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ARTICLE

Bridging Coordination of Acenaphthylene to a Pd₃ Chain or a Pd₄ Sheet Cluster

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The coordination behaviour of multinuclear clusters to fused arene ligands is of continuous interest due to its relevance to metal catalysts supported by graphitic carbon materials. Herein, we report the bridging coordination behaviour of acenaphthylene to a Pd₃ or a Pd₄ cluster. A bis-acenaphthylene Pd₃ chain cluster and an acenaphthylene-COT Pd₄ sheet cluster were isolated, and the μ_3 - π -coordination mode or the μ_4 -oxidative π -addition mode of the acenaphthylene ligand in each cluster was elucidated by X-ray structure analysis.

Introduction

The coordination behaviour of fused arenes has been studied extensively since the first discrete transition metal complex of naphthalene, Cr(η^6 -naphthalene)(CO)₃, was reported in 1958 by E. O. Fischer et al.¹ Among the characteristic coordination patterns of fused arenes, the multiple metal binding is of particular interest when considering their use as the ligands for metal clusters. The understanding of the multiple metal binding ability of fused arenes would also give an insight into how a multinuclear metal cluster is accommodated by extended sp²-carbon frameworks, that is related to carbon-supported metal catalysts and materials. While the multinuclear metal binding by fused arenes has been demonstrated through coordination of a few mononuclear moieties in a manner that there is no metal–metal bond; e.g., the early synthesis of [Fe₂(μ - η^6 : η^6 -phenanthrene)Cp₂][PF₆]₂, Cr₂(μ - η^6 : η^6 -naphthalene)(benzene)₂, La₃(μ_3 - η^2 : η^6 : η^6 -pyrene)Cp*₃(μ -Cl)₃(thf), and Ru₃(μ_3 - η^6 : η^6 : η^6 -triphenylene)(cod)₃,^{2,3} it has been shown that a dinuclear metal–metal bonded moiety can be introduced on a face of fused arenes.^{4–6} The acenaphthylene dinuclear complex Fe₂(μ - η^5 : η^3 -acenaphthylene)(CO)₅⁵ is one of the early examples in which a dinuclear metal–metal moiety is bound to multiple aromatic rings in a fused arene. More recently, our group has developed the sandwich-type bis-(fused arene) metal clusters, which allows systematic investigation of the bridging

coordination modes of various fused arenes to multinuclear metal–metal bonded moieties. For example, our group reported that perylene or fluoranthene binds a tetranuclear Pd–Pd–Pd–Pd chain through the μ_4 - η^2 : η^2 : η^2 : η^2 -mode.^{7,8} In contrast, tetracene can bind a Pd₅ sheet through the μ_5 - η^3 : η^2 : η^2 : η^2 : η^3 -mode.⁹ The multiple metal binding of several other fused arenes including naphthalene and anthracene have also been identified.^{4d,10–12} Through these studies, it has been proposed that the μ_3 - or higher order bridging coordination of fused arenes are classified by the following two modes; i) the π -coordination mode involving only even hapto-numbers such as η^2 for binding of each metal, and ii) the oxidative π -addition involving odd hapto-numbers such as η^3 in addition to η^2 for metal binding.^{4d,11}

In the course of our continuing investigation on the multiple metal binding ability of fused arenes, here we focused on acenaphthylene, whose coordination has been dominated by the oxidative π -addition mode, presumably because of the propensity to bind a metal atom at its five-membered cyclopentadienyl-like substructure. Indeed, Nagashima et al. and Cabeza et al. independently showed that acenaphthylene facially caps a Ru₃ or a Ru₄ site of ruthenium clusters through the μ_3 - η^5 : η^2 : η^3 - or μ_4 - η^5 : η^2 : η^3 : η^2 -oxidative π -addition mode (Scheme 1, **A** and **B**).^{13–16} Herein, we report the bridging coordination behaviour of acenaphthylene to a Pd₃ or Pd₄ cluster. The sandwich binding of a [Pd₃]²⁺ chain cluster is led by the μ_3 - η^2 : η^2 : η^2 - π -coordination mode of acenaphthylene (Scheme 1, **C**). On the other hand, the mixed-ligand sandwich coordination of acenaphthylene and cyclooctatetraene (COT) gave the Pd₄ sheet cluster, where the μ_4 - η^5 : η^2 : η^3 : η^2 -oxidative π -addition mode of acenaphthylene (Scheme 1, **B**) was identified. The facile ligand-exchange of the μ_3 - η^2 : η^2 : η^2 - π -coordinated acenaphthylene provides a good [Pd₃]²⁺ source for construction of some palladium clusters.

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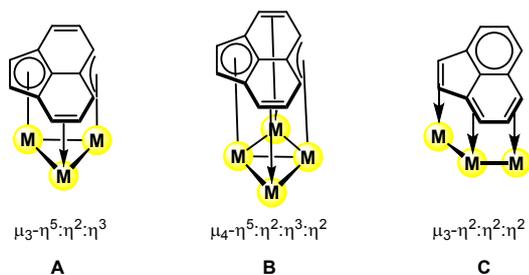
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Scheme 1. The bridging coordination modes of acenaphthylene to an M_3 or an M_4 moiety.

Results and Discussion

Bis(acenaphthylene)-Pd₃ Sandwich Complexes

Our group previously reported that the redox-condensation of a Pd–Pd complex with Pd⁰ in the presence of perylene or fluoranthene gives a Pd₄ chain sandwich cluster.^{7,8} The reaction of [Pd₂(CH₃CN)₆][BF₄]₂^{17,18} with Pd₂(dba)₃^{19–21} (0.5 equiv.) in the presence of acenaphthylene (5 equiv.), followed by the counter-anion exchange with NaBAR₄^F (Ar^F₄ = 3,5-(CF₃)₂C₆H₃)²² afforded [Pd₃(μ₃-acenaphthylene)₂(CH₃CN)₂][BAR₄^F]₂ in 77% yield as a mixture of two isomers (91:9) (eq. 1). The structure of one of the two isomers, **1**, was determined by the X-ray structure analysis (Figure 1). The bent-Pd₃ chain (Pd1–Pd2–Pd3 = 138.67(2)°) was held by two acenaphthylene ligands which are in an eclipsed arrangement. Such largely bent metal chain sandwich clusters in which the metal-chain is end-capped by ligands have been rarely isolated.^{23–25} The Pd–Pd bond lengths (2.5968(7) Å and 2.6693(7) Å) of the Pd₃ chain are in the range of normal Pd–Pd bond lengths,²⁶ and comparable to those in the previously isolated Pd₃ or Pd₄ chain sandwich clusters (Table 1). The μ₃-η²:η²:η²-coordination of the acenaphthylene ligands, which is attributed to the π-coordination mode (Scheme 1C), is distinct from the previously reported oxidative π-addition modes of acenaphthylene (Scheme 1A and B). The C–C bond lengths of the uncoordinated 6-membered ring (1.376(9)–1.418(9) Å) indicated the aromatic character of this ring. Although the structure of another isomer has not been identified yet, the isomer would have the staggered arrangement of the acenaphthylene ligands as shown in Scheme 1. Theoretical calculation of the model complex [Pd₃(μ₃-acenaphthylene)₂(HCN)₂]²⁺ suggested that the eclipsed sandwich cluster is slightly more stable than the staggered one (ΔG = 0.6 kcal/mol).

The ¹³C NMR analysis showed that **1** exhibited large up-field shifts (Δδ = 28–50 ppm) of the six coordinated carbon atoms (1-, 2-, 2A-, 3-, 4-, and 5-positions), that is consistent with the μ₃-η²:η²:η²-coordination of the acenaphthylene ligands in solution. Such large up-field shifts of the ¹³C resonances (Δδ > ca. 15 ppm) are commonly observed for the coordinating carbon atoms of olefins and arenes.²⁷ In the case of the perylene Pd₄ clusters [Pd₄(μ₄-perylene)₂(CH₃CN)₂][BAR₄^F]₂ and [Pd₄(μ₄-perylene)(μ₄-COT)(CH₃CN)₂][BAR₄^F]₂ where the eight carbons at the arm-chair edge are used in coordination for the former and the ten carbons at the naphthalene substructure are used for the latter, the coordinating carbons showed similar large Δδ values (Δδ = 27 ~ 50 ppm), while

the uncoordinated carbon atoms show much smaller Δδ values (Δδ = -4 ~ 8 ppm) (Scheme 2).^{7,8}

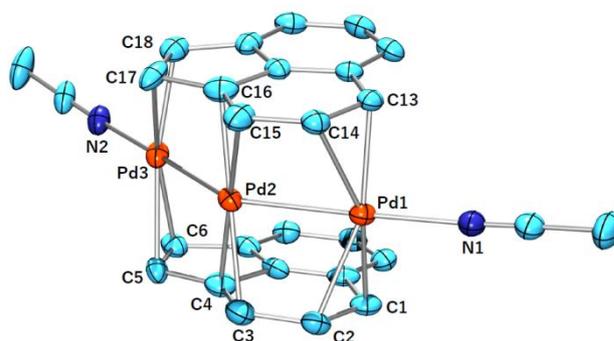
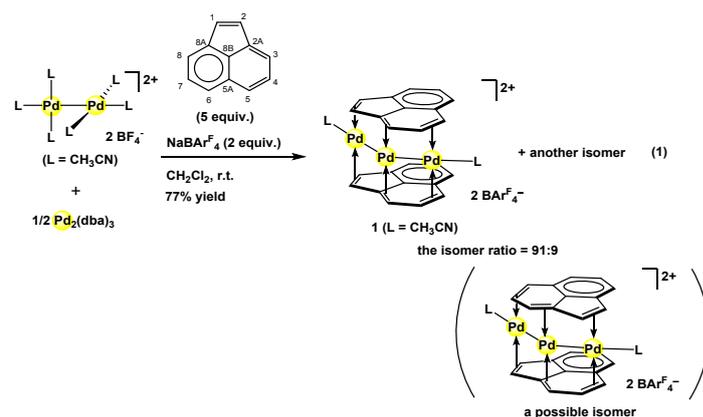
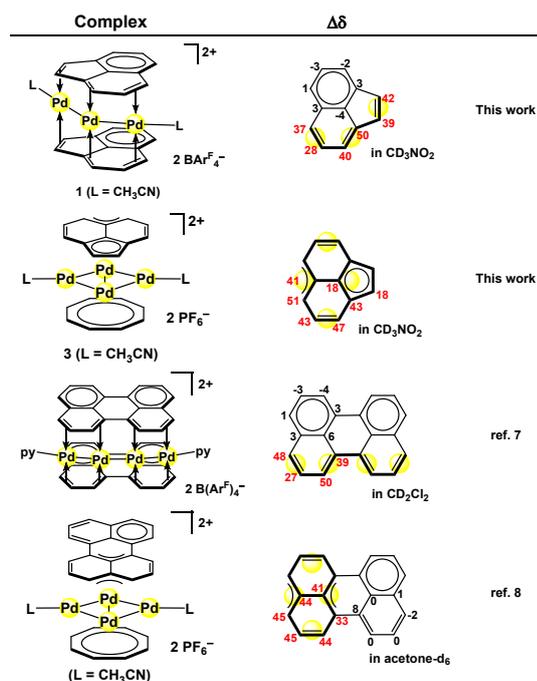


Figure 1. The ORTEP drawing of [Pd₃(μ₃-acenaphthylene)₂(CH₃CN)₂][BAR₄^F]₂ (**1**). (Ellipsoid set at 30% probability, BAR₄^F anions, solvent molecules, and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.5968(7), Pd2–Pd3 2.6693(7), Pd1–C1 2.237(6), Pd1–C2 2.314(6), Pd1–C13 2.215(5), Pd1–C14 2.350(6), Pd2–C3 2.190(7), Pd2–C4 2.129(6), Pd2–C15 2.232(7), Pd2–C16 2.159(7), Pd3–C5 2.331(6), Pd3–C6 2.208(6), Pd3–C17 2.344(6), Pd3–C18 2.200(6), Pd1–Pd2–Pd3 138.67(2), Pd2–Pd1–N1 178.25(14), Pd2–Pd3–N2 175.73(15).

Table 1. The Pd–Pd bond lengths for several Pd chain sandwich clusters in which the Pd chain termini are capped by CH₃CN or pyridine.

Complex	Pd–Pd (Å)
[Pd ₃ (μ ₃ -acenaphthylene) ₂ (CH ₃ CN) ₂][BAR ₄ ^F] ₂ (1)	2.5968(7), 2.6693(7)
[Pd ₄ (μ ₄ -perylene) ₂ (CH ₃ CN) ₂][BAR ₄ ^F] ₂	2.5575(7), 2.5376(7), 2.5627(7)
[Pd ₄ (μ ₄ -fluoranthene) ₂ (CH ₃ CN) ₂][BAR ₄ ^F] ₂	2.579(1), 2.622(1), 2.575(2)
[Pd ₃ (μ ₃ -1 ⁻ Bu-cycloheptatriene) ₂ (CH ₃ CN) ₃][BF ₄] ₂	2.7332(9), 2.7342(9)
[Pd ₄ (μ ₄ -1,8-diphenyloctatetraene) ₂ (py) ₂][BAR ₄ ^F] ₂	2.7463(8), 2.721(1), 2.7463(8)



Scheme 2. The up-field shifts ($\Delta\delta$) of coordinating carbons in several (fused arene)-Pd_n complexes, where $\Delta\delta = \delta_{\text{free ligand}} - \delta_{\text{arene ligand in complexes}}$.

Acenaphthylene-COT-Pd₄ Sandwich Complexes

Next, we examined the arene-exchange reaction of the triangular Pd₃ cluster [Pd₃(μ₃-anisole)(μ₃-COT)(CH₃CN)₃][PF₆]₂ (**2**) which shows a high μ₃-arene exchange reactivity.¹⁰⁻¹² The reaction of **2** with acenaphthylene (5 equiv.) proceeded at 60 °C, giving the Pd₄ sheet cluster [Pd₄(μ₄-acenaphthylene)(μ₄-COT)(CH₃CN)₂][PF₆]₂ (**3**), where an additional Pd⁰ atom incorporated into the sandwich framework was generated probably through decomposition of a portion of the starting complex **2**. We then confirmed that the addition of Pd₂(dba)₃ (0.5 equiv) to the reaction mixture at 40 °C gave **3** in 76% yield (eq. 2). The PPh₃-analogue of complex **3**, [Pd₄(μ₄-acenaphthylene)(μ₄-COT)(PPh₃)₂][PF₆]₂ (**3'**), was obtained by treatment of **3** with PPh₃ (2 equiv.) (eq. 2). The molecular structure of **3'** was determined by X-ray structure analysis (Figure 2). The acenaphthylene ligand facially coordinates to the rhombic Pd₄ sheet through the μ₄-η⁵:η²:η³:η²-oxidative π-addition mode, where the Pd–C bond lengths of the 5-membered ring carbons are in the range of 2.250(8)–2.472(10) Å. The ¹³C NMR analysis also supported that all carbon atoms of the acenaphthylene ligand are used in coordination to Pd; that is, large up-field shifts were observed for all carbon atoms of the acenaphthylene ligand ($\Delta\delta = 18$ –47 ppm) (Scheme 2). The rhombic Pd₄ sheet is distorted as the edge Pd–Pd bond lengths involving the η³-bound Pd2 (Pd1–Pd2 = 2.763(1) Å, Pd2–Pd3 = 2.777(1) Å) are slightly longer than those involving the η⁵-bound Pd4 (Pd3–Pd4 = 2.792(1) Å, Pd4–Pd1 = 2.785(1) Å). The diagonal Pd2–Pd4 (2.913(1) Å) is elongated in **3'**, compared to that in [Pd₄(μ₄-η³:η²:η³:η²-fused-arene)(COT)L₂][X]₂ (2.851(1) Å for naphthalene; 2.874(1) Å for perylene) (Table 2).^{8,10} Such distortion of the rhombic Pd₄ sheet in **3'** may be caused by the η⁵-coordination of the 5-membered ring to the Pd4 atom.

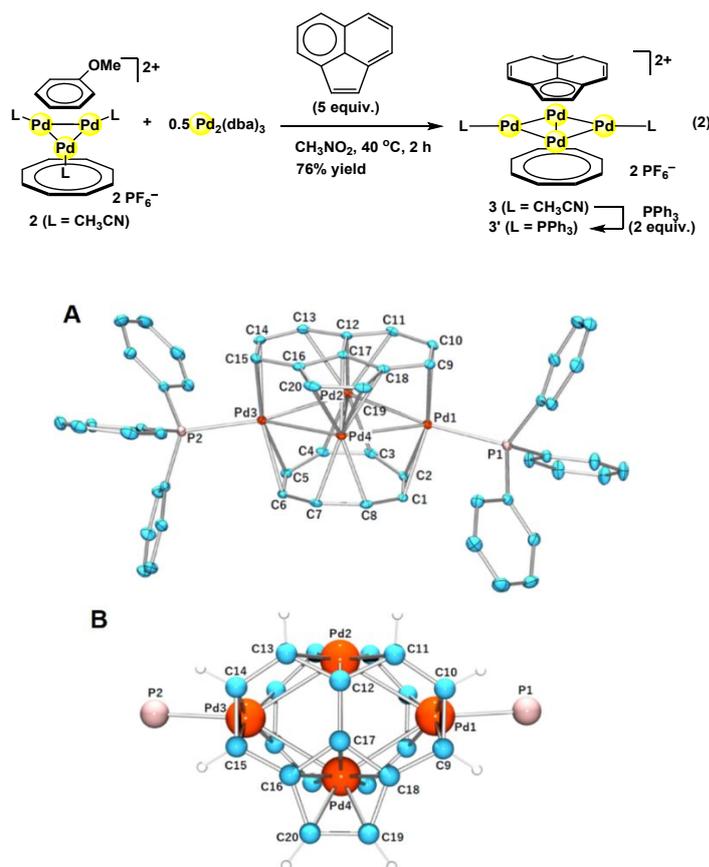


Figure 2. A: The ORTEP drawing of [Pd₄(μ₄-acenaphthylene)(μ₄-COT)(PPh₃)₂][PF₆]₂ (**3'**). (Ellipsoid set at 30% probability, PF₆ anions, solvent molecules, and protons are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.7628(7), Pd2–Pd3 2.7766(7), Pd3–Pd4 2.7921(7), Pd4–Pd1 2.7853(7), Pd1–C1 2.282(6), Pd1–C2 2.205(7), Pd1–C9 2.282(7), Pd1–C10 2.260(7), Pd2–C3 2.189(7), Pd2–C4 2.147(7), Pd2–C11 2.356(7), Pd2–C12 2.118(7), Pd2–C13 2.327(7), Pd3–C5 2.242(7), Pd3–C6 2.227(7), Pd3–C14 2.320(7), Pd3–C15 2.290(8), Pd4–C7 2.186(6), Pd4–C8 2.152(6), Pd4–C16 2.324(7), Pd4–C17 2.250(7), Pd4–C18 2.308(7), Pd4–C19 2.472(8), Pd4–C20 2.472(8). B: Top view of the molecular structure of complex **3'**.

Table 2. The Pd–Pd bond lengths for μ₄-fused arene-Pd₄ sandwich clusters (Å).

Complex	Pd–Pd (edge) (Å)	Pd–Pd (diagonal) (Å)
[Pd ₄ (μ ₄ -acenaphthylene)(μ ₄ -COT)(PPh ₃) ₂][PF ₆] ₂ (3')	2.7628(7), 2.7766(7), 2.7921(7), 2.7853(7)	2.913(1)
[Pd ₄ (μ ₄ -naphthalene)(μ ₄ -COT)(PCy ₃) ₂][BF ₄] ₂ (5')	2.7906(7), 2.8181(8), 2.7990(8), 2.8161(8)	2.8506(7)
[Pd ₄ (μ ₄ -perylene)(μ ₄ -COT)(CH ₃ CN) ₂][BARF ₄] ₂	2.711(1), 2.749(1), 2.715(1), 2.757(1)	2.874(1)

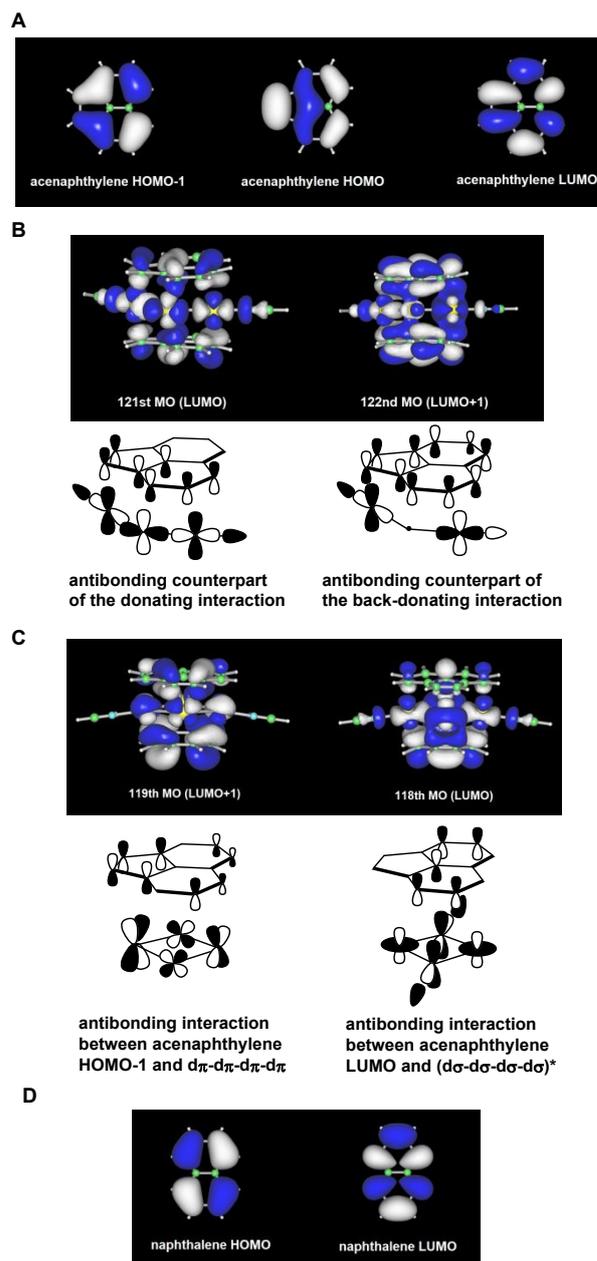
Theoretical Analysis

To gain further insight into the observed coordination modes of acenaphthylene, we carried out the Kohn-Sham orbital analysis on [Pd₃(μ₃-acenaphthylene)₂(HCN)₂]²⁺ (**1'**) and [Pd₄(μ₄-acenaphthylene)(μ₄-COT)(HCN)₂]²⁺ (**3''**). Geometrical optimization of **1'** and **3''** was performed with M06 functional.²⁸ Core electrons of Pd were replaced with Stuttgart-Dresden-

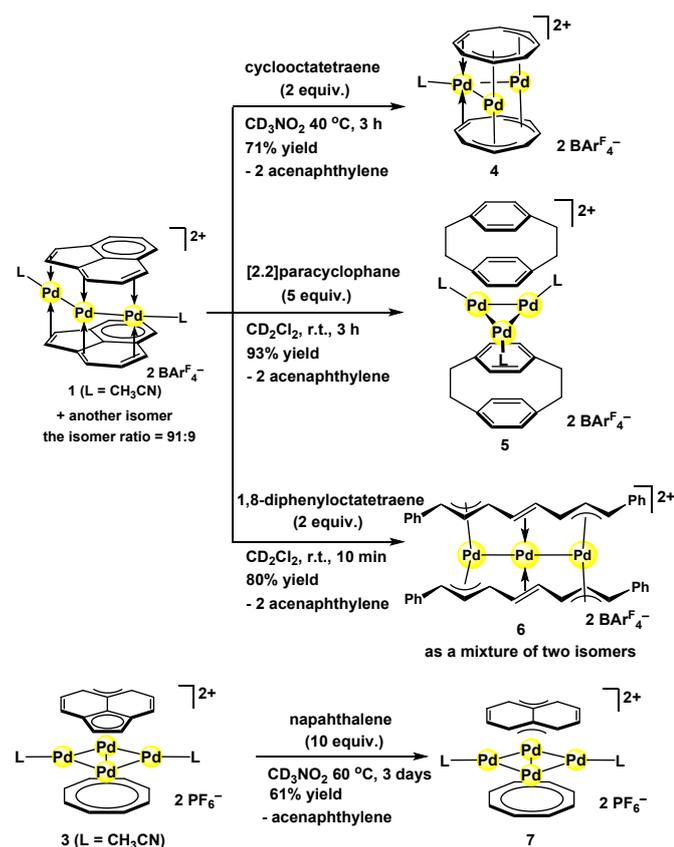
Bonn relativistic effect core potentials (ECPs) and their valence electrons were represented by (8s7p6d)/[6s5p3d] basis set.²⁹ The 6-311G(d) basis sets were used for other atoms.³⁰ The μ_3 - η^2 : η^2 : η^2 - π -coordination of the acenaphthylene ligands in **1'** is resulted mainly from the donating interaction between the acenaphthylene HOMO and the antibonding ($d\sigma$ - $d\sigma$ - $d\sigma$)* orbital of the Pd₃ chain, as well as from the back-donating interaction between the acenaphthylene LUMO and the non-bonding $d\sigma$ - \bullet - $d\sigma$ orbital of the Pd₃ chain (Scheme 3A, B). These donating and back-donating interactions are similar to those in the prototypal end-capped metal chain sandwich complexes of conjugated polyenes.²⁵ For **3''**, the HOMO-1 of acenaphthylene has an interaction with the $d\pi$ - $d\pi$ - $d\pi$ - $d\pi$ orbital of the Pd₄ sheet, where the antibonding counterpart is vacant (LUMO+1 (119th MO)) (Scheme 3A, C). It is noted that p-orbitals at 1- and 2-positions of the acenaphthylene carbons participated in this interaction, which is consistent with the η^5 -binding of the Pd₄ atom. Another important interaction for the acenaphthylene coordination involves the LUMO of acenaphthylene and ($d\sigma$ - $d\sigma$ - $d\sigma$ - $d\sigma$)* orbital of the Pd₄ sheet, whose antibonding counterpart is also vacant (LUMO (118th MO)) (Scheme 3C). The vacancy of this MO also leads to the Pd–Pd bonding at the edges of the Pd₄ sheet.

Exchange of the Bridging Acenaphthylene Ligand

Finally, we examined the ligand exchange of **1** and **3**. The acenaphthylene ligands in **1** were smoothly replaced with COT (2 equiv.) at 40 °C, giving the known bis-COT sandwich complex [Pd₃(μ_3 -COT)₂(CH₃CN)] [BAR^F₄]₂ (**4**)²⁴ in 71% yield after 3 h (Scheme 3). Addition of [2.2]paracyclophane (PCP) to **1** in the presence of CH₃CN (1 equiv.) at ambient temperature afforded [Pd₃(μ_3 -PCP)₂(CH₃CN)₃] [BAR^F₄]₂ (**5**) in 93% yield after 3 h. The replacement with 1,8-diphenyloctatetraene (DPOT) also proceeded smoothly to give [Pd₃(μ_3 -DPOT)₂] [BAR^F₄]₂ (**6**). These results showed that **1** can be used as a useful [Pd₃]²⁺ transfer reagent. Treatment of **3** with COT resulted in the gradual decomposition of **3**, where the formation of a bis-COT Pd₄ species was not detected. However, the μ_4 -acenaphthylene ligand in **3** was replaced gradually with naphthalene at 60 °C to give [Pd₄(μ_4 -naphthalene)(μ_4 -COT)(CH₃CN)₂] [PF₆]₂ (**7**)¹⁰ in 61% yield after 3 days (Scheme 4). This is not surprising because the μ_4 - η^3 : η^2 : η^3 : η^2 -coordination of naphthalene in **7** is closely related with that of the μ_4 -coordination of acenaphthylene in **3**, in view of the fact that the HOMO or the LUMO of naphthalene (Scheme 3D) is isolobal to the HOMO-1 or the LUMO of acenaphthylene, which is involved in the interaction with the $d\pi$ - $d\pi$ - $d\pi$ - $d\pi$ orbital or the ($d\sigma$ - $d\sigma$ - $d\sigma$ - $d\sigma$)* orbital, as mentioned above.



Scheme 3. A: The top views of the HOMO-1, the HOMO, and the LUMO of acenaphthylene. B: The 121st MO (LUMO) and the 122nd MO (LUMO+1) of **1'** and their schematic drawings highlighting the interaction between the acenaphthylene ligand and the Pd₃ chain, where one of the acenaphthylene ligands is omitted for clarity. C: The 119th MO (LUMO+1) and 118th MO (LUMO) of **3''** and schematic drawings highlighting interaction between the acetylene ligand and the Pd₄ sheet, where the COT ligand is omitted for clarity. D: The top views of the HOMO and the LUMO of naphthalene.



Scheme 4. The ligand exchange of complex 1 and 3.

Conclusions

The $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}\pi$ -coordination mode and $\mu_4\text{-}\eta^5\text{:}\eta^2\text{:}\eta^3\text{:}\eta^2$ -oxidative π -addition mode of acenaphthylene were revealed through isolation and structural characterization of the bis(acenaphthylene)-Pd₃ cluster **1** or the acenaphthylene-COT-Pd₄ clusters **3** and **3'**. The $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -acenaphthylene ligands undergo ligand-exchange facily, making **1** as the good starting material for synthesis of Pd₃ complexes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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