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Square Tetrapalladium Sheet Sandwich Complexes: Cyclononatetraenyl as a Versatile Face-Capping Ligand

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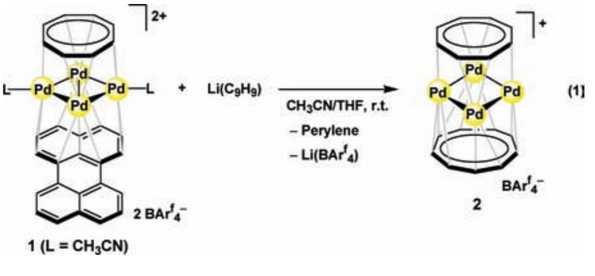
Among the monocyclic conjugated olefins formulated as $[C_nH_n]^x$, cyclopentadienyl anion ($C_5H_5^-$) is widely used as the auxiliary ligand for a mononuclear metal center, in part because of its stable and strong electron-donating properties associated with the η^5 coordination.[1,2] Cyclononatetraenyl anion ($C_9H_9^-$) is the next larger Hückel-aromatic $[C_nH_n]^-$ monoanion (Scheme 1) but has rarely been used as the ligand in transition-metal complexes.[3] A drawback is that the cyclononatetraenyl ligand bound to a mononuclear metal center is susceptible to skeletal rearrangement.[4,5] Because of its large ring size and possible strong electron-donating ability, however, cyclononatetraenyl is attractive as a planar π-coordinating ligand in metal sheet sandwich complexes, a recently discovered class of sandwich compounds.[6−9] Herein we report that cyclononatetraenyl acts as a stable π-coordinating ligand for an unprecedented square metal sheet sandwich complex.

Scheme 1. Cyclopentadienyl and Cyclononatetraenyl Anions

Lithium cyclononatetraenyl was prepared via ring-expansion of $C_8H_8^{2-}$ according to a literature procedure.[10] Initially, we examined the ligand-substitution reaction of the bisperylene Pd_4 chain complex[11] $[Pd_4(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-perylene})_2(CH_3CN)_2][BAr^f_4]_2$ (BAr^f_4 = $B\{3,5\text{-}(CF_3)_2(C_6H_3)\}_4$) with 2 equiv of $Li(C_9H_9)$. Although the starting materials were consumed immediately, the resultant black precipitates were insoluble in common organic solvents, and the product has not yet been identified. Next, we chose the Pd_4 rhombic sheet complex $[Pd_4(\mu_4\text{-}\eta^3{:}\eta^2{:}\eta^3{:}\eta^2\text{-perylene})(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_8H_8)(CH_3CN)_2][BAr^f_4]_2$ (**1**), which was recently synthesized and structurally characterized in our group,[7] as an alternative starting Pd_4 complex for the ligand-substitution reaction. Treatment of **1** with 1 equiv of $Li(C_9H_9)$ in CD_3CN resulted in the selective displacement of the perylene ligand to yield the cyclononatetraenyl−cyclooctatetraene mixed sandwich complex $[Pd_4(\mu_4\text{-}C_9H_9)(\mu_4\text{-}C_8H_8)][BAr^f_4]$ (**2**) almost quantitatively (eq 1):



Isolation of **2** was attained by passing the reaction mixture through a short neutral alumina column and then recrystallizing from CH_2Cl_2/cyclohexane. ^1H NMR spectra of **2** in CD_2Cl_2 at 298 K showed two sharp singlet signals at 4.55 ppm (9H, C_9H_9) and 3.55 ppm (8H, C_8H_8). The shape of the signals did not change at low temperature (183 K), indicating the rapid fluxional rotation of the $\mu_4\text{-}C_9H_9$ ligand. $^{13}C\{^1H\}$ NMR spectra at 298 K showed two sharp singlet signals at 80.9 ppm for the C_9H_9 ligand and 72.5 ppm for the C_8H_8 ligand.

The structure of **2** in the crystalline state was determined by X-ray diffraction analysis (Figure 1). Complex **2** forms a dimer, $\mathbf{2_2}$, in the crystalline state. In the monomeric unit **2** (Figure 1A), a nearly equilateral Pd_4 square sheet, in which the average Pd−Pd distance is 2.72 Å, is flanked by the planar C_9H_9 and C_8H_8 ligands. The C_9H_9 ligand coordinates to the Pd_4 square sheet in a $\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^3{:}\eta^3$ mode, where the C7 atom bridges two Pd atoms with relatively long Pd−C distances (2.57 and 2.62 Å). The C_8H_8 ligand coordinates to the Pd_4 square sheet in a $\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2$ mode. Square metal sheet sandwich complexes have not been isolated for any other metal elements.[12] The dimeric structure of the sandwich framework $[Pd_4(\mu_4\text{-}C_9H_9)(\mu_4\text{-}C_8H_8)]_2^{2+}$ is held together by a Pd_4−Pd_4 contact, with the Pd_4 planes forming a dihedral angle of 87° (Figure 1B). The Pd_4−Pd_4 contact [Pd1−Pd1* = 2.907(2) Å] is longer than the typical Pd−Pd bonding interaction.[13] Indeed, a much shorter Pd_3−Pd_3 contact [Pd_3−Pd_3 = 2.686(1) Å] is found in a dimer of the odd-valence-electron-number trinuclear sandwich complex $[Pd_3(\mu_3\text{-}C_7H_7)_2(CH_3CN)]_2[BAr^f_4]_2$.[9] The long Pd_4−Pd_4 contact in the $\mathbf{2_2}$ dimer may reflect the even number of valence electrons in the monomer **2**. ESI(+)-MS analyses of **2** showed a signal at *m/z* 647, for which the isotopomer peak separation was *m/z* 1.0 rather than 0.5, indicating the existence of the monomer **2** or the monomeric fragment of the dimer $\mathbf{2_2}$ under the electrospray ionization conditions.[14]

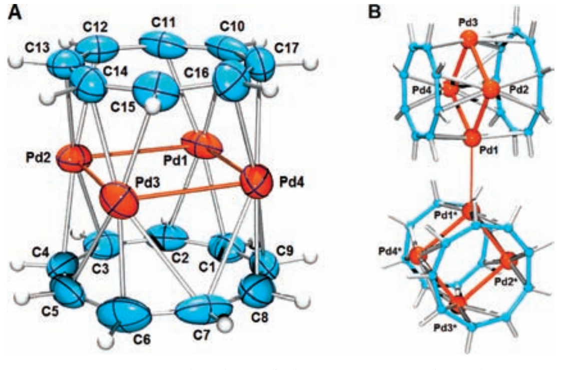


Figure 1. (A) ORTEP drawing of the monomer unit $[Pd_4(\mu_4\text{-}C_9H_9)(\mu_4\text{-}C_8H_8)][BAr^f_4]$ (**2**) (30% probability ellipsoids; the BAr^f_4 anion and a free solvent molecule have been omitted for clarity). (B) Ball-and-stick drawing of the dimeric structure $\mathbf{2_2}$ in the crystalline state. Selected bond lengths (Å) and angles (deg): Pd1−Pd2, 2.724(1); Pd2−Pd3, 2.700(1); Pd3−Pd4, 2.713(1); Pd4−Pd1, 2.728(1); Pd1−Pd1*, 2.907(2) Å; Pd1−Pd2−Pd3, 89.03(3); Pd2−Pd3−Pd4, 91.56(3); Pd3−Pd4−Pd1, 88.68(3); Pd4−Pd1−Pd2, 90.70(3); Pd1*−Pd1−Pd2, 142.60(4); Pd1*−Pd1−Pd4, 126.70(4).

Of interest is the fact that the complex **2** contains no acetonitrile ligands while the formal total valence electron count for the monomer **2** (56e) is four less than that for **1**.[15] Indeed, no sign of coordination of CH_3CN or

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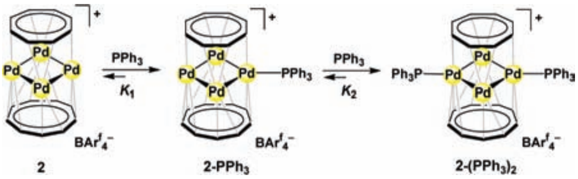
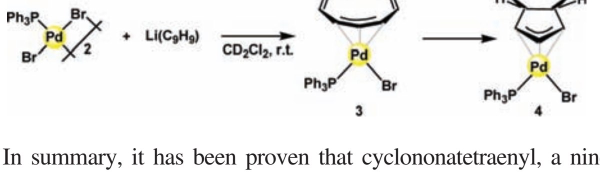
pyridine to **2** was detected by ^{1}H NMR analyses, even when excess CH_3CN or pyridine was added to the CD_2Cl_2 solution of **2** at 298 K. However, titration analyses using ^{1}H and ^{31}P NMR (CD_2Cl_2, 298 K) revealed that mono- and bis-PPh_3 adducts were generated at equilibrium (Scheme 2). The mono adduct **2-PPh$_3$** showed a pair of singlet resonances for the C_9H_9 ligand (4.40 ppm) and the C_8H_8 ligand (3.46 ppm). The bis adduct **2-(PPh$_3$)$_2$** showed singlet resonances shifted to higher field (4.15 ppm for the C_9H_9 ligand and 3.27 ppm for the C_8H_8 ligand). ^{31}P NMR spectra supported the coordination of PPh_3 ligands. The amount of **2-PPh$_3$** reached a maximum at [**2**]/[PPh_3] ≈ 1, where **2** and **2-(PPh$_3$)$_2$** coexisted. When 2 equiv of PPh_3 was added, **2-(PPh$_3$)$_2$** was the sole observable species.[16,17] The titration experiments showed that the first and the second coordination steps are in equilibrium, where each equilibrium lies almost at complete PPh_3 coordination.[18] During the titration experiments, no corresponding 2:1 adduct **2$_2$-PPh$_3$** or 2:3 adduct **2$_2$-(PPh$_3$)$_3$** was observed, indicating the monomeric form of the phosphine adducts of **2** in solution. The mono-PMe_2Ph adduct **2-PMe$_2$Ph** showed a sharp doublet signal ($^2J_{PH} = 10$ Hz) for the methyl protons of the PMe_2Ph ligand at both 293 and 193 K. This signal pattern is also consistent with the monomeric form of **2-PMe$_2$Ph**.[19] Thus, to date we have not obtained any observations that strongly support the dimeric structures **2$_2$-(PR$_3$)$_n$** ($n = 0-4$) in solution. In any case, it was proven that the complex **2** is coordinatively unsaturated and capable of accepting phosphine ligands. It is noteworthy that no decomposition of the Pd_4 square sheet sandwich framework was observed, even in the presence of 10 equiv of PPh_3 in CD_2Cl_2 solution.[20] Such a robust nature of the square metal sheet sandwich framework of Pd is in sharp contrast to the labile nature of mononuclear Pd sandwich complexes: for example, Pd(η^5-C_5H_5)(η^3-allyl) decomposes immediately under comparable conditions.[21]

Scheme 2. Addition of PPh_3 Ligands to **2**



As mentioned above, the cyclononatetraenyl ligand has rarely been used with a mononuclear transition-metal center,[3] probably because it is known that η^1-cyclononatetraenyl complexes undergo facile skeletal rearrangement.[4] We examined the coordination behavior of cyclononatetraenyl to a mononuclear Pd^{II} center. The reaction of $[Pd(PPh_3)Br_2]_2$ with $Li(C_9H_9)$ in CD_2Cl_2 at ambient temperature immediately afforded a product **3** that presumably was the η^3-cyclononatetraenyl complex. Complex **3** was gradually converted to the dihydroindenyl complex **4** within 12 h at ambient temperature (Scheme 3). Complex **4** was identified by ^{1}H, ^{13}C{^{1}H}, COSY, and HMQC NMR analyses.

Scheme 3. Mononuclear Pd Complexes Derived from $Li(C_9H_9)$



In summary, it has been proven that cyclononatetraenyl, a nine-membered aromatic anion, acts as a stable ligand for a tetranuclear square metal sheet. The present results suggest that the large carbocyclic ligands, which are sometimes incompatible with a mononuclear transition-metal center, can be utilized as the stable face-capping ligand for metal sheet clusters. The successful isolation of the first square metal sheet sandwich complex **2** in this work might expand the structural concept of the molecular sandwich compounds.

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Supporting Information Available: Experimental details of the preparation and characterization of **2**−**4** and details of the single-crystal X-ray structural analysis of **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The isotope pattern of the signal at *m/z* 647 was consistent with [Pd_4(C_9H_9)(C_8H_8)]$^+$ ($M_r = 647.0$). See Figure S1 in the Supporting Information.
(15) In the crystalline state, the Pd2, Pd3, and Pd4 atoms in **2** possess no capping ligand. While two para carbons, one from an Ar^f group in each of the BAr$^f_4$ anions, are located near the Pd2 and Pd4 atoms, Pd2$\cdots$C$_{para}$ (3.11 Å) and Pd4$\cdots$C$_{para}$ (3.34 Å) are out of the range of Pd−C bond lengths.
(16) **2-(PPh$_3$)$_2$** was generated as a single isomer. Although the trans/cis stereochemistry of **2-(PPh$_3$)$_2$** was not determined in this work, we assumed that the product is the trans isomer since **2-(PMe$_2$Ph)$_2$** is generated as the trans isomer (see ref 17). Only the trans isomer of **2-(PPh$_3$)$_2$** is shown in Scheme 2.
(17) The bis adduct **2-(PMe$_2$Ph)$_2$** showed a virtual triplet ^{1}H NMR signal for the methyl protons of PMe_2Ph ($J = 3$ Hz) at both 293 and 193 K. This signal pattern is consistent with the trans geometry of **2-(PMe$_2$Ph)$_2$** but inconsistent with the cis geometry, since the two methyl groups of a PMe_2Ph ligand in **2-(PMe$_2$Ph)$_2$** would be nonequivalent in the cis isomer.
(18) During the titration experiments (≤2 equiv), the concentration of free PPh_3 seemed too low to be determined by ^{1}H NMR analysis. Thus, K_1 and K_2 are both very large, and K_1/K_2 was estimated to be 33(3) at 298 K.
(19) The dimer **2$_2$-(PMe$_2$Ph)$_2$**, which is a chiral dication, might show two doublet signals for the diastereotopic methyl groups of the PMe_2Ph ligand. The observed signal pattern would be consistent with the dimer only when rotation about the Pd1−Pd1* bond or dissociation/association of the Pd_4 moiety is much faster than the NMR time scale.
(20) Addition of PPh_3 (>2 equiv) resulted in a shift of the proton resonances of **2-(PPh$_3$)$_2$** to higher field, indicating the formation of tris or higher adducts at equilibrium.
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