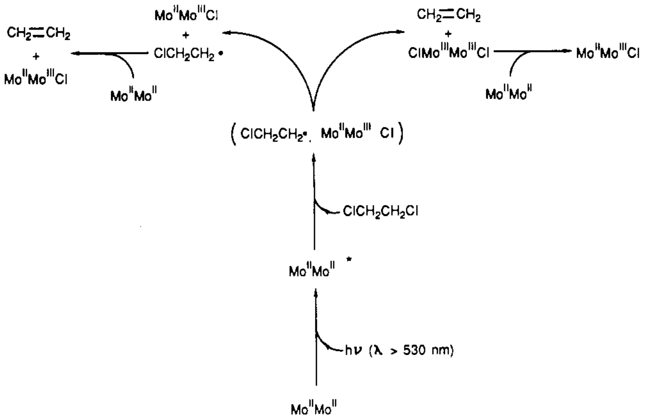

Figure 2. Proposed mechanism for the photochemical reduction of 1,2-dichloroethane by $Mo_2(O_2P(OC_6H_5)_2)_4$.

mixed-valence complex within the solvent cage, then the fully oxidized $Mo^{III}{}_2Cl_2$ complex is produced. The energetics of the dimolybdenum(II,II)/dimolybdenum(II,III) and dimolybdenum(II,III)/dimolybdenum(III,III) couples are such that comproportionation of $Mo^{III}{}_2Cl_2$ and unreacted dimolybdenum(II) diphenyl phosphate will yield the mixed-valence species. Thus, the stoichiometry of the photoreaction is independent of whether the radical reacts within or external to the solvent cage of the primary photoproducts.

Multielectron photochemistry has been observed from the lowest energy excited state of $M\overset{4}{-}M$ complexes. The dimolybdenum(II) diphenyl phosphate complex effectively promotes the two-electron reduction of halocarbon substrates upon excitation into the $\delta\delta^*$ excited state with the absorption of a single visible photon. Reaction from low-energy excited states of $M\overset{4}{-}M$ complexes has not been heretofore achieved, and hence the photoreduction of alkyl halides by $Mo_2(O_2P(OC_6H_5)_2)_4$ from its $\delta\delta^*$ excited state is a unique reaction pathway of $M\overset{4}{-}M$ complexes. The overall multielectron photochemistry is achieved by coupling the one-electron-oxidation-reduction chemistry of independent metal-metal cores. Efforts are currently underway to effect the multielectron transformation at a discrete electronically excited $M\overset{4}{-}M$ center.

Acknowledgment. We express our gratitude to Dr. Jay Winkler for providing us with access to the picosecond laser facilities at Brookhaven National Laboratory. Financial support of this work was provided by the National Science Foundation (Grant CHE-8705871). D.G.N. also gratefully acknowledges a Presidential Young Investigator Award administered by the National Science Foundation.

Registry No. DCE, 107-06-2; $Mo_2(O_2P(OC_6H_5)_2)_4$, 118494-24-9; $Mo_2(O_2P(OC_6H_5)_2)_4Cl$, 122967-43-5; $CH_2{=}CH_2$, 74-85-1; $(NH_4)_5Mo_2Cl_9$, 61583-95-7; $(C_6H_5O)_2PO_2^-$, 48168-03-2.

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Received June 19, 1989

Facile Regioselective Ligand Substitution for the In-Plane Bridging Acetates in Octakis(μ-acetato-*O*,*O'*)tetraplatinum(II)

Platinum(II) with d^8 electronic configuration has strong tendency to take a square-planar structure. Octakis(μ-acetato)tetraplatinum(II) (**1**), which was reported over a decade ago,[1,2] is unique in that each platinum(II) ion has an octahedral geometry and metal-metal direct bonds (metal-metal distance of 2.50 Å) exist. A complex with such unusual structural characteristics certainly deserves further investigations such as its electronic structure, route of formation, and various other properties, in view of recent extensive progress in studies of the chemistry of cluster complexes.

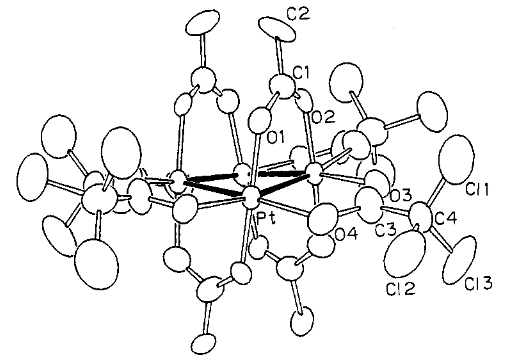

Figure 1. Structure of $Pt_4(\mu\text{-}CCl_3COO)_4(\mu\text{-}CH_3COO)_4$ showing the 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt-Pt = 2.49 (1); Pt-O(CH$_3$COO) = 2.01 (3), 2.00 (3); Pt-O(CCl$_3$COO) = 2.14 (5), 2.20 (4); Pt-Pt-Pt = 89.6 (1); Pt-Pt-O(CCl$_3$COO) = 85 (1), 84 (1); Pt-Pt-O(CH$_3$COO) = 82 (2), 84 (1), 94 (1), 97 (1).

While investigating reactivity of this cluster in solution, we found that only one of the two chemically different acetate groups is easily replaced by free carboxylate ions in solution. This paper reports the crystal structure of the new complex prepared by this facile regioselective substitution and kinetics of the acetate-exchange reaction as well as the theoretical studies on this unusual reactivity.

The substitution reaction is unexpectedly fast for the bridging carboxylates and is completed within a minute.[3] The new complex, $Pt_4(\mu\text{-}CH_3COO)_4(\mu\text{-}CCl_3COO)_4$ (**2**), was precipitated immediately from the solution of **1** in $CHCl_3$ by adding CCl_3COOH.[4] Figure 1 shows the ORTEP drawing of the new complex **2**,[5,6] which clearly shows that the in-plane acetates are replaced. Except for the difference in the in-plane ligands, the main structural features are very similar to those of the parent complex **1**. The Pt-Pt distance (2.49 Å) in **2** is similar to that in **1**. Somewhat longer in-plane Pt-O(CCl$_3$COO) distances than out-of-plane Pt-O(CH$_3$COO) distances are observed.

Kinetics of reaction 1 in $CDCl_3$ for the in-plane acetate exchange was studied by the ^1H NMR saturation transfer method.[7]

$$Pt_4(CH_3COO)_8 + {}^*CH_3COOH \rightarrow Pt_4(CH_3COO)_4({}^*CH_3COO)_4 + CH_3COOH \quad (1)$$

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(3) An example of the fast bridging carboxylate exchange: Teramoto, K.; Sasaki, Y.; Migita, K.; Iwaizumi, M.; Saito, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 446-452.

(4) Other carboxylic acids such as C_6H_5COOH and CF_3COOH also give similar complexes, e.g. $Pt_4(\mu\text{-}CH_3COO)_4(\mu\text{-}RCOO)_4$, on reacting with **1**.

(5) The complex **2** was recrystallized from CH_2Cl_2. Anal. Calcd for $Pt_4(\mu\text{-}CH_3COO)_4(\mu\text{-}CCl_3COO)_4{\cdot}2CH_2Cl_2$: C, 11.78; H, 0.89; Cl, 30.90. Found: C, 11.67; H, 0.90; Cl, 29.68.

(6) X-ray analysis: The compound $Pt_4(\mu\text{-}CH_3COO)_4(\mu\text{-}CCl_3COO)_4{\cdot}2CH_2Cl_2$ crystallizes in the tetragonal space group $I\bar{4}2d$, with a = 13.909 (2) Å, c = 23.372 (4) Å, V = 4522 (1) Å^3, and Z = 4. With the use of 626 unique reflections ($F_o > 3\sigma(F_o)$) collected at room temperature with Mo Kα (λ = 0.709 26 Å) radiation up to $2\theta = 50°$ on a Rigaku AFC-5R diffractometer, the structure was solved by the heavy-atom method and refined by block-diagonal least-squares techniques with anisotropic temperature factors for non-hydrogen atoms. The current R value is 0.053. Atomic positional and thermal parameters are provided as supplementary material.

(7) (a) Forsen, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2892-2901. (b) Recent application of this method: Cho, H.; Iwashita, T.; Ueda, M.; Mizuno, A.; Mizukawa, K.; Hamaguchi, M. *J. Am. Chem. Soc.* **1988**, *110*, 4832-4834 and references cited therein.

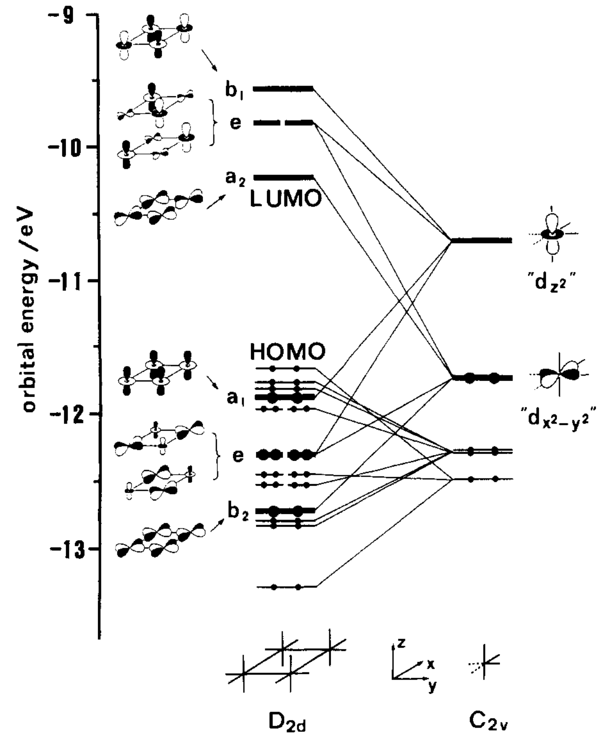

Figure 2. MO interaction diagram for $Pt_4(HCOO)_8$ (**3**) and its quaterly fragment.[12] MO's shown in thick lines are those involving Pt 6dσ orbitals.

Exchange rate is linearly dependent on the complex concentration and rate law 2 is derived.[8] At 25 °C, k_0 and k_1 are 0.36 s^{-1} and 4.4 M^{-1} s^{-1}, respectively, per each reaction site. Substitution of CD_3COO^- for the out-of-plane acetates was not at all observed after a month at 25 °C for the solution of **1** in $CDCl_3$ containing CD_3COOD.

$$\text{rate} = 4(k_0 + k_1[CH_3COOH])[\text{complex}] \qquad (2)$$

EHMO calculations[9] have been carried out for a model compound, $Pt_4(HCOO)_8$ (**3**), and its fragments,[10,11] where the Pt–O distances are assumed to be 2.01 (out-of-plane) and 2.16 Å (in-plane) as observed for **1**.[2] The MO study reasonably justifies the presence of the Pt–Pt bond and the regioselective substitution reaction.

The MO interaction diagram in Figure 2 shows levels near HOMO–LUMO, which are all associated with Pt 6d orbitals. The MO's shown in thick lines are those derived from dσ orbitals ("$d_{x^2-y^2}$" and "d_{z^2}")[12] of each quaterly fragment. These MO's are associated with the metal–ligand bonds, and therefore their character should relate to the regioselective lability. Four low-lying MO's of these are occupied by eight dσ electrons and result in the Pt–Pt single bonds.[13] With regard to metal–ligand interactions, all four orbitals are of antibonding type, and therefore the occupation of these MO's should weaken the metal–ligand bonds. The lower three orbitals are predominantly of $d_{x^2-y^2}$ character and are antibonding for in-plane ligands, and only the highest one is of d_{z^2} character and antibonding for out-of-plane ligands. The out-of-plane ligands are therefore more tightly bound to each metal ion than the in-plane ligands. The overlap population for the out-of-plane Pt–O bond in **3** was found to be larger than that for the in-plane Pt–O bond.[14]

These MO results indicating that the out-of-plane Pt-O bond is stronger than the in-plane bond are consistent with the observed regioselective ligand substitution as well as with the observed Pt–O distances.[1,2]

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 63612503) on the Priority Area of Dynamic Interactions and Electronic Processes of Macromolecular Complexes and a Grant-in-Aid for Scientific Research (No. 01430009) from the Ministry of Education, Science and Culture, Japan. We are grateful to Dr. M. Ebihara of the Institute for Molecular Science for the X-ray analysis.

Registry No. **1**, 60383-57-5; **2**·$2CH_2Cl_2$, 123358-56-5; **3**, 123380-75-6; Pt, 7440-06-4.

Supplementary Material Available: Tables of atomic positional and thermal parameters and interatomic distances and bond angles for $Pt_4(\mu\text{-}CH_3COO)_4(\mu\text{-}CCl_3COO)_4\cdot 2CH_2Cl_2$ (2 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Received September 7, 1989

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(8) NMR spectra were recorded on a JEOL JNM GSX-270 FT-NMR spectrometer. The reaction process can be observed by two independent approaches, by irradiating either the methyl signal of the coordinated acetates (in plane) at 2.45 ppm or that of the free acetic acid at 2.02 ppm. Two rate constants at a given reaction condition are in reasonable agreement to each other (maximum difference, 9%).

(9) Calculations were performed with the program FORTICON8: Howell, J.; Rossi, A.; Wallace, D.; Haraki, K.; Hoffmann, R. *QCPE* **1977**, No. 344.

(10) Orbital energies of the fragment MO's were estimated from the calculation in which all the overlaps between Pt atoms were set to be zero.

(11) For discussions on fragment MO's, see: Elian, M.; Hoffman, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. The quarterly fragment MO's of our complex are similar to those of MCl_4 rather than those of $M(CO)_4$. It should be noted that the coordination axes are taken in a different way from those in the above literature.

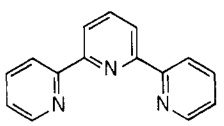
(12) The "$d_{x^2-y^2}$" and "d_{z^2}" orbitals actually contain some contributions of s and p orbitals, but for simplicity are designated as such.

(13) These four MO's are of bonding type with respect to Pt–Pt interaction, giving four Pt–Pt single bonds to stabilize the Pt_4 core, although the strong interaction takes place only in the b_2 orbital.

(14) This was the case even when the in- and out-of-plane Pt–O distances were assumed to be equal (2.01 or 2.16 Å).

Redox Regulation in Ruthenium(II) Complexes of 2,6-Bis(*N*-pyrazolyl)pyridine Ligands: Synthetically Versatile Analogues of 2,2′:6′,2″-Terpyridine

The redox reactions of ruthenium(II) complexes containing 2,2′:6′,2″-terpyridine (**1**) have been extensively investigated.[1-10]



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