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Synthetic, Structural, and Catalytic Studies of Well-Defined Allyl 1,2,3-Triazol-5-ylidene (*tz*NHC) Palladium Complexes

Takahiro Terashima,[a] Sayuri Inomata,[a] Kenichi Ogata,[a] and Shin-ichi Fukuzawa*[a]

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A series of allyl 1,2,3-triazol-5-ylidene (*tz*NHC) palladium complexes was prepared, and the structures of the complexes were fully characterized by NMR and X-ray diffraction analyses. The donor properties of these ligands were evaluated by studying the vibrational spectra of their carbonyliridium complexes and their X-ray photoelectron spectra. These evaluations showed that the structures of the *tz*NHC palladium complexes are almost identical to those of the corresponding imidazole carbene palladium complexes, and that the *tz*NHC ligands have stronger donor properties than the imidazole carbene ligands. The relationship between catalytic activity and structure was examined by carrying out a room-temperature Suzuki–Miyaura coupling reaction, and the cinnamylpalladium complex bearing 1,4-bis(2,6-diisopropylphenyl)-3-methyl-1,2,3-triazol-5-ylidene (TPr) was found to be the most active catalyst. (cinnamyl)(TPr)PdCl showed high activity in the room-temperature reaction performed with aryl chlorides regardless of the electronic and steric properties of the substituents, and was effective in reactions with sterically crowded arylboronic acids.

Introduction

N-Heterocyclic carbenes (NHCs) are widely used as ligands in metal-catalyzed reactions, and they sometimes function more effectively than traditional phosphane ligands.[1] NHCs can be broadly classified into two types: (**A**) normal carbenes such as imidazole carbenes whose carbene–metal bond is at the C2 position of the imidazolium moiety, [2] and (**B**) abnormal carbenes (*a*NHC) whose carbene–metal bond is at the C4 position (Figure 1).[3] The efficiency of the ligands in metal-catalyzed reactions depends on their donor properties, and a strong donor is often preferable for use in an active catalyst.[4] Recently, Albrecht et al. reported new 1,2,3-triazol-5-ylidene ligands (**C**) (this type of carbene is abbreviated as *tz*NHC to distinguish them from conventional NHCs), which are classified as abnormal carbenes.[5] The *tz*NHC ligands and their complexes have potential to show unique catalytic activity in organic reactions.[6] Albrecht et al. reported that their ruthenium complexes are more effective for the oxidation of alcohols than the corresponding (imidazol-2-ylidene)ruthenium complexes.[7] We have shown that the *trans*-bis(1,4-dimesityl-1,2,3-triazol-5-ylidene)palladium complex **1** [$(TMes)_2PdCl_2$] (TMes = 1,4-dimesityl-1,2,3-triazol-5-ylidene) is more effective in the Suzuki–Miyaura coupling reaction between sterically hindered aryl chlorides and arylboronic acids than the corresponding bis[1,3-dimesitylimidazol-2-ylidene]palladium complex **2** [$(IMes)_2PdCl_2$] (IMes = 1,3-dimesitylimidazol-2-ylidene) (Figure 2).[8] The *tz*NHC palladium complex also catalyzes Mizoroki–Heck coupling reactions with aryl chlorides to give higher product yields than those obtained with the imidazole (NHC)Pd complex.[9] The catalytic superiority of *tz*NHC complexes may be attributed to the stronger donor properties of the ligands relative to imidazole NHCs.

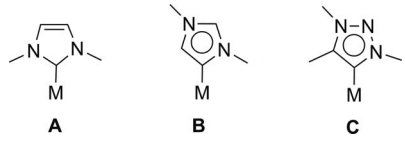

Figure 1. (**A**) Normal (traditional) carbene ligands, (**B** and **C**) abnormal N-heterocyclic carbene ligands.

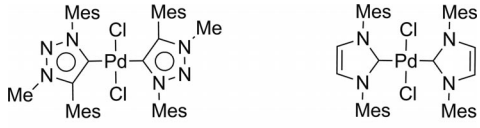

Figure 2. Bis(*tz*NHC)- and bis(NHC)palladium complexes.

Metal complexes bearing a single NHC ligand have sometimes been employed in cross-coupling reactions, because they exhibit higher activity than complexes bearing

[a] Department of Applied Chemistry, Institute of Science and Engineering, Chuo University,
1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan
Fax: +81-3-3817-1895
E-mail: orgsynth@kc.chuo-u.ac.jp

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two NHCs.[10] Therefore, a mono(*tz*NHC)metal complex is considered to be a more preferable active catalyst than a bis(*tz*NHC)metal complex. We have prepared 1,4-diarylated (η^3-allyl)(*tz*NHC)palladium complexes as mono(*tz*NHC)-palladium complexes. In this study, we have examined their electronic properties and catalytic activity in metal-catalyzed cross-coupling reactions.

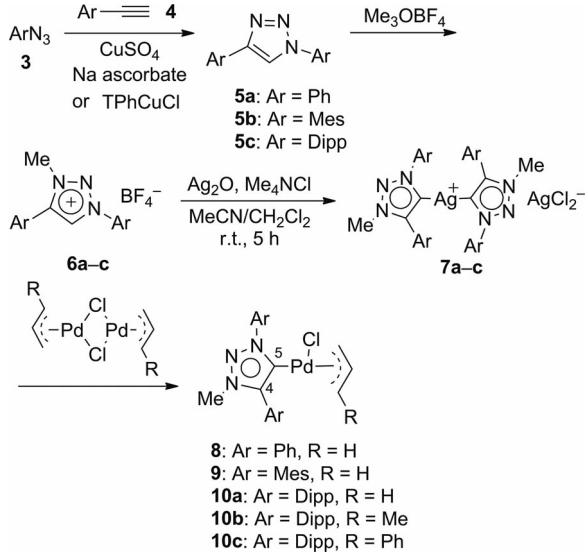
Results and Discussion

Synthesis and Structural Study of (R-allyl)(*tz*NHC)PdCl Complexes

1,4-Di(Ar)-1,2,3-triazoles (**5a**: Ar = Ph; **5b**: Ar = Mes) were readily prepared according to a reported method by the reaction of aryl azides with arylacetylenes in the presence of a copper(I) catalyst.[11] 1,4-Bis(2,6-diisopropylphenyl)-1,2,3-triazole [**5c**: Ar = 2,6-diisopropylphenyl (Dipp)] was prepared by the reaction of 2,6-diisopropylphenyl azide with (2,6-diisopropylphenyl)acetylene in the presence of the 1,3-diphenyl-1,2,3-triazole NHC copper(I) complex, which was originally developed by us, acting as a catalyst.[12] These 1,2,3-triazoles were treated with Me_3OBF_4 to afford the corresponding triazolium salts **6**.

In the synthesis of the (allyl)palladium complexes, shown in Scheme 1, the 1,2,3-triazolium salts **6** were treated with silver oxide at room temperature to afford the air-stable (1,2,3-triazol-5-ylidene)silver complexes **7**, which were subsequently treated with $[(allyl)PdCl]_2$ in CH_2Cl_2 at room temperature to give (allyl)(TPh)PdCl (**8**) and (allyl)(TMes)-PdCl (**9**) as air-stable pale yellow complexes. [The abbreviations we use in this paper for these *tz*NHC ligands are shown in Figure 3 (a commonly used abbreviation for imidazole NHC ligands is also shown in this figure).] These complexes were purified by preparative thick-layer chromatography (PTLC; eluent: EtOAc/hexane) and characterized by ^1H and ^{13}C NMR and combustion analyses. The ^{13}C NMR spectra show peaks for the carbene carbon atoms of **8** and **9** at δ = 166.6 and 169.5 ppm, respectively. The TPr (Ar = Dipp) palladium chloride (R-allyl)(TPr)-PdCl complexes [R-allyl = allyl (**10a**), crotyl (**10b**), cinnamyl (**10c**)] were similarly obtained as air- and thermally stable compounds by the above protocol. The peaks for the carbene carbon atoms of **10a**, **10b**, and **10c** were observed in their ^{13}C NMR spectra at δ = 171.8, 172.0, and 170.1 ppm, respectively.

We successfully obtained complexes **9** and **10a**–**10c** as single crystals suitable for X-ray diffraction analyses, and the structures of the complexes are shown in Figure 4.[13] The structures of all the (allyl)palladium complexes bearing the *tz*NHC ligands are similar to those of the corresponding Pd complexes bearing the imidazole NHC ligands: the Cl atoms are located *cis* to the carbene ligands, and the allyl moieties are η^3-coordinated to the Pd atoms with the terminal carbon atoms, C(3), *trans* to the C(5) atoms of the TMes ligands and the other terminal carbon atoms, C(1), *trans* to chlorine atoms.[14] In all the complexes, the length



Scheme 1. Synthesis of (R-allyl)(*tz*NHC)PdCl complexes.

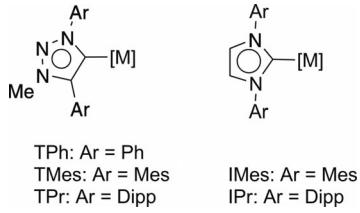


Figure 3. Abbreviations for the triazole and imidazole carbene ligands discussed herein.

of the bonds between Pd and the carbon atoms opposite to the *tz*NHC ligands are elongated due to the *trans* influence of *tz*NHC; the Pd–C(3) bonds are longer than the Pd–C(1) bonds. The triazole torsion angles, N(1)–N(2)–N(3)–C(4), are almost 0 °, indicating that the triazole rings are planar and aromatic systems. Table 1 lists selected bond lengths and angles for these (η^3-allyl)(*tz*NHC)Pd complexes. In **9** the Pd–C(3) bond is significantly longer than that in the corresponding imidazole (η^3-allyl)(NHC)Pd complex, (allyl)(IMes)PdCl, for which the Pd–C(3) bond length is 2.183(5) Å. The longer Pd–C(3) bond in the (η^3-allyl)-(*tz*NHC)Pd complex compared to that in (allyl)(IMes)PdCl may be attributed to the stronger *trans* influence of the *tz*NHC ligand compared to that of the imidazole ligand; the difference in the *trans* influence within these complexes results from the stronger donor property of the triazole NHC ligand relative to that of the imidazole NHC ligand. The length of the bonds between the Pd and the carbene carbon atoms in the triazole complexes [Pd–C(5) (TMes) 2.031(3) Å and Pd–C(5) (TPr) 2.043(2)] are almost the same as those in the corresponding imidazole (η^3-allyl)(NHC)Pd complexes [Pd–C(2) (IMes) 2.032(3) Å and Pd–C(2) (IPr) 2.040(11)] [IPr = 1,3-(2,6-diisopropylphenyl)-1,3-imidazol-2-ylidene].

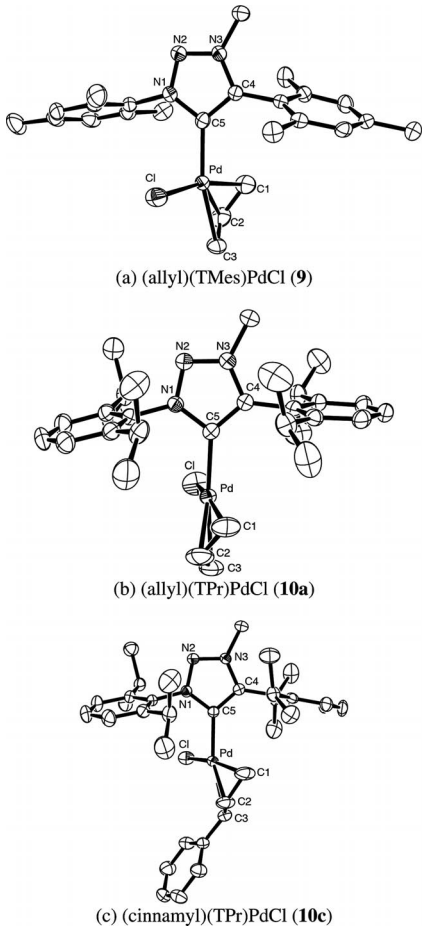


Figure 4. (a)–(c) Diagrams of the (R-allyl)(*tz*NHC)Pd complexes drawn with thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **9**, **10a** and **10c**.

	9	**10a**	**10c**
Pd–Cl	2.3892(7)	2.3614(7)	2.3618(8)
Pd–C(5)	2.031(3)	2.043(2)	2.023(3)
Pd–C(1)	2.096(3)	2.105(3)	2.106(4)
Pd–C(2)	2.121(3)	2.123(3)	2.162(4)
Pd–C(3)	2.212(3)	2.201(3)	2.256(3)
Cl–Pd–C(5)	95.64(6)	93.67(6)	93.00(8)
Cl–Pd–C(1)	166.00(8)	163.85(9)	166.04(9)
C(5)–Pd–C(1)	96.18(10)	101.30(10)	97.49(12)
C(5)–Pd–C(2)	129.25(10)	134.68(11)	132.74(11)
C(5)–Pd–C(3)	163.75(9)	169.09(9)	164.64(9)
N(1)–C(5)–C(4)	102.28(19)	101.85(18)	102.0(2)
N(1)–N(2)–N(3)–C(4)	0.2(3)	–0.6(2)	–1.0(3)

The bond length between Pd and the carbon atom *trans* to TPr in **10a** [Pd–C(3) 2.201(3) Å] is almost the same as that between Pd and the carbon atom *trans* to TMes in **9** [2.212(3) Å], suggesting that the *trans* influence of the TPr ligand is comparable to that of the TMes ligand. The Pd–C(3) bond length in the triazole complex **10a** is also the same as that within the corresponding imidazole (η^3-allyl)(NHC)Pd complex [(allyl)(IPr)PdCl: Pd–C(3) 2.210(6) Å]. The Pd–C(3) bond length in **9** is longer than in (allyl)(IMes)PdCl [Pd–C(3) 2.183(5) Å]. From these results, the order for the strength of the ligand *trans* influence may be represented as TPr ≈ TMes ≈ IPr > IMes.

Evaluation of the Donor Properties of the Triazol-5-ylidene Ligands in Their Carbonyliridium Complexes

The CO stretch vibrations of complexes can be used as a direct probe of the electronic properties of the TMes and TPr ligands, and to enable this analysis to be performed carbonyliridium complexes **11a** and **11b** (Figure 5) were prepared as follows:[15] treatment of the triazolium salt **6** with *t*BuOK resulted in the formation of the triazole carbene, to which was added $[Ir(cod)Cl]_2$, followed by excess carbon monoxide. The CO vibration frequencies of **11a** [ν(CO): 2062 and 1976 cm^{-1}; ν_{av}(CO): 2019 cm^{-1}] and **11b** [ν(CO): 2062 and 1976 cm^{-1}; ν_{av}(CO): 2019 cm^{-1}] were lower than those in the spectra of the corresponding imidazole NHC iridium complex analogues [IMes: ν_{av}(CO): 2023 cm^{-1}; IPr: ν_{av}(CO): 2024 cm^{-1}].[16] By applying a linear regression equation [TEP = 0.847ν_{av}(CO) + 336 cm^{-1}] to the data,[16,17] the Tolman electronic parameters (TEP) for **11a**, **11b**, and their imidazole NHC analogues were estimated: TEP(TMes) = 2046 cm^{-1} and TEP(TPr) = 2046 cm^{-1}, values that are higher than TEP(IMes) = 2051 cm^{-1} and TEP(IPr) = 2051 cm^{-1}. Thus, the vibrational study of these carbonyliridium complexes showed that the donor properties of *tz*NHC ligands are superior to those of imidazole NHCs, and that the donor strengths of TMes and TPr are comparable. Albrecht and Bertrand have suggested that the donor properties of *tz*NHC ligands would be superior to those of NHC ligands.[5,15,18]

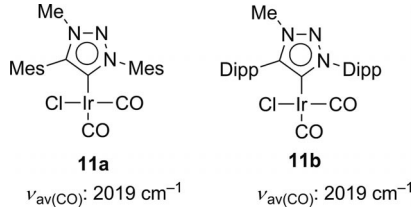


Figure 5. Carbonyl[1,4-di(Ar)-1,2,3-triazol-5-ylidene)iridium complexes.

The ^{13}C NMR shifts of the carbene carbon atoms of **11a** and **11b** are observed in their spectra at δ = 166.5 and 168.1 ppm, respectively. This result suggests that the order of donor strength should be TMes < TPr.[19]

The strong donor properties of the triazole carbenes were confirmed by X-ray photoelectron spectroscopy (XPS).[20] A comparison between the triazole carbene complex **10a** and a complex that is sterically identical to the imidazole NHC, i.e. (allyl)(IPr)PdCl, showed that the Pd 3d electron binding energies in the former are 0.5 eV less than those in

the latter [**10a**: 335.7 eV; (allyl)(IPr)PdCl: 336.2 eV; the signal for the 1s electron of C at 285 eV acted as a reference]; this indicates that TPr is a stronger donor than IPr. This result is consistent with the vibration study of the carbonyliridium complexes (Figure 6).

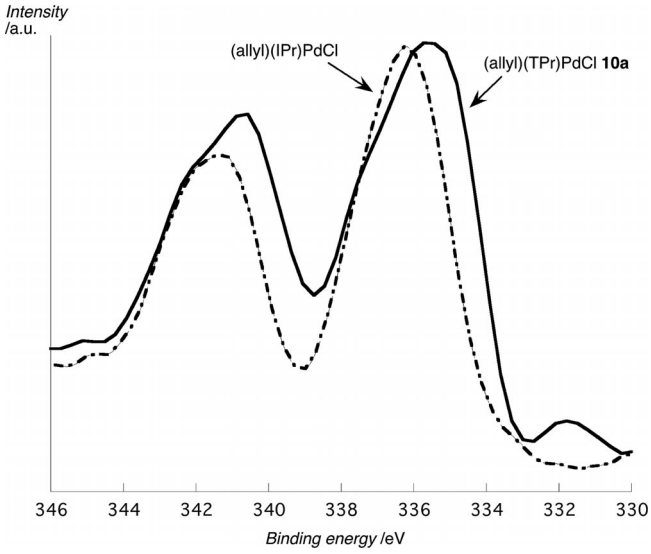


Figure 6. XPS spectra (palladium 3d level) for **10a** (solid line) and (allyl)(IPr)PdCl (dashed line).

Structure/Reactivity Study of the Complexes in Room-Temperature Suzuki–Miyaura Coupling Reactions with Aryl Chlorides

We expected the (η^3-allyl)(*tz*NHC)Pd complexes to be efficient active catalysts and therefore applied them in room-temperature Suzuki–Miyaura coupling reactions.[21] When we attempted the reaction of phenylboronic acids with *p*-chlorotoluene in the presence of **9** as the catalyst and *t*BuOK as a base, the reaction had hardly begun to proceed after 1 h. The replacement of **9** with **10a** still resulted in a low product yield (ca. 20%) after 1 h. It has been reported that the catalytic activity of the (η^3-allyl)(imidazole NHC)-Pd complex is low, and that of the corresponding (crotyl)- and (cinnamyl)Pd complexes is very high.[21a] Thus, the allyl ligand is not suitable for active (NHC)Pd catalysts. Subsequently, we evaluated the activity of the palladium complexes **10a**–**c** by monitoring a time-dependent Suzuki–Miyaura coupling reaction of *p*-chlorotoluene with phenylboronic acid. The yield vs. time graphs for reactions conducted with **10a**–**10c** and (cinnamyl)(IPr)PdCl are shown in Figure 7. The reactions were carried out in 2-propanol at room temperature with a palladium complex loading of 1.0 mol-% and with *t*BuOK as a base, and 1.1 equiv. of *p*-chlorotoluene. After the reaction, the yield was determined by gas chromatography (GC) with *n*-dodecane as an internal standard. As seen in the graph, when **10a** [(allyl)Pd] was used as a catalyst the reaction rate was slow, and the product yield was only 40% after 4 h. When either **10b** [(crotyl)Pd] or **10c** [(cinnamyl)Pd] was the catalyst the reaction was fast and the product yield reached around 80% after 0.5 h; the reaction with **10c** was complete after 4 h. The superior efficiency of (cinnamyl)Pd complexes as active catalysts could be attributed to the facile elimination of the cinnamyl group by *t*BuOK owing to the long bond between Pd and the *trans* allylic carbon atom (see Table 1) that leads to the formation of a (TPr)Pd^0 species.

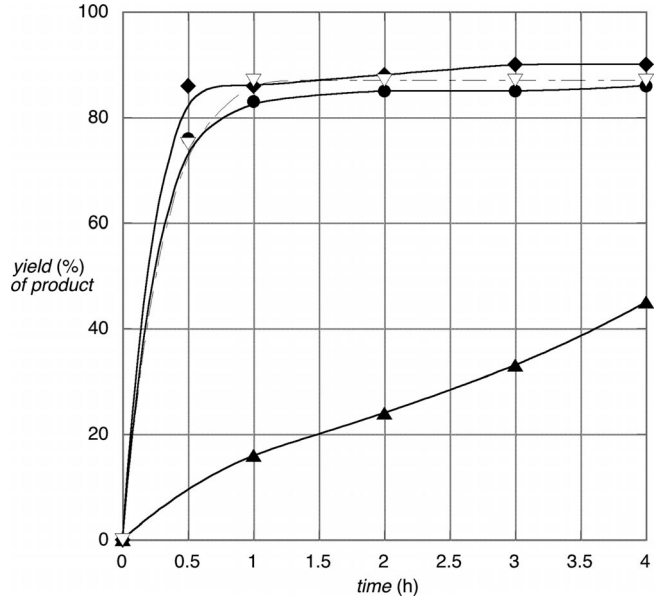
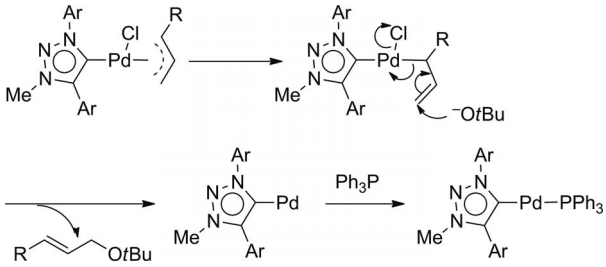


Figure 7. Time vs. yield (%) plots for (R-allyl)(*tz*NHC)PdCl-catalyzed Suzuki–Miyaura coupling reactions of *p*-chlorotoluene with phenylboronic acid. Black triangles **10a**; black dots **10b**; black diamonds **10c**; white triangles (cinnamyl)(IPr)PdCl (dashed line).

The (R-allyl)(imidazol-2-ylidene)Pd complexes showed similar catalytic activity, and their activation processes were studied by applying them to the Suzuki–Miyaura and Buchwald–Hartwig coupling reactions. The catalytic activity of **10c** was comparable to that of the corresponding (cinnamyl)(imidazole NHC)Pd complex [(cinnamyl)(IPr)PdCl] giving almost the same product yield after 1 h; **10c** gave a higher yield (99%) than the (IPr)Pd complex after 4 h.

The Pd–C(3) bond in the (cinnamyl)Pd complex **10c** is the longest of complexes **10a**–**c**, which explains why it is the most active catalyst for the C–C coupling reactions. Thus, the activation process for the Pd^0 complexes may be similar to Nolan's activation pathway for the (allyl)(imidazole NHC)Pd complex: the *tert*-butoxy anion attacks the allyl moiety, and then the allyl *tert*-butyl ether is eliminated from the palladium complex leading to the formation of the Pd^0 species (Scheme 2).[14,21a] We carried out a trapping experiment, to obtain the (*tz*NHC)Pd^0 species, with PPh_3 and observed, by ^{31}P NMR spectroscopy, the phosphane signal of the Pd complex (δ = 30.4 ppm). The formation of *tert*-butyl cinnamyl ether was observed by ^1H NMR measurement of the reaction mixture.[22]

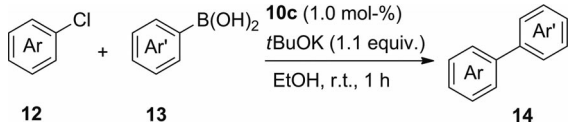


Scheme 2. Plausible pathway for the generation of (*tz*NHC)Pd^0.

Scope of the Room-Temperature Suzuki–Miyaura Coupling Reaction with (Cinnamyl)(TPr)PdCl (10c)

As **10c** was found to be the most active catalyst of those investigated for the room-temperature Suzuki–Miyaura coupling reaction with aryl chlorides, its substrate scope was examined with 1.0 mol-% of **10c** present in the reaction mixture; the results of this study are summarized in Table 2. Optimization experiments showed that ethanol was more suitable as the reaction solvent than 2-propanol, and that the product yield was sometimes high after short reaction times. Coupling products with phenylboronic acid were obtained in excellent yields with both electron-rich and -poor aryl chlorides, and the position of the substituent group on the benzene moiety had minimal effect on the yields (Entries 1–7). As for heteroaromatic chlorides, 2-chloropyridine coupled with phenylboronic acid to give the product in good yield, whereas a low yield was obtained for the coupling product prepared with 3-chloropyridine (Entries 8–9). It is noteworthy that the sterically crowded *o*-substituted aryl chlorides could couple with *o*-substituted phenylboronic acids to give the corresponding biaryls. The reaction of *o*-chlorotoluene with *o*-methoxyphenylboronic acid (**13**: Ar′ = *o*-MeOC$_6$H$_4$) gave a good yield for the coupling product, whereas the reaction of the sterically more crowded 2-chloro-1,3-dimethylbenzene with *o*-methoxyphenylboronic acid and 1-naphthylboronic acid gave the associated products in moderate yields (Entries 10–12).

Table 2. Details for the room-temperature Suzuki–Miyaura coupling reactions of various aryl chlorides with arylboronic acids.[a]



12 **13** **14**

Entry	Ar in **12**	Ar′ in **13**	Yield [%][b]
1	Ph	Ph	99
2	*p*-MeC$_6$H$_4$	Ph	99
3	*o*-MeC$_6$H$_4$	Ph	85
4	*p*-MeOC$_6$H$_4$	Ph	90
5	*m*-MeOC$_6$H$_4$	Ph	97
6	*p*-MeC(O)C$_6$H$_4$	Ph	93
7	*p*-O$_2$NCOC$_6$H$_4$	Ph	91
8	2-pyridyl	Ph	78
9	3-pyridyl	Ph	0
10	*o*-MeC$_6$H$_4$	*o*-MeOC$_6$H$_4$	82
11	2,6-Me$_2$C$_6$H$_3$	*o*-MeOC$_6$H$_4$	54
12	2,6-Me$_2$C$_6$H$_3$	1-C$_8$H$_{10}$	44

[a] **10c** (0.005 mmol), aryl chloride **12** (0.50 mmol), arylboronic acid **13** (0.53 mmol), *t*BuOK (0.55 mmol), ethanol (1.5 mL), room temp., 1 h. [b] Isolated yield.

The reaction could be carried out with a lower catalyst loading (*p*-chlorotoluene, phenylboronic acid, 0.1 mol-% **10c**, 99% yield; 0.05 mol-% **10c**, 57% yield) with an extended reaction time (15 h) and on a preparative scale (5 mmol scale).

Conclusions

A series of (allyl)palladium complexes bearing 1,2,3-triazol-5-ylidene (*tz*NHC) ligands was synthesized, and the structures of the complexes were characterized by NMR and X-ray diffraction analyses. The donor properties of the *tz*NHC ligands were evaluated by studying the vibrational spectra of their carbonyliridium complexes and their XPS spectra. It was found that the triazole carbene ligands have stronger donor properties than the corresponding imidazole carbene ligands. The catalytic activity of the (R-allyl)-(*tz*NHC)PdCl complexes in the room-temperature Suzuki–Miyaura coupling reaction was examined, and the (cinnamyl)Pd complex bearing TPr was found to be the most active catalyst of those synthesized. Complex (cinnamyl)(TPr)PdCl showed high activity in the room-temperature reaction with aryl chlorides, regardless of the electronic and steric properties of the substituents, and it was effective in the reaction with sterically crowded arylboronic acids.

Experimental Section

General: The ^{1}H and ^{13}C NMR spectra were recorded with a Varian Mercury 300 or 400 NMR (300 or 400 MHz) spectrometer with sample solutions prepared with $CDCl_3$. The chemical shifts are reported in δ units downfield from the internal reference (Me_4Si). IR spectra were recorded with an FT/IR-4100ST spectrometer. The GC–MS analyses were carried out with a Hewlett–Packard 5975B/6890N instrument equipped with a capillary column (helium as the carrier gas). The XPS spectra were measured with an AXIS His 165 X-ray photoelectron spectrometer with 1×10^{-9} Pa base pressure. The photon source consisted of an X-ray tube emitting Mg-K_α photons at 1253.6 eV. PTLC was conducted on 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. Compounds **5a**–**5c** were prepared by the copper-catalyzed click reaction of aryl azides with arylacetylenes, according to a method reported in the literature.[12] The triazolium salts **6a**–**6b** were prepared as previously reported.[12] All coupling products of the Suzuki–Miyaura reactions are previously reported compounds, and were identified by comparison of our data with that available in the literature.

Crystallography: The diffraction data were collected at –100 °C with a Rigaku R-AXIS RAPID diffractometer and with graphite-monochromated Mo-K_α radiation by an ω-scan technique to a maximum 2θ value of 55°. The structure solutions and refinements were carried out with the aid of the Crystal Structure crystallographic software packages.[23] The structures were solved by direct methods (SIR97)[24]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined with riding models.

CCDC-827678 (for **9**), -854140 (for **10a**), -854142 (for **10b**), -854141 (for **10c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of Triazolium Salt 6c: The triazole **5c** (0.71 mmol) and Me_3OBF_4 (154 mg, 1.04 mmol) were stirred under nitrogen in dry dichloromethane (15 mL) for 48 h. The reaction was quenched with MeOH (1 mL), and the solvent was removed under reduced pressure to give the crude product, which was then washed with diethyl ether and dried to give the triazolium salt. White solid; 254 mg, 76% yield; m.p. 222–223 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (d, J = 6.8 Hz, 6 H, CH_3), 1.22 (d, J = 6.8 Hz, 6 H, CH_3), 1.29 (d, J = 6.8 Hz, 6 H, CH_3), 1.33 (d, J = 6.8 Hz, 6 H, CH_3), 2.30–2.40 (m, 4 H, C*H*CH_3), 4.26 (s, 3 H, NCH_3), 7.39 (d, J = 6.3 Hz, 2 H), 7.41 (d, J = 6.3 Hz, 2 H), 7.63 (t, J = 8.1 Hz, 1 H), 7.65 (t, J = 8.1 Hz, 1 H), 8.55 (s, 1 H, tz*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.8, 23.6, 23.8, 24.7, 29.0, 31.7, 38.5, 117.2, 124.1, 124.6, 130.6, 133.0, 133.1, 142.0, 145.0, 148.9 ppm. $C_{27}H_{38}BF_4N_3{\cdot}0.5H_2O$: calcd. C 64.80, H 7.86, N 8.40; found C 65.18, H 7.91, N 8.43.

Synthesis of (Allyl)(1,2,3-triazol-5-ylidene)palladium Complexes (R-allyl)(*tz*NHC)PdCl: The following provides a general procedure for the synthesis of (R-allyl)(*tz*NHC)PdCl. Under nitrogen, Ag_2O (25 mg, 0.12 mmol) and Me_4NCl (24 mg, 0.22 mmol) were added to a solution of a triazolium salt **6a**–**6c** (70 mg, 0.22 mmol) in acetonitrile/dichloromethane (1:1, 12 mL) and the suspension was stirred in a Schlenk tube covered with foil at room temperature for 5 h. [(R-η^3-allyl)PdCl]$_2$ (42 mg, 0.11 mmol) was added to the solution that was then stirred overnight. The solvent was removed under vacuum, and the residue was extracted with dichloromethane and filtered through a Celite pad. The filtrate was concentrated, and then the crude palladium complex was purified by PTLC (silica gel; 20% EtOAc/hexanes).

(Allyl)(TPh)PdCl (8): Off-white solid; 93 mg, 99% yield; m.p. 100–101 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.87 (d, J = 11.7 Hz, 1 H, allyl), 2.90 (d, J = 7.0 Hz, 1 H, allyl), 3.10 (d, J = 14.1 Hz, 1 H, allyl), 4.14 (d, J = 7.0 Hz, 1 H, allyl), 4.17 (s, 3 H, NCH_3), 4.95–5.03 (m, 1 H, allyl-CH), 7.49–7.56 (m, 6 H), 7.95 (d, J = 8.2 Hz, 1 H), 8.33 (d, J = 7.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.4, 48.3, 71.1, 113.7, 123.9, 127.7, 128.6, 128.8, 129.5, 129.7, 130.0 139.9, 146.4, 166.6 (C-Pd) ppm. $C_{18}H_{18}ClN_3Pd$ (418.21): calcd. C 51.69, H 4.34, N 10.05; found C 51.39, H 4.21, N 10.01.

(Allyl)(TMes)PdCl (9): Pale yellow solid; 224 mg, 99% yield; m.p. 151 °C (dec). An analytically pure sample was obtained by recrystallization of **9** from CH_2Cl_2 and hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84 (d, J = 11.7 Hz, 1 H, allyl), 2.15–2.20 (m, 12 H, 4 CH_3), 2.33 (s, 3 H), 2.34 (s, 3 H), 2.88 (d, J = 13.5 Hz, 1 H, allyl), 3.10 (d, J = 7.6 Hz, 1 H, allyl), 3.84 (s, 3 H, NCH_3), 3.90 (dd, J = 7.0, 2.1 Hz, 1 H, allyl), 4.84–4.97 (m, 1 H, allyl-CH), 6.98 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.7, 20.4, 21.1, 21.2, 35.9, 47.5, 71.7, 113.8, 123.8, 128.5, 128.8, 134.7, 136.3, 138.3, 139.6 139.8, 145.0, 169.7 (C-Pd) ppm. $C_{24}H_{30}ClN_3Pd$ (502.37): calcd. C 57.38, H 6.02, N 8.36; found C 57.23, H 6.04, N 8.30.

(Allyl)(TPr)PdCl (10a): White solid; 119 mg, 78% yield; m.p. 170–171 °C (dec). An analytically pure sample was obtained by recrystallization of **10a** from toluene and hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (d, J = 6.9 Hz, 3 H, CH_3), 1.11 (d, J = 6.9 Hz, 3 H, CH_3), 1.16 (d, J = 6.9 Hz, 3 H, CH_3), 1.17 (d, J = 6.9 Hz, 3 H, CH_3), 1.30 (d, J = 6.9 Hz, 3 H, CH_3), 1.33 (d, J = 6.9 Hz, 3 H), 1.35 (d, J = 6.9 Hz, 3 H), 1.37 (d, J = 6.9 Hz, 3 H), 1.74 (d, J = 11.8 Hz, 1 H, allyl), 2.61 (sept, J = 6.8 Hz, 1 H, C*H*CH_3), 2.78 (sept, J = 6.8 Hz, 1 H, C*H*CH_3), 2.86 (d, J = 13.4 Hz, 1 H, allyl), 2.91–3.05 (m, 3 H, C*H*CH_3 and allyl), 3.85 (s, 3 H, NCH_3), 3.92 (dd, J = 1.9, 7.4 Hz, 1 H, allyl), 4.88 (m, 1 H, allyl-CH), 7.28–7.31 (d, J = 7.8 Hz, 4 H), 7.48 (t, J = 7.8 Hz, 1 H), 7.49 (t, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.5, 22.5, 24.1, 24.3, 24.5, 24.6, 25.3, 26.1, 28.7, 29.0, 30.9, 36.7, 48.5, 72.2, 113.7, 123.5, 123.6, 124.3, 130.6, 130.9, 136.7, 144.1 145.4, 149.4, 149.6, 171.8 (C-Pd) ppm. $C_{30}H_{42}ClN_3Pd$ (586.53): calcd. C 61.43, H 7.22, N 7.16; found C 61.07, H 7.27, N 7.11.

(Crotyl)(TPr)PdCl (10b): White solid; 79 mg, 63% yield; m.p. 167 °C (dec). An analytically pure sample was obtained by recrystallization of **10b** from benzene and hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.9 Hz, 3 H, CH_3), 1.13 (d, J = 6.9 Hz, 3 H, CH_3), 1.15 (d, J = 6.9 Hz, 3 H, CH_3), 1.15 (d, J = 6.9 Hz, 3 H, CH_3), 1.25–1.38 (m, 13 H), 1.42 (d, J = 6.2 Hz, 3 H, crotyl-CH_3), 2.60–2.69 (m, 2 H, 2 C*H*CH_3), 2.76–2.98 (m, 3 H, C*H*CH_3 and allyl), 3.55 (sext, J = 6.2 Hz, 1 H, crotyl-CH), 3.85 (s, 3 H, NCH_3), 4.59 (ddd, J = 11.6, 11.6, 6.5 Hz, 1 H, crotyl-CH), 7.27–7.31 (m, 4 H), 7.45–7.51 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.0, 22.6, 22.6, 24.1, 24.2, 24.4, 24.5, 25.4, 25.9, 28.7, 28.9, 30.9, 36.7, 43.9, 89.4, 112.6, 123.4, 123.5, 123.6, 124.6, 130.5, 130.8, 136.8, 144.3 145.3, 145.5, 149.4, 172.0 (C-Pd) ppm. $C_{31}H_{44}ClN_3Pd$ (600.56): calcd. C 62.00, H 7.38, N 7.00; found C 62.05, H 7.49, N 6.98.

(Cinnamyl)(TPr)PdCl (10c): Yellow solid; 94 mg, 68% yield; m.p. 78–80 °C. An analytically pure sample was obtained by recrystallization of **10c** from benzene and hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11–1.16 (m, 12 H), 1.27–1.41 (m, 12 H), 1.84 (d, J = 11.6 Hz, 1 H, cinnamyl), 2.81 (br. m, 5 H), 3.85 (s, 3 H, NCH_3), 4.42 (d, J = 12.7 Hz, 1 H, cinnamyl), 5.13–5.21 (m, 1 H, cinnamyl), 7.10–7.21 (m, 5 H), 7.29–7.32 (m, 4 H), 7.48–7.52 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5, 22.7, 24.1, 24.4, 25.5, 25.7, 28.8, 30.8, 36.7, 45.3, 89.8, 108.3, 123.5, 124.4, 126.3, 127.2, 128.1, 130.5, 130.9, 136.6, 138.1, 144.2 145.4, 149.3, 170.1 (C-Pd) ppm. $C_{36}H_{46}ClN_3Pd$ (662.63): calcd. C 65.25, H 7.00, N 6.34; found C 65.36, H 7.13, N 6.32.

(TMes)Ir(CO)$_2$Cl (11a): Yellow solid; 38 mg, 90% yield; m.p. 227–228 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.17 (s, 6 H, CH_3), 2.20 (s, 6 H, CH_3), 2.36 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 3.86 (s, 3 H, NCH_3), 7.03 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 20.6, 21.3, 21.4, 36.3, 122.5, 128.9, 129.2, 134.6, 135.5, 138.2, 140.5, 140.6, 146.6, 166.5 (C-Ir), 168.9 (CO), 181.0 (CO) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2062, 1976 [ν(CO)] cm^{-1}. $C_{23}H_{25}ClIrN_3O_2$ (603.14): calcd. C 45.80, H 4.18, N 6.97; found C 45.72, H 4.08, N 6.91.

(TPr)Ir(CO)$_2$Cl (11b): Yellow solid; 61 mg, 61% yield; m.p. 180–181 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (d, J = 6.9 Hz, 6 H, CH_3), 1.15 (d, J = 6.9 Hz, 6 H, CH_3), 1.36 (d, J = 6.7 Hz, 6 H, CH_3), 1.39 (d, J = 6.7 Hz, 6 H, CH_3), 2.67–2.83 (m, 4 H, 4 C*H*CH_3), 3.87 (s, 3 H, NCH_3), 7.34 (d, J = 7.8 Hz, 4 H), 7.49 (t, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2, 24.2, 24.8, 25.9, 29.3, 31.2, 37.1, 122.7, 123.8, 124.0, 131.3, 131.5, 135.6, 145.4, 149.5, 168.1 (C-Ir), 169.1 (CO), 180.7 (CO) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2062, 1976 [ν(CO)] cm^{-1}. $C_{29}H_{37}ClIrN_3O_2$ (687.30): calcd. C 50.7, H 5.43, N 6.11; found C 50.70, H 5.43, N 6.09.

General Procedure for the Room-Temperature Suzuki–Miyaura Coupling Reactions: Under nitrogen, a 20 mL Schlenk tube containing a stirring bar was charged with potassium *tert*-butoxide (62 mg, 0.55 mmol), palladium catalyst (0.005 mmol), arylboronic acid (64 mg, 0.53 mmol), aryl chloride (0.5 mmol) and dry EtOH (1.5 mL). The mixture was stirred at room temperature for 1 h. The reaction was quenched with water, and the mixture was extracted with EtOAc, dried with $MgSO_4$, and filtered. GC–MS analysis of

the organic layer showed the presence of the corresponding coupling product (biphenyl derivative). The solvent was removed under reduced pressure to give the crude product. The product was isolated by PTLC, and the yield was determined by GC with dodecane as an internal standard.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra of the palladium and iridium complexes.

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