Tetrahedron 67 (2011) 7263–7267

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

1,2,3-Triazol-5-ylidene–palladium complex catalyzed Mizoroki–Heck and Sonogashira coupling reactions

Sayuri Inomata, Hidekatsu Hiroki, Takahiro Terashima, Kenichi Ogata, Shin-ichi Fukuzawa *

Department of Applied Chemistry, Institute of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

ARTICLE INFO

Article history:
Received 28 June 2011
Received in revised form 18 July 2011
Accepted 18 July 2011
Available online 22 July 2011

Keywords:
1,2,3-Triazole
N-Heterocyclic carbene
Palladium
Cross coupling
Catalysis

ABSTRACT

The bis-1,4-dimesityl-1,2,3-triazol-5-ylidene–palladium complex (**1a**) successfully catalyzes the Mizoroki–Heck and Sonogashira coupling reactions with aryl bromides to give the corresponding alkenes and alkynes, respectively, in good to excellent yields. In the Mizoroki–Heck reaction, electron-rich, electron-poor, and functionalized aryl bromides and alkenes are tolerated, while the substrates are limited to electron-poor aryl halides in the Sonogashira coupling reaction. The palladium complex also catalyzes cross-coupling reactions with aryl chlorides to give higher yields of products than does the bis-IMes–Pd complex analogue (**2**), under specific conditions.

1. Introduction

Since its discovery 20 years ago, *N*-heterocyclic carbenes (NHCs) have gained rapid popularity as versatile ligands for metal complexes.[1] In particular, numerous Pd–NHC complexes have been prepared and their catalytic activity in cross-coupling reactions, such as Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions[2] have been investigated. The majority of NHC ligands is based on an imidazole framework and imidazol-2-ylidenes (**A**) and 1,2,4-triazol-5-ylidenes (**B**) (Fig. 1),[3] which are classified as normal NHCs are frequently used. Crabtree first reported an abnormally bonded NHC (*a*NHC, **C**) complex in which the imidazolium moiety was coordinated at the C4 position.[4] Nolan[5] and Hong[6] demonstrated that Pd–*a*NHC complex was more effective than the corresponding normal NHC complex in the Suzuki–Miyaura and Mizoroki–Heck reactions; and this enhanced catalytic activity may be due to the stronger σ-donor ability of *a*NHC compared with that of normal NHCs.

Albrecht first reported an *a*NHC ligand based on 1,2,3-triazol-5-ylidene (**D**) and its metal complexes.[7] Bertrand demonstrated that the donor property of 1,2,3-triazol-5-ylidene was superior to those of imidazol-2-ylidenes and 1,2,4-triazol-5-ylidenes in the vibrational spectra study of its iridium carbonyl complexes.[8] Abnormal NHC ligands and their complexes show potential use for unique catalytic activity in organic reactions.[9] Sankararaman prepared a pyrrolidinyl 1,2,3-triazol-5-ylidene–palladium complex and examined its catalytic effectiveness in the Suzuki–Miyaura coupling reaction,[10] with aryl bromides as the substrate. Based on these previous studies, we envision that the 1,4-dimesityl substituted 1,2,3-triazol-5-ylidene (TMes) ligand precursor should be an effective ligand as is its analogue, IMes [1,3-bis(mesityl)imidazol-2-ylidene], which is an effective imidazole-carbene ligand owing to its electronically rich and sterically hindered mesityl groups (Fig. 2).

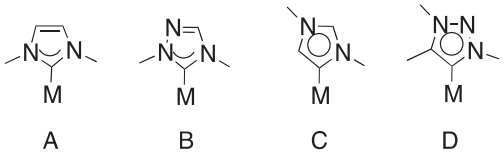


Fig. 1. Traditional NHCs (**A** and **B**) and *a*NHCs (**C** and **D**) bound to transition metals.

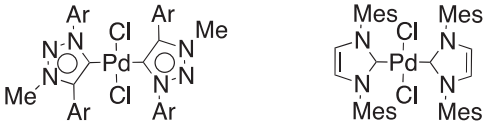


Fig. 2. *trans*-Bis(1,2,3-triazol-5-ylidene)palladium (**1**) and *trans*-bis(imidazol-2-ylidene)palladium (**2**).

* Corresponding author. E-mail address: orgsynth@kc.chuo-u.ac.jp (S.-i. Fukuzawa).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.07.045

In our preliminary study, we reported the synthesis of *trans*-$(TMes)_2PdCl_2$ (**1a**) and its catalytic behaviour in the Suzuki–Miyaura coupling reaction with aryl chlorides.[11] The reaction successfully yielded the coupling product in high amounts, and the complex proved to be particularly effective for the reaction between the sterically hindered aryl chlorides and aryl boronic acids. The palladium complex **1a** was revealed to have a higher catalytic activity than that of the corresponding imidazole NHC–Pd complex $[(IMes)_2PdCl_2]$ (**2**), under the same conditions.

We recently demonstrated that the 1,2,3-triazole NHC–copper complex was superior to the imidazole NHC–copper analogue in the CuAAC reaction.[12] The triazole NHC–copper complex significantly accelerated the reaction, and in the reaction between a sterically hindered alkyne and a sterically hindered azide, it successfully yielded a highly sterically crowded triazole. To establish the advantages of the 1,2,3-triazole NHC ligand and its palladium complexes in synthetic reactions, we extend the use of the palladium catalyst to other cross-coupling reactions. Previously we reported the Mizoroki–Heck coupling reaction between bromobenzene with *tert*-butyl acrylate using **1a** as a catalyst.[11] Herein, we describe Mizoroki–Heck and Sonogashira coupling reactions using **1** as a catalyst.

2. Results and discussion

To evaluate the activity of complex **1a**,**b**, we carried out a kinetic study of the Mizoroki–Heck coupling reaction of bromobenzene with *tert*-butyl acrylate. The yield versus time graphs are shown in Fig. 3 for **1a**,**b**. The reaction was carried out in dimethylacetamide (DMA) at 150 °C with loading 1.0 mol % of the palladium complex and was followed by gas chromatography (GC). The yield was determined by GC by using biphenyl as an internal standard. As seen in the graph, there was an initial 1-h induction period in the reaction with **1a**, and after this the reaction was accelerated and 80% product yield was achieved after 3 h. As expected, the Pd complex **1b** was less active catalyst giving 40% product yield after 8 h. The lower activity of **1b** was due to the poor electron-donor and low sterically crowded TPh ligand. During the initial 30 min the active TMes–Pd(0) complex was generated.[13] An induction period was also observed in the reaction with **1b**, and it took more than 3 h to generate the active catalyst, which was not as active as **1a**.

The reaction could be carried out with low catalyst loading or at lower temperature, however, the yield decreased although the reaction time was extended; 0.5 mol %, 85% (150 °C, 15 h), 0.1 mol %, 62% (150 °C, 15 h), 1 mol %, 56% (130 °C, 15 h) and 1.0 mol %, 7% (110 °C, 15 h). The coupling reactions between a variety of aryl bromides and *tert*-butyl acrylate were examined to explore the scope of the **1a** catalyzed Mizoroki–Heck coupling reaction. The results are summarized in Table 1. The trans-isomers were obtained as the sole products in excellent yields irrespective of the stereoelectronic properties of the benzene substituents. Electronically activated and deactivated aryl bromides tolerated the reaction, and the corresponding cinnamate esters were obtained in excellent yields (entries 1, 2 and 4–6). However, *o*-bromoanisole and *o*-nitrobromobenzene produced low product yields of 51% and 0%, respectively (entries 3 and 7). The coupling with other aromatic rings, such as 1-bromonaphthalene (entry 10) gave the corresponding α, β-unsaturated esters in quantitative yields. The heteroaromatic bromides, such as 3-bromopyridine and 2-bromothiophene (entries 12–13) coupled with *tert*-butyl acrylate to produce the corresponding products in low to moderate yields. On the other hand, the reaction with 2-bromopyridine hardly gave the coupling product (entry 11). Poor to low yields of the products may be due to heteroatoms coordinating with the palladium, therefore interfering with the catalysis role of the palladium complex.

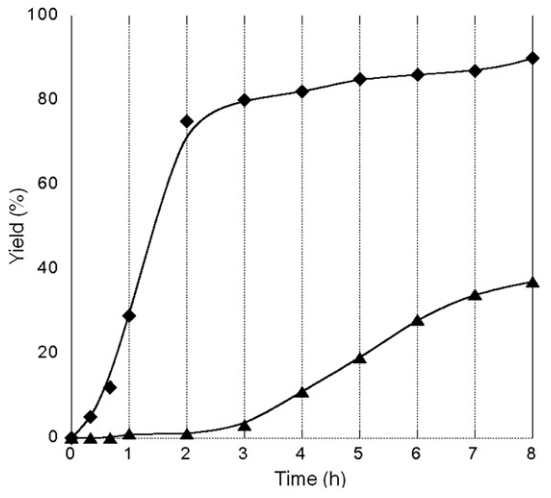
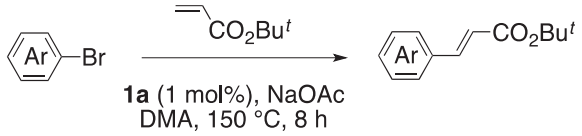


Fig. 3. Time versus yield (%) graph for the palladium catalyzed Mizoroki–Heck reaction of bromobenzene with *tert*-butyl acrylate: ◆**1a**; ▲**1b**.

Table 1
The scope of aryl bromides in the Mizoroki–Heck reaction with *tert*-butyl acrylate[a]



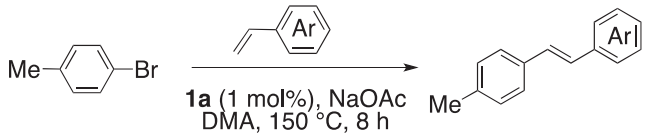
Entry	Ar	Yield[b] (%)
1	*o*-MeC_6H_4	92
2	*p*-MeC_6H_4	98
3	*o*-$MeOC_6H_4$	51
4	*p*-$MeOC_6H_4$	88
5	*p*-FC_6H_4	98
6	*p*-$CH_3COC_6H_4$	97
7	*o*-$NO_2C_6H_4$	0
8	*p*-$NO_2C_6H_4$	93
9	*m*-$NO_2C_6H_4$	94
10	1-$C_{10}H_8$	97
11	2-Pyridyl	0
12	3-Pyridyl	32
13	2-Thiophenyl	69

[a] Compound **1a** (0.005 mmol), aryl bromide (0.5 mmol), *tert*-butyl acrylate (0.75 mmol), NaOAc (1.0 mmol), DMA (1.5 mL); 150 °C, 8 h.
[b] Isolated yield: *trans*/*cis*≅99.9/0.1.

We then examined the reactions *p*-bromotoluene with various substituted styrenes under the same conditions as described above. The results are summarized in Table 2. The *trans*-stilbene derivatives were obtained from either electron-rich or electron-poor styrenes in good yields. However, the reaction with *o*-methylstyrene gave the corresponding coupling product in low yield probably due to steric hindrance. The reaction with 2-vinylpyridine gave the corresponding coupling product in low yield (entry 8); however, the reaction of 2-bromopyridine with *tert*-butyl acrylate did not give the coupling product at all (Table 1, entry 11).

As the above reactions with aryl and heteroaryl bromides and alkenes were tolerated, we were encouraged to attempt the reaction with aryl chlorides. Aryl chlorides have rarely been used for Mizoroki–Heck reaction, and addition of ammonium halide is often necessary to obtain a satisfactory yield product.[2c,14] It is interesting that moderate yields (64–69%) of products could be obtained in the reaction with *p*-chloronitrobenzene and *p*-chlorobenzonitrile in the absence of ammonium halide by using **1a** as a catalyst (entries 2 and 4, Table 3). On the other hand, bis-imidazole carbene $[(IMes)_2PdCl_2]$ (**2**) gave low yields of the products (45% and 27%,

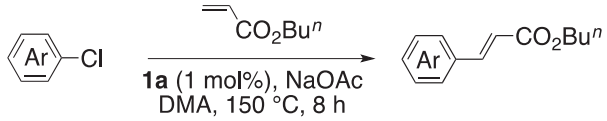
Table 2
The scope of styrenes in the Mizoroki–Heck reaction with *p*-bromotoluene[a]



Entry	Ar	Yield[b] (%)
1	C_6H_5	90
2	*p*-MeC_6H_4	98
3	*m*-MeC_6H_4	90
4	*o*-MeC_6H_4	73
5	*p*-$MeOC_6H_4$	96
6	*p*-$NO_2C_6H_4$	99
7	*p*-FC_6H_4	91
8	2-Pyridyl	48

[a] Compound **1a** (0.005 mmol), *p*-bromotoluene (0.5 mmol), alkene (0.75 mmol), NaOAc (1.0 mmol), DMA (1.5 mL); 150 °C, 8 h.
[b] Isolated yield: *trans*/*cis*≅97/3 to 81/19.

Table 3
Mizoroki–Heck reaction with aryl chlorides[a]



Entry	Ar	Yield[b] (%)
1	C_6H_5	0
2	*p*-NO_2	64
3[c]	*p*-NO_2	45
4	*p*-CNC_6H_4	69
5[c]	*p*-CNC_6H_4	27

[a] Compound **1a** (0.005 mmol), aryl chloride (0.5 mmol), *n*-butyl acrylate (0.75 mmol), NaOAc (1.0 mmol), DMA (1.5 mL); 150 °C, 8 h.
[b] Isolated yield: *trans*/*cis*≅99.9/0.1.
[c] Compound **2** was used as a catalyst.

respectively; entries 3 and 5 in Table 3). Thus, the palladium complex **1a** was superior to **2**. The reaction of chlorobenzene with *n*-butyl acrylate gave no coupling product under the conditions.

We can consider that the efficiency of **1a** is due to stronger donor property of the 1,2,3-triazolylidene ligand than that of the 2-imidazolylidene ligand. In order to estimate the donor property we measured oxidation potential of palladium complexes **1a** and **2** by cyclic voltammetry (Fig. 4). This electrochemical studies show that both complexes display irreversible oxidations, and oxidation potential of **1a** is lower than that of **2**. This result suggests that the 1,2,3-triazolylidene make the oxidation of Pd(II) more facile in comparison with the 2-imidazolylidene. We confirmed that its Ag complexes show no sign of significant oxidation, suggesting that the ligand is not readily oxidized but palladium is oxidized.[15]

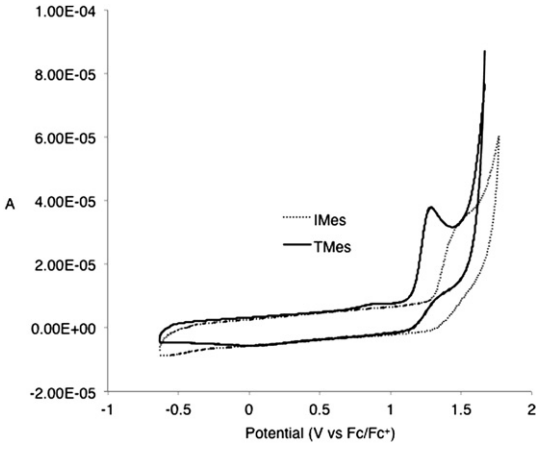
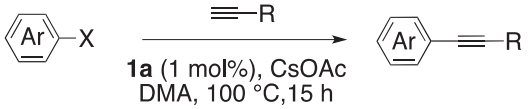


Fig. 4. Cyclic voltammograms for **1a** and **2** (dotted line).

The complex **1a** was evaluated in the Sonogashira coupling reactions of aryl halides with alkynes. The model reaction of *p*-bromonitrobenzene with phenylacetylene achieved maximum yields when CsOAc was used as a base, DMA as a solvent, and the reaction occurred at 100 °C for 15 h under copper-free conditions. Under these conditions, we examined the scope of the reaction of phenylacetylene with various aryl halides and the results are shown in Table 4. High yields of diaryl acetylenes were obtained in the reaction with electron-poor aryl halides (entries 1–5), while poor product yields were obtained in the reaction with electron-rich and neutral aryl bromides (entries 6 and 7).[16] When the reactions with *p*-chloronitrobenzene was carried out in the absence of ammonium halide at 130 °C, **1a** gave the coupling products in 63% (entry 2), while the imidazole–carbene complex (**2**) gave only 35% product yield (entry 3), suggesting **1a** again shows higher catalytic activity than **2**.

Table 4
The Sonogashira coupling reaction[a]

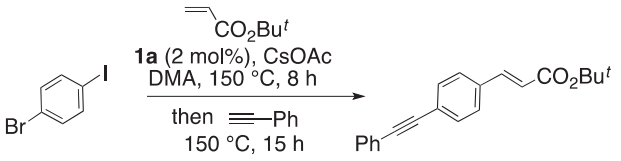


Entry	X	Ar	R	Yield[b] (%)
1	Br	*p*-$NO_2C_6H_4$	C_6H_5	94
2[c]	Cl	*p*-$NO_2C_6H_4$	C_6H_5	63[d]
3[c,e]	Cl	*p*-$NO_2C_6H_4$	C_6H_5	35[d]
4	Br	*p*-$CF_3C_6H_4$	C_6H_5	89
5	Br	*p*-AcC_6H_4	C_6H_5	93
6	Br	C_6H_5	C_6H_5	40
7	Br	*p*-$MeOC_6H_4$	C_6H_5	21
8	Br	*p*-AcC_6H_4	*p*-MeC_6H_4	89
9	Br	*p*-AcC_6H_4	*o*-MeC_6H_4	91
10	Br	*p*-AcC_6H_4	*p*-$CF_3C_6H_4$	54
11	Br	*p*-AcC_6H_4	*n*-C_6H_{13}	85
12	Br	*p*-AcC_6H_4	*i*-Pr_3Si	86

[a] Compound **1a** (0.005 mmol), aryl halide (0.5 mmol), phenylacetylene (1.0 mmol), CsOAc (1.0 mmol), DMA (3.0 mL); 100 °C, 15 h.
[b] Isolated yield.
[c] The reaction was carried out at 130 °C.
[d] GC conversion.
[e] Compound **2** was used as a catalyst.

To evaluate the applicability of the **1a** catalyst, we carried out the reaction using various substituted phenylacetylenes and terminal alkyl alkynes, by using *p*-bromoacetophenone as a counterpart (Table 4). For electron-neutral and electron-rich phenylacetylenes (*o*- and *p*-MeC_6H_4), the corresponding coupling products were obtained in good yields (entries 8 and 9). For electron-poor alkynes, such as *p*-trifluoromethylphenylacetylene, a moderate yield of product was obtained (entry 10). Terminal alkyl- and silylalkynes (entries 11 and 12) couple with *p*-bromoacetophenone to give the corresponding internal alkynes in a good yield. In summary, complex **1a** was effective for Sonogashira coupling between electron-poor aryl bromides and electron-rich alkynes.

As **1a** catalyzed both the Mizoroki–Heck and Sonogashira coupling reactions under similar conditions, we expect that the consecutive coupling reactions can occur in one-pot. We first carried out the reaction of *p*-bromoiodobenzene and *tert*-butyl acrylate using CsOAc in DMA at 150 °C for 8 h, and then phenylacetylene was added to the same flask and the reaction was left to continue at 150 °C for an additional 15 h (see Scheme 1). The tandem-coupling



Scheme 1. One-pot consecutive Mizoroki–Heck and Sonogashira coupling reactions.

product, i.e., *p*-alkynylcinnamate ester was obtained with 69% yield accompanied by small amounts of the double Mizoroki–Heck and Sonogashira products.

3. Conclusion

Electron-rich, electron-poor and functionalized aryl bromides and alkenes were tolerated in the Mizoroki–Heck reaction, while substrates were limited to electron-poor aryl halides in the Sonogashira coupling reaction. The bis-TMes–Pd complex **1a** was a more active catalyst than the bis-IMes–Pd complex analogue **2**, because it catalyzed the cross-coupling reactions with aryl chlorides to give relatively higher yields although the overall yields were low.

4. Experimental section

4.1. General

The GC/MS analyses were carried out using a Hewlett–Packard 5975B/6890N instrument equipped with a capillary column (helium as carrier gas). Preparative TLC was conducted using a 20×20 cm glass sheet coated with a 1 mm thick layer of Wakogel B-5F. All commercial compounds were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded using a Varian 300 MHz or 400 MHz NMR spectrometer as solutions in $CDCl_3$. The chemical shifts are reported in δ units downfield from the internal reference, Me_4Si. HRMS analyses were carried out using MICROMASS-LCT Spectrometer.

4.1.1. Preparation of the palladium complex. 1,4-Dimesityl-1,2,3-triazole (400 mg, 1.3 mmol) and Me_3OBF_4 (252 mg, 1.7 mmol) were stirred under a nitrogen atmosphere in dry dichloromethane (30 mL) for 18 h. The reaction mixture was quenched by 2 mL of MeOH and solvent was removed under reduced pressure to give the crude product, which was washed with diethyl ether and dried to give the triazolium salt quantitatively. Under an atmosphere of nitrogen, a solution of the salt (490 mg, 1.2 mmol) in CH_2Cl_2/CH_3CN (15 mL/15 mL) was added Ag_2O (142 mg, 0.6 mmol) and Me_4NCl (132 mg, 1.2 mmol) in a Schlenk tube. The mixture was stirred for 5 h in light shielding condition, then was added $PdCl_2(CH_3CN)_2$ (157 mg, 0.6 mmol). The mixture was stirred for 5 h and filtered through a pad of Celite. The solvent was removed under reduced pressure and the crude product was subjected to column chromatography on alumina (CH_2Cl_2, 100%) to give Pd complex **1a** (419 mg, 0.51 mmol, 85% yield) as light yellow solid. Mp: 270–272 °C. FT-IR (KBr): 2918, 1712, 1612, 1460, 1378, 1322, 1272, 1184, 1110, 1063, 1023, 848 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97 (s, 12H), 1.98 (s, 12H), 2.44 (m, 12H), 3.73 (s, 6H), 6.95 (m, 8H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 18.7, 21.0, 21.3, 21.4, 35.9, 124.6, 128.3, 128.8, 136.0, 136.5, 139.0, 139.3, 139.7, 143.8, 163.0 (C–Pd). Anal. Calcd. $C_{42}H_{50}Cl_2N_6Pd$: C, 61.80; H, 6.17; N, 10.30. Found: C. 61.89; H, 6.35; N, 10.11.

Compound **1b**:[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H) 3.98 (s, 3H), 7.16 (t, 2H, *J*=8.0 Hz), 7.24 (d, 2H, *J*=6.4 Hz), 7.38–7.44 (m, 6H), 7.47–7.57 (m, 2H), 7.85 (d, 4H, *J*=7.6 Hz), 8.26 (d, 2H, *J*=7.6 Hz), 8.31 (d, 2H, *J*=8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.1, 37.2, 124.5, 124.9, 125.3, 127.6, 127.9, 128.6, 128.9, 128.9, 129.0, 129.1, 129.2, 129.6, 130.5, 130.8, 131.5, 139.6, 139.8, 145.1, 158.2 (C–Pd), 158.4.

4.2. General procedure for Mizoroki–Heck reaction

Under an atmosphere of argon, a 5 mL vial containing a stirring bar was charged with **1** (0.005 mmol), NaOAc (82 mg, 1.0 mmol) and 1.5 mL of degassed DMA (dimethylacetamide), and subsequently were added aryl bromide (0.5 mmol) and alkene (0.75 mmol). The vial was placed in a 150 °C oil bath and the mixture was magnetically stirred for 8 h. The mixture was quenched with water, extracted with dichloromethane (20 mL×3). The combined extracts were dried ($MgSO_4$) and filtered. GC/MS analysis of the organic layer showed the presence of the corresponding coupling product (cinnamate or stilbene derivative). The solvent was removed under reduced pressure to give crude product. The product was isolated by PTLC and identified by GC/MS and spectroscopy with reference to analytical data of known compounds.

4.2.1. (E)-1-Methyl-2-(4-methylstyryl)benzene. White solid; 93.4 mg, 93% yield; mp: 44–47 °C. FT-IR (KBr): 3022, 2916, 1906, 1597, 1512, 1483, 1458, 975, 809, 718 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.44 (s, 3H), 6.98 (d, 1H, *J*=16.1 Hz), 7.17–7.23 (m, 5H), 7.30 (d, 1H, *J*=16.1 Hz), 7,43 (d, 2H, *J*=7.3 Hz), 7.59 (d, 1H, *J*=7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 21.3, 125.3, 125.6, 126.3, 126.5, 127.4, 129.4, 123.0, 130.4, 135.0, 135.8, 136.5, 137.6. MS (EI): *m*/*z*=208 [M^+].

4.2.2. (E)-1-Methyl-3-(4-methylstyryl)benzene. White solid; 76.2 mg, 73% yield; mp: 97–98 °C. FT-IR (KBr): 3018, 2919, 1909, 1599, 1512, 1490, 1449, 976, 967, 810 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.38 (s, 3H), 7.00–7.08 (m, 3H), 7.12–7.19 (m, 2H), 7.22–7.33 (m, 3H), 7.42 (d, 2H, *J*=8.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.5, 123.7, 126.5, 127.2, 127.9, 128.3, 128.5, 128.6, 129.5, 134.7, 137.5, 137.5, 138.2. MS (EI): *m*/*z*=208 [M^+].

4.2.3. (E)-2-(4-Methylstyryl)pyridine. Light yellow solid; 47.3 mg, 48% yield; mp: 76–78 °C. FT-IR (KBr): 3027, 1909, 1883, 1855, 1632, 1606, 1577, 1193, 1179, 1146, 1123, 975, 898 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.11–7.20 (m, 4H), 7.38 (d, 1H), 7.49 (d, 2H, *J*=8.0 Hz), 7.61 (d, 1H, *J*=16.0 Hz), 7.67 (d, 1H), 8.60 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 121.8, 121.9, 127.0, 127.1, 129.5, 132.7, 133.9, 136.5, 138.4, 149.6, 155.8. HRMS: calcd for $C_{14}H_{13}N$ [M+H]$^+$ 196.1126; found 196.1143.

4.3. General procedures for Sonogashira coupling

Under an atmosphere of air, a 5 mL vial containing a stirring bar was charged with **1a** (0.005 mmol), CsOAc (192.0 mg, 1.0 mmol) and DMA (3 mL), and subsequently were added aryl halide (0.5 mmol) and terminal alkyne (1.0 mmol). The vial was heated at 100 °C with magnetically stirring for 15 h. The mixture was quenched with water, extracted with dichloromethane, dried ($MgSO_4$) and filtered. GC/MS analysis of the organic layer showed the presence of the corresponding coupling product (diaryl alkyne or aryl alkyl alkyne). The solvent was removed under reduced pressure to give crude products. The product was isolated by PTLC or its yield was determined by GC by using biphenyl as an internal standard.

4.3.1. 1-(4-o-Tolylethynyl-phenyl)ethanone. Yellow solid; 106.3 mg, 91% yield; mp: 101–102 °C. FT-IR (KBr): 3343, 2994, 2216, 1677, 1595, 1456, 1403, 1358, 1263, 953, 839 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 2.62 (s, 3H), 7.16–7.28 (m, 3H), 7.51 (d, 1H, *J*=7.5 Hz), 7.59–7.63 (m, 2H), 7.93–7.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 26.6, 91.7, 92.5, 122.3, 125.6, 128.2, 128.4, 128.8, 129.5, 131.5, 132.0, 136.0, 140.3, 197.2. MS (EI): *m*/*z*=234 [M^+].

4.3.2. 1-(4-Acetylphenyl)-2-triisopropylsilylacetylene. Yellow oil; 130.1 mg, 86% yield. FT-IR (neat): 3359, 2943, 2156, 1687, 1600,

1463, 1402, 1359, 1263, 1015, 996, 883 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.13–1.14 (m, 21H), 2.60 (s, 3H), 7.55 (d, 2H, J=8.6 Hz), 7.89 (d, 2H, J=8.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.2, 18.6, 26.6, 94.7, 106.0, 128.1, 128.3, 132.1, 136.2, 197.2. MS (EI): m/z=300 [M^+].

4.4. Consecutive Mizoroki–Heck and Sonogashira coupling reaction

Under a nitrogen atmosphere, a 20 mL Schlenk tube containing a stirring bar was charged with **1a** (0.01 mmol), CsOAc (288 mg, 1.5 mmol) and DMA (3 mL), and subsequently were added *p*-bromoiodobenzene (142 mg, 0.5 mmol) and *tert*-butyl acrylate (73 μL, 0.5 mmol). The Schlenk tube was heated at 150 °C with magnetically stirring for 8 h. Then, phenylacetylene (82 μL, 0.75 mmol) was added to the tube and the mixture was stirred at the same temperature for additional 15 h. The mixture was quenched with water, extracted with dichloromethane, dried ($MgSO_4$) and filtered. GC/MS analysis of the organic layer showed the presence of the tandem-coupling product, (*E*)-*tert*-butyl 3-(4-(phenylethynyl)phenyl)acrylate. The solvent was removed under reduced pressure to give crude products, which was purified by PTLC (hexane/ethyl acetate=20/1). Yellow solid; 105.6 mg, 69% yield; mp: 117–119 °C. FT-IR (KBr): 3399, 2978, 2215, 1705, 1632, 1365, 1326, 139, 1160, 993, 831 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 9H), 6.39 (d, 1H, J=16.0 Hz, C=C*H*), 7.36 (d, 3H, J=5.4 Hz), 7.48–7.59 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.2, 80.6, 89.0, 91.3, 120.8, 122.9, 124.8, 127.8, 128.4, 128.5, 131.6, 131.9, 134.4, 142.6, 166.1. MS (EI): m/z=304 [M^+].

Acknowledgements

This study was financially supported by a Grant-in-Aid, No. 22550044, for Scientific Research from the Japan Society for the Promotion of Science (JSPS) and a Chuo University Grant for Special Research.

References and notes

1. For reviews on NHCs, see: (a) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2006; (b) *N-Heterocyclic Carbenes, from Laboratory Curiosities to Efficient Synthetic Tools*; Díez-González, S., Ed.; RSC: Cambridge, 2011; (c) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*; Cazin, C. S. J., Ed.; Spronger: Dordrecht, 2011; (d) Hahn, F. E.; Jahke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122; (e) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.
2. For reviews on NHC–Pd-catalyzed cross-coupling reactions, see: (a) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768; (b) Díez-González, S.; Nolan, S. P. *Top. Organomet. Chem.* **2007**, *21*, 47; (c) Whitcombe, N. J.; Hii, K. K.; Gibson, S. E. *Tetrahedron* **2001**, *57*, 7449 For recent 4 years research on Suzuki–Miyaura cross-coupling reactions, see: (d) Godoy, F.; Segarra, C.; Poyatos, M.; Peris, E. *Organometallics* **2011**, *30*, 684; (e) Antreas, S.; Alireza, R. *Chem. Commun.* **2010**, 2995; (f) Lee, D.-H.; Kim, J.-H.; Jun, B.-H.; Kang, H.; Park, J.; Lee, Y.-S. *Org. Lett.* **2010**, *10*, 1609; (g) Jin, Z.; Guo, S.-X.; Gu, X.-P.; Qiu, L.-L.; Song, H.-B.; Fang, J.-X. *Adv. Synth. Catal.* **2009**, *351*, 1575; (h) Organ, M. G.; Çalimsiz, S.; Sayah, M.; Hoi, K. H.; Lough, A. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2383; (i) Diebolt, O.; Braunstein, P.; Nolan, S. P.; Cazin, C. S. J. *Chem. Commun.* **2008**, 3190; (j) Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440. For recent 4 years research of Mizoroki–Heck reactions cross coupling reactions, see: (k) Saito, S.; Saika, M.; Yamasaki, R.; Azumaya, I.; Masu, H. *Organometallics* **2011**, *30*, 1366; (l) Sie, M.-H.; Hsieh, Y.-H.; Tsai, Y.-H.; Wu, J.-R.; Chen, S.-J.; Kumar, P. V.; Lii, J.-H.; Lee, H. M. *Organometallics* **2010**, *29*, 6473; (m) Lee, J.-Y.; Cheng, P.-Y.; Tsai, Y.-H.; Lin, G.-R.; Liu, S.-P.; Sie, M.-H.; Lee, H. M. *Organometallics* **2010**, *29*, 3901; (n) Ren, G.; Cui, X.; Yang, F.; Wu, Y. *Tetrahedron* **2010**, *66*, 4022; (o) Peh, G.-R.; Kantchev, E. A. B.; Zhang, C.; Ying, J. Y. *Org. Biomol. Chem.* **2009**, *7*, 2110; (p) Meyer, D.; Taige, M. A.; Zeller, A.; Hohlfeld, K.; Ahrens, S.; Strassner, T. *Organometallics* **2009**, *28*, 2142; (q) Liu, L-j.; Wang, F.; Shi, M. *Eur. J. Inorg. Chem.* **2009**, 1723; (r) Kantchev, E. A. B.; Peh, G.-R.; Zhang, C.; Ying, J. Y. *Org. Lett.* **2008**, *10*, 3949; (s) Taige, M. A.; Zeller, A.; Ahrens, S.; Goutal, S.; Herdtweck, E.; Strassner, T. *J. Organomet. Chem.* **2007**, *692*, 1519.
3. Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612.
4. Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274.
5. Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046.
6. Xu, X.; Xu, B.; Li, Y.; Hong, S. H. *Organometallics* **2010**, *29*, 6343.
7. Mathew, P.; Neels, A.; Albrecht, M. *J. Am. Chem. Soc.* **2008**, *130*, 13534.
8. Guisad-Barrious, G.; Bouffard, J.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 4759.
9. For reviews on abnormal NHCs see: (a) Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445; (b) Arnold, P. L.; Pearson, S. *Coord. Chem. Rev.* **2007**, *251*, 596.
10. Karthikeyan, T.; Sankararaman, S. *Tetrahedron Lett.* **2009**, *50*, 5834.
11. Nakamura, T.; Ogata, K.; Fukuzawa, S.-i. *Chem. Lett.* **2010**, *39*, 920.
12. Nakamura, T.; Terashima, T.; Ogata, K.; Fukuzawa, S.-i. *Org. Lett.* **2011**, *13*, 620.
13. (a) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815; (b) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371.
14. Frey, G. D.; Schüts, J.; Herdweck, E.; Herrmann, W. A. *Organometallics* **2005**, *24*, 4416.
15. Blakemore, J. D.; Chalkley, M. J.; Farnaby, J. H.; Guard, L. M.; Hazari, N.; Incarvito, C. D.; Luzik, E. D., Jr.; Suh, H. W. *Organometallics* **2011**, *30*, 1818.
16. The use of electron-rich aryl iodides instead of bromides gave the quantitative yields of products.
17. Saravanakumar, R.; Ramkumar, V.; Sankararaman, S. *Organometallics* **2011**, *30*, 1789.