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Extended Open-Chain Polyenides as Versatile Delocalized Anion Ligands for Metal Chain Clusters

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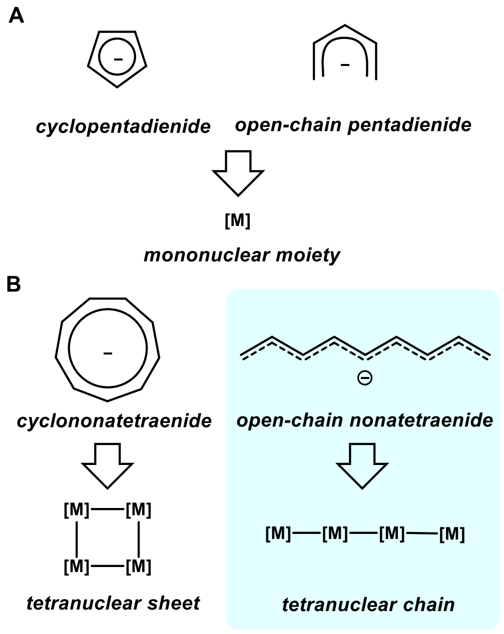
Abstract: *Although small cyclic- and open-chain unsaturated hydrocarbon anions such as cyclopentadienide and open-chain pentadienide are used as the strongly electron-donating auxiliary ligands for metal complexes, more extended π-conjugated unsaturated hydrocarbon anions have rarely been used in coordination chemistry, despite their potential ability to serve as the multiply bridging π-ligands for metal clusters. Here we report isolation of metal chain clusters bearing the multi-dentate, open-chain extended unsaturated hydrocarbon anion ligands. The extended open-chain π-conjugated polyenyl ligands effectively stabilized an oxidized palladium chain such as an unprecedented $[Pd_4]^{4+}$ chain.*

Unsaturated hydrocarbon anions (UHAs) play vital roles in the chemistry of transition metal complexes because of their utility as the strongly electron-donating auxiliary binders for mononuclear transition metal complexes. For example, cyclopentadienide (Cp^-) typically provides facile access to a series of mononuclear sandwich- and half-sandwich complexes which have a broad range of applications in catalysis and materials science (Scheme 1A).[1] Coordination behavior of pentadienide, an open-chain counterpart of Cp^-, has also been intensively studied, and its variable coordination modes to mono- and dinuclear metal centers have been established.[2,3] More extended π-conjugated UHAs are highly attractive as the multi-dentate bridging ligand for a metal assembly in a specific geometry. However, extended π-conjugated UHAs have rarely been used for synthesis of metal clusters. Our laboratory reported the use of an extended cyclic aromatic anion, cyclononatetraenide (CNT^-), that enabled the synthesis of a unique square M_4 sheet sandwich cluster (Scheme 1B, left-handed side).[4] On the other hand, it is virtually unexplored whether the extended open-chain UHAs[5] can bind a geometry-matching metal chain cluster (Scheme 1B, right-handed side).[6] While it has been shown by our group that neutral π-conjugated polyenes stabilize a chain cluster of group 10 metals in a low-oxidation state such as $[Pd_n]^{2+}$ chains,[7] open-chain π-conjugated polyenides may stabilize an elusive group 10 transition metal chain in a higher oxidation state through strong electron-donation,[7e,8f] widening the scope of metal clusters. Here we report isolation, unique coordination modes, and reactivity of open-chain polyenide Pd chain clusters by employing a carotenide (tricosaundecaenide) or a substituted nonatetraenide.



Scheme 1. Cyclic or open-chain polyenides for mono- or multinuclear metal centers: (**A**) cyclopentadienide and open-chain pentadienide for a mononuclear metal center; (**B**) cyclononatetraenyl and open-chain nonatetraenide for a tetranuclear metal sheet and chain, respectively.

Our group recently reported synthesis of extended metal chain sandwich complexes by employing β-carotene as the neutral multi-dentate unsaturated hydrocarbon support.[7f] During our investigation of the redox behavior of the bis-carotene Pd_{10} chain cluster $[Pd_{10}(\mu_{10}\text{-carotene})_2][B(Ar^F)_4]_2$ (**1**), we unexpectedly observed the polyene-to-polyenide transformation through oxidative deprotonation. Thus, oxidation of the meso isomer of **1** with $HB(Ar^F)_4$ (2.1 equiv.) in CH_2Cl_2 gave the tetracationic cluster $[Pd_{10}(\mu_{10}\text{-carotene})_2][B(Ar^F)_4]_4$ (**2**) in 86% yield (Scheme 2). In contrast to **1** which is in C_{2h} symmetry, complex **2** exhibited one set of carotene NMR resonances where all proton- or carbon chemical shifts were unequivalent, indicating C_s or a lower symmetry of **2**. Interestingly, deprotonation of **2** proceeded gradually in CD_2Cl_2 at room temperature to give a tricationic carotenyl-carotene Pd_{10} cluster $[Pd_{10}(\mu_{10}\text{-carotene})(\mu_{10}\text{-carotenyl})][B(Ar^F)_4]_3$ (**3**) (22% after 20 h). Treatment of **2** with Et_3N in CH_2Cl_2 gave **3** smoothly in 95% yield (Scheme 2).

The single-crystal X-ray structure analysis of **3** showed that the terminal polyenylic proton of one of the carotene ligands in **2**

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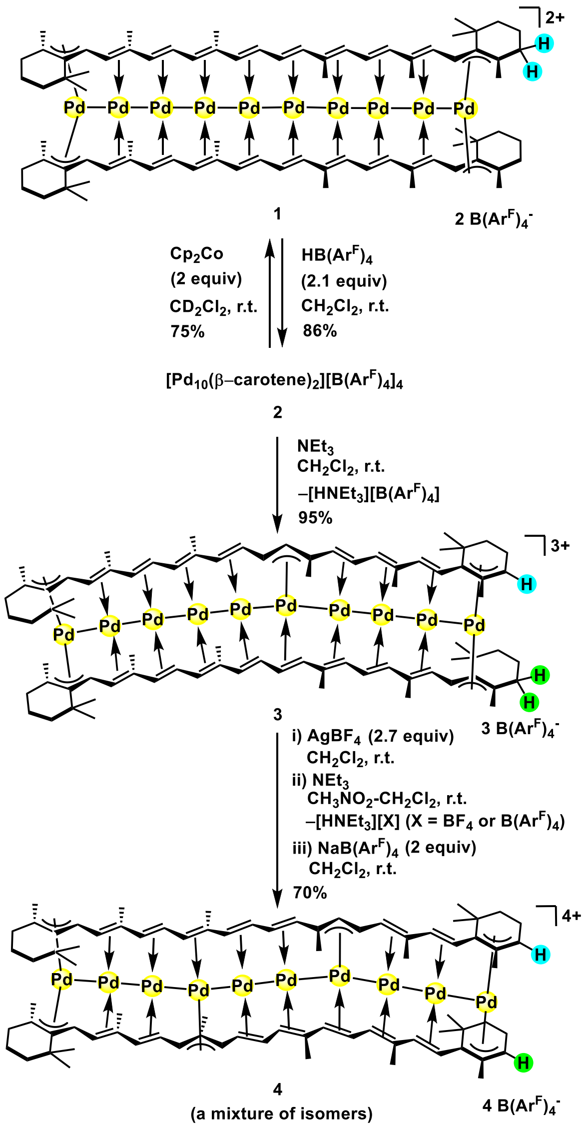
was deprotonated, and the resultant methine carbon (C4 atom) coordinated to the terminal Pd1 atom (Figure 1). This participation of the C4 atom in coordination causes the slippage of the next three inner Pd atoms (Pd2, Pd3 and Pd4) by one carbon, and the central Pd5 atom is bound in the η^3 fashion through C13, C14, and C15 atoms, giving a unique tri-η^3 coordination mode; μ_{10}-η^3:η^2:η^2:η^2:η^2:η^3:η^2:η^2:η^2:η^3. The coordination mode of another half part (Pd6, Pd7, Pd8, Pd9, and Pd10) is identical to that in **1**. The remaining carotene ligand adopted a μ_{10}-η^3:η^2:η^2:η^2:η^2:η^2:η^2:η^2:η^2:η^3 mode which is identical to that found in **1**. Consequently, the sandwich chain backbone is slightly bent at around the center (the Pd1···Pd5···Pd10 angle is 168.069(9)°), while each Pd–Pd length in **3** is in the range of normal Pd–Pd bond lengths.[9] The ^{1}H NMR spectra of **3** in CD_2Cl_2 showed a diagnostic down-field-shifted triplet resonance at δ 6.60 ppm (J = 5.5 Hz) which was assigned to the terminal polyenyl methine proton.



Scheme 2. Oxidative deprotonation of a bis-carotene complex $[Pd_{10}(\beta\text{-carotene})_2][B(Ar^F)_4]_2$ (**1**).

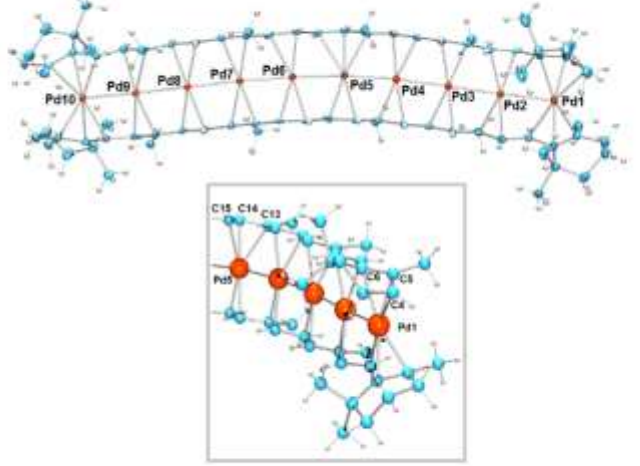
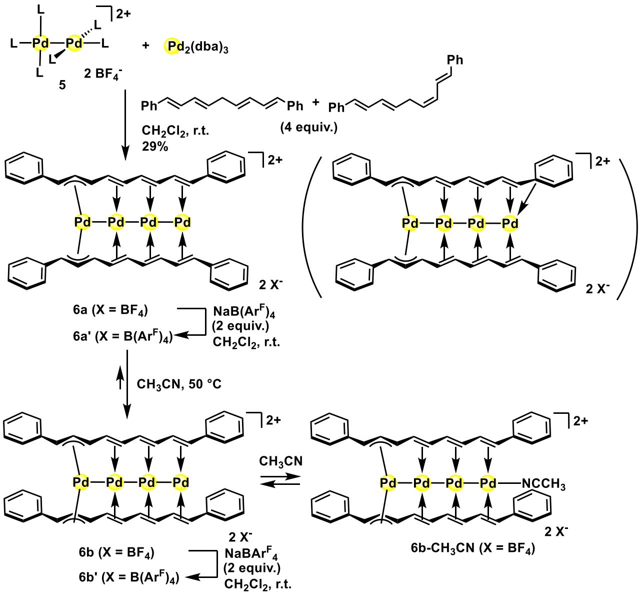


Figure 1. An ORTEP of $[Pd_{10}(\mu_{10}\text{–carotene})(\mu_{10}\text{–carotenyl})][B(Ar^F)_4]_3$ (**3**) (30% probability ellipsoids, $B(Ar^F)_4$ anions and solvent molecules are omitted for clarity). Selected bond lengths (Å): Pd1–Pd2 2.7143(9), Pd2–Pd3 2.6590(8), Pd3–Pd4 2.6432(9), Pd4–Pd5 2.6585(9), Pd5–Pd6 2.6542(9), Pd6–Pd7 2.6488(9), Pd7–Pd8 2.6314(9), Pd8–Pd9 2.6433(9), Pd9–Pd10 2.7438(9), Pd1–C4 2.233(16), Pd5–C13 2.384(11), Pd5–C14 2.136(11), Pd5–C15 2.416(9), Pd1–Pd2–Pd3 177.65(4), Pd2–Pd3–Pd4 173.42(4), Pd3–Pd4–Pd5 172.23(4), Pd4–Pd5–Pd6 172.75(4), Pd5–Pd6–Pd7 175.00(4), Pd6–Pd7–Pd8 174.71(4), Pd7–Pd8–Pd9 173.31(4), Pd8–Pd9–Pd10 178.39(4).

Although further deprotonation of **3** was not observed even in the presence of excess Et_3N, oxidation of **3** with $AgBF_4$ (2.7 equiv.) followed by treatment with Et_3N and counter anion exchange with $NaB(Ar^F)_4$ resulted in the deprotonation of the remaining carotene ligand, giving the tetracationic bis-carotenyl Pd_{10} chain cluster $[Pd_{10}(\mu_{10}\text{-carotenyl})_2][B(Ar^F)_4]_4$ (**4**) as a mixture of isomers (major/minor = 89/11) in 70% yield (Scheme 2). During the reaction, the two-electron-oxidized pentacationic intermediate $[Pd_{10}(\mu_{10}\text{-carotene})(\mu_{10}\text{-carotenyl})]^{5+}$ was detected through ESI(+)-MS analysis of the sample taken from the reaction mixture after 1 h. The ^{1}H NMR analysis of **4** showed a diagnostic down-field-shifted triplet resonance at δ 7.86 ppm (J = 3.6 Hz) for the terminal polyenyl methine proton of the major isomer. The X-ray structure analysis of **4** showed the disordered ten Pd atoms, making the discussion of the structure parameters difficult (see Supporting Information). However, it is evident that two carotenyl ligands, where the second deprotonation took place at the same side with the first deprotonation, flank the Pd_{10} chain in a tri-η^3 form, μ_{10}-η^3:η^2:η^2:η^3:η^2:η^2:η^2:η^2:η^2:η^3. It is noted that **4** contains formally four-electron-oxidized Pd_{10} chain compared to that of the dicationic bis-carotene Pd_{10} chain cluster **1**. This gives an implication that the extended open-chain polyenide effectively stabilizes a metal chain cluster in a high oxidation state.

Synthesis of **3** and **4** provides a proof that an extended open-chain polyenide has the ability to serve as the multi-dentate bridging ligand for a metal chain cluster. To gain further insight into the versatility of open-chain polyenide ligands, we next employed a shorter polyenide possessing terminal phenyl substituents. 1,9-Diphenyl-1,3,6,8-nonatetraene (DPNT-H) and its isomer are precursors of 1,9-diphenylnonatetraenide (DPNT$^-$), which is the open-chain counterpart of cyclononatetraenide (CNT$^-$). The DPNT-H was prepared as a mixture of *E*,*E*,*E*,*E*- and *E*,*E*,*Z*,*E*-isomers by the Wittig method.[5] The reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$ (**5**)[10] and $Pd_2(dba)_3$ in the presence of DPNT-H in CH_2Cl_2 at room temperature gave reddish brown precipitates of the DPNT sandwich complex [$Pd_4(\mu_4$-DPNT$)_2][BF_4]_2$ (**6a**) in 29% yield, where deprotonation of DPNT-H occurred in situ (Scheme 3). The counter-anion exchange with NaB($Ar^F)_4$ yielded [Pd_4(DPNT$)_2][B(Ar^F)_4]_2$ (**6a'**) which is soluble in CH_2Cl_2. The structure of **6a'** was confirmed by X-ray diffraction analysis (See Supporting Information). Although the disorder of four Pd atoms were found, the non-disordered DPNT ligands were arranged in a staggered sandwich form. It is noted that one of the phenyl rings of each DPNT ligand possibly coordinates to the terminal Pd atom through the ipso-carbon as shown in the parenthesis in Scheme 3, in order to decrease the coordinative unsaturation of the Pd_4 cluster.

Interestingly, the bis-DPNT Pd_4 cluster **6a** or **6a'** isomerized to thermodynamically more stable meso isomers **6b** or **6b'** in CH_3CN at 50 °C, where the equilibrium ratio of **6a'**/**6b'** was 4/96 (Scheme 3). Recrystallization from CH_3CN-Et_2O gave a single crystal of acetonitrile-capped Pd_4 chain cluster [Pd_4(DPNT$)_2(CH_3CN)][BF_4]_2$ (**6b-CH₃CN**), although the acetonitrile ligand in **6b-CH₃CN** easily dissociated in vacuo to recover **6b**. The X-ray structure analysis of **6b-CH₃CN** showed that the two eclipsed DPNT ligands coordinated to a Pd_4 chain through a mono-η^3 mode,[3c,d] μ_4-η^3:η^2:η^2:η^2, and the η^2-bound terminal Pd1 was capped by an acetonitrile ligand (Figure 2). Each Pd–Pd length (2.7356(11) Å, 2.7027(11) Å, and 2.7753(11) Å) is again in the range of normal Pd–Pd bond lengths.[9] Thus, the isomerization of **6a** to **6b** involves the face-inversion of the DPNT ligands on a Pd_4 chain.[11] It has been shown that the face-inversion of the neutral polyene (diphenyltetraene) ligands on a Pd_3 chain is sluggish in a thermal condition, while it proceeds smoothly under the visible-light irradiation.[11] In the present case, it was confirmed that the isomerization proceeded even in the dark. The more detailed mechanism of the thermal face-inversion process of **6a** to **6b** will be the subject of future study. It is noted that the formal oxidation state of the Pd_4 chain in **6** is the unprecedented $[Pd_4]^{4+}$, which indeed could not accessed by oxidation of the corresponding bis-diphenyltetraene-Pd_4 chain sandwich cluster [$Pd_4(\mu_4$-η^3:η^2:η^2:η^3-$Ph(CH=CH)_4Ph)_2]^{2+}$ with Ag^+ in CD_3CN.[7a,e]



Scheme 3. Synthesis of bis-1,9-diphenylnotatetraenyl Pd_4 chain clusters.

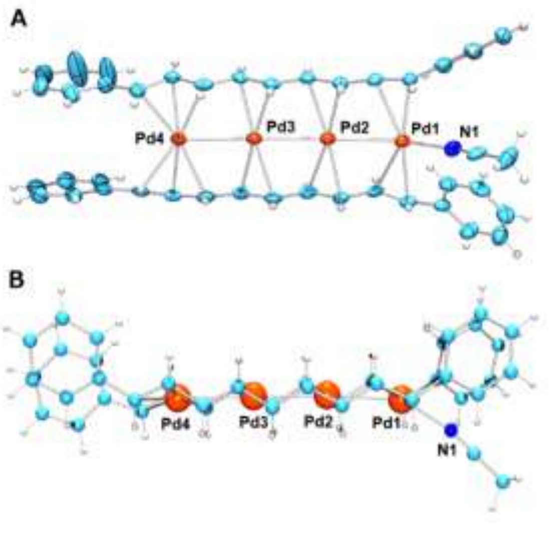
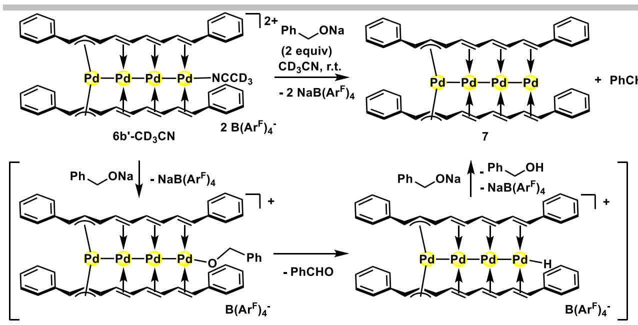


Figure 2 (**A**) An ORTEP of [Pd_4(DPNT$)_2(CH_3CN)][BF_4]_2$ (**6b-CH₃CN**) (30% probability ellipsoids, the BF_4 anions were omitted for clarity). Selected bond lengths (A) and angles (deg): Pd1–Pd2 2.7356(11), Pd2–Pd3 2.7027(11), Pd3–Pd4 2.7753(11), Pd1–N1 2.099(8), N1–Pd1–Pd2 152.65(18), Pd1–Pd2–Pd3 175.97(3), Pd2–Pd3–Pd4 179.25(3). (**B**) A ball and stick drawing of **6b-CH₃CN**.

Because **6b**, which has a rare $[Pd_4]^{4+}$ chain, is capable of accommodating a substrate at its unique Pd_4 axial site, we next demonstrated transformation of an organic substrate by using **6b**. We chose the oxidative transformation of an alkoxide as the model reaction, that is relevant to the Pd-catalyzed oxidation of alcohols. Thus, treatment of **6b'-CD₃CN** with $NaOCH_2Ph$ (2 equiv) in CD_3CN resulted in the immediate formation of benzaldehyde quantitatively, that accompanied precipitation of the neutral sandwich chain cluster $Pd_4(\mu_4$-DPNT$)_2$ (**7**) possessing a $[Pd_4]^{2+}$ chain (Scheme 4). The insoluble complex **7** was isolated in 48% yield. We confirmed that oxidation of **7** with acid or $AgBF_4$ recovered the dicationic complex **6b-CD₃CN**. The benzyloxide likely attacked at the axial coordination site of the Pd_4 chain and subsequent β-H elimination could give benzaldehyde. The Pd_4–H species might be quenched with remaining benzyloxide to give **7**. The coordination site of **6b'** is reminiscent of that of a pincer-type square planar Pd^{II} complex, where the trans position in **6b'** is occupied by Pd.[12] With such pincer-type coordination environment, it has been proposed that the β-H elimination of the pincer-type alkoxo-Pd^{II} complexes can be assisted by an external alcohol through a dissociative β-H elimination pathway.[13] We then confirmed that **6b** became an excellent catalyst for aerobic oxidation of alcohols. In the presence of a catalytic amount of Cs_2CO_3 (6 mol%) and MS4A, **6b** (2 mol%) efficiently catalyzed aerobic oxidation of benzyl alcohol to benzaldehyde almost quantitatively (>99% yield) at 80 °C in DMSO-toluene under the O_2 atmosphere (baloon).[14] No apparent induction period was observed for this catalytic process. Oxidation of 1-phenylethanol or cynnamyl alcohol to acetophenone (92% yield) or cynnamaldehyde (98% yield) also proceeded in a similar condition. While Pd chain cluster catalysts are of increasing interest recently,[15] these preliminary catalytic studies indicated that the organopalladium cluster catalysts can be produced by using unsaturated hydrocarbon anion ligands.



Scheme 4. Facile oxidation of benzyloxide with **6b'-CD$_3$CN**.

In summary, the present results provided the first experimental evidence that the extended open-chain UHAs behave as the excellent multi-dentate bridging ligands for metal chain clusters. The polyenides R–(CH)$_{2n+1}$–R stabilize either Pd$_n$ chain (**3** or **4**) or Pd$_{n-1}$ chain (**6**). Since UHAs such as Cp$^-$ have been widely used as the strong electron-donating auxiliary ligands for high-valent metal complexes, the extended open-chain polyenides may provide unique scaffolds for metal chain clusters in relatively high oxidation states. Further study on the use of extended π-delocalized anions for metal clusters and their use in catalysis are now ongoing in our laboratory.

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Keywords: Polyenyl • Metal Chain Clusters • Palladium Clusters

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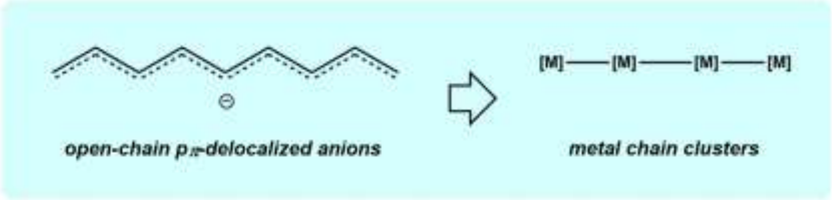
COMMUNICATION



We report that extended open-chain unsaturated hydrocarbon anions serve as the multiply bridging π-coordinating anions for extended metal chain clusters. The strong electron-donating property of the extended open-chain unsaturated hydrocarbon anions provides a way to access an oxidized state of metal chain clusters.

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Extended Open-Chain Polyenides as Versatile Delocalized Anion Ligands for Metal Chain Clusters