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

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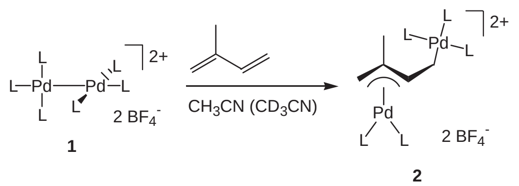
The reaction of a substitutionally labile dipalladium(I) complex $[Pd_2(CH_3CN)_6][BF_4]_2$ with isoprene or 1,3-butadiene in acetonitrile afforded $[Pd_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_5H_8)(CH_3CN)_5][BF_4]_2$ or $[Pd_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_4H_6)(CH_3CN)_5][BF_4]_2$. The structure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

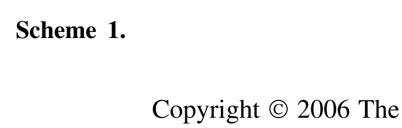
Coordination of 1,3-dienes to a mononuclear palladium center has been intensively studied in conjunction with the palladium-catalyzed transformation of those substrates.[1,2] However, the coordination of 1,3-dienes to a Pd–Pd bonded center has not been fully understood. Several dipalladium complexes containing $\mu\text{-}\eta^2{:}\eta^2$-1,3-diene ligands have been isolated, and some of those were structurally characterized by X-ray crystallographic studies.[3,4] On the other hand, the dinuclear addition of Pd–Pd bonded moieties to 1,3-dienes has not been reported.[5] 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-η^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).[6b] While the initial product of such $[4\pi + 2\sigma]$ addition may readily be converted to the more stable bi-η^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 η^1-allylpalladium is usually a less stable species.[7] Herein, we report that the reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**)[8] with 1,3-dienes in acetonitrile afforded the $\mu\text{-}\eta^3{:}\eta^1$-1,3-diene dipalladium complexes.

The reaction of **1** with excess amount of isoprene in CD_3CN at room temperature afforded $[Pd_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_5H_8)(CH_3CN)_5][BF_4]_2$ (**2**) almost quantitatively (eq 1).[9] No other isomer was formed. A considerable sp^3-hybridized character at the CH*CH*$_2$ terminal carbon is suggested by the geminal coupling constant ($J = 6.6$ Hz), as well as the high-field shifted $^{13}C\{^1H\}$ resonance ($\delta = 18.3$ ppm). The complex **2** was isolated in 55% yield after recrystallization from CH_3CN/Et_2O, and a single crystal suitable for X-ray structure analysis was obtained by recrystallization from CH_3CN/CH_2Cl_2/benzene. The molecular structure of **2** is shown in Figure 1.[10] 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_2 moiety in a $\mu\text{-}\eta^3{:}\eta^1$-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.



(1)

The reaction of **1** with 1,3-butadiene in CH_3CN afforded $[Pd_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_4H_6)(CH_3CN)_5][BF_4]_2$ (**3**) as a mixture of two isomers (49% isolated yield after recrystallization from CH_3CN/Et_2O, *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 ^{1}H NMR spectra; $J_{Hc\text{–}Hd} = 11.9$ Hz for syn isomer, $J_{Hc\text{–}Hd} = 7.9$ Hz for anti isomer (see Scheme 2 for the labels of the butadiene protons).[11] It should be noted that the isoprene complex **2** contained only syn isomer in CD_3CN 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



Scheme 1.

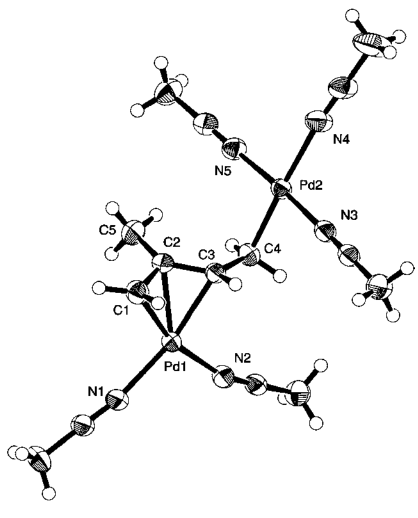
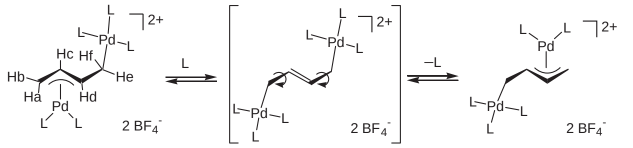


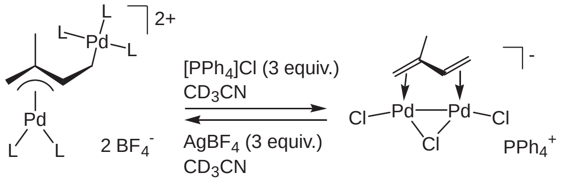
Figure 1. ORTEP drawing of $[Pd_2(\mu\text{-}\eta^3{:}\eta^1\text{-}C_5H_8)(CH_3CN)_5][BF_4]_2$ (**2**) (50% probability ellipsoids, BF_4 anions were omitted for clarity). Selected bond lengths (Å): Pd1–C1 2.094(6), Pd1–C2 2.132(5), Pd1–C3 2.162(5), Pd2–C4 2.041(5), Pd1–N1 2.091(5), Pd1–N2 2.103(5), 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 μ-η^3:η^1- and μ-η^1:η^3-complexes (**3-syn**).

−40 °C resulted in the coalescence of the four proton resonances (H_a, H_b, H_e, and H_f) and two proton resonances (H_c and H_d) at around 40 °C, and two broad resonances (δ 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 μ-η^3:η^1-mode and μ-η^1:η^3-mode, through a di-σ-bonded intermediate, as depicted in Scheme 2.

Then, we examined the transformation of the μ-η^3:η^1-complexes synthesized here to the μ-η^2:η^2-complexes. When the isoprene complex **2** was treated with $[PPh_4]Cl$ (3 equiv.), the known μ-η^2:η^2-isoprene trichloride complex $[Pd_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_5H_8)(\mu\text{-}Cl)Cl_2][PPh_4]$ (**4**)[3c] containing a Pd–Pd bond was formed almost quantitatively. Addition of $AgBF_4$ (3 equiv.) to the complex **4** in CD_3CN 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 $[Pd–Pd]^{2+}$ moiety was observed to take place from the bi-η^3-allyl dipalladium(II) complexes (i.e. the reverse reaction of Scheme 1), although no Pd–Pd complex having μ-η^2:η^2-bound triene ligand was detected.[6b]



2 **4** (2)

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 μ-η^3:η^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_3CN 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_3CN/Et_2O gave yellow microcrystals of **2** (53.3 mg, 55% yield). ^1H NMR data (CD_3CN) for **2** : δ 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), 2.64 (dd, $J = 5.7$ Hz, $J = 6.6$ Hz, 1H), 2.07 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 130.0 (C_2), 118.3 (CH_3CN), 89.4 (C_3), 61.9 (C_1), 19.2 (CH_3), 18.3 (C_4). Anal. Calcd for $C_{15}H_{23}N_5B_2F_8Pd_2$: 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, $\beta = 92.6824(8)°$, $V = 2409.7(1)$ Å^3, $Z = 4$, $F(000) = 1288$, $D_{calcd} = 1.818\ g\,cm^{-3}$, $\mu(Mo\ K\alpha) = 15.66\ cm^{-1}$, 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_3CN 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_3CN/Et_2O gave yellow microcrystals of **3** (56.4 mg, 49% yield). ^1H NMR (CD_3CN, −40 °C) for **3-syn**: δ 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, 5.6 Hz, 1H), 2.66 (dd, $J = 5.3$ Hz, 5.6 Hz, 1H). ^1H NMR (CD_3CN, −40 °C) for **3-anti**: δ 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 $C_{14}H_{21}N_5B_2F_8Pd_2$: C, 26.04; H, 3.28; N, 10.84%. Found: C, 25.26; H, 3.35; N, 10.58%.