Cationic Arylpalladium Complexes with Chelating Diamine Ligands, [PdAr(N−N)(solv)]BF_4 (N−N = *N,N,N′,N′*-tetramethylethylenediamine, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine). Preparation, Intermolecular Coupling of the Aryl Ligands, and Insertion of Alkyne and Allene into the Pd−C Bond

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Iodo(aryl)palladium complexes, [PdI{$C_6H_3(CF_3)_2$-3,5}(N−N)] (N−N = tmeda, bpy, 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy)), react with $AgBF_4$ in CH_3CN, acetone, and THF to yield stable cationic arylpalladium complexes [Pd{$C_6H_3(CF_3)_2$-3,5}(N−N)(solv)]BF_4. A similar reaction of $AgBF_4$ with [PdI($C_6H_3Me_2$-3,5)(bpy)] in CH_3CN gives [Pd($C_6H_3Me_2$-3,5)(bpy)-(CH_3CN)]BF_4. The complex does not change its NMR spectrum for 1 h at room temperature in CD_3CN but undergoes decomposition upon dissolution in acetone to release 3,3′,5,5′-tetramethylbiphenyl. Addition of $AgBF_4$ to acetone or THF solutions of [PdI(Ar)(bpy)] (Ar = Ph, $C_6H_3Me_2$-3,5) and of [PdI(Ar)(Me_2bpy)] (Ar = C_6H_4OMe-4, $C_6H_3Me_2$-3,5) does not lead to isolation of the cationic arylpalladium complexes and causes intermolecular coupling of the aryl ligands to yield the corresponding biaryls. The reaction of $AgBF_4$ with [PdI($C_6H_3Me_2$-3,5)(bpy)] in the presence of an excess amount of dimethyl acetylenedicarboxylate (DMAD) in CH_3CN gives [Pd(CZ═CZ−CZ═CZ−$C_6H_3Me_2$-3,5)(bpy)(CH_3CN)]BF_4 (Z = COOMe) via insertion of two acetylene molecules into the Pd−aryl bond. A similar reaction in acetone or THF causes insertion of three DMAD molecules into the Pd−aryl bond and cyclization of the formed Pd−$(CZ═CZ)_3$−Ar group to give the product containing a cyclopentadiene structure in the ligand. [PdI(CZ═CZ−$C_6H_3Me_2$-3,5)(bpy)] reacts with $AgBF_4$ in CH_3CN to form a cationic complex, [Pd(CZ═CZ−$C_6H_3Me_2$-3,5)(bpy)(CH_3CN)]BF_4. A series of cationic Pd complexes, formed through insertion of one, two, and three alkyne molecules into the Pd−aryl bond, are characterized by X-ray crystallography or NMR spectroscopy. Phenylallene reacts with [PdI($C_6H_3Me_2$-3,5)(bpy)] in the presence of $AgBF_4$ to give [Pd{η^3-CH_2C-($C_6H_3Me_2$-3,5)CHPh}(bpy)]BF_4 via insertion of the C═C double bond of the allene into the Pd−C bond of the cationic arylpalladium complex. The π-allylpalladium complex crystallizes exclusively in a form with a syn-oriented phenyl substituent but exists in solution as a mixture of the isomers with a syn or anti phenyl substituent.

Introduction

Palladium complex catalyzed carbonylation of aryl halides[1] and arylation of alkenes[2] involve insertion of small molecules such as CO and ethylene into the Pd−aryl bond as a crucial step. A number of mechanistic studies of such reactions have been carried out. Scheme 1(i) illustrates the associative insertion of CO into the Pd−C bond of [PdBr(Ar)(PR_3)$_2$], which is generally accepted as a plausible pathway in the Pd-catalyzed carbonylation of bromoarene in the presence of amine and alcohol to give carboxylic amides and esters.[3] The five-coordinate intermediates with a trigonal bipyramidal structure have been proposed based on results of kinetic studies of the overall carbonylation reactions. A detailed NMR study of the reaction of CO or CF_2═CF_2 with [PtMe(OMe)(dppe)] revealed the formation of the five-coordinate complex shown in Chart 1 at low temperature and the migratory insertion of CO or

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Scheme 1 . Two Pathways Proposed for Insertion of CO into the Pd−C Bond

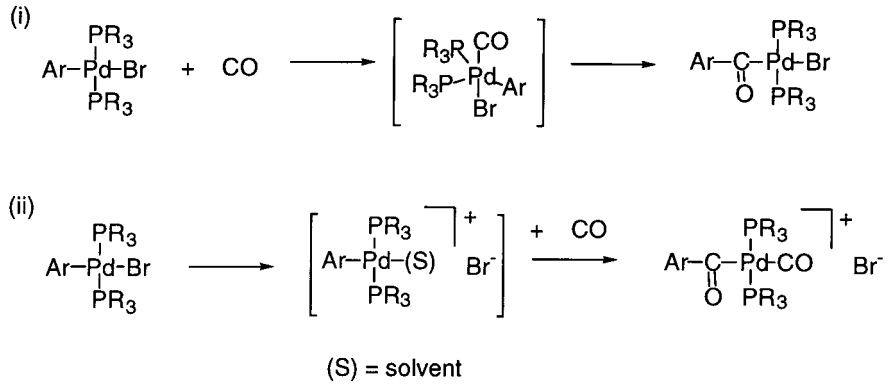


Chart 1

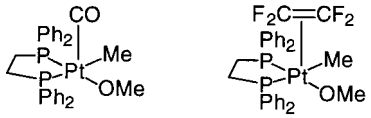
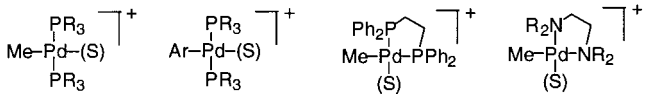


Chart 2



$CF_2{=}CF_2$ into the Pt−OMe bond on warming the solution of the complexes to room temperature.[4] Recently, several research groups suggested an alternative pathway for CO and alkene insertion into the Pd−C bond shown in Scheme 1(ii) based on the observation that $[PdR(solv)(L)_2]^+$ type complexes undergo insertion of the small molecules more easily than neutral $[PdR(X)(L)_2]$ (R = Me, Ph, X = Cl, Br, etc).[5,6] For example, *trans*-$[PdPh(solv)(PMe_3)_2]BF_4$ reacts with methyl acrylate at 5 °C to give methyl 2-phenylacrylate via insertion of the C=C double bond into the Pd−Ph bond followed by β-hydrogen elimination of the resulting alkylpalladium intermediate, whereas a similar reaction of *trans*-$[PdCl(Ph)(PMe_3)_2]$ requires heating at 70 °C.[6]

Structures of typical cationic organopalladium complexes with auxiliary phosphine or amine ligands are shown in Chart 2. Cationic alkyl and arylpalladium complexes with two monodentate phosphine ligands tend to have a geometry with two trans phosphine ligands but readily react with CO to cause insertion into the Pd−C bond. Since CO is initially coordinated at the trans position of the methyl or phenyl ligand, the reaction probably involves isomerization of intermediate *trans*-$[PdR'(CO)(PR_3)_2]^+$ into the cis isomer prior to the CO insertion (Scheme 2(i)). The cationic methylpalladium complexes with chelating diphosphine or diamine ligands undergo smooth migratory insertion of CO into the Pd−Me bond with keeping the cis geometry of the complexes throughout the reaction (Scheme 2(ii)). Thus, these complexes with the cis structure imposed by the chelating ligand have attracted recent attention not only as the reaction intermediates of Pd-catalyzed carbonylation and related reactions but also as catalysts of synthetic organic reactions and polymer synthesis including insertion of CO and/or alkenes into the Pd−C bond. Polymerization of alkenes[7] and alternating copolymerization of alkene and CO[5,8−14] catalyzed by cationic methylpalladium complexes have attracted recent attention. The living polymerization found in these studies afforded the polymers with regulated structures and

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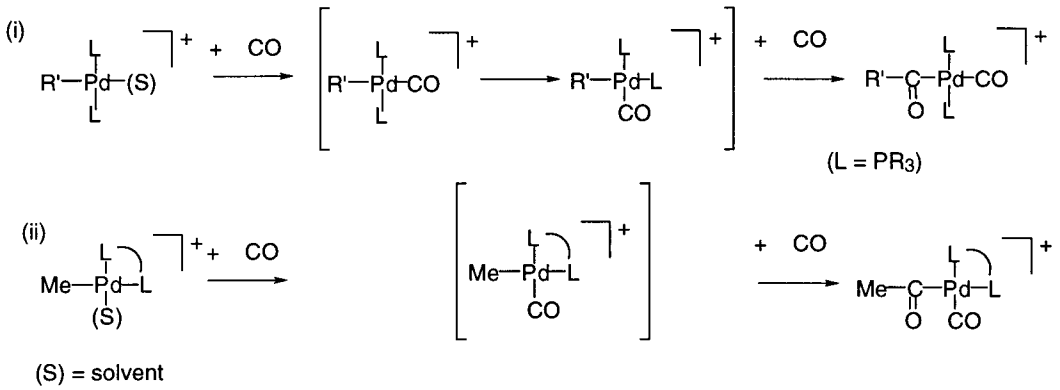
Scheme 2 . Insertion of CO into the Pd−C Bond of *trans*- and *cis*-[PdR′(L)$_2$(S)]+ Complexes

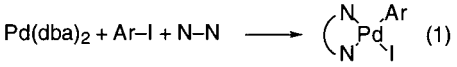


molecular weights. Although analogous cationic arylpalladium complexes with chelating ligands would also cause alkene or CO coordination and their smooth migratory insertion into the Pd−C bond, there have been only a few reports on preparation and detailed chemical properties of such cationic arylpalladium complexes with cis coordination.[15,16] De Felice et al. briefly reported preparation of [PdPh(bpy)(CH_3CN)]BF_4 and its reaction with unsaturated molecules.[15]

In this paper, we report the isolation of stable cationic palladium complexes with an aryl group containing CF_3 substituents and chelating diamine or bipyridine ligands. The complexes with nonfluorinated aryl groups are unstable in acetone or THF and tend to undergo intermolecular coupling of the aryl ligands in the solutions. This unique reaction of the cationic cis arylpalladium complexes and insertion of alkynes and allenes into the Pd−aryl bond are described.

Results

Cationic Arylpalladium Complexes with Chelating Diamine or Bipyridine Ligands. Iodo(aryl)palladium(II) complexes [PdI(Ar)(N−N)] (N−N = tmeda, bpy, Me_2bpy) were prepared by the oxidative addition of iodoarene to Pd(dba)$_2$ (dba = dibenzylideneacetone) in the presence of a bidentate ligand according to a previously described method (eq 1).[17,18]



	Ar	N–N
1a	Ph	tmeda
1b	C_6H_4OMe-4	tmeda
1c	$C_6H_3(CF_3)_2$-3,5	tmeda
2a	Ph	bpy
2c	$C_6H_3(CF_3)_2$-3,5	bpy
2d	$C_6H_3Me_2$-3,5	bpy
3b	C_6H_4OMe-4	Me_2bpy
3c	$C_6H_3(CF_3)_2$-3,5	Me_2bpy
3d	$C_6H_3Me_2$-3,5	Me_2bpy
3e	$C_6H_4CF_3$-4	Me_2bpy

The new complexes, **1c**, **2c**, **2d**, and **3b**−**3e**, were characterized by NMR spectroscopy and/or X-ray crystallography. Figure 1 displays the molecular structures of **1c** and **2c** determined by X-ray crystallography. Both

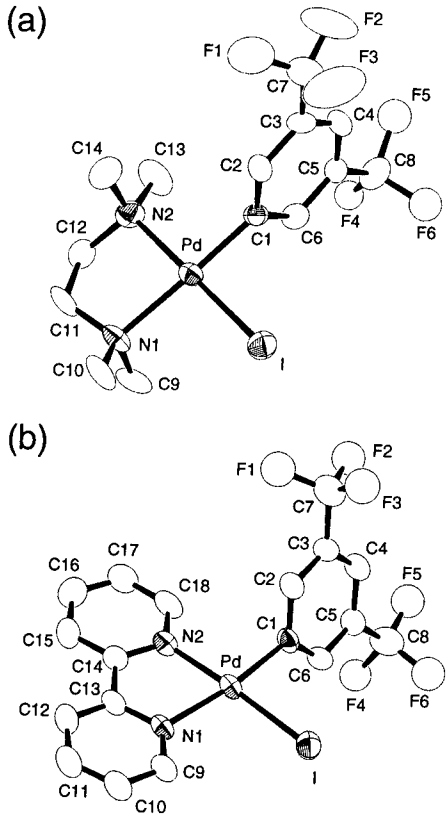


Figure 1. ORTEP drawing of **1c** (a) and **2c** (b) (50% probability). Selected bond lengths (Å) and angles (deg) for **1c**: Pd−I 2.583(1), Pd−N1 2.205(8), Pd−N2 2.134(9), Pd−C1 1.98(1), I−Pd−N1 96.4(3), I−Pd−N2 177.1(3), I−Pd−C1 88.4(3), N1−Pd−N2 83.5(4), N1−Pd−C1 172.8(4), N2−Pd−C1 91.9(4). Selected bond lengths (Å) and angles (deg) for **2c**: Pd−I 2.5737(7), Pd−N1 2.133(4), Pd−N2 2.082(5), Pd−C1 1.990(5), I−Pd−N1 98.6(1), I−Pd−N2 176.7(1), I−Pd−C1 88.5(2), N1−Pd−N2 78.6(2), N1−Pd−C1 172.3-(2), N2−Pd−C1 94.4(2).

of the square-planar complexes have Pd−C, Pd−N, and Pd−I bonds whose lengths are similar to those of [PdI-

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(16) Recently, the reaction of [Pd(dppp)(NCPh)$_2$](BF_4)$_2$ (dppp = 1,3-bis(diphenylphosphino)propane) with B(C_6F_5)$_3$ was reported to give [Pd(dppp)(C_6F_5)(NCPh)]BF_4. Isolation of the pure complex was not feasible, although the complex obtained in situ catalyzes alternating copolymerization of alkene and CO to give polyketones. See: Barlow, G. K.; Boyle, J. D.; Cooley, N. A.; Ghaffar, T.; Wass, D. F. *Organometallics* **2000**, *19*, 1470.

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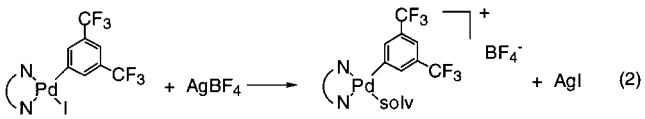
Table 1. Yield and Analytical Data of the Complexes

	yield (%)	elemental analysis (%)[a] C	H	N	I
1c	51	29.64 (29.89)	3.19 (3.40)	4.96 (4.98)	22.33 (22.56)
2c	59	35.93 (35.88)	1.70 (1.84)	4.66 (4.65)	21.64 (21.06)
3b	52	43.32 (43.49)	3.89 (3.65)	5.32 (5.34)	24.75 (24.19)
3c	66	38.21 (38.09)	2.56 (2.40)	4.57 (4.44)	19.73 (20.12)
3d	62	45.95 (45.96)	4.23 (4.05)	5.23 (5.36)	24.02 (24.28)
3e	70	40.56 (40.56)	2.88 (2.87)	4.96 (4.98)	22.06 (22.55)
4c-CH_3CN	74	33.70 (34.10)	3.86 (3.93)	7.58 (7.46)	
5c-CH_3CN	75	39.55 (39.80)	2.35 (2.34)	6.67 (6.96)	
5d-CH_3CN	96	48.26 (48.47)	4.32 (4.07)	8.43 (8.48)	
6c-CH_3CN	51	42.23 (41.84)	3.14 (2.87)	7.28 (6.65)	
9-CH_3CN	94	48.88 (48.97)	4.00 (4.11)	6.64 (6.59)	
10-CH_3CN	84	48.98 (49.29)	4.33 (4.14)	5.68 (5.39)	
11	46	56.63 (56.82)	4.52 (4.42)	4.67 (4.91)	

[a] Calculated values are in parentheses.

(Ph)(tmeda)], [PdI(C_6H_4Me-4)(tmeda)], and [PdI(Ph)(bpy)].[17,18] The distance between $H_{6'}$, bonded to C9, and I (2.982 Å) for **2c** is shorter than the sum of the van der Waals radii,[19] which implies the presence of an electrostatic interaction. Such H···I interaction has been found also in several Pd(II) and Pt(II) complexes.[20] Tables 1−3 summarize the yields and analytical values, as well as the ^{1}H and ^{13}C{^{1}H} NMR data of the complexes. The ^{1}H NMR spectrum of **2c** in $CDCl_3$ gives rise to the signals of the para and ortho hydrogens of 3,5-bis(trifluoromethyl)phenyl ligand at δ 7.42 and 7.88, which are at a lower magnetic field than those of **2d** (δ 6.52 and 6.99 in $CDCl_3$) caused by the presence of electron-withdrawing CF_3 groups. Figure 2a shows the spectrum of **2c** in CD_3CN, which exhibits the above signals at δ 7.53 and 7.93, respectively. The signals at δ 7.44, 7.64, 8.13, and 8.15 are assigned to the bpy hydrogens H_5, $H_{5'}$, H_4, and $H_{4'}$ (Chart 3), respectively, while doublets at δ 7.49 and 9.51 are due to H_6 and $H_{6'}$ hydrogens. A much lower magnetic field position of $H_{6'}$ than H_6 can be ascribed to the electrostatic interaction between $H_{6'}$ and I mentioned above. The signals of H_3 and $H_{3'}$ hydrogens are observed at δ 8.31 with severe overlapping. All these assignments are based on their coupling patterns and the ^{1}H−^{1}H COSY spectrum.

The iodo(aryl)palladium(II) complexes are stable in air and do not decompose below 50 °C in acetone. Addition of $AgBF_4$ to the Pd complexes with a 3,5-bis(trifluoromethyl)phenyl ligand, **1c**, **2c**, and **3c**, in polar solvents (CH_3CN, acetone, and THF) converts them into the cationic arylpalladium complexes, [Pd{$C_6H_3(CF_3)_2$-3,5}(N−N)(solv)]$^+BF_4^-$, accompanied by separation of AgI from the solution (eq 2).



(2)

1c: N–N = tmeda
2c: N–N = bpy
3c: N–N = Me_2bpy

	N–N	solvent
4c-CH_3CN	tmeda	CH_3CN
4c-acetone	tmeda	acetone
5c-CH_3CN	bpy	CH_3CN
5c-acetone	bpy	acetone
5c-THF	bpy	THF
6c-CH_3CN	Me_2bpy	CH_3CN

Acetonitrile-coordinated complexes **4c**-CH_3CN, **5c**-CH_3CN, and **6c**-CH_3CN are isolated as off-white solids in 51−75% yields and characterized by NMR spectroscopy and elemental analyses (Tables 1−3). The NMR spectra of the complexes do not change for 24 h or longer at room temperature. Figure 2b displays the ^{1}H NMR spectrum of **5c**-CH_3CN in CD_3CN. The singlets at δ 7.72 and 7.94 are assigned to the para and ortho phenyl protons. The former signal is shifted to a lower magnetic field by approximately 0.2 ppm from the corresponding neutral iodo(aryl)palladium complex **2c**. Most of the bipyridine hydrogen signals are observed at positions similar to those of **2c**; the multiplets due to H_5, $H_{5'}$, H_4, and $H_{4'}$ are positioned at δ 7.41, 7.72, 8.16, and 8.20, and a doublet of H_6 and overlapped signals of H_3 and $H_{3'}$ at δ 7.56 and 8.28, respectively. The $H_{6'}$ signal appears at a significantly higher magnetic field (δ 8.55) than **2c** (δ 9.51), suggesting that the low magnetic field position of **2c** is related to the H···I electrostatic interaction in solution. The position of the signal of acetonitrile (δ 1.95) is almost the same as the free solvent, which is due to a rapid exchange between the coordinated and uncoordinated solvents and a much smaller amount of coordinated CH_3CN than coordinated CD_3CN.[21]

The reactions of $AgBF_4$ with **1c** in acetone and with **2c** in acetone and THF also cause AgI formation. The ^{1}H NMR spectra of the resulting solutions indicate conversion of the complexes into the corresponding cationic arylpalladium complexes, **4c**-acetone, **5c**-acetone, and **5c**-THF. Addition of hexane to the solutions of the two latter complexes causes separation of the complexes as off-white solids. The ^{1}H NMR spectra of the solid products, however, show the signal of the coordinated solvents (acetone or THF) in a weaker peak intensity than expected from the formula (60% and 90% for **5c**-acetone and **5c**-THF, respectively). These NMR spectra as well as insufficient analytical results of the complexes seem to suggest partial conversion of the complexes into BF_4-coordinated Pd complex [Pd{$C_6H_3(CF_3)_2$-3,5}(N−N)(BF_4)] during the above procedure to obtain the products as a solid.[22]

Although cationic palladium complexes with nonfluorinated aryl ligands show a much lower stability than the complexes with a 3,5-bis(trifluoromethyl)phenyl ligand, it is possible to isolate the complexes in a CH_3CN

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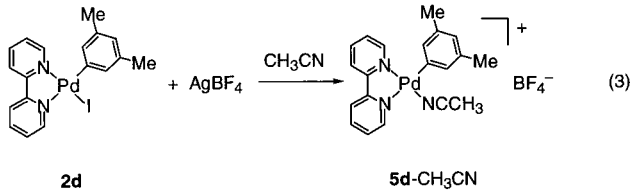
(21) The ^{1}H NMR signals of free and coordinated CH_3CN hydrogens show differences in the chemical shifts (by approximately 0.3 ppm) when the exchange of the molecule is slower than the NMR time scale. See: Yagyu, T.; Aizawa, S.; Hatano, K.; Funahashi, S. *Bull. Chem. Soc. Jpn*. **1996**, *69*, 1961.

Table 2. ^{1}H NMR Data of the Complexes[a]

	Ar			tmeda	bpy or Me_2bpy [b]					
	ortho	meta	para	*N*-CH_3 $-CH_2-$	H_3 $H_{3'}$	H_4 $H_{4'}$	H_5 $H_{5'}$	H_6 $H_{6'}$	4-CH_3 4′-CH_3	solvent
1c	7.71(s)		7.23(s)	2.21(s) 2.63(s) 2.49(m) 2.66(m)						
2c	7.88(s)		7.42(s)		8.1*	8.04(m)	7.39(m)	7.47(d) (5.4 Hz)		
					8.1*	8.04(m)	7.54(m)	9.63(d) (4.4 Hz)		
2c[c]	7.93(s)		7.53(s)		8.31*	8.13(m)	7.44(m)	7.49(d) (5.9 Hz)		
					8.31*	8.15(m)	7.64(m)	9.51(d) (5.4 Hz)		
2d[d]	6.99(s)		6.52(s)		8.06*	7.96(m)	7.32(m)	7.65(d) (5.9 Hz)		
					8.06*	7.96(m)	7.47(m)	9.56(d) (3.9 Hz)		
3b[e]	7.23*	6.72(d) (8.3 Hz)			7.83(s)		7.09(d) (5.9 Hz)	7.53(d) (5.4 Hz)	2.45(s)	
					7.83(s)		7.27(d) (5.4 Hz)	9.62(d) (5.4 Hz)	2.50(s)	
3c	7.88(s)		7.41(s)		7.9*		7.3(m)	7.16(d) (5.4 Hz)	2.47(s)	
					7.9*		7.3(m)	9.43(d) (5.9 Hz)	2.53(s)	
3d[f]	7.00(s)		6.52(s)		7.82(s)		7.11(d) (6.4 Hz)	7.52(d) (5.9 Hz)	2.44(s)	
					7.82(s)		7.26(d) (6.4 Hz)	9.40(d) (5.4 Hz)	2.50(s)	
3e	7.55(d) (8.3 Hz)	7.25*			7.85(s)		7.14(d) (4.9 Hz)	7.42(d) (5.4 Hz)	2.46(s)	
					7.83(s)		7.31(d) (5.4 Hz)	9.44(d) (5.4 Hz)	2.52(s)	
4c-CH_3CN[c]	7.94(s)		7.59(s)	2.41(s) 2.66(s) 2.69(m) 2.87(m)						1.95(s)
4c-acetone[g]	8.05(s)		7.47(s)	2.63(s) 2.65(s) 2.86(m) 3.08(m)						2.07(s)
5c-CH_3CN[c]	7.94(s)		7.72(s)		8.28*	8.16(m)	7.41(m)	7.56(d) (5.9 Hz)		1.95(s)
					8.28*	8.20(m)	7.72(m)	8.55(d) (4.9 Hz)		
5c-acetone[g]	8.11(s)		7.67(s)		8.66*	8.37(m)	7.64(m)	7.97(d) (5.5 Hz)		2.08(s)
					8.66*	8.39(m)	7.87(m)	8.48(d) (4.9 Hz)		
5c-THF[h]	8.13(s)		7.68(s)		8.62*	8.28(m)	7.48(m)	7.73(d) (5.4 Hz)		1.78(m)
					8.58*	8.26(m)	7.79(m)	8.6*		3.62(m)
5d-CH_3CN[c]	6.95(s)		6.75(s)		8.30*	8.14(m)	7.43(m)	7.84(d) (4.9 Hz)		1.95(s)
					8.32*	8.22(m)	7.73(m)	8.62(d) (4.9 Hz)		
6c-CH_3CN[c]	7.99(s)		7.73(s)		8.19(s)		7.24(d) (5.9 Hz)	7.47(d) (5.9 Hz)	2.49(s)	1.95(s)
					8.21(s)		7.57(d) (5.4 Hz)	8.47(d) (5.4 Hz)	2.57(s)	

[a] 400 MHz at 25 °C. In $CDCl_3$ unless otherwise stated. [b] Positions and splitting pattern of the peaks with asterisks are not determined precisely due to severe overlapping with other signals. [c] In CD_3CN. [d] 2.19 (s, *m*-CH_3). [e] 3.76 (s, *p*-OCH_3). [f] 2.20 (s, *m*-CH_3). [g] In acetone-d_6. [h] In THF-d_8.

solvated form. Addition of $AgBF_4$ to a CH_3CN solution of **2d** causes a change in the ^{1}H NMR signals, suggesting the formation of the cationic arylpalladium complex $[Pd(C_6H_3Me_2\text{-}3,5)(bpy)(CH_3CN)]^+BF_4^-$ (**5d**-CH_3CN) (eq 3).



2d **5d**-CH_3CN (3)

The complex is stable at room temperature in the solid state. The ^{1}H NMR spectrum of a CD_3CN solution of **5d**-CH_3CN does not change for 1 h at room temperature, but it appears to gradually decompose on standing the

Table 3. $^{13}C\{^1H\}$ NMR Data for Complexes[a]

	Ar				tmeda	bpy or Me_2bpy						
	ortho	meta	para	ipso	others	*N*-Me $-CH_2-$	C_2 $C_{2'}$	C_3 $C_{3'}$	C_4 $C_{4'}$	C_5 $C_{5'}$	C_6 $C_{6'}$	4-CH_3 4′-CH_3	others[b]
1c	136.2	127.7(q) ($^2J_{CF}$=32 Hz)	116.4(m)	148.4	123.6(q) (CF_3) ($^1J_{CF}$=273 Hz)	49.8, 49.9 58.4, 62.1							
2c	136.6(m)	128.7(q) ($^2J_{CF}$=32 Hz)	117.4(m)	148.1	123.7(q) (CF_3) ($^1J_{CF}$=275 Hz)		153.8 155.9	121.8 122.3	139.0 139.2	126.8 127.1	149.6 153.4		
2d	133.9	136.1	125.4	145.5	21.3 (CH_3)		153.6 155.5	121.6 121.9	138.5* 138.5*	126.3 126.5	150.3 152.7		150.3, 150.4, 153.5, 155.5
3b	136.4	113.6	133.7		55.2 (OCH_3)			122.2 122.5		127.0 127.3	149.7 152.3	21.6 21.6	156.6
3c	136.7(m)	128.5(q) ($^2J_{CF}$=32 Hz)	117.2(m)		123.8 (q, CF_3) ($^1J_{CF}$=273 Hz)			122.4 122.8		127.4 127.7	149.0 152.8	21.6 21.6	148.6, 150.9, 151.3, 153.6 155.8
4c-CH_3CN[c]	135.5(m)	129.6(q) ($^2J_{CF}$=32 Hz)	119.1(m)	152.1	124.9(q) (CF_3) ($^1J_{CF}$=272 Hz)	48.9, 51.9 59.0, 64.8							
5c-CH_3CN[c]	135.4(m)	130.3(q) ($^2J_{CF}$=32 Hz)	119.9(m)		124.7(q) (CF_3) ($^1J_{CF}$=272 Hz)			124.3 125.0	142.5 142.6	128.7 129.0	153.0 150.8		151.2, 154.0, 157.8
5c-acetone[d]	135.3(m)	129.7(q) ($^2J_{CF}$=32 Hz)	119.4(m)		124.6(q) (CF_3) ($^1J_{CF}$=272 Hz)			124.3 125.2	142.3 142.3	128.7 128.7	153.8 149.5		152.3, 154.2, 158.0
6c-CH_3CN[c]	135.5(m)	130.2(q) ($^2J_{CF}$=32 Hz)	119.8(m)		124.8(q) (CF_3) ($^1J_{CF}$=272 Hz)			125.5 124.9		129.0 129.2	152.3 149.9	21.8 21.5	151.7, 154.2 155.1, 155.3, 157.7

[a] 100 MHz at room temperature in $CDCl_3$ unless otherwise stated. [b] Aromtic carbons which are not assigned. [c] In CD_3CN. [d] In acetone-d_6.

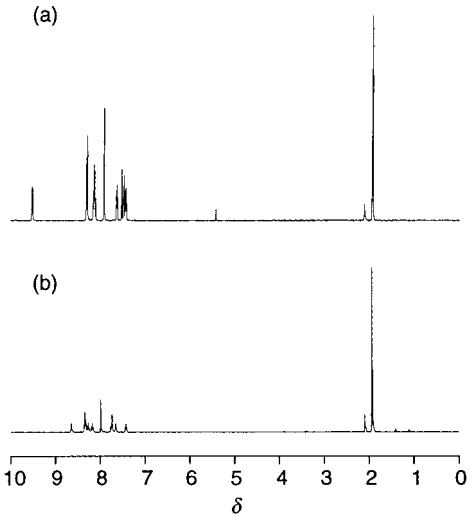
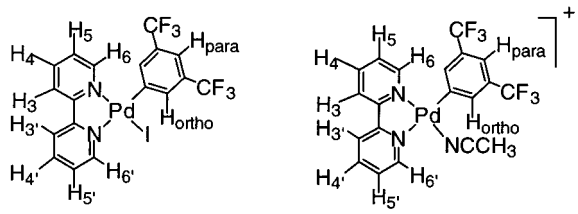


Figure 2. ^1H NMR spectra of (a) **2c** and (b) **5c**-CH_3CN in CD_3CN (400 MHz).

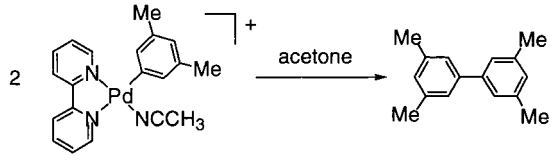
Chart 3



2c **5c**-CH_3CN

Designation of hydrogens in the NMR spectra.
H_n and $H_{n'}$ (n: 3-6) may be reverse

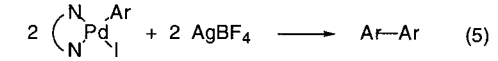
solution for a long period. Dissolution of **5d**-CH_3CN in acetone causes rapid decomposition accompanied by the release of 3,3′,5,5′-tetramethylbiphenyl in a 25% yield as shown in eq 4.



(4)

5d-CH_3CN

To obtain further scope and insight into the intermolecular coupling of the aryl ligands, the reactions of $AgBF_4$ with several iodo(aryl)palladium complexes were carried out. As shown in eq 5, the complexes containing bpy or Me_2bpy ligands, **2a**, **2d**, **3b**, and **3d**, react with $AgBF_4$ in acetone or THF to give the corresponding biaryls at room temperature. Characterization of the Pd-containing products formed in the reaction was not successful.



(5)

	Ar	N–N
2a	Ph	bpy
2d	$C_6H_3Me_2$-3,5	bpy
3b	C_6H_4OMe-4	Me_2bpy
3d	$C_6H_3Me_2$-3,5	Me_2bpy

Table 4. Yields of Biaryl in the Reaction of $AgBF_4$ with Arylpalladium Complexes[a]

		yields of biaryl (%)			
complex	solvent	1 h	6 h	24 h	
1a	CH_3CN				0 (6 d)
1a	acetone		0		
1b	CH_3CN				0 (5 d)
1c	CH_3CN				0 (5 d)
1c	acetone				0 (4 d)
2a	CH_3CN				0 (10 d)
2a	acetone	55	68	63	
2a	THF	3.9	28 (4 h)	83	
2d	acetone	87	95	96	
3b	acetone	56			
3c	acetone				0 (7 d)
3c	THF				0 (5 d)
3d	acetone	79			
3e	acetone				0 (2 d, at 50 °C)

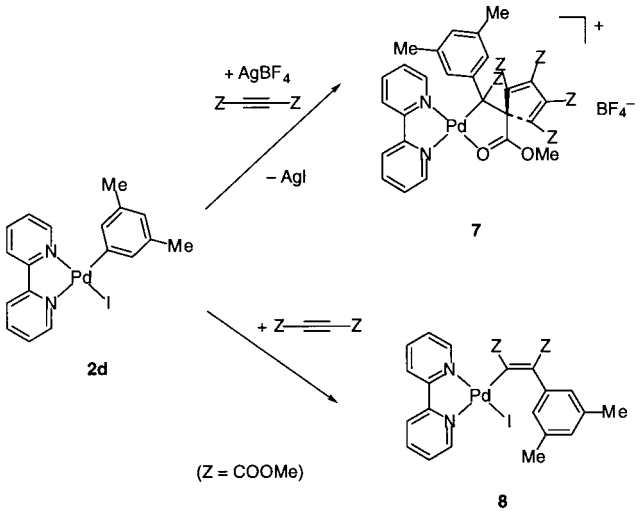
[a] Reactions were carried out at room temperature unless otherwise stated.

Table 4 summarizes the yields of the products and their variation depending on the kind of chelating ligand, aryl ligand, and solvent. Addition of $AgBF_4$ to acetone and THF solutions of **2a** gives biphenyl in 63% and 83% yields, respectively, after 24 h, whereas a similar reaction in CH_3CN does not give the coupling product at all. Complexes **2d** and **3d** with a 3,5-dimethylphenyl ligand react readily with $AgBF_4$ to form 3,3′,5,5′-tetramethylbiphenyl in 87% and 79% yields, respectively, after 1 h in acetone. The biaryl-forming reaction 5 takes place via the initial formation of a cationic intermediate, $[PdAr(N-N)(solv)]^+$, and subsequent intermolecular coupling of the aryl ligands. The stepwise pathway is demonstrated in reactions 3 and 4, which lead to the conversion of **2d** to its cationic derivative, **5d**-CH_3CN, and release of 3,3′,5,5′-tetramethylbiphenyl. The latter reaction involves an initial exchange of the coordinated CH_3CN with acetone to give $[Pd(C_6H_3Me_2\text{-}3,5)(bpy)(acetone)]^+$ followed by the bimolecular coupling of the aryl ligands.

Tmeda-coordinated complexes, **1a** and **1c**, react with $AgBF_4$ in acetone under similar conditions, probably giving the corresponding cationic arylpalladium complexes, but they do not produce the coupling products. Complexes **3c** and **3e** with CF_3 substituents on the aryl ligand do not give the biaryl even after the reaction with $AgBF_4$ for several days. CF_3 groups of the aryl ligand stabilize the Pd−aryl bond and prevent the aryl ligand transfer and/or their coupling reaction.

Insertion of Alkyne into the Pd−C Bond of Arylpalladium Complexes. Single and multiple insertion of alkynes into the Pd−C bond affords various organopalladium complexes depending on the alkyne and the supporting ligand bonded to the metal center; these have been studied in detail since the 1970s.[23] Maitlis reported insertion of three alkyne molecules into the Pd−C or Pd−Cl bond followed by cyclization of the resulting linear alkyne trimer bonded to the Pd center.[24] Clark et al. compared the reactions of alkynes with methylpalladium complexes, [PdCl(Me)(dppe)], $[Pd(NO_3)(Me)(dppe)]$, and $[PdMe(thf)(dppe)]^+$, and found more facile insertion of the alkyne into the Pd−Me bond of the cationic complex than that of the neutral ones having the same diphosphine ligand.[25] More recent studies by several research groups established the reactions involving single and multiple insertion of alkyne molecules into the Pd−C bond.[26−28] Recently, we reported that dimethyl acetylenedicarboxylate (DMAD) reacts with **2d** in the presence of $AgBF_4$ in acetone or THF, causing the insertion of three DMAD molecules into the Pd−C bond, followed by the addition of the Pd−C bond to a C=C double bond (Scheme 3).[29] Maitlis, Pfeffer, Vicente, and their respective co-workers also found that similar Pd complexes promote cyclotrimerization of alkynes to give the spirocyclic complexes.[24,26,27] The reaction of DMAD with **2d** takes place much more slowly in the absence of $AgBF_4$ to give the product $PdI(CZ{=}CZ{-}C_6H_3Me_2\text{-}3,5)(bpy)$ (**8**) via the single insertion of DMAD into the Pd−C bond, as reported previously.[29] Figure 3 shows the molecular structure of **8** determined by X-ray crystallography. The distances between $H_{6'}$ and I (2.917 and 2.955 Å) imply an electrostatic interaction similar to that for **2c**. Neither **7** nor **8** undergoes further insertion of DMAD into the Pd−C bond at room temperature. In this study, several reactions were conducted in order to obtain more detailed insights into the consecutive insertion of DMAD molecules into the Pd−C bond.

Scheme 3



The reaction of $AgBF_4$ with **8** in CH_3CN converts it into $[Pd(CZ{=}CZ{-}C_6H_3Me_2\text{-}3,5)(bpy)(CH_3CN)]BF_4$ (**9**-

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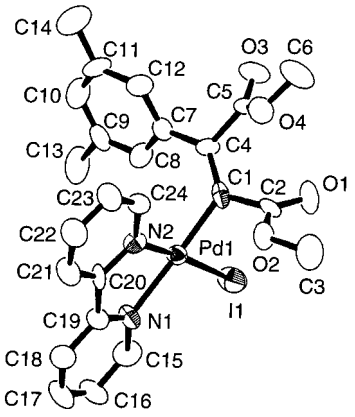


Figure 3. ORTEP drawing of **8** (50% probability). One of the two crystallographically independent molecules is shown. Selected bond lengths (Å) and angles (deg): Pd1−I1 2.583(1), Pd1−N1 2.10(1), Pd1−N2 2.06(1), Pd1−C1 2.00(1), I1−Pd1−N1 97.1(3), I1−Pd1−N2 174.1(3), I1−Pd1−C1 88.1(3), N1−Pd1−N2 79.1(4), N1−Pd1−C1 174.3(5), N2−Pd1−C1 95.5(5).

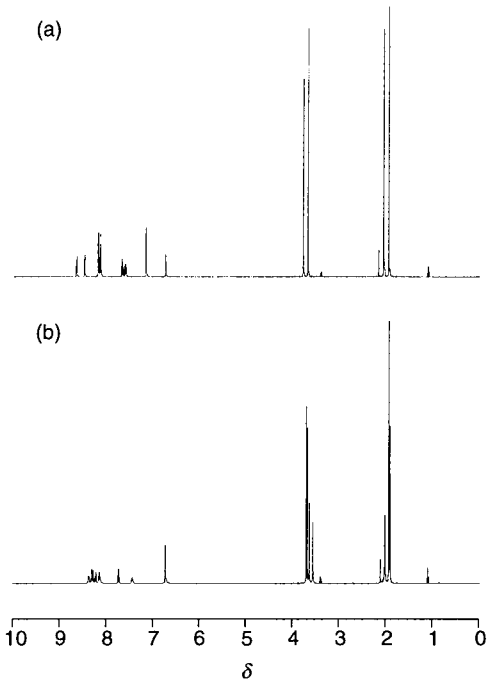
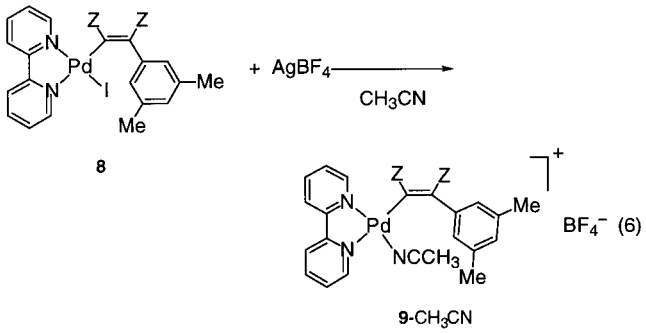


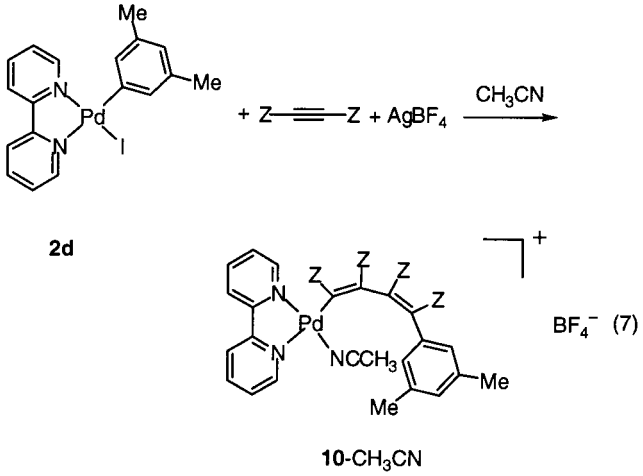
Figure 4. ^{1}H NMR spectra of (a) **9**−CH_3CN and (b) **10**-CH_3CN in CD_3CN (400 MHz).

CH_3CN) quantitatively (eq 6). Figure 4a shows the ^{1}H



NMR spectrum of **9**-CH_3CN in CD_3CN. All the signals are at reasonable positions for the structure as described below. The singlets at δ 2.07, 6.75, and 7.17 are assigned to methyl, para, and ortho hydrogens of the 3,5-dimethylphenyl ligand, respectively. Two OCH_3 hydrogen signals are observed at δ 3.69 and 3.79. The multiplets at δ 7.61, 7.68, 8.14, and 8.19 are assigned to H_5, $H_{5'}$, overlapped signals of $H_{3'}$ and $H_{4'}$, and overlapped signals of H_3 and H_4 of bpy, respectively. The doublets due to the H_6 and $H_{6'}$ hydrogens of bpy are close to each other (δ 8.48 and 8.65), whereas the corresponding signals of neutral and cationic aryl complexes **2d** and **5d**-CH_3CN exhibit much larger separations, approximately 2.0 and 1.0 ppm, respectively.

The 6:1 molar reaction of DMAD with **2d** in the presence of $AgBF_4$ in CH_3CN gives [Pd(CZ═CZ−CZ═CZ−$C_6H_3Me_2$-3,5)(bpy)(CH_3CN)]BF_4 (**10**-CH_3CN) at room temperature (eq 7). The reaction of DMAD with



9-CH_3CN in CH_3CN gives the same product via the insertion of a DMAD molecule into the Pd−vinyl bond. These results suggest the stepwise insertion of DMAD into the Pd−aryl bond of **5d**-CH_3CN, converting it into **9**-CH_3CN and further into **10**-CH_3CN. The reaction of excess DMAD with **10**-CH_3CN does not cause any further insertion of the alkynes into the Pd−vinyl bond at room temperature.

The perspective view of **10**-CH_3CN is presented in Figure 5. The molecule has a square-planar coordination around the Pd center and two inserted DMAD units between the aryl group and palladium center. The cis geometry of the C═C double bonds of **8** and **10**-CH_3CN indicates a cis addition of the Pd−C bond to the C≡C bond of DMAD in the insertion reaction. The aromatic ring of the $C_6H_3Me_2$-3,5 group and bpy ligand of **10**-CH_3CN are essentially parallel, being separated by a distance of 3.4 Å. The C13 atom on the aryl group is located at an apical coordination site of the palladium(II) center with a Pd−C distance of 3.417 Å. These structural parameters, including the interplane distance which is similar to or shorter than the sum of van der Waals radii,[19] are ascribed to an attractive interaction between the aryl group of the ligand and the Pd center or to a $\pi-\pi$ stacking between the aryl plane and bipyridine ligand. The intramolecular interaction of an organic ligand with the apical coordination site of the Pd(II) center was suggested in molecular structures of several organopalladium complexes, such as the dienylpalladium(II) complex shown in Chart 4.[30] Both this complex with an agostic interaction and **10**-CH_3CN in this study have an organic ligand containing a −CZ═

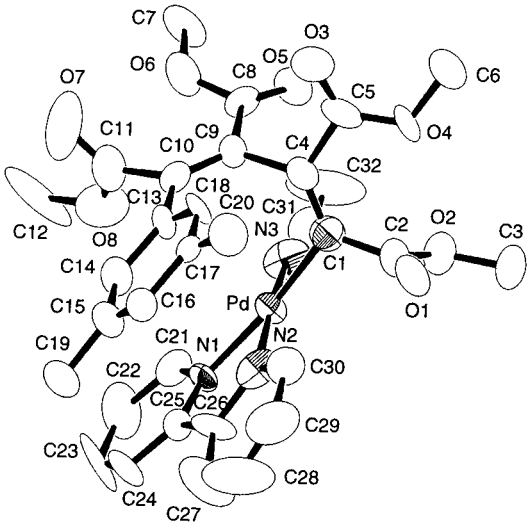
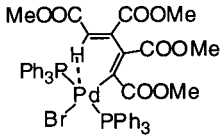


Figure 5. ORTEP drawing of **10**-CH_3CN (50% probability). BF_4^- anion is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−N1 2.07(2), Pd−N2 2.01(2), Pd−N3 1.96(2), Pd−C1 2.05(2), N1−Pd−N2 81.3(7), N1−Pd−N3 94.4(8), N1−Pd−C1 173.1(7), N2−Pd−N3 172.9(8), N2−Pd−C1 97.7(7), N3−Pd−C1 87.2(8).

Chart 4

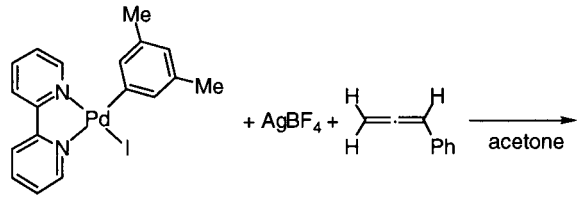


CZ−CZ═CZ− moiety with a cis geometry of two C═C double bonds and the single-bond cis structure. This situation seems to make the intramolecular interaction between the tethered organic ligand and the Pd center easy.

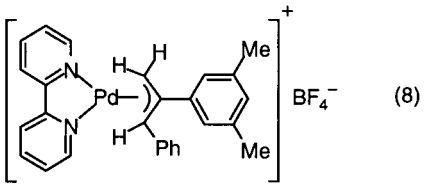
The ^1H and ^{13}C NMR spectra of **10**-CH_3CN in CD_3CN at room temperature indicate the presence of four different OCH_3 groups (Figure 4b). The ^1H NMR signal of the ortho phenyl hydrogens of 3,5-dimethylphenyl ligand is observed at δ 6.75, which is at a higher magnetic field than **9**-CH_3CN (δ 7.17) by 0.4 ppm. The large shift of the signal can be ascribed to the presence of interactions between the 3,5-dimethylphenyl ligand and the Pd center or the bipyridine ligand in the solution.

Scheme 4 summarizes insertion reactions of DMAD into the Pd−aryl bond of neutral or cationic arylpalladium complexes for forming various insertion products. The iodo ligand of **8** and the CH_3CN ligand of **10**-CH_3CN block further migratory insertion of DMAD into the Pd−C bond, while the reactions of DMAD with **2d** and with **9**-CH_3CN give the respective insertion products under similar conditions. An acetone-coordinated vinylpalladium complex, [Pd(CZ═CZ-$C_6H_3Me_2$-3,5)(bpy)(acetone)]BF_4 (**9**-acetone), was prepared from the reaction of $AgBF_4$ with **8** in acetone and characterized by NMR spectroscopy.[29] Addition of DMAD to **9**-acetone caused a smooth insertion of two alkyne molecules into the Pd−C bond to give **7**. The reaction probably involves the formation of [Pd(CZ═CZ−CZ═CZ−$C_6H_3Me_2$-3,5)(bpy)(acetone)]BF_4 (**10**-acetone) and further insertion of DMAD into the Pd−vinyl bond, but isolation of the intermediate **10**-acetone was prevented by a smooth reaction of DMAD with the complex giving **7**. In contrast with the above results, a similar reaction of **9**-CH_3CN leads to the isolation of **10**-CH_3CN, which does not undergo further insertion of DMAD into the Pd−vinyl bond.

The reaction of phenylallene with **2d** in the presence of $AgBF_4$ in acetone leads to the insertion of a C═C double bond into the Pd−aryl bond to give the π-allylpalladium complex [Pd{η^3-$CH_2C(C_6H_3Me_2$-3,5)CHPh}(bpy)]BF_4 (**11**), as shown in eq 8. A single insertion of



2d



(8)

11

allenes into the Pd−C bond has been reported to give π-allylpalladium complexes,[31] although several Pd complexes catalyze the polymerization of allenes via multiple insertion of allenes into the Pd−C bond.[32] Complex **11** does not undergo further insertion of allene into the Pd−π-allyl bond.

Figure 6 depicts the crystallographically determined molecular structure of **11** having a square-planar coordination with bipyridine and π-allyl ligands bonded to the Pd center.[33] Both of the two crystallographically independent molecules contain the syn-oriented phenyl substituent on the π-allyl ligand. The ^1H NMR spectrum of **11** indicates the presence of two isomeric forms in approximately 2:1 molar ratio in solution. The major isomer exhibits the ^1H NMR signals of π-allyl hydrogens at δ 4.20, 4.48, and 5.17, while the corresponding signals

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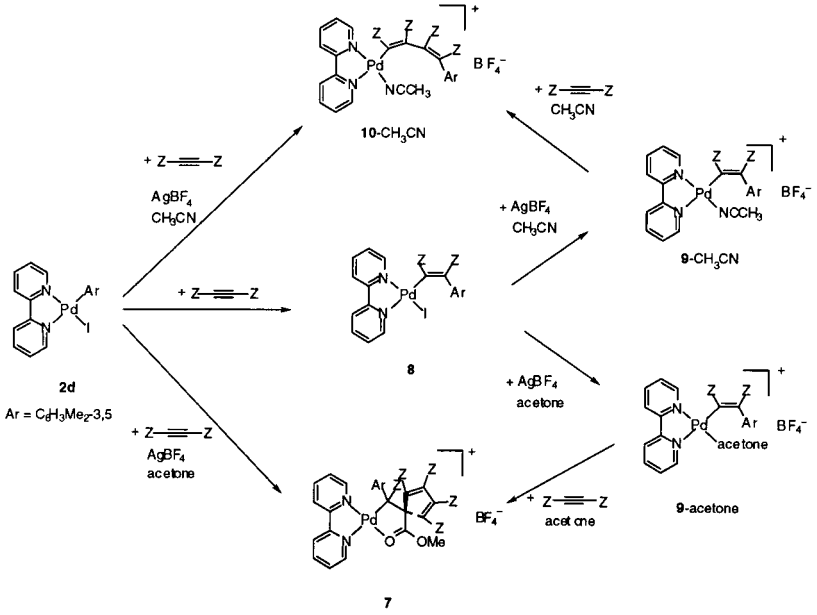
(33) Cationic π-allylpalladium complexes with a chelating pyridinepyrazole ligand have been reported recently. See: Satake, A.; Nakata, T. *J. Am. Chem. Soc.* **1998**, *120*, 10391.

Scheme 4



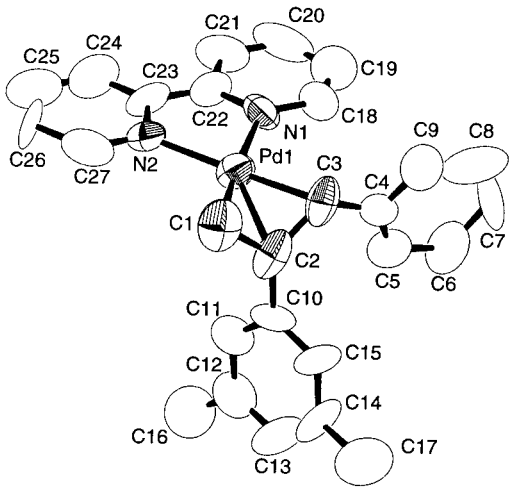
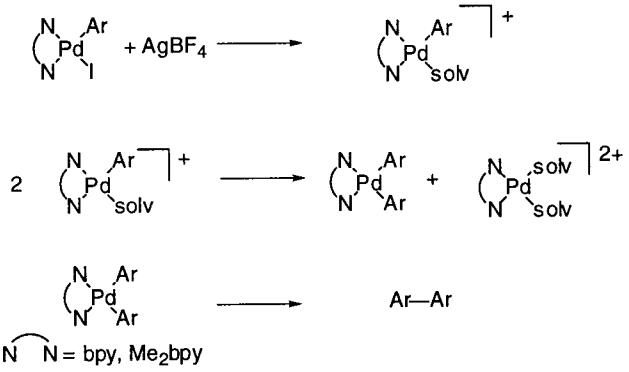


Figure 6. ORTEP drawing of **11** (50% probability). One of the two crystallographically independent molecules is shown. BF_4^- anion is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−N1 2.11(2), Pd1−N2 2.13(2), Pd1−C1 2.05(3), Pd1−C2 2.17(3), Pd1−C3 2.14(3), N1−Pd1−N2 76(1), N1−Pd1−C1 173(1), N1−Pd1−C2 138(1), N1−Pd1−C3 106(1), N2−Pd1−C1 109(1), N2−Pd1−C2 139(1), N2−Pd1−C3 174(1), C1−Pd1−C2 39(1), C1−Pd1−C3 68(1), C2−Pd1−C3 42(1).

of the minor isomer are observed at δ 4.36, 4.87, and 6.83. The signals at δ 5.17 and 6.83 are at lower magnetic field than the others and are assigned to the CH−Ph hydrogen of the π-allyl ligand. The former signal is at a higher position than the latter and is assigned to the hydrogen at the anti position of the isomer containing a syn-orientated Ph substituent. The latter signal of the minor complex is due to the CHPh hydrogen of the π-allyl ligand with an anti-orientated phenyl substituent. Since dissolution of crystals of a single isomer with a syn phenyl substituent of the π-allyl ligand results in the existence of a mixture of the isomers, the isomerization takes place rapidly in solution via a η^1-allylpalladium intermediate. The 2:1 ratio of the two isomers containing a syn- or anti-

Scheme 5



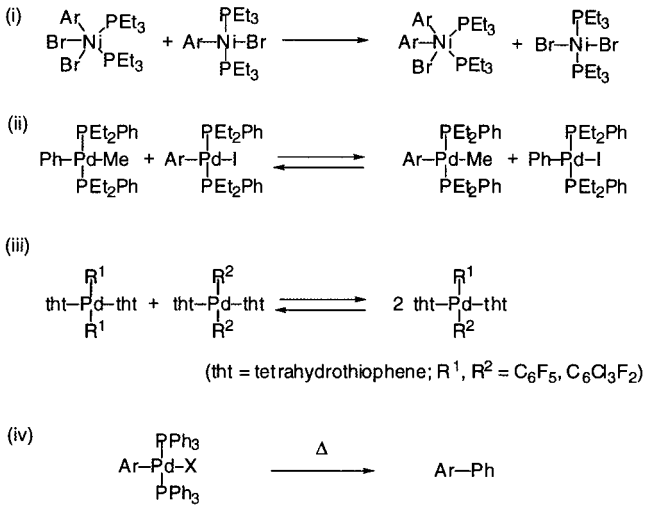
oriented substituent is smaller than that observed in most 1-substituted π-allylpalladium complexes which exist in the form with the syn substituent exclusively in solution.[34] Steric repulsion between the Ph group at the syn position and the 3,5-dimethylphenyl group at the central carbon of the π-allyl ligand seems to destabilize the syn isomer of **11** and makes differences in the relative stability between the syn and anti isomers small.

Discussion

The cationic arylpalladium complexes with chelating 2,2′-bipyridine or 4,4′-dimethyl-2,2′-bipyridine ligands obtained in this study undergo intermolecular coupling of the aryl ligands when a coordination site is occupied by a labile acetone or THF ligand. On the other hand, the neutral iodo(aryl)palladium complexes with the bpy ligand and previously reported *trans*-$[PdAr(PR_3)_2(solv)]^+$ [6] do not cause biaryl formation. Scheme 5 depicts a plausible pathway for the above coupling reaction involving intermolecular aryl ligand transfer to give

(34) Isolation or observation of 1-aryl-η^3-allylpalladium complex with anti-orientated substituents of the allyl ligand is rare but found in the literature. See: Ohta, T.; Hosokawa, T.; Murahashi, S.; Miki, K.; Kasai, N. *Organometallics* **1985**, *4*, 2080. Osakada, K.; Chiba, T.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 2602.

Scheme 6



diarylpalladium complexes that is responsible for the reductive elimination of the product. Results of previous experimental and theoretical studies indicated that reductive elimination of biaryl from cis diaryl complexes of group 10 metals takes place much more easily than the corresponding reductive elimination of alkanes from similar dialkyl complexes.[35] The disproportionation shown in Scheme 5, therefore, induces smooth intramolecular coupling of the aryl ligands of the resulting *cis*-diarylpalladium complex. Based on this mechanism, the rate-determining step of the reactions in Scheme 5 exists in the disproportionation via intermolecular aryl ligand transfer. An alternative pathway involving direct reductive elimination of biaryl from two arylpalladium complex molecules is less plausible than the above mechanism. Since coupling of two organic ligands bonded to the two metal centers of dinuclear transition metal complexes is quite rare[36] and is unfavorable according to results of the theoretical calculations,[37] the direct reductive elimination of biaryl from two aryl complexes would be even slower.

Several neutral nickel and palladium complexes were reported to undergo intermolecular aryl ligand transfer as summarized in Scheme 6. Earlier work by Kochi et al. established biaryl formation from monoarylnickel(II) complexes with PEt_3 ligands via Ni(I) and Ni(III) intermediates (Scheme 6(i)); the reaction of Ar−Br with $[NiAr(Br)(PEt_3)_2]$ at elevated temperature causes exchange of the aryl ligand and/or coupling of the aryl groups. The initially formed five-coordinate Ni(III) intermediate $[NiArBr_2(PEt_3)_2]$ undergoes aryl ligand exchange with the Ni(II) complex $[NiArBr(PEt_3)_2]$ to give $[NiAr_2Br(PEt_3)_2]$, which readily causes reductive elimination of biaryl.[38] Amatore et al. reported the electrochemical oxidation of arylnickel(II) complexes leading to biaryl formation.[39] Eventually, chemical and electrochemical oxidation of several Ni(0) and Ni(II) complexes results in isolation of the one-electron oxidation products containing Ni(I) and Ni(III) centers, respectively.[40] Ozawa and Yamamoto et al. observed smooth aryl ligand transfer in the reaction of iodo(aryl)palladium with methyl(aryl)palladium complexes to give the coupling products at room temperature (Scheme 6(ii)).[41] The reaction probably involves initial dissociation of a phosphine ligand to give a three-coordinate Pd(II) complex which is susceptible to aryl ligand transfer from the four-coordinate arylpalladium complex. Espinet et al. designed Pd complexes having both polyhalogeno aryl ligands and tht (tetrahydrothiophene) auxiliary ligands and achieved reversible conproportionation and disproportionation shown in Scheme 6(iii).[42] The Cl and F substituents on the aryl ligands stabilize the Pd−C bond and prevent intramolecular or intermolecular reductive elimination of biaryls during the reaction. The aryl ligand transfer in Scheme 6(ii) and (iii) was proposed to involve a dinuclear intermediate with a bridging aryl ligand coordinated to two square-planar Pd(II) centers. An initial dissociation of a neutral ligand is requisite in the formation of such intermediate complexes in aryl ligand transfer. Several transition metal complexes with bridging aryl ligands were isolated and structurally characterized.[43] Very recently, Grushin found that heating of $[Pd(Ph)I(PPh_3)_2]$ caused formation of biphenyl, but it is ascribed to the initial reductive elimination of PPh_4I and ensuing coupling of Ph groups bonded to Pd and bonded to P centers (Scheme 6(iv)).[44]

$AgBF_4$-promoted conversion of [PdI(Ar)(bpy)] to the cationic complexes shown in this study triggers a new type of transmetalation of the aryl ligand. A plausible mechanism of the facile aryl ligand transfer of the cationic complex is illustrated in Scheme 7. Mononuclear cationic arylpalladium complexes dimerize easily to form dinuclear intermediate Pd complexes with bridging aryl ligands accompanied by a loss of a solvent ligand. Cleavage of a Pd−C bond of the bridging aryl ligand leads to formation of the diarylpalladium complex with a bpy ligand or regeneration of the initial cationic arylpalladium complex. The transmetalation is promoted by the subsequent irreversible reductive elimination of biaryl from the diarylpalladium complex with a cis structure.

Similar disproportionation type transmetalation of *trans*-$[PdAr(PR_3)_2(solv)]^+$ appears to occur much less

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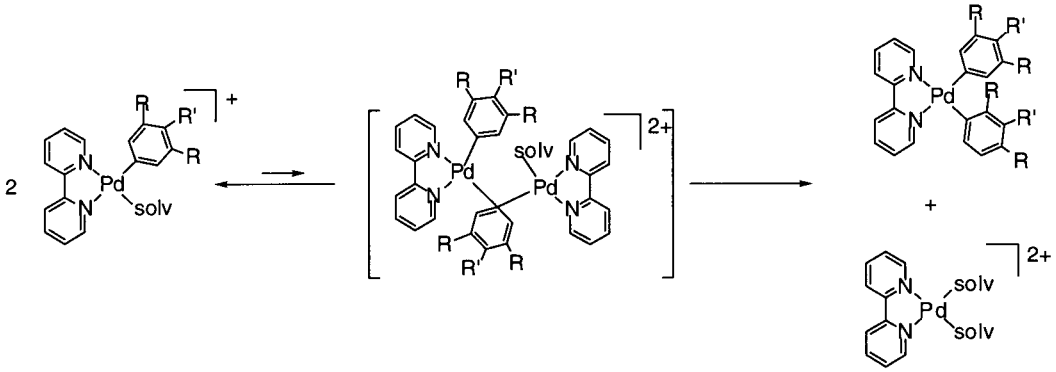
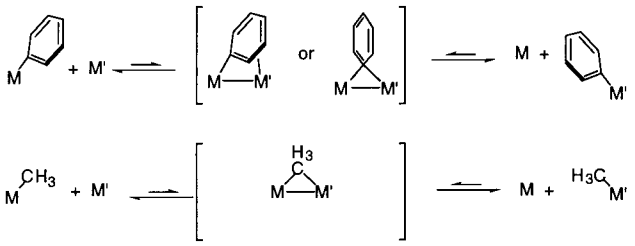
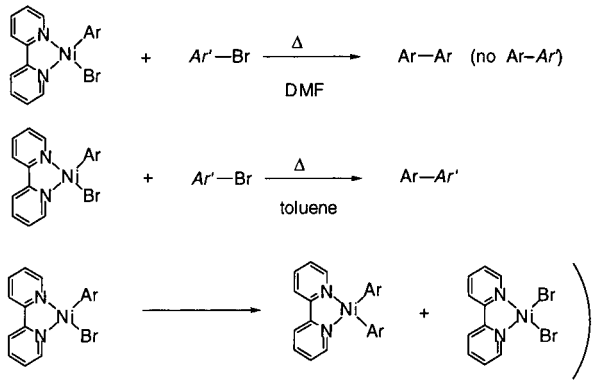
Scheme 7



Scheme 8



Scheme 9



smoothly than the bpy-coordinated complex. It may be due to lower thermodynamic stability of the products *trans*-[$PdAr_2(PR_3)_2$] and $[Pd(PR_3)_2(solv)_2]^{2+}$ than the starting monocationic complex or due to difficult direct coupling of the aryl ligands of the resulting *trans*-[$PdAr_2$-$(PR_3)_2$]. The complexes with a tmeda ligand also form no biaryls. Tmeda with a higher basicity than bpy and Me_2bpy may destabilize the bridging coordination of the aryl ligand to the two Pd centers in the reaction.

Cationic methylpalladium complexes with bipyridine or related diimine ligands are stable in solution, although analogous arylpalladium complexes in this study tend to cause intermolecular aryl ligand transfer. On the other hand, neutral arylpalladium complexes, *trans*-[$PdAr(C{\equiv}CPh)(PR_3)_2$] and *trans*-[$PdAr'(I)(PR'_3)_2$], undergo selective intermolecular alkynyl ligand transfer without transmetalation of the aryl ligand.[18,45] These results seem to suggest the order of reactivity of the metal−carbon bonds toward intermolecular transfer of the organic ligands, M−C≡CR > M−Ar > and M−R, which is opposite of that expected from relative thermodynamic stability of transition metal−carbon bonds in the order M−C≡CR > M−Ar > and M−R.[46]

Scheme 8 illustrates plausible intermediate complexes of transmetalation of aryl and methyl complexes of transition metals schematically. The intermolecular aryl ligand transfer involves the intermediate dinuclear complex with a bridging aryl ligand. Since the bridging coordination of the aryl group is partly stabilized by π-orbitals of the ligand, it is more stable than the bridging methyl coordination with a hypervalent carbon center. Thus, the low stability of the intermediate complex with a bridging methyl ligand hampers smooth transmetalation of the cationic methylpalladium complexes.

The mechanism of biaryl formation from monoarylpalladium complexes shown in Scheme 7 is related to the previously reported coupling of bromoarene promoted by $Ni(cod)_2$ in the presence of the bipyridine ligand in DMF giving biaryls.[47] Second-order kinetics of the reaction with respect to the concentration of Ni(II) complexes and negligible aryl ligand exchange with bromoarene added to the reaction mixture indicate that a pathway involving disproportionation of [NiBr(Ar)-(bpy)] gives [$NiAr_2$(bpy)], which releases biaryl product as shown in Scheme 9. A similar reaction in toluene occurs much more gradually and is accompanied by aryl group migration between the Ni complex and bromoarene, indicating another mechanism probably involving the Ni(I) and Ni(III) intermediates similarly to the reactions reported by Kochi et al.[38] The major role of DMF in this reaction is to promote initial dissociation of the bromo ligand to form a cationic arylnickel intermediate, which induces subsequent intermolecular aryl ligand transfer. Ishiguro et al. previously reported that a Br ligand of [$NiBr_2(bpy)_2$] is dissociated in DMF to form a stable cationic Ni complex in the solution on the basis of calorimetric measurements.[48] Aryl ligand transmetalation of [PdI(Ar)(bpy)] requires addition of $AgBF_4$ to generate the dinuclear intermediate with a bridging aryl ligand smoothly, while [NiAr(Br)(bpy)] appears to undergo dissociation of the bromo ligand upon dissolving it in DMF.

Milstein et al. reported the reaction of norbornene with [PdCl(Ph)(P−P)] (P−P = bis(diisopropylphosphi-

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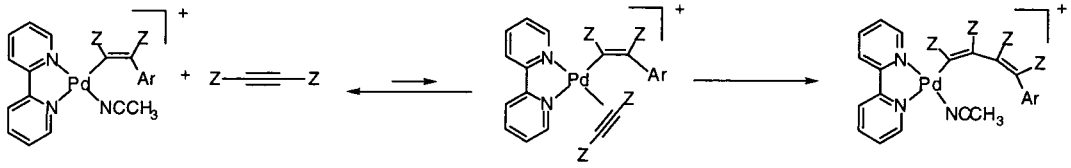
Scheme 10



no)propane) in DMF to give a mixture of phenylnorbornane, [$PdCl_2$(P−P)], and [Pd(norbornene)(P−P)].[49] They attributed the remarkable dependence of the reaction on the solvents (DMF ≫ dioxane) to the initial formation of cationic species, [PdPh(P−P)(norbornene)]Cl, followed by insertion of the C═C double bond into the Pd−Ph bond. Formation of the two Pd complexes is due to disproportionation type Cl ligand transfer from [PdCl(H)(P−P)]. In this case, intermolecular coupling of the Ph ligand was preceded by the insertion of norbornene to the Pd−Ph bond of the cationic phenylpalladium complex.

Scheme 10 depicts a plausible pathway for the coordination−insertion process of DMAD into the cationic arylpalladium complex, involving rapid and reversible exchange of the solvent molecule with DMAD to give an intermediate with π-coordinated DMAD and the insertion of the π-coordinated DMAD into the Pd−C bond. The kind of solvent coordinated to the metal center in the starting complex affects the equilibrium between the starting and intermediate complexes. CH_3CN is bonded to Pd firmly and is replaced with DMAD to a much smaller degree than acetone or THF ligand. Since the subsequent insertion process is not influenced by the solvent, insertion of DMAD into the Pd−C bond of the cationic arylpalladium complex with an acetone ligand takes place more easily than the corresponding CH_3CN-coordinated complex. Eventually, insertion of DMAD into the Pd−C bond of **10**-CH_3CN in CH_3CN is effectively suppressed, whereas the reaction of DMAD with **9**-acetone gives **7** via formation of [Pd(CZ═CZ−CZ═CZ−Ar)(acetone)(bpy)]$^+$ and the insertion of DMAD into the Pd−C bond of it.

Complexes **5d**-CH_3CN and [Pd($C_6H_3Me_2$-3,5)(bpy)(acetone)]BF_4, generated in situ from the addition of $AgBF_4$ to **2d** in acetone, exhibit a significantly different reactivity toward the disproportionation type transmetalation shown in Scheme 7. The former complex keeps its purity for 1 h at room temperature in CD_3CN, but the reaction of $AgBF_4$ with **2d** in acetone and dissolution of **5d**-CH_3CN in acetone cause rapid decomposition of the complex accompanied by liberation of the biaryl product once it is formed via [Pd($C_6H_3Me_2$-3,5)(bpy)(acetone)]BF_4. These complexes, however, react readily with DMAD to give **10**-CH_3CN and **7**, respectively.

The insertion of alkynes into the Pd−C bond of neutral iodo(aryl)palladium complexes is slower than that of the corresponding cationic complexes. Complex **8** does not undergo insertion of DMAD at all, whereas the cationic complexes **9**-CH_3CN and **9**-acetone are susceptible to insertion. Provided that insertion of DMAD into the Pd−C bond of the neutral complexes, [PdI(Ar)(bpy)], would proceed in a similar pathway to the cationic complexes (Scheme 10),[50] lower reactivity of the insertion of **8** than the cationic complexes could be ascribed to thermodynamically unfavorable displacement of the iodo ligand with π-coordinated DMAD. The degree of donor properties in the order I > CH_3CN > acetone is directly related to the equilibrium between the starting cationic complex and the intermediate with the π-coordinated DMAD. Since complex **2d** reacts with DMAD to give the insertion product, **8**, the reaction is controlled not only by the ligand that will be replaced with DMAD prior to insertion but also by the organic ligand attached to the Pd center. The controlled insertion reactions of DMAD into the Pd−C bond of various organopalladium complexes in this study have been attained by choosing a ligand that dominates the equilibrium to generate the DMAD-coordinated intermediates prior to the insertion.

Conclusion

Isolation of cationic arylpalladium complexes with a cis coordination imposed by chelating bipyridine ligands has long been of interest in this field because of its relevance to synthetic organic reactions using Pd complexes as a catalyst. Choosing a proper aryl group and solvent ligand enabled isolation and characterization of several [Pd(Ar)(N−N)(solv)]$^+$ complexes. The intermolecular coupling of the aryl ligand of the cationic arylpalladium complexes with a chelating bpy ligand is the main degradation pathway of the complexes and provides the reason for their lower stability in solution than the corresponding methylpalladium complexes. The labile solvent ligand serves to facilitate the initial intermolecular aryl ligand transfer to give *cis*-diarylpalladium complexes which are ready to release coupling products. The cationic arylpalladium complexes [Pd(Ar)(bpy)(solv)]$^+$ also exhibit a high reactivity toward insertion of alkynes into the Pd−aryl bond. The kind of organic ligands bonded to the metal center and of solvents used influence the reaction significantly. The coupling and insertion reactions of organopalladium complexes shown in this study are probably related not only to synthetic organic reactions promoted by cationic Pd complexes but also to those by noncationic Pd complexes in polar solvents.

Experimental Section

General Consideration, Measurement, and Materials. Manipulations of the palladium complexes were carried out under nitrogen or argon using standard Schlenk techniques.

(49) Portnoy, M.; Ben-David, Y.; Rousso, I.; Milstein, D. *Organometallics* **1994**, *13*, 3465.

(50) A previous report that demonstrates isolation of a Pt complex with a five-coordinate structure having π-coordinated DMAD to the Pt center suggests a possible associative insertion via a stable five-coordinate intermediate. See: De Felice, V.; De Renzi, A.; Giordano, F.; Tesauro, D. *J. Chem. Soc., Dalton Trans.* **1993**, 1927. The details of exchange between the solvent and DMAD, however, are not directly related to the different reactivity between the CH_3CN-coordinated complex and acetone or the THF-coordinated complexes toward alkyne insertion into the Pd−C bond.

Solvents were purified in usual manners and stored under argon. $Pd(dba)_2$[51] and [PdI(Ar)(N−N)] (**1a**−**3d**)[17,18] were prepared as described before. The other chemicals were commercially available. NMR spectra (^1H, $^{13}C\{^1H\}$, $^1H-^1H$ COSY, and $^1H-^{13}C\{^1H\}$ COSY) were recorded on JEOL EX-400 and Varian MERCURY300 spectrometers. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Preparation of [Pd{$C_6H_3(CF_3)_2$-3,5}(tmeda)(CH_3CN)]BF_4 (4c-CH_3CN). To a suspension of [PdI{$C_6H_3(CF_3)_2$-3,5}(tmeda)] (261 mg, 0.46 mmol) in dry CH_3CN (1.5 mL) was added dropwise a CH_3CN solution of $AgBF_4$ (ca. 0.5 M) with stirring until no generation of AgI was observed. After further stirring of the solution for 1 min at room temperature, the precipitated AgI was removed by filtration. Addition of Et_2O (50 mL) to the filtrate caused separation of **4c**-CH_3CN as an off-white air-stable solid, which was collected by filtration and dried under vacuum (192 mg, 0.34 mmol, 74%). The ^1H NMR spectrum of the complex in CD_3CN did not change for 5 days at room temperature.

Preparation of [Pd{$C_6H_3(CF_3)_2$-3,5}(tmeda)(acetone)]BF_4 (4c-acetone). To a suspension of [PdI{$C_6H_3(CF_3)_2$-3,5}(tmeda)] (257 mg, 0.46 mmol) in dry acetone (4 mL) was added dropwise an acetone solution of $AgBF_4$ (ca. 0.8 M) with stirring until no generation of AgI was observed. After further stirring the mixture for 1 min at room temperature, the precipitated AgI was removed by filtration. Solvent was evaporated under vacuum to give **4c**-acetone as a desiccated frothy off-white solid. Although the ^1H NMR spectrum of an acetone-d_6 solution of the complex indicated the proposed structure, its isolation was not feasible due to the high deliquesency.

Preparation of [Pd{$C_6H_3(CF_3)_2$-3,5}(bpy)(CH_3CN)]BF_4 (5c-CH_3CN). The cationic complex **5c**-CH_3CN was prepared by a procedure similar to that for **4c**-CH_3CN, using [PdI{$C_6H_3(CF_3)_2$-3,5}(bpy)] (573 mg, 0.95 mmol) as the starting material. The product **5c**-CH_3CN was obtained as an off-white air-stable solid (439 mg, 0.71 mmol, 75%) and did not change its ^1H NMR spectrum in CD_3CN for 24 h at room temperature.

Preparation of [Pd{$C_6H_3(CF_3)_2$-3,5}(bpy)(acetone)]BF_4 (5c-acetone). To a suspension of [PdI{$C_6H_3(CF_3)_2$-3,5}(bpy)] (784 mg, 1.3 mmol) in dry acetone (3 mL) was added dropwise an acetone solution of $AgBF_4$ (ca. 0.8 M) with stirring until no generation of AgI was observed. After further stirring of the solution for 1 min at room temperature, the precipitated AgI was removed by filtration. Addition of hexane (50 mL) to the filtrate caused separation of an off-white solid, which was collected by filtration and dried under vacuum. The obtained complex was kept for a few days at room temperature and then dissolved in a minimum amount of acetone. After removing insoluble Ag and Ag salts by filtration, hexane was added to the filtrate to give the cationic complex. The ^1H NMR spectra of the obtained complex in dry THF-d_8 and acetone-d_6 indicated that it contained the complex free from the coordinated solvent. Anal. Calcd for $C_{21}H_{17}BF_{10}N_2OPd$: C, 40.64; H, 2.76; N, 4.51. Found: C, 39.52; H, 2.90; N, 4.59. Disagreement of the analyses may be ascribed to the partial loss of the coordinated solvent during the purification procedure.

Preparation of [Pd{$C_6H_3(CF_3)_2$-3,5}(bpy)(thf)]BF_4 (5c-THF). To a suspension of [PdI{$C_6H_3(CF_3)_2$-3,5}(bpy)] (535 mg, 0.89 mmol) in dry THF (5 mL) was added dropwise a THF solution of $AgBF_4$ (ca. 0.6 M) with stirring until no generation of AgI was observed. After further stirring of the solution for 1 min at room temperature, the precipitated AgI was removed by filtration. Addition of hexane (50 mL) to the filtrate caused separation of an off-white solid, which was collected by filtration and dried in vacuo. The obtained complex was kept for a few days at room temperature and then dissolved in a minimum amount of THF. After removing insoluble Ag and Ag salts by filtration, hexane was added to the filtrate to give the cationic complex. The ^1H NMR spectrum in dry THF-d_8 indicated that it contained the complex partly free from the coordinated solvent. Anal. Calcd for $C_{22}H_{19}BF_{10}N_2OPd$: C, 41.64; H, 3.02; N, 4.41. Found: C, 39.52; H, 3.47; N, 4.37. Disagreement of the analyses may be ascribed to the partial loss of the coordinated solvent during the purification procedure.

Preparation of [Pd($C_6H_3Me_2$-3,5)(bpy)(CH_3CN)]BF_4 (5d-CH_3CN). To a suspension of [PdI{$C_6H_3Me_2$-3,5}(bpy)] (225 mg, 0.46 mmol) in dry CH_3CN (10 mL) was added dropwise a CH_3CN solution of $AgBF_4$ (ca. 0.5 M) with stirring at 0 °C until no formation of AgI was observed. After stirring for 1 min at 0 °C, the precipitated AgI was removed by filtration. Solvent was evaporated under vacuum to give **5d**-CH_3CN (218 mg, 0.44 mmol, 96%) as an off-white solid. This complex is stable for 1 h in CD_3CN at room temperature as monitored by the ^1H NMR spectrum.

Preparation of [Pd{$C_6H_3(CF_3)_2$-3,5}(Me_2bpy)(CH_3CN)]BF_4 (6c-CH_3CN). The cationic complex **6c**-CH_3CN was prepared by a procedure similar to that for **4c**-CH_3CN, using [PdI{$C_6H_3(CF_3)_2$-3,5}(Me_2bpy)] (364 mg, 0.58 mmol) as the starting material. The product (191 mg, 0.30 mmol, 51%) was obtained as an off-white air-stable solid. This complex is stable in CD_3CN for a month at room temperature.

Reaction of 5d-CH_3CN in Acetone-d_6. **5d**-CH_3CN (6.0 mg, 12 μmol) was placed into an NMR tube containing 0.60 mL of acetone-d_6. As soon as the complex was dissolved, a black solid precipitate was observed. Formation of 3,3′,5,5′-tetramethylbiphenyl was noted in the ^1H NMR spectrum and GC−MS. The yield of biaryl was estimated to be 25% (1.5 μmol) based on the peak area of para and ortho phenyl protons of biaryl compared with those of the complex.

Reactions of $AgBF_4$ with [PdI(Ar)(N−N)]. A typical procedure for the reactions of $AgBF_4$ with [PdI(Ar)(N−N)] is as follows. To a mixture of [PdI(Ar)(N−N)] (0.2−0.3 mmol) and two times molar $AgBF_4$ was added dry solvent (10 mL) with stirring at room temperature. After stirring the mixture for the prescribed time, excess NaI to BF_4^- anion (ca. 2:1) was added to the solution to quench the cationic or coordinatively unsaturated organopalladium complexes and stop the reaction. The resulting insoluble solid was removed by filtration, followed by extraction of the organic products with Et_2O. The products contained in the combined filtrate and extracts were analyzed by ^1H NMR and GC−MS spectra. The spectroscopic data from the biaryl products were compared with the authentic compounds, and their yields were estimated based on the ^1H NMR peak area relative to those of mesitylene added to the solution as an internal standard. The results obtained for the reactions conducted are summarized in Table 4.

Preparation of [Pd{CZ═CZ($C_6H_3Me_2$-3,5)}(bpy)(CH_3CN)]BF_4 (9-CH_3CN). A CH_3CN solution of $AgBF_4$ (ca. 0.5 M) was added dropwise to a solution of **8** (102 mg, 0.16 mmol) in dry CH_3CN (6 mL) with stirring until no generation of AgI was observed. The mixture was stirred for 5 min at room temperature, and the precipitated AgI was removed by filtration. Addition of Et_2O (50 mL) to the filtrate yielded an off-white solid, which was collected by filtration and dried under vacuum to give **9**-CH_3CN (95 mg, 0.15 mmol, 94%). This complex is stable in CD_3CN for 5 days at room temperature. ^1H NMR (400 MHz, CD_3CN): δ 1.95 (s, CH_3CN), 2.07 (s, 6H, CH_3C$_6$H$_3$), 3.69 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.75 (s, 1H, *p*-C$_6$H$_2$*H*), 7.17 (s, 2H, *o*-C$_6$H$_2$H), 7.61 (m, 1H, H_5-bpy), 7.68 (m, 1H, $H_{5'}$-bpy), 8.14 (m, 2H, $H_{3'}$, $H_{4'}$-bpy), 8.19 (m, 2H, H_3, H_4-bpy), 8.48 (d, 1H, H_6-bpy, J = 5.4 Hz), 8.65 (d, 1H, $H_{6'}$-bpy, J = 5.4 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 21.2 (*C*H$_3$C$_6$H$_3$), 52.6 (O*C*H$_3$), 52.8 (O*C*H$_3$), 124.3 (C_3-bpy), 124.6 ($C_{3'}$-bpy), 128.2 (*o*-*C*$_6$H$_3$), 128.7 (C_5, $C_{5'}$-bpy), 130.1 (*p*-*C*$_6$H$_3$), 137.5, 138.6, 140.1, 142.4 (C_4-bpy), 142.5 ($C_{4'}$-bpy), 150.6 (C_6-bpy), 153.9 ($C_{6'}$-bpy), 154.5, 157.4, 164.6, 171.7.

Preparation of [Pd{CZ═CZCZ═CZ($C_6H_3Me_2$-3,5)}(bpy)-(CH_3CN)]BF_4 (10-CH_3CN). To a dry CH_3CN (10 mL) solution

(51) Ukai, T.; Kawazura, H.; Ishii, Y. Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

Table 5. Crystallographic Data of the Palladium(II) Complexes

	1c	**2c**	**8**	**10**-CH_3CN	**11**
chemical formula	$C_{14}H_{19}N_2PdF_6I$	$C_{18}H_{11}N_2PdF_6I$	$C_{24}H_{23}O_4N_2PdI$ •$0.5C_3H_6O$	$C_{32}H_{32}O_8N_3PdBF_4$	$C_{27}H_{25}N_2PdBF_4$
fw	562.61	602.59	665.80	779.82	570.71
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No14)	$P2_1/c$ (No14)	$P2_1/n$ (No14)	$P2_1/c$ (No14)	$P2_1/c$ (No14)
a, Å	15.439(4)	13.562(2)	16.058(2)	7.629(1)	10.809(2)
b, Å	8.351(3)	8.785(1)	17.219(3)	22.120(7)	21.999(4)
c, Å	15.991(4)	16.994(2)	19.315(3)	20.788(7)	26.211(3)
β, deg	114.58(2)	109.732(8)	100.20(1)	91.77(2)	98.76(1)
V, Å^3	1874.9(9)	1905.9(5)	5256(1)	3506(1)	6160(2)
Z	4	4	8	4	8
μ, cm^{-1}	26.92	26.57	19.16	6.03	6.42
F(000)	1080	1144	2624	1584	2304
D_{calcd}, g cm^{-3}	1.993	2.100	1.683	1.477	1.231
cryst size, mm	0.40 × 0.11 × 0.09	0.50 × 0.38 × 0.06	0.38 × 0.25 × 0.10	0.30 × 0.30 × 0.30	0.75 × 0.20 × 0.13
2θ range, deg	5.0−55.0	5.0−55.0	5.0−55.0	5.0−55.0	5.0−55.0
no. of unique reflns	4601	4674	12 477	8241	11 332
no. of reflns used ($I>3.0\sigma(I)$)	2186	3038	3736	3386	3299
no. of variables	214	247	613	429	597
R	0.050	0.038	0.047	0.107	0.079
R_w	0.044	0.026	0.037	0.111	0.098

of [PdI($C_6H_3Me_2$-3,5)(bpy)] (469 mg, 0.95 mmol) and DMAD (880 mg, 6.2 mmol) was added $AgBF_4$ (290 mg, 1.5 mmol). The mixture was stirred for 3 days at room temperature to complete the separation of AgI, which was removed by filtration. Addition of Et_2O (50 mL) to the concentrated filtrate gave an off-white solid. Recrystallization from CH_3CN-Et_2O gave **10**-CH_3CN (624 mg, 84%). ^{1}H NMR (400 MHz, CD_3CN): δ 1.95 (s, CH_3CN), 2.03 (s(br), 6H, C$H_3C_6H_3$), 3.58 (s(br), 3H, OCH_3), 3.66 (s(br), 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 6.75 (s, 3H, *o*-, *p*-C_6H_3), 7.45 (m, 1H, H_5-bpy), 7.75 (m, 1H, $H_{5'}$-bpy), 8.1 (m, 2H, H_4, H_6-bpy), 8.24 (d, 1H, H_3-bpy, J = 7.3 Hz), 8.28 (m, 1H, $H_{4'}$-bpy), 8.32 (1H, $H_{3'}$-bpy, J = 8.2 Hz), 8.38 (d, 1H, $H_{6'}$-bpy, J = 5.4 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ 21.2 (*C*$H_3C_6H_3$), 52.6 (O*C*H_3), 53.1 (O*C*H_3), 53.2 (O*C*H_3), 53.5 (O*C*H_3), 124.3 (C_3, $C_{3'}$-bpy), 128.0, 128.7 (*o*-C_6H_3, C_5, $C_{5'}$-bpy), 132.4, 132.6 (*p*-C_6H_3), 136.1, 139.7, 142.2 (C_4-bpy), 142.7 ($C_{4'}$-bpy), 150.5 (C_6-bpy), 154.6 ($C_{6'}$-bpy), 154.9, 157.3, 163.0, 167.6, 169.9, 171.8.

Reaction of DMAD with 9-CH_3CN. To a CD_3CN (0.5 mL) solution containing **9**-CH_3CN (37 mg, 58 μmol) was added DMAD (36 μL, 0.21 mmol) at room temperature. Change in the ^{1}H NMR spectrum of the solution was recorded at room temperature.

Preparation of [Pd{η^3-$CH_2C(C_6H_3Me_2$-3,5)CHPh}(bpy)]-BF_4 (11). To a dry acetone (5 mL) solution containing a mixture of **2d** (104 mg, 0.21 mmol) and phenylallene (36.2 mg, 0.31 mmol) was added $AgBF_4$ (72 mg, 0.37 mmol) in one portion under argon. The mixture was stirred for 1 min at room temperature to complete the separation of AgI. Removal of the insoluble product by filtration and subsequent addition of hexane (50 mL) to the filtrate gave an off-white solid. Recrystallization from acetone−hexane gave **11** (55.5 mg, 0.097 mmol, 46%). The complex obtained contained only the isomer with the syn-oriented phenyl substituent, but the NMR spectra indicated the presence of isomers both with syn and anti orientations of the phenyl substituents. ^{1}H NMR (400 MHz, acetone-d_6): δ 2.19 (s, CH_3, major), 2.30 (s, CH_3, minor), 4.20 (m, H_a, major), 4.36 (d, $H_{a'}$, minor, J = 2.0 Hz), 4.48 (d, $H_{b'}$, major, J = 1.5 Hz),), 4.87 (m, $H_{b'}$, minor), 5.17 (s, major, H_c), 6.83 (s, minor, $H_{c'}$), 6.92 (d, H_6-bpy, J = 4.9 Hz), 7.03 (s, major, *p*-C_6H_3), 7.10, 7.12 (s, major, *o*-C_6H_3), 7.3−7.5 (m), 7.61 (m), 7.80 (m, $H_{5''}$-bpy), 7.91 (m, H_5-bpy), 7.95 (m, $H_{5''}$-bpy), 8.25 (m, $H_{4'''}$-bpy), 8.36 (m, $H_{4'}$-bpy), 8.44 (m, H_4-bpy), 8.65 (m, $H_{3'''}$-bpy), 8.66 (m, $H_{3''}$-bpy), 8.71 (d, $H_{3'}$-bpy, J = 8.3 Hz), 9.16 (d, $H_{6''}$-bpy, J = 5.4 Hz), 9.30 (d, H_6-bpy, J = 4.9 Hz), 9.61 (d, $H_{6'''}$-bpy, J = 4.9 Hz).

Crystal Structure Determination. Crystals of **1c**, **2c**, **8**, **10**-CH_3CN, and **11** suitable for X-ray diffraction study were obtained by recrystallization from acetone−hexane, $CH_2Cl_2-Et_2O$, acetone−Et_2O, CH_3CN-Et_2O, and acetone, respectively, and mounted in glass capillary tubes. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo Kα radiation (λ = 0.71069 Å) and $\omega-2\theta$ scan method, and an empirical absorption correction (Ψ scan) was applied. Calculations were carried out by using the program package TEXSAN for Windows. Atomic scattering factors were obtained from the literature.[52] Three fluorine atoms of the CF_3 group (**1c**), six fluorine atoms of two CF_3 groups (**2c**), three fluorine atoms of the BF_4^- anion (**10**-CH_3CN), and four fluorine atoms of two BF_4^- anions (**11**) were assigned to the two disordered positions with the occupancy of 1:1. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. Crystallographic data and details of refinement of the five complexes are summarized in Table 5.

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and distances, and thermal parameter of **1c**, **2c**, **8**, **10**-CH_3CN, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0007466

(52) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.