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Stereoretentive Elimination and Trans-olefination of the Dicationic Dipalladium Moiety $[Pd_2L_n]^{2+}$ Bound on 1,3,5-Trienes

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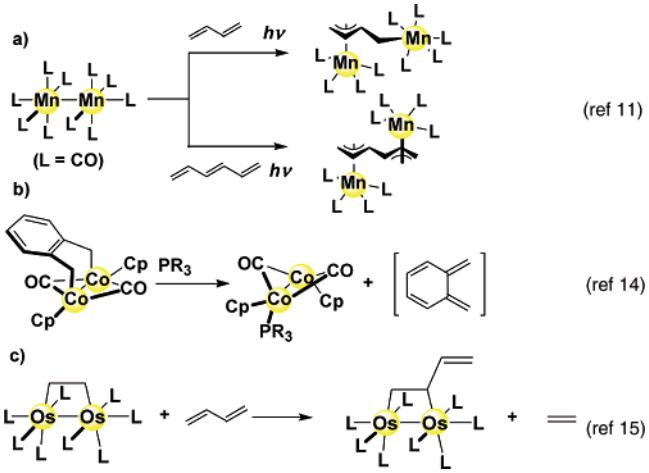
Abstract: The reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**) with 1,3,5-hexatriene, 1,6-diphenyl-1,3,5-hexatriene (DPHT), or 2,2,9,9-tetramethyl-3,5,7-decatriene (DBHT) afforded bi-η^3-allyldipalladium complexes **3**, **4**, or **5**. The reaction of **1** and DBHT proceeded in a stereospecific (syn) manner when the reaction was carried out in CD_2Cl_2 under aerobic conditions, while a mixture of two diastereomers was formed under N_2 atmosphere. The two diastereomers (**5-*E*,*Z*,*E*-antifacial** and **5-*E*,*E*,*E*-antifacial**) formed from DBHT were isolated, and the structure of **5-*E*,*Z*,*E*-antifacial**, which was kinetically formed from the reaction of **1** and (*E*,*E*,*E*)-DBHT, was determined by X-ray diffraction analysis. Addition of phosphine ligands (PPh_3 or dppm) to the dinuclear adduct **5-*E*,*Z*,*E*-antifacial** or **5-*E*,*E*,*E*-antifacial** in acetonitrile resulted in the stereospecific (syn) elimination of $[Pd_2(PPh_3)_2(CH_3CN)_4][BF_4]_2$ (**2**) or $[Pd_2(dppm)_2(CH_3CN)_2][BF_4]_2$ (**6**). During the PPh_3-induced dinuclear elimination, the phosphine adducts **7** that retain bi-η^3-allyldipalladium structure were observed initially. The phosphine adduct generated from **5-*E*,*E*,*E*-antifacial** was isolated and structurally characterized by X-ray diffraction analysis. The reaction of **1** and DPHT in CH_2Cl_2 afforded unique dipalladium sandwich compounds $[Pd_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-DPHT})_2][BF_4]_2$ (**8**). Interconversion between the sandwich complexes and half-sandwich complexes occurred in a stereoretentive manner. The structure of the sandwich complex **8-*E*,*Z*,*E*** formed from **4-*E*,*E*,*E*-antifacial** and (*E*,*Z*,*E*)-DPHT was determined by X-ray diffraction analysis. Transfer of the dipalladium moiety $[Pd_2(CH_3CN)_4]^{2+}$ from DPHT ligand of **4-*E*,*E*,*E*-antifacial** onto DBHT ligand proceeded in a stereoretentive manner. The observed stereoretentive dinuclear process is featured by the pairwise behavior of two palladium atoms sitting on the triene π-plane. In the dinuclear elimination, the two Pd atoms that are initially in the divalent state and bound on the opposite faces (antifacial) come to the synfacial positions to form a Pd−Pd bond prior to dissociation. These results represent the unique property of conjugated olefin as the multidentate ligands for metal−metal moieties.

Introduction

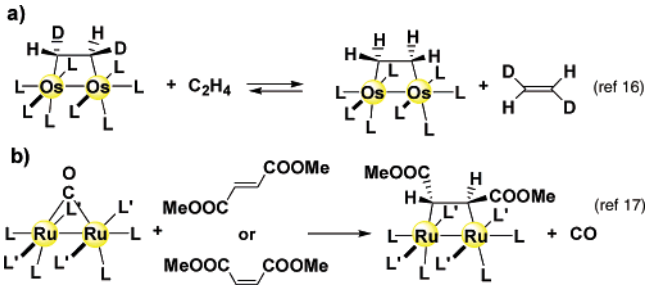
Conjugated sp^2-carbon frameworks act as unique π-coordinating polydentate ligands for multinuclear metal moieties.[1−7] We recently found that pπ-conjugated polyenes act as excellent template ligands for a linear palladium chain.[3−7] These findings prompted us to examine the mechanism of addition, elimination, and trans-olefination of a Pd−Pd bonded moiety to/from pπ-conjugated olefins. Historically, the interaction between metal−metal bonded species and olefin has received considerable attention as models for adsorption/desorption on metal surfaces.[8,9] It is known that some dinuclear metal−metal species add to conjugated olefin to afford "di-σ-bonded species" where a metal−metal bond is cleaved.[10−14] Typically, $Mn_2(CO)_{10}$ reacts with 1,3-butadiene or 1,3,5-hexatriene under the irradiation condition to form $Mn_2(\mu\text{-}\eta^3\text{:}\eta^1\text{-butadiene})(CO)_9$ or $Mn_2(\mu\text{-}\eta^3$:

(1) Markezich, R. L.; Whitlock, H. W. *J. Am. Chem. Soc.* **1971**, *93*, 5291.
(2) (a) Wadepohl, H.; Büchner, K.; Pritzkow, H. *Organometallics* **1989**, *8*, 2745. (b) Adams, R. D.; Wu, W. *Organometallics* **1993**, *12*, 1243. (c) Weng, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1998**, *17*, 4240. (d) Mashima, K.; Fukumoto, H.; Tani, K.; Haga, M.; Nakamura, A. *Organometallics* **1998**, *17*, 410. (e) Fukumoto, H.; Mashima, K. *Organometallics* **2005**, *24*, 3932.
(3) Murahashi, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H. *J. Am. Chem. Soc.* **1999**, *121*, 10660.
(4) Murahashi, T.; Nagai, T.; Mino, Y.; Mochizuki, E.; Kai, Y.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 6927.
(5) Murahashi, T.; Higuchi, Y.; Katoh, T.; Kurosawa, H. *J. Am. Chem. Soc.* **2002**, *124*, 14288.
(6) Tatsumi, Y.; Nagai, T.; Nakashima, H.; Murahashi, T.; Kurosawa, H. *Chem. Commun.* **2004**, 1430.
(7) It was also discovered that perylene binds a tetrapalladium chain through its tetraene edge: Murahashi, T.; Uemura, T.; Kurosawa, H. *J. Am. Chem. Soc.* **2003**, *125*, 8437.
(8) (a) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzner, W. R. *Chem. Rev.* **1979**, *79*, 91. (b) Muetterties, E. L. *Chem. Soc. Rev.* **1982**, *11*, 283.
(9) For adsorption of olefin on Pd or Pt surface: (a) Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A. *J. Am. Chem. Soc.* **1996**, *118*, 2942 and references therein. (b) Szulczewski, G.; Levis, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 3521. In this paper, it was proposed that desorption of di-σ-bonded ethylene from Pt(111) proceeds via a radical intermediate.
(10) (a) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923 and references therein. (b) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339 and references therein.
(11) (a) Kreiter, C. G.; Lipps, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 201. (b) Kreiter, C. G.; Lipps, W. *Chem. Ber.* **1982**, *115*, 973. (c) Kreiter, C. G.; Leyendecker, M. *J. Organomet. Chem.* **1985**, *292*, C18.
(12) Guggolz, E.; Oberdorfer, F.; Ziegler, M. L. *Z. Naturforsch., B: Chem. Sci.* **1981**, *36*, 1060.

Scheme 1. Typical Examples of Dinuclear Addition, Elimination, and Trans-olefination Involving Conjugated Olefins



Scheme 2. Stereochemistry of Some Dinuclear Processes



η^3-hexatriene)$(CO)_8$ (Scheme 1a).[11] The mechanism of dinuclear elimination of *o*-xylylene from the benzodicobaltacyclohexene (Scheme 1b) was studied by Hersh and Bergman, and they proposed the involvement of a retro-Diels−Alder-type dinuclear elimination process.[14] The dinuclear trans-olefination process has also been studied.[15] Typically, diosmacyclobutane reacts with 1,3-dienes to afford formal [2+2] cycloaddition products from Os=Os and the 1,3-diene with elimination of ethylene (Scheme 1c).[15b]

The mechanistic studies have been conducted concerning the dinuclear processes involving mono-olefin. Norton and co-workers revealed that the dinuclear trans-olefination process involving diosmacyclobutane and mono-olefin proceeds in a stereospecific (syn) manner (Scheme 2a), and they proposed a stepwise mechanism involving preequilibrium between μ-η^1:η^1-olefin and η^2-olefin complexes.[16] The dinuclear processes are not always stereoretentive. Johnson and Gladfelter reported that a Ru_2 center in $Ru_2(dmpm)_2(CO)_5$ (dmpm = $Me_2PCH_2PMe_2$) adds to mono-olefin in a nonstereospecific manner (Scheme 2b).[17] It should be mentioned that Halpern et al. reported that the Rh−Rh bonded species having rigid porphyrin ligands adds to styrene via a radical chain process.[18]

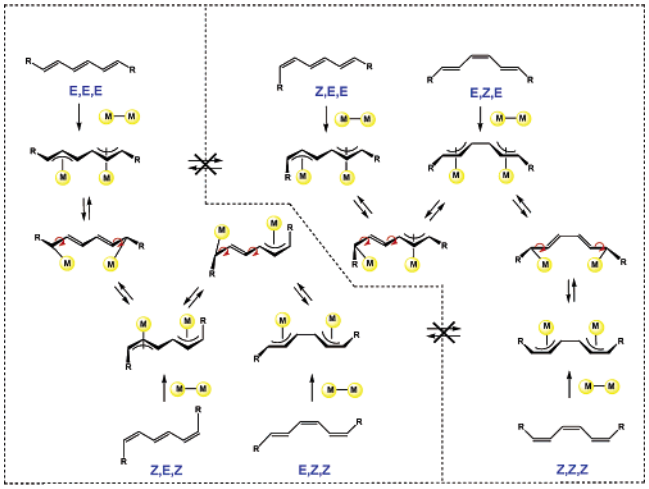
However, no systematic study has been undertaken of the dinuclear processes involving a pπ-conjugated olefin in which the stereochemistry is well documented, probably due to the lack of appropriate model systems. Involvement of concerted processes such as the dimetalla-Diels−Alder pathway and the migratory insertion pathway may result in highly stereospecific dinuclear reactions, while stepwise processes such as radical pathways should give rise to nonstereospecific reactions. It is also known that several olefin-bridged dimetal complexes without metal−metal bonds were synthesized by the reaction of cationic mononuclear olefin complexes with metal nucleophiles.[10] Typically, $[Re(CO)_5(\eta^2\text{-}C_4H_6)]^+$ reacted with $[Re(CO)_5]^-$ to afford $Re(CO)_5(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_4H_6)Re(CO)_5$.[19] Although the stereochemistry of such an ionic process has not been reported, a net stereospecific dinuclear addition may be involved if anti-attack of a metal nucleophile to the coordinated olefin takes place.

We recently developed the chemistry of Pd−Pd bonded complexes $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**)[20] and $[Pd_2(CH_3CN)_4(PPh_3)_2][BF_4]_2$ (**2**),[21] which are isolable but highly reactive with unsaturated hydrocarbons under mild conditions,[21−23] due to the substitutionally labile property of acetonitrile ligands on dipalladium centers. Furthermore, as the bridging ability of the nitrile or PPh_3 ligands is poor,[22] the dinuclear processes involving such Pd−Pd species might be free from strong geometrical constraints imposed by bridging auxiliary ligands often required to support M−M bonds in other complexes. In hopes of better understanding the dinuclear processes of the Pd_2^{2+} moiety embedded on conjugated olefin, we started examining the addition, elimination, and trans-olefination of the $[Pd_2L_n]^{2+}$ moiety.

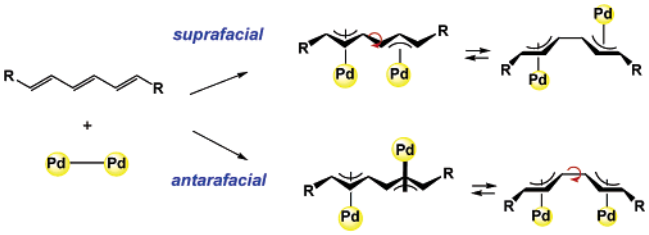
The syn and anti dinuclear additions to terminally disubstituted conjugated olefin can lead to different diastereomers. We elected 1,6-disubstituted 1,3,5-trienes as the conjugated olefin, which would give the addition products as stable bi-η^3-allyl dimetal complexes as found in Scheme 1a.[11] In Scheme 3, the two series of stereoisomers of bi-allyl complexes resulting from hypothetical suprafacial dinuclear addition to 1,6-disubstituted 1,3,5-hexatriene are summarized, where fast equilibria via $\pi-\sigma-\pi$ isomerization at the η^3-allylpalladium moiety[24] are assumed to be attained. For example, the trienes having odd numbers of olefinic *E* double bonds give one series of the products different from another derived from the trienes having even numbers of *E* double bonds (including zero *E*). Intercross-

(13) (a) Chisholm, M. H.; Huffman, J. C.; Lucas, E. A.; Lubkovsky, E. B. *Organometallics* **1991**, *10*, 3424. (b) Barry, J. T.; Bollinger, J. C.; Chisholm, M. H.; Glasgow, K. C.; Huffman, J. C.; Lucas, E. A.; Lubkovsky, E. B.; Streib, W. E. *Orgaometallics* **1999**, *18*, 2300.
(14) (a) Hersh, W. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 6992. (b) Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834. (c) Hersh, W. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5846.
(15) (a) Takats, J. *Polyhedron* **1988**, 931. (b) Spetseris, N.; Norton, J. R.; Rithner, C. D. *Organometallics* **1995**, *14*, 603. A related trans-dimetalation involving 1,3-diene was reported in ref 14c.
(16) (a) Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3468. (b) Hembre, R. T.; Ramage, D. L.; Scott, C. P.; Norton, J. R. *Organometallics* **1994**, *13*, 2995. (c) Ramage, D. L.; Wiser, D. C.; Norton, J. R. *J. Am. Chem. Soc.* **1997**, *119*, 5618. (d) Bender, B. R.; Ramage, D. L.; Norton, J. R.; Wiser, D. C.; Rappé, A. K. *J. Am. Chem. Soc.* **1997**, *119*, 5628.
(17) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1991**, *10*, 376.
(18) (a) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333. (b) Wayland, B. B.; Feng, Y.; Ba, S. *Organometallics* **1989**, *8*, 1438.
(19) Beck, W.; Raab, K.; Nagel, U.; Sacher, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 505.
(20) Murahashi, T.; Nagai, T.; Okuno, T.; Matsutani, T.; Kurosawa, H. *Chem. Commun.* **2000**, 1689.
(21) Murahashi, T.; Otani, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H. *J. Am. Chem. Soc.* **1998**, *120*, 4536.
(22) Murahashi, T.; Otani, T.; Okuno, T.; Kurosawa, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 537.
(23) Murahashi, T.; Okuno, T.; Nagai, T.; Kurosawa, H. *Organometallics* **2002**, *21*, 3679.
(24) $\pi-\sigma-\pi$-isomerism of allylpalladium complexes: (a) Vrieze, K.; MacLean, C.; Cosse, P.; Hilbers, C. W. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 1077. (b) Vrieze, K.; Volger, H. C. *J. Organomet. Chem.* **1967**, *9*, 537. (c) van Leeuwen, P. W. N. M.; Vrieze, K.; Praat, A. P. *J. Organomet. Chem.* **1969**, *20*, 219. (d) van Leeuwen, P. W. N. M.; Praat, A. P. *J. Organomet. Chem.* **1970**, *21*, 501. (e) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839.

Scheme 3. Two Series from Suprafacial Dinuclear Addition to 1,6-Disubstituted 1,3,5-Hexatrienes



Scheme 4



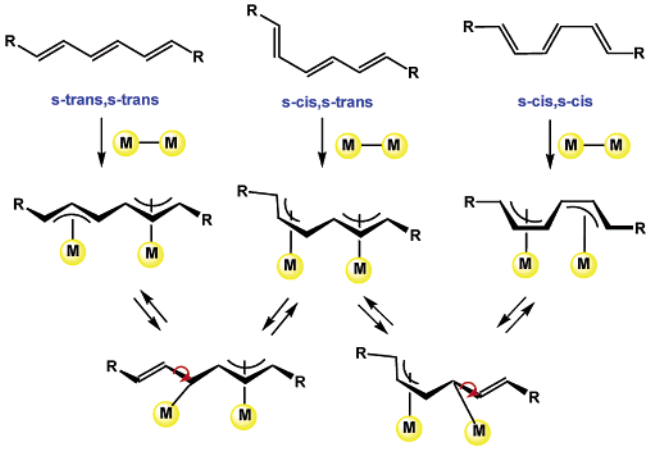
ing across the two series cannot be attained by conventional $\pi-\sigma-\pi$ allylic isomerization.[24,25] Thus, analysis of the product distribution of each series from an "odd *E* triene" or an "even *E* triene" would provide stereochemical information on the dinuclear processes involving 1,3,5-triene (Scheme 4).[26]

It is noticeable that the type of conformation, *s-cis* or *s-trans*, which a given 1,3,5-triene takes at any C−C single bond, does not affect the nature of the product series. For example, three conformers arising from *s-cis*/*s-trans* conformations of 1,6-disubstituted (*E*,*E*,*E*)-triene, that is, *s-trans*,*s-trans* triene, *s-cis*,*s-trans* triene, and *s-cis*,*s-cis* triene, give one series of products upon suprafacial dinuclear addition (Scheme 5).

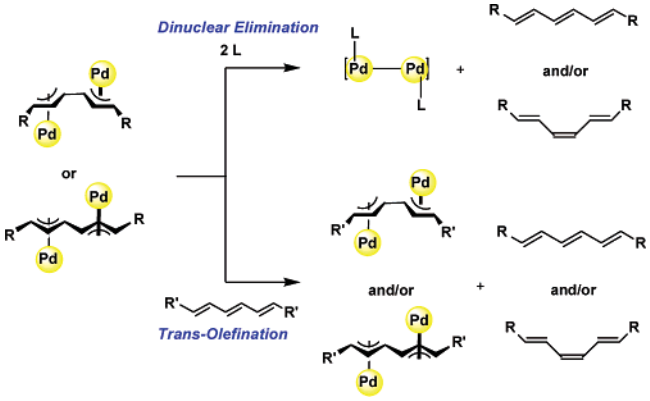
In a previous communication,[4] we reported that dinuclear addition of the complex **1** to 1,6-diphenyl-1,3,5-hexatriene (DPHT) afforded a mixture of isomers, each included in the different series. However, it was difficult to estimate the diastereoselectivity of the dinuclear addition step, as will be mentioned in section 1 in this Article, because the inter-series isomerization between two diastereomers proceeded competitively with the dinuclear addition reaction. As mentioned above, the intercrossing between two series cannot be explained by $\pi-\sigma-\pi$ allylic isomerization. The configurational lability of the η^3-allyl moiety[25] during the dinuclear addition reaction using DPHT hampers the stereochemical investigation of the dinuclear processes as well as isolation of the thermally unstable isomer.

The stereochemical study of the reverse reaction, dinuclear elimination, may also provide valuable information of the

Scheme 5. Intra-series Products from *s-cis* or *s-trans* Conformers of (*E*,*E*,*E*)-Triene through Suprafacial Dinuclear Addition



Scheme 6



dinuclear processes (Scheme 6),[26] if the dinuclear elimination process is much faster than the isomerization causing intercrossing between the series. The stereochemical information on the dinuclear trans-olefination process is also complementary to the dinuclear addition and elimination processes (Scheme 6).[26] For such studies, it is necessary to isolate the two series of products, separately.

In this contribution, we report successful isolation of two series of products by employing 2,2,9,9-tetramethyl-3,5,7-decatriene (DBHT).[27] It is proven that the dinuclear elimination and transfer of dipalladium moieties bound on trienes is highly stereospecific (syn). Furthermore, details of unique sandwich coordination of DPHT to a dipalladium center $[Pd_2]^{2+}$ are reported.

Results and Discussion

1.1. Dinuclear Addition Reactions Involving $[Pd_2(CH_3CN)_6][BF_4]_2$ (1) or $[Pd_2(\mu\text{-}PPh_3)_2(CH_3CN)_2][PF_6]_2$ (2′′) and 1,3,5-Hexatriene (HT). The homoleptic acetonitrile dipalladium(I) complex $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**) was prepared according to the reported method.[20] The structure of **1** was determined here by X-ray structure analysis (Figure 1). The Pd−Pd bond (2.486(1) Å) is the shortest among ever known $Pd^{I}-Pd^{I}$ bonds.[28] The Pd−N distances (2.165(9), 2.147(9) Å) trans to the Pd−Pd bond are longer than those (1.976(8), 2.001(8), 1.988(8), 1.987(8)

(25) (a) Kurosawa, H.; Ogoshi, S.; Chatani, N.; Kawasaki, Y.; Murai, S. *Chem. Lett.* **1990**, 1745. (b) Granberg, K. L.; Bäckvall, J. *J. Am. Chem. Soc.* **1992**, *114*, 6858.

(26) The half-sandwich type, bi-η^3-allyl dipalladium complexes can take two conformations where two Pd atoms are located either on the same face or opposite faces of the triene plane, with the latter being normally more stable.

(27) In this Article, 2,2,9,9-tetramethyl-3,5,7-decatriene is abbreviated as DBHT, which is derived from a conventional name "1,6-di-*t*-Bu-1,3,5-hexatriene".

(28) Murahashi, T.; Kurosawa, H. *Coord. Chem. Rev.* **2002**, *231*, 207.

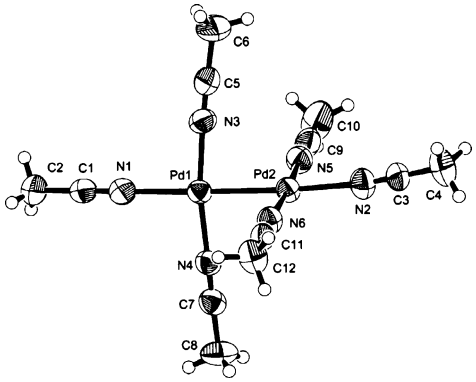


Figure 1. ORTEP drawing of **1** (50% probability ellipsoids, BF_4 anions were omitted for clarity). Selected bond distances (Å) and angles (deg): Pd1−Pd2 2.486(1), Pd1−N1 2.165(9), Pd2−N2 2.147(9), Pd1−N3 1.976(8), Pd1−N4 2.001(8), Pd2−N5 1.988(8), Pd2−N6 1.987(8), Pd1−Pd2−N6 86.4(2), Pd1−Pd2−N5 87.7(2), Pd1−Pd2−N2 174.7(2), Pd2−Pd1−N3 84.4(2), Pd2−Pd1−N4 86.6(2), Pd2−Pd1−N1 178.1(2).

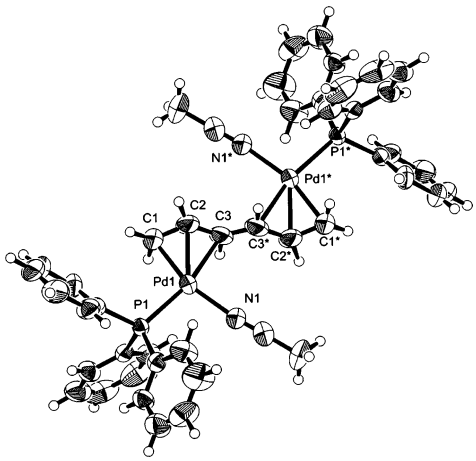


Figure 2. ORTEP drawing of **3b** (50% probablity ellipsoids, PF_6 anions were omitted for clarity). Selected bond distances (Å): Pd1−N1 2.067(9), Pd1−P1 2.305(2).

Å) cis to the Pd−Pd bond, probably due to a strong trans-influence of the Pd−Pd bond relative to that of acetonitrile ligand. The Pd−N lengths at the cis positions to the Pd−Pd bond are similar to those in the corresponding homoleptic mononuclear Pd(II) complex $[Pd(CH_3CN)_4][BF_4]_2$ (1.956(8) Å).[29]

Complex **1** reacted with 1,3,5-hexatriene (HT, a mixture of *E*- and *Z*-isomers) in acetonitrile at 25 °C for 1 h to afford a half-sandwich complex $[Pd_2(\mu\text{-}\eta^3{:}\eta^3\text{-hexatriene})(CH_3CN)_4][BF_4]_2$ (**3a**) in 75% isolated yield (eq 1). The ^{1}H NMR monitoring experiments in CD_3CN showed that complex **3a** was formed almost quantitatively. The similar product $[Pd_2(\mu\text{-}\eta^3{:}\eta^3\text{-hexatriene})(CH_3CN)_2(PPh_3)_2][PF_6]_2$ (**3b**) was obtained by the reaction of $[Pd_2(\mu\text{-}PPh_3)_2(CH_3CN)_2][PF_6]_2$ (**2″**)[22] with 1,3,5-hexatriene (a mixture of isomers) in CH_2Cl_2 (eq 2, 52% isolated yield), and its structure was determined by X-ray structure analysis (Figure 2). The two palladium atoms are bound on opposite faces of the *E-s-trans,s-trans*-1,3,5-hexatriene ligand through η^3-allyl coordination mode. Because of the disorder of the hexatriene ligand, it is difficult to discuss the structural parameters with regard to the coordination of 1,3,5-hexatriene ligand in **3b**. The formation of the identical product from a

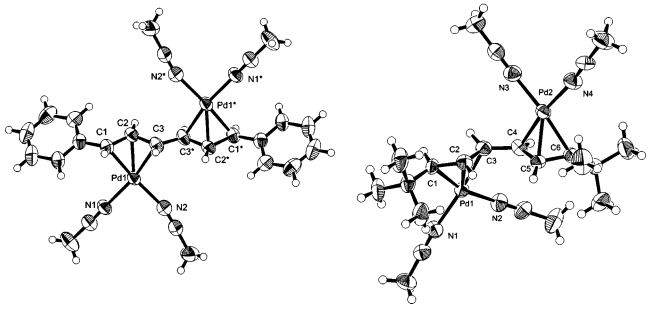
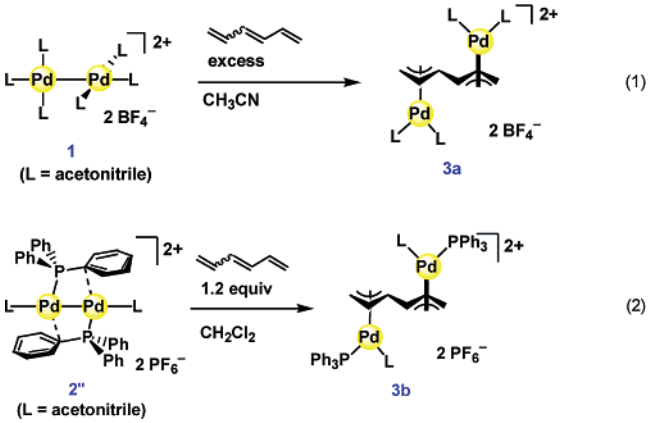


Figure 3. ORTEP drawings of **4-*E,E,E*-antifacial** (left) and **5-*E,Z,E*-antifacial** (right) (50% probability ellipsoids, BF_4 anions were omitted for clarity). Selected bond lengths (Å) for **4-*E,E,E*-antifacial**, Pd1−C1 2.132(4), Pd1−C2 2.129(4), Pd1−C3 2.128(4), C1−C2 1.393(5), C2−C3 1.411(5), C3−C3* 1.474(7); for **5-*E,Z,E*-antifacial**, Pd1−C1 2.159(8), Pd1−C2 2.111(9), Pd1−C3 2.121(8), Pd2−C4 2.113(9), Pd2−C5 2.111(9), Pd2−C6 2.179(9), C1−C2 1.40(1), C2−C3 1.39(1), C3−C4 1.49(1), C4−C5 1.39(1), C5−C6 1.42(1).

mixture of *E*-1,3,5-hexatriene and *Z*-1,3,5-hexatriene is understood by the involvement of rapid allylic $\pi-\sigma-\pi$ isomerization. When the isolated **3b** was dissolved in CD_3CN, partial dinuclear elimination involving dissociation of free 1,3,5-hexatriene from **3b** was observed,[30] where $[Pd_2(PPh_3)_2(CD_3CN)_4][PF_6]_2$ (**2′**)[21] was formed (37% after 4 h).

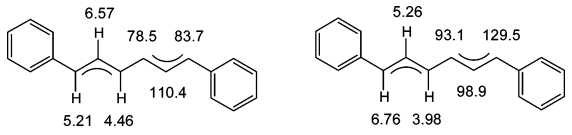


1.2. Dinuclear Addition Reactions Involving $[Pd_2(CH_3CN)_6][BF_4]_2$ (1) and 1,6-Diphenyl-1,3,5-hexatriene (DPHT). As was previously communicated,[4] the homoleptic acetonitrile dipalladium(I) complex $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**) reacted with *all-trans*-1,6-diphenyl-1,3,5-hexatriene ((*E,E,E*)-DPHT) in CH_3CN at 23 °C to afford a half-sandwich complex **4** as a mixture of two diastereomers (**4-*E,Z,E*-antifacial/4-*E,E,E*-antifacial** = 22/78 after crystallization) (eq 3).[4] The ^{1}H NMR monitoring experiments showed that the isomer ratio changed gradually (54/46 after 10 min, 46/54 after 1 h, 20/80 after 1 day). The major isomer of **4** was isolated by recrystallization, and its structure was determined by X-ray crystallographic analysis (Figure 3, left).[4] Two Pd atoms coordinated on opposite faces of the (*E,E,E*)-DPHT ligand, and the major isomer is abbreviated as **4-*E,E,E*-antifacial**. The η^3-coordination mode of each Pd atom as well as the single bond character of the central C3−C3* bond length (1.474(7) Å) indicated that the oxidation state of the dipalladium moiety in **4-*E,E,E*-antifacial** is 2 × Pd^{II}. ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **4-*E,E,E*-antifacial** (Scheme

(29) Gebauer, T.; Frenzen, G.; Dehnicke, K. *Z. Naturforsch., B: Chem. Sci.* **1992**, *47*, 1505.

(30) The *E*/*Z* ratio of the released 1,3,5-hexatriene could not be determined due to the overlap of those signals with the broad signals of **3b**.

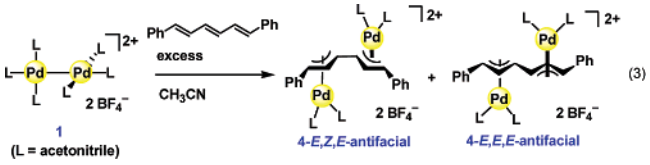
Scheme 7. ^{1}H and ^{13}C{^{1}H} NMR Chemical Shifts (ppm) for **4-*E,E,E*-Antifacial** and **8-*E,E,E*-Meso**[a]



4-*E,E,E*-antifacial[a] **8-*E,E,E*-meso**[b]

[a] (a)Measured in CD_3CN. (b) Measured in CD_2Cl_2.

7, left) are consistent with the bi-η^3-allyl palladium(II) structure. The allylic central carbons were less shielded than the allylic terminal carbons as typically observed for mononuclear η^3-allyl palladium(II) complexes. The minor isomer showed ^{1}H and ^{13}C NMR signal patterns similar to those of **4-*E,E,E*-antifacial**. The structure of the minor isomer is assumed as **4-*E,Z,E*-antifacial**, by referring to the crystal structure of **5-*E,Z,E*-antifacial** (Figure 3, right) derived from DBHT (vide infra). The reaction of **1** with (*E,Z,E*)-DPHT in CD_3CN also resulted in the formation of a mixture of **4-*E,Z,E*-antifacial** and **4-*E,E,E*-antifacial** (38/62 after 1 h, 16/84 after 1 day at 25 °C). Unfortunately, separation and isolation of **4-*E,Z,E*-antifacial** failed, due in part to the slow isomerization of **4-*E,Z,E*-antifacial** to **4-*E,E,E*-antifacial** at ambient temperature, as well as the poor solubility of DPHT in acetonitrile at −40 °C that caused low conversion in the low-temperature experiments.



1.3. Dinuclear Addition Reactions Involving $[Pd_2(CH_3CN)_6][BF_4]_2$ (1) and 2,2,9,9-Tetramethyl-3,5,7-decatriene (DBHT). Next, we chose 2,2,9,9-tetramethyl-3,5,7-decatriene (DBHT)[27] as the triene ligand. It was found that the isomer ratio of products was dependent on the reaction conditions including solvent and reaction atmosphere.

In acetonitrile, the reaction of **1** with (*E,E,E*)-DBHT (1 equiv) or (*E,Z,E*)-DBHT gave a mixture of two isomers, **5-*E,Z,E*-antifacial** and **5-*E,E,E*-antifacial** (isomer ratio = 76/24 from (*E,E,E*)-DBHT, 85% conversion after 5 min; 56/44 from (*E,Z,E*)-DBHT, 84% conversion after 5 min). The stereochemistry of these products was determined by X-ray crystallography on **5-*E,Z,E*-antifacial** (Figure 3, right) and the PPh_3 adduct of **5-*E,E,E*-antifacial** (Figure 4), as discussed later.

In CD_2Cl_2 under N_2, a mixture of two isomers was formed again (80/20 from (*E,E,E*)-DBHT, 69% conversion after 5 min; 61/39 from (*E,Z,E*)-DBHT, 49% conversion after 5 min) (Scheme 8). However, when each reaction in CD_2Cl_2 was carried out under aerobic conditions, the adduct was formed as the single isomer. From (*E,E,E*)-DBHT, **5-*E,Z,E*-antifacial** was formed quantitatively after 1 day (>99/<1, 51% conversion after 5 min) (Scheme 8). From (*E,Z,E*)-DBHT, **5-*E,E,E*-antifacial** was formed exclusively after 5 min (<1/>99, 26% conversion), while considerable mixing of the two isomers was observed after 1 day (77/23, 44% conversion).

The product **5-*E,Z,E*-antifacial**, which was exclusively formed from (*E,E,E*)-DBHT under aerobic conditions, was isolated in 76% yield, and its structure is shown in Figure 3, right. The coordination mode of the triene is μ-η^3:η^3, and the trend of C−C bond lengths for the triene part is similar to that in **4-*E,E,E*-antifacial**. However, the configuration around the C3−C4 bond (cisoid) in **5-*E,Z,E*-antifacial** is different from that of **4-*E,E,E*-antifacial** (transoid).

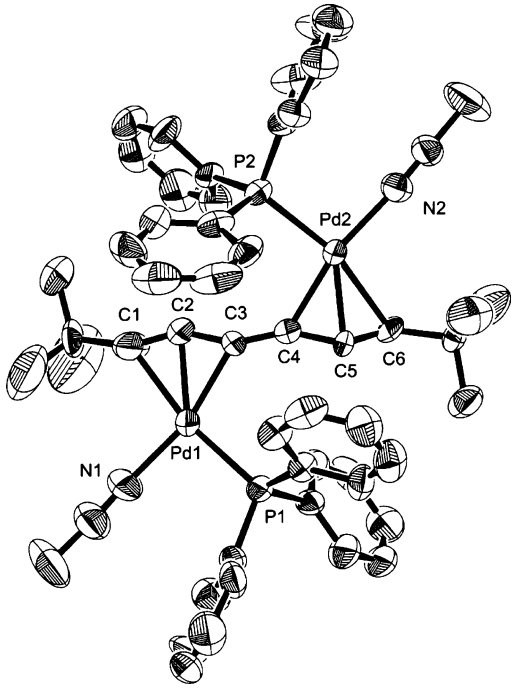
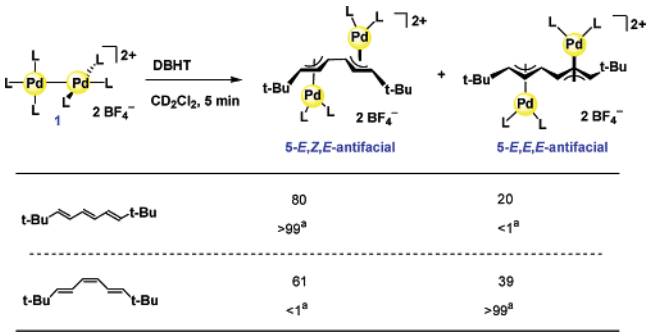


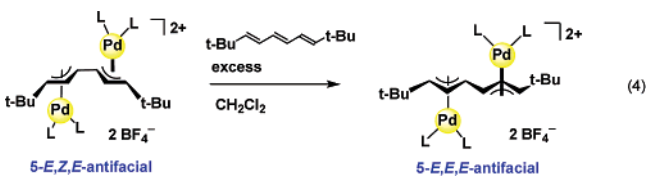
Figure 4. ORTEP drawing of **7-*E,E,E*-antifacial** (50% probability ellipsoids, BF_4 anions were omitted for clarity). Selected bond distances (Å): Pd1−N1 2.05(1), Pd1−P1 2.336(4), Pd2−N2 2.08(1), Pd2−P2 2.334(4).

Scheme 8 [a]



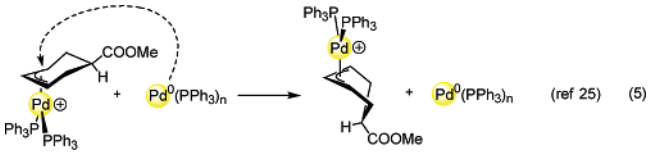
[a] (a) Under aerobic conditions.

5-*E,E,E*-Antifacial was isolated by stirring the mixture of **5-*E,Z,E*-antifacial** and free (*E,E,E*)-DBHT in CH_2Cl_2 overnight, followed by recrystallization (54% yield). The isomerization shown in eq 4 did not occur in the absence of free (*E,E,E*)-DBHT, while the role of (*E,E,E*)-DBHT in eq 4 remains elusive.[31] The isolated **5-*E,E,E*-antifacial** did not undergo isomerization even in the presence of excess (*E,E,E*)-DBHT.



Thus, two diastereomers derived from different series shown in Scheme 3 were successfully isolated as **5-*E,Z,E*-antifacial**

and **5-*E,E,E*-antifacial**. The stereospecific nature of the dinuclear addition process involving **1** and DBHT was observed only in the initial stage of the reactions carried out under aerobic conditions in CD_2Cl_2. It may well be that the dinuclear addition process is intrinsically stereospecific, but is competing with some other processes leading to the formation of the opposite series of products. The competitive occurrence of inter-series isomerization during the dinuclear addition process particularly under N_2 atmosphere is probably induced by some palladium species, for example, Pd^0, which could be generated by decomposition of reagent and product complexes.[32a] It is known that the cationic η^3-allylpalladium complex is subjected to nucleophilic anti-attack of Pd^0, which gives rise to the configurational lability of η^3-allylpalladium complexes (eq 5).[25] Similar anti-attack of a Pd^0 species at **5** may result in the inter-series isomerization, where a catalytic amount of Pd^0 species works effectively under inert condition. At present, involvement of inter-series isomerization makes the evaluation of the stereochemistry of the dinuclear addition process involving **1** and 1,3,5-trienes difficult.[32b]

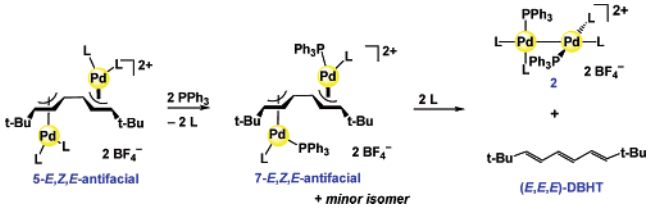


(ref 25) (5)

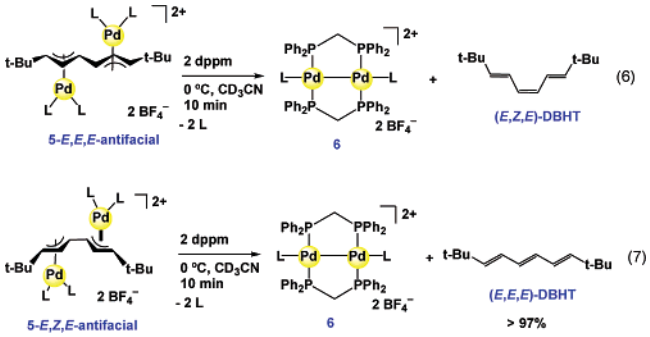
2. Phosphine-Induced Dinuclear Elimination from DBHT Half-Sandwich Complexes. From the viewpoint of the microscopic reversibility principle, elimination of a Pd−Pd bonded moiety from bi-η^3-allyl dipalladium(II) complexes is of great interest in relation to the dinuclear addition reactions discussed above. The major problem of the dinuclear addition processes is that the rate of dinuclear addition is competitive with that of inter-series isomerization particularly under N_2 atmosphere. However, as described in the Introduction, the stereochemical study of the reverse reaction, dinuclear elimination, may provide valuable information of the dinuclear processes, if the dinuclear elimination is much faster than the inter-series isomerization. We found that dinuclear elimination reactions from **5-*E,Z,E*-antifacial** or **5-*E,E,E*-antifacial** occurred rapidly by adding phosphines. Note that the choice of the solvent (CH_3CN) was important to the dinuclear elimination.

Treatment of **5-*E,E,E*-antifacial** with 2 equiv of dppm ($Ph_2PCH_2PPh_2$) in CD_3CN at 0 °C afforded (*E,Z,E*)-DBHT and $[Pd_2(dppm)_2(CH_3CN)_2][BF_4]_2$ (**6**)[33] almost quantitatively after 10 min (eq 6). According to this reaction, (*E,Z,E*)-DBHT was isolated in 81% yield. Thus, a thermodynamically unfavorable isomerization from (*E,E,E*)-DBHT to (*E,Z,E*)-DBHT was attained through the sequence of dinuclear addition of **1** to (*E,E,E*)-DBHT to give **5-*E,Z,E*-antifacial**, isomerization of **5-*E,Z,E*-antifacial** to **5-*E,E,E*-antifacial**, and dinuclear elimination from **5-*E,E,E*-antifacial**. When **5-*E,Z,E*-antifacial** was

Scheme 9. PPh_3-Induced Dinuclear Elimination from **5-*E,Z,E*-Antifacial**



treated with dppm (2 equiv) in the same condition, complex **6** and (*E,E,E*)-DBHT (>97%) were formed, where trace (*E,Z,E*)-DBHT (<3%) was observed (eq 7).



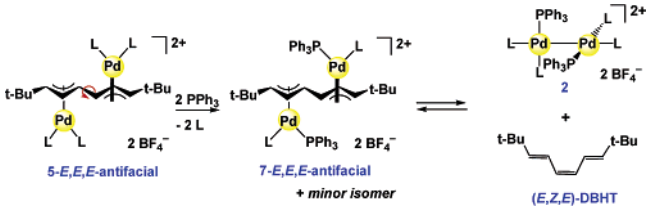
When **5-*E,Z,E*-antifacial** was treated with 2 equiv of PPh_3 in CD_3CN at 5−10 °C, a Pd−Pd bonded complex **2** and (*E,E,E*)-DBHT were formed quantitatively (Scheme 9). The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy at 5−10 °C. After 5 min, the starting materials disappeared and free (*E,E,E*)-DBHT (45%), the Pd−Pd bonded complex **2** (44%), and phosphine adduct **7-*E,Z,E*-antifacial** (55%) were observed. The phosphine adduct **7-*E,Z,E*-antifacial** was then gradually converted to free (*E,E,E*)-DBHT and **2**, and the yields of (*E,E,E*)-DBHT and **2** reached 97% and 96%, respectively, after 1 day, where a small amount of the phosphine adduct (3%) remained. During the reaction, the formation of (*E,Z,E*)-DBHT was not observed.

When the same reaction was carried out at −40 °C, the phosphine adduct **7-*E,Z,E*-antifacial** was generated almost quantitatively, and **7-*E,Z,E*-antifacial** remained as the sole species after warming the sample to 0 °C. **7-*E,Z,E*-Antifacial** existed as a mixture of two isomers (major/minor = 95/5). The $^{31}P\{^1H\}$ NMR signal for the major isomer was observed at δ 20.6 ppm as a broad singlet at −40 °C. In ^1H NMR spectra, the triene protons for the major isomer appeared as three signals at −40 °C, and the chemical shift pattern is similar to those found in **5**. Thus, it is reasonably assumed that the major isomer retains the μ-η^3:η^3-bi-allyl structure, as drawn in Scheme 9. On the other hand, the concentration of the minor isomer was too low to lead to structural estimation. However, upon warming the sample containing both isomers of the PPh_3 adduct to 25 °C, free (*E,E,E*)-DBHT and **2** were gradually formed. Thus, both isomers of **7-*E,Z,E*-antifacial** would retain the stereogenic identity of **5-*E,Z,E*-antifacial**.

Treatment of **5-*E,E,E*-antifacial** with 2 equiv of PPh_3 in CD_3CN at 5 °C resulted in the formation of two phosphine adducts, **7-*E,E,E*-antifacial** and a structurally unspecified minor product (**7-*E,E,E*-antifacial**/minor = 78/22 in CD_3CN at −40 °C, almost quantitative after 5 min) (Scheme 10). The formation of a small amount of **2** (2%) and free (*E,Z,E*)-DBHT (7%) was observed.

(31) The involvement of trans-olefination, which is described in section 4 in this Article, does not result in such isomerization.
(32) (a) One reviewer suggested a possibility of the involvement of some transient adduct between **1** and oxygen or water responsible for the stereospecific dinuclear addition under aerobic conditions. (b) Another transient active species Pd^{2+} may cause the isomerization[32c] of free (*E,Z,E*)-DBHT to free (*E,E,E*)-DBHT during the dinuclear addition process, resulting in slow formation of **5-*E,Z,E*-antifacial** in the reaction of **1** and (*E,Z,E*)-DBHT. (c) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 1, p 179, Vol. 2, p 111.
(33) Miedaner, A.; DuBois, D. L. *Inorg. Chem.* **1988**, *27*, 2479.

Scheme 10. PPh_3-Induced Dinuclear Elimination from **5-*E,E,E*-Antifacial**



The phosphine adducts then decreased gradually. After 3 days, the ratio of the phosphine adducts (**7-*E,E,E*-antifacial** + the minor product), the Pd−Pd complex **2**, and free (*E,Z,E*)-DBHT reached 1:1:1, and the ratio did not change for 15 days.

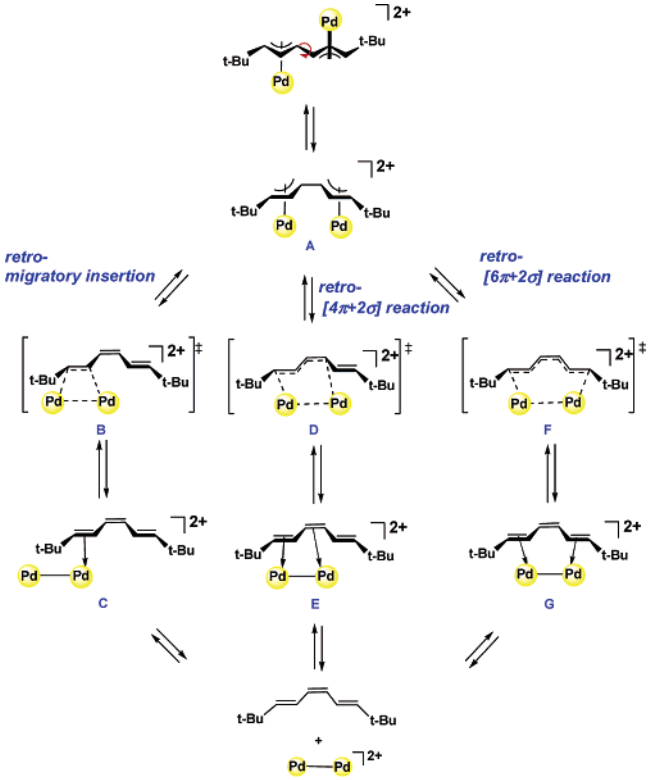
7-*E,E,E*-Antifacial was isolated and structurally characterized by X-ray structure analysis (Figure 4). Although the triene part was considerably disordered, the configuration of the triene moiety in the complex is reasonably concluded as *E,E,E* by comparing the distance between quaternary carbons of *t*-Bu groups (8.83 Å) with that in **5-*E,Z,E*-antifacial** (7.89 Å) and with the distance between ipso-carbons of Ph groups in **4-*E,E,E*-antifacial** (8.82 Å). When crystalline **7-*E,E,E*-antifacial** was dissolved in CD_2Cl_2, ^1H and $^{31}P\{^1H\}$ NMR spectra showed the presence of two species. The major set of the resonances was consistent with the structure found in the crystalline state; three trienyl proton signals and one phosphorus singlet were observed. On the other hand, the minor isomer showed six trienyl protons and two phosphorus doublet (J_{PP} = 13 Hz) signals. While the structure of the minor isomer cannot be decisively assumed from the NMR data,[34] the stereogenic identity of the triene in **7-*E,E,E*-antifacial** is retained in the minor isomer because warming the sample of a mixture of **7-*E,E,E*-antifacial** and the minor isomer in CD_3CN resulted in the selective conversion to (*E,Z,E*)-DBHT and **2**, as mentioned above. In CD_2Cl_2, **7-*E,E,E*-antifacial** and the minor isomer did not undergo dinuclear elimination at 25 °C.

When the complex **2** and free (*E,Z,E*)-DBHT were dissolved in CD_3CN, gradual formation of **7-*E,E,E*-antifacial** and the minor isomer was observed and the ratio reached (**7-*E,E,E*-antifacial** + minor isomer):**2**:DBHT = 1:1:1 after 1 day. In this case, however, trace free (*E,E,E*)-DBHT was observed (3%). Thus, the dinuclear elimination from the phosphine adducts **7-*E,E,E*-antifacial** is reversible. On the other hand, no reaction was observed when the mixture of compound **2** and free (*E,E,E*)-DBHT in CD_3CN was left for 1 day.

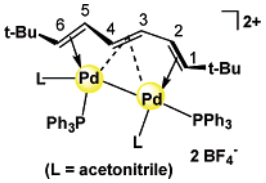
Thus, it is concluded that phosphine-induced dinuclear elimination from the half-sandwich DBHT dipalladium(II) complexes **5** is highly stereospecific. The observed stereochemistry is reasonably understood as the suprafacial (syn) elimination of the dipalladium(I) moiety from DBHT. The 180° rotation at the central C−C bond of the DBHT ligand in **7-*E,Z,E*-antifacial** or **7-*E,E,E*-antifacial** would give **7-*E,E,E*-synfacial** or **7-*E,Z,E*-synfacial**, respectively (Scheme 11). In the synfacial complexes, two Pd atoms are located at the juxtaposition with each other, allowing the Pd−Pd bond formation. As summarized in Scheme 11, there are three possible pathways for the stereoretentive elimination from the synfacial complexes: (a) retro-migratory insertion, (b) retro-dimetalla-[4π+2σ] reaction, and (c) retro-dimetalla-[6π+2σ] reaction. However, it is difficult to discriminate these three pathways on the basis of the experimental observations. It is noticeable that μ-η^2:η^2-1,3-diene dipalladium complexes that are related to the intermediate **E** in the retro-dimetalla-[4π+2σ] reaction are known.[21,35,36] Of particular interest is the structure of the bis-1,3-butadiene dipalladium(I) complex $[Pd_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-1,3-butadiene})_2(PPh_3)_2][PF_6]_2$, which shows an exceptionally long Pd−Pd length (3.1852(6) Å).[21] The long Pd−Pd separation may be regarded as the result of trapping of an intermediate of the dimetalla-[4π+2σ] process. The isolobal analogy between the dimetalla-[4π+2σ] reaction and the parent [4π+2π] Diels−Alder reaction can be understood qualitatively by considering the symmetry of frontier orbitals as shown in Scheme 12. The related retro-dimetalla-[4π+2π] process was proposed to be involved in the *o*-xylylene elimination from $[Co_2(o\text{-xylylene})Cp_2(\mu\text{-CO})_2]$ (Scheme 2a).[14]

The observed stereospecific dipalladium elimination from DBHT is featured by the pairwise behavior of two palladium

Scheme 11. Three Possible Pathways for Dinuclear Elimination from ***E,E,E*-Antifacial** Complexes



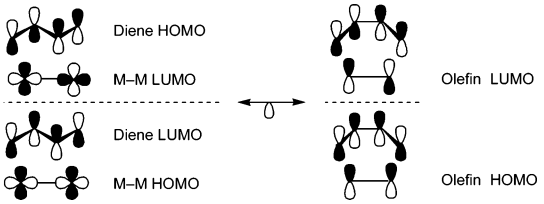
(34) The minor product showed six trienyl protons and two phosphorus doublet (J_{PP} = 13 Hz) signals. The J_{H2-H3} coupling constant (7.2 Hz) indicated the cis configuration at the C2−C3 bond in the minor product. It is also notable that the carbons of both *t*-Bu groups were *J*-coupled with phosphorus centers (J_{CP} = 3.8 Hz, J_{CP} = 3.8 Hz for methyl carbons, J_{CP} = 3.1 Hz, J_{CP} = 3.8 Hz for quaternary carbons). We assume a Pd−Pd bonded structure shown below as the minor product.



(35) (a) Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Rüegger, H. *Organometallics* **1993**, *12*, 4503. (b) Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Pregosin, P. S.; Rüegger, H. *Organometallics* **1996**, *15*, 2047.

(36) Murahashi, T.; Kanehisa, N.; Kai, Y.; Otani, T.; Kurosawa, H. *Chem. Commun.* **1996**, 825.

Scheme 12. Isolobal Analogy between the Dimetalla-[4π+2σ] Process and the [4π+2π] Diels−Alder Process



atoms sitting on the triene π-plane. The two Pd moieties in **5** are initially in the divalent state, and there is no Pd−Pd bond between them. When those are subjected to a condition for dissociation from DBHT, two palladium atoms come to the synfacial positions to form a Pd−Pd bond prior to dissociation.

3.1. Formation of Sandwich Dipalladium Complexes of 1,6-Diphenyl-1,3,5-hexatriene (DPHT). When complex **1** was treated with (*E*,*E*,*E*)-DPHT (excess) in dichloromethane, the sandwich complex **8-*E*,*E*,*E*-meso** was formed almost quantitatively (eq 8).[4] Although two isomers are possible for the complex **8-*E*,*E*,*E*** depending on the stacking manner of the two zigzag (*E*,*E*,*E*)-DPHT ligands, only meso isomer was observed throughout the monitoring experiments.[37] The complex **8-*E*,*E*,*E*-meso** was isolated in 77% yield after recrystallization.

The structure of **8-*E*,*E*,*E*-meso** was determined by X-ray structure analysis (Figure 5).[4] Two independent molecules were

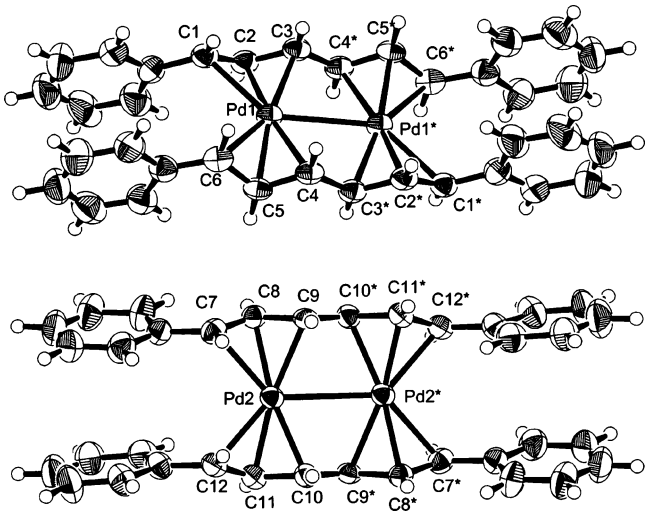
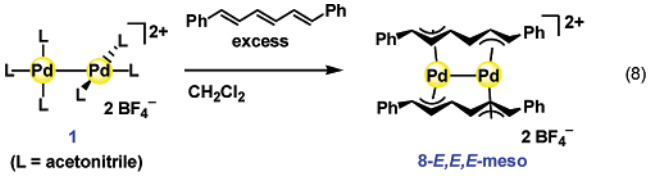


Figure 5. ORTEP drawings of **8-*E*,*E*,*E*-meso** (two independent molecules in a unit cell, 50% probability ellipsoids, BF_4 anions were omitted for clarity). Selected bond lengths (Å): Pd1−Pd1* 2.9156(6), Pd1−C1 2.378(4), Pd1−C2 2.176(3), Pd1−C3 2.193(3), Pd1−C4 2.231(3), Pd1−C5 2.168(3), Pd1−C6 2.355(4), Pd2−Pd2* 2.9400(5), 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), Pd2−C7 2.345(4), Pd2−C8 2.177(3), Pd2−C9 2.223(3), Pd2−C10 2.216(3), Pd2−C11 2.152(4), Pd2−C12 2.352(4), C7−C8 1.374(5), C8−C9 1.421(4), C9−C10* 1.403(5), C10−C11 1.431(4), C11−C12 1.383(5).

found in a unit cell, and each molecule shows similar structural parameters. The Pd−Pd distances (2.9156(6) and 2.9400(5) Å) are within the range of known Pd−Pd lengths (2.391−3.185 Å).[28] Although the coordination mode (μ-η^3:η^3-mode) of DPHT ligand in **8-*E*,*E*,*E*-meso** is the same as that in **4-*E*,*E*,*E*-antifacial**, the trend of C−C bond lengths in each triene part was quite different between the two complexes; the central C−C bond length (C3−C4* 1.395(5) Å or C9−C10* 1.403(5) Å) in **8-*E*,*E*,*E*-meso** is significantly shorter than that in **4-*E*,*E*,*E*-antifacial** (1.474(7) Å). The $^{13}C\{^1H\}$ NMR signal pattern of the triene part in **8-*E*,*E*,*E*-meso** was also considerably different from that in **4-*E*,*E*,*E*-antifacial** (Scheme 7). While **4-*E*,*E*,*E*-antifacial** showed ^{13}C chemical shifts of the allylic central carbons at lower field than those of allylic terminal carbons as mentioned in section 1.2, the chemical shift of the allylic terminal carbons in **8-*E*,*E*,*E*-meso** appeared at the field similar to or lower than that of the allylic central carbons (Scheme 7). Thus, the structural and spectroscopic aspects give little support to bi-η^3-allyl dianion character in **8-*E*,*E*,*E*-meso** and suggest the considerable contribution of the electronic structure involving less-reduced DPHT ligands and less-oxidized Pd−Pd moiety in **8-*E*,*E*,*E*-meso**.[38]

As mentioned in section 1.3, the reaction of **1** with DBHT (excess) in CD_2Cl_2 afforded no sandwich complex but half-sandwich complexes **5**. Probably, stacking of two DBHT planes required for formation of sandwich complexes is hampered by the steric congestion between *t*-Bu groups.



(8)

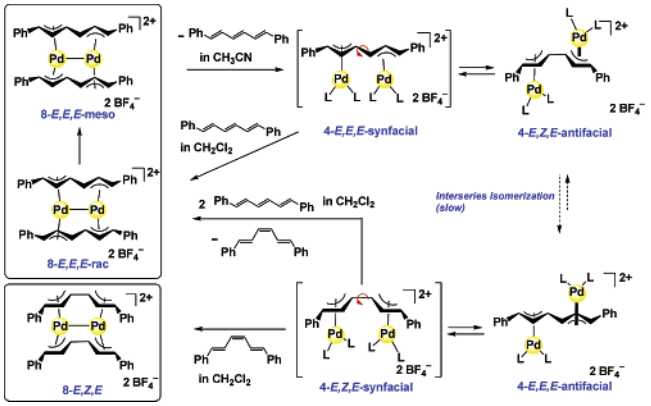
3.2. Interconversion between Half-Sandwich and Sandwich Complexes of 1,6-Diphenyl-1,3,5-hexatriene (DPHT). When the sandwich complex **8-*E*,*E*,*E*-meso** was dissolved in CD_3CN at −40 °C, one of the (*E*,*E*,*E*)-DPHT ligands was replaced by four acetonitrile ligands to give the half-sandwich complex **4-*E*,*Z*,*E*-antifacial** quantitatively.[4] Warming the sample to 25 °C then resulted in the isomerization of **4-*E*,*Z*,*E*-antifacial** to a mixture of **4-*E*,*Z*,*E*-antifacial**/**4-*E*,*E*,*E*-antifacial** (22/78) within 1 day in CD_3CN. When a solid sample of **4-*E*,*Z*,*E*-antifacial** obtained by evaporation of its CD_3CN solution at −40 °C was treated with (*E*,*E*,*E*)-DPHT (5 equiv) in CD_2Cl_2, the four acetonitrile ligands were immediately replaced by (*E*,*E*,*E*)-DPHT to generate the sandwich complex **8-*E*,*E*,*E*-rac** as a kinetic product.[39] Ultimately, **8-*E*,*E*,*E*-rac** isomerized to **8-*E*,*E*,*E*-meso** within 3 h at 23 °C (**8-*E*,*E*,*E*-rac**/**8-*E*,*E*,*E*-meso** = 2/98) (Scheme 13). Thus, the interconversion between half-sandwich and sandwich complexes occurred smoothly.

Treatment of **4-*E*,*E*,*E*-antifacial** with (*E*,*Z*,*E*)-DPHT (1 equiv) in CD_2Cl_2 gave a new sandwich complex **8-*E*,*Z*,*E*** as a single product, although the reaction was slow (13% conversion after 5 min) probably due to the poor solubility of **4-*E*,*E*,*E*-antifacial** in CD_2Cl_2. After 0.5 h, a mixture containing **8-*E*,*Z*,*E*** (17%), **8-*E*,*E*,*E*-meso** (21%), and **8-*E*,*E*,*E*-rac** (3%) was yielded, where a free DPHT existed as a mixture of (*E*,*Z*,*E*)-DPHT (19%) and (*E*,*E*,*E*)-DPHT (27%). Once isomerization of free (*E*,*Z*,*E*)-DPHT to free (*E*,*E*,*E*)-DPHT takes place due to

(37) There are two isomers for **8**, due to the two stacking modes (eclipsed and staggered) of zigzag conjugated polyenes. The existence of two isomers was revealed on the related sandwich complex $[Pd_3(\mu\text{-}\eta^3\text{:}\eta^2\text{:}\eta^3\text{-tetraene})]^{2+}$; see ref 5. In eq 8, **8-*E*,*E*,*E*-meso** was isolated as a single isomer. The structure of **8-*E*,*E*,*E*-rac** was reasonably assumed from the ^1H or $^{13}C\{^1H\}$ NMR signal pattern, which was similar to that of **8-*E*,*E*,*E*-meso**.

(38) The results of theoretical investigation on the electronic structure of **8** will be published elsewhere. It is notable that a related sandwich structure was found in $[Ni_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-pentadienyl})_2]$, see: (a) Rienäcker, R.; Yoshiura, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 677. (b) Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 678. (c) Böhm, M. C.; Gleiter, R. *Chem. Phys.* **1982**, *64*, 183.

Scheme 13. Interconversion between Sandwich and Half-Sandwich Complexes

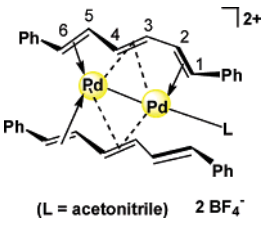


some palladium species as mentioned earlier, the Pd_2^{2+} moiety is trapped by free (*E*,*E*,*E*)-DPHT to form the stable sandwich complex **8-*E*,*E*,*E*-meso**.

The sandwich complex **8-*E*,*Z*,*E*** was isolated by a different method described in section 4, and its structure was determined by X-ray structure analysis (Figure 6). The Pd−Pd bond length in **8-*E*,*Z*,*E*** (2.770(1) or 2.767(1) Å) is shorter than that in **8-*E*,*E*,*E*-meso** (2.9156(6) or 2.9400(5) Å). In the crystal, the dication of **8-*E*,*Z*,*E*** held a pair of BF_4 anion and H_2O through supramolecular interaction at its concave space (Figure 7). BF_4^- and H_2O were connected through a hydrogen bond (F···O distance 2.82(1) or 2.84(1) Å). One of the four fluorine atoms of BF_4 and the oxygen atom of H_2O are located near the four hydrogen atoms of each *trans*,*cis*,*trans*-DPHT ligand (F···C distances 3.20−3.64 Å, O···C distances 3.29−3.69 Å).

Treatment of **4-*E*,*E*,*E*-antifacial** with (*E*,*E*,*E*)-DPHT (5 equiv) in CD_2Cl_2 at −40 °C afforded **8-*E*,*E*,*E*-rac**.[39] Interestingly, however, the formation of free (*E*,*Z*,*E*)-DPHT was also observed during the reaction (86% NMR yield).[4] It is reasonably assumed that (*E*,*Z*,*E*)-DPHT was released during the conversion of **4-*E*,*E*,*E*-antifacial** to **8-*E*,*E*,*E*-rac**, in view of the fact that (*E*,*Z*,*E*)-DPHT is thermodynamically less stable than (*E*,*E*,*E*)-DPHT. As depicted in Scheme 13, dissociation of (*E*,*Z*,*E*)-DPHT can be explained by the initial formation of **4-*E*,*Z*,*E*-synfacial**, which is a rotamer of **4-*E*,*E*,*E*-antifacial** at the central C−C bond of DPHT ligand. In **4-*E*,*Z*,*E*-synfacial**, two Pd atoms that are arranged co-facial are allowed to have a direct Pd−Pd

(39) The formation of another minor product (28% at 25 °C from **4-*E*,*Z*,*E*-antifacial** and 23% at 25 °C from **4-*E*,*E*,*E*-antifacial**) was observed. A slight amount of the minor product remained after 20 h during the reaction of **4-*E*,*E*,*E*-antifacial** and (*E*,*E*,*E*)-DPHT. Efforts to isolate this product failed, and the structure remains elusive. Because the minor product showed 12 nonaromatic C*H* proton resonances, the product is assumed as a sandwich complex having an unsymmetric structure. One possible structure is shown below. ^{1}H NMR signals (CD_2Cl_2, 23 °C) for −C*H*− of one DPHT, δ = 6.85 (H_2), 6.42 (d, J = 13.6 Hz, H_6), 5.37 (dd, J = 13.6 Hz, J = 10.4 Hz, H_5), 5.18 (dd, J = 12.8 Hz, J = 7.2 Hz, H_3), 4.78 (d, J = 14.0 Hz, H_1), 2.46 (dd, J = 12.8 Hz, J = 10.8 Hz, H_4); for −C*H*− of another DPHT, δ = 6.60 (H_1), 6.58 (H_6), 5.42 (dd, J = 13.6 Hz, J = 11.2 Hz, H_2), 5.05 (dd, J = 13.8 Hz, J = 11.2 Hz, H_5), 4.28 (t, J = 11.2 Hz, H_3), 3.88 (t, J = 11.2 Hz, H_4).



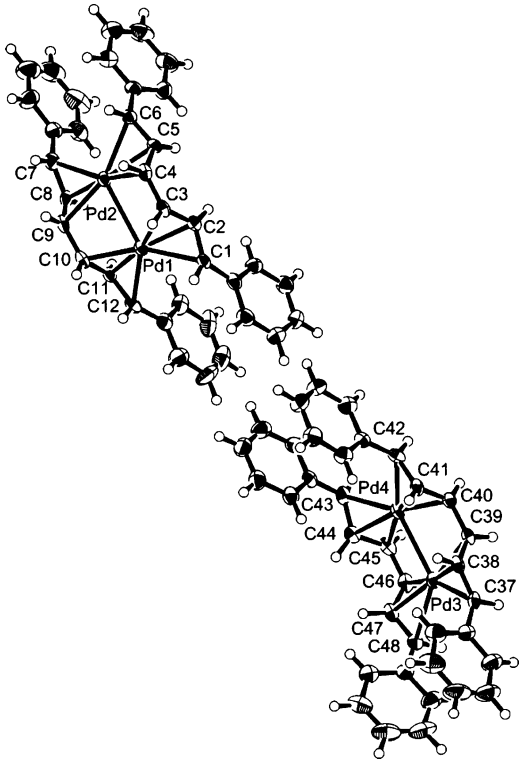


Figure 6. ORTEP drawings of **8-*E*,*Z*,*E*** (two independent molecules in a unit cell, 50% probability ellipsoids, BF_4 anions and water molecules were omitted for clarity). Selected bond lengths (Å): Pd1−Pd2 2.770(1), Pd1−C1 2.398(10), Pd1−C2 2.18(1), Pd1−C3 2.19(1), Pd2−C4 2.196(9), Pd2−C5 2.184(10), Pd2−C6 2.36(1), Pd2−C7 2.40(1), Pd2−C8 2.17(1), Pd2−C9 2.19(1), Pd1−C10 2.20(1), Pd1−C11 2.17(1), Pd1−C12 2.35(1), C1−C2 1.38(1), C2−C3 1.41(1), C3−C4 1.44(2), C4−C5 1.42(1), C5−C6 1.38(1), C7−C8 1.39(2), C8−C9 1.41(2), C9−C10 1.43(2), C10−C11 1.42(1), C11−C12 1.41(2), Pd3−Pd4 2.767(1), Pd3−C37 2.42(1), Pd3−C38 2.18(1), Pd3−C39 2.18(1), Pd4−C40 2.18(1), Pd4−C41 2.19(1), Pd4−C42 2.39(1), Pd4−C43 2.34(1), Pd4−C44 2.15(1), Pd4−C45 2.20(1), Pd3−C46 2.20(1), Pd3−C47 2.18(1), Pd3−C48 2.36(1).

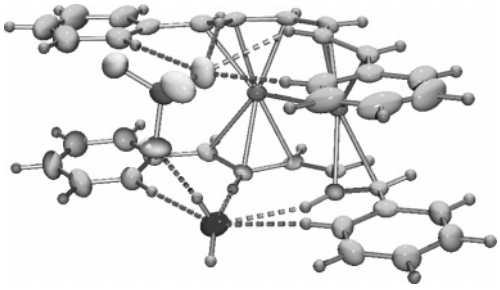
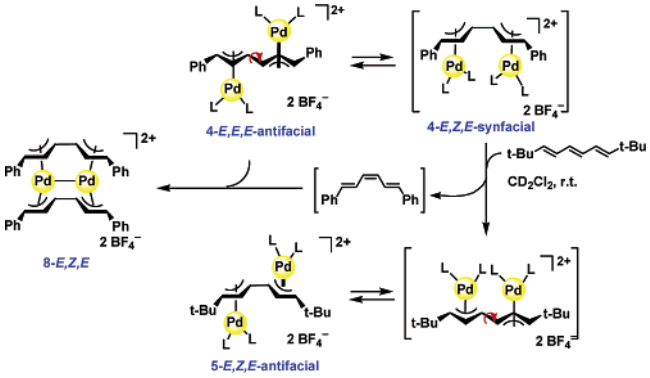


Figure 7. Supramolecular binding of the $[BF_4\cdots H_2O]^-$ moiety by the dication of **8-*E*,*Z*,*E*** in the crystalline state.

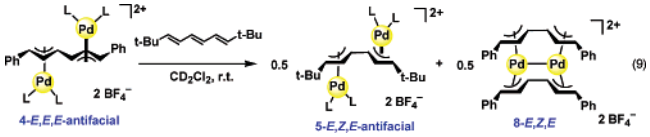
interaction, as suggested in the dinuclear elimination reaction involving DBHT. Two equivalents of (*E*,*E*,*E*)-DPHT then can bind the Pd−Pd moiety to release (*E*,*Z*,*E*)-DPHT (Scheme 13). This hypothesis is supported by the observation of the stereoretentive trans-olefination process described next.

4. Trans-olefination of $[Pd_2L_4]^{2+}$ Moiety between 1,3,5-Trienes. In the previous section, it is proposed that the transformation of **4-*E*,*E*,*E*-antifacial** to **8-*E*,*E*,*E*** in the presence of free (*E*,*E*,*E*)-DPHT may involve the replacement of (*E*,*Z*,*E*)-DPHT ligand with (*E*,*E*,*E*)-DPHT, from the observation of the release of free (*E*,*Z*,*E*)-DPHT during the reaction. The reaction of **4-*E*,*E*,*E*-antifacial** with the *t*-Bu analogue (*E*,*E*,*E*)-DBHT was then examined. When 1 equiv of (*E*,*E*,*E*)-DBHT was added

Scheme 14



to the solution of **4-*E,E,E*-antifacial** in CD_2Cl_2 at 0 °C, the formation of **5-*E,Z,E*-antifacial** (37%) and **8-*E,Z,E*** (33%) was observed after 1 h (eq 9). After 3 h, the yield of **5-*E,Z,E*-antifacial** reached 46%, while **8-*E,Z,E*** decreased to 23% probably due to the partial precipitation of **8-*E,Z,E*** (red precipitates were observed), and approximately one-half the amount of free (*E,E,E*)-DBHT remained.



This result suggests the involvement of stereoretentive ligation of (*E,E,E*)-DBHT and stereoretentive release of (*E,Z,E*)-DPHT (Scheme 14). Selective formation of the transferred product **5-*E,Z,E*-antifacial** indicates that the trans-olefination is mediated via syn addition of a Pd_2 unit. If the elimination of DPHT ligand in **4-*E,E,E*-antifacial** proceeds in a syn manner, (*E,Z,E*)-DPHT should be released via **4-*E,Z,E*-synfacial**. The formation of **8-*E,Z,E*** is reasonably understood by the immediate trap of the released (*E,Z,E*)-DPHT by the remaining **4-*E,E,E*-antifacial**, on the basis of the result described in section 3.2.

Conclusion

In summary, we have demonstrated the stereoretentive nature of dinuclear elimination and transfer of $[Pd_2L_n]^{2+}$ moieties between conjugated 1,3,5-trienes. From this study, several new aspects are gained on the role of conjugated olefin as the multidentate ligands for a dipalladium moiety: (a) a Pd_2^{2+} moiety derived from **1** adds to 1,3,5-trienes to form bi-η^3-allyldipalladium complexes; (b) dinuclear elimination from bi-η^3-allyldipalladium(II) complexes is induced by addition of phosphine (PPh_3 or dppm), and it proceeds in a stereospecific (syn) manner; (c) bis-μ-η^3:η^3-triene dipalladium sandwich complexes are reversibly formed from bi-η^3-allyldipalladium(II) complexes and triene in a stereoretentive manner; and (d) transfer of dipalladium moiety $[Pd_2L_4]^{2+}$ between 1,3,5-trienes (i.e., trans-olefination of $[Pd_2L_4]^{2+}$) proceeds stereoretentively. The observed highly stereoretentive dynamic behavior of Pd−Pd moieties on 1,3,5-trienes represents the pairwise behavior of a dinuclear metal moiety on the π-plane of sp^2-carbon framework; that is, multiple metal atoms behave in a correlated way on an extended sp^2-carbon framework through formation/cleavage of metal−metal bonds.

Experimental Section

General Considerations. Unless specified, all reactions were carried out using standard Schlenk techniques under dinitrogen atmosphere. ^1H and ^{13}C NMR spectra were obtained on either 270 (JEOL GSX-270), 400 (JEOL GSX-400, JEOL ECP-400), or 600 MHz (Varian UNITY-INOVA 600) instruments. The chemical shifts were referenced to the residual resonances of deuterated solvents. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. UV−vis spectra were recorded on a Shimadzu UV-3100PC. Unless specified, all reagents were purchased from commercial suppliers and used without purification. CH_2Cl_2, CD_2Cl_2, CH_3CN, and CD_3CN were distilled from CaH_2 prior to use. $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**),[20] $[Pd_2(CH_3CN)_4(PPh_3)_2][BF_4]_2$ (**2**),[20] $[Pd_2(CH_3CN)_4(PPh_3)_2][PF_6]_2$ (**2′**),[21] $[Pd_2(\mu\text{-}PPh_3)_2(CH_3CN)_2][PF_6]_2$ (**2″**),[22] $NaBAr_f$,[40] and (*E,E,E*)-DBHT[41] were prepared according to the literature. (*E,Z,E*)-DPHT was generously gifted from Prof. Tetsuro Majima (Osaka University). All monitoring experiments using DPHT or DBHT were carried out in J. Young resealable NMR tubes wrapped with aluminum foil.

Synthesis of $[Pd_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-Hexatriene})(CH_3CN)_4][BF_4]_2$ (3a). To a solution of $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**) (152.1 mg, 0.240 mmol) in CH_3CN was added 1,3,5-hexatriene (31.4 μL, 0.289 mmol), and the mixture was stirred for 1 h at room temperature. The yellow mixture was filtered, and the volatiles were removed in vacuo. Recrystallization from CH_3CN/Et_2O gave microcrystals of **3a** (113.9 mg, 75% yield). ^1H NMR (CD_3CN) δ = 6.01 (m), 4.37 (dd), 4.34 (d, J = 6.8 Hz), 3.34 (d, J = 12.7 Hz). Anal. Calcd for $Pd_2C_{14}H_{20}N_4B_2F_8$: C, 26.66; H, 3.20; N, 8.88. Found: C, 26.04; H, 3.16; N, 8.45.

Synthesis of $[Pd_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-Hexatriene})(CH_3CN)_2(PPh_3)_2][PF_6]_2$ (3b). To a solution of $[Pd_2(\mu\text{-}PPh_3)_2(CH_3CN)_2][PF_6]_2$ (**2″**) (70.0 mg, 0.0633 mmol) in CH_2Cl_2 was added 1,3,5-hexatriene (8.3 mL, 0.0760 mmol), and the mixture was stirred for 45 min at room temperature. The resultant mixture was filtered, and hexane was added to give a yellow powder. Recrystallization from CH_2Cl_2/hexane gave microcrystals of **3b** (39.5 mg, 52% yield). ^1H NMR ($CDCl_3$) δ = 7.6−7.4 (m), 6.32 (m), 5.55 (m), 3.42 (br d), 3.03 (br d), 2.05 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 26.2 (s). Anal. Calcd for $Pd_2C_{46}H_{44}N_2P_4F_{12}$: C, 46.44; H, 3.73; N, 2.35. Found: C, 46.27; H, 3.71; N, 2.26.

Synthesis of 4-*E,E,E*-Antifacial. $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**) (199.1 mg, 0.315 mmol) was dissolved in CH_3CN (30 mL), and (*E,E,E*)-DPHT (314.2 mg, 1.352 mmol) was added to the solution. The solution was stirred for 1.5 h at room temperature. The orange solution was filtered, and crystallization from CH_3CN/Et_2O afforded orange microcrystals of **4-*E,E,E*-antifacial** (136.0 mg, 55% yield). ^1H NMR (CD_3CN) δ = 7.70 (d, J = 7.3 Hz), 7.6−7.3 (m), 6.57 (br t), 5.21 (d, J = 11.1 Hz), 4.46 (br d). $^{13}C\{^1H\}$ NMR (CD_3CN) δ = 135.9 (s), 129.5 (s), 128.3 (s), 127.7 (s), 110.4 (s), 83.7 (s), 78.5 (s). Anal. Calcd for $Pd_2C_{26}H_{28}B_2F_8 \cdot H_2O$: C, 38.99; H, 3.78; N, 6.99. Found: C, 38.44; H, 3.60; N, 7.16.

Generation of 4-*E,Z,E*-Antifacial. The complex **4-*E,Z,E*-antifacial** was generated quantitatively by dissolving $[Pd_2((E,E,E)\text{-DPHT})_2][BF_4]_2$ (**8-*E,E,E*-meso**) in CD_3CN or CH_3CN at −40 °C. ^1H NMR (CD_3CN) δ = 7.78 (d, J = 7.8 Hz), 7.6−7.3 (m), 6.89 (br t), 5.17 (d, J = 11.1 Hz), 4.46 (br d). $^{13}C\{^1H\}$ NMR (CD_3CN) δ = 136.1 (s), 129.3 (s), 128.4 (s), 127.7 (s), 108.0 (s), 83.2 (s), 76.0 (s).

Synthesis of 5-*E,Z,E*-Antifacial. To a solution of $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**) (500.0 mg, 0.790 mmol) in CH_2Cl_2 (50 mL) was added (*E,E,E*)-DBHT (159.6 mg, 0.830 mmol), and the mixture was stirred for 50 min at room temperature under N_2. The mixture was filtered,

(40) (a) Kobayashi, H.; Sonoda, A.; Iwamoto, H.; Yoshimura, M. *Chem. Lett.* **1981**, *10*, 579. (b) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (c) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920. (d) Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579.
(41) Horner−Wadsworth−Simmons modified Wittig-type reaction was used. See: (a) Spangler, C. W.; McCoy, R. K.; Dembek, A. A.; Sapochak, L. S.; Gates, B. D. *J. Chem. Soc., Perkin Trans. 1* **1989**, 151. See for alternative synthesis and NMR data: (b) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

and crystallization from CH_2Cl_2/Et_2O gave a yellow powder (89.8 mg), which contained **5-*E,Z,E*-antifacial** and **5-*E,E,E*-antifacial**. The supernatant was separated from the powder, and Et_2O was added. Crystallization from this solution gave yellow microcrystals of **5-*E,Z,E*-antifacial** (446.8 mg, 76% yield). ^1H and $^{13}C\{^1H\}$ NMR spectra of this crystal in CD_3CN showed the presence of two intra-series isomers (93/7 at 25 °C).[42,43] For major isomer: ^1H NMR (CD_3CN) $\delta = 6.02$ (m), 4.22 (d, $J = 11.6$ Hz), 4.11 (m), 1.16 (s). $^{13}C\{^1H\}$ NMR (CD_3CN) $\delta = 110.1$ (s), 102.4 (s), 76.9 (s), 34.4 (s), 29.8 (s). For minor isomer: ^1H NMR (CD_3CN) $\delta = 5.53$ (m), 4.68 (d, $J = 12.7$ Hz), 4.35 (m), 1.15 (s). $^{13}C\{^1H\}$ NMR (CD_3CN) $\delta = 105.4$ (s), 100.7 (s), 73.5 (s), 34.6 (s), 29.9 (s). Anal. Calcd for $Pd_2C_{22}H_{36}N_4B_2F_8$: C, 35.56; H, 4.88; N, 7.54. Found: C, 35.65; H, 4.84; N, 7.72.

Synthesis of 5-*E,E,E*-Antifacial. To a solution of $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**) (500.0 mg, 0.790 mmol) in CH_2Cl_2 (40 mL) was added (*E,E,E*)-DBHT (457.6 mg, 2.371 mmol), and the mixture was stirred for 5 h at room temperature. The reaction mixture was filtered, and the volatiles were removed from the filtrate in vacuo. To the residue was added CH_2Cl_2 (200 mL), and the suspension was stirred overnight. The mixture was then concentrated, and Et_2O was added. The supernatant was decanted, and the residue was washed with Et_2O. The residue was then dissolved in CH_3CN, the solution was filtered, and toluene was added to generate a yellow precipitate. Recrystallization from CH_3CN/CH_2Cl_2/toluene gave a yellow powder of **5-*E,E,E*-antifacial** (314.1 mg, 54% yield) at the bottom of the vessel. The yellow crystalline materials on the wall of the vessel were a mixture of **5-*E,Z,E*-antifacial** and **5-*E,E,E*-antifacial**. ^1H NMR (CD_3CN) $\delta = 5.84$ (m), 4.26 (d, $J = 12.4$ Hz), 4.06 (m), 1.14 (s). $^{13}C\{^1H\}$ NMR (CD_3CN) $\delta = 112.6$ (s), 102.0 (s), 79.7 (s), 34.3 (s), 29.8 (s). Anal. Calcd for $Pd_2C_{22}H_{36}N_4B_2F_8$: C, 35.56; H, 4.88; N, 7.54. Found: C, 35.61; H, 4.88; N, 7.48.

Generation of 7-*E,Z,E*-Antifacial. In an NMR tube, **5-*E,Z,E*-antifacial** (7.0 mg, 0.0094 mmol) and PPh_3 (4.9 mg, 0.0188 mmol) were added, and CD_3CN (0.5 mL) was added. The temperature of the tube was kept at −40 °C. After 5 min, **5-*E,Z,E*-antifacial** disappeared, and only **7-*E,Z,E*-antifacial** was observed as a mixture of two isomers (>95/<5). For major: ^1H NMR (CD_3CN) $\delta = 7.6-7.4$ (m), 5.79 (br), 3.92 (br), 1.69 (br), 0.92 (br s). $^{31}P\{^1H\}$ NMR (CD_3CN) $\delta = 20.6$ (s). For minor: ^1H NMR (CD_3CN) $\delta = 7.19$, 6.98, 4.70, 4.42, 4.31, 3.46, 3.06. Only these signals were detected. $^{31}P\{^1H\}$ NMR (CD_3CN) $\delta = 18.2$ (only one signal was detected).

Synthesis of 7-*E,E,E*-Antifacial. To a solution of **5-*E,E,E*-antifacial** (100.0 mg, 0.135 mmol) in CH_3CN (3 mL) was added PPh_3 (70.6 mg, 0.269 mmol). The color immediately changed from yellow to orange. The mixture was stirred for 5 min, and the reaction mixture was filtered and poured into Et_2O to afford pale yellow precipitates. The powder was then washed with Et_2O and dried in vacuo to afford **7-*E,E,E*-antifacial** (127 mg, 79% yield). A single crystal suitable for X-ray analysis was obtained by recrystallization from CH_2Cl_2/benzene. For major: ^1H NMR (CD_2Cl_2, −40 °C) $\delta = 7.7-7.2$ (m), 4.69 (m, H_2, 2H), 3.95 (dd, $J = 13.2$ Hz, $J = 8.4$ Hz, H_1, 2H), 3.61 (m, H_3, 2H), 1.58 (s, C*H*$_3$CN, 6H), 0.59 (s, *t*-Bu, 18H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C) $\delta = 30.5$ (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) $\delta = 135.3-129.7$, 125.3 (s, CH_3CN), 119.4 (s, C_1), 111.6 (s, C_2), 76.1 (s, C_3), 34.4 (s, *C*(CH$_3$)$_3$), 29.8 (s, C(*C*H$_3$)$_3$), 2.8 (s, *C*H$_3$CN). For minor: ^1H NMR (CD_2Cl_2, −40 °C) $\delta = 7.7-7.2$, 5.24 (dd, $J = 14.8$ Hz, $J = 10.4$ Hz, H_1), 5.03 (dd, $J = 13.6$ Hz, $J = 9.2$ Hz, H_6), 4.42 (dd, $J = 11.2$ Hz, $J = 10.8$ Hz, H_4, 1H), 3.89 (dd, $J = 13.6$ Hz, $J = 10.8$ Hz, H_5, 1H), 3.72 (dd, $J = 14.8$ Hz, $J = 7.2$ Hz, H_2, 1H), 3.43 (dd, $J = 11.2$ Hz, $J = 7.2$ Hz, H_3, 1H), 1.95 (s, C*H*$_3$CN, 3H), 1.64 (s, C*H*$_3$CN, 3H), 0.78 (s, *t*-Bu, 9H), 0.61 (s, *t*-Bu, 9H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C) $\delta = 31.3$ (d, $J = 12.5$ Hz), 22.1 (d, $J = 12.5$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) $\delta = 135.3-129.7$, 125.3 (s, CH_3CN), 123.3 (s, C_6), 113.5 (s, C_1), 108.2 (s, C_2 or C_5), 108.0 (s, C_2 or C_5), 80.3 (s, C_3), 66.2 (s, C_4), 34.7 (d, $J = 3.1$ Hz, *C*(CH$_3$)$_3$), 34.1 (d, $J = 3.8$ Hz, *C*(CH$_3$)$_3$), 30.3 (d, $J = 4.6$ Hz, C(*C*H$_3$)$_3$), 30.0 (d, $J = 3.8$ Hz, C(*C*H$_3$)$_3$), 2.8 (s, *C*H$_3$CN). Anal. Calcd for $Pd_2C_{54}H_{60}N_2P_2B_2F_8$: C, 54.71; H, 5.10; N, 2.36. Found: C, 54.89; H, 5.15; N, 2.35.

Synthesis of (*E,Z,E*)-DBHT. (*E,Z,E*)-DBHT was conveniently obtained by the dipalladium-mediated isomerization from (*E,E,E*)-DBHT. To a solution of **5-*E,E,E*-antifacial** (300.0 mg, 0.404 mmol) in CH_3CN (10 mL) was added dppm (294.9 mg, 0.767 mmol), and the mixture was stirred for 10 min at 0 °C. The volatiles were removed in vacuo, and cold pentane (−20 °C) was added to the residue. The suspension was filtered immediately, and the volatiles were removed in vacuo to give a colorless powder of (*E,Z,E*)-DBHT (49.5 mg, 81% yield). NMR data were found in the literature.[41b] The compound that remained on the filter funnel was $[Pd_2(dppm)_2(CH_3CN)_2][BF_4]_2$.

Synthesis of 8-*E,E,E*-Meso. To a solution of $[Pd_2(CH_3CN)_6][BF_4]_2$ (**1**) (243.4 mg, 0.385 mmol) in CH_2Cl_2 (30 mL) was added (*E,E,E*)-DPHT (247.1 mg, 1.064 mmol), and the mixture was stirred for 2 h at room temperature. The reaction mixture was filtered, and crystallization from CH_2Cl_2/Et_2O gave a red powder of **8-*E,E,E*-meso** (251.8 mg, 77% yield). ^1H NMR (CD_2Cl_2) $\delta = 7.46$ (t), 7.05 (t), 6.78 (d), 6.76 (d, $J = 13.8$ Hz), 5.26 (m), 3.98 (m). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 132.0$ (s), 130.6 (br s), 130.0 (s), 129.7 (s), 129.4 (s), 98.9 (s), 93.1 (s). Anal. Calcd for $Pd_2C_{36}H_{32}B_2F_8$: C, 50.80; H, 3.79. Found: C, 50.51; H, 3.96. A single crystal suitable for X-ray analysis was obtained by recrystallization from CH_2Cl_2/*t*-Bu-benzene/*n*-hexane. ^1H NMR data of **8-*E,E,E*-rac**: ^1H NMR (CD_2Cl_2) $\delta = 5.95$ (d, $J = 13.5$ Hz), 5.79 (m), 3.67 (m).

Synthesis of 8-*E,Z,E*. The complex **4-*E,E,E*-antifacial** (15.0 mg, 0.0192 mmol) and (*E,E,E*)-DBHT (1.8 mg, 0.0095 mmol) were placed in an NMR tube. To the tube was added CD_2Cl_2 (0.5 mL), and the tube was supersonicated. After 2 h, the formation of **8-*E,Z,E*** (37% NMR yield) and **5-*E,Z,E*-antifacial** (41% NMR yield) was observed with trace (*E,Z,E*)-DPHT. The complex **8-*E,Z,E*** was obtained as red crystals together with **5-*E,Z,E*-antifacial** (yellow crystals) from the reaction of **4-*E,E,E*-antifacial** and (*E,E,E*)-DBHT in CH_2Cl_2 with stirring for 20 min followed by filtration and crystallization from CH_2Cl_2/toluene. A red crystal suitable for X-ray diffraction analysis was picked up from the crystalline mixture. ^1H NMR (CD_2Cl_2) $\delta = 7.39$ (m, *p*-Ph), 7.17 (d, $J = 13.5$ Hz, H_1), 6.93 (m, *o*-, *m*-Ph), 5.07 (m, H_2), 4.56 (m, H_3).

Table 1. X-ray Crystallographic Data of **1**, **3b**, and **5-*E,Z,E*-Antifacial**

	1	**3b**	**5-*E,Z,E*-antifacial**
formula	$C_{12}H_{18}N_6B_2F_8Pd_2$	$C_{46}H_{44}N_2P_4F_{12}Pd_2$	$C_{22}H_{36}N_4B_2F_8Pd_2$
fw	632.72	1189.4	742.96
space group	$P2_1/a$ (No. 14)	$C2/c$ (No. 15)	*Pbca* (No. 61)
a, Å	10.0193(6)	32.791(4)	17.2416(3)
b, Å	20.799(1)	8.962(2)	12.1588(3)
c, Å	12.0023(7)	19.133(3)	29.5145(5)
α, deg			
β, deg	112.696(2)	113.577(10)	
γ, deg			
V, Å^3	2307.5(3)	5153(1)	6187.3(4)
Z	4	4	8
D(calcd), g/cm^3	1.821	1.533	1.595
μ(Mo Kα), mm^{-1}	16.33	8.99	12.29
temp, K	273	296	277
R1	0.041	0.077	0.036

(42) The ^1H and ^{13}C NMR signal patterns of the major and minor isomers are quite similar (symmetric) to each other, and it is reasonably assumed that both isomers are the intra-series products, although it cannot be concluded that the isomer that was structurally determined by X-ray analysis is the major isomer in CD_3CN. For convenience, we abbreviate the two equilibrated isomers as **5-*E,Z,E*-antifacial** in this Article.

(43) The isolated **5-*E,Z,E*-antifacial** was poorly soluble in CD_2Cl_2. In the monitoring reactions of **1** and DBHT in CD_2Cl_2, however, **5-*E,Z,E*-antifacial** could be detected because **5-*E,Z,E*-antifacial** becomes soluble in the presence of free CH_3CN released from **1**. In these conditions, **5-*E,Z,E*-antifacial** existed as a mixture of two isomers (major/minor = 9/1) as observed in CD_3CN.

Table 2. X-ray Crystallographic Data of **7-*E,E,E*-Antifacial** and **8-*E,Z,E***

	7-*E,E,E*-antifacial	**8-*E,Z,E***
formula	$C_{54}H_{60}N_2B_2F_8P_2Pd_2$	$C_{36}H_{34}B_2F_8O_1Pd_2$
fw	1185.44	869.07
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	14.1209(4)	14.4348(3)
b, Å	17.2838(6)	14.8652(4)
c, Å	22.5026(9)	16.9596(4)
α, deg		72.4075(5)
β, deg	97.679(2)	90.278(1)
γ, deg		81.7435(7)
V, Å^3	5442.8(3)	3428.5(1)
Z	4	4
D(calcd), g/cm^3	1.447	1.684
μ(Mo Kα), cm^{-1}	7.84	11.22
temp, K	223	213
R1	0.065	0.042

X-ray Crystallographic Studies. The crystallographic data were summarized in Tables 1 and 2. All measurements were made on a Rigaku AFC5R diffractometer (for **3b**) or Rigaku RAXIS-RAPID imaging plate diffractometer (for **1**, **5-*E,E,E*-antifacial**, **7-*E,E,E*-antifacial**, and **8-*E,Z,E***) with graphite monochromated Mo Kα radiation. The calculations were carried out with the teXsan crystal structure analysis software package of Molecular Structure Corp. The structures were solved by heavy-atom Patterson methods and refined by full-matrix least-squares procedures. The non-hydrogen atoms were refined anisotropically. Detailed crystallographic data were collected in the Supporting Information.

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Supporting Information Available: Details of the X-ray single-crystal structural analyses for **1**, **3b**, **5-*E,Z,E*-antifacial**, **7-*E,E,E*-antifacial**, and **8-*E,Z,E***. This material is available free of charge via the Internet at http://pubs.acs.org.

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