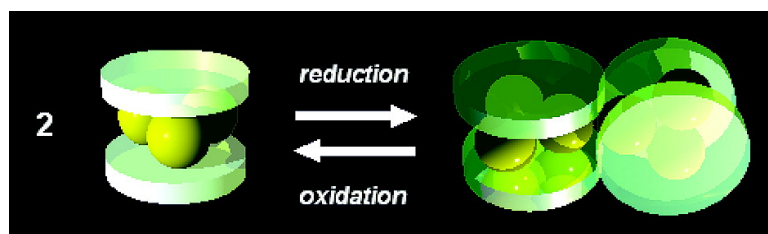


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## Reductive Coupling of Metal Triangles in Sandwich Complexes

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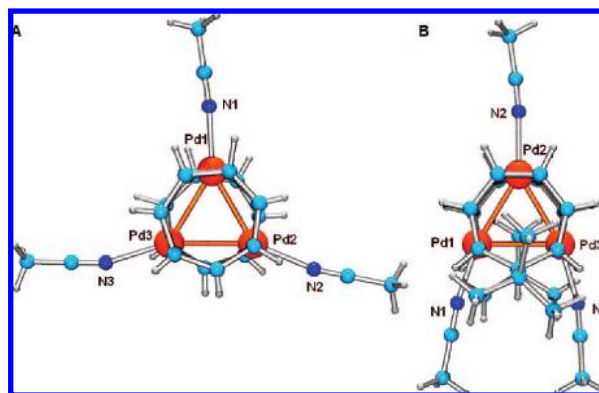
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Recently, we found that metal sheet sandwich complexes are isolable.<sup>1</sup> Planar mono- or polycyclic aromatic ligands act as the binder for the Pd<sub>3</sub>, Pd<sub>4</sub>, or Pd<sub>5</sub> sheet.<sup>1–3</sup> This finding expands the scope of the structural concept of sandwich compounds. It is intriguing to elucidate the redox properties of such metal sheet sandwich complexes in view of the widely developed redox chemistry of metallocenes and other mononuclear sandwich complexes.<sup>4–10</sup> Herein, we report the unique redox behavior of the trinuclear metallocenoids of seven-membered carbocyclic ligands; the cycloheptatrienyl complex [Pd<sub>3</sub>(μ<sub>3</sub>-C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>L<sub>3</sub>]<sup>2+</sup> (**1**) and the cycloheptatriene complex [Pd<sub>3</sub>(μ<sub>3</sub>-C<sub>7</sub>H<sub>7</sub>R)<sub>2</sub>L<sub>3</sub>]<sup>2+</sup> (**2**), where the latter representing the first trimetal sandwich complex of nonaromatic carbocyclic ligands is thought to have the different total electrons around the metals than those of the former. Remarkably, reduction of either bis-cycloheptatrienyl or bis-cycloheptatriene Pd<sub>3</sub> complex led to the novel type dimerization via Pd<sub>3</sub>–Pd<sub>3</sub> coupling with the two parallel carbocyclic ligands remaining sandwich-coordinated.

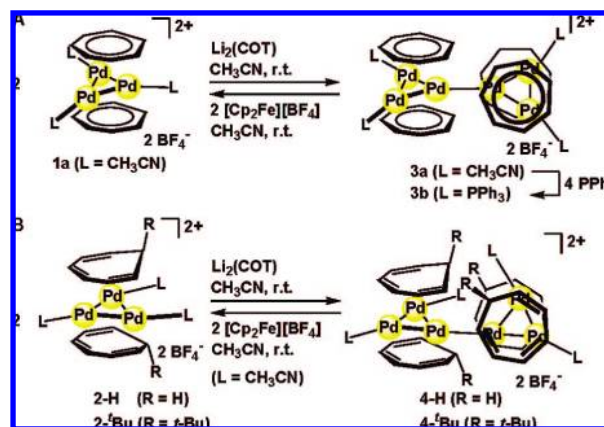
The cycloheptatrienyl tripalladium complex [Pd<sub>3</sub>(μ<sub>3</sub>-C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> (**1a**)<sup>1</sup> was conveniently prepared by an improved method: The reaction of Pd<sub>2</sub>(dba)<sub>3</sub> and [C<sub>7</sub>H<sub>7</sub>][BF<sub>4</sub>] in the presence of NaOAc (5 equiv) in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN in 1 h gave an orange powder of **1a** in 87% yield. The X-ray crystallographic analysis showed that **1a** contains a nearly equilateral Pd<sub>3</sub> triangle (Pd–Pd = 2.7393(2), 2.7562(2), and 2.7631(2) Å) (Figure 1A). The cycloheptatriene tripalladium sandwich complexes [Pd<sub>3</sub>(μ<sub>3</sub>-C<sub>7</sub>H<sub>7</sub>R)<sub>2</sub>(CH<sub>3</sub>CN)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> (**2-H**; R = H, **2-tBu**; R = *t*-Bu) were newly synthesized by the reaction of [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub><sup>11</sup> and 0.5 equiv of Pd<sub>2</sub>(dba)<sub>3</sub> in the presence of excess cycloheptatriene or *tert*-butylcycloheptatriene.<sup>12</sup> While **2-H** gradually decomposed to **1a** in CD<sub>3</sub>CN at 25 °C, **2-tBu** was stable for a day in the same condition. The structure of **2-tBu** was successfully determined by X-ray crystallographic analysis (Figure 1B). Interestingly, the geometry of the Pd<sub>3</sub> moiety is obviously different from that of the cycloheptatrienyl complex **1a**. In **2-tBu**, the Pd<sub>3</sub> moiety is an isosceles triangle, where the base Pd–Pd (Pd1–Pd3 = 2.7905(8) Å) is longer by 0.06 Å than Pd1–Pd2 (= 2.7342(9) Å) and Pd2–Pd3 (= 2.7332(9) Å). Furthermore, the orientation of the acetonitrile ligands bound to the base Pd atoms (Pd1 and Pd3) is nearly trans to the apex Pd2 atom (e.g., Pd2–Pd1–N1 = 193°, Pd3–Pd1–N1 = 108°), while the acetonitrile ligands in **1a** are oriented midway between the trans positions of two neighboring Pd atoms (Pd2–Pd1–N1 = 153°, Pd3–Pd1–N1 = 147° in **1a**). Such marked difference in the Pd<sub>3</sub>L<sub>3</sub> geometry is presumably due to the difference of the total electron count (i.e., 46e for **2** and 48e for **1**) and thus probably of the oxidation state of the Pd<sub>3</sub> moiety.

One-electron reduction of **1a** with Li<sub>2</sub>(C<sub>8</sub>H<sub>8</sub>) (0.5 equiv) in CH<sub>3</sub>CN gave the soluble, deep green, air-sensitive dimer dication [Pd<sub>6</sub>(μ<sub>3</sub>-C<sub>7</sub>H<sub>7</sub>)<sub>4</sub>(CH<sub>3</sub>CN)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> (**3a**) in 78% isolated yield (Scheme 1A).<sup>13</sup> Monitoring the reaction of **1a** with Co(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> in CD<sub>3</sub>CN showed the immediate disappearance of **1a** (δ = 4.84 ppm for



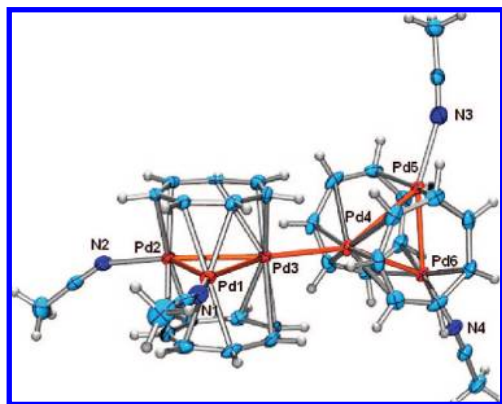
**Figure 1.** Top view (ball-stick drawings) of (A) the bis-cycloheptatrienyl complex **1a** and (B) the bis-*tert*-butylcycloheptatriene complex **2-tBu** from the X-ray determined molecular structures. The BF<sub>4</sub><sup>−</sup> anions were omitted for clarity.

### Scheme 1

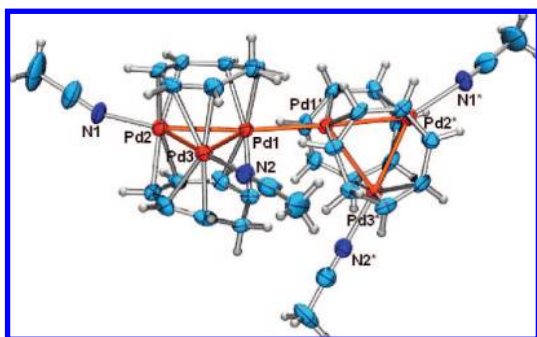


cycloheptatrienyl protons) and the appearance of a high-field shifted sharp singlet resonance for cycloheptatrienyl protons of **3a** (δ = 4.05 ppm in CD<sub>3</sub>CN). Oxidation of **3a** with ferrocenium salt [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (2 equiv) in CD<sub>3</sub>CN gave **1a** and ferrocene almost quantitatively (Scheme 1A). Addition of PPh<sub>3</sub> (4 equiv) to **3a** gave the tetrakis-triphenylphosphine complex [Pd<sub>6</sub>(μ<sub>3</sub>-C<sub>7</sub>H<sub>7</sub>)<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> (**3b**). Further addition of PPh<sub>3</sub> resulted in decomposition of **3b** to ditropyl (C<sub>7</sub>H<sub>7</sub>–C<sub>7</sub>H<sub>7</sub>), [Pd<sub>3</sub>(μ<sub>3</sub>-C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> (**1b**), Pd(PPh<sub>3</sub>)<sub>n</sub>, and black precipitates.

The structure of **3a** was determined by X-ray crystallographic analysis (Figure 2). Two Pd<sub>3</sub> triangles are connected directly through a Pd–Pd bond (Pd3–Pd4 = 2.696(1) Å). Each Pd<sub>3</sub> triangle is flanked by nearly eclipsed C<sub>7</sub>H<sub>7</sub> ligands, where the Pd<sub>3</sub> triangle is interestingly distorted to an isosceles triangle; that is, the base Pd–Pd (Pd1–Pd2 = 2.6855(9) Å) is shorter by 0.07 Å and others



**Figure 2.** ORTEP drawing of  $[\text{Pd}_6(\text{C}_7\text{H}_7)_4(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$  (**3a**) (50% probability ellipsoids,  $\text{BF}_4$  anions and a free  $\text{CH}_3\text{CN}$  molecule were omitted for clarity). Selected bond lengths ( $\text{\AA}$ ) and angles (deg): Pd1–Pd2 2.685(9), Pd2–Pd3 2.814(1), Pd3–Pd1 2.800(1), Pd3–Pd4 2.696(1), Pd4–Pd5 2.854(1), Pd5–Pd6 2.6719(8), Pd6–Pd4 2.793(1), Pd1–Pd2–Pd3 61.17(2), Pd2–Pd3–Pd1 57.15(2), Pd1–Pd3–Pd4 148.47(3), Pd3–Pd4–Pd5 146.36(3), Pd4–Pd5–Pd6 60.62(2), Pd5–Pd6–Pd4 62.92(2).



**Figure 3.** ORTEP drawing of  $[\text{Pd}_6(\text{C}_7\text{H}_8)_4(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$  (**4-H**) (50% probability ellipsoids,  $\text{BF}_4$  anions and a free  $\text{CH}_3\text{CN}$  molecule were omitted for clarity). Selected bond distances ( $\text{\AA}$ ) and angles (deg): Pd1–Pd1\* 2.643(1), Pd1–Pd2 2.791(1), Pd2–Pd3 2.741(1), Pd3–Pd1 2.834(1), Pd2–N1 2.223(9), Pd3–N2 2.12(1), Pd1\*–Pd1–Pd2 175.16(3), Pd1–Pd2–Pd3 61.62(3), Pd2–Pd3–Pd1 60.06(3), Pd2–Pd1–Pd3 58.32(3), Pd1–Pd2–N1 152.6(3), Pd2–Pd3–N2 185.6(3).

(Pd2–Pd3 = 2.814(1)  $\text{\AA}$ , Pd1–Pd3 = 2.800(1)  $\text{\AA}$ ) are longer by ca. 0.05–0.06  $\text{\AA}$  than the mean Pd–Pd length (2.753  $\text{\AA}$ ) of the equilateral  $\text{Pd}_3$  triangle in **1a**. The dihedral angle between the two  $\text{Pd}_3$  triangles is  $90^\circ$ , in order to avoid the steric congestion between the bis-cycloheptatrienyl tripalladium moieties. The acetonitrile ligands in **3a** are still oriented midway between the trans positions of two neighboring Pd atoms (Pd3–Pd1–N1 =  $151^\circ$ , Pd2–Pd1–N1 =  $148^\circ$ ).  $^1\text{H}$  NMR spectra of **3a** showed a sharp singlet signal for cycloheptatrienyl protons even at low temperature, indicating that the  $\text{C}_7\text{H}_7$  rings still rotate faster than the NMR time scale in the dimer dication.

One-electron reduction of the bis-cycloheptatriene complex **2-H** or **2'-Bu** with  $\text{Co}(\text{C}_5\text{H}_5)_2$  (1 equiv) or  $\text{Li}_2(\text{C}_8\text{H}_8)$  (0.5 equiv) afforded the air-sensitive dimer complex **4-H** or **4'-Bu** as a single product (Scheme 1B). Oxidation of **4-H** or **4'-Bu** with ferrocenium salt  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{BF}_4]$  (2 equiv) in  $\text{CD}_3\text{CN}$  gave **2-H** or **2'-Bu** almost quantitatively. The structure of **4-H** was determined by X-ray crystallographic analysis (Figure 3). One of the acetonitrile ligands bound to the base Pd atoms in **2-H** is displaced by a Pd–Pd bond (Pd1–Pd1\* = 2.643(1)  $\text{\AA}$ ), resulting in the nearly linear Pd2–Pd1–Pd1\*–Pd2\* connection (Pd2–Pd1–Pd1\* =  $175^\circ$ ). Each  $\text{Pd}_3$  moiety is distorted

from the isosceles triangle, due to the lengthening of the Pd1–Pd2 and Pd1–Pd3. In **4-H** with  $\text{C}_2$  symmetry, two cycloheptatriene ligands in each  $\text{Pd}_3(\text{C}_7\text{H}_8)_2$  moiety is nonequivalent. This is consistent with the NMR signal pattern of **4-H** in  $\text{CD}_3\text{CN}$ ; that is,  $^1\text{H}$  NMR spectra of **4-H** in  $\text{CD}_3\text{CN}$  showed two sets of eight signals for cycloheptatriene protons. Other isomers such as a dimer generated via a  $\text{Pd}_3$ – $\text{Pd}_3$  coupling at the apex Pd2 atom should have shown NMR signal patterns different from the observed one.

A simple M–M bonded dimer of mononuclear metallocenes has rarely been isolated; that is, only a few examples of the third-row  $d^5$  metallocene dimers,  $\text{Cp}_2\text{Re–ReCp}_2$  and  $[\text{Cp}_2\text{Os–OsCp}_2]^{2+}$ , are known.<sup>8,9</sup> Feasible formation of the stable dimers **3** and **4** is probably due to the less steric coverage of each metal atom by the carbocyclic ligands; that is, each metal atom in the tripalladium sandwich complexes is located beneath the rim of the carbocyclic rings, enabling access of another molecule with each parallel sandwich framework retained. On the other hand, a metal atom in mononuclear metallocenes is located beneath the centroid of the cyclopentadienyl rings, where bending of the metallocene framework is required for the formation of M–M bonded dimer.<sup>8b</sup>

In summary, one-electron reduction of the cycloheptatrienyl and cycloheptatriene  $\text{Pd}_3$  sandwich complexes yielded dimers with novel bitriangle  $\text{Pd}_6$  moieties, where the parallel sandwich frameworks are retained. The  $\text{Pd}_3$  triangle geometry varies within the sandwich framework possibly due to the different electronic demands of cycloheptatrienyl and cycloheptatriene ligands for the  $[\text{Pd}_3]^{2+}$  core both in the monomer and the dimers. Further study to explore the promising redox chemistry of metal sheet sandwich complexes is now underway in our laboratory.

**Supporting Information Available:** Experimental details of the preparation and characterization of **1–4** and details of the X-ray single-crystal structural analyses for **1a**, **2-Bu**, and **4-H**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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