

Perylene–Tetrapalladium Sandwich Complexes

Tetsuro Murahashi,* Tomohito Uemura, and Hideo Kurosawa*

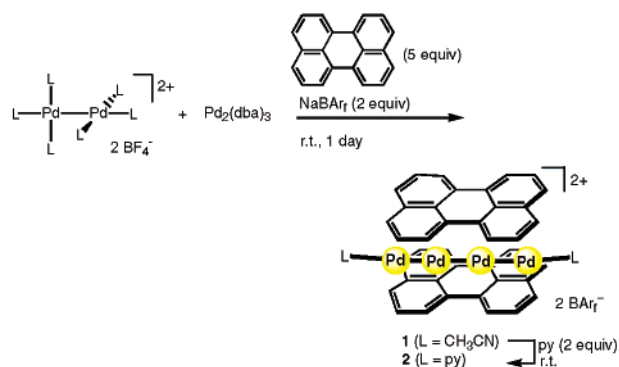
Department of Applied Chemistry and Frontier Research Center, Faculty of Engineering, Osaka University, Suita, Osaka, 565-0871, Japan

Received April 28, 2003; E-mail: tetsu@chem.eng.osaka-u.ac.jp; kurosawa@chem.eng.osaka-u.ac.jp

In relation to carbon-supported metal catalysts or carbon-based functional materials containing metals, it seems of great significance to know how a multimetal aggregate having metal–metal bonds is accommodated by sp^2 carbon frameworks, such as graphite, carbon nanotubes, etc.^{1,2} Particularly interesting is the behavior of multiple metals within the space made by stacking extended sp^2 carbon frameworks. However, this has been difficult to study due to the lack of appropriate molecular models. While the coordination of arene to two or three metal atoms has been intensively investigated,^{3–5} there are few reports on molecular complexes in which two polycyclic aromatic hydrocarbon (PAH) ligands sandwich multiple metals.⁶ Recently, we found that $p\pi$ -conjugated polyene ligands having a one-dimensional sp^2 carbon framework are able to bind a linear polypalladium chain.^{7–10} These findings prompted us to investigate the system in which PAHs act as a two-dimensionally extended sp^2 carbon ligand. Herein, we report the first perylene sandwich complex having a tetranuclear metal–metal chain.

The reaction of a homoleptic solvated dipalladium complex $[Pd_2(CH_3CN)_6][BF_4]_2$ with perylene (excess) and $NaBAR_f$ (2 equiv, $BAR_f = B\{3,5-(CF_3)_2C_6H_3\}_4$) in CH_2Cl_2 afforded a wine-red product **1** in 34% yield. The product **1** was obtained more efficiently by addition of 1 equiv of $Pd_2(dba)_3$ as the Pd^0 source (67% yield after recrystallization from CH_2Cl_2 /benzene) (Scheme 1). The molecular

Scheme 1



structure of **1** was determined by X-ray structure analysis (Figures 1 and 2).¹¹ Figure 1 shows that the Pd–Pd–Pd–Pd chain is sandwiched by two perylene ligands via a μ - η^2 : η^2 : η^2 -coordination mode. The tetrapalladium chain is slightly bent at Pd2 (5.8°) and Pd3 (11.5°) and is end-capped by acetonitrile ligands. As shown in Figure 2, the two perylene ligands are stacked in an eclipsed manner (intramolecular separation, ca. 4.2 Å), and these coordinate to the Pd₄ chain with the C₈ carbon array at the edge position. Complex **1** is the first example of a bis-arene sandwich complex having a metal–metal bond chain.¹²

The acetonitrile ligands in **1** were readily replaced by pyridine ligands to form **2** (Scheme 1). While both **1** and **2** gradually decomposed in CD_2Cl_2 solution at ambient temperature, complex

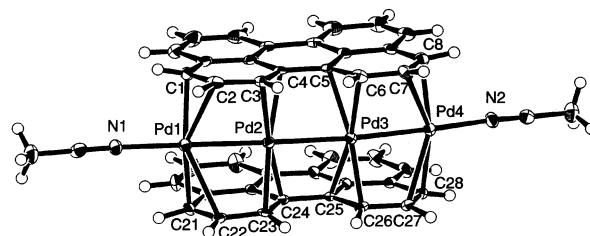


Figure 1. ORTEP drawing for **1** (50% probability ellipsoids, counteranions, solvent, and free perylene are omitted for clarity). Selected bond lengths (Å) and angles (deg): Pd1–Pd2 2.5575(7), Pd2–Pd3 2.5376(7), Pd3–Pd4 2.5627(7), Pd1–C1 2.195(7), Pd1–C2 2.421(7), Pd2–C3 2.159(6), Pd2–C4 2.256(6), Pd3–C5 2.278(6), Pd3–C6 2.142(7), Pd4–C7 2.457(7), Pd4–C8 2.190(7), Pd1–C21 2.198(7), Pd1–C22 2.496(6), Pd2–C23 2.175(6), Pd2–C24 2.241(6), Pd3–C25 2.251(6), Pd3–C26 2.162(6), Pd4–C27 2.452(7), Pd4–C28 2.196(7), C1–C2 1.38(1), C2–C3 1.438(10), C3–C4 1.430(9), C4–C5 1.467(9), C5–C6 1.421(9), C6–C7 1.437(10), C7–C8 1.39(1), C21–C22 1.40(1), C22–C23 1.429(9), C23–C24 1.431(9), C24–C25 1.478(9), C25–C26 1.423(9), C26–C27 1.438(9), C27–C28 1.379(10), Pd1–Pd2–Pd3 174.20(3), Pd2–Pd3–Pd4 168.54(3).

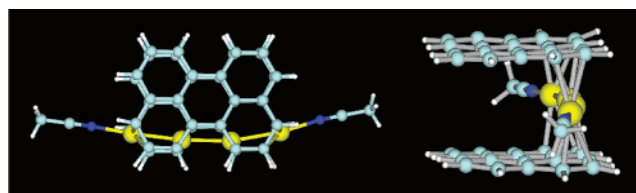
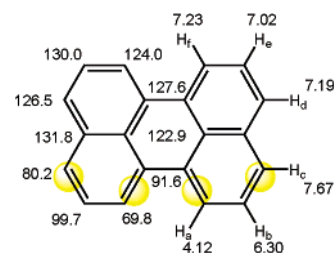


Figure 2. Top (left) and side views (right) of the crystal structure of **1** (counteranions, solvent, and free perylene are omitted for clarity).

2 remained unchanged for 1 day in the presence of free perylene. The sandwich structure of **2** is maintained in CD_2Cl_2 solution, as deduced by 1H , $^{13}C\{^1H\}$ NMR analyses with aid of C–H COSY (Scheme 2). Particularly, the eight coordinated carbons appeared at higher field regions (δ 99.7–69.8) in the $^{13}C\{^1H\}$ NMR spectra compared to their uncoordinated counterparts.¹³

Scheme 2 $^{13}C\{^1H\}$ NMR Chemical Shifts (Left) and 1H NMR Chemical Shifts (Right) of **2** in CD_2Cl_2 in the Presence of Free Perylene



Particularly interesting is that perylene favorably binds a multipalladium unit in the chain form rather than other shapes, such as a triangle.³ Moreover, perylene binds the Pd₄ chain at the C₈ edge. Some useful implications were obtained from the MO analysis of

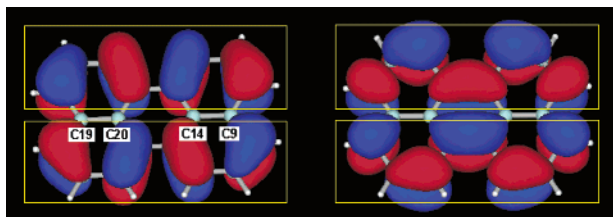
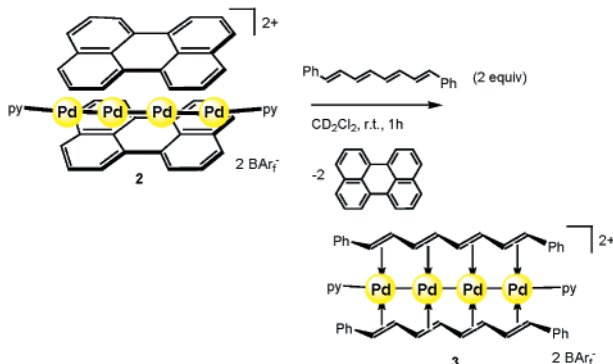


Figure 3. HOMO (left) and LUMO (right) of ground-state perylene (HF/6-31G(d) level, C_2 symmetry). The symmetry at C_8 carbon arrays (the parts surrounded by yellow rectangles) in each case bears resemblance to that of conjugated tetraene.

peryene prior to the full MO analysis of **1**.¹⁴ The HOMO and LUMO of perylene are shown in Figure 3. Both HOMO and LUMO are antisymmetric with respect to the vertical pseudo-mirror plane containing C9, C14, C19, and C20 atoms. This suggests the inability of perylene to interact with a Pd–Pd moiety that lies across such a pseudo-mirror plane. On the other hand, the electronic delocalization along the upper or lower edge framework consisting of eight carbons appears quite similar, in terms of the orbital sign, to that of the linear octatetraene molecules (Figure 3). Thus, it is proposed that one of the C_8 edges in perylene behaves as the binder to the Pd₄ moiety as *all-s-trans*-tetraene (DPOT) does in the bis- μ - η^2 : η^2 : η^2 -tetraene–tetrapalladium chain complex [Pd₄(*all-trans*-DPOT)₂(py)₂][BARf]₂ (**3**, DPOT = 1,8-diphenyl-1,3,5,7-tetraene).^{7,15}

Next, we investigated the substitution reaction of perylene ligands in **2** with *all-trans*-DPOT. The reaction facily occurred in CD₂-Cl₂ at ambient temperature to afford **3** quantitatively (Scheme 3).

Scheme 3



On the other hand, the coordinated DPOT ligands in **3** were not displaced, even by excess perylene. It should be mentioned that no loss of a Pd atom was observed during the substitution reaction. Thus, the transfer of the Pd₄²⁺ chain occurs cleanly from the perylene sandwich to the DPOT sandwich.

In summary, it has been proven that perylene favorably binds a Pd₄ chain in a sandwich manner. This is the first example showing that a PAH ligand behaves as the supporting ligands for a metal–metal bond chain.¹² Actually, the successful synthesis is probably attributed to the template effect of perylene to assemble metal atoms in a chain form. A systematic elucidation of the correlation between the electronic structures in PAHs and the shape of metal–metal bonded framework formed in contact with the PAH ligands is of

great interest and is now in progress in our group. Furthermore, the catalytic property of perylene sandwich complexes is also under investigation.

Acknowledgment. This work was supported by Grants-in-aid for Scientific Research, Ministry of Education, Culture, Sports, Science and Technology of Japan, and CREST of Japan Science and Technology Corporation. We thank Mr. T. Zaïke for MO calculations of perylene. Thanks are also due to the Analytical Center, Faculty of Engineering, Osaka University, for the use of NMR facilities.

Supporting Information Available: Text giving experimental details of the preparation and characterization of **1** and **2** (PDF), and details of the X-ray single-crystal structural analyses for **1** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For some examples, see: (a) Chambers, A.; Nemes, T.; Rodriguez, N. M.; Baker, R. T. K. *J. Phys. Chem. B* **1998**, *102*, 2251. (b) Park, C.; Baker, R. T. K. *J. Phys. Chem. B* **1998**, *102*, 5168. (c) Park, C.; Baker, R. T. K. *J. Phys. Chem. B* **1999**, *103*, 2453 and references therein.
- (2) For recent examples, see: (a) Fischer, J. E. *Acc. Chem. Res.* **2002**, *35*, 1079. (b) Lago, R. M.; Tsang, S. C.; Lu, K. L.; Chen, Y. K.; Green, M. L. H. *Chem. Commun.* **1995**, 1355. (c) Kong, J.; Chapline, M.; Dai, H. *Adv. Mater.* **2001**, *13*, 1384.
- (3) Deeming, A. J. *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raitby, P. R., Eds.; Wiley-VCH: Weinheim, 1999; Vol. 1, Chapter 1.14, p 236, and references therein.
- (4) For several recent examples of non-sandwich PAH complexes having more than two metal atoms, see: (a) Bochkarev, M. N. *Chem. Rev.* **2002**, *102*, 2089 and references therein. (b) Schneider, J. J.; Wolf, D.; Denninger, U.; Goddard, R.; Krüger, C. J. *Organomet. Chem.* **1999**, *579*, 139.
- (5) Several coordination polymers involving bonding between PAHs and transition metal atoms were revealed in a crystalline state. (a) Munakata, M.; Wu, L.-P.; Ning, G.-L. *Coord. Chem. Rev.* **2000**, *198*, 171 and references therein. (b) Munakata, M.; Wu, L.-P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K. *Inorg. Chem.* **1997**, *36*, 4903. (c) Cotton, F. A.; Dikarev, E. V.; Petrukina, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 11655.
- (6) To the best of our knowledge, there are no reports of a bis-arene complex in which more than three metal centers are sandwiched by two arene ligands. For a dinuclear arene sandwich complex, Allegra et al. first showed that benzene binds a dinuclear metal–metal moiety in a sandwich manner: (a) Allegra, G.; Immirzi, L.; Porri, L. *J. Am. Chem. Soc.* **1965**, *87*, 1394. (b) Allegra, G.; Cassagrande, G. T.; Immirzi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289.
- (7) Murahashi, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H. *J. Am. Chem. Soc.* **1999**, *121*, 10660.
- (8) Murahashi, T.; Nagai, T.; Okuno, T.; Matsutani, T.; Kurosawa, H. *Chem. Commun.* **2000**, 1689.
- (9) Murahashi, T.; Nagai, T.; Mino, Y.; Mochizuki, E.; Kai, Y.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 6927.
- (10) Murahashi, T.; Higuchi, Y.; Katoh, T.; Kurosawa, H. *J. Am. Chem. Soc.* **2002**, *124*, 14288.
- (11) In the crystalline state, complex **1** and 0.5 equiv of free perylene form infinite π -stacking columns having a composition of $\cdots(\mathbf{1}\cdots\mathbf{1}\cdots\text{perylenes})_n\cdots$. Crystal data for $2(\mathbf{1})\cdot(\text{C}_{20}\text{H}_{16})\cdot 2(\text{CH}_2\text{Cl}_2)$: $\text{C}_{238}\text{H}_{126}\text{Pd}_8\text{F}_{96}\text{N}_4\text{Cl}_4$, $M = 5901.74$, space group $P1$ (No. 2), $a = 17.6632(1)$ Å, $b = 19.4810(1)$ Å, $c = 19.6861(3)$ Å, $\alpha = 91.886(1)^\circ$, $\beta = 113.958(1)^\circ$, $\gamma = 113.9237(8)^\circ$, $V = 5497.9(1)$ Å³, $Z = 1$, $F(000) = 2902$, $D_c = 1.782$ g cm⁻³, $\mu(\text{MoK}\alpha) = 8.27$ cm⁻¹, 1589 variables refined with 17 736 reflections with $I > 3\sigma(I)$ to $R = 0.045$.
- (12) Bera, J. K.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 4453 and references therein.
- (13) The H_c protons in Scheme 2 are deshielded, possibly due to the magnetic anisotropic effect of the closely located pyridine ligand.
- (14) (a) Optimization of perylene (C_2 symmetry) was performed at the B3LYP/6-31G(d) level by use of the Gaussian 98 program. For a recent MO analysis of perylene analogues, see: (b) Adachi, M.; Nagao, Y. *Chem. Mater.* **2001**, *13*, 662.
- (15) While **1** contains the same coordination mode as that in **3**, the Pd–Pd distances in **1** (outer Pd–Pd 2.5575(7)/2.5627(7) Å, inner Pd–Pd 2.5376(7) Å) are shorter than those in **3** (outer Pd–Pd 2.7463(8), inner Pd–Pd 2.721(1) Å).

JA0358246