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Reversible Interconversion between Dinuclear Sandwich and Half-Sandwich Complexes: Unique Dynamic Behavior of a Pd−Pd Moiety Surrounded by an sp^2-Carbon Framework

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Elucidation of the chemical behavior of an assembly of multiple metals bound on sp- or sp^2-carbon networks is crucial in understanding and development of carbon-supported metal catalysts or metal-containing organic functional materials.[1,2] Several approaches along this line have been previously made, typically using (oligo)fulvalenes[2d−e,3] or π-conjugated linear polyenes[4,5] as a carbon network having long-scale pπ-conjugation. There are two primary aggregation forms, sandwich and half-sandwich complexes with such carbon networks. While both are known to exhibit unique properties within the framework of each form, some remarkably new chemical behavior would be expected to arise if a dynamic interconversion is introduced between the two forms. Herein, we reveal a novel interconversion between the sandwich and half-sandwich systems which involves making and breaking of metal−metal bonds, by utilizing a 1,3,5-triene-Pd$_2$ combination, the new and smallest member of the recently developed polyene-Pd$_n$ sandwich chain compounds.[5]

The reaction of a Pd−Pd single-bonded complex [Pd$_2$(CH$_3$CN)$_6$][BF$_4$]$_2$[6] with excess *all-trans*-DPHT (= 1,6-diphenyl-1,3,5-hexatriene) in CH$_2$Cl$_2$ afforded the red-colored sandwich dipalladium complex [Pd$_2$(μ-η^3: η^3-DPHT)$_2$][BF$_4$]$_2$ (**1-meso**) in 77% yield after recrystallization (eq 1). The structure of **1-meso** was determined by X-ray structure analysis (Figure 1). Each unit cell contained two independent molecules (**1A** and **1B**) having quite similar structures. The Pd−Pd lengths (2.9156(6) Å for **1A**/2.9400(5) Å for **1B**) were in the range of a Pd−Pd-bonding interaction.[7] The terminal phenyl rings were face-to-face stacking over each other via mean separations of 3.48 Å for **1A**/3.38 Å for **1B**. Each Pd is formally in the +III oxidation state.[8] However, the trend in the C−C bond lengths at DPHT, with particular attention to the central C3−C4* length, is different from that of a Pd$_2$−DPHT half-sandwich complex described below where DPHT acts as a more genuine bi-η^3-allyl ligand, but retains that of the original DPHT to some extent.[9] Furthermore, ^{1}H and ^{13}C NMR spectra of **1-meso** in CD$_2$Cl$_2$[10] showed the considerably lower-field shifted triene terminal H1 protons (δ 6.65) and C1 carbons (δ 129.45) compared to those of typical bis-η^3-allyl Pd species.[11] The C−H coupling constants of **1-meso** (C1 158.2 Hz, C2 166.4 Hz, C3 165.8 Hz) indicated that the coordinated triene-part maintains nearly sp^2-character at the carbon atoms. Thus, the structural and spectroscopic aspects give little support to bi-η^3-allyl dianion character for each DPHT ligand of **1-meso** despite the obvious μ-η^3: η^3-coordination mode, and suggest considerable contribution of the less-reduced DPHT ligands lying on the Pd−Pd unit.[12]

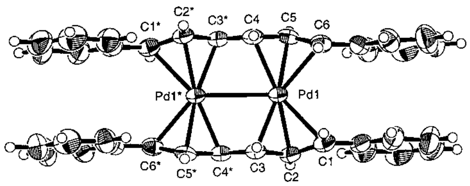
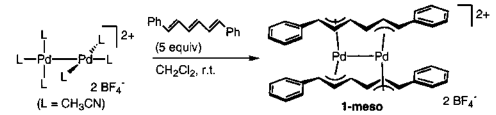


Figure 1. ORTEP drawing of **1-meso** (Only one of the two independent molecules in a unit cell (**1A**) was shown, 50% probability, BF$_4$ anions were omitted for clarity). Selected bond lengths (Å). Pd1−Pd1* 2.9156(6), Pd1−C1 2.378(4), Pd1−C2 2.176(3), Pd1−C3 2.193(3), Pd1−C4 2.231(3), Pd1−C5 2.168(3), Pd1−C6 2.355(4), C1−C2 1.376(6), C2−C3 1.424(5), C3−C4* 1.395(5), C4−C5 1.430(5), C5−C6 1.385(5).



(1)

When the solvent of eq 1 was changed to CH$_3$CN, the yellow-colored half-sandwich complex [Pd$_2$(η^3: η^3-DPHT)(CH$_3$CN)$_4$][BF$_4$]$_2$ (**2**) was obtained as a mixture of two isomers (the ratio 78/22 for **2** in CD$_3$CN at 23 °C) (eq 2). The major isomer was isolated (55% yield for **2**) by recrystallization from the mixture, and its structure was identified as **2-antifacial** by X-ray structure analysis (Figure 2). Two Pd atoms are bound on the opposite faces of the *all-trans*-DPHT framework through η^3-allyl coordination mode. The central C3−C3* length (1.474(7) Å), which emphasizes the C−C single bond character, is in accordance with the 2e-reduced state of DPHT which forms bi-η^3-allyl substructure in **2-antifacial**. The minor isomer showed the ^{1}H and ^{13}C NMR patterns and chemical shifts similar to those of **2-antifacial**.[13] The symmetric DPHT signal pattern of this isomer rules out a possibility of the η^3-η^1-η^3-allyl interconverted diastereomeric

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[1] For selected recent examples: (a) Chambers, A.; Nemes, T.; Rodriguez, N. M.; Baker, R. T. K. *J. Phys. Chem. B.* **1998**, *102*, 2251. (b) Pham-Huu, C.; Keller, N.; Charbonniere, L. J.; Ziessel, R.; Ledoux, M. J. *J. Chem. Soc., Chem. Commun.* **2000**, 1871. (c) Sloan, J.; Hammer, J.; Zwiefka-Sibley, M.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1998**, 347.

[2] For recent reviews: (a) Kingsborough, R. P.; Swager, T. M. *Adv. Inorg. Chem.* **1999**, *48*, 123. (b) Nguyen, P.; Gômez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515. (c) Lehn, J.-M. *Supramolecular Chemistry*, VCH: Weinheim, 1995. (d) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637. (e) Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383.

[3] For selected examples: (a) Vollhardt, K. P. C.; Cammack, J. K.; Matzger, A. J.; Bauer, A.; Capps, K. B.; Hoff, C. D. *Inorg. Chem.* **1999**, *38*, 2624. (b) Boese, R.; Cammack, J. K.; Matzger, A. J.; Pflug, K.; Tolman, W. B.; Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1997**, *119*, 6757. (c) Boese, R.; Myrabo, R. L.; Newman, D. A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 549.

[4] For metal−polyene (triene or longer polyene) systems: (a) Whitlock, H. W.; Reich, C.; Woessner, W. D. *J. Am. Chem. Soc.* **1971**, *93*, 2483. (b) Wadepohl, H.; Büchner, K.; Pritzkow, H. *Organometallics* **1989**, *8*, 2745. (c) Adams, R. D.; Wu, W. *Organometallics* **1993**, *12*, 1243. (d) Mashima, K.; Fukumoto, H.; Tani, K.; Haga, M.; Nakamura, A. *Organometallics* **1998**, *17*, 410. (e) Weng, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1998**, *17*, 4240.

[5] Murahashi, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H. *J. Am. Chem. Soc.* **1999**, *121*, 10660.

[6] Murahashi, T.; Nagai, T.; Okuno, T.; Matsutani, T.; Kurosawa, H. *J. Chem. Soc., Chem. Commun.* **2000**, 1689.

[7] Murahashi, T.; Otani, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H.; Sakaki, S. *J. Am. Chem. Soc.* **1998**, *120*, 4536 and references therein.

[8] In the related edge-sharing bi-square-planar dinuclear complexes, some are defined as Pt(III)−Pt(III) rather than Pt(I)−Pt(I): (a) Usón, R.; Forniés, J.; Falvello, L. R.; Tomás, M.; Casas, J. M.; Martín, A.; Cotton, F. A. *J. Am. Chem. Soc.* **1994**, *116*, 7160. (b) Alonso, E.; Casas, J. M.; Cotton, F. A.; Feng, X.; Forniés, J.; Fortuño, C.; Tomas, M. *Inorg. Chem.* **1999**, *38*, 5034. For Pd(I)−Pd(I): (c) Kostic, N. M.; Fenske, R. F. *Inorg. Chem.* **1983**, *22*, 666. Pd(III) complexes are very rare: recently, a dipalladium(III) complex with bi-octahedral geometry was structurally characterized; (d) Cotton, F. A.; Gu, J.; Murillo, C. A.; Timmons, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 13280.

[9] Benet-Buchholtz, J.; Boese, R.; Haumann, T. In *The Chemistry of Dienes and Polyenes*; Rappoport, Z., Ed.; John Wiley & Sons: New York, 1997; pp 25−65.

[10] (a) Selected NMR data for **1-meso**: ^{1}H NMR (CD$_2$Cl$_2$) δ 6.76 (d, J = 13.8 Hz, 4H, H$_1$) 5.26 (m, 4H, H$_2$) 3.98 (m, 4H, H$_3$). ^{13}C NMR (CD$_2$Cl$_2$) δ 129.5 (s, C1) 98.9 (s, C2) 93.1 (s, C3). (b) For **1-rac**: ^{1}H NMR (CD$_2$Cl$_2$) δ 5.95 (d, J = 13.5 Hz, 4H, H$_1$) 5.79 (m, 4H, H$_2$) 3.67 (m, 4H, H$_3$).

[11] Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J. C.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 425.

[12] The electronic structure of **1** is still elusive without completion of high level molecular orbital calculations.

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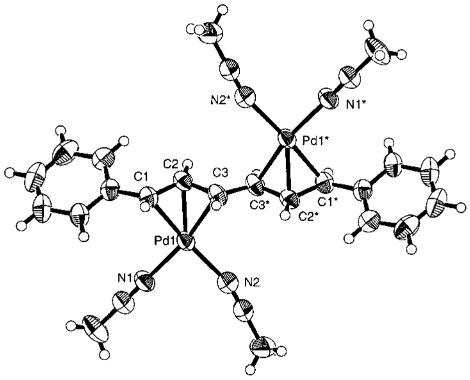


Figure 2. ORTEP drawing of **2-antifacial** (50% probability, BF_4 anions were omitted for clarity). Selected bond lengths (Å) Pd1−C1 2.132(4), Pd1−C2 2.129(4), Pd1−C3 2.128(4), C1−C2 1.393(5), C2−C3 1.411(5), C3−C3* 1.474(7).

Chart 1

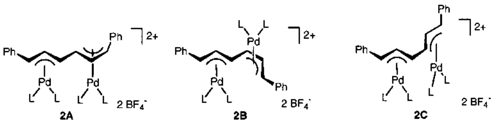
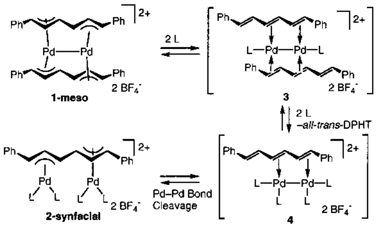
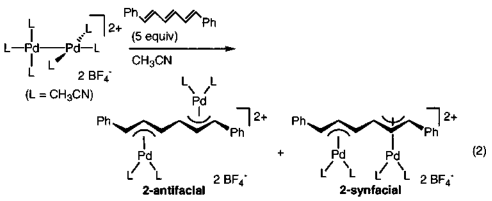


Chart 2

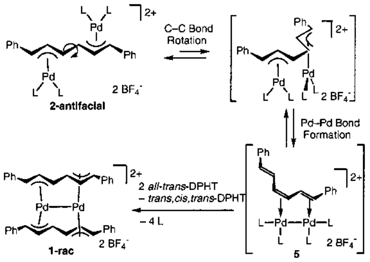


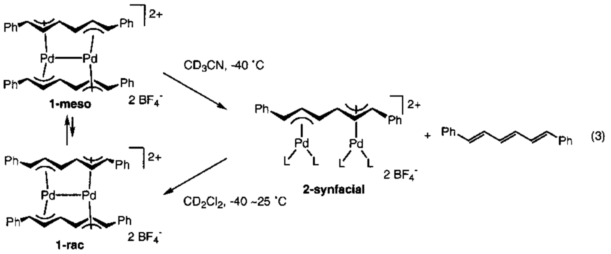
isomer of **2-antifacial** such as **2A** or **2B** (Chart 1). This, together with the characteristic reactivities of the two isomers with DPHT described below, led us to assume the structure of the minor isomer as **2-synfacial** (eq 2), rather than a rotational isomer of **2-antifacial** (**2C** in Chart 1). In eq 2, triene acts as a 2e-oxidant[4b] and Pd−Pd bond in $[Pd_2(CH_3CN)_6]^{2+}$ is cleaved.



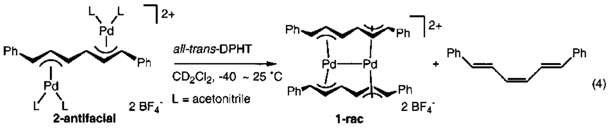
Then, we examined the interconversion between the obtained sandwich and half-sandwich dipalladium complexes. When **1-meso** was dissolved in CD_3CN at −40 °C, one of the DPHT ligands was replaced by four acetonitrile ligands to form **2-synfacial** quantitatively (eq 3).[14] Although no intermediate was observed during this reaction, it would be reasonable to assume that initially two acetonitrile ligands coordinate to the Pd−Pd center to afford μ-η^2:η^2-sandwich intermediate[7] (**3**) (Chart 2). Then one π-bound DPHT ligand would be replaced by additional acetonitrile ligands, and the resulting mono-μ-η^2:η^2-DPHT Pd−Pd complex **4** would rearrange to **2-synfacial** exclusively via Pd−Pd bond cleavage.

Chart 3





When **2-synfacial** thus formed and *all-trans*-DPHT (5 equiv) were co-dissolved in CD_2Cl_2 at −40 °C, the four acetonitrile ligands were immediately replaced by DPHT to generate **1-rac** as a kinetic product (eq 3).[15] Ultimately, **1-rac** isomerized to **1-meso** within 3 h at 23 °C (**1-rac**/**1-meso** = 2/98) (eq 3).[16] Interestingly, the similar treatment of **2-antifacial** with *all-trans*-DPHT afforded not only **1-rac** but *trans,cis,trans*-DPHT (86% NMR yield) (eq 4), the latter of which was never found in the corresponding reaction of **2-synfacial**.[17] This observation strongly suggests that the coordinated DPHT in **2-antifacial** is replaced by *all-trans*-DPHT *in a stereoretentive manner*. Probably, as depicted in Chart 3, the reaction began with C−C bond rotation of **2-antifacial** to bring two Pd atoms close to facilitate Pd−Pd bond formation, yielding an intermediate **5**. The *trans,cis,trans*-DPHT ligand of **5** would then be replaced by *all-trans*-DPHT to lead to **3**, and eventually to **1-rac**.



In summary, we prepared the dinuclear metallo-sandwich and half-sandwich compounds of the triene−Pd_2 combination, and revealed the reversibly interconverting process between them. These new aspects might represent a case where the electronic state of the multiple metal unit, for example the presence or absence of the metal−metal bonding, depends significantly on the number of the contacting sp^2-carbon frameworks.

Supporting Information Available: Characterization data and crystallographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Selected NMR data for **2-antifacial**: ^1H NMR (CD_3CN) δ 7.70 (d, J = 7.3 Hz, 4H, *o*-Ph), 6.57 (br t, 2H, H_2), 5.21 (d, J = 11.1 Hz, 2H, H_1), 4.46 (br d, 2H, H_3). ^{13}C NMR (CD_3CN) δ 110.4 (s, C_2) 83.7 (s, C_1), 78.5 (s, C_3). For **2-synfacial**: ^1H NMR (CD_3CN) δ 7.78 (d, J = 7.8 Hz, 4H, *o*-Ph), 6.89 (br t, 2H, H_2), 5.17 (d, J = 11.1 Hz, 2H, H_1), 4.46 (br d, 2H, H_3). ^{13}C NMR (CD_3CN) δ 108.0 (s, C_2) 83.2 (s, C_1), 76.0 (s, C_3).

(14) **2-synfacial** isomerized to the equilibrium mixture of **2-synfacial/2-antifacial** (22/78) within 24h in CD_3CN at 23 °C. This spontaneous isomerization cannot be simply explained by the conventional η^3-η^1-η^3 allyl interconversion mechanism. The mechanistic study will be reported in a future article.

(15) The formation of another minor product (28% at 25 °C from **2-synfacial** and 23% at 25 °C from **2-antifacial**) was observed. Although its structure has been still elusive, it showed two sets of nonequivalent DPHT ligands (12 nonaromatic C*H* protons), and is tentatively assigned as $[Pd_2(\mu\text{-}\eta^3\text{:}\ \eta^3\text{-DPHT})(\mu\text{-DPHT})(CH_3CN)]^{2+}$ (see Supporting Information).

(16) This suggests that **1-meso** is thermodynamically more stable than **1-rac**. On the other hand, meso-isomer is minor in typical mononuclear bis-η^3-allyl Pd complexes such as $Pd(\eta^3\text{-}C_3H_5)_2$ (meso/racemic 30/70).[11]

(17) Other *cis*-DPHTs such as *trans,trans,cis*-DPHT were not observed.