J. Am. Chem. Soc. **1998,** *120,* 13280−13281

The First Dinuclear Complex of Palladium(III)

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Received September 10, 1998

The number of compounds of Pd^{III} that have been isolated and characterized is extremely limited. In the realm of aqueous chemistry there is no aqua ion nor any classical anionic complexes, PdX_6^{3-}; the latter have been made only in the solid state under strenuous conditions.[1] There are no binary compounds ("PdF_3" being a mixed Pd^{II}, Pd^{IV} compound[2]).

Only in 1987 was the compound $(H_3O)[PdL_2](ClO_4)_4 \cdot 3H_2O$ (L = 1,4,7-trithiacyclononane) reported with a structure determination.[3] Since then there have been no others unambiguously established, although in 1988 a powdered material believed to be $[PdL'_2](PF_6)_3$ (L′ = 1,4,7-triazacyclononane), which behaved electrochemically in accord with that formula, was prepared.[4] Three reported attempts to make and isolate dinuclear complexes were unsuccessful. In this laboratory[5] $Pd_2(DTolF)_4$, $DTolF^-$ = $[(p\text{-tolyl})NC(H)N(p\text{-tolyl})]^-$, was oxidized to $[Pd_2(DTolF)_4](PF_6)$ which was crystallographically characterized. In it, the Pd−Pd distance of 2.637(6) Å is little different from that, 2.622(3) Å, in the unoxidized starting material. No product containing a Pd_2^{6+} core could be isolated although a $Pd_2^{5+} \rightarrow Pd_2^{6+}$ oxidation wave was seen at +1.19 V, and the EPR spectrum of the Pd_2^{5+} compound was considered indicative of ligand rather than M_2 core oxidation. Contemporaneously, Bear and co-workers[6] prepared the similar *N*,*N*′-diphenylbenzamidinate compound. They saw only one oxidation wave, but from their EPR spectrum they concluded that a genuine $Pd_2^{4+} \rightarrow Pd_2^{5+}$ oxidation had occurred. Finally, attempts were made[7] to oxidize the $Pd_2(pyt)_4$ (pyt^- = 2-thiopyridinate anion) molecule which appears to generate an unstable $Pd_2(pyt)_4X_2$ species during cyclic voltammetry, but no Pd_2^{5+} or Pd_2^{6+} products were actually isolated.

Recently, use of the binitrogen-donor ligand hpp (the anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine) has proven to be effective in stabilizing metal−metal bonds in paddlewheel complexes for V,[8] Cr,[8] Mo,[8] Nb,[9] and Ru.[10] The isolation of $[Mo_2(hpp)_4][BF_4]_2$,[11] the first Mo_2^{6+} compound of its kind, intensified our interest in other previously unstable systems—the oxidized forms of palladium being among them.

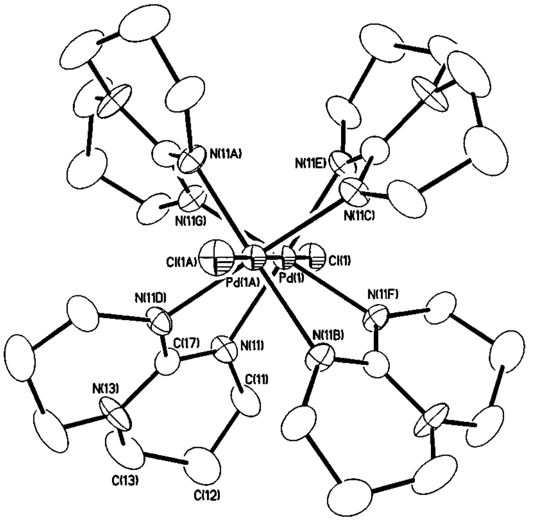

Figure 1. Thermal ellipsoid plot of **2**; atoms are drawn at the 50% probability level. Selected bond distances and angles are Pd(1)−Pd(1a) 2.391(2) Å, Pd(1)−N(11) 2.034(6) Å, Pd(1)−Cl(1) 2.474(4) Å, N(11)−Pd(1)−N(11f) 89.81(2)°, N(11)−Pd(1)−N(11e) 173.5(3)°, N(11)−C(17)−N(11d) 120.4(9)°, N(11)−Pd(1)−Pd(1a)−N(11d) 24.0(3)°.

We report here the first single bond between two trivalent palladium atoms. A reaction of Pd(II)acetate with Lihpp in THF produces the orange complex $Pd_2(hpp)_4$, **1**.[12] The cyclic voltammogram of **1** in CH_2Cl_2 showed a quasi-reversible oxidation at −0.12 V and an irreversible oxidation at +0.82 V, indicating that oxidation products obtained under these conditions are likely to be unstable. However, the two electron oxidation of **1** with $PhI \cdot Cl_2$ resulted in the formation of the dark complex $Pd_2(hpp)_4Cl_2$, **2**.[13] Reproducibly a small amount of **2** was obtained from several reactions, even when different temperatures, solvents, and oxidizing agents such as $NOPF_6$ and $NOBF_4$ were used. All invariably gave a mixture of products. Unfortunately, the only way to separate them was to hand-pick them. The presence of **2** was confirmed in each case by checking the cell dimensions by X-ray diffraction. The crystals themselves are quite stable, even in air, but the solutions are very unstable and always became orange. The identity of the other products has not yet been determined. We are continuing our efforts to improve the yield of this synthesis.

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(12) Palladium(II) acetate (0.897 g, 4 mmol) was added at 0 °C to Lihpp (8.0 mmol) in 70 mL THF and stirred overnight, resulting in a dark-orange solution and some light-orange solid. The mixture was heated to boiling and filtered on a frit; the filtrate was evaporated to dryness and extracted with 20 mL toluene. The solution was filtered through Celite and evaporated to dryness. The residue was washed with hexanes and filtered in air. The orange solid was collected in 71% yield (1.08 g, 1.41 mmol). Crystals suitable for single-crystal X-ray diffraction were grown from a THF solution of **1** carefully layered with hexanes. ^1H NMR showed **1** to be diamagnetic. The elemental analysis, done by Canadian Microanalytical Service was satisfactory. ^1H NMR (C_6D_6, ppm) $\delta = 1.74$ (quin), 2.70 (t), 3.73 (t). UV/vis (toluene): $\lambda_{max} = 290$ nm. IR (KBr, cm^{-1}): 2931.8(s), 2807.3(s), 1573.1(vs), 1513.0(vs), 1467.4(m), 1439.0(s), 1381.9(s), 1361.7(w), 1334.0(w), 1319.2(m), 1305.2(m), 1279.7(s), 1261.6(m), 1219.4(w), 1199.5(vs), 1082.5(s), 1025.8(m), 801.5(m), 745.0(w), 700.0(w), 465.6(w), 415.7(w).

(13) (a) $PhI \cdot Cl_2$ (0.018 g, 0.065 mmol) was dissolved in 2 mL CH_3CN and added via cannula to 10 mL of a toluene solution of $Pd_2(hpp)_4$ (0.10 g, 0.13 mmol). The orange solution became dark green and was stirred for 1 h at room temperature. A dark precipitate separated from the solution and was collected on a frit. A dichloromethane solution of the dark solid was stored at 0 °C for 48 h and then carefully layered with hexanes. A few very small, dark crystals of **2** grew within a few days; they were suitable for single-crystal X-ray diffraction. A small quantity of orange powder always precipitated along with the crystals of **2**. (b) The layering of a solution of $Pd_2(hpp)_4$ in toluene with a solution of $PhI \cdot Cl_2$ in acetonitrile affords dark crystals of **2** at the interface within 24 h. The crystals became oily and orange within 72 h.

10.1021/ja9832313 CCC: $15.00

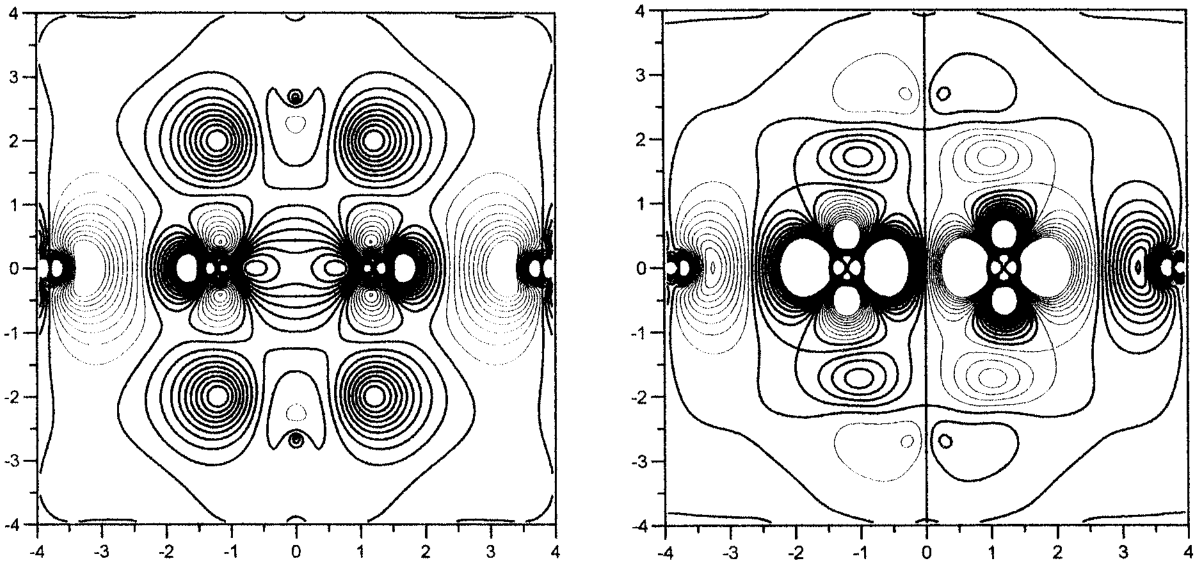

Figure 2. Contours of the HOMO (left) and LUMO (right) of the molecule $Pd_2(hpp)_4Cl_2$ showing the Pd−Pd single bond on the plane formed by the Cl−Pd−Pd−Cl unit and four nitrogen atoms from two hpp ligands. Positive and negative contours are in heavy and light lines, respectively. Both are antibonding with respect to the Pd−Cl interaction.

The structures[14,15] of both centrosymmetric complexes, **1** and **2**, are very similar; only **2** is shown in Figure 1. In each complex the two palladium atoms are bridged by four hpp ligands, resulting in a paddlewheel-type structure. Additionally, two axial chloride ions are present in **2**. There is formally no metal−metal bond in **1** although the intermetallic separation is quite short (2.555(1) Å). In similar complexes containing binitrogen-donor ligands, the Pd−Pd separations are comparable although slightly longer (e.g., 2.576(1) Å in Pd_2(*N,N′*-diphenylbenzamidinato)$_4$,[6] 2.5627(7) Å in Pd_2(*N,N′*-diphenyltriazenato)$_4$[16]); the shortest published separation was found in Pd_2(6-methyl-2-hydroxypyridinato)$_4$[17] (2.546(1) Å).

The unprecedented Pd−Pd bond distance of 2.391(2) Å found in **2** is 0.164 Å shorter than that in **1** and 0.097 Å shorter than the shortest Pd−Pd distance ever reported for any type complex (in this case a Pd(I)−Pd(I) acetonitrile complex[18]). It is also worth noting that the Pd−Pd single bond distance in **2** is 0.36 Å shorter than the Pd−Pd distance in the metal itself.[19] The magnitude of the shortening of the Pd−Pd distance provides strong evidence that the oxidation does occur in the dipalladium unit and that the electron-rich single bond configuration of $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ can be appropriately assigned to the metal−metal interaction.

To specify in detail how the Pd−Pd bond is formed, we have performed a high-level calculation[20] of the electronic structure of the $Pd_2(hpp)_4Cl_2$ molecule, in which the geometry was optimized, giving results in excellent agreement with experiment: Pd−Pd, 2.402 Å vs 2.391 Å (obs) and for the torsion angle 22.6° vs 24°(obs). The HOMO/LUMO gap is calculated to be 167 kcal mol^{-1}. The HOMO and LUMO are depicted in Figure 2, where it is clear that the Pd−Pd bond is a σ-bond formed mainly by a $d_{z^2} - d_{z^2}$ overlap.

Spectroscopic studies on $Pd_2(hpp)_4Cl_2$ as well as attempts to isolate the one electron oxidation product are in progress.

Acknowledgment. We are grateful to Dr. Marina Petrukhina for invaluable assistance, to Dr. Isabel Pascual for helpful discussion, and to the National Science Foundation for support.

Supporting Information Available: Figures of **1** and **2** and tables of crystallographic data including diffractometer and refinement data, atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters (14 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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(14) $Pd_2(hpp)_4$ crystallizes in space group $P\bar{1}$ with the following unit cell parameters: $a = 8.388(2)$ Å, $b = 9.352(2)$ Å, $c = 10.036(2)$ Å, $\alpha = 87.47(2)°$, $\beta = 70.80(2)°$, $\gamma = 81.19(2)°$, $V = 734.7(3)$ Å^3, and $Z = 1$. Refinement converged for 1898 unique reflections and 191 parameters to give R1 = 0.046 and wR2 = 0.144 and a goodness-of-fit (GOF) = 1.108. Selected bond distances and angles: Pd(1)···Pd(1a) 2.555(1) Å, Pd(1)−N(11) 2.037(6) Å, Pd(1)−N(21) 2.020(6) Å, Pd(1)−N(22a) 2.039(6) Å, Pd(1)−N(12a) 2.054(6) Å, N(11)−Pd(1)−N(21) 89.1(3)°, N(12a)−Pd(1)−N(22a) 92.3(2)°, N(11)−Pd(1)−N(12) 173.4(2)°, N(11)−C(17)−N(12) 121.8(7)°, N(21)−C(27)−N(22) 122.0(7)°, N(11)−Pd(1)−Pd(1a)−N(12) 1.9°.

(15) $Pd_2(hpp)_4Cl_2$ crystallizes in space group *P*4/*nnc* with the following unit cell parameters: $a = 10.502(3)$ Å, $c = 14.500(8)$ Å, $V = 1559.2(1)$ Å^3, and $Z = 2$. Refinement converged for 534 unique relections and 53 parameters to give R1 = 0.047 and wR2 = 0.092 and a goodness-of-fit (GOF) = 1.392.

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(20) The Hartree−Fock self-consistent-field (SCF) method was used to locate the energy minimum structure of $Pd_2(hpp)_4Cl_2$. Both standard 3-21G[21] basis set and the valence double-ζ basis set were used. In the later, a [10s8p5d1f] contraction of the (17s13p8d1f) primitive set by Huzinaga[22] plus two p and one f functions was used for Pd, and the valence double-ζ basis set augmented with d- and p-like polarization functions (6-31G(d,p)) was for all the ligand atoms. Gaussian-94 software was used for the calculations.

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