Sandwich Compounds

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Sandwich Complexes Containing Bent Palladium Chains**

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Since the landmark discovery of ferrocene in 1951–52,[1] organometallic sandwich compounds have been the subject of extensive research owing to the wide utility of these as molecular materials and catalysts.[2] Recently, we developed one-dimensional sandwich chain complexes as a new class of extended organometallic sandwich compounds.[3,4] It has been proven that all-*trans*,all-s-*trans* conjugated polyenes serve as template ligands for a linear palladium chain (for example,

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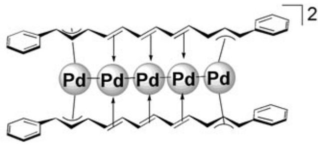
compound **1**).[3a,5] It is of continued interest to know how other pπ-conjugated ligands which have different conjugation geometries from the linear ones can accommodate a multinuclear metal moiety in a sandwich framework.[6] A simple way to attain a nonlinear pπ-conjugation geometry is the incorporation of a *cis* or s-*cis* segment into the *trans*,s-*trans* polyene sequence. Herein, we report the unique coordination behavior of the *o*- or *p*-phenylene-inserted polyenes 1,2-bis(4-phenyl-1,3-butadienyl)benzene (*o*-BPBB) (**2**)[7] and 1,4-bis(4-phenyl-1,3-butadienyl)benzene (*p*-BPBB) (**3**),[8] which leads to the formation of the remarkable sandwich complexes containing bent polypalladium chains.



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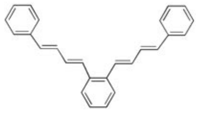

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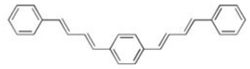

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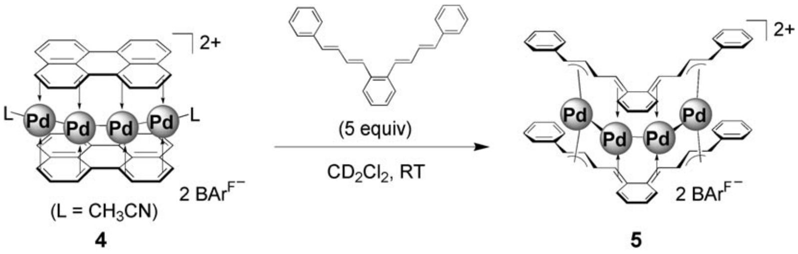
Treatment of the bis(perylene)tetrapalladium complex $[Pd_4(perylene)_2L_2][BAr^F]_2$ (**4**; L = CH_3CN, $BAr^F = B\{3,5\text{-}(CF_3)_2C_6H_3\}_4$)[6] with *o*-BPBB (**2**, 5 equiv) resulted in the quantitative formation of the bis(*o*-bpbb)-tetrapalladium complex $[Pd_4(o\text{-bpbb})_2][BAr^F]_2$ (**5**, Scheme 1). Complex **5** was alternatively isolated in 69% yield by the reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$[3b] and $[Pd_2(dba)_3]$ (1 equiv; dba=dibenzylideneacetone) with an excess of *o*-BPBB and subsequent anion exchange from BF_4 to BAr^F. Complex **5** was stable in CD_2Cl_2 for one week at ambient temperature.



Scheme 1. Synthesis of $[Pd_4(o\text{-bpbb})_2][BAr^F]_2$ (**5**).

The molecular structure of **5** was determined by X-ray crystallographic analysis (Figure 1).[9] In the structure, a Pd_4 chain is sandwiched between two *o*-bpbb ligands through μ_4-η^3:η^2:η^2:η^3 coordination. The Pd_4 chain is bent at Pd2 and Pd2* (Pd1-Pd2-Pd2* 149.93(3)°) along the *cisoid* pπ-conjugation framework of C10-C11-C24*-C23*. This arch-shaped geometry of the Pd_4 chain is in sharp contrast to the linear Pd_4 chain in $[Pd_4(dpdp)_2]^{2+}$.[5] In **5**, each Pd−Pd bond length (Pd1−Pd2 2.701(1) Å, Pd2−Pd2* 2.584(1) Å) is in the range of normal Pd−Pd bonds.[10] The internal Pd2−Pd2* bond (2.584(1) Å) is somewhat shorter than the corresponding bond in $[Pd_4(dpdp)_2]^{2+}$ (2.676(1) Å).[5] The CH(*o*-C_6H_4)CH units of the *o*-bpbb ligands in **5** may be regarded as an *o*-xylylene moieties in view of the η^2(C10,C11):η^2(C23*,C24*) coordination mode and the single-bond character of the C11−C24* bond (1.51(1) Å).[11,12]

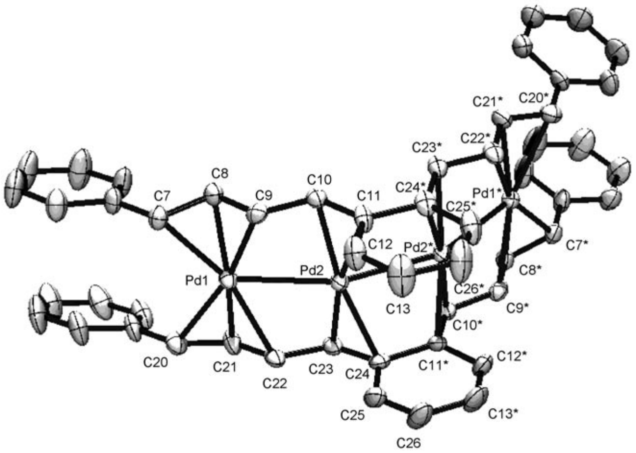
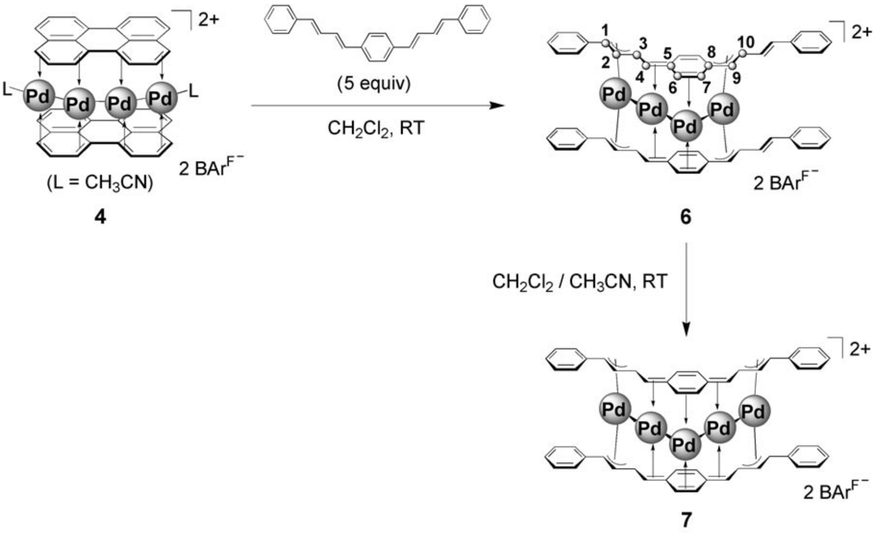


Figure 1. ORTEP drawing of **5** (30% probability thermal ellipsoids; counterions, solvent molecules, and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: Pd1-Pd2 2.701(1), Pd2-Pd2* 2.584(1), C9-C10 1.44(1), C10-C11 1.42(1), C11-C24* 1.51(1), C11-C12 1.42(1), C12-C13 1.37(1), C13-C26* 1.40(2), C25-C26 1.32(2), C24-C25 1.44(1), C23-C24 1.43(1), C22-C23 1.45(1); Pd1-Pd2-Pd2* 149.93(3).

We then carried out the reaction of *p*-BPBB (**3**) with complex **4** (Scheme 2). The reaction proceeded smoothly in CH_2Cl_2 at ambient temperature to afford the bis(*p*-bpbb)tetrapalladium complex $[Pd_4(p\text{-bpbb})_2][BAr^F]_2$ (**6**) as a brown precipitate (81% yield of isolated product). The structure of **6** was deciphered on the basis of ^1H, $^{13}C\{^1H\}$ NMR, H−H COSY, HMQC, HMBC, and NOE analyses in $[D_6]$acetone. The upfield shift of the $^{13}C\{^1H\}$ NMR signals for C1–C10 in **6** (δ = 115–82 ppm) relative to those of free *p*-BPBB indicated that the carbon atoms C1–C10 are involved in the coordination to the Pd_4 chain (Scheme 2).[13] The conformation of the *p*-bpbb ligands in **6** was determined by difference NOE experiments.[14]

Complex **6** transformed spontaneously into the bis(*p*-bpbb)pentapalladium complex $[Pd_5(p\text{-bpbb})_2][BAr^F]_2$ (**7**) in CD_2Cl_2/CD_3CN (v/v = 1:1; 41% yield after two days). During the transformation, partial decomposition of **6** might generate Pd^0 species, a part of which is trapped by the remaining Pd_4 complex **6** to form the Pd_5 complex **7**.[15] The yield of complex **7** was not greatly improved when 0.5 equivalents of $[Pd_2(dba)_3]$ was added to a solution of **6** (49% yield). Isolated **7** underwent no decomposition or isomerization over one week in CD_2Cl_2 at ambient temperature.



Scheme 2. Synthesis of [Pd_4(*p*-bpbb)$_2$][BAr^F]$_2$ (**6**) and [Pd_5(*p*-bpbb)$_2$][BAr^F]$_2$ (**7**).

The structure of **7** was determined by X-ray structure analysis (Figure 2).[16] A unique V-shaped Pd_5 chain is sandwiched between *p*-bpbb ligands through μ_5-η^3:η^2:η^2:η^2:η^3 coordination. The Pd_5 chain is bent at the central Pd3 atom (Pd2-Pd3-Pd4 121.81(4)°), which is coordinated by the *p*-phenylene moieties. This bent arrangement is in stark contrast to the linear Pd_5 chain in complex **1**. As a consequence of bending, the apex Pd atom (Pd3) in complex **7** has a unique four-coordinate "butterfly-type" geometry (**A**, Scheme 3).[17] In the known bent M-M-M chain complexes of Group 10 transition metals, one or two ligands interact with the apex M atom from the in-plane direction with respect to the M-M-M plane (**B** and **C**, Scheme 3).[18] Complex **7** was found to be inert toward MeCN and pyridine. Each Pd–Pd bond length in **7** (Pd1–Pd2 2.722(1) Å, Pd2–Pd3 2.713(1) Å, Pd3–Pd4 2.721(1) Å, Pd4–Pd5 2.733(1) Å) is in the range of normal Pd–Pd bonds.[10]

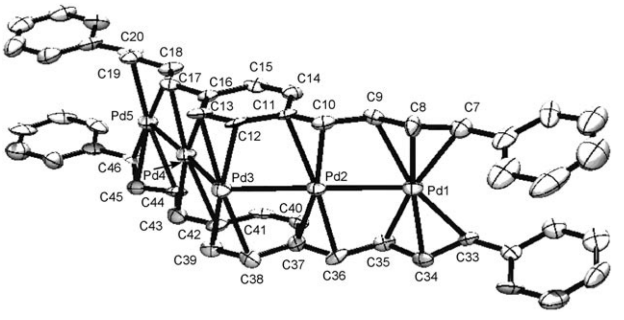
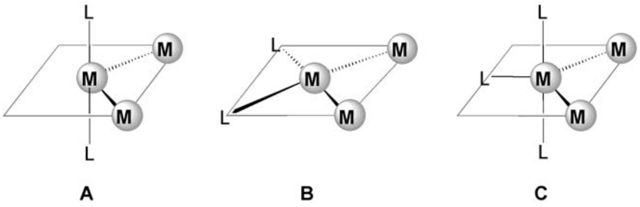


Figure 2. ORTEP drawing of **7** (50% probability thermal ellipsoids; counterions, solvent molecules, and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: Pd1-Pd2 2.722(1), Pd2-Pd3 2.713(1), Pd3-Pd4 2.721(1), Pd4-Pd5 2.733(1), C10-C11 1.42(1), C11-C12 1.45(1), C11-C14 1.43(1), C12-C13 1.37(1), C13-C16 1.42(1), C14-C15 1.34(1), C15-C16 1.45(1), C16-C17 1.42(1), C36-C37 1.44(1), C37-C38 1.46(1), C37-C40 1.42(1), C38-C39 1.38(1), C39-C42 1.44(1), C40-C41 1.36(1), C41-C42 1.44(1), C42-C43 1.45(1); Pd1-Pd2-Pd3 177.34(4), Pd2-Pd3-Pd4 121.81(4), Pd3-Pd4-Pd5 176.45(4).

A formal quinoid character of the CH(*p*-C_6H_4)CH moieties of the *p*-bpbb ligands in **7** may be suggested by the η^2(C10,C11):η^2(C12,C13):η^2(C16,17) and η^2(C36,C37):η^2(C38,C39):η^2-(C42,43) coordination modes, as well as by the alternation in C–C bond lengths in the sequences C11-C14-C15-C16 (1.43(1), 1.34(1), 1.45(1) Å) and C37-C40-C41-C42 (1.42(1), 1.36(1), 1.44(1) Å).[19,20]

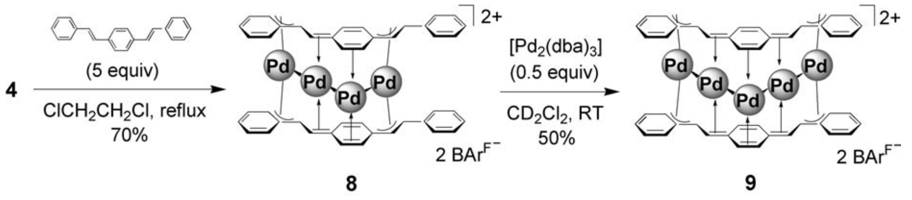
The bent sandwich chain complexes **8** and **9** were also prepared from 1,4-bis(2-phenylethenyl)benzene (*p*-BPEB),[21] according to Scheme 4.



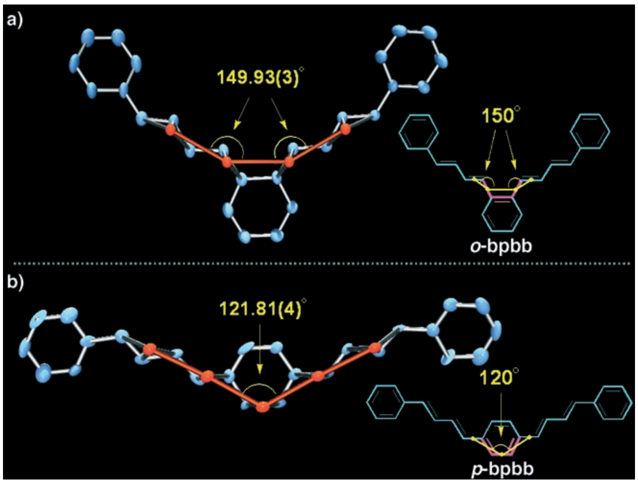
Scheme 3. Schematic representation of the coordination geometry at the apex metal atom in bent M-M-M chains of Group 10 metals.

The bending of polypalladium chains in **5** and **7** occurred along the *cisoid* C_4 moieties (shown in purple, Scheme 5) at the phenylene units of the ligands. It is noticeable that the bending angles of the polypalladium chains (149.93(3)° (**5**) and 121.81(4)° (**7**)) reflect the angles of the pπ-conjugated skeleton (150° in *o*-bpbb, 120° in *p*-bpbb; Scheme 5).[22]

Thus, it is reasonably concluded that the bending of the polypalladium chains in **5** or **7** is caused by the template effect of pπ-conjugated sp^2-carbon frameworks. This result suggests



Scheme 4. Synthesis of [Pd_4(*p*-bpeb)$_2$][BAr^F]$_2$ (**8**) and [Pd_5(*p*-bpeb)$_2$][BAr^F]$_2$ (**9**).



Scheme 5. Template roles of pπ-conjugated sp^2-carbon frameworks for shaping the Pd chains. a) The arch-shaped Pd$_4$ chain on *o*-bpbb; b) the V-shaped Pd$_5$ chain on *p*-bpbb.

the potential utility of *carbon π templates* in controlling the shape of the metal assembly. Further studies on the construction of different shapes of polypalladium assemblies, such as zigzag and ring shapes, by using appropriate unsaturated hydrocarbons as carbon π templates are currently in progress.

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[7] *o*-BPBB was prepared by the Wittig reaction; the experimental details are given in the Supporting Information.

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[9] Crystal data for **5**: $C_{122}H_{80}B_2F_{48}Cl_{12}Pd_4$, $M_r = 3330.55$, monoclinic, space group $C2/c$ (no. 15), $a = 23.060(1)$, $b = 25.619(2)$, $c = 25.149(2)$ Å, $\beta = 116.352(3)°$, $V = 13313(1)$ Å^3, $Z = 4$, $F(000) = 6568$, $\rho_{calcd} = 1.661$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 8.87$ cm^{-1}, $T = 133$ K, 835 variables refined with 24034 reflections with $I > 3\sigma(I)$ to $R1 = 0.091$. CCDC-604663 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[13] A possible coordination mode of *p*-bpbb in **6** is μ_4-η^3:η^2:η^2:η^3. The same coordination mode was found in the analogous Pd$_4$ complex [Pd$_4${Ph{all-*trans*,s-*trans*-(CH = CH)$_4$}Ph}$_2$][BAr^F]$_2$.[3a]

[14] The NOE signals were observed between H4 and H6 and between H7 and H9 in **6**.

[15] During the reaction, a yellow precipitate of *p*-BPBB was generated.

[16] Crystal data for **7**: $C_{124}H_{83}B_2NF_{48}Cl_6Pd_5$, $M_r = 3265.29$, monoclinic, space group $P2_1/n$ (no. 14), $a = 16.9054(3)$, $b = 24.2244(4)$, $c = 29.8064(4)$ Å, $\beta = 90.8575(6)°$, $V = 12205.0(3)$ Å^3, $Z = 4$, $F(000) = 6432$, $\rho_{calcd} = 1.777$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 9.79$ cm^{-1}, $T = 133$ K, 1668 variables refined with 35196 reflections with $I > 3\sigma(I)$ to $R1 = 0.077$. CCDC-604664 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[21] T. W. Campbell, R. N. McDonald, *J. Org. Chem.* **1959**, *24*, 1246.

[22] The angles 150° and 120° in Scheme 5 are defined by the midpoints of the C–C bonds, such that all C–C bond lengths and C-C-C angles are fixed as being equivalent.