

Photoinduced Face-Inversion of Conjugated Tetraene Ligands on a Pd–Pd–Pd Moiety

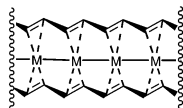
Tetsuro Murahashi,* Yutaka Higuchi, Tetsuya Katoh, and Hideo Kurosawa*

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

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We recently reported one-dimensional organometallic sandwich compounds made of conjugated polyenes and a polypalladium chain (Scheme 1), possessing unique rodlike molecular shape and ladderlike contiguous π -coordination bonds.¹ They are expected to show unique photochemical behavior in view of the photochemical characteristics of each component.^{2–4} For example, photoexcitation of α,ω -diphenylpolyenes results in cis–trans isomerization and/or radiation.^{2a,b} It has also been known that dinuclear M–M single or even multiple bonded complexes undergo photoinduced homolysis of the metal–metal bond affording metal-radicals.³ Furthermore, metal–metal bonded complexes with unsaturated hydrocarbon ligands show photoinduced rearrangement involving M–M, M–C, C–C, and C–H bond cleavage and formation.⁴ Herein, we wish to report our finding that photoirradiation of [Pd₃{Ar(CH=CH)₄Ar₂}[BAr_F]₂ (1)^{1a} (BAr_F = B(3,5-(CF₃)₂C₆H₃)₄) results in an unusual photochemical event: the face-inversion of the multihapto-coordinated μ -olefin ligands on a metal–metal chain.⁵

Scheme 1



The complex [Pd₃{Ph(CH=CH)₄Ph₂}[BAr_F]₂ (**1**)^{1a} was prepared according to the already published method.⁶ The complex **1** contained two isomers: **1-rac** and **1-meso** (eq 1).⁷ These undergo no thermal interconversion (vide infra), and each preparative experiment gave different isomer ratios in the range of ca. 6/4–7/3, probably due to subtle changes in crystallization conditions. The *p*-*t*-Bu substituted derivative [Pd₃{*t*-BuC₆H₄(CH=CH)₄C₆H₄-*t*-Bu₂}[BAr_F]₂ (**2**) or (**2'**) (counteranions = BF₄) was also prepared in a similar manner. In this case, **2-rac** or **2'-rac** was obtained almost exclusively. The structures of **1-meso** and **2'-rac** were determined by X-ray crystallographic analyses (Figure 1, a single crystal of **1-meso** was obtained from a meso-rich solution prepared by the method mentioned below).⁸ Both structures have the same coordination bond: the μ - η^3 : η^2 : η^3 -mode with similar structural parameters, for example, Pd–Pd distances of 2.7959(7) Å for **1-meso**, 2.7890(5) Å for **2'-rac**, except for the stacking mode of two tetraene ligands as shown in Figure 1.

Thermal interconversions between rac and meso isomers were not observed in **1** and **2** (60 °C in ClCD₂CD₂Cl). However, in the presence of free tetraene, slow interconversion was observed at 25 °C (10 days for completion). Thermal equilibrium states were achieved for each complex starting from a ratio of mixtures indicated in Table 1. The meso isomer is thermally more stable

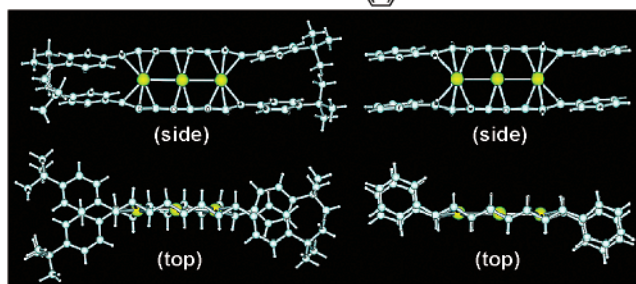
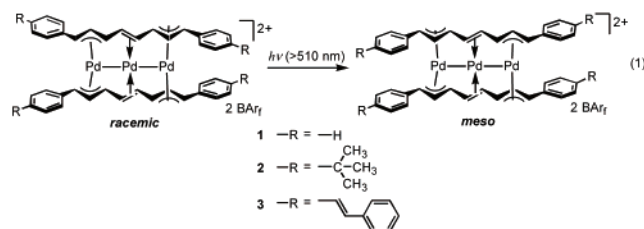


Figure 1. X-ray structures of **2'-rac** (left) and **1-meso** (right).

Table 1. Rac/Meso Ratios for **1–3**^a

	thermal equil. ^b	PSS
1 (R = H)	7/93 (52/48)	1/99 (73/27)
2 (R = <i>t</i> -Bu)	99/1 (30/70)	21/79 (99/1)
3 (R = styryl)	<i>c</i>	1/99 (59/41)

^a The values in the parentheses show the starting ratios. ^b 25 °C, CD₂Cl₂, in the presence of 6 equiv of free tetraene. ^c Not observed because of the insolubility of the free tetraene.

than the rac one for **1**.^{1b} On the other hand, sterically encumbered **2** favors the rac form rather than the meso. Probably, the net isomerization occurs during the replacement of the tetraene ligand by free tetraene.⁹

Interestingly, when complex **1** (rac/meso 73/27) in CD₂Cl₂ in a Pyrex tube was irradiated with a Xenon lamp (>510 nm) at room temperature in the absence of free tetraene, the gradual isomerization proceeded without forming any byproducts. After irradiation for 7 h, the rac/meso ratio reached 1/99 at the PSS (photo stationary state). More interestingly, irradiation with visible light (>510 nm) of **2-rac** resulted in a thermally unfavorable rac to meso isomerization (**2-rac/2-meso** 21/79 at the PSS which was achieved after 38 h) (Table 1).¹⁰

A *p*-styryl-substituted diphenyltetraene complex **3** was also examined as a model of a sandwich complex having tetraene ligands with more extended sp²-conjugation. The complex **3** was obtained as a mixture of rac and meso isomers (the ratio ~6/4).¹¹ A considerably faster visible light-induced rac to meso isomerization of **3** was observed as compared to the case of **1** in the same condition (6 h for **1** and 0.5 h for **3** were required for complete isomerization from ca. 6/4 rac/meso mixtures).

* To whom correspondence should be addressed. E-mail: tetsu@chem.eng.osaka-u.ac.jp (T.M.); kurosawa@chem.eng.osaka-u.ac.jp (H.K.).

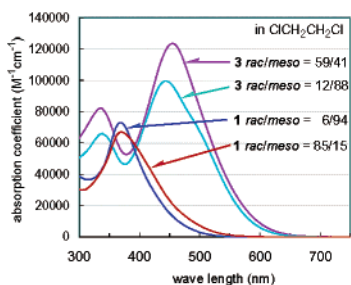


Figure 2. Absorption spectra of **1** and **3**.

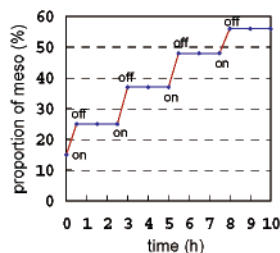


Figure 3.

The absorption spectra for rac-major and meso-major mixtures for **1** and **3** are shown in Figure 2. The rac and meso isomers for each complex show slightly different absorptions, probably due to a geometrical difference at each metal center or difference in the degree of π -stacking at the phenyl moieties (phenyl–phenyl separation in **1-meso** was 3.47 Å).¹² Absorption bands of **3** are considerably red-shifted with larger coefficients as compared to those of **1**, probably due to effective electronic or charge delocalization along the molecular chain. Examination of the effect of wavelength on the isomerization of **1** showed that UV-irradiation (366 nm, high pressured Hg lamp, 3 min) drove the **1-rac/1-meso** ratio from 1/99 to \sim 2/8.¹³ Irradiation at 546 nm then resulted in the recovery of the initial absorption of the 1/99 mixture.

The mechanism of the present face-inversion is of great interest. Repeated light on–off experiments on the isomerization of **1** in the absence of free tetraene ligands (Figure 3) clearly indicated that the isomerization is driven by photonic energy. Thus, it can be ruled out that the isomerization was catalyzed by any undetectable palladium species or tetraene generated during the irradiation. It seems unlikely that complete dissociation of tetraene is involved, because this should form a highly unsaturated transient species, for example, $[\text{Pd}_3(\text{tetraene})]^{2+}$ undergoing no decomposition or precipitation.¹⁴ It should be noted that scrambling of tetraene ligands was induced by irradiation of a mixture of **1** and **2**.¹⁵ This implies a possibility of an intermolecular polyene exchange between photoactivated complexes having loosely bound polyene ligands,¹⁶ while an intramolecular face-inversion would also occur, particularly in a dilute condition.^{6,17} It is reasonably assumed that photoexcitation would weaken the contiguous π -coordination bonds between the tetraene and Pd_3 unit all at once due to the electronic conjugation.¹⁸

In summary, the intriguing behavior of tetraene Pd_3 sandwich complexes, photoinduced face-inversion of the tetraene ligand on a Pd–Pd–Pd array, was found. Such a process would originate from the unique electronic structure of the polyene sandwich compounds as well as from the π -stacking of the $p\pi$ -conjugated ligands.¹⁹ The present strategy will be applied to the preparation of a structurally well-organized organic/inorganic hybrid material by employing an oligo- or polymer-sized conjugate molecule with a tetraene substructure and a Pd_3^{2+} linker. The full photochemical property of the polyene-polymetal hybrid compounds is now under investigation.

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Supporting Information Available: Text giving experimental details of preparation and characterization of **1–3**, and details of X-ray single-crystal structural analyses for **1-meso** and **2'-rac** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Rac and meso refer to the relative stacking mode (staggered and eclipsed) of two polyene frameworks.
- (8) Crystal data for **1-meso**: $\text{C}_{106}\text{H}_{64}\text{Pd}_3\text{B}_2\text{F}_8\text{Cl}_2$, $M = 2661.32$, space group $P1$ (No. 2), $a = 14.5246(7)$, $b = 16.0632(4)$, $c = 12.9564(9)$ Å, $\alpha = 106.848(9)$, $\beta = 100.968(5)$, $\gamma = 70.382(8)^\circ$, $V = 2710.6(3)$ Å³, $Z = 1$, $F(000) = 1314$, $D_c = 1.630$ g/cm³, $\mu(\text{Mo K}\alpha) = 6.71$ cm⁻¹, 745 variables refined with 6151 reflections collected at 296 K with $I > 3\sigma(I)$ to $R = 0.075$. Crystal data for **2'-rac**: $\text{C}_{64}\text{H}_{78}\text{Pd}_3\text{B}_2\text{F}_8$, $M = 1340.13$, space group $P1$ (No. 2), $a = 15.3395(7)$, $b = 21.4748(9)$, $c = 9.2123(3)$ Å, $\alpha = 95.812(2)$, $\beta = 96.587(1)$, $\gamma = 95.1087(8)^\circ$, $V = 2983.5(2)$ Å³, $Z = 2$, $F(000) = 1364$, $D_c = 1.492$ g/cm³, $\mu(\text{Mo K}\alpha) = 9.59$ cm⁻¹, 694 variables refined with 7971 reflections collected at 223 K with $I > 3\sigma(I)$ to $R = 0.031$.
- (9) Ligand exchange was observed in the reaction of **1** with free $\text{Ar}(\text{CH}=\text{CH})_4\text{Ar}$ ($\text{Ar} = p\text{-}t\text{-BuC}_6\text{H}_4$) or the reaction of **2** with free $\text{Ph}(\text{CH}=\text{CH})_4\text{Ph}$.
- (10) In this case, however, formation of a slight amount of unidentified product was also observed (8%, δ 1.10 (s) and 1.03 (s) for $t\text{-Bu}$ region).
- (11) The ¹H NMR signals of **3-rac** and **3-meso** were assigned by comparison with those of **1** or **2**, respectively (see Supporting Information).
- (12) The average value of intramolecular {(phenyl carbon)⋯(phenyl plane)} distances (the shortest distance 3.303 Å, the longest 3.624 Å).
- (13) Similar meso to rac isomerization by UV irradiation was not observed for **2** and **3** at this stage.
- (14) Attempts to detect $[\text{Pd}_3(\text{tetraene})]^{2+}$ or its equivalents by NMR spectroscopic methods failed.
- (15) No scrambling was observed in the dark. The scrambled products were observed in the initial stage of the irradiation (0.5 h) and gradually increased concomitantly with isomerization of each complex (after 16 h of irradiation, **2**/(scrambled complexes, isomer ratio ca. 1/6) = ca. 1/2).
- (16) Photoassisted exchange of unsaturated hydrocarbon ligands is known, for example: Top, S.; Kaloun, E. B.; Toppi, S.; Herrbach, A.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **2001**, *20*, 4554 and references therein.
- (17) As a possible intramolecular mechanism, two consecutive rotations about one of three C–C single bonds of the tetraene framework would cause a net face-inversion.
- (18) Electronic conjugation is supported by the X-ray crystal structures (nearly planar tetraene as well as the linear Pd_3 skeleton) and NMR data ($J_{\text{C-H}}$ for coordinated tetraene carbons for **1** are in the range of 153–164 Hz).
- (19) It has been experimentally and theoretically proved that the electronic state of an assembly of $p\pi$ -conjugated molecules depends significantly on the intermolecular space as well as orientation. For selected recent literature: (a) Bartholomew, G. P.; Bazan, G. C. *Acc. Chem. Res.* **2001**, *34*, 30. (b) McQuade, D. T.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 5885. (c) Reitzel, N.; Greve, D. R.; Kjaer, K.; Howes, P. B.; Jayaraman, M.; Savoy, S.; McCullough, R. D.; McDevitt, J. T.; Bjørnholm, T. *J. Am. Chem. Soc.* **2000**, *122*, 5788 and references therein. (d) Cornil, J.; dos Santos, D. A.; Crispin, X.; Silbey, R.; Brédas, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 1289. (e) Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B.-L.; Sugauma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. *J. Am. Chem. Soc.* **1998**, *120*, 2047.

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