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Stepwise growth of polypalladium chains in 1,4-diphenyl-1,3-butadiene sandwich complexes†

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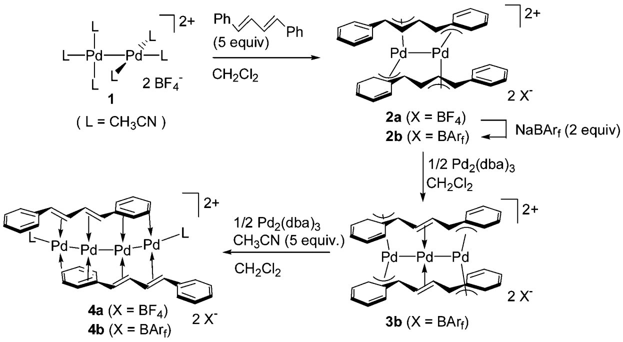
A series of 1,4-diphenyl-1,3-butadiene multinuclear palladium sandwich complexes are synthesized by stepwise growth of palladium chains within a sandwich framework.

Considerable efforts have been devoted to the chemistry of organopalladium complexes containing Pd–Pd bonds, and recent reports revealed that unsaturated hydrocarbon ligands are capable of binding palladium assemblies having more than three Pd atoms.[1] Typically, a linear π-conjugated sequence in conjugated polyenes binds a polypalladium chain in a sandwich manner.[2] The polyene-polypalladium sandwich complexes are prepared by the reaction of a dinuclear complex $[Pd_2(CH_3CN)_6]^{2+}$ with a Pd^0 complex in the presence of polyene ligands, where the Pd atoms are assembled into the space between two polyene ligands. While the mechanism of the metal aggregation during the formation of polyene-polypalladium sandwich complexes has not been identified, one possible way is the stepwise growth of polypalladium chains under the template effect of two polyene ligands. Furthermore, the stepwise preparation is of interest from a viewpoint of size-controllable preparation of not only one-dimensional but other shaped metal assemblies.[3,4] Herein, we wish to report the synthesis of tri- and tetranuclear palladium sandwich complexes having 1,4-diphenyl-1,3-butadiene (DPBD) ligands from the dinuclear DPBD-sandwich complex by stepwise incorporation of Pd^0 atoms (Scheme 1).

The dinuclear palladium sandwich complex **2a** was readily prepared almost quantitatively as a wine-red precipitate by the treatment of homoleptic acetonitrile dipalladium(I) complex[5] **1** with an excess amount of DPBD in CH_2Cl_2 at room temperature.‡ While **2a** was insoluble in most of non-coordinative organic solvents, a single crystal suitable for X-ray crystallographic analysis§ was obtained from 1,2-dichloroethane. Cationic parts of **2a** were disordered in the crystal and two structures were refined with occupancy factor 4 : 1. The crystal structure for the major counterpart is shown in Fig. 1.¶ The DPBD ligands coordinated to the Pd–Pd moiety through μ_2-η^3:η^3 coordination mode. The Pd–C_{ortho} length [2.559(10) Å] is much longer than those in the typical π-benzyl palladium complex (*e.g.* 2.25 Å in [Pd(η^3-benzyl-)(phen)]$^+$),[6] while the Pd–C_{ortho} length in the related sandwich complex $[Pd_4\{Ph(CH{=}CH)_4Ph\}_2]^{2+}$ (**5**)[2a] was also rather long (2.421(8) Å). The μ_2-η^3:η^3 coordination of conjugated triene to a Pd_2 moiety was reported in the related sandwich complex $[Pd_2\{Ph(CH{=}CH)_3Ph\}_2]^{2+}$ (**6**).[2b] The Pd–Pd length [2.844(1) Å] in **2a** is shorter than that of **6** [2.9156(6) Å].



Scheme 1 Preparation of sandwich complexes **2**, **3**, and **4**.

The complex **2b**,‡ which was obtained by exchange of the counteranions to BAr_f (= $B(3,5\text{-}(CF_3)_2C_6H_3)_4$), was soluble in CH_2Cl_2. The complex **2b** showed only two broad vinylic ^1H resonances at δ 6.8 and 4.2 in CD_2Cl_2 at room temperature, probably due to rapid slide motion of DPBD in a manner similar to that of the tetraene ligand in **5**.[2a]

The addition of 0.5 equiv. of $Pd_2(dba)_3$ to the CD_2Cl_2 solution of **2b** led to formation of the trinuclear complex **3b** almost quantitatively (red color, 66% isolated yield after recrystallization).‖ The structure of **3b** was determined by X-ray crystallographic analysis (Fig. 2). The linear Pd–Pd–Pd chain was held between DPBD ligands which are located in almost superimposed positions with each other. Each phenyl ring deviates from the parallel stacking position (the dihedral angle between upper and lower phenyl planes = 25°) in order to make a direct contact between terminal Pd atoms and one of the *ortho*-carbons [Pd1–C1 2.41(1) Å, Pd1–C8 2.50(1) Å]. The similar μ_3-η^3:η^2:η^3 coordination mode was found in $[Pd_3\{Ph(CH{=}CH)_4Ph\}_2]^{2+}$ (**7**).[2a]

Further addition of 0.5 equiv. of $Pd_2(dba)_3$ to the solution of **3b** in the presence of CH_3CN (2–5 equiv.) afforded the tetranuclear sandwich complex **4b** (88% yield) in CD_2Cl_2. In the absence of CH_3CN, no tetranuclear complex was formed. The tetranuclear complex **4b** was identified by a separate preparation of the BF_4 salt (**4a**) and the subsequent anion exchange (from BF_4 to BAr_f). Thus, treatment of **1** with $Pd_2(dba)_3$ in CH_2Cl_2 in the presence of DPBD afforded a moderate yield of **4a**.** The structure of **4a** was determined by X-ray crystallographic analysis (Fig. 3). The Pd_4 chain is held by DPBD ligands through μ_4-η^2:η^2:η^2:η^2 coordination, and is capped by CH_3CN ligands. Interestingly, the Pd_4 chain is significantly bent [Pd1–Pd2–Pd3 161.43(9)°, Pd2–Pd3–Pd4 161.63(9)°], probably due to the template effect of the bent pπ-

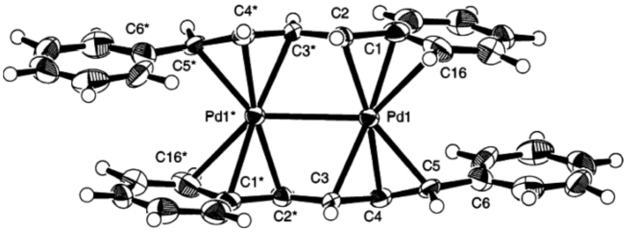


Fig. 1 ORTEP drawing of **2a** (BF_4^- were omitted for clarity).

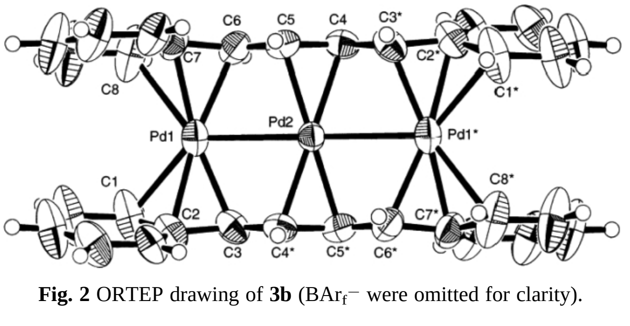


Fig. 2 ORTEP drawing of **3b** (BAr_f^- were omitted for clarity).

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† Electronic supplementary information (ESI) available: structural details. See http://www.rsc.org/suppdata/cc/b4/b403098b/

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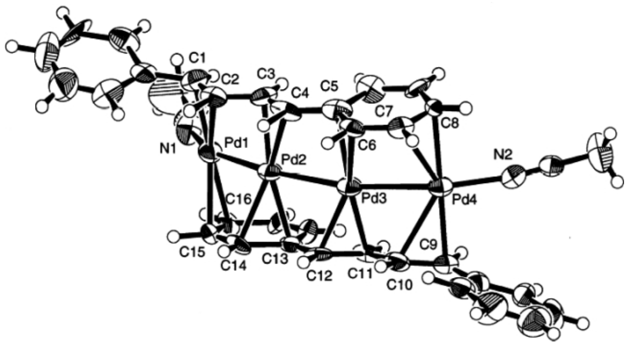

Fig. 3 ORTEP drawing of **4a** (BF_4^- were omitted for clarity).

conjugated sequence comprised of s-*trans*,s-*trans*,s-*cis* tetraene units used in coordination. In stark contrast, a virtually linear Pd_4 chain was identified in the analogous sandwich complex $[Pd_4\{Ph(CH{=}CH)_4Ph\}_2(py)_2]^{2+}$ (**8**),[2a] in which the linear s-*trans*,s-*trans*,s-*trans* tetraenes are coordinated to the Pd_4 chain *via* the same coordination mode. The Pd–Pd lengths [Pd1–Pd2 2.638(3) Å, Pd2–Pd3 2.641(3) Å, Pd3–Pd4 2.643(3) Å] in **4a** are shorter than those of **8** [2.7463(8) Å, 2.721(1) Å].

Thus, it is revealed that the Pd^0 atom is incorporated into the DPBD sandwich framework in a stepwise manner. To the best of our knowledge, this is the first example of the stepwise construction of the molecular one-dimensional metal chains between two unsaturated hydrocarbon ligands having no hetero-atom donor sites.[4b,c] It should be mentioned that the DPBD ligands effectively change their coordination mode according to the stepwise growth of the Pd chain.[7,8] This result also gives the implication that the stepwise incorporation method may be useful to construct metal chains of specific sizes in an organometallic framework.

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Notes and references

‡ **2a**and **2b**: to a suspension of $[Pd_2(CH_3CN)_6][BF_4]_2$ (212.7 mg, 0.3361 mmol) in CH_2Cl_2 was added $Ph(CH{=}CH)_2Ph$ (378.8 mg, 1.836 mmol), and the mixture was stirred for 12 h at ambient temperature. The red precipitate was collected, washed with CH_2Cl_2 and dried under vacuum to give $[Pd_2(Ph(CH{=}CH)_2Ph)_2][BF_4]_2$ (**2a**) (265.4 mg, 99% yield), which was analyzed as the BAr_f (= $B(3,5\text{-}(CF_3)_2C_6H_3)_4$) salt (**2b**), obtained on treatment of **2a** with 2 equiv. of $NaBAr_f$ in CH_2Cl_2.[2a] Anal. calcd. (found) for $C_{96}H_{52}B_2F_{48}Pd_2$: C, 49.03 (48.32); H, 2.23 (2.29)%. Crystal data for **2a**: $C_{32}H_{28}B_2F_8Pd_2{\cdot}C_2H_4Cl_2$, M_r = 897.94, space group $C2/c$ (no. 15), a = 20.479(1), b = 7.9523(4), c = 22.452(2) Å, β = 114.108(2)°, U = 3337.4(4) Å^3, Z = 4, F_{000} = 1776, D_c = 1.787 g cm^{-3}, μ(Mo-Kα) = 13.08 cm^{-1}, 238 variables refined with 2818 reflections with $I > 2\sigma(I)$ to R = 0.058.

§ Throughout this work, some H atoms were found from difference Fourier maps and others were sited at calculated positions.

¶ In **2a**, the Pd_2 complex lies about an inversion center. The coordination geometry of the minor counterpart is essentially the same as the major one.

‖ **3b**: $[Pd_2(Ph(CH{=}CH)_2Ph)_2][BAr_f]_2$ (**2b**) (596.3 mg, 0.2535 mmol) was dissolved in $Ph(CH{=}CH)_2Ph$-saturated CH_2Cl_2 (80 mL). Then $Pd_2(dba)_3$ (131.4 mg, 0.1269 mmol) was added and the solution was stirred for 2 h at ambient temperature. **3b** was obtained after recrystallization from CH_2Cl_2–n-hexane (411.7 mg, 66% yield). The ^1H NMR monitoring experiment revealed the quantitative formation of **3b**. ^1H NMR (CD_2Cl_2) δ 8.04 (t, J = 7.8 Hz, 4H), 7.70 (m, 20H), 7.63 (s, 8H), 7.10 (m, 2H), 6.34 (d, J = 8.4 Hz, 4H), 4.19 (dd, J = 3.0 Hz, J = 8.6 Hz, 4H), 3.22 (dd, J = 3.0 Hz, J = 8.9 Hz, 4H). $^{13}C\{^1H\}$NMR (CD_2Cl_2) δ 134.96 (C_{para}), 133.03 (C_{meta}), 132.33 (C_{meta}), 123.28 (C_{ortho}), 122.68 (C_{ortho}), 99.81 (C_{ipso}), 90.45, 81.09. Anal. calcd. (found) for $C_{96}H_{52}B_2F_{48}Pd_3{\cdot}CH_2Cl_2$: C, 45.81 (45.69); H, 2.14 (2.17)%. Crystal data for **3b**: $C_{96}H_{52}B_2F_{48}Pd_3{\cdot}6CH_2Cl_2$, M_r = 2967.81, space group $P2_1/c$ (no. 14), a = 17.981(2), b = 12.556(5), c = 26.639(5) Å, β = 102.91(1)°, U = 5861(2) Å^3, Z = 2, F_{000} = 2920, D_c = 1.681 g cm^{-3}, μ(Mo-Kα) = 8.50 cm^{-1}, 785 variables refined with 8505 reflections with $I > 2\sigma(I)$ to R = 0.087. The Pd2 atom lies on an inversion center in **3b**.

** **4a**: to a suspension of $[Pd_2(CH_3CN)_6][BF_4]_2$ (300.0 mg, 0.4741 mmol) in CH_2Cl_2 was added $Ph(CH{=}CH)_2Ph$ (489.0 mg, 2.371 mmol), $Pd_2(dba)_3$ (490.8 mg, 0.4741 mmol) and the mixture was stirred for 2 h at ambient temperature. **4a** was obtained after recrystallization from CH_2Cl_2–xylene–CH_3CN (290.4 mg, 56% yield). ^1H NMR (CD_2Cl_2) δ 7.65 (t, J = 6.5 Hz, 2H), 7.53–7.42 (m, 6H), 7.37–7.31 (m, 4H), 6.57 (td, J = 7.0 Hz, J = 1.3 Hz, 2H), 6.36 (t, J = 6.7 Hz, 2H), 5.14 (d, J = 7.3 Hz, 2H), 4.97 (d, J = 12.7 Hz, 2H), 4.96 (d, J = 8.3 Hz, 2H), 4.41 (dd, J = 12.7 Hz, J = 10.7 Hz, 2H), 4.11 (d, J = 12.7, 2H), 2.76 (dd, J = 12.5 Hz, J = 10.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 137.61–128.0 (uncoordinated Ph, 6C), 123.66 (C_{meta}), 110.00 (C_{ortho}), 101.70 (C_{ortho}), 106.68 (C_{meta}), 95.60 (C_{ipso}), 88.82, 88.10, 86.04 (C_{para}), 79.88, 73.93. Anal. calcd. (found) for $C_{36}H_{34}B_2F_8N_2Pd_4{\cdot}CH_2Cl_2$: C, 37.70 (37.32); H, 3.08 (3.24); N, 2.38 (2.20)%. Crystal data for **4a**: $C_{36}H_{34}B_2F_8N_2Pd_4{\cdot}2CH_2Cl_2$, M_r = 1263.75, space group Pc (no. 7), a = 12.0844(6), b = 7.6585(3), c = 23.967(1) Å, β = 95.888(2)°, U = 2206.4(2) Å^3, Z = 2, F_{000} = 1228, D_c = 1.902 g cm^{-3}, μ(Mo-Kα) = 19.11 cm^{-1}, 518 variables refined with 3586 reflections with $I > 2\sigma(I)$ to R = 0.075. There is no crystallographically imposed symmetry in **4a**. ^1H NMR (CD_2Cl_2) for **4b** (DPBD ligands) δ 7.55–7.35 (m, 12H), 6.54 (t, J = 6.6 Hz, 2H), 6.24 (t, J = 7.2 Hz, 2H), 5.01 (d, J = 6.8 Hz, 2H), 4.96 (d, J = 12.9 Hz, 2H), 4.64 (d, J = 7.5 Hz, 2H), 4.36 (dd, J = 12.6 Hz, J = 10.6 Hz, 2H), 3.88 (d, J = 12.5 Hz, 2H), 2.57 (dd, J = 12.5 Hz, J = 10.6 Hz, 2H). CCDC 233253–233255. See http://www.rsc.org/suppdata/cc/b4/b403098b/ for crystallographic data in .cif or other electronic format.

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