J|A|C|S
COMMUNICATIONS

High Yield Syntheses of Stable, Singly Bonded Pd_2^{6+} Compounds

F. Albert Cotton,*[,†] Igor O. Koshevoy,[‡] Pascual Lahuerta,*[,‡] Carlos A. Murillo,*[,†] Mercedes Sanaú,[‡]
M. Angeles Ubeda,*[,‡] and Qinliang Zhao[†]

Department of Chemistry, Laboratory for Molecular Structure and Bonding, P.O. Box 30012, Texas A&M University, College Station, Texas 77842-3012, and Departamento de Química Inorgánica, Facultad de Química, Universitat de Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

Received August 12, 2006; E-mail: cotton@tamu.edu; murillo@tamu.edu; pascual.lahuerta@uv.es; angeles.ubeda@uv.es

Compounds with metal−metal bonds have grown in number and importance since the discovery of $Re_2Cl_8^{2-}$ ion nearly 40 years ago.[1] There are now thousands of derivatives,[2] with the most prominent structural motif being that of the paddlewheel in which a metal−metal bonded unit, M_2^{n+}, is surrounded by eight equatorially bonded atoms and sometimes two axial groups. In many of these molecules the symmetry is roughly D_{4h} or a variation thereof. Some of these compounds have useful applications, for example, those having singly bonded Rh_2^{4+} and Pt_2^{6+} units which have been extensively used in catalysis[3] and medicine.[4] Mixed valence species, such as those in the platinum blues, have also been widely studied.[5] Even though there are known paddlewheel compounds for most of the transition elements, very little is known about analogues of Pt_2^{6+} in group 10. Indeed, there is only one compound spectroscopically characterized with a proposed Ni_2^{6+} core[6] and only one structurally characterized compound containing a Pd_2^{6+} core, namely $Pd_2(hpp)_4Cl_2$ (hpp = the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine).[7] The Pd_2^{4+} precursor contains no metal−metal bond because of the d^8 configuration of the Pd(II) atoms, which in a paddlewheel compound will give rise to a $\sigma^2\pi^4\delta^2\sigma^{*2}\pi^{*4}\delta^{*2}$ configuration with a bond order of zero. The compound $Pd_2(hpp)_4Cl_2$ was prepared in low yield and mixed with other compounds. Because the crystals had to be manually separated from other solids, progress in development of the Pd_2^{6+} chemistry using this compound has been hampered.

Here we report high yield syntheses of very pure paddlewheel compounds having Pd−Pd single bonds and the general formula *cis*-$Pd_2(C_6H_4PPh_2)_2(O_2CR)_2Cl_2$ with R = CH_3 (**1**), CF_3 (**2**), and CMe_3 (**3**),[8] obtained by oxidation of the corresponding *cis*-$Pd_2(C_6H_4PPh_2)_2(O_2CR)_2$ compounds[9] with $PhI{\cdot}Cl_2$.[10] Compounds **1** and **3** are stable in solutions of chlorinated solvents for over 48 h, and crystals may be stored for weeks at ambient temperature and in air without apparent decomposition. However, **2** slowly decomposes in solution and as a solid at ambient temperature. It appears that the electron donating ability by the carboxylate substituents has an important impact in stabilizing the products, and it should be noted that it was not possible to oxidize *cis*-$Pd_2(C_6F_4PPh_2)_2(O_2CMe)_2$. All compounds are diamagnetic as shown by sharp singlets at −13.8, −8.8, and −14.0 ppm in the ^{31}P NMR spectra for **1**, **2**, and **3**, respectively, and by the position of the signals in the ^1H NMR spectra which are in the expected region for orthometalated phosphines bridging a dinuclear unit.[11]

The structures of **2** and **3** show a Pd_2^{6+} unit bridged by two carboxylate groups and cisoid orthometalated phosphine ligands in a head-to-tail arrangement. There are also two chloride groups in axial positions, as shown in Figure 1 for **3**. There is a twist in the orthometalated ligands; the molecules are chiral but crystals are racemic. For both **2** and **3** the Pd−Pd distances (2.5434(4) and 2.5241(9) Å, respectively) are much shorter than those in the precursors[9] (2.7229(8) and 2.6778(15) Å, respectively) but longer than that in the only known compound with a Pd_2^{6+} unit, $Pd_2(hpp)_4Cl_2$ (2.391(2) Å). The latter has guanidinate ligands which are known for the high electron donating ability.

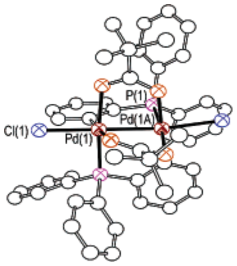

Figure 1. The structure of **3** with displacement ellipsoids drawn at the 40% probability level. Hydrogen atoms are not shown.

Because the shortened Pd−Pd distances and the diamagnetism of **1**−**3** suggest the presence of a Pd−Pd single bond, the electronic properties and the nature of the Pd−Pd interaction were probed with hybrid HF/DFT calculations on the simplified model *cis*-$Pd_2(C_6H_4PMe_2)_2(O_2CH)_2Cl_2$ having C_2 symmetry. The calculations favored the singlet state by 19.1 kcal·mol^{-1}.

As shown in Tables 1 and S2, the optimized geometry of the singlet state resulted in good agreement with the experimental values. The calculated Pd−Pd distance (2.611 Å) is overestimated but by only 0.068 Å relative to that in **2**. The very large HOMO/LUMO gap of 2.54 eV (58.6 kcal·mol^{-1}) accounts for the observed diamagnetism. As shown in Figure 2, the HOMO originates from the direct overlap of two lobes of the d_{z^2} orbitals that provides a significant accumulation of electron density along the metal−metal bond, whereas the LUMO is the antibonding interaction of these two d_{z^2} orbitals. Accordingly, there is a single bond between these two palladium atoms, and the electronic configuration of $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ may be assigned to the Pd_2^{6+} unit. This is similar to what was calculated using a Hartree−Fock self-consistent field method for $Pd_2(hpp)_4Cl_2$.[7]

Since the interaction between the d_{z^2} orbitals of the palladium atoms and the p_z orbitals from the axial chloride atoms is antibonding in character, the effect of the axial Cl^- ions on the Pd_2 unit was explored by DFT calculations, and a fragment analysis were performed on both *cis*-$Pd_2(C_6H_4PMe_2)_2(O_2CH)_2Cl_2$ and [*cis*-$Pd_2(C_6H_4PMe_2)_2(O_2CH)_2]^{2+}$ models. The results (Tables 1 and S2) show that the axial Cl atoms do influence other bonding distances, but their effect on the Pd−Pd bond appears to be most significant when compared to the model devoid of axial interactions. The calculations for this model show very short Pd−Pd bond distances. These are shorter by ca. 0.1 Å than those in the model with axial chloride ligands. The reason for the elongation of the Pd−Pd bond

---

[†] Texas A&M University.
[‡] Universitat de Valencia.

10.1021/ja0656595 CCC: $33.50 © 2006 American Chemical Society

Table 1. Experimental and Calculated Bond Parameters (Å and deg)

	2·$2CH_2Cl_2$	**3**	*cis*-$Pd_2(C_6H_4PMe_2)_2(O_2CH)_2Cl_2$		[*cis*-$Pd_2(C_6H_4PMe_2)_2(O_2CH)_2$]$^{2+}$
spin			0	1	0
energy (au)			−2856.762	−2856.732	−1935.682
Pd−Pd	2.5434(4)	2.5241(9)	2.611	2.816	2.493
Pd−P(1)	2.2511(11)	2.2621(19)	2.293	2.330	2.356
Pd−O(1)	2.140(3)	2.103(4)	2.130	2.134	2.108
Pd−C(1)	2.021(4)	2.028(7)	2.063	2.041	2.029
Pd−Cl	2.4144(11)	2.4262(18)	2.510	2.569	

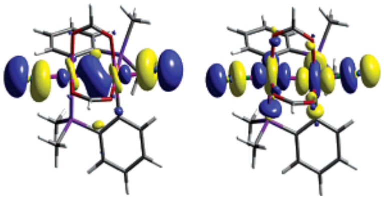

Figure 2. Frontier orbital plot of the HOMO (left) and the LUMO (right) for the model *cis*-$Pd_2(C_6H_4PMe_2)_2(O_2CH)_2Cl_2$ showing the Pd−Pd single bond along the Cl−Pd−Pd−Cl unit. Both are antibonding with respect to the Pd−Cl interaction. Positive and negative contours are in yellow and blue, respectively. Orbitals are drawn using an isosurface value of 0.04.

by axial Cl interactions is similar to that in $W_2(hpp)_4Cl_2$ compounds described recently,[12] and is due to metal-based σ interactions that are perturbed by the pσ orbitals of the Cl^- ions. This is shown in more detail elsewhere because of space limitations in a communication (see Supporting Information).

A time-dependent DFT calculation on the optimized geometry of the dication *cis*-$Pd_2(C_6H_4PMe_2)_2(O_2CH)_2Cl_2$ allowed the assignment of the low-energy transitions in **1** and **3**. The absorptions at ca. 500 nm correspond to the HOMO−LUMO transition (calcd at 488 nm, $f = 0.0657$) and the relatively strong absorption at about 381 nm ($\epsilon = 2.0 \times 10^4$ M^{-1} cm^{-1} for **3**) to a LMCT transition (calcd at 431 nm, $f = 0.2458$).

In conclusion, a general method has been found for the syntheses of singly bonded Pd_2^{6+} compounds having the formula *R,S-cis*-$Pd_2(C_6H_4PPh_2)_2(O_2CR)_2Cl_2$. When the alkyl group in the carboxylate ligands is an electron donor, the compounds are stable. Such stability opens the way for exploration of the chemistry of these rare Pd^{3+} compounds.[13] Of special interest will be the resolution of the optical isomers and production of supramolecular entities by replacement of the labile carboxylate ligands in a similar way as the Rh analogues[11] and exploration of possible catalytic potential, such as that in Pt_2^{6+} compounds.[3b]

Acknowledgment. At TAMU we thank the Robert A. Welch Foundation and Texas A&M University for financial support. At UV we thank MEC of Spain (Project NO. CTQ2005-08351) for financial assistance and a grant to I.O.K. We also thank Dr. F. Estevan for help with some experiments and Dino Villagrán for helpful discussions on DFT and the Laboratory for Molecular Simulation at TAMU for software.

Supporting Information Available: X-ray crystallographic data for **2**·$2CH_2Cl_2$ and **3** in CIF format and synthetic and experimental procedures, characterization data, an ellipsoid plot of **2**, additional discussion on the effect of the axial Cl atoms on the Pd−Pd distance and DFT results on the precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Robinson, W. T.; Fergusson, J. E.; Penfold, B. R. *Proc. Chem. Soc., London* **1963**, 116. (b) Bertrand, J. A.; Dollase, W. A.; Cotton, F. A. *J. Am. Chem. Soc.* **1963**, *85*, 1349.

(2) Cotton, F. A., Murillo, C. A., Walton, R. A., Eds.; *Multiple Bonds between Metal Atoms*, 3rd ed.; Springer Science and Business Media, Inc.: New York, 2005.

(3) (a) For Rh_2 compounds see for example: Doyle, M. P.; Ren, T. *Prog. Inorg. Chem.* **2001**, *49*, 113. (b) For Pt_2 compounds see for example: Matsumoto, K.; Ochiai, M. *Coord. Chem. Rev.* **2002**, *231*, 229.

(4) See for example: (a) Chifotides, H. T.; Dunbar, K. R. *Acc. Chem. Res.* **2005**, *38*, 146. (b) Matsumoto, K. In *Cisplatin: Chemistry and Biochemistry of a Leading Anticancer Drug*; Lippert, B., Ed. Wiley-VCH: Weinheim, Germany, 1999; p 455.

(5) See for example: (a) Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszczak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434. (b) Lippert, B. *Coord. Chem. Rev.* **1999**, *182*, 263 and references therein.

(6) Berry, J. F.; Bothe, E.; Cotton, F. A.; Ibragimov. S. A.; Murillo, C. A.; Villagrán, D.; Wang, X. *Inorg. Chem.* **2006**, *45*, 4396.

(7) Cotton, F. A.; Gu, J.; Murillo, C. A.; Timmons, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 13280.

(8) The compounds were synthesized as follows: A sample of the corresponding *cis*-$Pd_2(C_6H_4PPh_2)_2(O_2CR)_2$ compound (0.042 mmol) was suspended in 6 mL of diethyl ether and then cooled to −10 °C. A slight excess of $PhI{\cdot}Cl_2$ (13 mg, 0.055 mmol) in 1 mL of acetonitrile was added dropwise over a period of 5 min to the yellow suspension while the mixture was under stirring. The color changed from yellow to red. The reaction mixture was stirred at about −5 °C for 1 h. The pale red-orange solution was decanted off and the red precipitate was washed (3 × 3 mL) with a 5:1 v/v mixture of diethyl ether/acetonitrile and then dried to give the products in high yield (**1**, 90%; **2**, 78%; **3**, 96%). (For **1**) $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): −13.8 (s). ^1H NMR ($CDCl_3$, 20 °C): 8.22 (m, 2H), 7.74 (m, 1H), 7.42 (m, 4H), 7.20 (m, 4H), 6.99 (m, 1H), 6.80 (m, 1H), 6.74 (m, 1H), 1.14 (s, 3H). For characterization data for **2** and **3** see Supporting Information.

(9) Koshevoy, I. O.; Lahuerta, P.; Sanaú, M.; Ubeda, M. A. *J. Chem. Soc., Dalton Trans.* Accepted.

(10) Lucas, H. J.; Kennedy, E. R. *Org. Synth.* **1942**, *22*, 69.

(11) See for example: Cotton, F. A.; Murillo, C. A.; Stiriba, S.-E.; Wang, X.; Yu. R. *Inorg. Chem.* **2005**, *44*, 8223 and references therein.

(12) Cotton, F. A.; Donahue, J. P.; Gruhn, N. E.; Lichtenberger, D. L.; Murillo, C. A.; Timmons, D. J.; Dorn, L. O.; Villagrán, D.; Wang, X. *Inorg. Chem.* **2006**, *45*, 201.

(13) The compound $Pd_2(hpp)_4Cl_2$ (see ref 7) is one of a only a handful containing authentic Pd^{III} species. See (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999. (b) Jasper, Jr. S. A.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1998**, *37*, 6060 and references therein. (c) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Roberts, Y. V.; Lavery, A. J.; Schröder, M. *J. Organomet. Chem.* **1987**, *323*, 261. (d) McAuley, A.; Whitcombe, T. W. *Inorg. Chem.* **1988**, *27*, 3090. (e) Yamashita, M.; Miya, S.; Kawashima, T.; Manabe, T.; Sonoyama, T.; Kitagawa, H.; Mitani, T.; Okamoto, H.; Ikeda, R. *J. Am. Chem. Soc.* **1999**, *121*, 2321. (f) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1987**, 987. (g) Blake, A. J.; Gordon, L. M.; Holder, A. J.; Hyde, T. I.; Reid, G.; Schröder, *J. Chem. Soc., Chem. Commun.* **1988**, 1452. (h) Blake, A. J.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3363.

JA0656595