

Organometallic Sandwich Chains Made of Conjugated Polyenes and Metal–Metal Chains

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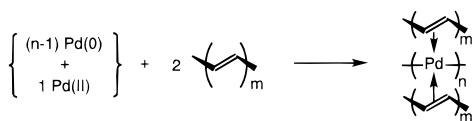
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The combination of multiple low-dimensionally extended molecules by chemical bonding of considerable strength would become a powerful methodology for the construction of new functional molecular organizations. Among the extended systems, conjugated polyenes such as polyacetylene are among the most ubiquitous and simple sp^2 -carbon chain frameworks, of which a number of fascinating properties have been intensively explored.¹ Another extended framework made of only transition metals, such as a metal–metal bond chain, is likewise fascinating.² We aimed to directly combine both kinds of intriguing chains by utilizing a $p\pi$ -electron sequence of conjugated polyenes for the bonding with a metal–metal bonded array.^{3,4} Here, we report synthesis and structures of one-dimensionally expanded organometallic sandwich complexes, made of two conjugated polyenes $-(CH)_m-$ and a metal–metal bond chain $-Pd_n^{2+}-$. The *full-hybrid* chain-linkage is revealed to be attained by two modes of *sequential* coordination bonds.

The “naked” Pd_n^{2+} chain, though unstable for isolation, can be a discrete molecular ion consisting of $(n - 1)$ Pd–Pd bonds with $2(n - 1)$ electrons,⁵ which are expected to be supplied by a combination of $\{1Pd(II) + (n - 1)Pd(0)\}$ because a high-valent Pd(II) can be regarded as a $0e$ -contributor and a low-valent Pd(0) as a $2e$ -contributor along the Pd–Pd bond direction. As shown in Chart 1, we assembled mononuclear palladium substrates

Chart 1



bearing the correct number of electrons and substitutional lability^{6,7} along the conjugated polyene chains, forming a linear Pd–Pd bond chain.

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(3) A few π -coordinated acyclic polyene–transition metal complexes have been reported: (a) Whitlock, H. W.; Reich, C.; Woessner, W. D., *J. Am. Chem. Soc.* **1971**, *93*, 2483. (b) Wadehoff, 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.

(4) For a recent review for metal-containing organic $p\pi$ -systems, see: Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123 and references therein.

(5) Zhang, T.; Drouin, M.; Harvey, P. D. *Inorg. Chem.* **1999**, *38*, 1305.

(6) $[Pd(CH_3CN)_4][BF_4]_2$: Schramm, R. F.; Wayland, B. B. *J. Chem. Soc., Chem. Commun.* **1968**, 898.

(7) $[Pd_2(dba)_3 \cdot CHCl_3]$: (a) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253. For an example of its use for multi-palladium complexes, see: (b) Fox, G. A.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 3718.

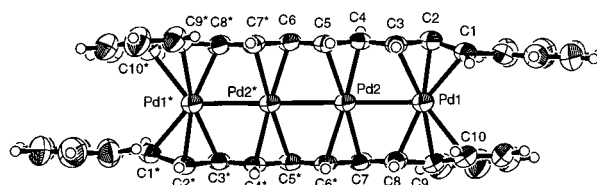
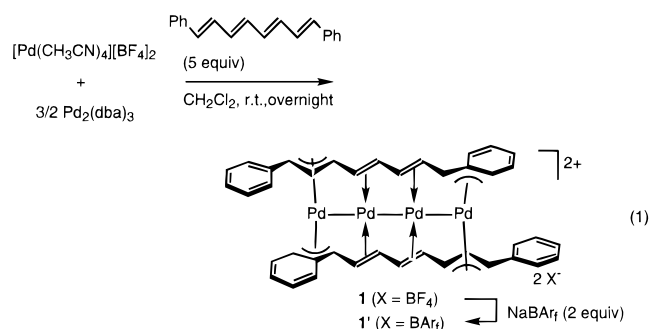


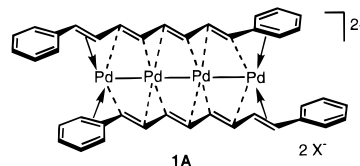
Figure 1. ORTEP drawing of **1'** (BAR_f anions were omitted for clarity). Selected bond distances (Å) and angles (deg): Pd1–Pd2 = 2.7322(8), Pd2–Pd2* = 2.654(1), Pd1–C1 = 2.282(7), Pd1–C2 = 2.168(7), Pd1–C3 = 2.242(6), Pd2–C4 = 2.182(6), Pd2–C5 = 2.219(6), Pd2*–C6 = 2.223(6), Pd2–C7 = 2.185(6), Pd1–C8 = 2.236(7), Pd1–C9 = 2.206(7), Pd1–C10 = 2.421(8), C1–C2 = 1.393(10), C2–C3 = 1.420(10), C3–C4 = 1.425(10), C4–C5 = 1.410(9), C5–C6 = 1.419(10), C6–C7* = 1.408(10), C7–C8 = 1.42(1), C8–C9 = 1.454(10), C9–C10 = 1.43(1), Pd1–Pd2–Pd2* = 178.25(4), C1–C2–C3 = 119.9(7), C2–C3–C4 = 122.0(7), C3–C4–C5 = 123.8(7), C4–C5–C6 = 122.9(6), C5–C6–C7* = 123.7(7), C6*–C7–C8 = 122.3(7), C7–C8–C9 = 125.7(7).

As an initial model, the Pd₄ sandwich chain of *all-trans*-1,8-diphenyl-1,3,5,7-octatetraene (DPOT, **1'**) was synthesized according to eq 1 (74% isolated yield, counteranions were ex-



changed from BF₄ to BAR_f (=B(3,5-(CF₃)₂C₆H₃)₄)⁸ to improve the solubility and crystallinity, and its crystal structure is shown in Figure 1.⁹ The component three chains were bound in a sandwich manner through $\eta^3: \eta^2: \eta^2: \eta^3$ -coordination mode. The alternative description of **1** is **1A** in Chart 2 involving three

Chart 2



bridging C=C ligands in each DPOT, which may accord to the general formula shown in Chart 1. In the crystal structure, Pd–Pd–Pd–Pd skeleton is highly linear (Pd2–Pd1–Pd1* = 178.25(4)°), and each Pd–Pd length (outer, 2.7322(8) Å; inner, 2.654(1) Å) is normal and consistent with the four-centered, six-electron bond of the Pd₄ core.

The ¹H NMR spectra of **1'** in CD₂Cl₂ or acetone-*d*₆ showed only sharp symmetrical DPOT signals at 23 °C, which were

(8) (a) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (b) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

(9) Crystal data: C₁₀₄H₆₀B₂F₄₈Pd₄·3Et₂O·2H₂O, *M* = 2927.16, space group *P*2₁/*c* (no. 14), *a* = 13.094(2), *b* = 24.229(2), and *c* = 19.497(4) Å, β = 104.42(1)°, *U* = 5990(1) Å³, *Z* = 2, *F*(000) = 2912, *D*_c = 1.623 g cm⁻³, μ (Mo K α) = 7.17 cm⁻¹, 833 variables refined with 10 335 reflections collected at 223 K with *I* > 3 σ (*I*) to *R* = 0.072.

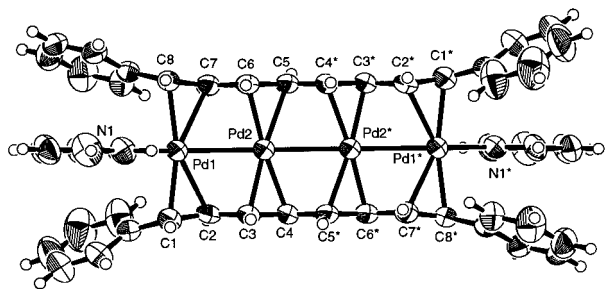
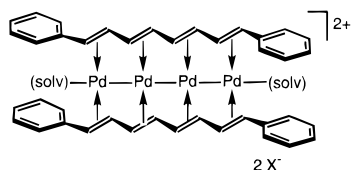


Figure 2. ORTEP drawing of **2'** (BARf anions were omitted for clarity). Selected bond distances (Å) and angles (deg): Pd1–Pd2 = 2.7463(8), Pd2–Pd2* = 2.721(1), Pd1–C1 = 2.188(7), Pd1–C2 = 2.344(7), Pd2–C3 = 2.129(6), Pd2–C4 = 2.218(7), Pd2–C5 = 2.203(6), Pd2–C6 = 2.142(6), Pd1–C7 = 2.337(6), Pd1–C8 = 2.202(6), C1–C2 = 1.407(10), C2–C3 = 1.46(1), C3–C4 = 1.412(10), C4–C5* = 1.46(1), C5–C6 = 1.410(9), C6–C7 = 1.451(10), C7–C8 = 1.402(9), Pd1–N1 = 2.152(5), Pd1–Pd2–Pd2* = 174.50(4), N1–Pd1–Pd2 = 152.0(2), C1–C2–C3 = 120.5(7), C2–C3–C4 = 120.9(8), C3–C4–C5* = 118.9(8), C4*–C5–C6 = 120.6(8), C5–C6–C7 = 121.8(8), C6–C7–C8 = 121.4(7).

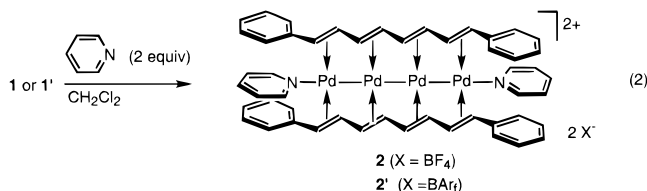
significantly broadened at $-90\text{ }^\circ\text{C}$.¹⁰ Although we were unable to obtain well-characterizable resonances at temperatures lower than $-90\text{ }^\circ\text{C}$, the spectral aspects suggest occurrence of a facile slippage of the DPOT ligands along the Pd₄ array, forming a symmetrical $\eta^2:\eta^2:\eta^2:\eta^2$ -complex (Chart 3).¹¹ It is possible that

Chart 3



this complex, which may or may not be coordinated with solvents at the terminals of Pd₄ chain, lies as an equilibrium species with the asymmetrical form **1'** or as an intermediate in the ¹H NMR symmetrization process of **1'**.

In any case, such an alternative coordination mode was clearly confirmed by the reaction of **1** or **1'** with 2 equiv of pyridine to give the pyridine association product **2** or **2'** (eq 2, quantitative in CD₂Cl₂).¹² The crystal structure of **2'** is shown in Figure 2.¹³



Each Pd–Pd (Pd1–Pd2 = 2.7463(8) Å, Pd2–Pd2* = 2.721(1) Å) is again within a four-centered, six-electron Pd₄ bond length. The $-(\text{CH})_8-$ parts are maintained planar, although each phenyl group of DPOT leaps up from the $-(\text{CH})_8-$ plane to avoid the steric congestion with pyridine ligands being accommodated at both ends of the Pd₄ chain, which also brought about the slight

(10) ¹H NMR (CD₂Cl₂, 25 °C) of the $-(\text{CH})_8-$ part of **1'**: δ 4.89 (d, J = 13.2 Hz), 3.93 (dd, J = 11.3, 12.7 Hz), 3.27 (m), 3.00 (m).

(11) A related facile change of coordination mode of ethylene between η^2 -C₂H₄ and μ - $\eta^1:\eta^1$ -C₂H₄ on Os–Os has been reported: Ramage, D. L.; Wisner, D. C.; Norton, J. R. *J. Am. Chem. Soc.* **1997**, *119*, 5618. Bender, B. R.; Ramage, D. L.; Norton, J. R.; Wisner, D. C.; Rappé, A. K. *J. Am. Chem. Soc.* **1997**, *119*, 5628.

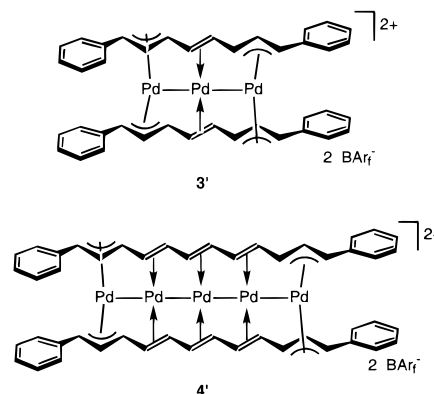
(12) ¹H NMR (CD₂Cl₂, 25 °C) of the $-(\text{CH})_8-$ part of **2'**: δ 5.37 (d, J = 12.7 Hz), 4.19 (t, J = 11.3 Hz), 3.42 (m), 3.24 (m).

(13) Crystal data: C₁₁₄H₇₀N₂B₂F₈Pd₄·2C₆H₁₄, M = 2999.32, space group $P1$ (no. 2), a = 13.417(3), b = 19.297(6), and c = 13.369(3) Å, α = 106.00(3), β = 94.42(2), and γ = 100.98(4)°, U = 3235(1) Å³, Z = 1, $F(000)$ = 1494, D_c = 1.539 g cm⁻³, $\mu(\text{Mo K}\alpha)$ = 6.64 cm⁻¹, 858 variables refined with 10 431 reflections collected at 223 K with $I > 3\sigma(I)$ to R = 0.064.

deviation of Pd1–Pd2–Pd2* angle (174.50(4)°) from 180° and the bent N1–Pd1–Pd2 angle (152.0(2)°) (N1 shifted away from the terminal Ph, on the mirror plane of the dication).

In addition to the preparation of the Pd₄ chain (eq 1), the Pd₃ sandwich chain of DPOT, [Pd₃(DPOT)₂][BARf]₂ (**3'**, Chart 4)

Chart 4



obtained by reducing the amount of added Pd(0) from 3 to 2 equiv. The Pd₅ chain of *all-trans*-1,12-diphenyl-1,3,5,7,9,11-dodecahexaene (DPDH), [Pd₅(DPDH)₂][BARf]₂ (**4'**, Chart 4), was also prepared from the reaction mixture {1Pd(II) + 4Pd(0) with excess DPDH}. The indicated structures of both Pd₃ and Pd₅ sandwich complexes were assigned by ¹H NMR spectra, showing sharp symmetrical polyene resonances even at the lower temperatures (see Supporting Information). Thus, in principle, there may be no limitation of the present synthetic strategy (Chart 1) with regard to the chain lengths.

It is noticeable that the bond length-alternation of the free *all-trans*-DPOT ($d_{\text{C}=\text{C}}$ = 1.335 Å (av) vs $d_{\text{C}-\text{C}}$ = 1.443 Å (av)),¹⁴ was considerably reduced in **1'** and **2'** (d = 1.414 Å (av)/ d = 1.413 Å (av) for **1'** and d = 1.408 Å (av)/ d = 1.46 Å (av) for **2'**), presumably due to the considerably strong donating/back-donating interactions.^{15,16} Moreover, all the present sandwich chain complexes were thermally stable, and no degradation was observed, even in solution, due to the cooperative strengthening of the chain–chain binding by the sequential Pd–C bonds.¹⁷

In conclusion, we designed and prepared novel organometallic sandwich chains, where a metal–metal bond chain is held in the “ π -electron corridor” of two conjugated polyenes through two coordination modes. Investigation of the chemical and physical properties of the present complexes as well as synthesis of potential “metallo-sandwich wires” having much longer chains is currently in progress.

Acknowledgment. This work was supported by Grants-in-aid for Scientific Research, Ministry of Education, Science and Culture of Japan, and CREST of Japan Science and Technology Corp.

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

JA992387F

(14) Benet-Buchholz, J.; Boese, R.; Haumann, T. In *The Chemistry of Dienes and Polyenes*; Rappoport, Z., Ed.; John Wiley & Sons: New York, 1997; pp 25–65.

(15) Strong donating/back-donating interactions between Pd₂ and bis- μ - η^2 - η^2 -C₄H₆ ligands have been proposed in [Pd₂(μ - η^2 : η^2 -C₄H₆)₂(PH₃)₂]²⁺: Murahashi, T.; Otani, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H.; Sakaki, S. *J. Am. Chem. Soc.* **1998**, *120*, 4536.

(16) It should be mentioned that a recent theoretical prediction suggested that when two intrinsically Peierls distortion materials, polyacetylene and transition metal chain, are linked to each other via σ - or π -bonds, there would no longer be a tendency for each to undergo a simple pairing distortion: Goldberg, N.; Tang, H.; Kroohs, N.; Hoffmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 10294.

(17) No pyridine adduct was observed when the Pd₅ sandwich complex **4'** was treated with excess pyridine under the same condition as for the formation of **2'**. This may imply stronger cooperative strengthening in **4'** than in **1'**. The Pd₃ complex **3'** and pyridine led to unidentified decomposition products.