Di- and Trinuclear Sandwich Complexes of a Cross-conjugated Fulvene

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ARTICLE

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We report di- and trinuclear palladium sandwich complexes of cross-π-conjugated fulvenes. Structural and theoretical analysis revealed that a fulvene sandwich framework holds a metal–metal bonded moiety, where the dinuclear and trinuclear bindings are featured by strong donation and back-donation, respectively. The trinuclear fulvene sandwich complex undergoes unique reversible extrusion of a Pd atom from inside to outside the sandwich framework.

Introduction

Our group and others have developed the multinuclear sandwich complexes in which an extended π-conjugated unsaturated hydrocarbon holds a metal–metal bonded moiety.[1-3] It has been shown that cyclic π-conjugated unsaturated hydrocarbons such as arene, cycloheptatriene, cycloheptatrienyl (tropylium), cylooctatetraene, and cyclononatetraenyl serve as the excellent binder for M_3 or M_4 metal sheet, giving a layered ligand–metal–ligand sandwich structure.[2] These findings using cyclic π-conjugated ligands extend the structural concept of sandwich complexes which had been limited to mono- and dinuclear complexes. However, it has not been verified whether cross-π-conjugated ligands act as the binder for a metal sheet sandwich complex, although the use of cross-π-conjugated ligands have brought unique features of mononuclear sandwich and half-sandwich complexes.[4,5] Among the cross-π-conjugated unsaturated hydrocarbons, here we focused on fulvenes (or pentafulvenes).[4,5] Fulvene has the ability to coordinate either in a simple neutral olefin mode or in a dianionic oxidatively π-addition mode (Figure 1A). The representative examples of the olefin mode include the η^4-fulvene ligands in Fe(η^4-6,6-diphenylfulvene)$_2$ (Figure 1A), which exhibits an interesting radical reactivity and a redox property due to the propensity to adopt the cyclopentadienyl-like η^5-mode through oxidative π-addition.[6] The oxidative π-addition mode is more commonly found in mononuclear metal complexes in relation to the substituted cyclopentadienyl complexes. Ti(η^6-6,6-diphenylfulvene)$_2$ is one of the typical sandwich complexes of this type (Figure 1A).[7] It should be mentioned that the HOMO of fulvene is composed of pπ-orbitals at C(1), C(2), C(3), and C(4) atoms, where there is no contribution from C(5) and C(6) atoms. On the other hand, the LUMO of fulvene is mainly contributed by the p orbital at C(6) atom in addition to C(1), C(2), C(3), and C(4) atoms (Figure 1B). Therefore, the η^4-coordination using C(1), C(2), C(3), and C(4) atoms is advantageous for a donating interaction through efficient overlap of metal orbitals with the HOMO of fulvene. On the other hand, the η^6-coordination involving C(6) atom could lead to an efficient overlap of a metal orbital with the LUMO of fulvene, which is advantageous for a back-donating interaction.[7a] The bridging coordination in an oxidative π-addition mode has been observed in several di- and multinuclear complexes, as found in the classic diiron carbonyl complex $Fe_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-fulvene})(CO)_6$.[8] A hexaruthenium carbide carbonyl cluster accommodates fulvene in an olefin mode to

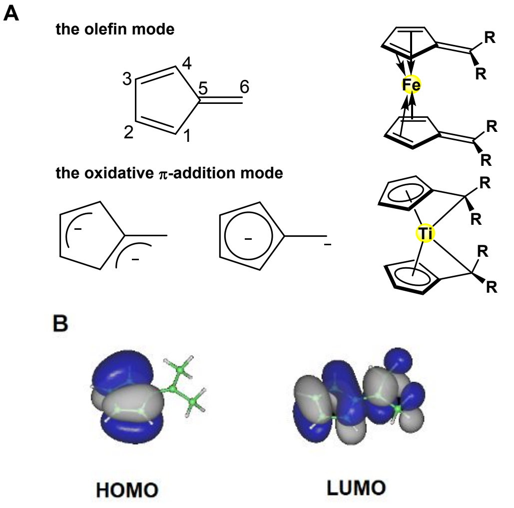

Figure 1. **A**: The neutral olefin mode and the dianionic oxidative π-addition mode of fulvene and typical examples of fulvene mononuclear sandwich complexes. **B**: The HOMO and the LUMO of 6,6-dimethylfulvene (M06/6-311G(d) level).

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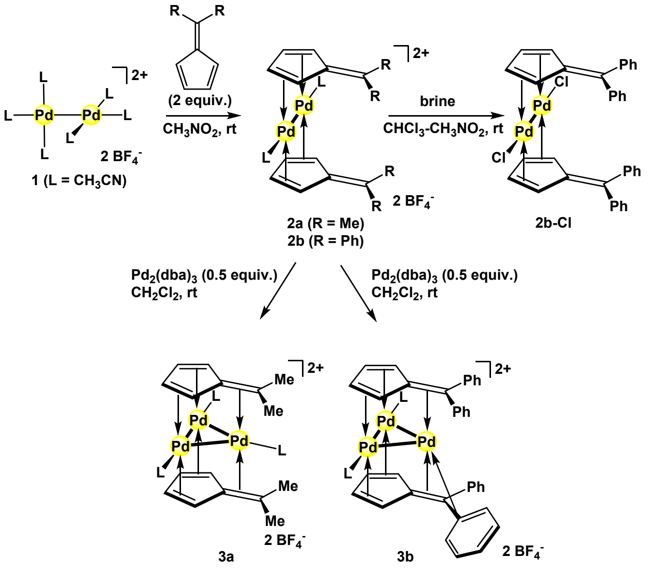
afford Ru$_6$C(μ-η^2:η^2-6,6-diphenylfulvene)(CO)$_{15}$. The face-capping μ$_3$-coordination of fulvene has rarely been observed, and the only known cluster Ru$_6$C(μ$_3$-6,6-diphenylfulvene)(CO)$_{14}$ contains a μ$_3$-fulvene ligand in a μ$_3$-η^3:η^2:η^1-oxidative π-addition mode.[9] Due to the lack of fulvene di- and trinuclear sandwich complexes, however, it remains elusive whether and how fulvene holds a metal–metal bonded moiety in its sandwich framework. Herein, we report that bridging coordination of fulvene provides stable di- and trinuclear palladium sandwich complexes. Structural and theoretical analysis revealed that coordination of fulvenes leads to unique metal–metal bonding inside its sandwich framework. We also found that the mode of μ$_3$-bridging coordination of fulvene changes reversibly between the neutral olefin mode and the dianionic oxidative π-addition modes, that accompanies the reversible extrusion of a Pd moiety from the metal sheet.

Results and Discussion

Synthesis and Structures of Di- and Trinuclear Palladium Fulvene Sandwich Complexes

We at first synthesized the dinuclear palladium sandwich complexes by the reaction of [Pd$_2$(CH$_3$CN)$_6$][BF$_4$]$_2$ (**1**)[10] with 6,6-dimethylfulvene or 6,6-diphenylfulvene. The incorporation of the fulvene ligands proceeded smoothly, resulting in the formation of [Pd$_2$(μ-η^2:η^2-C$_6$H$_4$R$_2$)$_2$(CH$_3$CN)$_2$][BF$_4$]$_2$ (**2a**, R = Me; **2b**, R = Ph). The complexes **2a** and **2b** were isolated in 81% yield and 64% yield, respectively (Scheme 1). The single crystals suitable for X-ray structure analysis were obtained for the dicationic complex **2b** and the neutral dichloro-complex Pd$_2$(μ-6,6-diphenylfulvene)$_2$Cl$_2$ (**2b-Cl**), where the latter was synthesized by treatment of **2b** with brine. In these dinuclear sandwich complexes, the 6,6-diphenylfulvene ligands flank the Pd$_2$ moiety through an eclipsed fashion, despite the steric congestion between the fulvene ligands (Figure 2). In each complex, the fulvene ligands coordinate in a μ-η^2:η^2-mode by using C(1), C(2), C(3), and C(4) atoms, where C(5) and C(6) atoms remain uncoordinated. The deviation of C–C bond lengths of the fulvene ligand from those of free 6,6-diphenylfulvene[11] is small, where C1–C2/C2–C3/C3–C4 bond alternation of the free fulvene (1.35 Å/1.47 Å/1.35 Å) diminishes slightly in **2b** (1.38 Å/1.44 Å/1.38 Å or **2b-Cl** (1.39 Å/1.45 Å/1.40 Å), and C5–C6 bond length in **2b** (1.377(10) Å) or in **2b-Cl** (1.368(3) Å) is similar to that of the free fulvene (1.368(2) Å). The Pd–Pd lengths in **2b** (2.4992(8) Å) and **2b-Cl** (2.5261(3) Å) are in the range of normal Pd–Pd bond lengths.[12,13]

Interestingly, the dinuclear sandwich complex **2a** or **2b** smoothly accommodated a Pd^0 moiety in CH$_2$Cl$_2$ through binding to C(5) and C(6) atoms, affording the trinuclear sandwich complexes [Pd$_3$(μ$_3$-η^2:η^2:η^2-6,6-dimethylfulvene)$_2$(CH$_3$CN)$_3$][BF$_4$]$_2$ (**3a**) in 80% yield and [Pd$_3$(μ$_3$-η^2:η^2:η^2-6,6-diphenylfulvene)(μ$_3$-η^2:η^2:η^4-6,6-diphenylfulvene)(CH$_3$CN)$_2$][BF$_4$]$_2$ (**3b**) in 69% yield, respectively (Scheme 1). The X-ray structure analysis unequivocally showed that the third Pd atom, which is either acetonitrile-capped or uncapped, is accommodated in a fulvene sandwich framework (Figure 3). In the complex **3a**, the fulvene ligand coordinates to the Pd$_3$ moiety through a μ$_3$-η^2:η^2:η^2-olefin mode, where the extent of the bond alternation at C1–C2/C2–C3/C3–C4 (1.41 Å/1.44 Å/1.41 Å) further diminished, and C5–C6 bond length was considerably elongated (1.404(6) Å). The Pd2 atom is ligated by one acetonitrile ligand. The Pd1–Pd1* length (2.5058(6) Å) is much shorter than the Pd1–Pd2 (2.8694(5) Å), resulting in the isosceles Pd$_3$ triangle (Figure 3A). On the other hand, in the complex **3b**, the Pd3 atom is not ligated by acetonitrile ligand. Instead, one of the phenyl groups of one 6,6-diphenylfulvene ligand participates in the coordination in a π-benzyl manner, where rather long Pd3–C5 (2.545(3) Å) and Pd3–C8 (2.535(3) Å) distances are at a border of the Pd–C coordination distance. As a result, each fulvene ligand coordinates in a distinct mode; one in a μ$_3$-η^2:η^2:η^2-olefin mode, and the other in a μ$_3$-η^2:η^2:η^4-olefin mode. The Pd$_3$ moiety in **3b** adopted a distorted isosceles triangle (Pd1–Pd2 = 2.5010(3) Å, Pd1–Pd3 = 2.8128(3) Å, and Pd2–Pd3 = 2.8691(3) Å), where the Pd1–Pd2 length is similar to that in the dinuclear complex **2b**. The base L–Pd–Pd–L skeleton in **3a** or **3b** is almost linear (N1–Pd–Pd1* = 172.74(11)° for **3a**; N1–Pd1–Pd2 = 177.64(9)°, Pd1–Pd2–N2 = 176.78(9)° for **3b**). ^{1}H NMR spectra of **3b** exhibited only one set of resonances for 6,6-diphenylfulvene ligands at 20 °C and even at -90 °C, indicating the fluxional behaviour involving rapid exchange between the μ$_3$-η^2:η^2:η^2-ligand and the μ$_3$-η^2:η^2:η^4-ligand on the NMR timescale.



Scheme 1. Synthesis of di- and trinuclear sandwich complexes of 6,6-disubstituted fulvenes.

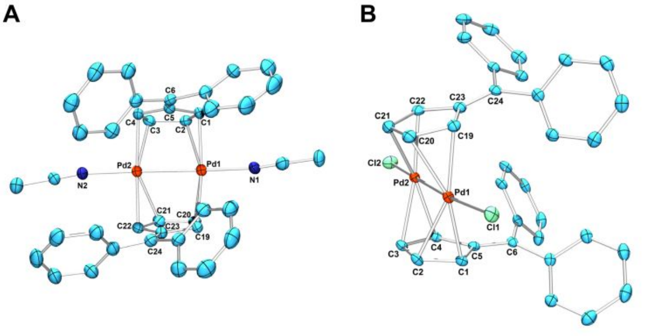


Figure 2. (**A**) ORTEP of [Pd$_2$(μ-6,6-diphenylfulvene)$_2$(CH$_3$CN)$_2$][BF$_4$]$_2$ (**2b**). Ellipsoids set at 30% probability. BF$_4$ anions and protons are omitted for clarity. The selected bond lengths (Å): Pd1–Pd2 2.4992(8), C1–C2 1.382(10), C2–C3 1.439(11), C3–C4 1.380(10),

C4–C5 1.475(10), C5–C1 1.487(10), C5–C6 1.377(10). (**B**) ORTEP of $Pd_2(\mu$-6,6-diphenylfulvene$)_2Cl_2$ (**2b-Cl**). Ellipsoids set at 30% probability. BF_4 anions and protons are omitted for clarity. The selected bond lengths (Å): Pd1–Pd2 2.5261(3), C1–C2 1.392(4), C2–C3 1.452(4), C3–C4 1.400(4), C4–C5 1.471(3), C5–C1 1.476(3), C5–C6 1.368(3).

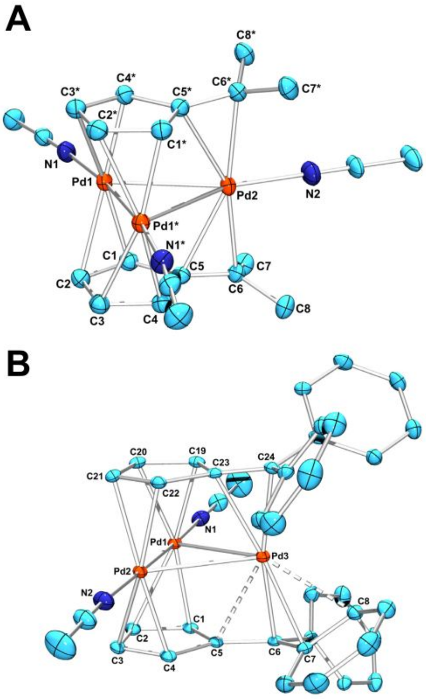


Figure 3. (**A**) ORTEP of $[Pd_3(\mu_3$-6,6-dimethylfulvene$)_2(CH_3CN)_3][BF_4]_2$ (**3a**), Ellipsoids set at 30% probability. BF_4 anions and protons are omitted for clarity. The selected bond lengths (Å) and angles (degrees): Pd1–Pd1* 2.5058(6), Pd1–Pd2 2.8694(5), C1–C2 1.406(7), C2–C3 1.438(6), C3–C4 1.406(7), C4–C5 1.482(5), C5–C1 1.471(6), C5–C6 1.404(6), Pd1–Pd1*–Pd2 64.111(8), Pd1–Pd2–Pd1* 51.780(15). (**B**) ORTEP of $Pd_3(\mu_3$-6,6-diphenylfulvene$)_2(CH_3CN)_2][BF_4]_2$ (**3b**). Ellipsoids set at 30% probability. BF_4 anions and protons are omitted for clarity. The selected bond lengths (Å) and angles (degrees): Pd1–Pd2 2.5010(3), Pd2–Pd3 2.8691(3), Pd1–Pd3 2.8128(3), Pd1–C1 2.171(3), C1–C2 1.403(5), C2–C3 1.444(5), C3–C4 1.404(5), C4–C5 1.482(4), C5–C1 1.469(5), C5–C6 1.407(4), C19–C20 1.409(5), C20–C21 1.439(5), C21–C22 1.393(5), C22–C23 1.481(4), C23–C19 1.488(4), C23–C24 1.405(4), Pd1–Pd2–Pd3 62.732(9), Pd2–Pd3–Pd1 52.218(8), Pd3–Pd1–Pd2 65.050(9).

DFT Analysis of Di- and Trinuclear Palladium Fulvene Sandwich Complexes

To gain further insight into the electronic structures of the di- and trinuclear sandwich complexes of fulvene, we carried out the DFT calculations for the model complexes, $[Pd_2(6,6$-dimethylfulvene$)_2(HCN)_2]^{2+}$ (**2a'**) and $[Pd_3(6,6$-dimethylfulvene$)_2(HCN)_3]^{2+}$ (**3a'**). The Kohn-Sham MO analysis of **2a'** showed that the coordination of fulvene to the Pd_2 moiety is featured by the strong donating interaction between the fulvene HOMO and the dσ antibonding orbital of Pd_2 (Figure 4a), where the C(5) and C(6) atoms of fulvene are not involved in the coordination due to the absence of the p-orbitals at these carbon atoms in the HOMO of fulvene (Figure 1B). The natural atomic charge analysis showed that each fulvene ligand in **2a'** possesses the positive charge (+0.50), supporting the strong donating interaction between the Pd_2 moiety and fulvene ligands. The presence of the Pd–Pd σ-bond is suggested by the Mayer bond index for Pd–Pd (0.43). Noteworthy is that the back-donating interaction between the fulvene LUMO and the dσ bonding orbital of Pd_2 is not efficient because the η^4-coordination does not involve the C(6) atom which is a major contributor to the LUMO of fulvene. This is in sharp contrast to the fact that the back-donating interaction is strongly involved in the μ-η^2:η^2-coordination of s-trans 1,3-butadiene.[14]

In the trinuclear sandwich complex **3a'**, the MO analysis showed that the donating interaction involving the fulvene HOMO is quite similar to that in the dinuclear complex, where p orbitals of C(5) and C(6) atoms are not involved in the interaction. The MO (106th MO) which is antibonding with respect to the ligand-Pd_2 donating interaction is shown in Figure 4. The orientation of the nitrile ligands bound to the base Pd atom is trans to the base Pd–Pd bond, that makes the base Pd–Pd moiety a good acceptor through raising the Pd–Pd dσ antibonding orbital energy by antibonding interaction with nitrile p orbitals. The MO analysis also showed that the back-donating interaction is efficient in the trinuclear sandwich complex. The interaction between the out-of-phase combination of the fulvene LUMOs and the dπ orbitals of the Pd_3 moiety contributes to the back-donation, where the d orbital of the apical Pd atom efficiently overlaps with the p orbitals at C(6) atom of the fulvene ligands (Figure 4b). The in-phase combination of the fulvene LUMOs also interacts with the dσ orbitals of the Pd_3 moiety, where the d orbital of the apical Pd atom overlaps well with the p orbital of the C(6) atom, leading to the back-donation (Figure 4c). The MOs (107th and 108th MOs) which are antibonding with respect to the back-donating interactions are shown in Figure 4. The decrease of the extent of bond length alternation as well as the elongation of C(5)–C(6) bond in the trinuclear complexes **3a** or **3b** are consistent with the occupation of the bonding MOs of the back-donating interaction involving the fulvene LUMOs. The less positive natural charge (+0.37) at each fulvene ligand in the trinuclear sandwich complex **3a'** than that in the dinuclear sandwich complex **2a'** suggests the strong back-donating interaction in **3a'**. The Mayer bond index (0.43) for the μ-η^2:η^2-bound base Pd–Pd bond in **3a'** is identical to that in **2a'**, indicating that the Pd–Pd σ-bond is maintained after accommodation of the apical Pd atom. The Mayer bond indices for equilateral Pd–Pd are smaller (0.14) than that of the base Pd–Pd, but non-zero, indicating that there is a weak Pd–Pd bond for the equilateral Pd–Pd.

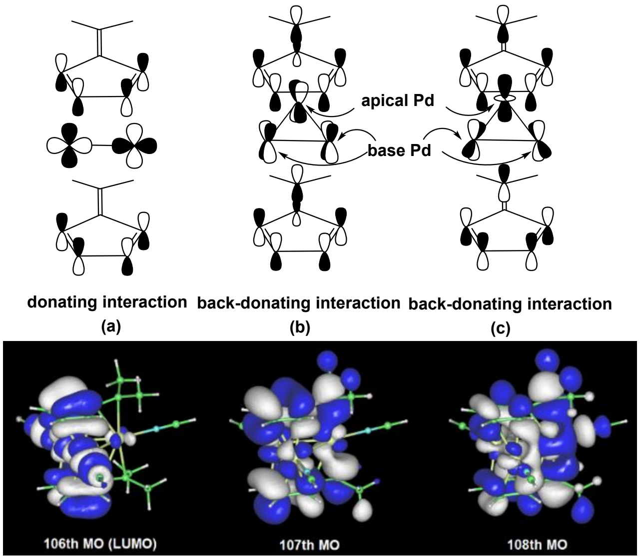
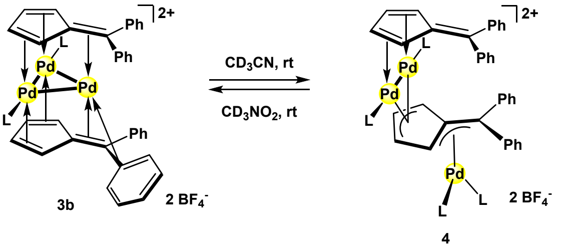

donating interaction (a) back-donating interaction (b) back-donating interaction (c)

Figure 4. The donating interaction (a) for the di- and trinuclear sandwich complexes, and the back-donating interactions (b), (c) for the trinuclear sandwich complexes. Several antibonding MOs for the trinuclear sandwich complexes are shown at the bottom.

Reversible Translocation of a Pd Moiety inside and outside the Fulvene Sandwich Framework

We found that dissolving **3b** in CD_3CN resulted in the immediate and almost quantitative conversion to $[Pd_3(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_4Ph_2)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^3\text{-}C_6H_4Ph_2)(CH_3CN)_4][BF_4]_2$ (**4**) (the molar ratio of **3b**:**4** = 5:95), where additional two acetonitrile ligands added to **3b** (Scheme 2). A single crystal of **4** was obtained by recrystallization from a CH_3CN-toluene solution. X-ray structure analysis (Figure 5) showed that in the transformation of **3b** to **4**, ligation of two acetonitrile ligands induces the oxidative π-addition of the Pd moieties, where the equilateral Pd–Pd bonds are cleaved and the C(5)–C(6) bond of one of the fulvene ligands rotates to extrude the apical Pd atom outside of the sandwich framework. As a result, one of the fulvene ligands changed the coordination mode, where dinuclear Pd–Pd moiety (Pd–Pd = 2.5410(5) Å) is held through an μ-η^2:η^1-allyl mode and the extruded Pd through an η^3-π-allyl mode. We confirmed that dissolving the crystals of **4** in CD_3NO_2 regenerated **3b** quantitatively through liberation of two acetonitrile ligands. The reversible conversion between **3b** and **4** demonstrated for the first time that the μ_3-fulvene ligand can switch between the olefin and oxidative π-addition modes with M–M bond cleavage and formation, which might be a unique behaviour exhibited by the cross-π-conjugated ligands. It is noted that the dimethylfulvene complex **3a** remained intact in CD_3CN.



Scheme 2. Acetonitrile-induced reversible conversion of 6,6-disubstituted fulvene Pd_3 complex.

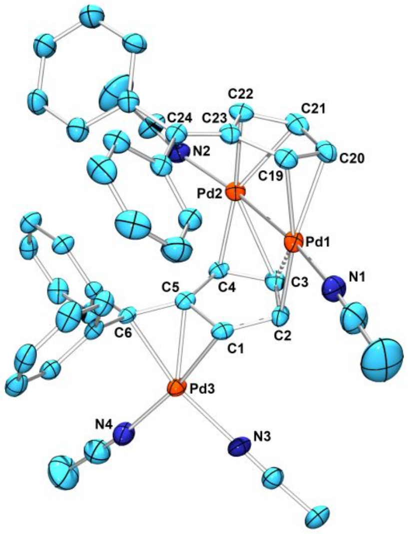


Figure 5. ORTEP of $[Pd_3(\mu\text{-}6,6\text{-diphenylfulvene})(\mu_3\text{-}6,6\text{-diphenylfulvene})(CH_3CN)_4][BF_4]_2$ (**4**). Ellipsoids set at 30% probability. BF_4 anions and protons are omitted for clarity. The selected bond lengths (Å): Pd1–Pd2 2.5409(6), C1–C2 1.471(7), C2–C3 1.412(7), C3–C4 1.431(7), C4–C5 1.458(7), C5–C1 1.430(7), C5–C6 1.438(7), C19–C20 1.380(8), C20–C21 1.458(9), C21–C22 1.381(8), C22–C23 1.471(8), C23–C19 1.479(8), C23–C24 1.368(7).

Conclusions

The di- and trinuclear sandwich complexes of fulvene were isolated and structurally characterized for the first time. The fulvene ligands can hold a Pd_2 or Pd_3 moiety through μ-η^2:η^2- or μ_3-η^2:η^2:η^2-olefin mode. The dinuclear sandwich binding by fulvene is characterized by strong donating interaction, while the trinuclear sandwich binding is featured by the strong back-bonding interaction in addition to the donating interaction. The μ_3-fulvene ligand can switch between the olefin and oxidative π-addition modes with M–M bond cleavage and formation, resulting in the reversible translocation of a Pd moiety between the inside and outside positions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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