Vinyl- and Dienylpalladium Complexes Formed via Insertion of Alkyne into Sterically Hindered Pd–Aryl Bonds

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[PdI($C_6H_3Me_2$-2,6)(bpy)] reacts with excess amounts of dimethyl acetylenedicarboxylate to produce [PdI{CZ=CZ-($C_6H_3Me_2$-2,6)}(bpy)] (**2**, Z = COOMe) and [PdI{CZ=CZ–CZ=CZ($C_6H_3Me_2$-2,6)}(bpy)] (**3**). Crystallographic study revealed the molecular structures of **2** and **3** the latter of which has an *s*-trans dienyl ligand.

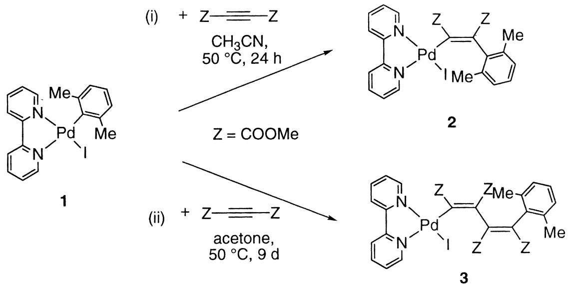
Insertion of a carbon–carbon triple bond into a transition metal–carbon bond is important since it is often involved as a crucial step in the transition metal complex catalyzed synthetic organic reactions and polymerization of the unsaturated molecules. Recently we reported the reaction of dimethyl acetylenedicarboxylate (DMAD) with Pd complexes having a 3,5-dimethylphenyl ligand, which led to insertion of one, two, or three molecules into the Pd–Ar bond depending on the reaction conditions.[1] Late transition metal complexes with a 2,6-dimethylphenyl ligand have attracted current attention owing to the stable metal–carbon bond and unique reactivity.[2] In this paper we report the reactions of DMAD with a 2,6-dimethylphenylpalladium(II) complex with a bipyridine ligand and the structures of the products.

Results and Discussion

The iodo arylpalladium(II) complex [PdI($C_6H_3Me_2$-2,6)-(bpy)] (**1**), prepared from the literature method,[3,4] reacts with excess amounts of DMAD at 50 °C and produces [PdI{CZ=CZ($C_6H_3Me_2$-2,6)}(bpy)] (**2**, Z = COOMe) and [PdI{CZ=CZ–CZ=CZ($C_6H_3Me_2$-2,6)}(bpy)] (**3**), as shown in Scheme 1. Complexes **2** and **3** were isolated from recrystallization of the products of the reactions (i) and (ii), respectively. Extremely low solubility of **3** in acetone helped its isolation from the reaction mixture containing the three Pd complexes. ^{1}H NMR analyses of the reaction mixture of DMAD (0.32 M) with **1** (0.043 M) in acetone-d_6 over 2 weeks revealed initial formation of **2** and its gradual conversion into **3**. The reaction (i) requires more severe conditions than insertion of a DMAD molecule into Pd–Ar bond of [PdI($C_6H_3Me_2$-3,5)(bpy)] (24 h at room temperature or a few hours at 50 °C). The reaction (ii) produces the dienylpalladium complex in 68% isolated yield after 9 d, whereas a similar reaction of DMAD with [PdI($C_6H_3Me_2$-3,5)(bpy)] at 50 °C gives the corresponding dienylpalladium complex in less than 20% yield after 6 days.

Figure 1 depicts molecular structures of **1–3** determined by X-ray crystallography. The 4-aryl-1,3-dienyl ligand of **3** has an *s*-trans structure as shown in Fig. 1c. It contrasts with the recently reported [Pd{CZ=CZ–CZ=CZ($C_6H_3Me_2$-3,5)}-(MeCN)(bpy)]$^+$ whose crystallographic study revealed an *s*-cis structure of the ligand and the presence of π–π interaction between the aryl group and the bpy ligand. The dihedral angle between aryl plane and the C–C double bond plane of **3** is large (114°), due to a steric repulsion between the *ortho* methyl and COOMe groups of the ligand.

Table 1 summarizes the ^{1}H and ^{13}C{^{1}H} NMR data of the complexes. The ^{1}H NMR spectrum of **3** exhibits the signals of aryl hydrogens of the 4-aryl-1,3-dienyl ligand at positions close to those of **1** and **2**. On the other hand, peak positions of the aryl hydrogens of [Pd{CZ=CZ–CZ=CZ($C_6H_3Me_2$-3,5)}-(MeCN)(bpy)]$^+$, having a π–π interaction between the bpy and



Scheme 1.

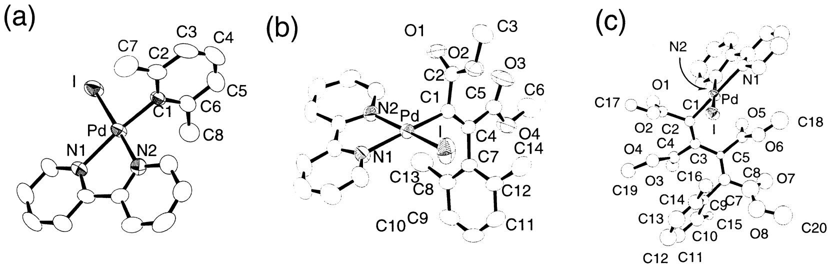


Fig. 1. ORTEP drawing of (a) **1**, (b) **2**, and (c) **3** (50% probability). Atoms except Pd and I of **3** are refined isotropically due to insufficient collected data/parameter ratio. Selected bond distances (Å) are summarized below. **1**: Pd–I 2.5718(8), Pd–N1 2.145(5), Pd–N2 2.064(5), Pd–C1 1.997(6). **2**: Pd–I 2.5577(7), Pd–N1 2.124(4), Pd–N2 2.084(4), Pd–C1 2.007(4). **3**: Pd–I 2.573(5), Pd–N1 2.16(3), Pd–N2 2.00(4), Pd–C1 1.95(4).

Table 1. ^{1}H and ^{13}C{^{1}H} NMR Data in $CDCl_3$

	^{1}H$^{a)}$								^{13}C{^{1}H}
	Ar			bpy				OCH_3	
	meta	para	CH_3	H^3, $H^{3'}$	H^4, $H^{4'}$	H^5, $H^{5'}$	H^6, $H^{6'}$		
1	6.8(m)	6.8(m)	2.63	8.05*	7.97(m)	7.53(m)	9.61(d, 5)		
				8.05*	7.95(m)	7.28(m)	7.41(d, 6)		
2	6.8(m)	7.0(m)	1.97	7.94(d, 8)	8.03(m)	7.58(m)	9.36(d, 6)	3.62,	174.2, 162.8, 158.2, 155.4, 154.1, 154.0, 153.7, 139.4, 139.1, 138.9, 135.5, 133.9, 127.7, 126.8, 126.7, 126.5, 126.2, 121.7, 121.6, 51.9, 22.3, 21.6
	7.0(m)		2.41	7.90(d, 7)	7.86(m)	7.24(m)	9.43(d, 5)	3.85	
3	6.64(d, 7)	6.87 (dd, 7, 7)	2.16	8.0*	8.0*	7.49(m)	9.81(d, 5)	3.16, 3.46	173.0, 168.7, 168.3, 163.5, 160.6, 154.7, 153.9, 152.9 139.6, 139.1, 138.8, 137.8, 136.8, 133.4,133.3, 128.3 127.6, 126.8, 126.7, 121.7, 121.3,52.4, 51.9, 51.9 51.5, 21.9, 21.1
	6.94(d, 7)		2.46	8.0*	8.0*	7.49(m)	8.58(d, 5)	3.61, 3.64	

a) Positions of the peaks with asterisks are not precise due to overlapping with other signals.

aryl group, and those of $[Pd\{CZ{=}CZ(C_6H_3Me_2\text{-}3,5)\}(MeCN)(bpy)]^+$ differ by ca. 0.4 ppm.[1] The above contrast of the NMR data suggests that the dienyl ligand of **3** prefers the *s*-trans structure and is free from the π–π interaction with the bpy ligand in solution.

The palladium complex with a sterically demanding aryl ligand, **1**, undergoes insertion of one or two DMAD molecules, although it requires heating at 50 °C for a long time. The presence of ortho methyl groups influences the reaction rate of the first and second insertion as well as structure of the insertion product.

Experimental

Complex **1** was prepared from the reaction of 2,6-dimethyliodobenzene with $[Pd(dba)_2]$[3] (dba = dibenzylideneacetone) in the presence of 2,2′-bipyridine and recrystallized from CH_2Cl_2–hexane (1.47 g, 41%).[4] Anal. Calcd for $C_{18}H_{17}IN_2Pd$: C, 43.71; H, 3.46; N, 5.66; I, 25.65%. Found: C, 43.67; H, 3.42; N, 5.73; I, 25.54%.

Preparation of 2. A mixture of $[PdI(C_6H_3Me_2\text{-}2,6)(bpy)]$ (197 mg, 0.398 mmol) and DMAD (0.60 cm^3, 4.9 mmol) in 6 cm^3 of dry CH_3CN was stirred for 1 day at 50 °C. Cooling the reaction mixture at room temperature caused separation of a yellow solid which was collected by filtration and recrystallized from CH_2Cl_2–hexane to give **2** (125 mg, 49%). Anal. Calcd for $C_{24}H_{23}IN_2O_4Pd$: C, 45.27; H, 3.64; N, 4.40; I, 19.93%. Found: C, 45.41; H, 3.64; N, 4.31; I, 19.65%.

Preparation of 3. A mixture of $[PdI(C_6H_3Me_2\text{-}2,6)(bpy)]$ (390 mg, 0.788 mmol) and DMAD (0.65 cm^3, 5.3 mmol) in 10 cm^3 of dry acetone was stirred for 9 days at 50 °C. Cooling the reaction mixture at room temperature caused separation of a yellow solid which was collected by filtration and recrystallized from CH_2Cl_2–hexane to give **3** (414 mg, 68%). Anal. Calcd for $C_{30}H_{29}IN_2O_8Pd$: C, 46.26; H, 3.75; N, 3.60; I, 16.29%. Found: C, 46.34; H, 3.75; N, 3.60; I, 16.33%.

Crystal Structure Determination. Crystals of **1**–**3** suitable for X-ray diffraction study were mounted in glass capillary tubes under argon. Intensities were collected on a Rigaku AFC-5R or -7R automated four-cycle diffractometers by using Mo-$K\alpha$ radiation (λ = 0.71069 Å) and ω-2θ scan method, and an empirical absorption correction (ψ scan) was applied. Calculations were carried out using a program package TEXSAN for Windows. **1** ($C_{18}H_{17}IN_2Pd$): 1.03 × 0.70 × 0.15 mm, $M_r = 494.65$, monoclinic, $P2_1/n$, $a = 9.583(1)$, $b = 12.148(1)$, $c = 15.074(2)$ Å, $\beta = 95.39(1)°$, $V = 1747.1(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.880$ g cm^{-3}, $\mu = 2.828$ mm^{-1}, $F(000) = 952$, $R(R_w) = 0.038(0.038)$ for 2744 reflections with $I > 3\sigma(I)$. **2** ($C_{24}H_{23}IN_2O_4Pd$): 0.55 × 0.43 × 0.25 mm, $M_r = 636.76$, monoclinic, $P2_1/n$, $a = 10.172(2)$, $b = 15.527(2)$, $c = 15.454(3)$ Å, $\beta = 100.86(2)°$, $V = 2397.0(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.764$ g cm^{-3}, $\mu = 2.095$ mm^{-1}, $F(000) = 1248$, $R(R_w) = 0.034(0.024)$ for 3645 reflections with $I > 3\sigma(I)$. **3** ($C_{30}H_{29}IN_2O_8Pd$): 0.24 × 0.18 × 0.11 mm, $M_r = 778.87$, triclinic, $P\bar{1}$, $a = 11.154(7)$, $b = 17.39(1)$, $c = 8.650(6)$ Å, $\alpha = 99.62(5)$, $\beta = 96.75(6)$, $\gamma = 71.91(6)°$, $V = 1569(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.649$ g cm^{-3}, $\mu = 1.627$ mm^{-1}, $F(000) = 772$, $R(R_w) = 0.123(0.127)$ for 1920 reflections with $I > 3\sigma(I)$.

All the data of the crystallographic study except F_o-F_c tables are deposited as Document No. 74044 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data are deposited also at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 163005 and 163006.

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