## Dinuclear Addition of the Pd–Pd Moieties to 1,3-Dienes

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The reaction of a substitutionally labile dipalladium(I) complex  $[Pd_2(CH_3CN)_6][BF_4]_2$  with isoprene or 1,3-butadiene in acetonitrile afforded  $[Pd_2(\mu-\eta^3:\eta^1-C_5H_8)(CH_3CN)_5][BF_4]_2$  or  $[Pd_2(\mu-\eta^3:\eta^1-C_4H_6)(CH_3CN)_5][BF_4]_2$ . The structure of the isoprene complex was determined by X-ray crystallographic analyses. The interconversion between the  $[Pd_2(\mu-\eta^3:\eta^1-C_5H_8)-(CH_3CN)_5][BF_4]_2$  and  $[Pd_2(\mu-\eta^2:\eta^2-C_5H_8)(\mu-Cl)Cl_2][PPh_4]$  occurred facilely.

Coordination of 1,3-dienes to a mononuclear palladium center has been intensively studied in conjunction with the palladium-catalyzed transformation of those substrates.<sup>1,2</sup> However, the coordination of 1,3-dienes to a Pd-Pd bonded center has not been fully understood. Several dipalladium complexes containing  $\mu$ - $\eta^2$ : $\eta^2$ -1,3-diene ligands have been isolated, and some of those were structurally characterized by X-ray crystallographic studies.<sup>3,4</sup> On the other hand, the dinuclear addition of Pd-Pd bonded moieties to 1,3-dienes has not been reported.<sup>5</sup> We recently reported that the dinuclear addition of  $[Pd_2L_n]^{2+}$  (L = acetonitrile) to 1,3,5-trienes proceeds smoothly to afford the bi- $\eta^3$ -allyl type dipalladium complexes  $[Pd_2{R(CH=CH)_3R}]L_4[PF_6]_2$  $(R = Ph and t-Bu).^{6}$  Through a mechanistic study including demonstration of highly stereospecific nature of the reverse reactions; i.e. dinuclear elimination reactions, we proposed that the dimetalla- $[4\pi + 2\sigma]$  Diels-Alder type process is possibly involved in the dinuclear addition reactions of 1,3,5-trienes (Scheme 1).<sup>6b</sup> While the initial product of such  $[4\pi + 2\sigma]$  addition may readily be converted to the more stable bi- $\eta^3$ -allyl form, it seems of considerable interest to examine what type of structure is taken by an analogous  $[4\pi + 2\sigma]$  adduct involving 1.3-diene, particularly because the  $\eta^1$ -allylpalladium is usually a less stable species.<sup>7</sup> Herein, we report that the reaction of  $[Pd_2(CH_3CN)_6][BF_4]_2$  (1)<sup>8</sup> with 1,3-dienes in acetonitrile afforded the  $\mu$ - $\eta^3$ : $\eta^1$ -1,3-diene dipalladium complexes.

The reaction of **1** with excess amount of isoprene in CD<sub>3</sub>CN at room temperature afforded  $[Pd_2(\mu-\eta^3:\eta^1-C_5H_8)(CH_3CN)_5]$ - $[BF_4]_2$  (**2**) almost quantitatively (eq 1).<sup>9</sup> No other isomer was formed. A considerable sp<sup>3</sup>-hybridized character at the CH*CH*<sub>2</sub> terminal carbon is suggested by the geminal coupling constant (J = 6.6 Hz), as well as the high-field shifted <sup>13</sup>C{<sup>1</sup>H} resonance ( $\delta = 18.3$  ppm). The complex **2** was isolated in 55% yield after recrystallization from CH<sub>3</sub>CN/Et<sub>2</sub>O, and a single crystal suitable for X-ray structure analysis was obtained by recrystallization from CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>/benzene. The molecular structure of **2** is



Scheme 1.

shown in Figure 1.<sup>10</sup> The Pd–Pd bond in **1** was cleaved during the formation of **2**. Two palladium atoms are located at the opposite faces of the pseudo-plane composed of the diene carbons (C1, C2, C3, and C4). The isoprene ligand coordinated to the Pd<sub>2</sub> moiety in a  $\mu$ - $\eta^3$ : $\eta^1$ -mode. As expected, the C3–C4 bond length (1.488(8) Å) is longer than the C1–C2 and C2–C3 bond lengths (1.411(8) and 1.407(7) Å) due to its C–C single-bond character.



The reaction of **1** with 1,3-butadiene in CH<sub>3</sub>CN afforded  $[Pd_2(\mu-\eta^3:\eta^1-C_4H_6)(CH_3CN)_5][BF_4]_2$  (**3**) as a mixture of two isomers (49% isolated yield after recrystallization from CH<sub>3</sub>CN/Et<sub>2</sub>O, *syn/anti* = 93/7 at -40 °C). The *syn-* or *anti*-allyl structure in each isomer was assumed by the *J*-coupling constants in the <sup>1</sup>H NMR spectra;  $J_{Hc-Hd} = 11.9$  Hz for syn isomer,  $J_{Hc-Hd} = 7.9$  Hz for anti isomer (see Scheme 2 for the labels of the butadiene protons).<sup>11</sup> It should be noted that the isoprene complex **2** contained only syn isomer in CD<sub>3</sub>CN solution, as was confirmed by difference NOE measurements. Relatively large geminal coupling constant at one of the butadiene termini was observed (J = 5.6 Hz). Raising the temperature from



**Figure 1.** ORTEP drawing of  $[Pd_2(\mu-\eta^3:\eta^1-C_5H_8)(CH_3CN)_5]$ -[BF<sub>4</sub>]<sub>2</sub> (**2**) (50% probability ellipsoids, BF<sub>4</sub> anions were omitted for clarity). Selected bond lengths (Å): Pd1–C1 2.094(6), Pd1– C2 2.132(5), Pd1–C3 2.162(5), Pd2–C4 2.041(5), Pd1–N1 2.091(5), Pd1–N2 2.103(5), Pd2–N3 2.001(5), Pd2–N4 2.041(5), Pd1–N5 1.999(5), C1–C2 1.411(8), C2–C3 1.407(7), C3–C4, 1.488(8), C2–C5 1.472(7).



Scheme 2. Interconversion between  $\mu$ - $\eta^3$ : $\eta^1$ - and  $\mu$ - $\eta^1$ : $\eta^3$ - complexes (3-syn).

-40 °C resulted in the coalescence of the four proton resonances (H<sub>a</sub>, H<sub>b</sub>, H<sub>e</sub>, and H<sub>f</sub>) and two proton resonances (H<sub>c</sub> and H<sub>d</sub>) at around 40 °C, and two broad resonances ( $\delta$  3.2 and 5.2 ppm) with relative intensities of 2:1 appeared at 70 °C. This temperature-dependent NMR behavior can be explained by the occurrence of rapid exchange between  $\mu$ - $\eta^3$ : $\eta^1$ -mode and  $\mu$ - $\eta^1$ : $\eta^3$ -mode, through a di- $\sigma$ -bonded intermediate, as depicted in Scheme 2.

Then, we examined the transformation of the  $\mu$ - $\eta^3$ : $\eta^1$ -complexes synthesized here to the  $\mu$ - $\eta^2$ : $\eta^2$ -complexes. When the isoprene complex **2** was treated with [PPh<sub>4</sub>]Cl (3 equiv.), the known  $\mu$ - $\eta^2$ : $\eta^2$ -isoprene trichloride complex [Pd<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ - $C_5H_8$ )( $\mu$ -Cl)Cl<sub>2</sub>][PPh<sub>4</sub>] (**4**)<sup>3c</sup> containing a Pd–Pd bond was formed almost quantitatively. Addition of AgBF<sub>4</sub> (3 equiv.) to the complex **4** in CD<sub>3</sub>CN gave the complex **2** in a quantitative manner (eq 2). During the interconversion of eq 2, the dimetalla-[ $4\pi$  +  $2\sigma$ ] process is probably involved. Similarly to the Pd–Pd bond formation in the forward reaction of eq 2, the dinuclear elimination of a [Pd–Pd]<sup>2+</sup> moiety was observed to take place from the bi- $\eta^3$ -allyl dipalladium(II) complexes (i.e. the reverse reaction of Scheme 1), although no Pd–Pd complex having  $\mu$ - $\eta^2$ : $\eta^2$ -bound triene ligand was detected.<sup>6b</sup>



In summary, it has been proven that the dinuclear addition of a  $[Pd_2L_n]^{2+}$  moiety to isoprene or 1,3-butadiene takes place to afford the  $\mu$ - $\eta^3$ : $\eta^{1-1}$ .3-diene dipalladium complexes.

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- 9 Synthesis of **2**: To a solution of **1** (94.4 mg, 0.149 mmol) in CH<sub>3</sub>CN was added isoprene (60.0 µL, 0.600 mmol) and the mixture stirred for 30 min at room temperature. The yellow reaction mixture was filtered. Recrystallization from CH<sub>3</sub>CN/Et<sub>2</sub>O gave yellow microcrystals of **2** (53.3 mg, 55% yield). <sup>1</sup>H NMR data (CD<sub>3</sub>CN) for **2** :  $\delta$  4.26 (dd, J = 11.4 Hz, J = 5.7 Hz, 1H), 3.93 (s, 1H), 2.86 (s, 1H), 2.78 (dd, J = 11.4 Hz, J = 6.6 Hz, 1H), 2.07 (s, 3H). <sup>13</sup>C<sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  130.0 (C<sub>2</sub>), 118.3 (CH<sub>3</sub>CN), 89.4 (C<sub>3</sub>), 61.9 (C<sub>1</sub>), 19.2 (CH<sub>3</sub>), 18.3 (C<sub>4</sub>). Anal. Calcd for C<sub>15</sub>H<sub>23</sub>N<sub>5</sub>B<sub>2</sub>F<sub>8</sub>Pd<sub>2</sub>: C, 27.30; H, 3.51; N, 10.61%. Found: C, 27.24; H, 3.57; N, 10.66%.
- 10 Crystal data for **2**:  $C_{15}H_{23}Pd_2B_2F_8N_5$ ,  $M_r$  659.79, space group  $P2_1/n$  (No. 14), a = 13.3229(4) Å, b = 10.3235(2)Å, c = 17.5397(5) Å,  $\beta = 92.6824(8)^\circ$ , V = 2409.7(1) Å<sup>3</sup>, Z = 4, F(000) = 1288,  $D_{calcd} = 1.818$  g cm<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 15.66 cm<sup>-1</sup>, 289 variables refined with 3774 reflections with  $I > 3\sigma(I)$  to R = 0.034.
- 11 Synthesis of **3**: To a solution of **1** (113.4 mg, 0.179 mmol) in CH<sub>3</sub>CN was bubbled 1,3-butadiene gas for 5 min and the mixture stirred for 30 min at room temperature. The yellow reaction mixture was filtered. Recrystallization from CH<sub>3</sub>CN/Et<sub>2</sub>O gave yellow microcrystals of **3** (56.4 mg, 49% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN, -40 °C) for **3-syn**:  $\delta$  5.73 (ddd, J = 12.0 Hz, J = 6.8 Hz, J = 11.9 Hz, 1H), 4.41 (ddd, J = 11.9 Hz, J = 5.3 Hz, J = 12.1 Hz, 1H), 4.00 (d, J = 6.8 Hz, 1H), 3.00 (d, J = 12.0 Hz, 1H), 2.72 (dd, J = 12.1 Hz, 5.6Hz, 1H), 2.66 (dd, J = 5.3 Hz, 5.6Hz, 1H). <sup>1</sup>H NMR (CD<sub>3</sub>CN, -40 °C) for **3-anti**:  $\delta$  5.56 (dt, J = 12.1 Hz, J = 7.9 Hz, 1H), 5.35 (ddd, 1H), 4.07 (d, J = 7.9 Hz, 1H), 3.41 (d, J = 12.1 Hz, 1H), 2.3 (m). Anal. Calcd for C<sub>14</sub>H<sub>21</sub>N<sub>5</sub>B<sub>2</sub>F<sub>8</sub>Pd<sub>2</sub>: C, 26.04; H, 3.28; N, 10.84%. Found: C, 25.26; H, 3.35; N, 10.58%.