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Palladium Complexes with Carbene and Phosphine Ligands: Synthesis, Structural Characterization, and Direct Arylation Reactions between Aryl Halides and Alkynes

Kai-Ting Chan, Yi-Hua Tsai, Wu-Shien Lin, Jia-Rong Wu, Shih-Jung Chen, Fu-Xing Liao, Ching-Han Hu, and Hon Man Lee*

Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan, Republic of China

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The new palladium complexes with NHC and phosphine ligands, cis-$PdCl_2(L^2)(PPh_3)$ (**2**), cis-$PdBr_2(L^2)(PPh_3)$ (**3**), and cis-$PdCl_2(L^3)(PPh_3)$ (**4**) were prepared following a general protocol of a one pot reaction between $PdCl_2(COD)$, PPh_3, and the ligand precursors $LH\cdot Y$ (Y = Cl, Br, BF_4) (L^2 = 1,3-dibenzylimidazolin-2-ylidene; L^3 = 1,3-dibenzylimidazol-2-ylidene). The cis-$PdCl_2(L^3)(PCy_3)$ complex (**5**) was prepared by the ligand substitution reaction between **4** and PCy_3. The palladium complexes with NHC and pyridine complexes, trans-$PdCl_2(L)(py)$ (**6**: L = L^2; 7: L = L^3) were obtained by heating a mixture of $PdCl_2(COD)$ and $LH\cdot BF_4$ in pyridine. A similar reaction condition using CH_3CN as solvent with KO^tBu as base afforded cis-$PdCl_2(L^3)_2$ (**8**). Complexes **2**−**8** were successfully characterized by X-ray crystallographic studies, among which, intriguingly, two polymorphs of **8** were obtained. Thermogravimetric analysis showed that the cis-$PdX_2(NHC)(PR_3)$ complexes are more thermally stable than the trans-$PdCl_2(NHC)(py)$ complexes. Together with the known cis-$PdCl_2(L^1)(PCy_3)$ (**1**) (L^1 = 1-benzyl-3-(*N*-phenylacetamido)imidazol-2-ylidene), they were screened for the direct arylation reaction between aryl halides and alkynes. The result indicate that the carbene/phosphine complexes **1**−**5** are superior precatalysts than **6**−**8** with higher activities than the commonly-used system of $Pd(OAc)_2/2PPh_3$.

Introduction

Palladium complexes with N-heterocyclic carbene ligands (NHCs) have been proven remarkably successful in catalyzing Suzuki-type cross-coupling reactions for the construction of biaryl motifs.[1−9] These reactions, however, required the use of organometallic reagents as substrates.[10−13] The construction of the biaryl motif without the need of a preliminary organometallic reagent is more challenging and has attracted much attention because of the reduced waste and fewer reaction steps.[14−18] This direct arylation reaction involves a kinetically significant aryl C−H bond activation step, and reactive aryl halides, most commonly aryl iodides, were required as substrates.[15] $Pd(OAc)_2/2PPh_3$ represents a widely used catalytic system for direct arylations.[15,19,20] Lately, there has been growing interest in using palladium NHC complexes in catalyzing direct arylations.[21−23] In this regard, Sames et al. reported that palladium NHC complexes of the type $PdI_2(NHC)(PPh_3)$ efficiently catalyze the C−H arylation of SEM-protected azoles.[22] These types of mixed carbene/phosphine complexes offer the distinct features of a strong donating effect from a robust NHC ligand as well as a stabilization effect from a labile phosphine ligand. These types of palladium complexes have already been applied commonly in cross-coupling reactions.[3,24−26]

*To whom correspondence should be addressed. Tel: +886 4 7232105, ext. 3523. Fax: +886 4 7211190. E-mail: leehm@cc.ncue.edu.tw.

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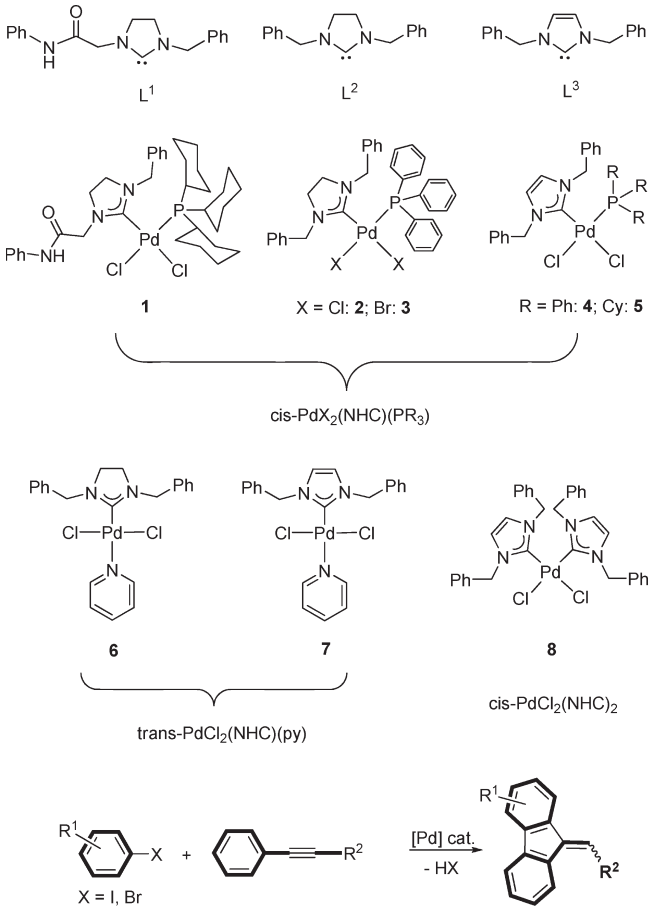
Chart 1. NHC Ligands and Their Pd(II) Precatalysts for the Direct Arylation Reactions of Alkynes with Aryl Halides



Palladium carbene complexes of the type *trans*-$PdCl_2$(NHC)(py′) (py′ = 3-chloropyridine), known as PEPPSI complexes, share a similar concept and have been highly successful in catalyzing various cross-coupling reactions.[9,27]

In a previous report, we had shown that *cis*-$PdCl_2(L^1)$-(PCy_3) (**1**) is a highly robust precatalyst for Suzuki cross-coupling reactions.[26] This spurred us to check the catalytic performance of complexes of the type PdX_2(NHC)(PR_3) as well as $PdCl_2$(NHC)(py) in the direct arylation reactions of alkynes with aryl halides for the formation of fluorene compounds (Chart 1). Molecular and polymeric materials containing fluorene skeletons have been attracting interest because they have rich optical properties which can be applied in optoelectronic applications.[28−30] Most recently, Gevorgyan et al. described an alternative approach of palladium-catalyzed hydroarylation of *o*-alkynyl biaryls to prepare relevant fluorene derivatives with high regioselectivity.[31] The cascade reaction in Chart 1 affords fluorene derivatives from easily available substrates but is typically catalyzed by a high loading of $Pd(OAc)_2$ (5 mol %) and PPh_3 (10 mol %) at high temperature over a long duration using aryl iodides as substrates.[20] Considering these harsh catalytic conditions required, robust palladium carbene complexes may exhibit better activities. In this regard, we showed that palladium complexes with rigid bidentate phosphine and NHC groups are effective catalytic precursors for the direct arylation reactions between phenyl halides and diphenylacetylene.[23] However, extended hours were still needed for utilizing unreactive phenyl bromide as substrate. We anticipated that the new catalyst systems PdX_2(NHC)(PR_3) and $PdCl_2$(NHC)(py) will perform better due to the easy availability of vacant coordination sites and their still-good thermal stability. The catalytic performance of $PdCl_2(NHC)_2$ will also be studied and compared with those of PdX_2(NHC)(PR_3) and $PdCl_2$-(NHC)(py). Instead of one robust and one labile ligands, two robust NHC ligands are present in $PdCl_2(NHC)_2$. The L^1 ligand in **1** is an unsymmetrical ligand bearing benzyl and amido groups. Herein, we investigate the saturated monodentate NHC ligand of 1,3-dibenzylimidazolin-2-ylidene (L^2) and the unsaturated 1,3-dibenzylimidazol-2-ylidene (L^3). Our interest in these ligands is based on the fact that these symmetrical ligands are easily accessible at low cost. Also, in contrast to the ubiquitously used IMes and IPr ligands, these ligands contain *N*-benzyl groups which are more conformationally flexible, giving rise to plausible better accommodation of steric bulk on the palladium coordination sphere. The results illustrate that, among the three types of precatalysts screened, $PdCl_2$(NHC)(PR_3) complexes represent a promising class of precatalysts for the direct arylations, capable of utilizing the unreactive yet cheap aryl bromides as substrates in producing fluorene derivatives.

Results and Discussion

Preparation of Ligand Precursors. The organic salts $L^2H\cdot Y$ (Y = Cl,[32] BF_4[33]) and $L^3H\cdot Y$ (Y = Cl,[34] BF_4) were the ligand precursors for the NHC ligands L^2 and L^3, respectively. The salts $L^2H\cdot Cl$ and $L^3H\cdot Cl$ were prepared by reacting benzyl chloride with 1-benzylimidazole and 1-benzyl-4,5-dihydro-1*H*-imidazole, respectively. The $L^2H\cdot BF_4$ and $L^3H\cdot BF_4$ salts were similarly prepared, but $NaBF_4$ was also added for anion exchange. Either the chloride or the tetrafluoroborate salts can be used for the preparation of Pd(NHC) complexes; the tetrafluoroborate salts were preferred by us because of their nonhygroscopic nature. The difference in electronic properties between $[L^2H]^+$ and $[L^3H]^+$ ions is reflected by the more upfield chemical shift of the ^1H NMR signals of the saturated species compared with the unsaturated compound. For example, the signals for the methylene proton and the proton on the C-2 carbon in $L^2H\cdot BF_4$ are observed at 4.63 and 8.50 ppm, respectively, whereas those in $L^3H\cdot BF_4$ are observed at 5.27 and 9.05 ppm, respectively. Some iridium complexes with L^2 and L^3 have been reported recently.[35]

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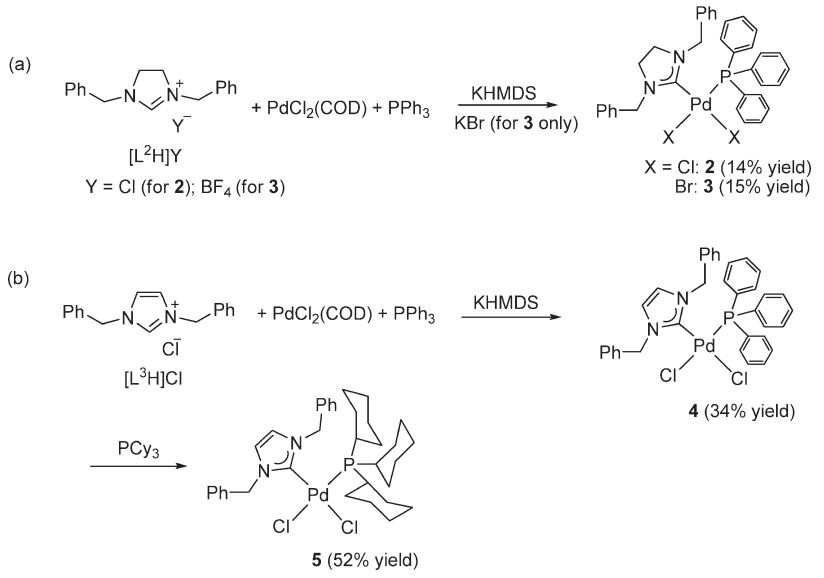
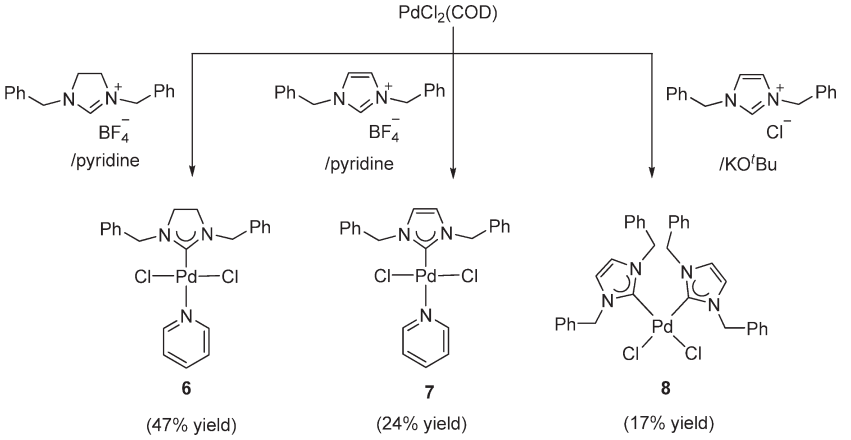
Scheme 1. Synthesis of Cis Palladium Complexes Bearing NHC and Phosphine Ligands



Scheme 2. Synthesis of Phosphine-Free Palladium NHC Complexes



Preparation of *cis*-$PdCl_2$(NHC)(PR_3) Complexes. The new palladium complexes with NHC and phosphine ligands **2**−**5** were prepared according to our previously reported procedure for **1** (Scheme 1).[26] Pure complexes were obtained, albeit in low yields. As an example, a one-plot reaction between $L^2H\cdot Cl$, $PdCl_2(COD)$, and PPh_3 in the presence of KHMDS afforded the pure *cis*-$PdCl_2(L^2)(PPh_3)$ (**2**). The complex *cis*-$PdCl_2(L^3)(PCy_3)$ (**5**) was prepared by a ligand displacement reaction between *cis*-$PdCl_2(L^3)(PPh_3)$ (**4**) and PCy_3.

The successful formation of **2**−**4** is indicated by the disappearance of signal due to the proton upon the C-2 carbon of the ligand precursor and the downfield coordination shift of the $^{31}P\{^1H\}$ NMR signal (for example, from ca. −6 ppm in free PPh_3 to ca. 27 ppm in **2**). The ^{31}P NMR resonance for PCy_3 in **5** is even more downfield than that of PPh_3 in **4** (ca. 49 vs 27 ppm). As noted by us earlier in relevant systems,[26] the saturated carbenic carbons resonate as much as 30 ppm more downfield than the unsaturated carbenic carbons (ca. 193 ppm in **2** and **3** vs 160 ppm in **4** and **5**). This drastic difference in chemical shift reflects the variation of electronic properties between the saturated and unsaturated carbene ligands. Complexes **1**−**5** have the desirable air and moisture stability and dissolve readily in halogenated solvents. The cis coordination in complex **1** had been established.[26] Complexes **2**−**5** are similar cis complexes, as revealed by subsequent structural studies (vide infra). Those NHC/phosphine complexes bearing large aryl groups typically adopt a trans configuration.[25,36−38] Complexes **2**−**5** are cis compounds, reflecting the smaller steric bulk of the benzyl groups.

Preparation of Phosphine-Free Pd(NHC) Complexes. New palladium complexes with NHC and pyridine ligands **6** and **7** were prepared according to Scheme 2. The general procedure involves the heating of mixture of the appropriate tetrafluoroborate salt and $PdCl_2(COD)$ in pyridine at 130 °C overnight.[39] The protocol is similar to those unsaturated carbene compounds published by Ghosh et al.,[40] except that our

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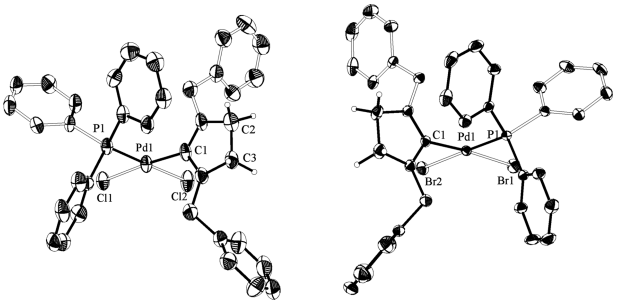

Figure 1. Molecular structures of **2** (left) and **3** (right) with 50% probability ellipsoids for non-H atoms. Hydrogen atoms, except those on the heterocyclic ring, have been omitted for clarity.

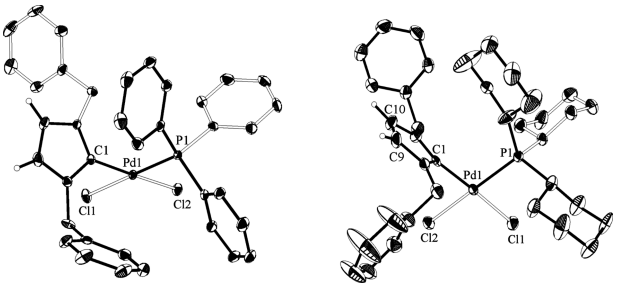

Figure 2. Molecular structures of **4** (left) and **5** (right), with 50% probability ellipsoids for non-H atoms. Hydrogen atoms, except those on the heterocyclic ring, have been omitted for clarity. Only one of the independent molecules in the asymmetric unit of **5** is shown.

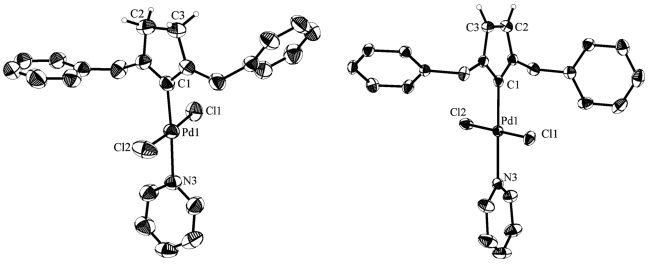

Figure 3. Molecular structure of **6** (left) and **7** (right), with 50% probability ellipsoids for non-H atoms. Hydrogen atoms, except those on the heterocyclic ring, have been omitted for clarity. Only one of the independent molecules in the asymmetric unit of **6** is shown.

procedure did not involve the addition of K_2CO_3. Purification with column chromatography gave pure complexes **6** and **7** in low yields. They are trans complexes, as revealed by subsequent X-ray structural studies (vide infra). The cis palladium bis(NHC) complex **8** was prepared by stirring a mixture of $L^3H \cdot Cl$ and $PdCl_2(COD)$ in the presence of potassium *tert*-butoxide. A low 17% yield was obtained for the pure complex **8** after column chromatography. Notably, the chloride salt of $L^3 \cdot Cl$ was necessary for the preparation of **8**. The use of the tetrafluoroborate salt instead did not afford the desirable product.

The most important spectroscopic feature in the *trans*-$PdCl_2(NHC)(py)$ complexes is again the 30 ppm downfield shift of the carbene resonance in the saturated carbene complex **6** compared to that in the unsaturated analogue **7** (ca. 181 vs 150 ppm). The carbene signal in **8** resonates at an

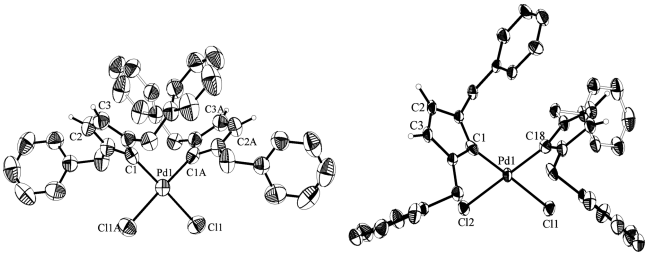

Figure 4. Molecular structures of **8**: (left) $C2/c$ unit cell, with 50% probability ellipsoids for non-H atoms (symmetry code A: $1 - x$, y, $0.5 - z$); (right) $P2_1/c$ unit cell, with 50% probability ellipsoids for non-H atoms. Hydrogen atoms, except those on the heterocyclic ring, have been omitted for clarity.

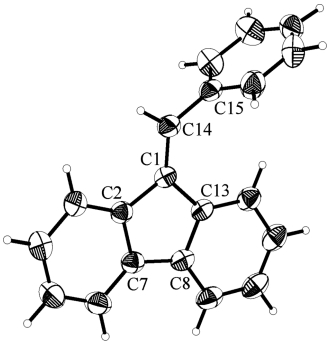

Figure 5. Molecular structure of **9** with 30% probability ellipsoids for non-H atoms. Only one orientation of the disordered phenyl ring is shown.

intermediate chemical shift of ca. 161 ppm. The structure of **8** was established to be a cis palladium bis(NHC) complex by an X-ray structural study (vide infra), in contrast to the more commonly observed trans complexes.[41−44] The *cis*-$PdI_2(L^4)_2$ complex (L^4 = 1,3-dimethylimidazol-2-ylidene) is a closely related compound reported in the literature.[45] Complexes **6**−**8** are also air and moisture stable and dissolve readily in halogenated solvents.

Crystallographic Studies. All the new Pd(NHC) complexes described in this paper have been successfully structurally characterized. Figures 1−4 display their thermal ellipsoid plots. The molecular structure of the organic product 9-benzylidene-9*H*-fluorene (**9**) was also determined (Figure 5). Selected bond distances and angles for the *cis*-$PdCl_2(NHC)(PR_3)$ complexes are given in Table 1, whereas those for the phosphine-free Pd(NHC) complexes and the organic compound **9** are shown in Table 2. Complexes **2**−**5** are revealed as cis complexes. Due to the cis disposition of two bulky organic ligands, they display distorted square coordination geometry with C−Pd−P angles greater than the ideal 90°. For example, complex **5** bearing L^3 and the bulky PCy_3 ligands has a large C−Pd−P angle of 95.77(14)°, whereas the corresponding angle in **4**, due to the smaller bulk of PPh_3, is 92.85(5)°. A perusal of Table 1 reveals that there is no significant difference in the geometrical parameters between

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Table 1. Selected Bond Distances (Å) and Angles (deg) of 2−5

2		**3**·C_3H_7NO		**4**		**5**	
Pd1−C1	1.981(6)	Pd1−C1	1.9903(18)	Pd1−C1	1.9784(17)	Pd1−C1	1.997(5)
Pd1−P1	2.2583(18)	Pd1−P1	2.2640(4)	Pd1−P1	2.2599(4)	Pd1−P1	2.2785(14)
Pd1−Cl1	2.3590(17)	Pd1−Br1	2.4750(2)	Pd1−Cl1	2.3570(4)	Pd1−Cl1	2.3468(12)
Pd1−Cl2	2.3487(18)	Pd1−Br2	2.4784(2)	Pd1−Cl2	2.3482(4)	Pd1−Cl2	2.3684(14)
C1−Pd1−P1	91.59(18)	C1−Pd1−P1	92.03(5)	C1−Pd1−P1	92.85(5)	C1−Pd1−P1	95.77(14)
C1−Pd1−Cl2	85.64(18)	C1−Pd1−Br2	83.39(5)	C1−Pd1−Cl1	84.89(5)	C1−Pd1−Cl2	85.72(15)
Cl1−Pd1−P1	91.09(6)	Br1−Pd1−P1	89.979(13)	Cl2−Pd1−P1	90.929(16)	Cl1−Pd1−P1	87.78(5)
Cl1−Pd1−Cl2	91.66(7)	Br1−Pd1−Br2	92.472(8)	Cl1−Pd1−Cl2	91.472(16)	Cl1−Pd1−Cl2	90.69(5)
C1−Pd1−Cl1	176.3(2)	C1−Pd1−Br1	176.20(5)	C1−Pd1−Cl2	174.51(5)	C1−Pd1−Cl1	176.06(15)
P1−Pd1−Cl2	177.20(7)	P1−Pd1−Br2	176.683(13)	P1−Pd1−Cl1	176.886(16)	P1−Pd1−Cl2	177.88(5)

Table 2. Selected Bond Distances (Å) and Angles (deg) of 6−9

6		**7**		**8** (form I)		**8** (form II)		**9**	
Pd1−C1	1.953(3)	Pd1−C1	1.9682(18)	Pd1−C1	1.982(4)	Pd1−C1	1.986(7)	C1−C14	1.315(2)
Pd1−N3	2.099(3)	Pd1−N3	2.0932(16)	Pd1−Cl1	2.3539(11)	Pd1−C18	1.985(6)	C1−C2	1.475(2)
Pd1−Cl1	2.3046(13)	Pd1−Cl1	2.3086(5)			Pd1−Cl1	2.3591(15)	C1−C13	1.470(2)
Pd1−Cl2	2.3021(13)	Pd1−Cl2	2.3075(5)			Pd1−Cl2	2.3675(15)	C7−C8	1.455(2)
C1−Pd1−Cl1	89.45(11)	C1−Pd1−Cl1	91.37(6)	C1−Pd1−C1A	95.3(2)	C1−Pd1−C18	92.8(2)	C1−C14−Cl5	127.90(16)
C1−Pd1−Cl2	88.17(11)	C1−Pd1−Cl2	88.32(6)	C1−Pd1−Cl1A	85.42(10)	C1−Pd1−Cl2	88.87(17)	C2−C1−Cl4	126.22(14)
Cl1−Pd1−N3	92.37(10)	Cl1−Pd1−N3	89.55(5)	Cl1−Pd1−Cl1A	94.19(6)	Cl1−Pd1−Cl2	92.42(6)	Cl3−C1−C14	128.22(15)
Cl2−Pd1−N3	89.90(10)	Cl2−Pd1−N3	90.80(5)	C1−Pd1−Cl1	175.89(11)	Cl1−Pd1−C18	86.11(17)	C1−C2−C7	108.67(13)
C1−Pd1−N3	176.75(13)	C1−Pd1−N3	178.55(7)			C1−Pd1−Cl1	175.0(2)	C1−C13−C8	108.39(14)
Cl1−Pd1−Cl2	176.57(4)	Cl1−Pd1−Cl2	178.08(2)			C18−Pd1−Cl2	177.48(18)		

the saturated carbene complex **2** and its unsaturated counterpart **4**. Generally, for complexes **2**−**5**, the difference in trans influence of the carbene and the phosphine ligands is not obvious. For example, the Pd−Cl distance trans to PCy_3 in one of the independent molecules of **5** is 2.3684(14) Å, longer than that of 2.3468(12) Å trans to the carbene. The reverse trend is observed in the other independent molecule (see the Supporting Information). The Pd−carbene distances in these complexes are within the normal range of similar compounds published in the literature.[42,43,46,47]

The structural determinations established that the $PdCl_2$(NHC)(py) complexes **6** and **7** adopt trans coordination (Figure 3). For the structure of **6**, there are two independent molecules in an asymmetric unit; their geometrical parameters are similar, and only one of the molecules is used for structural discussion (see also the Supporting Information). The Pd−C bond in **6** (1.953(3) Å) is slightly shorter than that in **7** (1.9682(18) Å), seemingly indicating that coordination of the saturated carbene L^2 is stronger than that of the unsaturated carbene L^3. The Pd−C distance is also strongly influenced by the N-substituents, as relevant $PdCl_2$(NHC)(py) compounds bearing unsaturated carbene can also have short Pd−C distances as in **6**.[40,48] The Pd−C distances in the two *trans*-$PdCl_2$(NHC)(py) complexes are slightly shorter than those in the *cis*-PdX_2(NHC)(PR_3) complexes (ca. 1.96 Å vs 1.99 Å). The Pd−Cl distances of ca. 2.31 Å in the *trans*-$PdCl_2$(NHC)(py) complexes are also shorter than those of ca. 2.36 Å in **2**, **4**, and **5**. Interestingly, while the Pd−C bonds in **6** and **7** are similar to those in the related Pd−PEPPSI−IPr complex,[27] their Pd−N bonds are markedly shorter (2.099(3) and 2.0932(16) Å vs 2.1372 Å), reflecting the stronger coordination of the pyridine as compared to that of 3-chloropyridine.

The structure of complex **8** was also established by X-ray crystallography. Intriguingly, two polymorphic single crystals were obtained (Figure 4). One of them crystallizes in the monoclinic space group $C2/c$ (form I), whereas the other crystallizes in the monoclinic space group $P2_1/c$ (form II). The presence of two polymorphic structures confirms unambiguously the flexible conformation of the *N*-benzyl groups on the carbene ligands. In form I, the two benzyl groups for each ligand are in an anti orientation with respect to each other, whereas in form II one of the ligands contains two benzyl groups which are in a syn orientation. The Pd−C distances in these two structures are comparable to those in the related *cis*-$PdI_2(L^4)_2$ complex.[45] However, their C−Pd−C angles are somewhat larger than that of the known compound (95.3(2) and 92.8(2)° vs 90.2(1)°),[45] attributable to the larger steric bulkiness of benzyl compared to that of methyl groups.

The organic product 9-benzylidene-9*H*-fluorene (**9**), obtained from a direct arylation reaction between phenyl halide and diphenylacetylene (vide infra), was also successfully studied by X-ray crystallography (Figure 5). It crystallizes in the monoclinic space group $C2/c$ with a full molecule in an asymmetric unit. The molecule is disordered over two overlapping orientations related by a 2-fold rotation operation along the C1−C14 bond with 50:50 site occupancies. The phenyl ring and the fluorene fragment are nearly normal to each other with a dihedral angle of 86.57(9)°, which is in sharp contrast to that of 51.22(5)° in the closely related structure of 9-pentafluorophenylmethylene-9*H*-fluorene.[49]

(46) Fürstner, A.; Seidel, G.; Kremzow, D.; Lehmann, C. W. *Organometallics* **2003**, *22*, 907.
(47) Chamizo, J. A.; Morgado, J.; Castro, M.; Bernes, S. *Organometallics* **2002**, *21*, 5428.
(48) Ray, S.; Mohan, R.; Singh, J. K.; Samantaray, M. K.; Shaikh, M. M.; Panda, D.; Ghosh, P. *J. Am. Chem. Soc.* **2007**, *129*, 15042.
(49) Plater, M. J.; Howie, R. A.; Schmidt, D. M. *Acta Crystallogr.* **2003**, *E59*, o89.

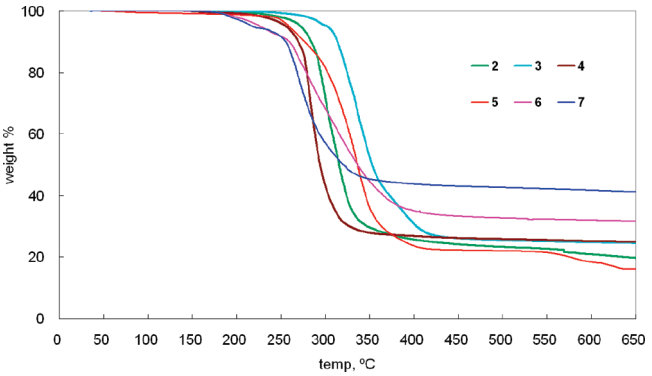
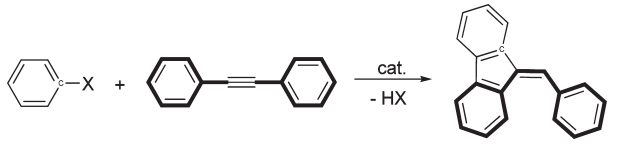


Figure 6. Thermogravimetric analyses of **2**−**7**.

Table 3. Direct Arylation Reactions between Phenyl Halides and Diphenylacetylene[a]



entry	cat.	X	time (h)	yield (%)	time (h)	yield (%)[a]
1	**1**	I	12	89	24	
2	**2**	I	12	87	24	
3	**3**	I	12	97	24	
4	**4**	I	12	72	24	
5	**5**	I	12	84	24	
6	**6**	I	12	82	24	
7	**7**	I	12	58	24	
8	**8**	I	12	88	24	
9	$PdCl_2/2PPh_3$	I	12	61	24	
10	$Pd(OAc)_2/2PPh_3$	I	12	67	24	
11	**1**	Br	12	97	24	>99
12	**2**	Br	12	97	24	>99
13	**3**	Br	12	93	24	>99
14	**4**	Br	12	82	24	>99
15	**5**	Br	12	93	24	>99
16	**6**	Br	12	23	24	60
17	**7**	Br	12	40	24	49
18	**8**	Br	12	30	24	35
19	$PdCl_2/2PPh_3$	Br	12	42	24	54
20	$Pd(OAc)_2/2PPh_3$	Br	12	39	24	59

[a] Reaction conditions: 5 mol % of catalyst, 0.25 mmol of phenyl halide, 0.25 mmol of diphenylacetylene, 0.50 mmol of NaOAc, 0.25 mmol of *n*-Bu_4NCl, 5 mL of DMF, 120 °C, isolated yield (an average of several runs).

Computational Studies. To understand the relative stability between the cis and the trans forms of $PdX_2(NHC)(PR_3)$, we conducted density functional theory computations using the B3LYP functional. The studies indicated that in the gas phase the trans form of complex **4** is, in contrast with our structural study, more stable than the cis compound by ca. 7.0 kcal/mol in Gibbs free energy. Since a polar solvent was employed in the preparation of complexes **2**−**5**, the solvent effect may play a key role in the relative stability between the two isomers. When the solvent correction was included using the polarizable continuum model (PCM, nitromethane as solvent), the experimentally found cis structure indeed becomes lower in energy than the trans isomer by 2.7 kcal/mol. The stability of the cis form in polar solvent over the trans form is attributed to the difference of the dipole moments of the two isomers. The DFT optimized structures of **4** are illustrated in the Supporting Information, and the selected bond distances and bond angles of the cis isomer were comparable to those obtained by the X-ray structural study (vide infra). The computational studies are fully consistent with our previous results obtained for complex **1**.[26]

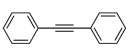
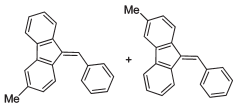
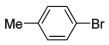
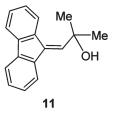
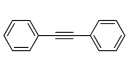
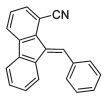
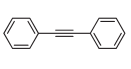
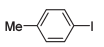
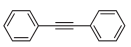
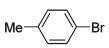
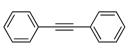
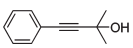
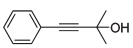
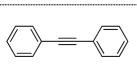
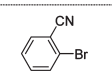
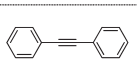
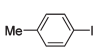
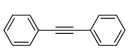
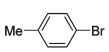
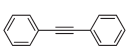
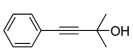
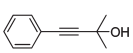
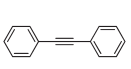
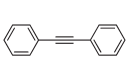
Thermogravimetric Analysis (TGA). To understand the robustness of the new complexes, TGA was conducted on the $PdX_2(NHC)(PR_3)$ complexes **2**−**5** and $PdCl_2(NHC)(py)$ complexes **6** and **7** (Figure 6). The analyses clearly indicate the high robustness of all these complexes. In general, the $PdX_2(NHC)(PR_3)$ complexes are thermally more stable than the $PdCl_2(NHC)(py)$ complexes. Complexes **2**−**5** are thermally stable up to ca. 250 °C, with complex **3** being the most thermally stable compound. In contrast, complexes **6** and **7** start thermal decomposition above ca. 200 °C.

Catalytic Transformations. Complexes **1**−**8** were screened as precatalysts for the direct arylation reactions between aryl halides and alkynes. We employed the conditions initially utilized by Larock et al.,[20] involving 5 mol % of precatalyst, 0.25 mmol of phenyl halide, 0.25 mmol of diphenylacetylene, 0.50 mmol of NaOAc, and 0.25 mmol of *n*-Bu_4NCl in 5 mL of DMF at 120 °C for a duration of 12 or 24 h. We began our investigation using phenyl iodide and diphenylacetylene as the benchmark reaction (Table 3). Entries 1−8 illustrate that good to excellent yields of 9-benzylidene-9*H*-fluorene can be achieved using all the new palladium carbene precatalysts. The effectiveness among these complexes is more obvious when less reactive phenyl bromide was used as substrate. Entries 11−15 vs 16−18 clearly reveal the higher efficiency of *cis*-$PdX_2(NHC)(PR_3)$ complexes over the *trans*-$PdCl_2(NHC)(py)$ and *cis*-$PdCl_2(NHC)_2$ complexes. Indeed, complexes **1**−**5** afford quantitative production of the product after prolonging the reaction time to 24 h (entries 11−15). The results indicated that complexes **1**−**5** are superior precatalysts to the reported $Pd(OAc)_2/2PPh_3$ system,[20,50] which gives inferior activities under the same conditions (entries 11−15 vs 20). Intriguingly, while $Pd(OAc)_2$ has been generally employed as the precatalyst for direct arylation,[20,50] the simple $PdCl_2$ complex has never been tested. We showed that the simple $PdCl_2$ complex in the presence of PPh_3 also represents a viable catalytic system, delivering activities comparable to those of the $Pd(OAc)_2/2PPh_3$ system (entries 9 and 19 vs 10 and 20).[20,50] Unfortunately, none of the precatalysts were able to utilize the unreactive but economic attractive phenyl chloride as substrate.

The substrate scope of the *cis*-$PdCl_2(NHC)(PR_3)$ complexes was briefly investigated, using complexes **1**, **4**, and **5** as representative examples (Table 4). In general, they are capable of utilizing aryl iodides effectively to form fluorene products **10**−**12** and the use of aryl bromides affords lower yields. By far, complex **1** is the most efficient among the three complexes tested. Entry 1 illustrated that a 60% yield of a mixture of **10a** and **10b** (*Z*/*E* ratio 42:58) was obtained with complex **1** as precatalyst using 4-iodotoluene and diphenylacetylene as substrates (entry 1). A comparable yield (58%) of the fluorene product can also be obtained with the less reactive 4-bromotoluene (entry 2). Contrastingly, inferior yields of 46 and 47% were obtained using **4** and **5** as precatalysts (entries 8 and 14). The similar activities between

(50) Larock, R. C.; Tian, Q. *J. Org. Chem.* **2001**, *66*, 7372.

Table 4. Direct Arylation Reactions between Aryl Halides and Alkynes[a]

entry	cat.	aryl halide	alkyne	product	yield (%)[a] *Z*/*E* ratio
1	**1**			 **10a** + **10b**	60 (42:58)
2	**1**			**10a** + **10b**	58 (36:64)
3	**1**			 **11**	85
4	**1**			**11**	60
5	**1**			 **12**	86
6	**1**			**12**	76
7	**4**			**10a** + **10b**	49 (40:60)
8	**4**			**10a** + **10b**	46 (38:62)
9	**4**			**11**	71
10	**4**			**11**	34
11	**4**			**12**	75
12	**4**			**12**	58
13	**5**			**10a** + **10b**	51 (37:63)
14	**5**			**10a** + **10b**	47 (43:57)
15	**5**			**11**	75
16	**5**			**11**	37
17	**5**			**12**	77
18	**5**			**12**	60

[a] Reaction conditions: 5 mol % of catalyst, 0.25 mmol of aryl halide, 0.25 mmol of alkyne, 0.50 mmol of NaOAc, 0.25 mmol of *n*-Bu_4NCl, 5 mL of DMF, 120 °C, isolated yield (an average of several runs). The *Z*/*E* ratio was determined by ^1H NMR spectroscopy.

4 and **5** suggested that the labile phosphines do not take part in the rate-determining step of the catalytic cycle (entries 7−12 vs 13−18). Using complex **1** as precatalyst, a decent yield of **11** (60%) can be obtained from the reaction between phenyl bromide and 2-methyl-4-phenylbut-3-yn-2-ol in 24 h (entry 4); also, the reaction between 2-bromobenzonitrile and diphenylacetylene gave the single stereoisomer of **12** in pure form with a yield of 76% (entry 6).

Conclusions. On the basis of the conformationally flexible 1,3-dibenzylimidazolin-2-ylidene (L^2) and 1,3-dibenzylimidazol-2-ylidene (L^3), we prepared and structurally characterized *cis*-$PdX_2(NHC)(PR_3)$, *trans*-$PdCl_2(NHC)$(py), and *cis*-$PdCl_2(NHC)_2$. An interesting aspect of the structural studies is the observation of two genuine polymorphic forms of **8** due to the flexibility of *N*-benzyl conformations. Together with the previously reported complex **1**, these three types of complexes were tested for the direct arylation reactions of alkynes with aryl halides. The screening sheds light on the modular design of effective palladium precatalysts for the catalytic process. Palladium complexes bearing one robust NHC ligand and one labile phosphine ligand, *cis*-$PdX_2(NHC)(PR_3)$, are confirmed to deliver good activities, capable of utilizing less reactive aryl bromides as substrates. The activities from PCy_3 and PPh_3 ligands are essentially the same. The catalytic performance from these types of complexes is superior to that of the commonly used system of $Pd(OAc)_2/2PPh_3$. The inefficiency of the *cis*-$PdCl_2(NHC)_2$ precatalyst further confirmed that one labile ligand is essential. In contrast, replacement of the phosphine ligand with a pyridine ligand results in inferior activities from the *trans*-$PdCl_2(NHC)(py)$ complexes. Their poorer thermal stability compared to that of *cis*-$PdX_2(NHC)(PR_3)$ may contribute to their lower efficiency. The use of aryl chlorides as substrates and better control of regioselectivity are, however, challenges for further studies.

Experimental Section

General Procedure. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All solvents used were purified according to standard procedures.[51] Commercially available chemicals were purchased from Aldrich or Acros. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.13, 75.48, and 121.49 MHz, respectively, on a Bruker AV-300 spectrometer. The chemical shifts for ^1H and ^{13}C spectra were referenced by the residual solvent signals relative to tetramethylsilane at 0 ppm. The chemical shifts for ^{31}P spectra were referenced to an external reference of 85% phosphoric acid at 0 ppm. Elemental analyses were performed on a Heraeus CHN-OS Rapid elemental analyzer at the National Chung Hsing University, Taiwan, or a Thermo Flash 2000 CHN-O elemental analyzer at NCUE. ESMS spectra were collected on a Finnigan/Thermo Quest MAT 95XL mass spectrometer at NCHU. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 6 thermogravimetric analyzer under flowing N_2 gas (40 mL/min), and the heating rate was 20 °C/min. 9-Benzylidene-9*H*-fluorene[20] and **10**−**12**[19] were previously reported.

Synthesis of $L^3H\cdot BF_4$. A mixture of 1-benzylimidazole (1.50 g, 9.49 mmol), benzyl bromide (1.13 mL, 9.49 mmol), and $NaBF_4$ (5.21 g, 47.4 mmol) in DMF (5 mL) was stirred at room temperature for 4 h. Upon addition of diethyl ether into the solution, a white precipitate was formed. The supernatant liquid was removed, and the residual solid was redissolved in dichloromethane. The organic layer was washed twice with water. After drying with anhydrous $MgSO_4$, the solvent was removed completely under vacuum. The residue was washed with diethyl ether. The white solid was filtered on a frit and dried under vacuum. Yield: 2.31 g, 72%. Mp: 87−90 °C. Anal. Calcd for $C_{17}H_{17}BF_4N_2$: C, 60.74; H, 5.10; N, 8.33. Found: C, 60.54; H, 5.02; N, 7.97. ^1H NMR ($CDCl_3$): δ 5.27 (s, 4H, CH_2), 7.12 (s, 2H, imi *H*), 7.30−7.36 (m, 10H, Ph *H*), 9.05 (s, 1H, NC*H*N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 53.4 (Ph*C*H_2), 122.1 (imi *C*), 128.9 (Ph *C*), 129.4 (Ph *C*), 129.5 (Ph *C*), 132.7 (Ph *C*), 135.7 (N*C*HN).

Synthesis of *cis*-$PdCl_2(L^2)(PPh_3)$ (2). A mixture of $L^2H\cdot Cl$ (0.447 g, 1.32 mmol), KHMDS (0.263 g, 1.32 mmol), $PdCl_2$(COD) (0.378 g, 1.32 mmol), and PPh_3 (0.347 g, 1.32 mmol) in DMF (10 mL) was stirred at room temperature for 1 day. After the mixture was cooled, the solvent was removed completely under vacuum. The residue was extracted with dichloromethane. The organic layer was washed twice with water. After drying with anhydrous $MgSO_4$, the solvent was removed completely under vacuum. The residue was washed with THF. The off-white solid was filtered on a frit and dried under vacuum. Yield: 0.123 g, 14%. Mp: 264−266 °C dec. Anal. Calcd for $C_{35}H_{33}Cl_2N_2PPd$: C, 60.93; H, 4.82; N, 4.06. Found: C, 60.61; H, 5.08; N, 3.76. ^1H NMR ($CDCl_3$): δ 2.66−2.72 (m, 2H, NCH_AH$_B$C), 3.03−3.09 (m, 2H, NCH$_A$$H_B$C), 4.05 (d, $^2J_{HH}$ = 14.0 Hz, 2H, PhCH_AH$_B$N), 5.51 (d, $^2J_{HH}$ = 14.0 Hz, 2H, PhCH$_A$$H_B$N), 7.19−7.29 (m, 10H, Ph *H*), 7.38−7.52 (m, 9H, Ph *H*), 7.71−7.77 (m, 6H, Ph *H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 47.4 (N*C*H_2), 54.8 (Ph*C*H_2), 128.3 (Ph *C*), 128.5 (d, $^3J_{PC}$ = 11.1 Hz, Ph *C*), 129.0 (d, $^2J_{PC}$ = 40.4 Hz, Ph *C*), 129.8 (Ph *C*), 130.5 (Ph *C*), 131.4 (d, $^4J_{PC}$ = 2.5 Hz, Ph *C*), 134.0 (Ph *C*), 134.5 (d, $^1J_{PC}$ = 11.1 Hz, Ph *C*), 192.2 (N*C*N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.2. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of diethyl ether into a DMF solution of the solid mixture.

Synthesis of *cis*-$PdBr_2(L^2)(PPh_3)$ (3). A mixture of $L^2H\cdot BF_4$ (0.217 g, 0.643 mmol), KHMDS (0.128 g, 0.643 mmol), $PdCl_2$(COD) (0.114 g, 0.643 mmol), PPh_3 (0.169 g, 0.643 mmol), and KBr (0.192 g, 1.61 mmol) in CH_3CN (15 mL) was heated at room temperature for 1 day. The workup procedure is same as that for **2**. An off-white solid was obtained. Yield: 0.0747 g, 15%. Mp: 285 °C dec. Anal. Calcd for $C_{35}H_{33}Br_2N_2PPd$: C, 53.97; H, 4.27; N, 3.60. Found: C, 53.90; H, 4.73; N, 3.40. ^1H NMR ($CDCl_3$): δ 2.66−2.72 (m, 2H, NCH_AH$_B$C), 3.03−3.09 (m, 2H, NCH$_A$$H_B$C), 4.05 (d, $^2J_{HH}$ = 13.8 Hz, 2H, PhCH_AH$_B$N), 5.45 (d, $^2J_{HH}$ = 13.8 Hz, 2H, PhCH$_A$$H_B$N), 7.16−7.25 (m, 10H, Ph *H*), 7.37−7.51 (m, 9H, Ph *H*), 7.69−7.75 (m, 6H, Ph *H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 47.4 (N*C*H_2), 54.8 (Ph*C*H_2), 128.2 (Ph *C*), 128.4 (d, $^3J_{PC}$ = 11.0 Hz, Ph *C*), 128.9 (d, $^2J_{PC}$ = 45.2 Hz, Ph *C*), 130.2 (Ph *C*), 130.9 (Ph *C*), 131.3 (d, $^4J_{PC}$ = 2.4 Hz, Ph *C*), 133.9 (Ph *C*), 134.5 (d, $^1J_{PC}$ = 11.0 Hz, Ph *C*), 193.1 (d, $^2J_{PC}$ = 3.2 Hz, N*C*N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.4. Crystals suitable for X-ray crystallography were obtained by vapor diffusion of diethyl ether into a DMF solution of the solid mixture.

Synthesis of *cis*-$PdCl_2(L^3)(PPh_3)$ (4). A mixture of $L^3H\cdot Cl$ (1.09 g, 3.82 mmol), KHMDS (0.76 g, 3.82 mmol), Pd(COD)Cl_2 (1.09 g, 3.82 mmol), and PPh_3 (1.00 g, 3.82 mmol) in DMF (10 mL) was stirred at room temperature for 1 day. The workup procedure was same as that for **2**. Yield: 0.892 g, 34%. Mp: 264−268 °C dec. Anal. Calcd for $C_{35}H_{31}Cl_2N_2PPd$: C, 61.11; H, 4.54; N, 4.54. Found: C, 61.12; H, 3.97; N, 4.53. ^1H NMR ($CDCl_3$): δ 4.50 (d, $^2J_{HH}$ = 14.1 Hz, 2H, PhCH_AH$_B$N), 5.68 (d, $^2J_{HH}$ = 14.1 Hz, 2H, PhCH$_A$$H_B$N), 6.37 (s, 2H, imi *H*), 7.14−7.31 (m, 16H, Ph *H*), 7.39−7.51 (m, 9H, Ph *H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 54.4 (*C*H_2), 121.4 (imi *C*), 128.4 (d, $^3J_{PC}$ = 10.9 Hz, Ph *C*), 128.5 (Ph *C*), 128.9 (d, $^2J_{PC}$ = 35.8 Hz, Ph *C*), 129.2 (Ph *C*), 129.9 (Ph *C*), 131.5 (d, $^4J_{PC}$ = 2.3 Hz, Ph *C*), 133.9 (Ph *C*), 134.0 (d, $^1J_{PC}$ = 11.1 Hz, Ph *C*), 160.5 (N*C*N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.4. Crystals suitable for X-ray crystallography were obtained by slow evaporation of a $CHCl_3$ solution of the solid mixture.

Synthesis of *cis*-$PdCl_2(L^3)(PCy_3)$ (5). A solution of **4** (0.572 g, 0.831 mmol) and PCy_3 (0.349 g, 1.25 mmol) in dichloromethane (15 mL) was stirred for 1 day at room temperature. The solvent was then removed completely under vacuum. The residue was washed with diethyl ether. The white powder that remained was

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Table 5. Crystallographic Data for 2−5

	2	**3**·C_3H_7NO	**4**	**5**·C_4H_8O
empirical formula	$C_{35}H_{33}Cl_2N_2PPd$	$C_{35}H_{33}Br_2N_2PPd\cdot C_3H_7NO$	$C_{35}H_{31}Cl_2N_2PPd$	$C_{35}H_{49}Cl_2N_2PPd\cdot C_4H_8O$
formula wt	689.90	851.92	687.89	742.09
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	15.7000(4)	11.5499(4)	15.6908(2)	16.8134(4)
b, Å	18.927(5)	16.3133(6)	11.1879(2)	16.3899(4)
c, Å	21.459(5)	19.1900(7)	17.9775(3)	27.0373(7)
α, deg	90	90	90	90
β, deg	90	96.7120(10)	96.9448(14)	103.143(2)
γ, deg	90	90	90	90
V, Å^3	6377(3)	3590.9(2)	3132.74(9)	7255.5(3)
T, K	150(2)	150(2)	100(2)	100(2)
Z	8	4	4	8
no. of unique data	8354	9214	6779	14 688
no. of params refined	371	417	370	811
R1[a] ($I > 2\sigma(I)$)	0.0622	0.0224	0.0228	0.0591
wR2[b] (all data)	0.1767	0.0594	0.0568	0.1566

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o^2)]^{1/2}$.

Table 6. Crystallographic Data for 6−9

	6	**7**	**8** (form I)	**8b** (form II)	**9**
empirical formula	$C_{22}H_{23}Cl_2N_3Pd$	$C_{22}H_{21}Cl_2N_3Pd$	$C_{34}H_{32}Cl_2N_4Pd$	$C_{34}H_{32}Cl_2N_4Pd$	$C_{20}H_{14}$
formula wt	506.73	504.72	673.94	673.94	254.31
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1/c$	$C2/c$
a, Å	19.941(12)	9.0547(7)	15.823(5)	7.5602(9)	23.555(15)
b, Å	10.116(6)	25.3595(18)	14.132(5)	33.767(4)	7.215(5)
c, Å	22.057(13)	9.7807(7)	15.342(5)	12.2325(15)	19.145(13)
α, deg	90	90	90	90	90
β, deg	93.222(11)	111.7780(10)	114.275(17)	95.880(3)	119.881(11)
γ, deg	90	90	90	90	90
V, Å^3	4442(4)	2085.6(3)	3127.2(17)	3106.3(6)	2821(3)
T, K	150(2)	150(2)	150(2)	150(2)	150(2)
Z	8	4	4	4	8
no. of unique data	11 720	4338	3413	5314	3754
no. of params refined	505	253	186	370	224
R1[a] ($I > 2\sigma(I)$)	0.0454	0.0219	0.0373	0.0627	0.0506
wR2[b] (all data)	0.1348	0.0572	0.1145	0.1876	0.1766

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o^2)]^{1/2}$.

then collected on a frit and dried under vacuum. Yield: 0.306 g, 52%. Mp: 241−243 °C dec. Anal. Calcd for $C_{35}H_{49}Cl_2N_2PPd$: C, 59.54; H, 6.99; N, 3.97. Found: C, 53.25; H, 6.83; N, 3.65. ^{1}H NMR ($CDCl_3$): δ 1.07−2.49 (m, 33H, Cy *H*), 5.03 (d, $^2J_{HH}$ = 13.9 Hz, 2H, PhCH_AH_BN), 6.14 (d, $^2J_{HH}$ = 13.9 Hz, 2H, PhCH_AH_BN), 7.22 (s, 2H, imi *H*), 7.24−7.35 (m, 6H, Ph *H*), 7.46−7.54 (m, 4H, Ph *H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 25.6 (Cy *C*), 26.8 (d, $^3J_{PC}$ = 11.0 Hz, Cy *C*), 29.5 (Cy *C*), 36.2 (d, $^1J_{PC}$ = 23.8 Hz, Cy *C*), 54.3 (CH_2), 122.5 (imi *C*), 128.4 (Ph *C*), 129.1 (Ph *C*), 135.4 (Ph *C*), 159.6 (N*C*N). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 48.6. Crystals suitable for X-ray crystallography were obtained by slow evaporation of a THF solution of the solid mixture.

Synthesis of *trans*-$PdCl_2(L^2)$(py) (6). A solution of $L^2H\cdot BF_4$ (0.152 g, 0.449 mmol) and $PdCl_2$(COD) (0.192 g, 0.674 mmol) in pyridine (20 mL) was heated at 130 °C for 12 h. After the mixture was cooled, the solvent was removed completely under vacuum. The residue was extracted with dichloromethane. The organic layer was washed twice with water. After drying with anhydrous $MgSO_4$, the solvent was removed completely under vacuum. The residue was washed with THF. After removal of the solvent under vacuum, the crude solid was purified by column chromatography with hexane−ethyl acetate (1:1) as eluent to give a yellow solid. Yield: 0.106 g, 47%. Mp: 204−206 °C. Anal. Calcd for $C_{22}H_{23}Cl_2N_3Pd$: C, 52.14; H, 4.57; N, 8.29. Found: C, 52.02; H, 4.51; N, 8.20. ^{1}H NMR ($CDCl_3$): δ 3.42 (s, 4H, NCH_2), 5.42 (PhCH_2), 7.27−7.39 (m, 8H, Ph *H*, py *H*), 7.56 (d, 4H, $^3J_{HH}$ = 6.9 Hz, Ph *H*), 7.73 (t, 1H, $^3J_{HH}$ = 5.7 Hz, py *H*), 8.96 (m, 2H, py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 47.6 (NCH_2), 54.5 (PhCH_2), 124.3 (py *C*), 128.0 (Ph *C*), 128.7 (2 overlapping signals, Ph *C*), 135.1 (Ph *C*), 138.0 (py *C*), 181.4 (N*C*N), 151.1 (py *C*). Crystals suitable for X-ray crystallography were obtained by vapor diffusion of diethyl ether into a pyridine solution of the solid mixture.

Synthesis of *trans*-$PdCl_2(L^3)$(py) (7). The procedure was same as that for **6**. A solution of $L^3H\cdot BF_4$ (1.50 g, 4.46 mmol) and $PdCl_2$(COD) (1.30 g, 4.46 mmol) in pyridine (20 mL) was used. A yellow solid was obtained. Yield: 0.529 g, 24%. Mp: 197−199 °C. Anal. Calcd for $C_{22}H_{21}Cl_2N_3Pd$: C, 52.35; H, 4.19; N, 8.32. Found: C, 52.39; H, 4.10; N, 8.43. ^{1}H NMR ($CDCl_3$): δ 5.89 (CH_2), 6.71 (imi *H*), 7.34−7.44 (m, 8H, Ph *H*, py *H*), 7.52−7.55 (m, 4H, Ph *H*), 7.77 (t, 1H, $^3J_{HH}$ = 9.0 Hz, py *H*), 9.01 (d, $^3J_{HH}$ = 6.0 Hz, 2H, py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 54.7 (CH_2), 121.7 (imi *C*), 124.4 (py *C*), 128.4 (Ph *C*), 128.9 (2 overlapping signals, Ph *C*), 135.3 (Ph *C*), 138.0 (py *C*), 149.9 (N*C*N), 151.2 (py *C*). Crystals suitable for X-ray crystallography were obtained by vapor diffusion of diethyl ether into a DMF solution of the solid mixture.

Synthesis of *cis*-$PdCl_2(L^3)_2$ (8). A solution of $L^3H\cdot Cl$ (2.38 g, 8.34 mmol), KO^{t}Bu (0.94 g, 8.34 mmol), and $PdCl_2$(COD) (1.20 g, 4.17 mmol) in CH_3CN (10 mL) was stirred at room temperature for 12 h. The workup procedure was same as that for **2**. The crude product was then purified by column chromatography using 1:1 acetone−hexane as eluent. A white solid was obtained. Yield: 0.478 g, 17%. Mp: 237−242 °C dec. Anal. Calcd for $C_{34}H_{32}Cl_2N_4Pd$: C, 60.59; H, 4.79; N, 8.31. Found: C, 60.28; H, 4.77; N, 8.09. ^{1}H NMR ($CDCl_3$): δ 5.25 (d, $^2J_{HH}$ = 14.5 Hz, 2H, PhCH_AH_BN), 5.96 (d, $^2J_{HH}$ = 14.5 Hz, 2H, PhCH_AH_BN), 6.54 (s, 2H, imi *H*), 7.11−7.14 (m, 8H, Ph *H*),

7.24−7.27 (m, 12H, Ph *H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 54.6 (CH_2), 121.6 (imi *C*), 128.3 (Ph *C*), 128.5 (Ph *C*), 129.0 (Ph *C*), 134.7 (Ph *C*), 161.3 (N*C*N). Crystals of forms I and II suitable for X-ray crystallography were obtained by vapor diffusion of diethyl ether into a methanol solution of the solid mixture. Forms I and II are visually indistinguishable.

Catalytic Direct Arylation. In a typical reaction, a mixture of aryl halides (0.25 mmol), diphenylacetylene (0.25 mmol), NaOAc (0.50 mmol), *n*-Bu_4NCl (0.25 mmol), and palladium(II) precatalyst (5 mol %) in 5 mL of DMF was stirred at 120 °C for the periods of time indicated in Tables 3 and 4. In the standard workup, the reaction mixture was cooled to ambient temperature, diluted with diethyl ether, washed with brine, and dried with anhydrous $MgSO_4$. The solution was then filtered. The solvent and any volatiles were removed completely under high vacuum to give a crude product which was purified by column chromatography. Crystals of 9-benzylidene-9*H*-fluorene (**9**) suitable for X-ray diffraction study were obtained by slow evaporation of a hexane solution containing the compound.

X-ray Data Collection. Typically, the crystals were removed from the vial with a small amount of mother liquor and immediately coated with Paratone-N oil on a glass slide. A suitable crystal was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.710 73 Å) at 150(2) K. The data were corrected for Lorentz and polarization effects using the Bruker SAINT software, and an absorption correction was performed using the SADABS program.[52]

Solution and Structure Refinements. All the structures were solved by direct methods and refined by full-matrix least-squares methods against F^2 with the SHELXTL software package.[53] All non-H atoms were refined anisotropically; H atoms were fixed at calculated positions and refined with the use of a riding model. Crystallographic data are given in Tables 5 and 6. The file numbers CCDC-747061 (**2**), CCDC-747062 (**3**·C_3H_7NO), CCDC-747063 (**4**), CCDC-747064 (**5**·C_4H_8O), CCDC-747065 (**6**), CCDC-747066 (**7**), CCDC-747067 (**8a**), CCDC-747068 (**8b**), and CCDC-747069 (**9**) contain the supplementary crystallographic data for this paper. These data can obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. We used the three-parameter hybrid of exact exchange and Becke's exchange energy functional,[54] plus Lee, Yang, and Parr's gradient-corrected correlation energy functional (B3LYP).[55] The 6-31G(d) basis sets for H, C, N, P, and Cl were used. For Pd we used the LANL2DZ effective core potential plus basis functions.[56] The solvation free energies were computed using the polarizable continuum model (PCM).[57] Within the PCM model, we incorporated nitromethane as our solvent. The Gaussian03 suite of programs was used in our study.[58]

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Supporting Information Available: CIF files giving full crystallographic data for all the structures and figures giving molecular structures of **5** and **6** (the other independent molecules) and optimized structures of cis and trans isomers of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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