Cluster Binding

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Modulation of Benzene or Naphthalene Binding to Palladium Cluster Sites by the Backside-Ligand Effect**

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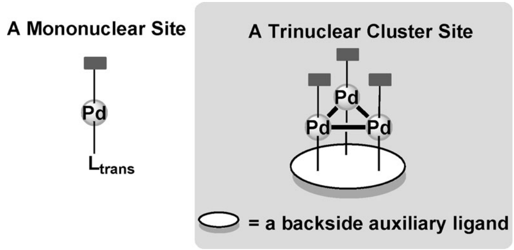
Abstract: *The backside-ligand modulation strategy to enhance the substrate binding property of Pd clusters is reported. The benzene or naphthalene binding ability of Pd_3 or Pd_4 clusters is enhanced significantly by the backside cyclooctatetraene ligand, leading to the formation of the first solution-stable benzene- or naphthalene Pd clusters. The present results imply that the ligand design of the metal clusters, especially for the backside ligand of the metal cluster site, is crucial to acquire a desired reactivity of metal clusters.*

Much attention has been focused on the roles of metal clusters in catalysis. It is of particular interest to explore the substrate binding and activation modes at the bridging coordination sites of metal clusters, as multiple metal atoms of a metal cluster site may facilitate some elementary reactions in catalytic cycles, or bring new modes of substrate binding and transformation.[1] Despite the importance of palladium in catalysis, however, the way that Pd clusters bind substrates at their μ_n-bridging coordination sites ($n \geq 3$) has not been extensively investigated and thus poorly characterized.[2] This is mainly due to the difficulty to generate reactive molecular Pd clusters in homogeneous systems.[3] To overcome this problem, it is necessary to develop a ligand system which not only supports a Pd cluster core, but also bring a suitable environment for substrate binding at a Pd cluster site through electronic and/or steric effects. In designing the ligand systems for reactive Pd clusters, we focused on the roles of the backside auxiliary ligand, as the property of a metal cluster site may be largely affected by electronic effects of the backside ligand, in view of the well-established *trans* influence and *trans* effect in the mononuclear metal systems (Scheme 1).[4] Herein, we report that the backside carbocyclic ligands have a large effect on the substrate binding property at a Pd_3 cluster site, through demonstration of the significantly enhanced benzene binding ability of a Pd_3 cluster as compared to known Pd complexes. Furthermore, it was also confirmed that the backside-ligand-modulation strategy can be applied to the naphthalene binding at a μ_4-Pd_4 cluster site.



Scheme 1. The *trans* ligand of a mononuclear Pd site and the backside ligand of a trinuclear Pd cluster site.

We chose benzene as the target substrate in examining the backside-ligand effect on the substrate binding at a μ_3-Pd_3 cluster site, as benzene is one of the weakest coordinating substrates in organopalladium chemistry. In fact, mononuclear Pd complexes that bind benzene stably in solution have not been reported.[5,6] The lack of solution-stable benzene-Pd complexes would have raised a question on the involvement of benzene–Pd π-adducts in Pd-catalyzed benzene transformations.[7] The μ_3-benzene coordination to molecular Pd clusters is unprecedented, while the potential ability of Pd clusters to bind benzene may be indicated by the Pd surface chemistry; that is, it has been proposed that adsorbed benzene on Pd surface adopts μ_3- or μ_4-bridging coordination modes.[8] Our laboratory recently addressed the arene binding ability of Pd_3 clusters,[9] and disclosed that [2.2]paracyclophane, which is a distorted and intramolecularly π-stacking arene having much stronger coordinating ability than benzene, afforded the μ_3-arene Pd_3 cluster, through the redox-condensation of $[Pd_2(CH_3CN)_6][BF_4]_2$ and $[Pd_2(dba)_3]$ in the presence of the cyclophane. In this case, however, a similar reaction using benzene instead of [2.2]paracyclophane did not afford any benzene–Pd_3 cluster (Scheme 2a).

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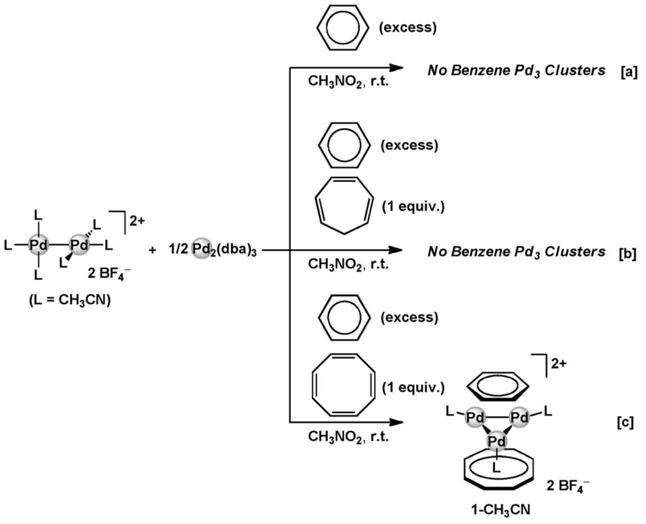


Scheme 2. Examination of potential backside carbocyclic ligands for the formation of μ_3-benzene Pd_3 clusters.

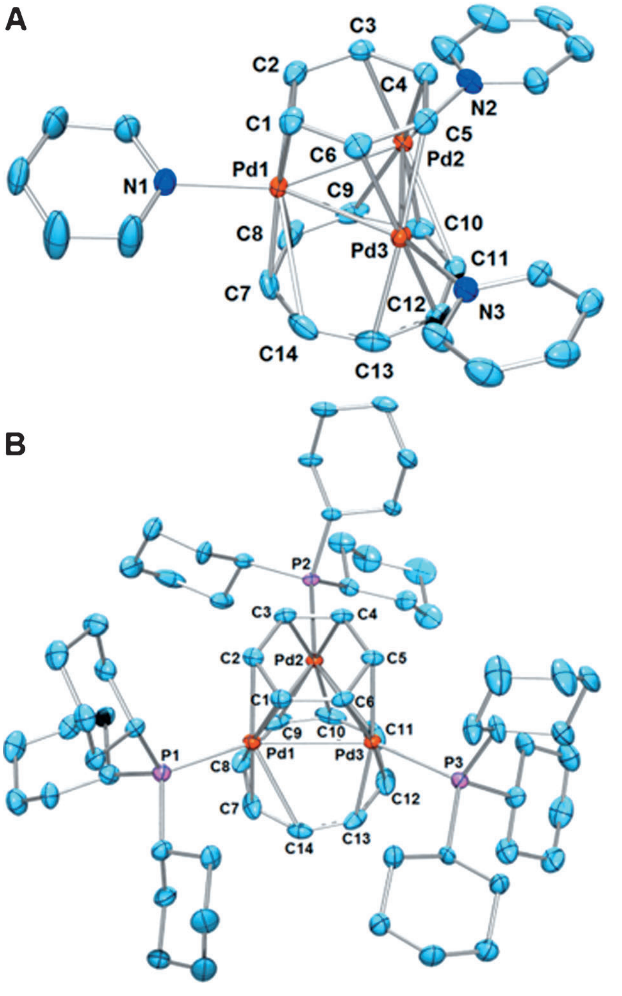
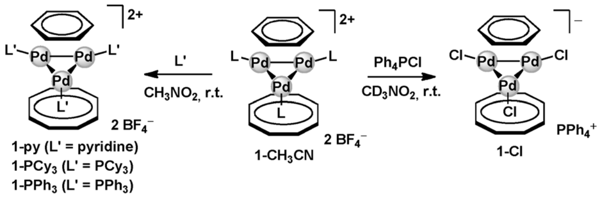


Figure 1. A) ORTEP of $[Pd_3(\mu_3\text{-}C_6H_6)(\mu_3\text{-}C_8H_8)(py)_3][BF_4]_2$ (**1-py**) (ellipsoids set at 50% probability, BF_4 anions are omitted for clarity). Selected bond lengths [Å]: Pd1–Pd2 2.7331(3), Pd2–Pd3 2.7624(3), Pd3–Pd1 2.7519(3), Pd1–C1 2.197(3), Pd1–C2 2.202(3), Pd2–C3 2.208(3), Pd2–C4 2.202(3), Pd3–C5 2.214(3), Pd3–C6 2.203(3), C1–C2 1.420(5), C2–C3 1.428(4), C3–C4 1.421(4), C4–C5 1.426(5), C5–C6 1.416(4), C6–C1 1.435(4), C9–C10 1.420(4), C10–C11 1.406(5), C11–C12 1.405(5), C12–C13 1.426(5), C13–C14 1.403(4), C14–C7 1.421(6). B) ORTEP of $[Pd_3(\mu_3\text{-}C_6H_6)(\mu_3\text{-}C_8H_8)(PCy_3)_3][BF_4]_2$ (**1-PCy$_3$**) (ellipsoids set at 30% probability, BF_4 anions and a solvent molecule are omitted for clarity). Selected bond lengths [Å]: Pd1–Pd2 2.8979(9), Pd2–Pd3 2.8784(8), Pd1–Pd3 2.9169(9), Pd1–C1 2.203(11), Pd1–C2 2.208(10), Pd2–C3 2.198(10), Pd2–C4 2.221(10), Pd3–C5 2.187(10), Pd3–C6 2.193(10).

We sought to develop the backside ligand which enhances the arene binding ability of Pd_3 clusters. Several unsaturated carbocyclic compounds were tested as the additive for the reaction in Scheme 2a. Addition of a cyclic π-conjugated triene, 1,3,5-cycloheptatriene (CHT), which is known to behave as an excellent μ_3-binder of a Pd_3 cluster,[9b,10] to the redox-condensation reaction mentioned above did not yield any benzene–Pd_3 complex (Scheme 2b). We then tested a larger neutral π-carbocyclic ligand, cyclooctatetraene (COT), as the potential backside ligand.[9b,11,12] Interestingly, addition of COT (1 equiv) to a mixture of $[Pd_2(CH_3CN)_6][BF_4]_2$, $[Pd_2(dba)_3]$, and excess benzene gave the unprecedented μ_3-benzene Pd_3 complex $[Pd_3(\mu_3\text{-benzene})(\mu_3\text{-COT})(CH_3CN)_3][BF_4]_2$ (**1**-CH_3CN) in 83% yield (Scheme 2c). The benzene–Pd_3 complex **1**-CH_3CN remained intact in CD_3NO_2 solution for two days at ambient temperature,[13] even in the presence of CH_3CN (10 equiv). To our further surprise, the μ_3-benzene ligand remained intact in the presence of more strongly coordinating ligands such as pyridine, phosphines, or chloride. Thus, in each case, substitution of the equatorial CH_3CN ligands took place to afford $[Pd_3(\mu_3\text{-benzene})(\mu_3\text{-COT})(L)_3][BF_4]_2$ (**1**-py, **1**-PCy_3, **1**-PPh_3) or $[Pd_3(\mu_3\text{-benzene})(\mu_3\text{-COT})Cl_3][PPh_4]$ (**1**-Cl) (Scheme 3). It was confirmed that the benzene ligand in **1**-PPh_3 or **1**-py remained coordinated in CD_3NO_2 solution in the presence of excess free PPh_3 or pyridine (7 equiv) at ambient temperature.[14] In contrast, the known mono- and dinuclear palladium complexes of benzene immediately release the benzene ligand in the presence of these strongly coordinating ligands.[5,6]



Scheme 3. The μ_3-benzene Pd_3 clusters containing pyridine, phosphines, and chloride Ligands.

The structures of **1**-py and **1**-PCy_3 were determined by X-ray crystallographic analysis (Figure 1). The benzene ring capped the nearly equilateral Pd_3 triangle (Pd–Pd = 2.7331(3) Å, 2.7624(3) Å, 2.7519(3) Å in **1**-py; Pd–Pd = 2.8979(9) Å, 2.8784(8) Å, 2.9169(9) Å in **1**-PCy_3) through the μ_3-η^2:η^2:η^2-coordination mode. The C–C lengths (1.416(4)–1.435(4) Å) of the μ_3-benzene ligand in **1**-py are slightly longer than those of free benzene, where a reduced bond length alternation was retained.[15,16] Such trend of C–C lengths in the μ_3-benzene ligand is comparable to that predicted for the μ_3-benzene adsorbed on a Pd(111) surface.[8] The planar COT ligand supported the Pd_3 triangle at the backside through μ_3-η^3:η^3:η^2-coordination mode.

Apparently, COT might play important roles in the formation of μ_3-benzene Pd_3 complex **1**, as any μ_3-benzene clusters were not obtained in the absence of COT, as mentioned above (Scheme 2). To gain insights into the stabilization effect of the backside COT ligand, we carried out DFT calculations[17] on the model ions $[Pd_3(benzene)(COT)(CH_3CN)_3]^{2+}$ (**A**) and $[Pd_3(benzene)_2(CH_3CN)_3]^{2+}$ (**B**), where the latter is a model of the expected but unobtainable product in Scheme 2a.[18] The calculation results supported that the backside coordination of COT stabilizes the benzene–Pd_3 cluster effectively; that is, the benzene dissociation energy for **A** ($D_{calc} = 105$ kcal mol^{-1}) is larger than the first benzene dissociation energy for **B** ($D_{calc} = 88$ kcal mol^{-1}). The replacement of one of the benzene ligands in **B** with COT to form **A** and free benzene was calculated to be exothermic ($\Delta H = -43$ kcal mol^{-1}). The different electronic effects of the backside COT and benzene ligands exerting on $[Pd_3L_3]^{2+}$ is reflected by the distinct geometries of the Pd_3 core in **A** and **B**; that is, pseudo-C_{3v} symmetry in **A** (a nearly equilateral Pd_3 triangle; Pd–Pd = 2.79 Å, 2.79 Å, 2.82 Å); C_{2v} symmetry in **B** (a distorted isosceles Pd_3 triangle; Pd–Pd = 2.77 Å, 2.77 Å, 2.68 Å; Figure 2a,b).[19] MO analysis suggested that this geometrical difference of the Pd_3 core is related to the difference of the π-electron number of the backside ligand: The highest occupied molecular orbital (HOMO) and the next-HOMO of **A** are essentially degenerated as a result of the MO interactions between the degenerated e′ orbitals of the pseudo-C_{3v} symmetric $[Pd_3L_3]$ fragment[5c,20] and the in-phase combination of the COT-benzene ligand orbitals (Figure 2c). When two 6π benzene ligands are the sandwich ligands, where the sum of the ligand π-electrons (12 e) are two less than that of the COT-benzene ligand system (14 e), these degenerated orbitals are each half-occupied, and hence the structure is subjected to Jahn–Teller distortion as found in **B**.

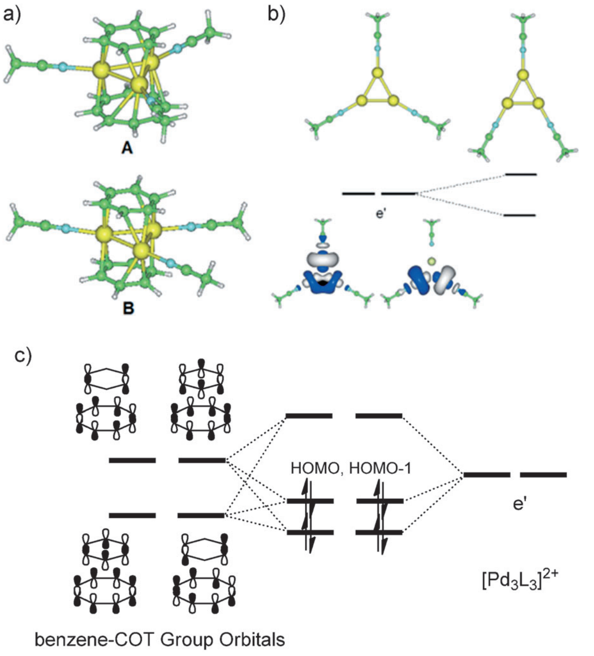
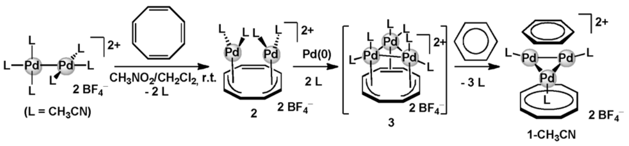


Figure 2. a) The optimized structures of $[Pd_3(benzene)(COT)L_3]^{2+}$ (**A**) and $[Pd_3(benzene)_2L_3]^{2+}$ (**B**). b) The degenerate e′ orbitals of the C_{3v}-symmetric Pd_3L_3 triangle, which are resolved by the Jahn–Teller distortion. c) A qualitative molecular orbital diagram between the ligand π-orbitals and the e′ orbitals of $[Pd_3L_3]^{2+}$ fragment in $[Pd_3(benzene)(COT)L_3]^{2+}$.

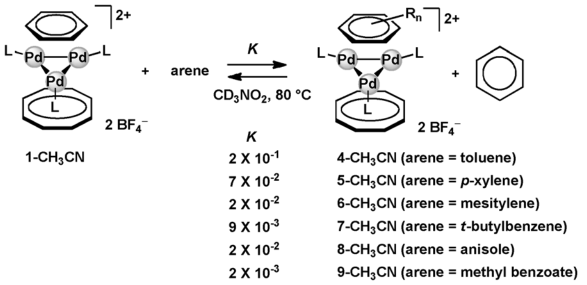
It is noted that COT may assist the Pd assembly not only with a thermodynamic cause but kinetic one in the formation of **1**-CH_3CN (Scheme 2c). As the binding of benzene by $[Pd_2(CH_3CN)_6][BF_4]_2$ is thermodynamically unfavorable,[6d] and $[Pd_2(dba)_3]$ did not react with benzene, $[Pd_2(CH_3CN)_6][BF_4]_2$ might have reacted with COT to afford the dinuclear complex **2**.[21] We confirmed that the dinuclear adduct **2** did not react with benzene. Thus, a reactive half-sandwich Pd_3-COT species **3** can be formed by addition of an Pd^0 moiety to **2** (Scheme 4). When compared with $[Pd^I_2]^{2+}$ in $[Pd_2(CH_3CN)_6][BF_4]_2$ or $[Pd^{II}_2]^{2+}$ in **2**, the low-valent $[Pd_3]^{2+}$ moiety in **3**, that is, formally +2/3 for each Pd, might have advantage in binding benzene and releasing CH_3CN ligands, in view of the weaker coordination ability of CH_3CN to Pd in lower oxidation states.



Scheme 4. A plausible mechanism of COT-assisted benzene binding by a Pd_3 cluster.

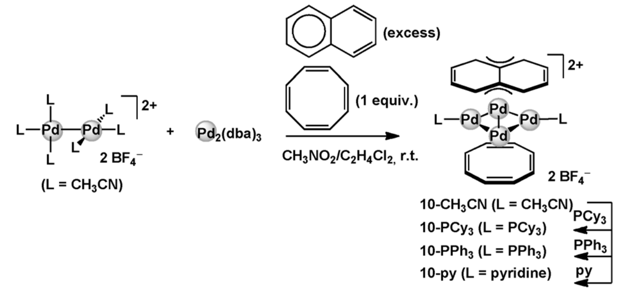
The μ_3-Pd_3 cluster site supported by the backside COT ligand showed the arene-exchangeable property, while known μ_3-benzene M_3 clusters (M = Ru, Os, Rh) did not show exchange of the μ_3-benzene ligand with free arenes even at elevated temperature.[15,16] The exchange of the μ_3-benzene ligand in **1**-CH_3CN with free arenes took place at 80 °C in CD_3NO_2 with [D$_6$]benzene, toluene, *p*-xylene, mesitylene, *tert*-butylbenzene, anisole, and methylbenzoate representing substrates (Scheme 5).[22] The equilibrium constant K_{eq} for each substituted benzene was smaller than 1, indicating that steric effects contributed to the thermodynamic stability of μ_3-arene Pd_3 complexes.

The backside-ligand modulation strategy can be applied to the naphthalene binding by a Pd_4 sheet cluster. Thus, the



Scheme 5. The μ_3-arene exchange equilibrium of the Pd_3 clusters.

tetranuclear complex [Pd_4(μ_4-naphthalene)(μ_4-COT)(CH_3CN)$_2$][BF_4]$_2$ (**10**-CH_3CN) was formed by the reaction of [$Pd_2(CH_3CN)_6$][BF_4]$_2$ and $Pd_2(dba)_3$ (1 equiv) in the presence of excess naphthalene and COT (1 equiv) in 62% yield (Scheme 6).[23] It is noted that any naphthalene Pd_4 complex was not obtained in the absence of COT. The PCy_3 complex **10**-PCy_3, PPh_3 complex **10**-PPh_3, or pyridine complex **10**-py was prepared by treatment of **10**-CH_3CN with 2 equiv of PCy_3, PPh_3, or pyridine, and the structure of **10**-PCy_3 was determined by X-ray crystallographic analysis (Figure 3). The naphthalene ligand facially capped the rhombic Pd_4 sheet through μ_4-η^3:η^2:η^3:η^2-mode. To the best of our knowledge, the μ_4-bridging coordination of naphthalene to a tetranuclear cluster was unprecedented for any metal elements. The COT ligand coordinated to the Pd_4 sheet through μ_4-η^2:η^2:η^2:η^2-coordination mode.[24] During the formation of μ_4-naphthalene Pd_4 cluster **10**-CH_3CN, COT could assemble Pd on its face, but naphthalene may also work as the directing ligand for the Pd assembly. Indeed, **10**-CH_3CN was formed by the reaction of **1**-CH_3CN with naphthalene at 80 °C, where decomposition of a portion of **1**-CH_3CN might provide Pd^0.



Scheme 6. Naphthalene binding by a Pd_4 sheet cluster supported by the backside COT ligand.

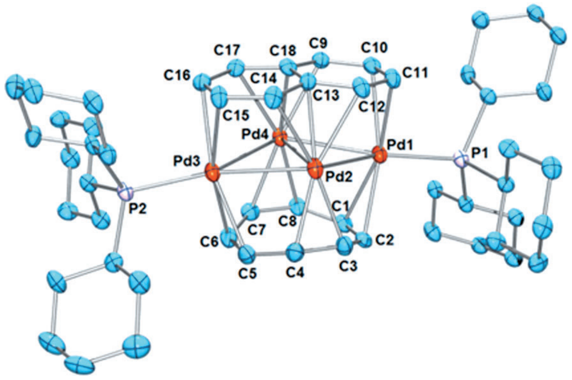


Figure 3. ORTEP of [$Pd_4(\mu_4\text{-}C_{10}H_8)(\mu_4\text{-}C_8H_8)(PCy_3)_2$][$BF_4$]$_2$ (**10-PCy**$_3$) (ellipsoids set at 30% probability, BF_4 anions are omitted for clarity). Selected bond lengths [Å]: Pd1–Pd2 2.8161(8), Pd2–Pd3 2.7990(8), Pd3–Pd4 2.8181(8), Pd4–Pd1 2.7906(7), Pd2–Pd4 2.8506(7).

In summary, it has been shown that the backside COT ligand of the Pd_3 clusters significantly enhances the benzene binding ability at the Pd_3 cluster site, leading to the first μ_3-benzene–Pd_3 clusters that are stable in solution. Theoretical analysis supported the electronic stabilization effect of the backside COT ligand. The naphthalene binding by Pd_4 clusters was also attained by using a Pd_4 sheet bearing the backside COT ligand. These new aspects might represent a promising backside-ligand-modulation strategy to control the reactivity of metal clusters. Further reactivity study on the backside-ligand-modulated metal clusters are now ongoing in our laboratory.

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[1] a) E. L. Muetterties, *Science* **1977**, *196*, 839; b) B. F. G. Johnson, M. Gallup, Y. V. Roberts, *J. Mol. Catal.* **1994**, *86*, 51; c) *Catalysis by Di- and Polynuclear Metal Cluster Complexes* (Eds.: R. D. Adams, F. A. Cotton), Wiley-VCH, New York, **1998**; d) *Metal Clusters in Chemistry* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1999**; e) H. Suzuki, *Eur. J. Inorg. Chem.* **2002**, 1009; f) P. J. Dyson, *Coord. Chem. Rev.* **2004**, *248*, 2443; g) S. Hu, T. Shima, Z. Hou, *Nature* **2014**, *512*, 413.

[2] a) R. S. Paton, J. M. Brown, *Angew. Chem. Int. Ed.* **2012**, *51*, 10448; *Angew. Chem.* **2012**, *124*, 10598; b) T. Murahashi, H. Kurosawa, *Coord. Chem. Rev.* **2002**, *231*, 207, and references therein.

[3] As a rare system which can provide triply bridging coordination site of Pd clusters, [$Pd_3(dppm)_3(CO)$]$^{2+}$ has been developed and its reactivity with RX or alkyne has been investigated: a) F. Lemaître, D. Lucas, K. Groison, P. Richard, Y. Mugnier, P. D. Harvey, *J. Am. Chem. Soc.* **2003**, *125*, 5511; b) R. J. Puddephatt, L. Manojlović-Muir, K. W. Muir, *Polyhedron* **1990**, *9*, 2767; c) L. Manojlovic-Muir, K. W. Muir, B. R. Lloyd, R. J. Puddephatt, *J. Chem. Soc. Chem. Commun.* **1983**, 1336; For other systems: d) K. Y. Monakhov, C. Gourlaouen, P. Braunstein, *Chem. Commun.* **2012**, *48*, 8317; e) A. D. Burrows, D. M. P. Mingos, S. Menzer, R. Vilar, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **1995**, 2107.

[4] R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 6th ed., Wiley, Hoboken, **2014**.

[5] All known benzene mono- or dinuclear Pd complexes are highly labile in a solution containing any competitive substrates with weakly coordinating ability, such as H_2O, Et_2O, or acetone. For non-chelating arene mononuclear Pd complexes, see: a) D. J. Mabbott, B. E. Mann, P. M. Maitlis, *J. Chem. Soc. Dalton Trans.* **1977**, 294; b) T. A. Stromnova, M. V. Dayneko, A. V. Churakov, L. G. Kuz'mina, J. Campora, P. Palma, E. Carmona, *Inorg. Chim. Acta* **2006**, *359*, 1613; c) T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki, H. Kurosawa, *Science* **2006**, *313*, 1104; d) M. D. Walter, R. A. Moorhouse, S. A. Urbin, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* **2009**, *131*, 9055.

[6] For dinuclear Pd complexes bearing non-chelating μ-arenes, see: a) G. Allegra, G. T. Casagrande, A. Immirzi, L. Porri, G. Vitulli, *J. Am. Chem. Soc.* **1970**, *92*, 289; b) M. Gorlov, A. Fischer, L. Kloo, *Inorg. Chim. Acta* **2009**, *362*, 605; c) J. Åkerstedt, M. Gorlov, A. Fischer, L. Kloo, *J. Organomet. Chem.* **2010**, *695*, 1513; d) T. Murahashi, K. Takase, M. Oka, S. Ogoshi, *J. Am. Chem. Soc.* **2011**, *133*, 14908; e) T. Murahashi, S. Kimura, K. Takase, S. Ogoshi, K. Yamamoto, *Chem. Commun.* **2013**, *49*,

4310; f) S. Lin, D. E. Herbert, A. Velian, M. W. Day, T. Agapie, *J. Am. Chem. Soc.* **2013**, *135*, 15830.

[7] a) B. Biswas, M. Sugimoto, S. Sakaki, *Organometallics* **2000**, *19*, 3895; b) J. Guihaumé, E. Clot, O. Eisenstein, R. N. Perutz, *Dalton Trans.* **2010**, *39*, 10510; c) S. I. Gorelsky, D. Lapointe, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 10848; d) S. I. Gorelsky, D. Lapointe, K. Fagnou, *J. Org. Chem.* **2012**, *77*, 658.

[8] a) F. Mittendorfer, C. Thomazeau, P. Raybaud, H. Toulhoat, *J. Phys. Chem. B* **2003**, *107*, 12287; b) C. Morin, D. Simon, P. Sautet, *J. Phys. Chem. B* **2004**, *108*, 5653, and references therein.

[9] a) T. Murahashi, M. Fujimoto, Y. Kawabata, R. Inoue, S. Ogoshi, H. Kurosawa, *Angew. Chem. Int. Ed.* **2007**, *46*, 5440; *Angew. Chem.* **2007**, *119*, 5536; b) T. Murahashi, K. Takase, K. Usui, S. Kimura, M. Fujimoto, T. Uemura, S. Ogoshi, K. Yamamoto, *Dalton Trans.* **2013**, *42*, 10626.

[10] a) T. Murahashi, K. Usui, Y. Tachibana, S. Kimura, S. Ogoshi, *Chem. Eur. J.* **2012**, *18*, 8886; b) T. Murahashi, Y. Hashimoto, K. Chiyoda, M. Fujimoto, T. Uemura, R. Inoue, S. Ogoshi, H. Kurosawa, *J. Am. Chem. Soc.* **2008**, *130*, 8586.

[11] T. Murahashi, S. Kimura, K. Takase, T. Uemura, S. Ogoshi, K. Yamamoto, *Chem. Commun.* **2014**, *50*, 820.

[12] Previously, we observed that a (μ_3-[2.2]paracyclophane)–Pd$_3$–(μ_3-COT) complex was formed by treatment of a bis-μ_3-[2.2]paracyclophane Pd$_3$ complex with excess COT.[9a] This implied the relatively stable arene–Pd$_3$–COT structure compared to the bis(arene) Pd$_3$ structure.

[13] A ^{1}H NMR spectra of **1**-CH$_3$CN in CD$_3$NO$_2$ showed two sharp singlet signals for benzene protons ($\delta = 5.43$ ppm) and COT protons ($\delta = 4.79$ ppm) in high-field region compared to that of free benzene or COT. The ^{13}C NMR signals for the benzene and COT ligands also appeared at high-field region ($\delta = 73$ ppm for C_6H_6; $\delta = 82$ ppm for C_8H_8).

[14] In the case of PCy$_3$, gradual decomposition of **1**-PCy$_3$ was observed. When less than 3 equiv of PPh$_3$ was added to the solution of **1**-CH$_3$CN, gradual decomposition of the μ_3–benzene–Pd$_3$ framework was observed. This result may reflect the unstable nature of [Pd$_3$(benzene)(COT)(PPh$_3$)$_2$L]$^{2+}$ or [Pd$_3$(benzene)(COT)(PPh$_3$)L$_2$]$^{2+}$.

[15] For a review of μ_3-arene clusters, see: D. Braga, P. J. Dyson, F. Grepioni, B. F. G. Johnson, *Chem. Rev.* **1994**, *94*, 1585.

[16] For selected examples of μ_3-arene clusters, see: a) H. Wadepohl, M. J. Calhorda, M. Herrmann, C. Jost, P. E. M. Lopes, H. Pritzkow, *Organometallics* **1996**, *15*, 5622; b) A. Inagaki, Y. Takaya, T. Takemori, H. Suzuki, M. Tanaka, M. Haga, *J. Am. Chem. Soc.* **1997**, *119*, 625; c) J. P.-K. Lau, Z.-Y. Lin, W.-T. Wong, *Angew. Chem. Int. Ed.* **2003**, *42*, 1935; *Angew. Chem.* **2003**, *115*, 1979.

[17] DFT calculations were performed at B3LYP-D level of theory.

[18] The composition of the model ion **B** containing three CH$_3$CN ligands is reasonable, in light of the composition of a related complex [Pd$_3$(μ_3-[2.2]paracyclophane)$_2$(CH$_3$CN)$_3$][B(Ar^F)$_4$]$_2$.[9a]

[19] An isosceles triangle geometry of [Pd$_3$L$_3$]$^{2+}$ core was experimentally identified in the structures of related bis(cycloheptatriene) M$_3$ complexes [Pd$_3${μ_3-C$_7$H$_7$(*t*Bu)}$_2$(CH$_3$CN)$_3$][BF$_4$]$_2$ and [Pd$_2$Pt(μ_3-CHT)$_2$(CH$_3$CN)$_3$][BF$_4$]$_2$.[10]

[20] The HOMO and HOMO-1 (e′ orbitals) of a neutral D_{3h}-symmetric [Pd$_3$L$_3$] fragment are degenerate: M. T. Reetz, E. Bohres, R. Goddard, M. C. Holthausen, W. Thiel, *Chem. Eur. J.* **1999**, *5*, 2101.

[21] T. Murahashi, N. Kato, S. Ogoshi, H. Kurosawa, *J. Organomet. Chem.* **2008**, *693*, 894.

[22] The (μ_3-substituted benzene)–Pd$_3$ complexes were prepared according to the reaction shown in Scheme 2c, where each substituted arene was used instead of benzene. See the Supporting Information.

[23] The ^{13}C NMR analysis in CD$_3$NO$_2$ showed the upfield-shifted signals for all naphthalene carbons ($\delta = 93$ ppm, 85 ppm, 84 ppm) and COT carbons ($\delta = 68$ ppm), indicating the structure found in the crystalline state was retained in solution.

[24] a) T. Murahashi, R. Inoue, K. Usui, S. Ogoshi, *J. Am. Chem. Soc.* **2009**, *131*, 9888; b) T. Murahashi, N. Kato, T. Uemura, H. Kurosawa, *Angew. Chem. Int. Ed.* **2007**, *46*, 3509; *Angew. Chem.* **2007**, *119*, 3579.