Energy Capture by a Tetranuclear Metal Cluster Complex. Synthesis and Characterization of $PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})[Si(OMe)_3](\mu\text{-H})$ and Its Metastable Photoisomer

Richard D. Adams,* Jeffrey E. Cortopassi, Jeffrey Aust, and Michael Myrick

Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

Received April 28, 1993

UV irradiation is one of the principle modes for activation of metal carbonyl cluster complexes.[1,2] Generally, this produces ligand elimination or the cleavage of metal–metal bonds. We have now discovered a novel photoinduced reorganization of the metal–metal bonding in a tetranuclear metal cluster complex that yields an energetically excited metastable isomer, which was isolated and structurally characterized.

The complex $PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})[Si(OMe)_3](\mu\text{-H})$ (**1**, dppm = bis(diphenylphosphino)methane) was obtained in 50% yield from the reaction of $Os_3(CO)_{10}(\eta^1\text{-dppm})[Si(OMe)_3](\mu\text{-H})$ with $Pt(COD)_2$ at 68 °C.[3] Complex **1** was characterized crystallographically and was found to consist of a planar butterfly cluster of four metal atoms, with the platinum atom located in one of the "hinge" sites, see Figure 1.[5] The cluster is nearly planar, with the Pt,Os(1), Os(3)–Pt,Os(2),Os(3) dihedral angle of 176.4°. The dppm ligand bridges the Pt–Os bond to the wingtip atom Os(2), and a $Si(OMe)_3$ ligand is coordinated to the other wingtip atom Os(1) that is bonded to the platinum atom. A hydride ligand bridges the Pt–Os(1) bond. Compound **1** contains only 60 valence electrons, which is 2 fewer than the total required by the 18-electron rule for each metal atom.

When compound **1** was irradiated (UV) for 6 h, it was converted to an isomer $(PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})[Si(OMe)_3](\mu\text{-H}),\ \mathbf{2})$.[6] Compound **2** slowly converts back to **1** under thermal conditions. A kinetic analysis showed the transformation to be first order in **2**, with the activation parameters $\Delta H^* = 24.3$ kcal/mol and $\Delta S^* = 6.0$ eu. Its half-life is 4.6 h at 47 °C.[7] At 25 °C, the reconversion is sufficiently slow that **2** can be isolated in a pure form. In fact, it has been possible to grow crystals of **2** and to characterize it structurally by an X-ray diffraction analysis.[8] An ORTEP diagram of the molecular structure of **2** is shown in Figure 2. This molecule also consists of a planar $PtOs_3$ butterfly cluster of four metal atoms, but in contrast to **1**, the platinum atom lies in a

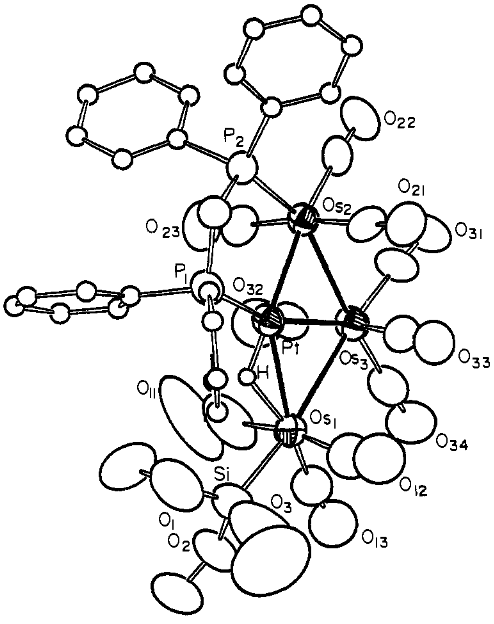


Figure 1. ORTEP diagram of $PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})[Si(OMe)_3](\mu\text{-H})$ (**1**). Selected interatomic distances (Å) are Pt–Os(1) = 2.738(1), Pt–Os(2) = 2.633(1), Pt–Os(3) = 2.769(1), Os(1)–Os(3) = 3.102(1), Os(2)–Os(3) = 2.954(1), Os(1)–Si = 2.366(6). The Pt,Os(1),Os(3)–Pt,Os(2),Os(3) dihedral angle is 176.4°.

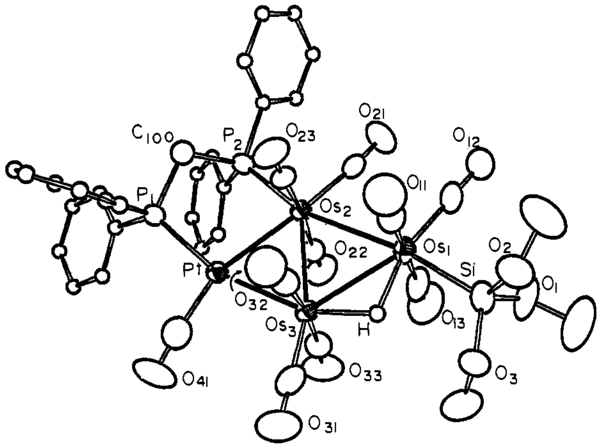


Figure 2. ORTEP diagram of $PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})[Si(OMe)_3](\mu\text{-H})$ (**2**). Selected interatomic distances (Å) are Pt–Os(2) = 2.7574(8), Pt–Os(3) = 2.6254(9), Os(1)–Os(2) = 3.099(1), Os(1)–Os(3) = 2.8881(8), Os(2)–Os(3) = 2.9143(9), Os(1)–Si = 2.388(4). The Pt,Os(2),Os(3)–Os(1),Os(2),Os(3) dihedral angle is 171.9°.

---

(1) (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (b) Bensten, J. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 4530. (c) Desrosiers, M. F.; Wink, D. A.; Trautman, R.; Friedman, A. E.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1917. (d) Foley, H. C.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 7176.

(2) Poë, A. J. In *Metal Clusters*; Moskovits, M., Ed.; Wiley-Interscience: New York, 1986.

(3) $Os_3(CO)_{10}(\eta^1\text{-dppm})[Si(OMe)_3](\mu\text{-H})$ was prepared in 73% yield by the addition of dppm to $Os_3(CO)_{10}(NCMe)[Si(OMe)_3](\mu H)$[4] in refluxing methylene chloride over a 5-h period. IR ν_{CO} (cm^{-1} in hexane): 2107 (w), 2064 (m), 2043 (s), 2021 (vs), 2010 (m), 2002 (s), 1988 (w), 1975 (w). ^1H NMR (δ in $CDCl_3$): 7.57–7.16 (m, phenyl, H, 20H), 3.68 (dd, CH_2, 2H), 3.43 (s, OCH_3, 9H), –19.11 (dd, Os–H, $^2J_{P\text{-}H} = 11.4$ Hz, $^4J_{P\text{-}H} = 0.7$ Hz, 1H). Red $PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})[Si(OMe)_3](\mu\text{-H})$ (**1**) was obtained in 50% yield by the addition of $Pt(COD)_2$ (0.059 mmol) to $Os_3(CO)_{10}(\eta^1\text{-dppm})[Si(OMe)_3](\mu\text{-H})$ in a refluxing 50-mL hexane solution for 10 min. The product **1** was isolated by TLC on silica gel using a 7/4 hexane/acetone solvent mixture. IR ν_{CO} (cm^{-1} in hexane): 2096 (m), 2058 (m), 2028 (m), 2016 (vs), 1997 (m), 1960 (w). ^1H NMR (δ in $CDCl_3$): 7.57–7.22 (m, Ph, 20H), 4.67 (t, CH_2, $^2J_{P\text{-}H} = 11.0$ Hz, $^3J_{Pt\text{-}H} = 58.8$ Hz, 2H), 3.20 (s, OCH_3, 9H), –2.01 (dd, Os–H–, Pt, $^1J_{Pt\text{-}H} = 770.3$ Hz, $^2J_{P\text{-}H} = 6.6$ Hz, $^3J_{P\text{-}H} = 1.2$ Hz, 1H). UV/visible λ_{max} (ϵ) (in CH_2Cl_2): 384 (11 120 M^{-1} cm^{-1}), 438 (8007 M^{-1} cm^{-1}), 520 (3481 M^{-1} cm^{-1}) nm. Anal. Calcd (found) for **1**: C, 29.4 (30.2); H, 2.08 (2.11).

(4) Adams, R. D.; Cortopassi, J. E.; Pompeo, M. P. *Inorg. Chem.* **1992**, *31*, 2563.

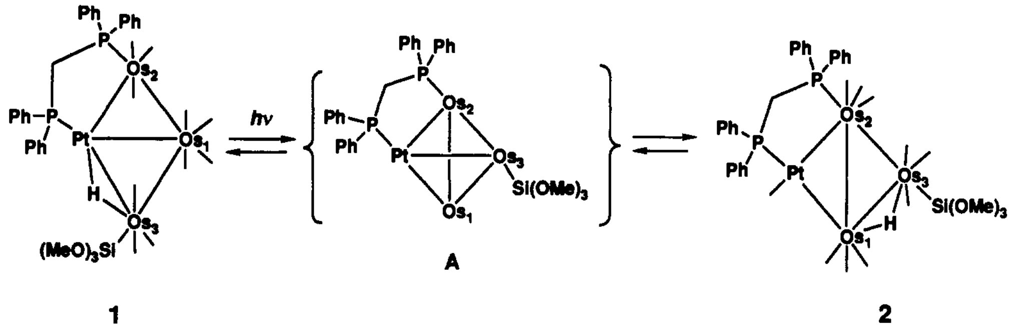
(5) Crystal data for **1**: space group = $P2_1/c$, $a = 15.838(4)$ Å, $b = 12.768(4)$ Å, $c = 22.820(5)$ Å, $Z = 4$, 3473 reflections, $R = 0.034$. All diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. An empirical absorption correction was applied to the data.

(6) A 41.2-mg sample of **1** was dissolved in 40 mL of a hexane/methylene chloride 3/1 solution and irradiated (high-pressure Hg lamp) for 6 h. The product was separated from unreacted **1** by TLC using a 7/4 (v/v) hexane/acetone solvent to yield 14.2 mg of brown $PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})[Si(OMe)_3](\mu\text{-H})$ (**2**) (43% yield based on **1** consumed). IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2096 (w), 2050 (m), 2012 (vs), 1998 (m, sh), 1969 (w), 1945 (m). ^1H NMR (δ in $CDCl_3$): 7.42–7.29 (m, phenyl H, 20H), 5.16 (t, CH_2, $^2J_{P\text{-}H} = 11.0$ Hz, 2H), 3.55 (s, OCH_3, 9H), –14.52 (dd, Os_2–H, $^2J_{P\text{-}H} = 12.0$ Hz, $^3J_{P\text{-}H} = 1.8$ Hz, 1H). UV/visible λ_{max} (ϵ) (in CH_2Cl_2): 402 (9532 M^{-1} cm^{-1}), 490 (4210 M^{-1} cm^{-1}) nm. Anal. Calcd (found) for $\mathbf{2}\cdot C_6H_6$: C, 32.4 (32.6); H, 2.35 (2.16). Samples of **1** that were heated to 80 °C for 12 h showed no evidence of formation of **2** by NMR spectroscopy, indicating that **2** is formed by a true photo process.

(7) The transformations of **2** to **1** at five different temperatures were followed by ^1H NMR spectroscopy. No other products were observed spectroscopically. Plots of ln[**2**] vs time produced straight lines. $\Delta H^* = 24.3$ kcal/mol, $\Delta S^* = 6.0$ eu, $t_{1/2} = 4.6$ h at 47 °C.

0002-7863/93/1515-8877$04.00/0

Scheme I



wingtip site and is not bonded to the osmium atom containing the $Si(OMe)_3$ ligand.

The structure of **2** implies that the **1**-to-**2** transformation occurred by a major rearrangement of the metal–metal bonding. This could have occurred by the formation of a tetrahedral-like intermediate (**A**) through the formation of a bond between the wingtip metal atoms Os(2) and Os(3) in **1**, see Scheme I. In **A**, all of the metal atoms would obey the 18-electron rule. Butterfly–tetrahedral cluster transformations have been observed previously in platinum-containing tetranuclear metal clusters, and sometimes both structural types exist together in equilibrium.[9] Intermediate **A** could be transformed to **2** by cleavage of the Pt–Os(3) bond accompanied by the shift of a CO ligand to the Pt atom. The thermal transformation of **2** back to **1** could also occur via a tetrahedral-like intermediate by reformation of the Pt–Os(3) bond followed by an opening of the Os(2)–Os(3) bond. The intermediates need not be identical. In fact, it seems likely that the intermediate created photolytically might be electronically excited. Indeed, **2** itself is thermodynamically unstable with respect to **1**. Although the transformation produces almost no side products, the quantum yield for the transformation of **1** to **2** measured at 345 nm is very low, 0.003. It was found that the rate of formation of **2** could be enhanced by a factor of 3 when polychromatic radiation was used in the presence of the sensitizer, acetophenone.[10,11]

The most important feature of this study is that it demonstrates for the first time that a metal cluster complex can capture energy by undergoing a transformation to a metastable species. Materials that efficiently capture photon energy and then release it thermally after an appreciable delay could, in principle, be of value in energy conversion and solar energy storage processes.[11,12]

Acknowledgment. This research was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for **1** and **2** (22 pages); listing of observed and calculated structure factors for **1** and **2** (50 pages).

---

(8) Crystal data for $\mathbf{2}\cdot C_6H_6$: space group = $P\bar{1}$, a = 12.966(2) Å, b = 15.952(3) Å, c = 12.626(3) Å, α = 104.03(2)°, β = 101.14(2)°, γ = 72.34(1)°, Z = 2, 3789 reflections, R = 0.028.

(9) Braunstein, P.; de Méric de Bellefon, C.; Bouaoud, S.-E.; Grandjean, D.; Halet, J.-F.; Saillard, J.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 5282.

(10) The quantum yield was measured at 345 nm on 5.0×10^{-3} M solutions of **1** in C_6D_6 solvent by irradiation with an Innova 300 argon ion continuous wave laser that delivered 8.7×10^{-7} einstein/s.

(11) Phillippopoulos, C.; Marangozis, J. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 458.

(12) (a) Lichtin, N. N. *CHEMTECH* **1980**, *10*, 252. (b) Sweet, E. M.; King, R. B.; Hanes, R. M.; Ikai, S. *Adv. Chem. Ser.* **1979**, *173*, 244. (c) Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677. (d) Kutal, C. *Adv. Chem. Ser.* **1977**, *168*, 158. (e) Fendler, J. *J. Phys. Chem.* **1985**, *89*, 2730.