Multinuclear Sandwich Complexes

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Rearrangement of a Pd$_4$ Skeleton from a 1D Chain to a 2D Sheet on the Face of a Perylene or Fluoranthene Ligand Caused by Exchange of the Binder Molecule**

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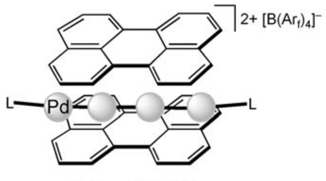
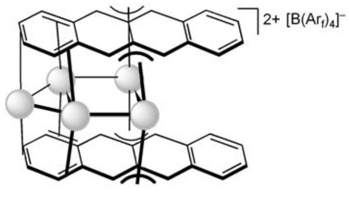
We recently reported stable multinuclear sandwich complexes of polycyclic aromatic hydrocarbon (PAH) ligands, the bis(perylene) Pd$_4$ chain complex **1** and the bis(naphthacene) Pd$_5$ sheet complex **2**.[1,2] These compounds are very rare examples of organometallic sandwich complexes in which more than three metal atoms are stabilized between two cyclic unsaturated hydrocarbon ligands.[3–5] It seems reasonable that the shape of a stable palladium assembly in such a compound should be more or less dependent on the geometry of the π network of the PAH ligands. However, certain PAH ligands could be capable of binding palladium assemblies with a variety of shapes. A change from one shape to another could be brought about by some change in the coordination environment around the palladium assembly, for example, a change in the end-capping ligands or exchange of one of the facial PAH ligands with another unsaturated hydrocarbon ligand to form a mixed sandwich complex. Herein, we demonstrate a chain-to-sheet rearrangement of a Pd$_4$ moiety on a perylene or fluoranthene ligand, which is induced by μ$_4$-facial coordination of 1,3,5,7-cyclooctatetraene (cot).



1a (L = CH$_3$CN)
1b (L = pyridine)



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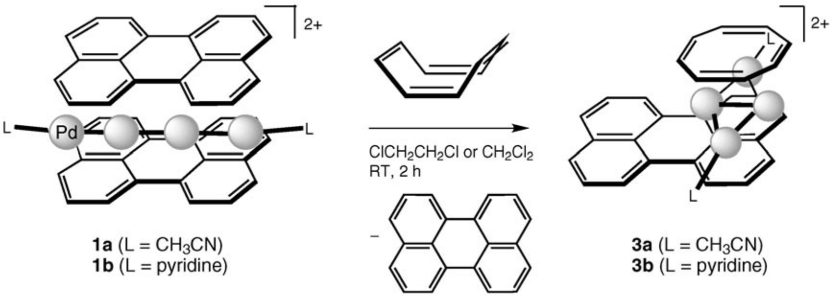
The perylene ligands in **1** are easily replaced with pπ-conjugated polyene ligands to afford a bis(polyene) Pd$_4$-chain sandwich complex.[1,5c] We expected that a change in the shape of the Pd$_4$ moiety may take place when one of the perylene ligands in **1** is exchanged for a different unsaturated hydrocarbon, such as cot, whose π-network geometry apparently mismatches the geometry of the μ$_4$-coordination site of a Pd$_4$ chain.[6] Interestingly, treatment of **1** with excess cot resulted in quantitative displacement of one of the perylene ligands with cot to form a mixed sandwich Pd$_4$ complex [Pd$_4$(perylene)(cot)L$_2$][B(Ar$_f$)$_4$]$_2$ (**3a** L = CH$_3$CN, **3b** L = pyridine; [B(Ar$_f$)$_4$]$^-$ = [B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$^-$; Scheme 1). Other possible products, such as a bis(cot) sandwich complex, were not generated during the reaction, even though excess cot (10 equiv) was used. After recrystallization, **3a** or **3b** was isolated in good yield (75 or 87%, respectively). The compositions of **3a** and **3b** were confirmed by elemental analysis.



Scheme 1. Synthesis of the perylene–cot mixed sandwich Pd$_4$ complexes from the bis(perylene) Pd$_4$ sandwich complexes. Counterions are [B(Ar$_f$)$_4$]$^-$.

The structure of **3a** was revealed by X-ray crystallographic analysis (Figure 1).[7] The complex **3a** has a rhombic Pd$_4$ sheet between cot and perylene ligands. The Pd–Pd bond lengths along the edge (2.711(1), 2.715(1), 2.749(1), and 2.757(1) Å) are in the range of normal Pd–Pd bonds.[3c] The diagonal Pd2–Pd4 separation (2.874(1) Å) is longer than the edge distances, but is still within the range of a Pd–Pd bonding interaction. The other diagonal separation (Pd1···Pd3 4.619(1) Å) is out of the range of a Pd–Pd interaction. The rhombic Pd$_4$ sheet is held by ten carbon atoms of the perylene ligand through a μ$_4$-η^2:η^3:η^2:η^3 coordination mode. The Pd1

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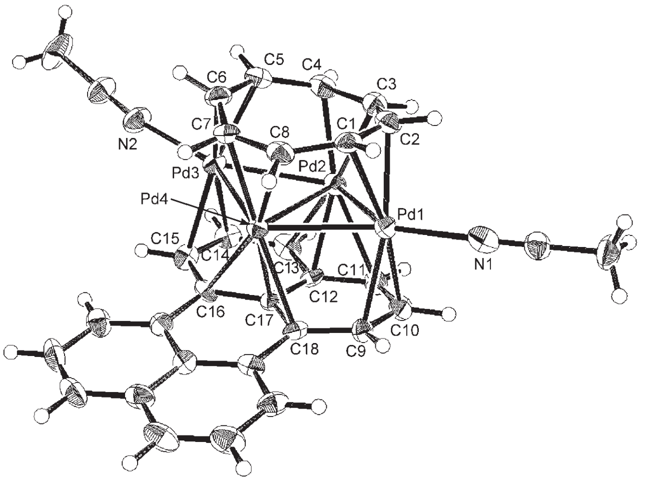
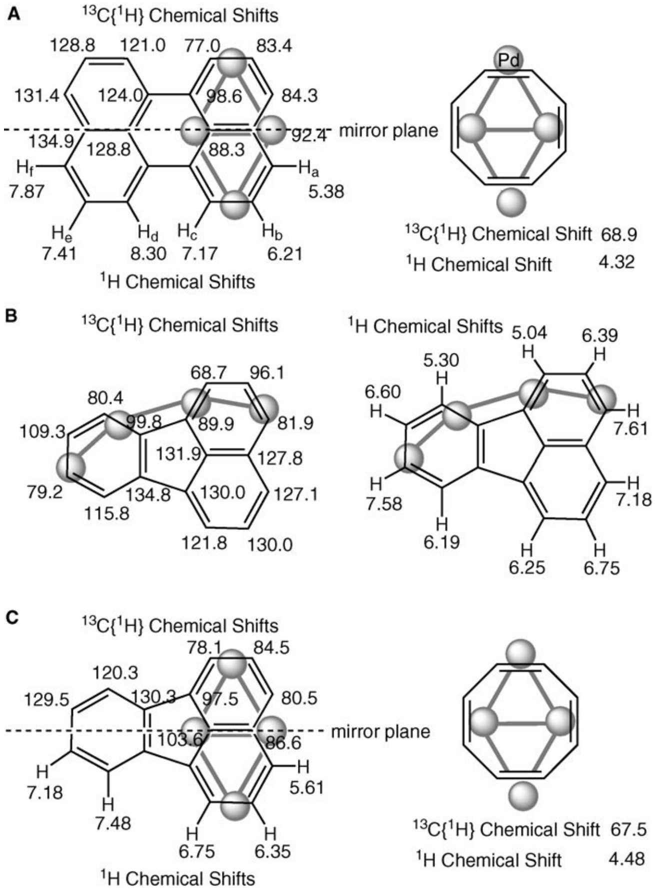


Figure 1. Molecular structure of **3a**; probability ellipsoids set at 50%; $[B(Ar_f)_4]^-$ counterions and free perylene omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.749(1), Pd2–Pd3 2.711(1), Pd3–Pd4 2.757(1), Pd4–Pd1 2.715(1), Pd2–Pd4 2.874(1), Pd1–N1 2.19(1), Pd3–N2 2.19(1), Pd1–C1 2.24(1), Pd1–C2 2.21(1), Pd2–C3 2.21(1), Pd2–C4 2.19(1), Pd3–C5 2.22(1), Pd3–C6 2.21(1), Pd4–C7 2.193(10), Pd4–C8 2.188(10), Pd1–C9 2.27(1), Pd1–C10 2.25(1), Pd2–C11 2.37(1), Pd2–C12 2.172(10), Pd2–C13 2.32(1), Pd3–C14 2.29(1), Pd3–C15 2.27(1), Pd4–C16 2.404(9), Pd4–C17 2.163(9), Pd4–C18 2.346(10), C1–C2 1.41(2), C2–C3 1.45(2), C3–C4 1.41(2), C4–C5 1.45(2), C5–C6 1.41(2), C6–C7 1.45(1), C7–C8 1.42(2), C8–C1 1.42(2); Pd1-Pd2-Pd4 57.68(3), Pd4-Pd2-Pd3 59.06(3), Pd2-Pd3-Pd4 63.43(3), Pd3-Pd4-Pd2 57.51(3), Pd2-Pd4-Pd1 58.85(3).

and Pd3 atoms coordinated to CH_3CN are connected to the perylene ligand through η^2 coordination, while Pd2 and Pd4 are η^3-coordinated to the perylene ligand. The cot ligand is bound to the Pd_4 sheet by a μ_4-η^2:η^2:η^2:η^2 coordination mode. The cot ligand is slightly puckered towards a tub conformation with the dihedral angle between the C3-C2-C1-C8 plane and the C4-C5-C6-C7 plane being 25° (Figure 1). Along with the puckering of the cot ligand, the Pd_4 rhombus is also slightly bent along the Pd2–Pd4 diagonal (the dihedral angle between the Pd1-Pd2-Pd4 and the Pd2-Pd3-Pd4 planes is 13°; Figure 1). The bond alternation in the C_8 ring of the cot ligand is diminished (short 1.41(2) Å, long 1.45(2) Å) as compared to free cot (short 1.33 Å, long 1.47 Å).[8] The μ_4-η^2:η^3:η^2:η^3 coordination of naphthalene or a naphthalene substructure is unprecedented.[9] Furthermore, μ_4-η^2:η^2:η^2:η^2 coordination of cot to a tetranuclear metal moiety in the face-capping mode is also unprecedented.[10]

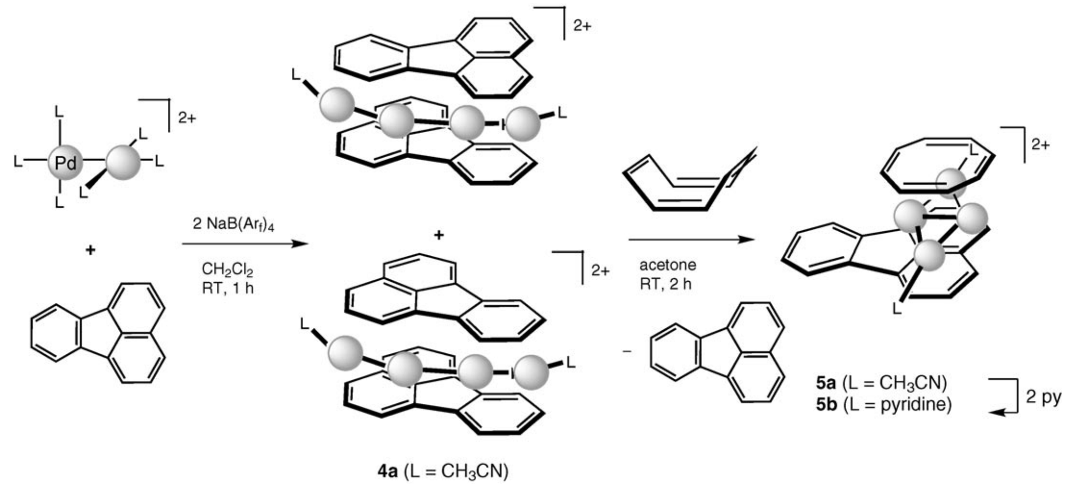
The ^1H and $^{13}C\{^1H\}$ NMR, H–H correlation spectroscopy (COSY), heteronuclear multiple-quantum correlation (HMQC), and heteronuclear multiple-bond correlation (HMBC) analyses of **3a** and **3b** indicated that the perylene-cot mixed sandwich structure is maintained in CD_2Cl_2 solution. The ^1H and $^{13}C\{^1H\}$ NMR chemical shifts for the perylene ligand in **3a** are shown in Scheme 2A. The ten carbon atoms that constitute one of the naphthalene substructures in the perylene ligand exhibit ^{13}C signals shifted upfield compared to those of the ten carbon nuclei in the other naphthalene substructure. This suggests that one of the naphthalene substructures in the perylene ligand is involved in coordination to the Pd_4 core. The upfield-shifted ^1H NMR



Scheme 2. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts [ppm] of the unsaturated hydrocarbon ligands A) **3a** in $[D_6]$acetone, B) **4a**-major in CD_2Cl_2, and C) **5a** in $[D_6]$acetone.

signals were also observed for protons bound to the coordinated carbon atoms (Scheme 2A). The signal for cot was a sharp singlet in the ^1H and $^{13}C\{^1H\}$ NMR spectra at 25°C (Scheme 2A) but also at −80°C. This result indicates that the cot ligand bound to the Pd_4 rhombus rotates faster than the NMR time scale, since the averaged signal is seen even at −80°C. The NMR analysis of the complex **3b** showed a similar signal pattern from the perylene and cot ligands to that of **3a**.

To verify whether the chain-to-sheet transformation of a Pd_4 moiety takes place on the face of other PAH ligands, we employed fluoranthene as the ligand. The bis(fluoranthene) Pd_4 complex $[Pd_4(\text{fluoranthene})_2(CH_3CN)_2][B(Ar_f)_4]_2$ (**4a**) was obtained as a mixture of two isomers by the reaction of $[Pd_2(CH_3CN)_6](BF_4)_2$[11] with fluoranthene (5 equiv) and $NaB(Ar_f)_4$ (2 equiv) in 31% yield (Scheme 3). The isomer ratio varied with each batch (major/minor ca. 1:1–2:1). The structure of **4a** was determined by X-ray crystallographic analysis (Figure 2).[7] Two fluoranthene ligands flank a bent Pd_4 chain (Pd1-Pd2-Pd3 157.72(6)°, Pd2-Pd3-Pd4 154.67(6)°).[5c] The Pd–Pd bond lengths (2.579(1), 2.622(1), and 2.575(1) Å) are in the normal range.[3c] One of the fluoranthene ligands is disordered such that C29 and C30 occupy two positions. One position is as shown in Figure 2, forming a six-membered ring with atoms C27, C28, C31, and



Scheme 3. Synthesis of the bis(fluoranthene) Pd_4 complex **4a** (two isomers: non-eclipsed (top), eclipsed (bottom)) and fluoranthene–cot mixed sandwich Pd_4 complexes **5a** and **5b**. Counterions are $[B(Ar_f)_4]^-$.

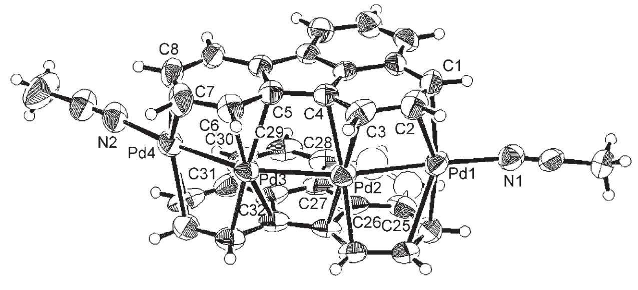
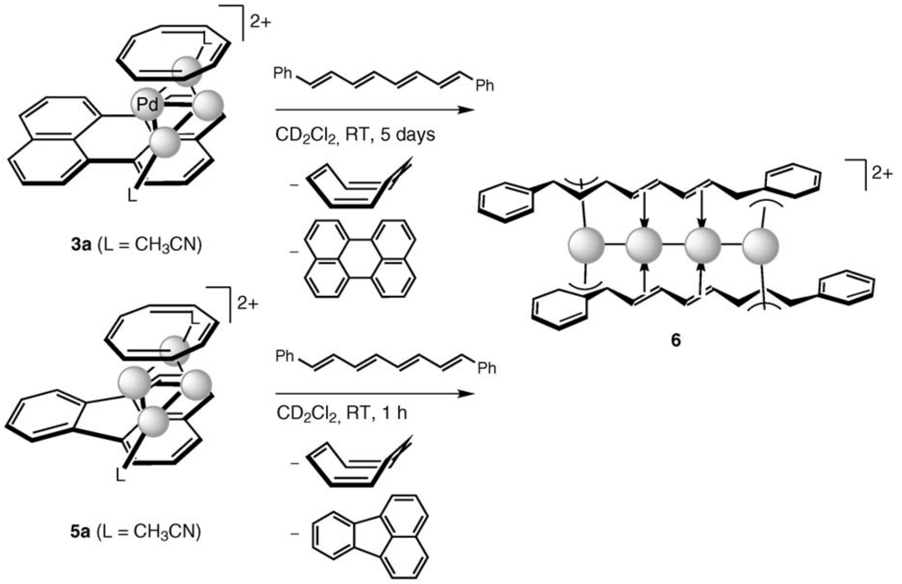


Figure 2. Molecular structure of **4a**; probability ellipsoids set at 50%; $[B(Ar_f)_4]^-$ counterions, and free fluoranthene and solvent molecules omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.579(1), Pd2–Pd3 2.622(1), Pd3–Pd4 2.575(2), Pd1–C1 2.21(1), Pd1–C2 2.35(1), Pd2–C3 2.16(1), Pd2–C4 2.21(1), Pd3–C5 2.26(1), Pd3–C6 2.20(1), Pd4–C7 2.57(2), Pd4–C8 2.21(1); Pd1-Pd2-Pd3 157.72(6), Pd2-Pd3-Pd4 154.67(6), N1-Pd1-Pd2 176.7(3), Pd3-Pd4-N2 173.9(4).

C32; In the other (empty circles in Figure 2), they are positioned so as to form a six-membered ring with C25–C28. Thus, the X-ray crystallographic analysis indicates that the structures of the two isomers are of non-eclipsed (C_2 symmetric), and eclipsed (C_s symmetric) geometries, as shown in Scheme 3. The $^{13}C\{^1H\}$ NMR resonances for the eight carbon atoms at the tetraene edge position of the fluoranthene ligands appeared at higher chemical shifts (Scheme 2B), consistent with the molecular structure determined by X-ray structure analysis.

Treatment of **4a** with cot (5 equiv) in acetone gave the fluoranthene–cot mixed sandwich complex $[Pd_4(\text{fluoranthene})(\text{cot})(CH_3CN)_2][B(Ar_f)_4]_2$ (**5a**) in 79% yield (Scheme 3). The composition of **5a** was confirmed by elemental analysis. The $^{13}C\{^1H\}$ NMR chemical shifts showed that the resonances of the ten carbon atoms of a naphthalene substructure in the fluoranthene ligand appeared in the upfield region (Scheme 2C). This result strongly indicates that the Pd_4 moiety in **5a** is held by the naphthalene substructure of the fluoranthene ligand, just like in the structure of **3a**. The chemical shifts of the singlet ^1H and $^{13}C\{^1H\}$ NMR resonances for the cot ligand were similar to those of **3a**. Complex **5a** was easily transformed to bis(pyridine) complex **5b** by treatment with pyridine (2 equiv; 74% yield; Scheme 3).

Finally, the sheet-to-chain rearrangement of the Pd_4 skeleton was also observed when complex **3a** or **5a** was treated with 1,8-diphenyl-1,3,5,7-octatetraene (dpot; Scheme 4); the cot and PAH ligands were displaced with dpot ligands to give the known Pd_4 chain sandwich complex $[Pd_4(\mu\text{-}\eta^3{:}\eta^2{:}\eta^2{:}\eta^3\text{-dpot})_2][B(Ar_f)_4]_2$ (**6**).[5a] The conversion



Scheme 4. Sheet-to-chain rearrangement of the Pd_4 moiety. Counterions are $[B(Ar_f)_4]^-$.

from **5a** (almost quantitative after 1 h) was much faster than from **3a** (60% yield after 5 days, as determined by NMR spectroscopy).

In summary, it has been shown that the Pd_4 moiety rearranges from a 1D chain to a 2D rhombic sheet on the face of perylene or fluoranthene during the binding of cot. This unique rearrangement is attributed to the "slippery" nature of the sp^2 carbon plates, where metal atoms can change their positions with a low barrier owing to the labile nature of metal–carbon(sp^2) bonds.[12,13] The results obtained here suggest that a small metal cluster laid on a graphene face may flexibly change its shape during binding, activation or release of various substrates. Further studies to gain mechanistic insight into the observed skeletal rearrangement coupled with exchange of the binder molecule are now underway.

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