Single and Multiple Insertion of Carbon−Carbon Triple Bonds into the Palladium−Aryl Bond of Cationic and Neutral Arylpalladium Complexes with a 2,2′-Bipyridine Ligand

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Received January 18, 2000

Dimethyl acetylenedicarboxylate reacts with $PdI(C_6H_3Me_2$-3,5)(bpy) in the presence of $AgBF_4$, causing rapid insertion of three acetylene molecules into the Pd−C bond to afford $[Pd\{C(CCOOMe-CZ{=}CZ-CZ{=}CZ)(Z)(C_6H_3Me_2$-3,5)$\}$(bpy)]$BF_4$ (Z = COOMe), whereas a similar reaction without $AgBF_4$ gives the product of a single insertion of the carbon−carbon triple bond, $Pd(I)(CZ{=}CZC_6H_3Me_2$-3,5)(bpy).

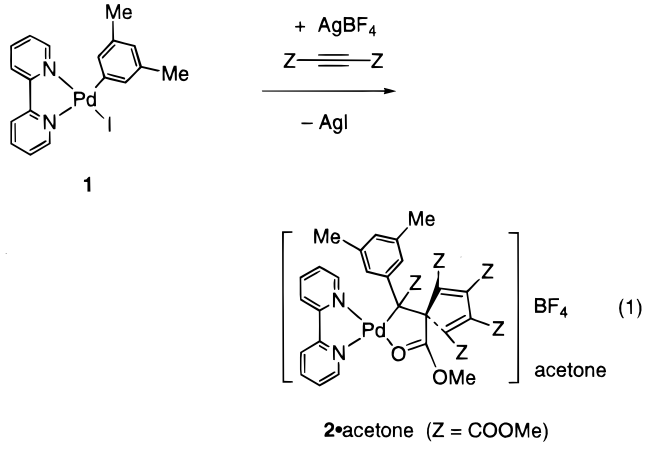
Introduction

Insertion of a carbon−carbon double or triple bond into a transition metal−carbon σ-bond is an important reaction of organotransition metal complexes involved in various synthetic organic reactions as well as polymer synthesis catalyzed by transition metals. Several studies have been reported where cationic alkylpalladium complexes bring about the efficient carbonylation of organic halides, Mizorogi−Heck coupling of organic halides with alkenes, and polymerization of unsaturated molecules.[1−5] The reaction of metal salts of anions such as BF_4^-, ClO_4^-, and BAr_4^- with methylpalladium halide complexes provides a convenient route to cationic methylpalladium complexes with tertiary phosphine ligands or with a chelating diamine or diimine ligand, as shown in Scheme 1. The cationic complexes thus formed contain a metal center with Lewis acid character and a labile coordination site occupied by a solvent molecule. They exhibit high reactivity toward coordination of alkenes or CO and their insertion into the Pd−methyl bond.[1,2,6,7] Cationic arylpalladium complexes with chelating ligands[8] have attracted much less attention than the corresponding methylpalladium complexes, which initiate alkene polymerization and copolymerization of alkenes and CO, and than the arylpalladium complexes with two trans phosphine ligands.

In this paper we report on the reaction of dimethyl acetylenedicarboxylate (DMAD) with an arylpalladium iodo complex with a 2,2′-bipyridine ligand in the presence of $AgBF_4$. The smooth multiple insertions of DMAD into the Pd−aryl bond is compared with the results of the reaction without addition of $AgBF_4$.

Results and Discussion

$PdI(C_6H_3Me_2$-3,5)(bpy) (**1**) reacts with DMAD in the presence of $AgBF_4$ in acetone to result in the insertion of three acetylene molecules into the Pd−aryl bond at



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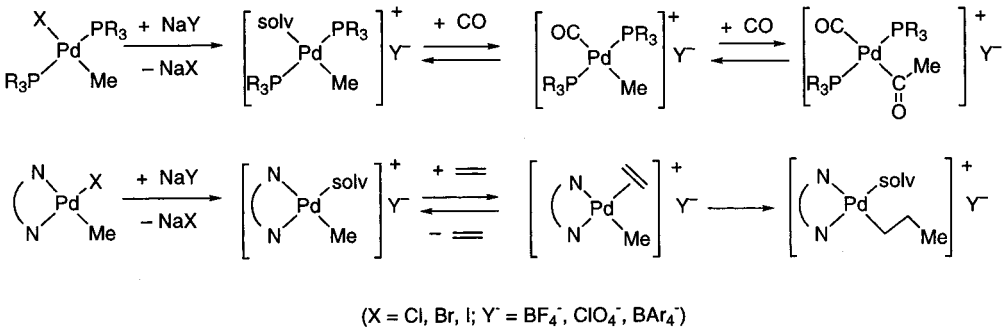
10.1021/om0000360 CCC: $19.00
Publication on Web 04/29/2000

Scheme 1



(X = Cl, Br, I; Y^- = BF_4^-, ClO_4^-, BAr_4^-)

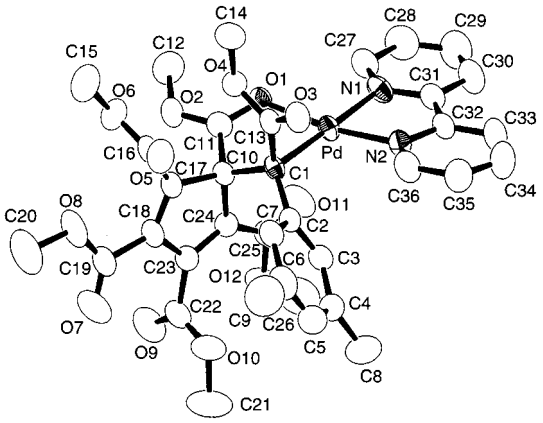


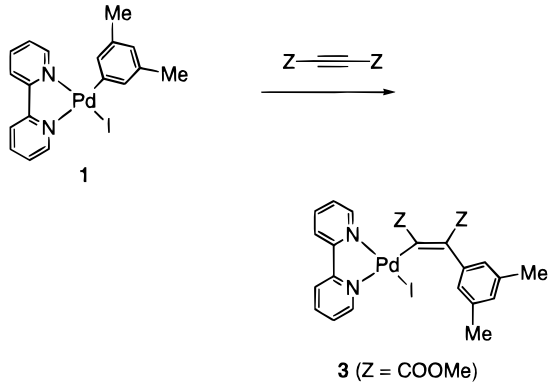
Figure 1. ORTEP drawing of **2** (50% probability). BF_4^- anion and solvated acetone are omitted for simplicity. Selected bond lengths (Å) and angles (deg): Pd−O1 2.055(5), Pd−N1 2.087(6), Pd−N2 2.031(7), Pd−C1 2.099(7), C1−C2 1.47(1), C1−C10 1.59(1), C10−C11 1.52(1), O1−C11 1.242(9), C10−C17 1.546(9), C17−C18 1.33(1), C18−C23 1.46(1), C23−C24 1.34(1), C10−C24 1.54(1), O1−Pd−N1 93.8(3), O1−Pd−N2 171.3(3), O1−Pd−C1 84.0(3), N1−Pd−N2 80.6(3), N1−Pd1−C1 177.2(3), N2−Pd−C1 101.8(3), Pd−C1−C2 119.8(5), Pd−O1−C11 113.8(5), Pd−C1−C10 101.9(5), C1−C10−C11 109.7(6), C1−C10−C17 113.1(6), C1−C10−C24 112.0(6), C10−C17−C18 109.9(7), C17−C18−C23 110.4(7), C18−C23−C24 108.8(7), C10−C24−C23 110.8(7), O1−C11−C10 119.7(8).

room temperature to give [Pd{C(CCOOMe−CZ=CZ−CZ=CZ)(Z)($C_6H_3Me_2$-3,5)}(bpy)]BF_4·acetone (**2**·acetone; Z = COOMe) (eq 1). The NMR spectra of the mixture exhibited growth of signals of **2** from the beginning of the reaction. All the Pd complexes were converted into **2** within 6 h at room temperature.

Figure 1 shows the molecular structure of **2**·acetone with a slightly distorted square planar coordination around the Pd center. The coordination sites are occupied by the two N-donor atoms of bpy and the C and O atoms of the O-chelating alkyl ligand composed of a cyclic trimer of the acetylene derivative attached to the 3,5-dimethylphenyl group. The Pd−N1 bond is longer than the Pd−N2 bond because of the larger trans influence of the alkyl ligand than of the carbonyl oxygen bonded to Pd. The cyclopentadiene ring of the acetylene trimer ligand lies almost perpendicular to the five-membered chelate ring. The torsion angle C13−C1−C10−C11 is 65.9(8)°, indicating the syn orientation of the two COOMe groups around the C1−C10 bond.

The ^1H and ^{13}C NMR spectra of **2** contain six ^1H and ^{13}C NMR signals of OCH_3 groups, indicating the presence of a single diastereomer with six inequivalent OMe groups. Pairs of signals due to ortho hydrogens (δ 7.06 and 7.18) and methyl hydrogens of the aryl group (δ 1.98 and 2.22) which are assigned by $^1H-^1H$ and $^1H-^{13}C$ COSY appear as somewhat broad peaks at 25 °C and are broadened further upon warming to 40 °C, suggesting that rotation of the C−C bond between the 3,5-dimethylphenyl group and the tertiary carbon bonded to Pd is hindered significantly and occurs much more slowly than rotation about the typical C−C single bond. Severe steric repulsion between the aryl and substituted cyclopentadienyl groups of the ligand appears to render the bond inflexible. The reaction shown in eq 1 in THF and the recrystallization of the product from CH_2Cl_2−Et_2O gives the same product in a CH_2Cl_2 solvated form (**2**·CH_2Cl_2).

DMAD reacts slowly with **1** in the absence of $AgBF_4$ to give PdI{C(COOMe)=C(COOMe)$C_6H_3Me_2$-3,5}(bpy) (**3**) via the single insertion of DMAD (eq 2). Complete



1

3 (Z = COOMe)

(2)

conversion of **1** into **3** requires 24 h in acetone and 48 h in CH_2Cl_2 even when 5 times molar DMAD to **1** is added to the reaction mixture. The produced complex **3** does not undergo further insertion of the substrate into the Pd−vinyl bond at room temperature, probably due to the negligible dissociation of the iodo ligand. We exam-

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Scheme 2

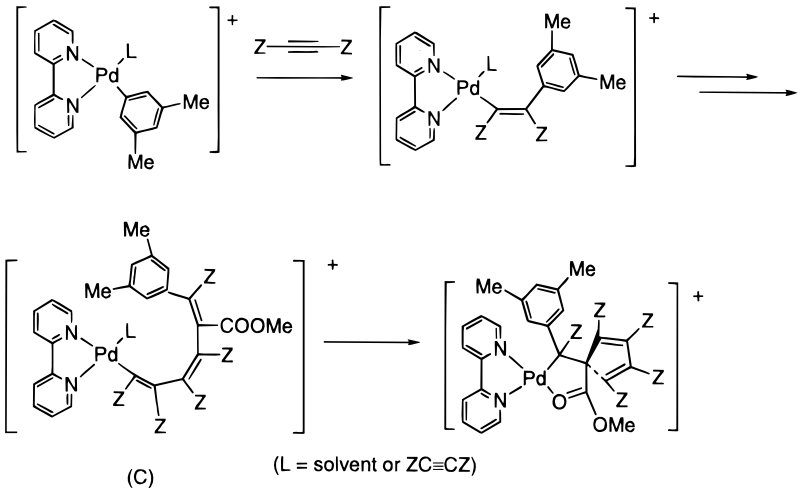
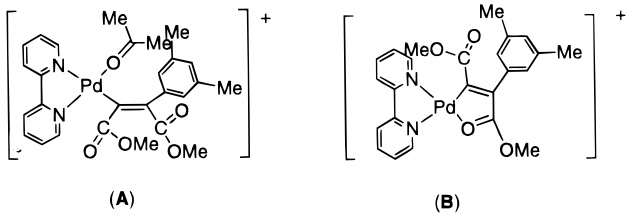


Chart 1



ined the reaction of DMAD with **3** in the presence of $AgBF_4$ with the expectation of the initial conversion of **3** into a cationic vinylpalladium complex which reacts with DMAD more readily. The ^1H NMR spectrum of an acetone-d_6 solution of **3** upon the addition of $AgBF_4$ immediately indicated the formation of a new species showing signals at δ 8.47 and 8.52 accompanied by deposition of AgI. The signals were assigned to the cationic complex [Pd{C(COOMe)═C(COOMe)$C_6H_3Me_2$-3,5}(acetone)(bpy)]BF_4 (Chart 1 (**A**)), although small signals are also observed at δ 4.32 and 4.41, which may be attributed to the complex with *Z* configuration of the C═C double bond (Chart 1 (**B**)). The spectrum exhibited a negligible change for 3 days at room temperature. The addition of excess DMAD to the solution causes rapid and quantitative formation of **2**, as revealed by the NMR spectral changes shown in Figure 2.

Scheme 2 summarizes a plausible pathway of the reaction 1 giving **2**. The cationic arylpalladium complex formed via the elimination of the iodo ligand from **1** undergoes consecutive insertion of acetylene molecules into the Pd−aryl bond. The resulting vinylpalladium complex containing a trimer of the acetylene in the ligand (**C**) causes the addition of the Pd−C bond to the C═C bond adjacent to the aryl group, giving a stable product with the O-chelating alkyl ligand. The structure of **2** indicates that each insertion occurs mostly with cis stereochemistry. Similar cyclotrimerization of DMAD was reported in its reaction with $PdCl_2$ and those with orthopalladated arylamines and arylamides in the presence of tertiary amine.[9,10] These nonionic complexes generate coordinatively unsaturated species that are responsible for ensuing coordination and insertion of the three alkyne molecules into a Pd−Cl or Pd−C bond. Recently a cationic methylpalladium complex with a 2,2′-bipyridine ligand was reported to undergo insertion of acetylene to the Pd−Me bond, giving a complex with a cyclic trimer of the acetylene as the π-allylic ligand.[11]

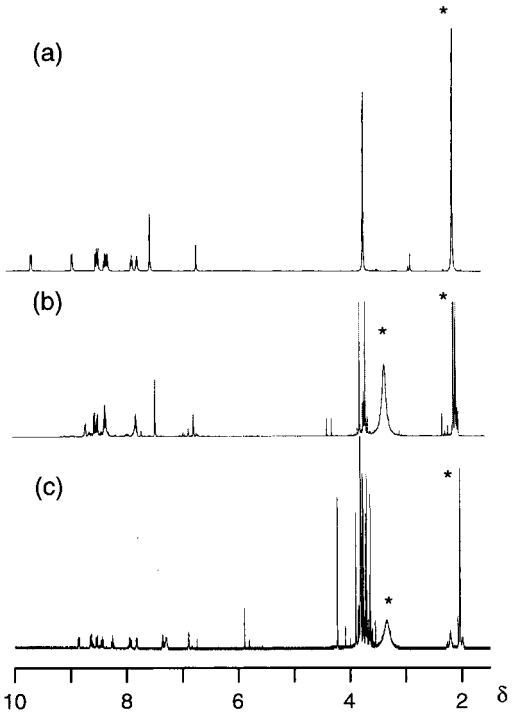


Figure 2. Change in the ^1H NMR spectra (acetone-d_6) during the reaction of **3** with DMAD. The spectra (a) of **3**, (b) after addition of $AgBF_4$, and (c) after further addition of DMAD (25 °C). Signals with asterisks are due to the solvent and water contaminated with $AgBF_4$. The signals in (b) can be assigned to the cationic vinyl complex in Chart 1.

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The reaction probably involves an intermediate Pd complex containing the cyclic acetylene as the tertiary alkyl ligand similarly to **2**.

In summary, the cationic and neutral arylpalladium complexes with a bipyridine ligand react with DMAD at different rates to give **2** and **3**, repsectively. The neutral arylpalladium complex **1** with an iodo ligand reacts with DMAD, whereas the vinylpalladium complex **3** does not cause further insertion of the carbon−carbon triple bond. Upon treatment with $AgBF_4$, complexes **1** and **3** react readily with DMAD to undergo the insertion of three or two acetylene molecules into the Pd−C bond.

Experimental Section

General Consideration, Measurement, and Materials. Manipulations of the palladium complexes were carried out under nitrogen or argon using standard Schlenk techniques. NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{1}H−^{1}H COSY, and ^{1}H−^{13}C COSY) were recorded on JEOL EX-400 and Lambda-500 spectrometers. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder. Complex **1** was prepared according to the literature method to prepare analogous arylpalladium complexes as follows.[12] To a benzene solution (15 mL) of Pd(dba)$_2$ (2.25 g, 3.91 mmol) were added bpy (826 mg, 5.29 mmol) and 3,5-$Me_2C_6H_3I$ (0.90 mL, 0.62 mmol). The mixture was stirred for 3 h with gentle heating below 50 °C. After evaporation of the solvent, the CH_2Cl_2-soluble fraction of the product was recrystallized from CH_2Cl_2−hexane to give **1** (1.03 g, 53.2%). Anal. Calcd for $C_{18}H_{17}IN_2Pd$: C, 43.71; H, 3.46; N, 5.66; I, 25.65. Found: C, 43.47; H, 3.50; N, 5.64; I, 25.96. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.19 (s, 6H, C*H*$_3$C$_6$H$_3$), 6.52 (s, 1H, *p*-C$_6$H$_2$*H*), 6.99 (s, 2H, *o*-C$_6$H*H*$_2$), 7.32 (m, 1H, *H*$_{5'}$-bpy), 7.47 (m, 1H, *H*$_5$-bpy), 7.65 (d, 1H, *H*$_{6'}$-bpy, J = 5.9 Hz), 7.96 (m, 2H, *H*$_4$ and *H*$_{4'}$-bpy), 8.06 (m, 2H, *H*$_3$ and *H*$_{3'}$-bpy), 9.56 (d, 1H, *H*$_6$-bpy, J = 3.9 Hz).

Preparation of 2·Acetone. To a dry acetone solution (25 mL) of [PdI($C_6H_3Me_2$-3,5)(bpy)] (125 mg, 0.253 mmol) and DMAD (0.124 mL, 1.01 mmol) was added $AgBF_4$ (71.2 mg, 0.366 mmol). The mixture was stirred at room temperature to complete the separation of AgI, which was removed by filtration. The addition of Et_2O to the filtrate gave **2** in an acetone-solvated form (**2**·acetone) as yellow crystals (202 mg, 85%). Anal. Calcd for $BC_{36}F_4H_{35}N_2O_{12}Pd\cdot C_3H_6O$: C, 49.89; H, 4.40; N, 2.98. Found: C, 49.97; H, 4.49; N, 2.79. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.98 (s(br), 3H, C*H*$_3$C$_6$H$_3$), 2.12 (s, 6H, acetone), 2.22 (s(br), 3H, C*H*$_3$C$_6$H$_3$), 3.66 (s, 3H, OC*H*$_3$), 3.68 (s, 3H, OC*H*$_3$), 3.70 (s, 3H, OC*H*$_3$), 3.77 (s, 3H, OC*H*$_3$), 3.89 (s, 3H, OC*H*$_3$), 4.15 (s, 3H, OC*H*$_3$), 6.85 (s, 1H, *p*-C$_6$H$_2$*H*), 7.06 (s(br), 1H, *o*-C$_6$H*H*$_2$), 7.10 (m, 1H, *H*$_{5'}$-bpy), 7.18 (s(br), 1H, *o*-C$_6$H*H*$_2$), 7.63 (d, 1H, *H*$_{6'}$-bpy, J = 5.8 Hz), 7.77 (m, 1H, *H*$_5$-bpy), 8.09 (m, 1H, *H*$_{4'}$-bpy), 8.24 (m, 1H, *H*$_4$-bpy), 8.45 (d, 1H, *H*$_{3'}$-bpy, J = 8.2 Hz), 8.54 (d, 1H, *H*$_3$-bpy, J = 8.2 Hz), 8.60 (d, 1H, *H*$_6$-bpy, J = 4.9 Hz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 21.0 (*C*H$_3$C$_6$H$_3$), 21.3 (*C*H$_3$C$_6$H$_3$), 30.8 (*C*H$_3$-acetone), 49.9, 52.2 (OCH$_3$), 52.5 (OCH$_3$), 52.9 (OCH$_3$), 53.0 (OCH$_3$), 53.1 (OCH$_3$), 57.7 (OCH$_3$), 78.3, 123.9 (*C*$_3$-bpy), 123.9 (*C*$_{3'}$-bpy), 126.3 (*C*$_{5'}$-bpy), 127.8 (*C*$_5$-bpy), 129.0 (*o*-C$_6$H$_3$), 129.7 (*o*-C$_6$H$_3$), 130.1 (*p*-C$_6$H$_3$), 132.1, 133.7, 135.4, 136.9, 141.4 (*C*$_{4'}$-bpy), 141.6 (*C*$_4$-bpy), 146.4, 148.8 (*C*$_6$-bpy), 150.0, 152.1 (*C*$_{6'}$-bpy), 153.3, 157.3, 159.9, 162.2, 163.3, 164.2, 173.7, 185.6, 207.0 (*C*O-acetone).

Similar reaction in THF and ensuing recrystallization of the product from CH_2Cl_2−Et_2O gives **2**·CH_2Cl_2. Yield: 198 mg (85%). Anal. Calcd for $BC_{36}F_4H_{35}N_2O_{12}Pd\cdot CH_2Cl_2$: C, 46.01; H, 3.86; N, 2.90. Found: C, 46.22; H, 4.09; N, 2.86.

Table 1. Crystallographic Data and Details of Refinement of 2·acetone

chemical formula	$C_{39}H_{41}BF_4N_2O_{13}Pd$	μ, cm^{-1}	5.237
		F(000)	960
fw	938.96	D_{calcd}, g cm^{-3}	1.482
cryst syst	triclinic	cryst size, mm	0.75 × 0.28 × 0.15
space group	$P\bar{1}$ (No. 2)		
a, Å	14.113(4)	2θ range, deg	5.0−55.0
b, Å	15.078(4)	no. of unique reflns	9677
c, Å	10.365(3)		
α, deg	100.76(2)	no. of reflns used ($I \geq 3\sigma(I)$)	5271
β, deg	101.28(2)		
γ, deg	96.56(2)	no. of variables	508
V, Å^3	2105(1)	$R(F_o)$[a]	0.064
Z	2	$R_w(F_o)$[a]	0.061

[a] Weighting scheme, $[\{\sigma(F_o)\}^2]^{-1}$.

Preparation of 3. A mixture of [PdI($C_6H_3Me_2$-3,5)(bpy)] (55 mg, 0.11 mmol) and DMAD (72 mg, 0.51 mmol) in 10 mL of dry acetone was stirred for 24 h at room temperature. After the removal of a small amount of insoluble solid by filtration, the solvent was removed under reduced pressure. Recrystallization of the remaining solid from CH_2Cl_2−hexane yielded **3** as yellow crystals (53 mg, 75%). Anal. Calcd for $C_{24}H_{23}IN_2O_4Pd$: C, 45.27; H, 3.64; N, 4.40; I, 19.93. Found: C, 45.50; H, 3.76; N, 4.37; I, 19.55. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.07 (s, 6H, C*H*$_3$C$_6$H$_3$), 3.68 (s, 3H, OC*H*$_3$), 3.81 (s, 3H, OC*H*$_3$), 6.65 (s, 1H, *p*-C$_6$H$_2$*H*), 7.24 (m, 1H, *H*$_5$-bpy), 7.30 (s, 2H, *o*-C$_6$H*H*$_2$), 7.43 (m, 1H, *H*$_{5'}$-bpy), 7.80 (d, 1H, *H*$_{3'}$-bpy, J = 8.2 Hz), 7.87 (m, 1H, *H*$_{4'}$-bpy), 7.88 (d, 1H, *H*$_3$-bpy, J = 8 Hz), 7.91 (m, 1H, *H*$_4$-bpy), 8.80 (d, 1H, *H*$_{6'}$-bpy, J = 5.5 Hz), 9.35 (d, 1H, *H*$_6$-bpy, J = 4.6 Hz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 21.2 (*C*H$_3$C$_6$H$_3$), 51.8 (OCH$_3$), 52.0 (OCH$_3$), 122.2 (*C*$_{3'}$-bpy), 122.2 (*C*$_3$-bpy), 126.2 (*C*$_{5'}$-bpy), 126.5 (*C*$_5$-bpy), 128.0 (*o*-C$_6$H$_3$), 128.6 (*p*-C$_6$H$_3$), 134.5, 136.5, 138.9 (*C*$_{4'}$-bpy), 139.3, 139.4 (*C*$_4$-bpy), 151.0 (*C*$_{6'}$-bpy), 153.2 (*C*$_6$-bpy), 153.6, 155.2, 158.2, 164.3, 173.3.

Reaction of 3 with DMAD in Acetone-d_6 in the Presence of $AgBF_4$. A mixture of **3** (12 mg, 0.019 mmol) and $AgBF_4$ (30 mg, 0.15 mmol) in 0.5 mL of acetone-d_6 was stirred for 1 min at room temperature. After the removal of an insoluble solid by filtration, the solution was transferred to an NMR tube under argon. The ^{1}H NMR spectrum exhibited signals at δ 2.08 (s, 6H, C*H*$_3$C$_6$H$_3$), 3.67 (s, 3H, OC*H*$_3$), 3.77 (s, 3H, OC*H*$_3$), 6.76 (s, 1H, *p*-C$_6$H$_2$*H*), 7.45 (s, 2H, *o*-C$_6$H*H*$_2$), 7.8 (m, 2H, *H*$_5$ and *H*$_{5'}$-bpy), 8.3 (m, 3H, *H*$_4$, *H*$_{4'}$ and *H*$_{6'}$-bpy), 8.47 (d, 1H, *H*$_3$-bpy, J = 7.8 Hz), 8.52 (d, 1H, *H*$_{3'}$-bpy, J = 8.3 Hz), 8.69 (d, 1H, *H*$_6$-bpy, J = 4.9 Hz), which remained unchanged for 3 days at room temperature. To this solution was added 6.0 μL (0.049 mmol) of dimethyl acetylenedicarboxylate, after which a change of the ^{1}H NMR spectrum was observed for 1 day at room temperature.

Crystal Structure Determination. Crystals of **2**·acetone suitable for X-ray diffraction study were obtained by recrystallization from acetone−Et_2O and mounted in glass capillary tubes under argon. 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 the ω−2θ 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.[13] Three fluorine atoms were assigned to the two disordered positions (F2−F7) with 50:50 occupancy. A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotoropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. Crystallo-

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graphic data and details of refinement are summarized in Table 1.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan. T.Y. is grateful for the fellowship from JSPS (Japan Society for Promotion of Science).

Supporting Information Available: Table of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, and thermal parametere of **2**·acetone. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0000360