} mol) in EtOH (1 mL). The vial was placed in a preheated oil bath at 80 °C and stirred for 1 h. After cooling to 20–25 °C, the reaction mixture was evaporated to dryness under a stream of dinitrogen followed by addition of 1.0 equiv of 1,2-dimethoxyethane as NMR internal standard, and extraction of the reaction mixture with three 0.20-mL portions of $CDCl_3$. All fractions were joined and analyzed by ^1H NMR spectroscopy. The product peak assignments were based on the authentic samples or on published data [47–53], whereas quantifications were performed

upon integration of the selected peak of the product relatively to the peak of the standard.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.06.001.

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