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The First Dirhodium Tetracarboxylate Molecule without Axial Ligation: New Insight into the Electronic Structures of Molecules with Importance in Catalysis and Other Reactions

F. Albert Cotton,*,† Elizabeth A. Hillard,† and Carlos A. Murillo*,†,‡

Department of Chemistry and Laboratory for Molecular Structure and Bonding, P.O. Box 30012 Texas A&M University, College Station, Texas 77842-3012 and Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

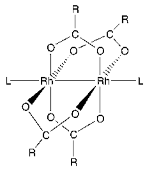
Received January 30, 2002

One of the most remarkable and important new classes of homogeneous catalysts,[1] which has been developed in recent years (and which is still growing in scope),[1b,c] is based on dirhodium tetracarboxylates and similar paddlewheel species with bridging ligands that are stereoelectronic equivalents of a carboxyl group (e.g., amidato anions). The first such catalysts to be employed were the acetate, $Rh_2(O_2CCH_3)_4(H_2O)_2$ and other $Rh_2(O_2CR)_4L_2$ compounds.[2] The acetate itself, the first compound of the entire class of Rh_2^{4+} compounds, was reported in 1962,[3] although the simplest member of the class, the tetraformate, had been reported, but incorrectly formulated, a little earlier.[4] As first reported, the structure, **I**, was somewhat imprecise although qualitatively correct; an accurate structure was published in 1970.[5]

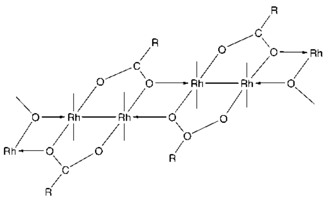
Their role as catalysts is far from the only reason for wide interest in compounds of the general type $Rh_2L^{br}_4$ (where L^{br} is any η^2-μ_2 ligand). Other important features of their chemistry relate to their potential as therapeutic agents,[6] their interactions with DNA and nucleosides,[7] their utility in forming supramolecular structures,[8] and the exceptional ability of $Rh_2(O_2CCF_3)_4$ to function as a powerful difunctional Lewis acid.[9]

A key factor in stabilizing $Rh_2(O_2CR)_4L_2$ compounds is the formation of a Rh−Rh single bond, and this bond length is generally in the range 2.34−2.41 Å; mononuclear rhodium(II) compounds are almost unknown.[10]

The work reported here, which provides important new data bearing on the question of electronic structure, begins with the solution of a synthetic problem. In *all* previously known $Rh_2(O_2CR)_4$ compounds, there has been axial ligation. Even two structurally characterized compounds, $Rh_2(O_2CC_3H_7)_4$ and $Rh_2(O_2CCF_3)_4$, whose formulas do not have exogenous ligands, have structures in which the molecules form infinite chains[11,12] in such a way that each molecule has its axial sites occupied by oxygen atoms from its neighbors, as shown in **II**. This means that all theoretical work bearing on how axial ligation affects the electronic structure of an $Rh_2(O_2CR)_4$ molecule has been untested by experiment.



I



II

For many years, the problem of isolating a paddlewheel compound, $M_2(O_2CR)_4$, with no axial ligands, especially when the metal is Cr or Rh, for which the $M_2(O_2CR)_4$ compounds have a very strong affinity for axial ligands, remained unsolved for several reasons. (1) Merely driving the solvent off of a crystalline $M_2(O_2CR)_4L$ or $M_2(O_2CR)_4L_2$ compound leaves an amorphous product from which structural information cannot be obtained. (2) It is impractical to design and synthesize a compound with an R group capable of blocking the axial positions completely. An R group that might be able to accomplish this would tend to be so bulky as to make the compound nonvolatile and to create a severe solubility problem in any solvent that is not able to be an axial ligand. (3) Solubility or volatility alone do not, of course, suffice because, as noted, these give crystals in which the molecules form self-ligating chains.

A workable strategy for overcoming these difficulties was found several years ago and applied successfully to give the first example of a crystalline $Cr_2(O_2CR)_4$ compound that was totally lacking in axial ligation.[13] That strategy was to employ an R group that meets two requirements:[14] (1) It can block the formation of chains of type **II**, even though the axial positions are still accessible to many ligands. (2) This R group renders the $M_2(O_2CR)_4$ compound soluble in one or more noncoordinating solvents from which crystals may be grown. In the case of $Cr_2(O_2CR)_4$, we used the R group 2,4,6-triisopropylphenyl. This choice has the added practical advantage that the needed acid, TiPBH, is commercially available at relatively low cost. We have now applied our strategy to what we believe is the second most difficult case, namely, $Rh_2(O_2CR)_4$, and have prepared the first dirhodium compound without axial ligation, $Rh_2(TiPB)_4$, **1**, where TiPB is the anion of 2,4,6-triisopropyl benzoic acid. We also report on the structure of **1**·2.90acetone, $Rh_2(TiPB)_4(Me_2CO)_2\cdot 0.90Me_2CO$, for comparison.

The reaction[15] between NaTiPB and $RhCl_3\cdot 3H_2O$ in C_2H_5OH at reflux temperature gave a solution with the characteristic green color of many $Rh_2(O_2CR)_4L^{ax}_2$ compounds[16] with axial oxygen donor molecules. Thus, this solution presumably contained $Rh_2(TiPB)_4(C_2H_5OH)_2$. After vacuum distillation of the solvent, redissolution of the solid in acetone, followed by subsequent cooling yielded **1**·2.90acetone. The blue-green crystals of **1**·2.90acetone were then placed under vacuum at 130 °C to drive off both the axial and interstitial acetone molecules, affording a yellow-green solid. This solid was recrystallized by slow evaporation of a hexane solution to yield crystals of **1**.[17]

In **1**, the four carboxylato groups bridge the singly bonded Rh_2^{4+} unit, giving the typical paddlewheel arrangement shown in Figure 1. The structure is similar (but not isomorphous) to that of the

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* To whom correspondence should be addressed. E-mail: (F.A.C.) cotton@tamu.edu; (C.A.M.) murillo@tamu.edu.
† Texas A&M University.
‡ University of Costa Rica.

10.1021/ja025760j CCC: $22.00 © 2002 American Chemical Society

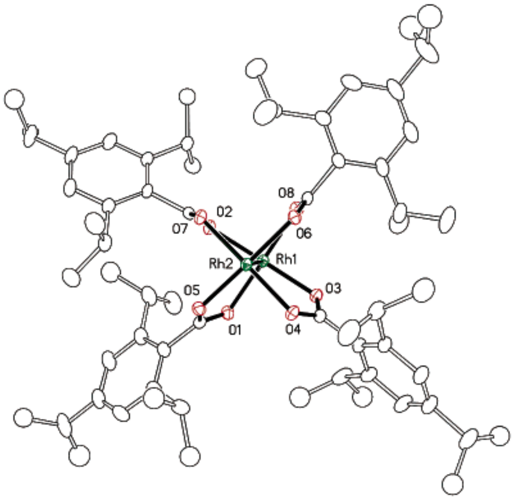

Figure 1. Thermal ellipsoid plot of **1**, shown at the 30% probability level. Hydrogen atoms and disordered groups of minor occupancy have been omitted for clarity. Selected bond distances (Å) for **1**: Rh−Rh, 2.3499(4), Rh(1)−O, 2.026[2], Rh(2)−O, 2.038[2]. The structure of **1**·2.90acetone is similar but two axial ligands are found with Rh−O distances (Å) of 2.295(3) and 2.32(1). Other relevant distances are: Rh−Rh, 2.3700(5), Rh(1)−O_{eq}, 2.043[3], Rh(2)−O_{eq}, 2.030[3].

chromium and molybdenum analogues.[13,18] A major difference is that **1** exhibits an internal twist angle of 13.15°, which is not present in the Cr and Mo compounds. This is not surprising, as the single bond in **1** does not entail any net δ bonding, while the short, quadruple bonds found in the chromium and molybdenum compounds assuredly do. In **1**·2.90acetone, it is clear that, although TiPB is bulky enough to block the carboxyl oxygen atoms and prevent the self-association found in $Rh_2(O_2CC_3H_7)_4$ and $Rh_2(O_2CCF_3)_4$, the axial position itself is not protected from coordination by acetone.

It is interesting that in **1** the Rh−Rh distance of 2.3499(4) Å is only *slightly* shorter, by ca. 0.02 Å, than that in **1**·2.90acetone, (2.3700(4) Å). Dichromium complexes have a strong affinity for such ligands, and the Cr−Cr bond in $Cr_2(TiPB)_4$ is dramatically shortened by ca. 0.4 Å when deprived of axial ligands. Although the Mo−Mo bond in $Mo_2(TiPB)_4$ also shows only a slight shortening of ca. 0.02 Å when compared to $Mo_2(O_2CCR)_4L_2$, it is well-known that dimolybdenum paddlewheel compounds do not have a strong affinity for axial ligands. It is now seen for the first time that the Rh−Rh bond length is also almost insensitive to the complete removal of axial ligands, even though the colors of $Rh_2(O_2CR)_4L_2$ compounds are very sensitive to the identity of the ligands L.

Because of the great variety of fascinating and important chemical properties possessed by $Rh_2(O_2CR)_4$ compounds, and the presence of Rh−Rh bonding, their electronic structures have been the subject of extensive investigation[19−21] by both experimental and theoretical methods. The earliest quantitative calculations, by Norman and Kolari,[20a] produced a $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$ configuration for $Rh_2(O_2CH)_4$ and a $\pi^4\sigma^2\delta^2\pi^{*4}\delta^{*2}$ for $Rh_2(O_2CH)_4(H_2O)_2$, each with a σ^* LUMO and a single bond. The ordering of the bonding orbitals in the two compounds was attributed to the interaction of the symmetric and antisymmetric combinations of the two H_2O σ lone pair orbitals with the Rh−Rh σ and σ^* orbitals, respectively, which destabilizes these orbitals relative to those of the anhydrous compound. This destabilization of the σ-bonding orbital corresponds to only a slight weakening of the Rh−Rh bond, which is what we have found comparing the structures of **1** and **1**·2.90acetone. Some EPR[22,23] spectroscopic confirmation of the Norman and Kolari results has already been published.

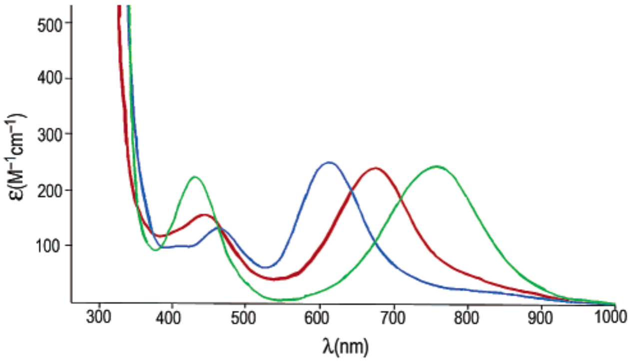

Figure 2. Electronic spectra of **1** (green), **1**·$2H_2O$ (red), and **1**·2acetone (blue) in hexanes. For **1**, $\lambda(\epsilon)$, nm(M^{-1} cm^{-1}): 760(251), 430(225), for **1**·$2H_2O$: 670(250), 445(164), for **1**·2acetone: 610(255), 460(123).

The assignment of the visible and UV spectra of $Rh_2(O_2CR)_4L_2$ compounds, which have a great variety of colors,[16] has been the subject of several studies.[20b,c] There are always two principal bands, A at 600−700 nm and B at around 450 nm. The assignment of the A band to the HOMO−LUMO, $\pi^*(Rh_2)\rightarrow\sigma^*(Rh_2)$, transition is strongly favored on the evidence previously available,[20b] while the assignment of band B is still uncertain, although it has been attributed to a $\pi^*(Rh-O)\rightarrow\sigma^*(Rh-O)$ transition.[20c]

Room-temperature electronic spectra for **1**, **1**·$2H_2O$, and **1**·2acetone are displayed in Figure 2. The pale yellow solution of **1** in hexanes gives a spectrum that shows a very low-energy peak at 760 nm. After a drop of water was added, the solution became pale green in color, and the low-energy peak shifted to 670 nm. A solution of **1**·2acetone in hexanes gave a spectrum where the peak appears at 610 nm. Contrary to ref 16, we observe a much lower-energy peak for the water adduct (670 vs 587 nm), perhaps reflecting the different media (hexanes vs H_2O). Band B displays an inverse behavior from band A: peaks appear at 430, 445, and 460 nm, for the anhydrous, hydrated, and acetone adduct, respectively. The lesser degree of sensitivity of band B toward the nature of the axial ligand suggests only a small Rh contribution to the orbitals involved, but we are not prepared to speculate any further. It should be pointed out, however, that the molar absorptivity of band B is slightly greater for the $Rh_2(TiPB)_4$ compound than for the bis-adducts, 225 vs 164 (water) and 123 (acetone) M^{-1} cm^{-1}, perhaps suggesting some ligand involvement.

The extremely low-energy of band A when there is no ligation at all provides further, and very persuasive evidence that the assignment to the $\pi^*(Rh_2)\rightarrow\sigma^*(Rh_2)$ is correct.

Acknowledgment. We thank Johnson Matthey for a generous loan of rhodium and Drs. Lee M. Daniels and Xiaoping Wang for crystallographic advice. We are grateful to the National Science Foundation for financial support. E.A.H. also thanks the NSF for a predoctoral fellowship.

Supporting Information Available: Thermal ellipsoid plots of **1** and **1**·2.90acetone and IR and NMR spectra (PDF) and crystallographic data in CIF format for compounds **1** and **1**·2.90acetone. This material is available free of charge via the Internet at http://www.acs.org.

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(14) (a) It is important to emphasize that the two requirements of bulkiness and the presence of solubilizing substituents must be met. It has been known that bulk alone was not enough to block the axial positions. For example, even with the very bulky carboxylate ligand 2,4,6-tri-tolylbenzoate, pyridine molecules had been found occupying the axial positions of the corresponding tetracarboxylate dirhodium units. See: Callot, H. J.; Albrecht-Gary, A.-M.; Al Joubbeh, M.; Metz, B.; Metz, F. *Inorg. Chem.* **1989**, *28*, 3633. (b) Further discussion on this topic will be provided on a follow-up paper in which we will show the road to the target compound and a plethora of $Rh_2(O_2CR)_4L_{2-n}$ compounds, $n = 0, 1, 2$. See: Cotton, F. A.; Hillard, E. A.; Liu, C. Y.; Murillo, C. A.; Wang, W.; Wang, X. Manuscript in preparation.

(15) Sodium ethoxide (0.17 g, 2.5 mmol) was dissolved in 30 mL of ethanol, and TiPBH (0.55 g, 2.2 mmol) was added. Once the TiPBH had dissolved, $RhCl_3 \cdot 3H_2O$ (0.15 g, 0.55 mmol) was added, affording an orange-brown suspension. The mixture was refluxed 18 h, yielding a green solution as well as a deposit of rhodium metal. The suspension was filtered over Celite and the solvent removed in vacuo. The blue-green solid was extracted with 20 mL of chloroform, dried in vacuo, and redissolved in 30 mL of acetone. The solution was concentrated to ca. 5 mL and placed in the freezer at −10 °C. After 12 h, a crop of green-blue parallelogram-shaped crystals had grown. The mother liquor was decanted, and the crystals were washed with 5 mL of acetone. The yield was 15%. Interstitial acetone (0.90 occupancy) was removed in vacuo at room temperature. Anal. for $C_{70}H_{104}Rh_2O_{10}$, Calcd (Found): C, 64.11 (64.11); H, 7.99 (7.70). ^1H NMR δ (ppm, in benzene-d_6) 7.037 (s, 8 H, aromatic), 3.306 (septet, 8 H, *o*-methyne), 2.683 (septet, 4 H, *p*-methyne), 1.832 (12 H, acetone methyl), 1.211 (d, 48 H, *o*-methyl) 1.139 (d, 24 H, *p*-methyl). IR (KBr): 3455, 2963, 2871, 1693, 1604, 1573, 1553, 1460, 1401, 1319, 1261, 1236, 1159, 1105, 1020, 944, 877, 811, 749, 650, 558, 506, 460 cm^{-1}. UV/vis $\lambda(\epsilon)$, nm(M^{-1} cm^{-1}) in hexane: 610(255), 460(123). Crystal data for **1**·2.90acetone: triclinic, space group $P1$, $a = 14.776(1)$ Å, $b = 16.429(1)$ Å, $c = 17.464(2)$ Å, $a = 65.457(1)°$, $\beta = 78.709(2)°$, $\gamma = 87.445(2)°$, $V = 3778.5(6)$ Å^3, $Z = 2$, $T = 213(2)$ K; cell parameters were refined with 5061 reflections within a 2θ range of 4.79−54.945°. A total of 13143 unique reflections ($2\theta \leq 50.00°$) were measured. Full-matrix least-squares refinement of F^2 (577 parameters) converged to R = 0.0684, wR2 = 0.1472 (all data).

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(17) Crystals of **1**·2.90acetone were dried in vacuo at 130 °C for 12 h. The solid changed color from blue-green to green to yellow-green. Yield was quantitative, based on $Rh_2(TiPB)_4(acetone)_2$. Anal. for $C_{64}H_{92}Rh_2O_8$, Calcd (Found): C, 64.31 (63.94); H, 7.76 (7.51). ^1H NMR δ (ppm, in CD_2Cl_2): 6.911 (s, 8 H, aromatic), 2.847 (m, 12 H, methyne), 1.202 (d, 24 H, *p*-methyl), 1.043 (d, 48 H, *o*-methyl). IR (KBr): 3429, 2963, 2871, 1609, 1569, 1551, 1460, 1401, 1318, 1261, 1157, 1102, 1023, 944, 874, 808, 750, 652, 564, 509, 466 cm^{-1}. UV/vis $\lambda(\epsilon)$, nm(M^{-1} cm^{-1}) in hexane: 760(251), 430(225). Crystal data for **1**: monoclinic, space group $P2_1/n$, $a = 13.6919(8)$ Å, $b = 30.832(2)$ Å, $c = 15.1279(9)$ Å, $\beta = 97.350(1)°$, $V = 6333.7(7)$ Å^3, $Z = 4$, $T = 213(2)$ K; cell parameters were refined with 5412 reflections within a 2θ range of 4.494−54.92°. A total of 14415 unique reflections ($2\theta \leq 55.00°$) were measured. Full-matrix least-squares refinement of F^2 (612 parameters) converged to R = 0.0789, wR2 = 0.1163 (all data).

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JA025760J