Structures of two haptotropic isomers generated by the sliding of 1,3,5-triene ligands on a Pd–Pd–Pd chain†

Tetsuro Murahashi,* Yukari Mino, Koji Chiyoda, Sensuke Ogoshi and Hideo Kurosawa

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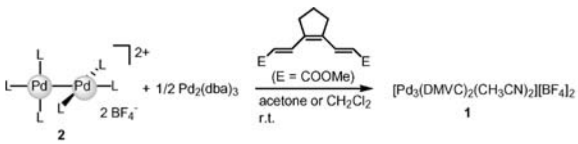
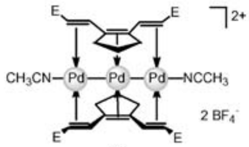
Two haptotropic isomers of $[Pd_3(\mu_3\text{-DMVC})_2(CH_3CN)_2][BF_4]_2$ (DMVC = 1,2-di-(*E*)-carbomethoxyvinylcyclopentene) were structurally determined by X-ray crystallographic analyses; a monoclinic crystal contained a symmetric sandwich complex (μ_3-η^2:η^2:η^2-coordination of DMVC ligands) and a triclinic crystal contained an unsymmetric sandwich complex (μ_3-η^2:η^3:η^1-coordination of DMVC ligands), where the latter are connected to each other by C–H···O hydrogen bonds.

We recently revealed that pπ-conjugated olefins and polycyclic aromatic hydrocarbons act as versatile sandwich ligands for metal chains or sheets.[1,2] The ligand–metal connection in such multinuclear sandwich complexes is comprised of an array of contiguous multiple π-coordination bonds, which exhibit unique hapticity changes. For example, sliding of tetraene ligands on the Pd_4 chain takes place when the diphenyltetraene-tetrapalladium sandwich complex accepts two terminal ligands or two electrons (Scheme 1).[1a,j] Such sliding of the polyene ligands on a metal–metal chain involves a set of 1,2-migrations of the polyene carbon from one palladium atom to a neighboring palladium atom. Similar 1,2-migration is involved in the interconversion between a bridging olefin and a terminal olefin bound to a dinuclear moiety (Scheme 2(A)).[3] Such bimodal coordination behavior in olefins has long been investigated in the field of metal surface chemistry due to its importance in heterogeneous catalytic transformations.[4] However, it is very rare that the occurrence of *both* terminal and bridging modes is structurally determined at the molecular level *without* changing the molecular composition, because one of these is usually much more stable than the other.[3] Herein, we report the structural determination of two sliding isomers of a triene-trimetal complex, where each can be attributed to either the terminal or bridging mode (Scheme 2(B)). This was unexpectedly observed during crystallization of a triene-tripalladium sandwich complex $[Pd_3(\mu_3\text{-DMVC})_2(CH_3CN)_2][BF_4]_2$ (**1**; DMVC = 1,2-di-(*E*)-carbomethoxyvinylcyclopentene).

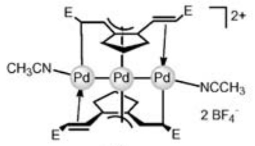
We recently reported that an *ortho*-phenylene-inserted *trans*-conjugated polyene uniquely acts as the binder of a bent metal chain, where the *ortho*-phenylene moiety provides a *cis*-C=C unit for the coordination.[1h] In the course of this study, we chose DMVC as the *trans*,*cis*,*trans*-1,3,5-triene, and we carried out the reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$ (**2**)[1b] and 0.5 equiv. of $Pd_2(dba)_3$ with an excess of DMVC[5] in acetone or CH_2Cl_2. After 1.5 h, a single product, **1**, was obtained as an orange powder (67% yield from the reaction in acetone) (eqn (1)).



(1)

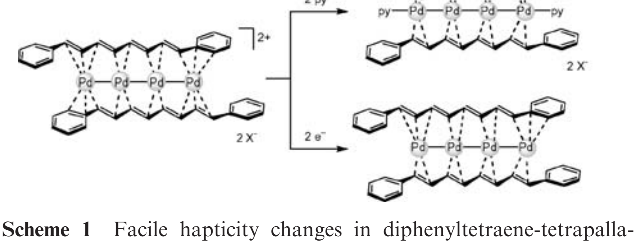


s-**1**



u-**1**

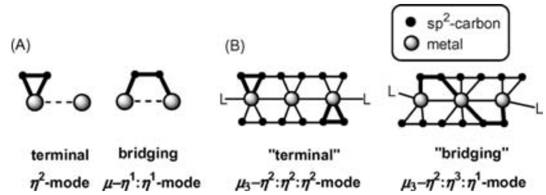
Two kinds of crystals of **1** were obtained: a monoclinic crystal of space group $P2_1/n$ (no. 14) from a reaction mixture in CH_2Cl_2, and a triclinic crystal of space group $P\bar{1}$ (no. 2) from a reaction mixture in CH_2Cl_2 where *n*-hexane had been added. The X-ray structure analyses show that both crystals contained the sandwich complex **1**, in which a linear Pd–Pd–Pd chain is flanked by two staggered DMVC ligands (Fig. 1, Fig. 2 and Table 1).‡ No solvent molecules were found in either crystal.[6] Interestingly, the coordination mode of the DMVC ligands is different in each case, *i.e.* a μ_3-η^2:η^2:η^2-mode in the monoclinic crystal (*s*-**1**) and a μ_3-η^2:η^3:η^1-mode in the triclinic crystal (*u*-**1**). The linear Pd–Pd–Pd skeletons in both crystals are almost identical (Pd–Pd = 2.7651(5) Å for *s*-**1** and 2.755(1) Å for *u*-**1**). The unsymmetric property in *u*-**1** arises from a slight sliding of the DMVC ligands on the Pd–Pd–Pd array from a symmetrical position in *s*-**1**, which



Scheme 1 Facile hapticity changes in diphenyltetraene-tetrapalladium sandwich complexes (ref. 1*a* and 1*j*).

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, PRESTO, Japan Science and Technology Agency (JST), Suita, Osaka, 565-0871, Japan.
E-mail: tetsu@chem.eng.osaka-u.ac.jp; Fax: +81 6 6879-7394;
Tel: +81 6 6879-7394

† Electronic supplementary information (ESI) available: Experimental details of the preparation and characterization of **1**, details of the X-ray structure analyses of *s*-**1** and *u*-**1**. See DOI: 10.1039/b806824k



Scheme 2 Pictorial models of olefin coordination modes.

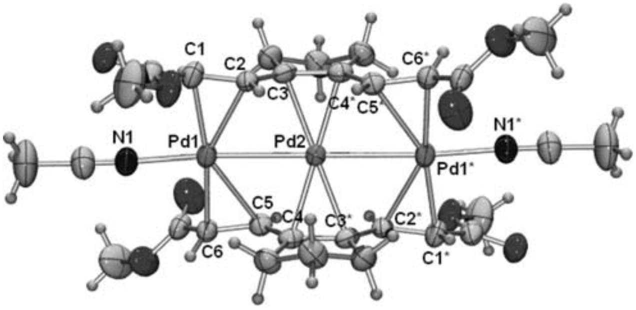


Fig. 1 ORTEP drawing of *s*-**1** (50% probability ellipsoids, BF_4 anions are omitted for clarity).

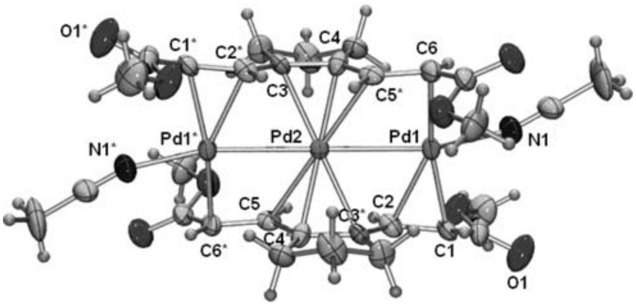


Fig. 2 ORTEP drawing of *u*-**1** (50% probability ellipsoids, BF_4 anions are omitted for clarity).

Table 1 Selected interatomic distances (Å) and angles (°) of *s*-**1** and *u*-**1**

	s-**1**	*u*-**1**
Space group	$P2_1/n$	$P\bar{1}$
Pd1–Pd2	2.7651(5)	2.755(1)
C1–Pd1	2.187(7)	2.20(1)
C2–Pd1	2.341(6)	2.29(1)
C3–Pd2	2.255(6)	2.32(1)
C4–Pd2	2.206(6)	2.19(1)
C5–Pd2	**2.496(7)**	**2.35(1)**
C5–Pd1	**2.407(6)**	**2.53(1)**
C6–Pd1	2.134(6)	2.12(1)
Pd1–N1	2.044(7)	2.06(1)
C1–C2	1.39(1)	1.41(2)
C2–C3[a]	1.43(1)	1.43(2)
C3–C4[a]	1.42(1)	1.43(2)
C4–C5[a]	1.43(1)	1.40(2)
C5–C6[a]	1.38(1)	1.43(2)
Pd1–Pd2–Pd1	180	180
Pd2–Pd1–N1	**175.6(2)**	**166.5(4)**

[a] The asterisk labels of C2–C6 are omitted in Table 1. Therefore, it is required to use an asterisk where necessary when the structures are referred from Fig. 1 and Fig. 2.

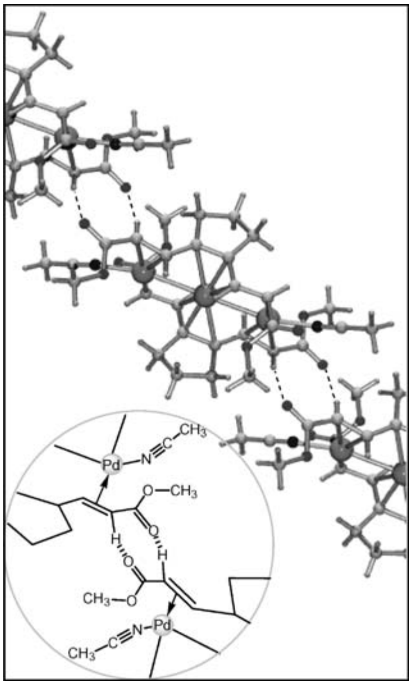
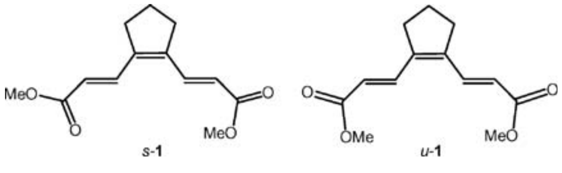


Fig. 3 An infinite C–H···O hydrogen-bonded array in the crystal of *u*-**1**.

results in the shortening of the C5–Pd2 bond and the lengthening of the C5–Pd1 bond (C5–Pd2 = 2.496(7) Å and C5–Pd1 = 2.407(6) Å in *s*-**1**; C5–Pd2 = 2.35(1) Å and C5–Pd1 = 2.53(1) Å in *u*-**1** (Table 1)). Notably, the long C5–C6* bond (1.43(2) Å) in *u*-**1**, compared to 1.38(1) Å in *s*-**1**, suggests an increased single bond character of C5–C6* bond, which is consistent with the μ_3-η^2:η^3:η^1-mode. Furthermore, the orientation of the CH_3CN ligands is different in *s*-**1** and *u*-**1**; *i.e.* the CH_3CN ligands lie almost on the Pd–Pd–Pd axis (Pd2–Pd1–N1 175.6(2)°) in *s*-**1**, while their orientation considerably deviates from the Pd–Pd–Pd axis (Pd2–Pd1–N1 = 166.5(4)°) in *u*-**1**. Such differences in orientation of the CH_3CN ligands are mainly due to the differences in their intermolecular contacts. As shown in Fig. 3, each dication of *u*-**1** is connected by C–H···O hydrogen bonds to form an infinite chain in the crystal. The distance (*D*) between C1 and the carbonyl oxygen atom O1 of the neighboring dication is 3.38 Å, which is in the range of normal C–H···O hydrogen bonds (3.0 ∼ 4.0 Å).[7] Thus, the hydrogen-bonded contacts between dications cause steric congestion around the CH_3CN ligand, giving rise to the deviation of the orientation of the CH_3CN ligands from the Pd chain axis. Consequently, the steric congestion and CH_3CN deviation may push the DMVC ligand slightly away, causing bond recombination at the C5 atom. Such intermolecular C–H···O hydrogen bonds were not



Scheme 3 Conformations of the DMVC ligands in *s*-**1** and *u*-**1**.

observed in the crystal of *s*-**1**. Notably, the conformation of the –CH=CH–COOMe moiety is different between *s*-**1** and *u*-**1**, as shown in Scheme 3, which might also be caused by the near contact of the neighboring dication in *u*-**1** and absence of such a contact in *s*-**1**.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of *s*-**1** and *u*-**1** in CD_3NO_2 or acetone-d_6 showed only one set of symmetric signals for the DMVC ligands, even at low temperature (−90 °C in acetone-d_6). According to the above discussion that the unsymmetric structure of *u*-**1** is attained due to the intermolecular C–H···O hydrogen bonds in the solid state, perhaps *s*-**1** is the only isomer in solution, although the possibility that rapid conversion between *s*-**1** and *u*-**1** occurs in solution cannot be ruled out at this stage.

Thus, *s*-**1** and *u*-**1** have been identified as novel sliding isomers derived from different intermolecular contacts in the solid state. These results provide direct evidence that the ligand–metal hapticity change in polyene-multimetal complexes occurs in a facile manner, without a change in molecular composition. It should be mentioned that crystal packing forces sometimes cause a change in the nature of intramolecular bonding. An interesting example for trimetal chain complexes was recently reported, where the crystal packing forces affected the Co–Co–Co bond distances in a series of tricobalt chain complexes.[8–10] In the present case, the Pd–Pd–Pd distances are almost identical in *s*-**1** and *u*-**1**, while the coordination mode of the DMVC ligands differs between them. Further study of the unique behavior of pπ-conjugated polyene ligands bound to a metal chain is ongoing in our laboratory.

Notes and references

‡ Crystal data for *s*-**1**: $C_{30}H_{38}O_8F_8B_2N_2Pd_3$, M_r = 1047.45, monoclinic, space group $P2_1/n$ (no. 14), T = 293 K, a = 10.3565(1), b = 12.3481(3), c = 14.3451(3) Å, β = 95.920(2)°, U = 1824.71(6) Å^3, Z = 2, F(000) = 1032, D_c = 1.906 g cm^{-3}, μ(Mo-K$_\alpha$) = 15.55 cm^{-1}, 16 626 reflections collected, 4167 unique (R_{int} = 0.072), 241 variables with 2480 observed reflections ($I > 2\sigma(I)$) to R = 0.051, Rw = 0.143. CCDC 685830.

Crystal data for *u*-**1**: $C_{30}H_{38}O_8F_8B_2N_2Pd_3$, M_r = 1047.45, triclinic, space group $P\bar{1}$ (no. 2), T = 296 K, a = 10.0065(1), b = 11.0597(8), c = 8.7843(8) Å, α = 96.218(6), β = 94.476(5), γ = 68.120(6)°, U = 896.1(1) Å^3, Z = 1, F(000) = 516, D_c = 1.941 g cm^{-3}, μ(Mo-K$_\alpha$) = 15.83 cm^{-1}, 7764 reflections collected, 3985 unique (R_{int} = 0.096), 277 variables with 2078 observed reflections ($I > 2\sigma(I)$) to R = 0.081, Rw = 0.221. CCDC 685831.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b806824k

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