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1,2,3-Triazol-5-ylidene bearing a pyridine auxiliary based bidentate PEPPSI type palladium(II) complex: Synthesis, structure, and application in the direct arylation of pyridine *N*-oxide

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Abstract

A novel PEPPSI (pyridine enhanced precatalyst preparation stabilization and initiation) type palladium(II) complex has been synthesized and fully characterized by NMR, HR-MS, as well as elemental analysis. The molecular structure was finally confirmed by single crystal X-ray diffraction, and it revealed that the pyridyl-armed 1,2,3-triazole ligand is coordinated to the palladium in bidentate fashion. This air and moisture insensitive complex has proven to be a suitable catalyst for the arylation of pyridine *N*-oxides and 2-bromopyrroles with a broad functional group tolerance, demonstrating that the robustness and high efficiency of our complex.

Keywords: Mesoionic carbene, PEPPSI, *N*-heterocyclic carbene, 1,2,3-Triazol-5-ylidene, Bidentate palladium(II) complex, Arylation

1. Introduction

Transition-metal-catalyzed cross coupling has been recognized as one of the most powerful carbon–carbon bond formation processes [1–3]. The development of catalysts, especially the evolution of ligands is critical for homogeneous catalysis. In this area, phosphine-based ligands have been predominant for a long time until *N*-heterocyclic carbene–palladium (NHC–Pd) type precatalysts exhibited their effectiveness and versatilities [4]. Since then, a broad variety of complexes containing imidazole-, triazole-, or tetrazole-based carbene have been introduced [5,6].



Fig. 1. Representative NHC-palladium complexes.

The mesoionic carbenes (MICs) [7], also known as abnormal carbenes (aNHCs), are similar to normal NHCs except that the canonical resonance structures cannot be depicted without the introduction of extra charges [8]. Carbenes based on 1,2,3-triazoles which could be readily accessed through Click reaction [7,9,10] are well studied. The first typically trisubstituted triazolylidenes with alkyls in the N1 and N3 positions and aryls in the C4 or C5 position were reported by Albrecht in 2008 [11] (Fig. 1, left). The presence of triazole unit offers an interesting alternative to the traditional framework and has been found to render interesting variation in catalysis. Importantly, these ligands usually exhibit strong σ -donating properties, easily tunable steric properties, excellent air and moisture stability, as well as high dissociation energies [12].

Recently, chelated MICs assembled with a donor group are readily established themselves as privileged ligands in homogeneous catalysis [13–17]. As a consequence, the discovery of PEPPSI complexes is an important breakthrough in cross coupling chemistry (Fig. 1, center left) [18,19]. This combined electronic effect renders the metal more electron rich [20,21], allowing for more favorable oxidative

insertion. In this class of tightly bonded complexes, the pyridyl group readily departs in *situ* [22] to generate a vacant site to promote the coupling process [23].

It has been demonstrated that triazolylidene-based palladium complexes show enhanced thermal stability (above 100 °C), and documented that catalysts bearing both NHCs and auxiliary ligands such as N- [24], (Fig. 1, center right) P- [25], and other donors [26] exhibit enhanced catalytic activities in several coupling reactions [27]. In order to enhance the structure rigidity and overcome the drawbacks of free pyridine donors, we envisioned that a 1,2,3-triazole backbone with an additional pyridyl arm (Fig. 1, right) could coordinate with palladium in bidentate fashion to provide both bulky steric hindrance and strong electronic donation, and therefore a more efficient cross coupling reaction could be conducted on this basis. Accordingly, we reported herein a preparation of a 1,2,3-triazole based PEPPSI type palladium complex and its application in cross coupling reaction.

2. Results and discussion



Scheme 1 Sequential procedure for the synthesis of palladium complex 5.

2.1 Synthesis and characterization of palladium complex 5

The complex **5** was synthesized through a four-step procedure in good overall yield (Scheme 1). The protocol was started with the reaction between

4-(ethoxycarbonyl)pyridine 1-oxide (1) and NaN₃ in the presence of stoichiometric amount of toluenesulfonyl chloride (TsCl) as internal activator at elevated temperature, tetrazole **2** was generated as the majority form in the tetrazole/azide equilibrium. The mixture was then subjected to a copper catalyzed Click reaction with phenylacetylene to deliver the triazole **3** in 85% isolated yield. The following step of the reaction sequence was a quaternization of a triazole nitrogen atom with trimethyloxonium tetrafluoroborate ([Me₃O]BF₄) under ice cold to room temperature conditions in DCM to give triazolium tetrafluoroborate **4**, which was isolated as a white powder. Next, treatment of **4** with Ag₂O under dark yields Agl(carbene)₂ complex, which served as a carbene transfer agent, reacted with palladium precursor in a appropriate molar ratio. It has proved that Pd(CH₃CN)₂Cl₂ was the choice of reagent. In this step the initial brown mixture gradually turned yellow, indicating the completion of the reaction. Finally, 1,2,3-triazol-5-ylidene based PEPPSI type palladium complex **5** was recrystallized in 68% yield as a yellow solid, exhibiting stable properties towards air and moisture.

The complex was characterized thoroughly by various spectroscopic methods. High resolution mass spectrometry (HR-MS) of the complex **5** showed single ions with a *m*/*z* value corresponding to the [(pyridyl-armed-1,2,3-triazol-5-ylidene)PdCl]⁺ ion, indicating the NHC-Pd complex composition. Likewise, elemental analysis for **5** was in agreement with a [(pyridyl-armed-carbene)PdCl₂]_n formulation which again ruled out the possibility of a non-chelating complex. The structural assignment was ultimately confirmed by the X-ray crystallographic structure determination (vide infra).

2.2 X-ray crystallographic analyses of the complex 5



Fig. 2 The molecular structure of the complex 5, hydrogen atoms are omitted for clarity.

Single crystal suitable for the X-ray diffraction studies was obtained by slow diffusion of diethyl ether into a chloroform solution at room temperature. An oak ridge thermal ellipsoid plot (ORTEP) drawing of 5 is depicted in Fig. 2. Most of NHC-palladium complexes possess the square-planar coordination around the central palladium atom with either *trans* or *cis* arrangements of the X groups (e.g., chloride or acetate). Among the monocarbene complexes, the trans isomers are the most prevalent with the donor group usually completing the coordination of the metal center [28]. The cis arrangement is less populated and is likely to occur when the additional donor group is directly bonded to the NHC fragment to form a four- to eight-membered palladacycle [15,29]. As expected, the geometry of complex 5 around palladium is square planar sphere with the triazole ligand and the attached pyridyl donor disposed at a cis position and the other two chlorine atoms also placed in cis fashion, respectively. As a consequence, a five-membered chelate ring is formed through the functionalized pyridine donor to the metal centre (Figure 1). For the classic PEPPSI type complexes with free pyridyl donors, the triazolylidene rings is usually nearly perpendicular to the plane containing a palladium atom, X groups, carbene carbon and pyridine nitrogen [30]. In this complex, however, the triazolylidene ring, pyridine ring, the palladium, as well as two chlorine atoms are almost coplanar.

Pd1–Cl1	0.2353(2)	C14–N1	0.1362(10)	
Pd1–C8	0.1986(8)	C10–N2	0.1424(10)	
Pd1–N1	0.2039(6)	C8–N2	0.1355(10)	
N2–N3	0.1335(9)	C9–N4	0.1472(10)	
N3–N4	0.1316(9)	C8–C7	0.1385(11)	
CI1-Pd1-CI2	91.57(8)	N2-C10-C11	124.1(7)	
CI1-Pd1-N1	94.06(19)	C10–N2–C8	123.0(7)	
CI1-Pd1-C8	175.3(2)	C10-N2-N3	121.0(6)	
Cl2–Pd1–C8	93.1(2)	C8–N2–N3	115.9(6)	
Cl2-Pd1-N1	174.31(19)	N2-C8-C7	103.4(7)	
C8–Pd1–N1	81.3(3)	N2-C8-Pd1	110.3(5)	
Pd1-N1-C10	115.7(5)	C7-C8-Pd1	146.2(6)	
Pd1-N1-C14	129.1(6)	C8–C7–N4	104.5(7)	
N1-C10-N2	109.4(7)	C7-N4-C3	115.4(6)	
N1-C10-C11	126.4(7)	N2-N3-N4	100.8(6)	

Table 1 Selected bond lengths (nm) and elected bond angles (°) of complex 5.

Selected principal bond lengths and interbond angles are shown in Table 1. The $Pd-C_{trz}$ (trz = triazolylidene) bond length is 1.986(8) Å, which is in line with those of related triazolylidene–palladium complexes (Table 1) [31]. The Pd–Cl bond distance *trans* to the triazole carbene Pd1–Cl1, is 2.353(2) Å, 0.087 Å longer than the other Pd–Cl distances *trans* to the pyridyl nitrogen atom, Pd1–Cl2. This bond elongation phenomenon is usually observed and could be attribute to the *trans* effect of the NHC ligands [15,29]. Compared with other carbenes, the Pd1–N1 bond length, 2.039(6) Å, is 0.01–0.04 Å shorter than nitrogen containing groups chelated complexes [15,29], and 0.06–0.09 Å shorter than complexes with free pyridyl donors [32], indicating the stability of the resulting coordination. The bite angle of C(7)–Pd(1)–N(1) is 81.3(3)°, similar with previous reports [32]. The palladium and atoms bonded around are exactly in a plane and there is no out-of-plane distortion, with the summation of the four angles around the palladium central being 360.03 °. Other structural parameters are unexceptional.

2.3 Direct arylation of pyridine N-oxide

Table 2 Identification reaction conditions for the palladium complex 5 catalyzed cross coupling reaction pyridine *N*-oxide and 2-bromopyrrole^a

	⊖ ⊖ ⊖ O 6a	L _н	+ Br	ba N s R 7f	5 (x mol ⁴ se (1.5 e tetracosa (15 mg olvent (2 temperat N ₂	%) quiv.) ane) mL) ure	R N ⊖ 0 8aa–8af	
Entry	R	х	Base	Solvent	T (°C)	t (h)	Conversion (%) ^b	Yield (%) ^c
1	H (7a)	1	NaOH	DMF	100	18	<5	ND^{d}
2	Me (7b)	1	NaOH	DMF	100	18	70	58
3	Ph (7c)	1	NaOH	DMF	100	18	72	55
4	Bn (7d)	1	NaOH	DMF	100	18	76	70
5	Ts (7e)	1	NaOH	DMF	100	18	92	tracee
6	NMe ₂ (7f)	1	NaOH	DMF	100	18	<5	ND^d
7	Bn (7d)	1	K_2CO_3	DMF	100	18	>99	91
8	Bn (7d)	1	K_2CO_3	DMF	100	12	97	87
9	Bn (7d)	1	Cs_2CO_3	DMF	100	18	92	83
10	Bn (7d)	1	<i>t</i> BuOK	DMF	100	18	88	82
11	Bn (7d)	1	K_2CO_3	dioxane	100	12	72	64
12	Bn (7d)	1	K ₂ CO ₃	toluene	100	12	60	55
13	Bn (7d)	1	K ₂ CO ₃	DMF	80	24	85	77
14	Bn (7d)	-	K ₂ CO ₃	DMF	100	12	33	28 ^f
15	Bn (7d)	-	K ₂ CO ₃	DMF	100	12	42	40 ^g
16	Bn (7d)	-	K ₂ CO ₃	DMF	100	12	47	44 ^h
17	Bn (7d)	0.5	K ₂ CO ₃	DMF	100	18	95	88
18	Bn (7d)	0.2	K ₂ CO ₃	DMF	100	18	83	80

^a Reaction conditions: pyridine *N*-oxide **6a** (0.40 mmol, 1.0 equiv.), 2-bromopyrrole **7a-7f** (0.48 mmol, 1.2 equiv.), base (0.60 mmol, 1.5 equiv.), indicated amount of catalyst **5**, tetracosane (15 mg) in solvent (2.0 mL, 0.2 M) under an inert atmosphere at the indicated temperature for the indicated reaction time.

^b Determined by GLC analysis with tetracosane as the internal standard.

^c Isolated yield after purification by flash column chromatography on silica gel.

^d ND = Not determined.

^e Complicate.reaction system with up to 10 compounds formed in situ.

^f Pd(OAc)₂ (10 mol%) was used as catalyst instead of catalyst **5**.

 g Pd(OAc)₂ (10 mol%) was used as catalyst instead of catalyst **5**, PPh₃ (20 mol%) was introduced as ligand.

^h Pd(OAc)₂ (10 mol%) was used as catalyst instead of catalyst **5**, 1,4-bis(diphenylphosphino)butane (DPPB, 20 mol%) was introduced as ligand.

Palladium catalyzed cross coupling reaction has established itself as a benchmark

process for the formation of biaryl compounds [33]. The steric and electronic features of ligands bound to palladium modify the activity of the metal center and their structures play a central role in catalysis. Consequently, catalytic performance studies of the palladium complex 5 with pyridyl-functionalized triazole ligand have been focused on this type of transformation. Pyridine N-oxide 6a and protected 2-bromopyrroles 7a-7f were employed as model substrates to furnish biaryl product **8aa-8af.** As illustrated in Table 2, initial protecting group screening (entries 1-6) at 100 °C in the presence of 1 mol% catalyst loading indeed provided desired products, in which benzyl was the best choice of accessory to give biaryl product 8ad in 70% yield (entry 4). However, tosyl (Ts, 7e), dimethylamino (7f), as well as unprotected 7a substrates remained almost unreacted (entries 1 and 6) or resulted in a mess mixture (entry 5). To our delight, both conversions and yields, as determined by GLC analysis with the introduction of tetracosane as internal standard, increased dramatically immediately when other bases such as potassium carbonate (K₂CO₃) or cesium carbonate (Cs₂CO₃) were employed instead (entries 7 and 9) even with a shortened reaction time (entry 8). Other solvents such as dioxane and toluene gave rise to moderate conversions and yield under the identical reaction conditions (entries 11 and 12). The detrimental effect was observed when the reaction temperature was lowered to 80 °C, reactivity disparities could not bridged even with a prolonged reaction time (entry 13). In order to clearly determine the real influence of the complex 5 compared to other Pd sources, we introduced Pd(OAc)₂ as catalyst instead. As illustrated in entries 14-16, poor to moderate yield were obtained. It is worthy to mention that phosphorus containing ligands were crucial to promote the transformation, in which 1,4-bis(diphenylphosphino)butane (DPPB) showed better reactivity than PPh₃. Our palladium complex indeed showed better reactivity towards the desired cross coupling over ordinary palladium salts. Furthermore, reducing the catalyst loading by half did not lead to much different, however, continuously decreasing would generate poor results noticeable (entries 17-18). From the viewpoint of reactivity and economic, we chose entry 14 as the optimal conditions for further investigation. It is worthy mentioning that the undesired side reactions such as homocoupling of

2-bromopyrroles, deoxygenation, and debromination of the substrates were almost suppressed.

 Table 3 Variation of the coupling partners in the palladium complex 5 catalyzed biaryl

 formation reaction^a



^a Except for other statement, all reactions were proceeded under the following reaction conditions: pyridine *N*-oxide (0.40 mmol, 1.0 equiv.), 2-bromopyrrole (0.48 mmol, 1.2 equiv.), K_2CO_3 (0.60 mmol, 1.5 equiv.), catalyst **5** (0.002 mmol, 0.5 mol%), and tetracosane (15 mg) in DMF (2.0 mL) under N₂ atmosphere at 100 °C for 18 h; isolated yield reported. ^b Reactions proceeded for 24 h.

Encouraged by these results, we extended our investigations to the other substrates derivatives to broaden the application of our catalyst. A series of coupling partners

were examined under the optimized conditions and the results were presented in Table 3. It can be concluded that the electronic and steric profiles of pyridine *N*-oxides didn't exhibit significant influences on the reactivities and efficiency, good to excellent results were achieved accordingly (**8ad-8jd**). It was worth mentioning that quinoline *N*-oxide and pyridine *N*-oxide performed equally well (**6a** \rightarrow **8ad** *vs* **6k** \rightarrow **8kd**). Additionally, however, pyrroles bearing other substituent normally exhibited slightly lower reactivities (**8ag-8ai**).

2.4 Mercury-poisoning test

The mercury drop test is a widely used protocol to confirm the formation of palladium(0) nanoparticles resulting from decomposition of homogeneous palladium complexes, since mercury(0) is able to poison the "naked" metal particles [34,35] The direct arylation of pyridine N-oxide initiated by complex 5 was accompanied by the formation of fine black solid in situ. The coordination between the bulky armed ligand and palladium atom would loosen during the catalysis process. Therefore, the possibility of formation of highly active palladium species as the active catalyst prompted us to perform mercury poisoning tests. Based on an identical condition with entry 9 of Table 2, we applied the experimental set-up with the addition of an excess amount of (200 equiv.) mercury. The most noticeable decrease in conversion (full conversion to 38%) was observed when mercury is added at the very beginning of the catalysis. Otherwise, the addition of mercury after 3 h resulted in small variations in the yields (97% to 91%), suggesting that the molecular nature of the active catalyst species. We isolated this solid material at relative lower reaction temperature (Table 2, entry 13, at 50 oC for 2 h) and characterized with transmission electron microscope (TEM), fine palladium nanoparticles were observed (refer to the Supplementary material in detail).

3. Conclusions

To sum up, we developed a novel and stable triazolylidene-based PEPPSI complex with a five-membered palladacycle. The complex was prepared by convenient method

and full characterized. It was confirmed by the crystal structure that the existence of a coplaner containing the triazole ring, pyridine ring, palladium central, as well as chlorides. The resulting complex exhibited very high reactivity towards the cross coupling between pyridine *N*-oxide and 2-bromopyrrole with very low catalyst loading. The rigid backbone based complex exhibited an air stabilization effect on the catalytic process, and the reaction could be performed in the presence of air and moisture. The cross coupling reaction was applicable for a broad substrate scope with high functional group tolerance under mild conditions, and a series of biaryl compounds were prepared in high yields. Mercury poisoning experiment, together with TEM characterization were established to preliminary proof the in *situ* generation of palladium(0) nanoparticles from the decomposition of the complex, which was recognized as highly catalytically active intermediate. Further investigation of the catalytic potential and structure modifications of the palladium complex is currently undertaking in our laboratory.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships

that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found in the online version, at: XXX.

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Highlights

- Design and synthesis of a PEPPSI type bidentate palladium complex.
- The complex was applied to the arylation of pyridine *N*-oxides and bromopyrroles.
- Mercury poisoning test was performed.
- Pd(0) nanoparticles were generated in *situ* as highly catalytically active species.

Graphical abstract