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Biscarbene Palladium(II) Complexes. Reactivity of Saturated Versus Unsaturated *N*-Heterocyclic Carbenes

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A series of designed palladium biscarbene complexes including saturated and unsaturated *N*-heterocyclic carbene (NHC) moieties have been prepared by the carbene transfer methods. All of these complexes have been characterized by ^{1}H and ^{13}C NMR spectroscopy as well as X-ray diffraction analysis. The reactivity of $Pd-C_{(saturated\ NHC)}$ is distinct from that of $Pd-C_{(unsaturated\ NHC)}$. The $Pd-C_{(saturated\ NHC)}$ bonds are fairly stable toward reagents such as CF_3COOH, $AgBF_4$ and I_2, whereas $Pd-C_{(unsaturated\ NHC)}$ bonds are readily cleaved under the similar conditions. Notably, the catalytically activity of these palladium complexes on Suzuki−Miyaura coupling follows the order: $(sat\text{-}NHC)_2PdCl_2$ > $(sat\text{-}NHC)(unsat\text{-}NHC)PdCl_2$ > $(unsat\text{-}NHC)_2PdCl_2$.

Introduction

The chemistry of palladium complexes stands as an important class of catalysts in useful organic reactions, particularly in the coupling reactions.[1] It is known that the properties of ligands can influence critically the activity of metal complexes. Recently, the uses of *N*-heterocyclic carbenes (NHCs) with palladium complexes often show better stability and reactivity than those of the TM-phosphine counterparts in analogous catalytic reactions.[2] For instance, Herrmann and co-workers have demonstrated that the biscarbene palladium complexes are not only stable compounds but also serve as excellent catalysts in Heck coupling reactions.[3] And, many examples with stable palladium biscarbene complexes that show other remarkable catalytic activities have also been reported.[4−7]

Among this context, most known palladium biscarbene complexes contain two identical carbene ligands except a dicoordinated palladium(0) species.[8] Less investigation has been endeavored to the complexes with different NHC ligands,

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(1) There are a number of reviews and books for palladium-catalyzed reaction, for example: (a) *Palladium in Organic Synthesis*; Tsuji, J., Ed.; Springer: Berlin, Germany, 2005. (b) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., De Meijere, A., Eds.; Wiley: New York, NY, 2002.

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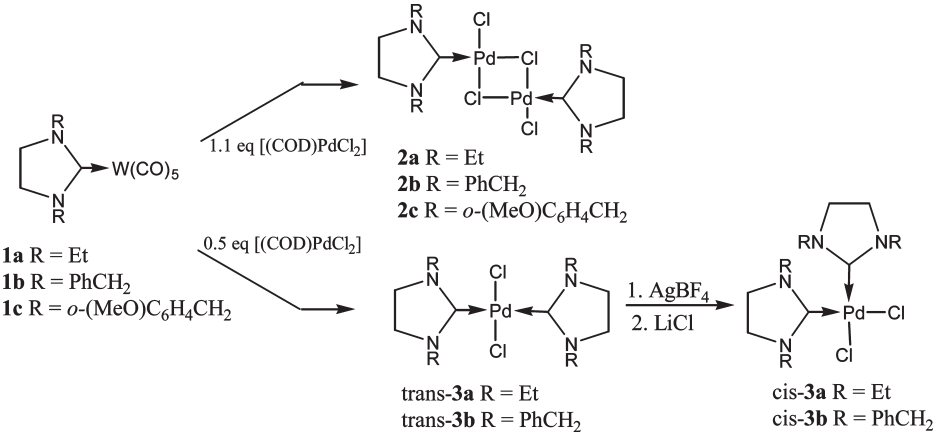
Scheme 1



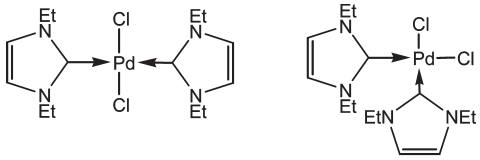
although they are expected to exhibit interesting properties due to distinguishable trans influence. In this work, we report the preparation of a series of designed biscabene palladium complexes, particularly comprising both saturated and unsaturated NHCs. With such species, the differences of donating ability between saturated and unsaturated NHCs to the palladium(II) centers as well as the reactivity of these complexes have been compared by means of spectroscopic analyses, single crystal structures, and chemical reactions.

Results and Discussion

Synthesis and Characterization. Both mono- and bis-(saturated NHC) palladium complexes (Scheme 1) were prepared according to the previously reported procedure via a carbene transfer reaction of tungsten carbene complexes with Pd(II) ions.[9] Reactions of **1** with [(COD)$PdCl_2$] in dichloromethane always result in a mixture of **2** and **3**. However, carrying out the reaction by a slow addition of **1** into a dichloromethane solution of [(COD)$PdCl_2$] leads to **2** as the sole product. In contrast, a procedure with reverse addition yields the homobiscarbene species *trans*-**3** exclusively. Conversion of *trans*-**3** into thermodynamically more stable *cis*-**3** is a fairly slow process at room temperature but is accelerated in the presence of silver salt in an acetonitrile solution (see Scheme 1).

It is noted to mention that complexes **2** do not convert into the corresponding biscarbene complexes **3** either thermally or even by the addition of silver salts. This observation clearly indicates that the carbene does not transfer from one palladium metal center to the other. Mixed bis(NHC) complexes of palladium(II) can be acquired by double carbene transfer reactions: the transfer of a carbene moiety either from (NHC)$W(CO)_5$ or (NHC)AgX to the palladium center (Scheme 2). Thus, reaction of **2a** with an excess of **1b** at room temperature for 72 h generated a mixture of bis-NHC palladium complexes *trans*- and *cis*-**4** in a ratio of 2:1.

Silver NHCs have been successfully used in transmetalation reactions for the preparation of a wide range of metal carbene complexes.[2g] Thus, the carbene transfer reaction between unsaturated silver−carbene **6a** and **2a** takes place to provide *trans*-**5a**, bearing both saturated and unsaturated NHCs as the kinetic product that slowly isomerizes to yield a mixture of *trans*- and *cis*-**5a** in a ratio of 1:1. Complex *trans*-**5b** that contains sterically bulky *N*-substitutents on NHC did not transform into its *cis*-isomer, presumably energetically unfavored. For the purpose of comparison, the homo unsaturated NHC palladium complex **7** was prepared by the similar method. Reaction of [(COD)$PdCl_2$] with excess of **6a** provides a mixture of *cis*- and *trans*-**7** in a ratio of 1:1.



All palladium complexes, which are air stable, were isolated as solids; complexes **2c**, *trans*- and *cis*-**3a**, and *cis*-**7** were even in crystalline forms. The spectral data of complexes **2a**−**b** and **3a**−**b** are consistent with the reported data.[9b] The newly prepared species could be easily characterized by the determination of their ^1H and ^{13}C NMR spectral data. The coordination of the NHC ligands to the palladium is confirmed by the appearance of a downfield shift in the ^{13}C NMR spectra for the carbenic carbon (Table1). It is noticed that there is an average difference of 20−30 ppm between the chemical shifts due to unsaturated and saturated carbenic carbons (such as *trans*-**3a** vs *trans*-**7**, *cis*-**3a** vs *cis*-**7**, or *cis*-**4** vs *cis*-**5a**), in agreement with the reported data.[10,11]

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Scheme 2

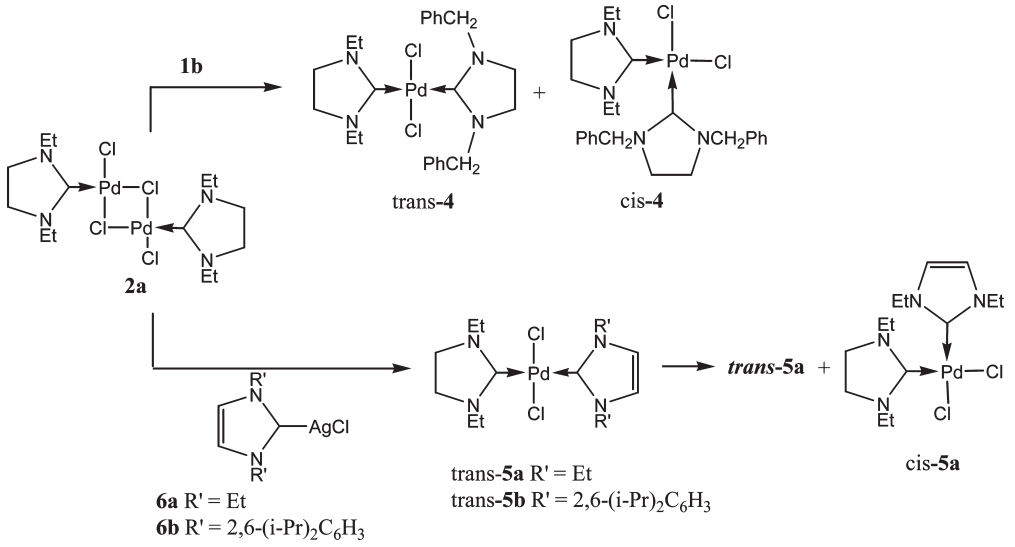


Table 1. ^{13}C Shifts of the Carbene Carbons for Complexes

complex	^{13}C NMR $C_{(NHC)}$−Pd	complex	^{13}C NMR $C_{(NHC)}$−Pd
2a	173.3[a]	*trans*-**4**	198.7, 197.9
2b	174.5	*cis*-**4**	198.2, 197.8
2c	182.9	*trans*-**5a**	197.1, 170.1
trans-**3a**	198.1	*cis*-**5a**	198.2, 168.8
cis-**3a**	189.1	*trans*-**5b**	195.8, 178.1
trans-**3b**	199.1	*cis*-**7**	168.9
		trans-**7**	169.1

[a] Ref 9b.

Crystallography. To further confirm the geometrical arrangement and the bonding around the metal center, X-ray diffraction studies were carried out on complexes **2c**, *trans*-**3a**, *cis*-**3a**, and *cis*-**7**. The complexes were crystallized by a slow vaporization from saturated solutions in CH_2Cl_2/hexanes at ambient temperature. The crystal structures of **2c**, *trans*-**3a**, *cis*-**3a**, and *cis*-**7** are shown in Figures 1−4, respectively, and the selected bond lengths are shown in Table 2.

The C−C distances of the imidazole rings in **3a** lie in the range of 1.50−1.52 Å, typical for a single bond, whereas those in *cis*-**7** appear to be 1.378(4) Å, typical for a double bond, showing the difference between saturated and unsaturated NHCs. The nonplanarity of the heterocycle in *cis*-**3a**, caused by the two sp^3 carbons in the NHC backbone, is also different from the structure of *cis*-**7**, in which the heterocycle is in a planar arrangement. Other than these observations, the structural difference between *cis*-**3a** and -**7** (caused by saturated or unsaturated NHC) is negligible.

There is a rather small difference in the Pd−$C_{(carbene)}$ as well as Pd−Cl bond lengths in complexes *cis*-**3a** of the saturated NHC and *cis*-**7** of the unsaturated NHC, that is consistent with the reported data.[10b] The slightly longer Pd−$C_{(carbene)}$ bond distance in *trans*-**3a** than that in *cis*-**3a** (ca. 0.06 Å) is attributed to the good trans influence from the strong donating NHC ligands. Generally speaking, little difference in the carbene character between the saturated and unsaturated NHCs in the investigated biscarbene palladium system may be drawn from the crystallographic data. In another words, the structural and NMR data appear not able to differentiate the electronic power between the saturated and unsaturated NHCs.

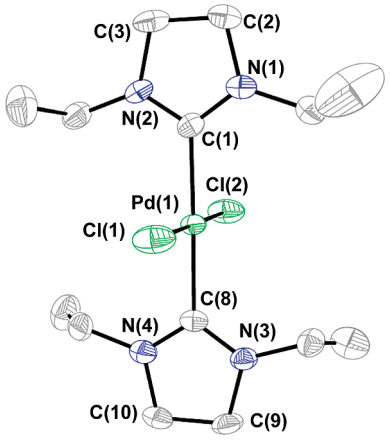


Figure 1. ORTEP plot of complex *trans*-**3a** (drawn with 30% probability ellipsoids).

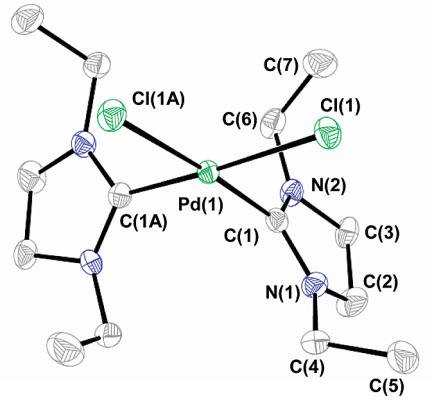


Figure 2. ORTEP plot of complex *cis*-**3a**.

Reaction of Pd−NHC Complexes with $AgBF_4$. In a previous work, we have found that reaction of *trans*-**3a** with $AgBF_4$ in CH_2Cl_2 (or $CHCl_3$) with a trace of moisture yielded the corresponding imidazolium **9** (Scheme 3, path a). It is believed that the NHC moiety is first transferred from Pd to Ag and followed by the protonation. However, treatment of *trans*-**3a** with $AgBF_4$ in an acetonitrile solution under refluxing conditions

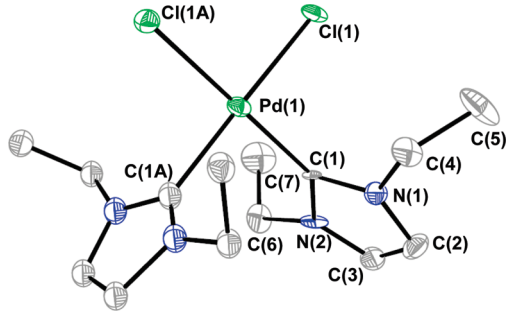


Figure 3. ORTEP plot of complex *cis*-**7**.

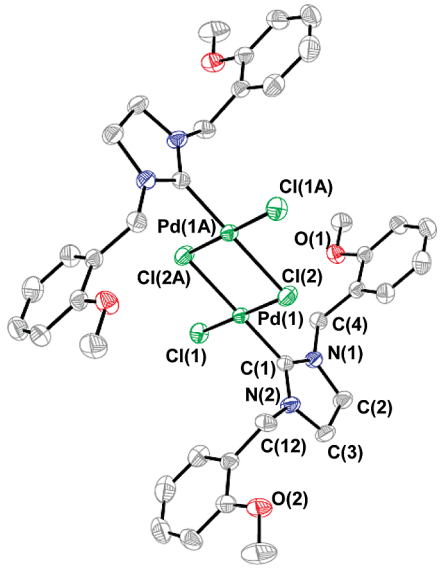


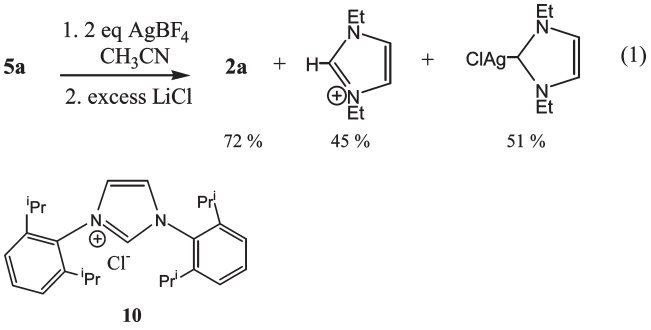
Figure 4. ORTEP plot of complex **2c**.

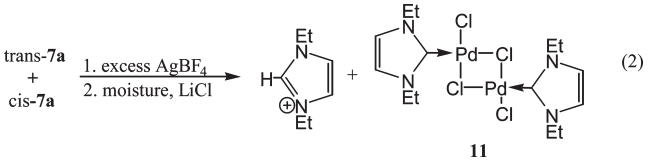
Table 2. Selected Bond Distance and Bond Angles of NHC−Pd Complexes

complex	*trans*-**3a**	*cis*-**3a**	*cis*-**7**	**2c**
Pd−$C_{(carbene)}$	2.051(5)	1.988(3)	1.986(3)	1.943(3)
Pd−$C_{(carbene)}$	2.046(5)	1.988(3)	1.986(3)	1.943(3)
Pd−Cl(1)	2.307(2)	2.3653(7)	2.3842(6)	2.3319(9)
Pd−Cl(2)	2.315(2)	2.3654(7)	2.3843(6)	2.2980(9)
C−$C_{(imi\text{-}ring)}$	1.50(1)	1.519(5)	1.378(4)	1.524(5)
C−$C_{(imi\text{-}ring)}$	1.519(9)	1.519(5)	1.378(4)	1.524(5)
$C_{(carbene)}$−N	1.319(7)	1.330(4)	1.345(4)	1.325(4)
$C_{(carbene)}$−N	1.314(6)	1.335(4)	1.346(4)	1.320(4)
$C_{(carbene)}$−N	1.303(6)	1.330(4)	1.345(4)	1.325(4)
$C_{(carbene)}$−N	1.321(6)	1.335(4)	1.346(4)	1.320(4)
C−Pd−C	178.1(3)	91.13(15)	88.7(1)	−

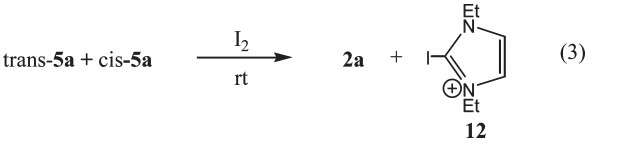
resulted the isomerization of a *trans*-cation **I** to a *cis* one (Scheme 3, path b). Presumably, the abstraction of chloride by the silver ion generates an acetonitrile coordinating intermediate **I** that may facilitate the isomerization. From these observations, it appears that the coordinating ability of the solvent molecules plays a remarkable effect on the stabilization of NHC palladium complexes.

Unlike *trans*-**3a**, treatment of **5a** with $AgBF_4$ in CH_3CN at 80 °C for 48 h caused the selective cleavage of Pd−$C_{(unsaturated\ NHC)}$, yielding **2a**, silver−carbene, and imidazolium salt (eq 1). Obviously, the unsaturated NHC moiety may be transferred from Pd(II) back to Ag(I) but not the saturated NHC. Upon the addition of chloride, the fragment of [(saturated NHC)$PdCl_2$] readily underwent the dimerization via the chloride bridging to form **2a**. The formation of the 1,3-diethylimidazolium salt is presumably due to the protonation of the carbene, and the source of the proton is probably from a trace of water in the reaction medium.[9b] Similarly, reaction of **5b** with $AgBF_4$ under the same conditions also resulted in the formation of the corresponding imidazolium salt **10**. One would expect that complex **7**, which has two unsaturated NHC moieties, might also undergo Pd−C cleavage upon treatment with silver ions. Indeed, reaction of complex **7** with an excess of $AgBF_4$ provided 1,3-diethylimidazolium salt (71%) and the chloride-bridged dimer **11** (18%) (eq 2).



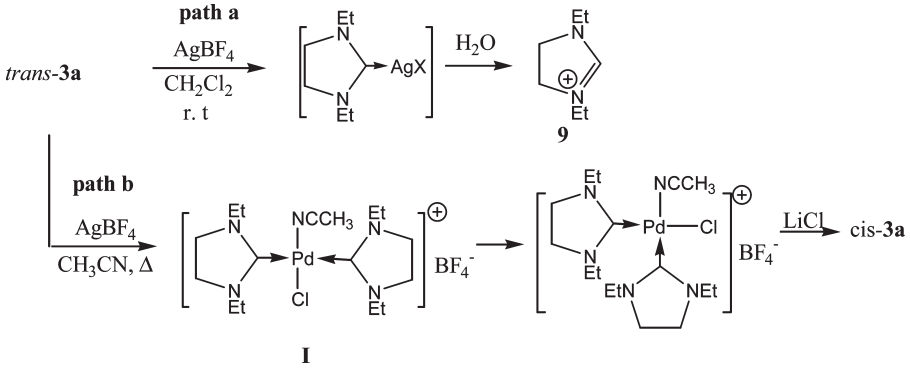


Reactivity Toward I_2. Complexes **2a**, **3a**−**b**, and **4** are stable toward iodine in the dichloromethane solution even under refluxing conditions. But, complex **5a** reacts with iodine at room temperature for 8 h to provide **2a** and 2-iodoimidazolium salt **12** quantitatively (eq 3). Complex **7** behaves similarly, and it reacts with iodine to produce the iodo-substituted imidazolium salt **12** and the chloride-bridged complex **11** in a ratio of 2:1 by the NMR integration.

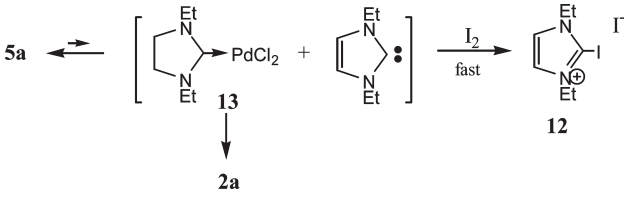


Since the NHC palladium complexes **2a**, **3a**−**b**, and **4** are inert toward I_2, the decomposition of **5a** or **7** through the oxidative addition of I_2 toward the metal center, which demands a Pd(IV) intermediate, is quite unlikely. As discussed in the previous section, the formation of **2a** is due to the dimerization of [(saturated NHC)$PdCl_2$], generated by the dissociation of the unsaturated NHC moiety from **5a**. A plausible mechanism for the formation of **12** is shown in Scheme 4. The unsaturated NHC moiety is dissociated from the metal center to yield the intermediate **13** and the free carbene, which then reacts with I_2 directly to form **12**. It has been demonstrated that the reaction of free NHC with I_2 would provide

Scheme 3

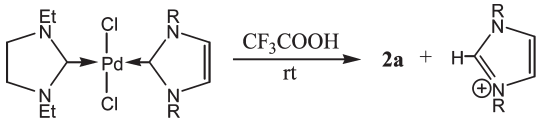


Scheme 4



2-iodo-imidazolium salt easily.[12] Compound **12** is stable toward the Pd(II) species, and it is not likely to regenerate the carbene species under this reaction conditions. We were not able to detect any free carbene species by NMR or MS analysis of the crude reaction mixture. It may be that the concentration of these species, if formed, was low in the presence of iodine. From these observations, it indicates that the unsaturated NHC moiety on these biscarbene palladium complexes could dissociate from the metal center.

Reactivity Toward CF_3COOH. All studied carbene palladium complexes are stable toward air and water. In order to investigate further the stability of the Pd−$C_{(carbene)}$ bonds, all palladium complexes were subjected to react with trifluoroacetic acid. The reaction of *trans*-**5b** with an excess of CF_3COOH in $CDCl_3$ in a sealed NMR tube was monitored by ^1H NMR spectroscopy (eq 4). After 12 h, both **2a** and 1,3-bis(2,6-diisopropylphenyl)imidazolium salt were obtained quantitatively (eq 4). These two products were confirmed by both ^1H and ^{13}C NMR spectroscopies. Obviously, the unsaturated NHC moiety is readily protonated by acid to yield the imidazolium ion, and the residual palladium fragment undergoes the dimerization via the bridging chloride. Similarly, reaction of a mixture of *trans*- and *cis*-**5a** with excess of CF_3COOH showed the same reaction pattern, i.e., the reaction products were **2a** and 1,3-diethylimidazolium salt. In contrast to unsaturated NHCs, complexes *trans*- and *cis*-**3a** and **3b** were retained in the solution of $CF_3COOH/CDCl_3$ over a temperature range (room temperature to 50 °C) for an even longer period. As expected, complex **7** is also sensitive toward CF_3COOH. Thus, complex **7** was readily decomposed in the presence of trifluoroacetic acid to yield 1,3-diethylimidazolium salt accompanied with a trace amount of the chloride-bridged palladium species **11**.



trans-**5a** R = Et
trans-**5b** R = 2,6-(i-Pr)$_2$C$_6$H$_3$

R = Et
R = 2,6-(i-Pr)$_2$C$_6$H$_3$

These results clearly demonstrate the difference of the reactivity between Pd−$C_{(saturated\ NHC)}$ and Pd−$C_{(unsaturated\ NHC)}$. It is known that the basicity of saturated NHCs is stronger that that of the corresponding unsaturated one.[13] One would expect that protonation should occur at the site of the saturated NHCs. However, Pd−$C_{(saturated\ NHC)}$ is stable toward acid, indicating that ligands of saturated NHCs do not dissociate from the metal center. On the other hand, the dissociation of unsaturated NHCs from [$(NHC)_2$-$PdCl_2$] takes place, then yielding the imidazolium salt in the presence of acid. Again, the Pd−$C_{(carbene)}$ cleavage by CF_3COOH reveals a similar trend, as illustrated in the cleavage of these bonds in the presence of I_2 or silver ions, suggesting that the strength of Pd−$C_{(saturated\ carbene)}$ is more stable than that of Pd−$C_{(unsaturated\ carbene)}$.

These NHC complexes are stable toward common organic bases, such as pyridine and amines. However, the reactions of bis(NHC)palladium complexes with hydroxide cause their decomposition, as evidenced by the generation of palladium black.

Catalysis. Suzuki−Miyaura coupling is one of the most efficient methods for the construction of C−C bonds through Pd(II)-involved catalysis. The auxiliary ligands in such processes are known to play important roles.[14] The Pd−NHC complexes indicate that they can better stabilize the Pd(II)-center as well as enhance their

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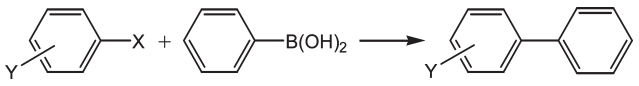
Table 3. Results of the Coupling Reaction of Aryl Halides with Phenylbonoric Acid[a]



entry	substrates	additives[b]	base	yield
1	*p*-chloroacetophenone	$^tBu_3P$, TBAB	Cs_2CO_3	23%
2	*p*-chloroacetophenone	$^tBu_3P$, TBAB	K_2CO_3	33%
3	*p*-chloroacetophenone	$^tBu_3P$, TBAB	KF	33%
4	*p*-chloroacetophenone	$^tBu_3P$, TBAB	K_3PO_4	74%
5	*p*-chloroacetophenone	TBAB	K_3PO_4	63%
6	*p*-chloroacetophenone	$^tBu_3P$	K_3PO_4	>99%
7	*o*-chlorotoluene	$^tBu_3P$	K_3PO_4	57%
8	chlorobenzene	$^tBu_3P$	K_3PO_4	42%
9	*p*-chlorobenzoic acid	$^tBu_3P$	K_3PO_4	20%

[a] Reaction conditions: *p*-chloroacetophenone (0.2 mmol), phenylbonoric acid (0.3 mmol), *trans*-**3a** (2×10^{-3} mmol), additives, base (0.4 mmol) in water (5 mL), and refluxing temperature for 24 h. [b] $^tBu_3P$ (4×10^{-3} mmol), TBAB = tetrabutylammonium bromide (0.5 mmol).

catalytic activity, comparing to their TM−phosphine counterparts.[15] Aiming to explore if the electronic modification would have any significant effect on the catalytic activity, the Suzuki−Miyaura reactions with the use of our new Pd-carbene complexes were examined.

The reaction of *p*-chloroacetophenone and phenylbonoric acid, with loading of 1 mol % *trans*-**3a** and the added $^tBu_3P$ and/or tetrabutylammonium bromide (TBAB), was found to achieve a quantitative yield of the coupling product in the presence of K_3PO_4 in water at 100 °C for 24 h, as listed in entry 6 of Table 3. Entries 7−9 of Table 3 show the feasibility of other aryl halides in the comparable reactions. The correlation of yields versus the substituted aryl halides appears to be similar to that of other catalytic systems. It may be noticed that the addition of $^tBu_3P$ is essentially to acquire the high conversion presumably due to the further stabilization of the active palladium species upon the catalysis.

In order to explore to NHC ligand effect on the catalysis, we selected the coupling of *p*-chloroacetophenone with phenylboronic acid and the optimized reaction conditions that were used for *trans*-**3a**. All palladium complexes are subjected to test their catalytic activity on the Suzuki−Miyaura coupling reaction, and the results are summarized in table 4.

Gratifyingly, higher reactivity due to both *trans*- and *cis*-**3a** in these coupling reactions was confirmed by as our prediction. The complexes **5** and **7** with unsaturated NHCs appear to be less active as the analogues with saturated NHCs, again supporting that the higher stability of the Pd-center possesses a higher catalytically activity.[16] In fact, we did observe the precipitation of palladium black out the reaction mixture with the use of **7** as the precatalyst during the catalytic reactions but not

Table 4. Results of the Suzuki−Miyaura coupling catalyzed Various Pd(II) Complexes[a]

complex	**2a**	*trans*-**3a**	*cis*-**3a**	**4**	**5a**[b]	*trans*-**5b**	**7**[b]
yield (%)	50	>99	>99	95	81	74	47

[a] Reaction conditions: *p*-chloroacetophenone (0.2 mmol), phenylbonoric acid (0.3 mmol), Pd(II) complex (2×10^{-3} mmol), $^tBu_3P$ (4×10^{-3} mmol) in water (5 mL), refluxing temperature for 24 h, yields given based on the average of two runs. [b] Mixture of *cis*- and *trans*-isomers.

complex **3a**. This might explain the more stable complex providing a better activity.

Summary

In this study, we demonstrate the synthetic approach to prepare both symmetrical and unsymmetrical biscarbene palladium complexes. The comparison of spectroscopic and structural and catalytic activities of these palladium complexes has been presented. As compared to unsaturated NHC complexes, saturated NHC palladium counterparts show better stability toward acid as well as iodine. From these investigations, it reveals that the unsaturated NHC moiety could dissociate from the biscarbene palladium complexes but not from the saturated NHCs. In terms of catalytically reactivity, bis-saturated NHC palladium complexes appear to be better precatalysts in the Suzuki−Miyaura coupling reaction.

Experimental Section

General Information. All reactions, manipulations, and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after a degassed process. Tungsten carbene complexes **1a**−**c**,[9a,b] **6a**−**b**[17] were prepared accordingly to the method reported previously.

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on a Bruker either AM-300 or AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for the ^1H and ^{13}C NMR.

General Procedure for Complexes 2a−c. A solution of **1** (0.09 mmol) in CH_2Cl_2 (5 mL) was added slowly to a solution of $[(COD)PdCl]_2$ (0.09 mmol) in CH_2Cl_2 (5 mL) with stirring. The resulting solution turned into a dark color immediately. After stirring at room temperature for 8 h, the reaction mixture was filtered through Celite. The filtrate was concentrated, and the residue was recrystallized to yield the desired complex.

Complex 2a. Yellow solids (61%): ^1H NMR ($CDCl_3$, 300 MHz): δ 4.22 (q, 8H, $-CH_2-$, $^3J_{HH}$ = 7.3 Hz), 3.63 (s, 8H, imi-*H*), 1.37 (t, 12H, $-CH_3$, $^3J_{HH}$ = 7.3 Hz), which is identical to the reported data.[9b]

Complex 2b. Yellow solids (42%): ^1H NMR ($CDCl_3$, 300 MHz): δ 7.46−7.50 (m, 8 H, Ar−*H*), 7.36−7.28 (m, 12 H, Ar−*H*), 5.41 (s, 8 H, $-CH_2Ph$), 3.37 (s, 8 H, imidazole−*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.5 (M=*C*), 134.3, 128.8, 128.7, 128.2 (*Ph*), 54.7, 47.7. Anal. calcd. for $C_{34}H_{36}Cl_4N_4Pd_2$: C, 47.74; H, 4.24; N, 6.55. Found: C, 47.39; H, 4.08; N, 6.39.

Complex 2c. Yellow solids (36%):^1H NMR ($CDCl_3$, 400 MHz): δ 4.22 (q, J = 7.3 Hz, 8H, $-CH_2-$), 3.63 (s, 8H, imidazole−*H*),

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1.37 (t, J = 7.3 Hz, 12H, $-CH_3$). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 182.9 (Pd=*C*), 156.9, 129.2, 128.9, 122.8, 120.2, 110.8, 55.4, 48.8, 47.9. Anal. calcd. for $C_{38}H_{44}Cl_4N_4O_4Pd_2$: C, 46.79; H, 4.55; N, 5.74. Found: C, 46.68; H, 4.75; N, 5.58.

General Procedure for Complexes 3a−b. A solution of $[(COD)PdCl]_2$ (0.16 mmol) in CH_2Cl_2 (15 mL) was added slowly to a solution of **1** (0.33 mmol) in CH_2Cl_2 (15 mL) with stirring at room temperature. The resulting solution turned into a dark color immediately. After stirring for 8 h, the reaction mixture was filtered through Celite. The filtrate was concentrated, and the residue was recrystallized from CH_2Cl_2/hexane to yield the desired complex.

Complex *trans*-3a. Colorless crystalline solids (55%): ^1H NMR ($CDCl_3$, 400 MHz): δ 4.03 (q, 4H, $-CH_2-$, $^3J_{HH}$ = 7.2 Hz), 3.53 (s, 4H, imidazole−*H*), 1.34 (t, 6H, $-CH_3$, $^3J_{HH}$ = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.1 (M=*C*), 47.9, 44.3, 13.7. HR-FAB-MS calcd. m/z for $C_{14}H_{28}N_4{}^{35}Cl^{106}Pd$ $[M-Cl]^+$: 393.1037. Found: 393.1027. Anal. calcd. for: $C_{14}H_{28}Cl_2N_4Pd$: C, 39.13; H, 6.57; N, 13.04. Found: C, 39.29; H, 6.82; N, 12.80.

Complex *cis*-3a. A solution of *trans*-**3a** (4.7 mg) in CH_3CN (1 mL) was added to a flask loaded with $AgBF_4$ (5.5 mg). The mixture was stirred at refluxing temperature for 24 h, and then LiCl (3.1 mg) was added. After stirring for another 24 h, the solvent was removed, and the ^1H NMR spectrum of the reaction product showed only a single species *cis*-**3a** presented. This residue was recrystallized from CH_2Cl_2/hexane to give the desired complex *cis*-**3a** as white solids (2.1 mg, 45%): ^1H NMR ($CDCl_3$, 400 MHz): δ 4.07 (q, J = 7 Hz, 4H, $-CH_2-$), 3.87 (q, J = 7 Hz, 4H, $-CH_2-$), 3.55−3.61 (m, 8H, imidazole−*H*), 1.20 (t, J = 7 Hz, 12H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.1 (M=*C*), 47.2, 45.3, 13.1. Anal. calcd. for $C_{14}H_{28}Cl_2N_4Pd$: C, 39.13; H, 6.57; N, 13.04. Found: C, 38.83; H, 6.86; N, 12.94.

Complex *trans*-3b. Light-yellow solids (80%): ^1H NMR ($CDCl_3$, 400 MHz): δ 7.45−7.41 (m, 12 H), 7.19 (m, 8 H), 5.25 (s, 8 H), 3.31 (s, 8H), which is identical to the reported data.[9b]

Complex *cis*-3b. Light-yellow solids (78%): ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32−7.38 (m, 8H, Ar−*H*), 7.24−7.39 (m, 12H, Ar−*H*), 5.57 (d, J = 14.1 Hz, 4H, −CH*H*Ph), 4.76 (d, J = 14.1 Hz, 4H, −CH*H*Ph), 3.33−3.42 (m, 4H, imidazole−H), 3.14−3.25 (m, 4H, imidazole−H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.2 (M=*C*), 134.9, 128.8, 128.3, 128.1 (*Ph*), 54.7, 47.9. Anal. calcd. for $C_{34}H_{36}Cl_2N_4Pd$: C, 60.23; H, 5.35; N, 8.26; Found: C, 59.94; H, 5.29; N, 7.88.

Complexes *trans*-4 + *cis*-4. A mixture of **2a** (5.0 mg, 8.24 × 10^{-3} mmol) and **1b** (18.9 mg, 3.3 × 10^{-2} mmol) in dichloromethane (4 mL) was stirred at room temperature for 72 h. The excess of **1b** was removed by chromatography. A mixture of *trans*- and *cis*-**4** was obtained as white solids (5.3 mg, 58%). However, neither *trans*- nor *cis*-**4** could be obtained in pure form not even by chromatography.Complex *trans*-**4**: ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58−7.60 (m, 4H, Ar−*H*), 7.21−7.37 (m, 6H, Ar−*H*), 5.28 (s, 4H, $-CH_2Ph$), 4.00 (q, J = 7 Hz, 4H, $-CH_2CH_3$), 3.55 (s, 4H, imidazole−*H*), 3.31 (s, 4H, imidazole−*H*), 1.28 (t, J = 7 Hz, 6H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.7 (M=*C*), 197.2 (M=*C*), 136.0, 128.6, 128.5, 127.5, 54.1, 47.9, 47.9, 44.4, 13.6. Complex *cis*-**4**: ^1H NMR ($CDCl_3$, 400 MHz): δ 7.51−7.53 (m, 4H, Ar−*H*), 7.21−7.37 (m, 6H, Ar−*H*), 5.24 (s, 4H, $-CH_2Ph$), 3.70−4.08 (m, 4H, $-CH_2CH_3$), 3.55 (s, 4H, imidazole−*H*), 3.31 (s, 4H, imidazole−*H*), 1.34−1.39 (m, 6H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.2 (M=*C*), 197.8 (M=*C*), 135.9, 128.6, 128.5, 127.5, 54.1, 47.9, 47.9, 44.3, 13.7. Anal. calcd. for $C_{24}H_{32}Cl_2N_4Pd$: C, 52.04; H, 5.82; N, 10.12. Found: C, 51.72; H, 5.59; N, 9.82.

Complexes *trans*-5a + *cis*-5a. A mixture of **2a** (50.0 mg, 8.24 × 10^{-2} mmol) and **6a** (51.4 mg, 0.165 mmol) in $CHCl_3$ was heated at 60 °C for 12 h. After filtration of silver salt, the solution was treated with excess of Et_4NCl. The reaction mixture was then concentrated, and the residue was recrystallized from CH_2Cl_2/ether to give the desired products (*trans*-**5a** + *cis*-**5a**) as light-yellow solids (61 mg, 87%). Complex *trans*-**5**: ^1H NMR ($CDCl_3$, 400 MHz): δ 6.79 (s, 2H, imidazole−*H*), 4.50 (q, J = 7.3 Hz, 4H, $-CH_2CH_3$), 4.11 (q, J = 7.3 Hz, 4H, $-CH_2CH_3$), 3.58 (s, 4H, imidazole−*H*), 1.60 (t, J = 7.3 Hz, 6H, $-CH_3$), 1.40 (t, J = 7.3 Hz, 6H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.1 (M=*C*), 170.1 (M=*C*), 119.7, 47.9, 45.5, 44.4, 16.5, 13.7. Complex *cis*-**5**: ^1H NMR ($CDCl_3$, 400 MHz): δ 6.83 (d, J = 3.9 Hz, 1H, imidazole−*H*), 6.80 (d, J = 3.9 Hz, 1H, imidazole−*H*), 4.47−4.56 (m, 4H, $-CH_2CH_3$), 4.00−4.13 (m, 4H, $-CH_2CH_3$), 3.55 (s, 4H, imidazole−*H*), 1.58−1.67 (m, 6H, $-CH_3$), 1.33−1.42 (m, 6H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.2 (M=*C*), 168.8 (M=*C*), 119.7, 47.9, 45.5, 44.4, 16.5, 13.7. Anal. calcd. for $C_{14}H_{26}Cl_2N_4Pd$: C, 39.31; H, 6.13; N, 13.10. Found: C, 39.02; H, 5.89; N, 12.99.

Complex *trans*-5b. A mixture of **2a** (10.0 mg, 1.65 × 10^{-2} mmol) and **6b** (20.5 mg, 3.3 × 10^{-2} mmol) in $CHCl_3$ was heated at 60 °C for 36 h. After filtration of silver salt, the solution was treated with excess of Et_4NCl. The reaction mixture was then concentrated, and the residue was recrystallized from CH_2Cl_2/ether to give the desired product as light-yellow solids (16.1 mg, 71%): ^1H NMR ($CDCl_3$, 400 MHz): δ 7.44 (t, J = 7.7 Hz, 2H, Ar−*H*), 7.31 (d, J = 7.7 Hz, 2H, Ar−*H*), 7.05 (s, 2H, imidazole−*H*), 3.45 (q, J = 7.2 Hz, 4H, $-CH_2CH_3$), 3.29 (s, 4H, imidazole−*H*), 3.09−3.16 (m, 4H, $-CH(Me)_2$), 1.37 (d, J = 6.8 Hz, 12H, $-CH(CH_3)(CH_3)$), 1.05 (d, J = 6.8 Hz, 12H, $-CH(CH_3)(CH_3)$), 0.89 (t, J = 7.2 Hz, 6H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.8 (M=*C*), 178.1 (M=*C*), 147.1, 135.8, 129.5, 123.8, 123.4, 47.5, 43.7, 28.6, 26.4, 22.7,13.1. Anal. calcd. for $C_{34}H_{50}Cl_2N_4Pd$: C, 59.00; H, 7.28; Cl, 10.24; N, 8.10. Found: C, 58.76; H, 7.04; N,7.88.

Complexes *trans*-7 + *cis*-7. A mixture of **6a** (50 mg, 016 mmol) and $[(COD)PdCl]_2$ (23 mg, 0.08 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 8 h. A solution of LiCl (50 mg) was added to the reaction mixture. After filtration of salts, ether was slowly added to the reaction solution, and yellow solids precipitated (25 mg, 73%), which was identified as a mixture of *trans*- and *cis*-isomers. Complex *trans*-**7**: ^1H NMR ($CDCl_3$, 400 MHz): δ 6.84 (s, 4H, imidazole−*H*), 4.49−4.60 (m, 8H, $-CH_2CH_3$), 1.59−1.66 (m, 12H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 119.95, 119.8, 45.6, 16.4. Complex *cis*-**7**: ^1H NMR ($CDCl_3$, 400 MHz): δ 6.82 (s, 4H, imidazole−*H*), 4.40−4.58 (m, 8H, $-CH_2CH_3$), 1.53−1.59 (m, 12H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 120.1, 119.92, 45.7, 16.3. Anal. calcd. for $C_{14}H_{24}Cl_2N_4Pd$: C, 39.50; H, 5.68; N, 13.16. Found: C, 38.92; H, 5.64; N, 12.96.

Typical Procedure Reaction of Biscarbene Palladium with $AgBF_4$. A solution of **5a** (20 mg, 4.7 × 10^{-2}mmol) in CD_3CN (1 mL) was added to a flask loaded with $AgBF_4$ (18.2 mg, 9.5 × 10^{-2} mmol). The mixture was stirred at refluxing temperature for 48 h, and then LiCl (10 mg) was added. After stirring for another 24 h, the reaction mixture was filtrated to remove all solids, and the ^1H NMR spectrum of the solution was taken. The signals of spectrum were identified as a mixture of **2a**, 1,3-diethylimidazolium salt, and **6a**, which are essentially identical to the authentic samples.

Typical Procedure for Reaction of Biscarbene Palladium with I_2. A solution of **5a** (18 mg, 4.2 × 10^{-2}mmol) in $CDCl_3$ (1 mL) was added to a NMR tube loaded with I_2 (22 mg, 8.6 × 10^{-2} mmol). The mixture was stirred at room temperature for 10 h. After that, the reaction mixture was filtrated, and the ^1H NMR spectrum of the solution was taken. The signals of spectrum were identified as a mixture of **2a** and 2-iodo-1, 3-diethylimidazolium salt **10**, which are essentially identical to the authentic samples.

Compound 10. Complex **7** (7.3 mg, 7.8 × 10^{-3} mmol) and I_2 (3.5 mg, 1.4 x10^{-2} mmol) were dissolved in CH_2Cl_2 (1 mL). The resulting mixture was stirred at room temperature for 10 h. The reaction mixture was filtrated through Celite, and the filtrate was chromatographed on silica gel to separate **10** from **2a**.

Table 5. Crystal Data of **2c**, *trans*-**3a**, *cis*-**3a** and *cis*-**7**

complex	*trans*-**3a**	*cis*-**3a**	*cis*-**7**	**2c**
formula	$C_{14}H_{28}Cl_2N_4Pd$	$C_{14}H_{28}Cl_2N_4Pd$	$C_{14}H_{24}Cl_2N_4Pd$	$C_{40}H_{48}Cl_8N_4O_4Pd_2$
fw	429.70	429.70	425.67	1145.22
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$Pna2_1$	$C2/c$	$C2/c$	$P2_1/n$
a, Å	17.8170(3)	10.0204(3)	10.1228(2)	10.1320(1)
b, Å	8.3450(1)	11.0892(3)	11.1158(2)	13.9446(2)
c, Å	12.5420(2)	16.3857(5)	15.4894(3)	17.1902(2)
α, deg	90	90	90	90
β, deg	90	94.360(3)	91.205(2)	106.787(1)
γ, deg	90	90	90	90
V, Å^3; Z	1864.78(5), 4	1815.48(9), 4	1742.53(6), 4	2325.25(5), 2
d (calc.), Mg/m^3	1.595	1.572	1.623	1.636
F(0,0,0)	920	880	864	1152
crystal size, mm^3	0.25 × 0.20 × 0.10	0.20 × 0.15 × 0.10	0.20 × 0.15 × 0.10	0.30 × 0.20 × 0.15
rflns collected	10 779	10 834	11 807	16 626
independent rflns	4230 [R(int) = 0.0489]	2088 [R(int) = 0.0610]	2003 [R(int) = 0.0355]	5332 [R(int) = 0.0324]
θ range, deg	2.29−27.46	2.74−27.49	3.00−27.49	1.91−27.48
refined method	full-matrix least-squares on F^2			
goodness of fit on F^2	1.229	0.886	0.807	1.112
R indices [$I > 2\sigma(I)$]	$R1$ = 0.0694 w$R2$ = 0.1485	$R1$ = 0.0386 w$R2$ = 0.1029	$R1$ = 0.0266 w$R2$ = 0.0914	$R1$ = 0.0386 w$R2$ = 0.1004
R indices (all data)	$R1$ = 0.0817 w$R2$ = 0.1555	$R1$ = 0.0416 w$R2$ = 0.1049	$R1$ = 0.0309 w$R2$ = 0.0945	$R1$ = 0.0571 w$R2$ = 0.1204

Compound **10** was obtained as light-yellow solids (2.3 mg, 80%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (s, 2H, imidazole−*H*), 4.28 (q, J = 7 Hz, 4H, −CH_2−), 1.51 (t, J = 7 Hz, 6H, −CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 123.9, 96.0, 48.0, 15.5. ESI-MS calcd for $[M-I]^+$ $C_7H_{12}IN_2$ m/z = 251.00. Found 250.94.

Complex 11. A mixture of **6a** (100 mg, 0.32 mmol), $[(COD)PdCl]_2$ (135 mg, 0.35 mmol), and LiCl (50 mg) in dichloromethane (1 mL) was stirred for 8 h. The reaction mixture was filtered, and the filtrate was concentrated. The residue was chromatographed on silica gel with elution of ethyl acetate. A yellow band was collected and concentrated to yield **11** as yellow solids (54 mg, 56%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.91 (s, 4 H, imidazole−*H*), 4.67 (q, J = 7 Hz, 8H, −CH_2−), 1.63 (t, J = 7 Hz, 12H, −CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.8(M=*C*), 121.5, 46.1, 16.1. Anal. calcd. for $C_{14}H_{24}Cl_4N_4Pd_2$: C, 27.88; H, 4.01; N, 9.29. Found: C, 27.36; H, 4.21; N, 9.26.

Typical Procedure for Reaction of Biscarbene Palladium with CF_3COOH. A solution of **5a** (18 mg, 4.2×10^{-2}mmol) in $CDCl_3$ (1 mL) was added to a NMR tube loaded with an excess of CF_3COOH. The tube was immersed into a sonication bath for 12 h. The spectrum of the sample showed signals corresponding to **2a** and 1,3-diethylimidazolium salt, which are essentially identical to the authentic samples.

Catalysis-General Procedure. A mixture of aryl halide (0.2 mmol), phenylboronic acid (0.3 mmol), palladium complex (0.002 mmol), phosphine (0.004 mmol), and K_3PO_4 was placed in flask under nitrogen atmosphere. Then, degassed water (5 mmol) was syringed into the reaction mixture. The resulting mixture was heated for 24 h. The reaction mixture was extracted with dichloromethane (5 mL x 2). The organic extracts were dried and concentrated. The residue was chromatographed on silica gel to give the desired organic product. Products obtained in this work were characterized by spectral methods particularly with ^{1}H NMR, and the data were consistent with those reported.

4-Acetylbiphenyl [18]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (d, J = 8 Hz, 2H, Ar−*H*), 7.65 (d, J = 8 Hz, 2H, Ar−*H*), 7.59 (d, J = 7 Hz, 2H, Ar−*H*), 7.44−7.38 (m, 3 H), 2.60 (s, 3H, −CH_3).

2-Methylbiphenyl [18]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40−7.31 (m, 5H, Ar−*H*), 7.25−7.20-(m, 4H, Ar−*H*), 2.25 (s, 3H, −CH_3).

Biphenyl [18]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, J = 7 Hz, 4H, Ar−*H*), 7.48 (m, 4H), 7.39 (m, 2H).

Biphenyl-4-carboxylic acid [18]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, J = 8 Hz, 2H, Ar−*H*), 7.78−7.73 (m, 4H, Ar−*H*), 7.53−7.42 (m, 3H, Ar−*H*).

Crystallography. Crystals suitable for X-ray determination were obtained for **2c**, *trans*-**3a**, *cis*-**3a**, and *cis*-**7** by recrystallization at room temperature. Cell parameters were determined by a Siemens SMART CCD diffractometer. Crystal data of these complexes are summarized in Table 5. The structure was solved using the SHELXS-97 program[19] and refined using the SHELXL-97 program[20] by full-matrix least-squares on $F2$ values. Other crystallographic data are deposited as Supporting Information.

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Supporting Information Available: Complete description of the X-ray crystallographic structural determination of **2c**, *trans*-**3a,** *cis*-**3a**, and *cis*-**7** including: tables of atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles are given as cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

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