corporation of deuterium was followed by ^1H and ^2H NMR spectroscopy. Exchange of deuterium into the terminal vinyl position was about half-complete after 10 min at room temperature, and exchange into the secondary vinyl position was about 10 times slower. After 27 days, ^2H NMR spectroscopy showed that all of the vinyl positions of **4** were fully deuterated but the methyl group of **4** had less than 5% deuterium. This indicates that the agostic intermediate III must undergo in-place rotation and deprotonation several thousand times faster than the agostic interaction is broken.

The possibility that the agostic intermediate III might be significantly more stable than its diastereomer IV and thus inhibit exchange into the methyl group was tested by examining deuterium incorporation into the 2-methylpropene complex $C_5H_5(CO)_2Re(CH_2{=}CMe_2)$ (**5**)[7] since its agostic intermediate V is symmetric (Scheme III). The exchange rate of deuterium into **5** with CF_3CO_2D was approximately the same as that as into **3**, but deuterium was found only in the vinyl position of **5** and not in the methyl groups.

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Unsaturation in a High-Nuclearity Metal Carbonyl Cluster Complex. Synthesis, Structures, and Interconversions of $Pt_2Os_4(CO)_{12}(COD)_2$ and $Pt_2Os_4(CO)_{11}(COD)_2$

Richard D. Adams* and Wengan Wu

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

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Summary: The two new platinum-osmium carbonyl cluster complexes $Pt_2Os_4(CO)_{12}(COD)_2$ (**1**) and $Pt_2Os_4(CO)_{11}(COD)_2$ (**2**) were obtained from the reaction of $Pt_2Os_4(CO)_{18}$ with 1,5-cyclooctadiene (COD) at 97 °C. Both compounds consist of a bicapped Os_4 tetrahedron. Compound **1** is coordinatively saturated, while compound **2** is coordinatively unsaturated. The latter contains several unusually short metal-metal bonds and readily adds CO to give **1** in good yield.

An important feature of coordinatively unsaturated complexes is their ability to add new ligands under mild conditions.[1] Although there are relatively few examples of coordinatively unsaturated cluster complexes,[2] this feature may play a key role in the future development of these compounds as catalysts.[3] We now wish to report a new example of coordination unsaturation in a high-nuclearity metal carbonyl cluster complex and the observation that the complex can add and eliminate CO without the formal cleavage of a metal-metal bond.

From the reaction of $Pt_2Os_4(CO)_{18}$[4] with 1,5-cyclooctadiene (COD) in refluxing heptane solvent we have isolated the two new complexes $Pt_2Os_4(CO)_{12}(COD)_2$ (**1**; 55% yield) and $Pt_2Os_4(CO)_{11}(COD)_2$ (**2**; 9% yield).[5] The structures of both complexes have been determined by single-crystal X-ray diffraction methods, and ORTEP drawings of their molecular structures are shown in Figure

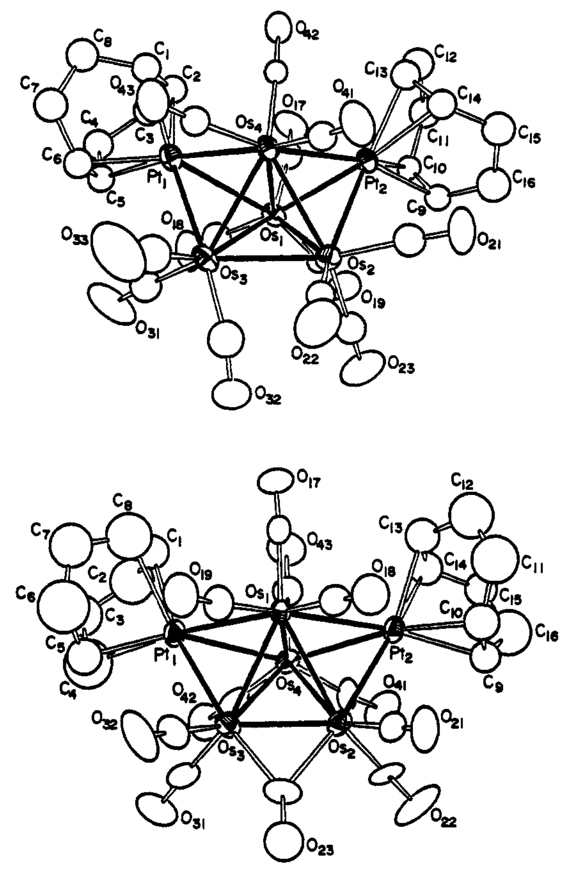

Figure 1. ORTEP diagrams of $Pt_2Os_4(CO)_{12}(COD)_2$ (**1**; top) and $Pt_2Os_4(CO)_{11}(COD)_2$ (**2**; bottom) showing 50% probability thermal ellipsoids. Selected bond distances (Å) for **1** [**2**] are as follows: Os(1)–Os(2) = 2.859 (1) [2.835 (1)], Os(1)–Os(3) = 2.759 (1) [2.834 (1)], Os(1)–Os(4) = 2.832 (1) [2.705 (1)], Os(1)–Pt(1) = 2.975 (1) [2.857 (1)], Os(1)–Pt(2) = 2.737 (1) [2.883 (1)], Os(2)–Os(3) = 2.786 (1) [2.530 (1)], Os(2)–Os(4) = 2.785 (1) [2.831 (1)], Os(2)–Pt(2) = 2.855 (1) [2.614 (1)], Os(3)–Os(4) = 2.868 (1) [2.838 (1)], Os(3)–Pt(1) = 2.741 (1) [2.609 (1)], Os(4)–Pt(1) = 2.711 (1) [2.865 (1)], Os(4)–Pt(2) = 2.784 (1) [2.840 (1)].

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[5] A 36-mg amount of $Pt_2Os_4(CO)_{18}$ was allowed to react with 0.36 mL of COD in heptane solvent at 97 °C for 4.5 h. The products were isolated by TLC on silica gel. The first band yielded 20.5 mg of red-brown **1** (55%), and the second band yielded 3.6 mg of yellow-brown **2** (9%). IR for **1** (ν_{CO}, cm^{-1}; in hexane): 2059 (m), 2022 (w), 2005 (vs), 1955 (w), 1944 (w). IR for **2** (ν_{CO}, cm^{-1}; in CH_2Cl_2): 2014 (vs), 1991 (vs), 1982 (sh), 1952 (w), 1926 (vw), 1844 (vw, br). ^1H NMR for **1** (δ; in $CDCl_3$): 5.69 (t, 8 H, $^2J_{Pt-H}$ = 61.5 Hz), 2.36 (m, 8 H), 1.92 (m, 8 H). ^1H NMR for **2** (δ; in C_6D_6): 5.03 (s, br, 4 H), 4.33 (s, br, 4 H), 1.36 (s, br, 8 H), 0.71 (s, br, 8 H).

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1.[6] Both compounds are structurally similar and consist of a central tetraosmium core arranged in a tetrahedral geometry with two Pt(COD) groupings capping triangular faces. The M_6 cluster is thus very similar to that of the parent osmium cluster $Os_6(CO)_{18}$.[7]

Complex 1 is electronically saturated and exhibits no unusual distortions. Each osmium atom contains three terminal carbonyl ligands. All six osmium–osmium bonds lie within the range 2.786 (1)–2.868 (1) Å, which is similar to the range of values found in $Os_6(CO)_{18}$ (2.732–2.808 Å) for the central Os_4 grouping.[7] The osmium–platinum distances span a fairly wide range (2.711 (1)–2.975 (1) Å), but none are unusually long or unusually short.[8]

On the other hand, complex 2, which has one less carbonyl ligand than 1, is electron-deficient by the amount of two electrons. The structure of 2 shows that several of its metal–metal bonds are considerably shorter than those in 1. For example, the Os(2)–Os(3) distance in 2 is 2.530 (1) Å. It is over 0.25 Å shorter than the corresponding distance in 1 and is nearly 0.20 Å shorter than the corresponding Os–Os distance observed in $Os_6(CO)_{18}$.[7] It is one of the shortest Os–Os distances ever observed in an osmium cluster complex.[10] Os–Os triple-bond distances range from 2.182 (1) Å[12] to 2.467 (1) Å.[13] Although the Os(2)–Os(3) bond contains a bridging carbonyl ligand, structural characterizations of the few osmium cluster complexes that have been shown to contain bridging carbonyl ligands show that these bridging ligands do not produce a significant shortening of osmium–osmium bonds.[14] In addition, three of the other metal–metal bonds in 2 are also substantially shorter than those in 1. These are Os(1)–Os(4) (2.705 (1) Å in 2 vs 2.832 (1) Å in 1), Pt(1)–Os(3) (2.609 (1) Å in 2 vs 2.741 (1) Å in 1), and Pt(2)–Os(2) (2.614 (1) Å in 2 vs 2.855 (1) Å in 1). It is believed that the shortening of the metal–metal bonds in 2 is a direct consequence of its electronic unsaturation, although differences in the coordination of the COD ligands to the platinum atoms may also affect these and some of the other metal–metal bond distances. The shortness of the Os(2)–Os(3) bond suggests the unsaturation is greatest at this position.

We have found that the reactivity of 2 is also indicative of unsaturation. For example, when 2 was exposed to CO (1 atm/25 °C) in CH_2Cl_2 solvent, it was converted to 1 in 84% yield in 15 min. The thermal decarbonylation of 1 to 2 at 97 °C in heptane solvent is fraught with much decomposition, but 2 can be obtained in low yield (7%). In contrast, compound 2 was obtained cleanly from 1 when its solutions were exposed to UV radiation at 25 °C in the presence of a nitrogen purge (77% yield after 11 h). We expect that compound 2 will show enhanced reactivity to the addition of a wide range of small molecules. These studies are in progress.

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Supplementary Material Available: Tables of crystal data, positional parameters, intramolecular bond distances and angles, and anisotropic thermal parameters for the structural analysis of compounds 1 and 2 (23 pages); listings of structure factor amplitudes (40 pages). Ordering information is given on any current masthead page.

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(6) Dark brown crystals of 1 were grown from solution in a CH_2Cl_2/hexane solvent mixture by slow evaporation of solvent at 10 °C. Crystal data for 1: space group $P\bar{1}$, $a = 11.217$ (2) Å, $b = 17.295$ (3) Å, $c = 8.866$ (2) Å, $\alpha = 92.88$ (2)°, $\beta = 105.82$ (2)°, $\gamma = 104.23$ (2)°, $Z = 2$. Dark brown crystals of 2 were grown from solution in a CH_2Cl_2/hexane solvent mixture by slow evaporation of solvent at 25 °C. Crystal data for 2: space group $P2_1/c$, $a = 8.622$ (2) Å, $b = 21.917$ (5) Å, $c = 16.767$ (3) Å, $\beta = 95.61$ (2)°, $Z = 4$. Both structures were solved by a combination of direct methods and difference Fourier techniques. Compound 1 was refined with 3084 reflections to the final R values $R = 0.038$ and $R_W = 0.043$. Compound 2 was refined with 2698 reflections to the final R values $R = 0.033$ and $R_W = 0.034$. Diffraction data were collected on a Rigaku AFC6S diffractometer by using Mo Kα radiation. Calculations were performed on a MICROVAX II computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Data were corrected for absorption.

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Reaction of Diethylaluminum Chloride with Diaza-18-crown-6. Synthesis and Molecular Structure of $[(EtAl)_2 \cdot \text{diaza-18-crown-6}]^{2+}$: A Novel Aza Crown Ether Stabilized Square-Pyramidal Coordination of Aluminum

Mark F. Self, William T. Pennington, Janeen A. Laske, and Gregory H. Robinson*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634-1905

Received November 2, 1990

Summary: The crystalline complex $[(EtAl)_2 \cdot \text{diaza-18-crown-6}][EtAlCl_3]_2$ has been prepared and its structure determined by X-ray diffraction. The $[(EtAl)_2 \cdot \text{diaza-18-crown-6}]^{2+}$ cation contains two five-coordinate aluminum atoms, both residing in square-pyramidal environments. The title compound appears to have resulted from an interesting disproportionation of diethylaluminum chloride.

The interactions of aluminum species with oxygen-based ligands represent one of the fundamental cornerstones of organoaluminum chemistry. The last decade has witnessed an impressive body of work in this area. Particularly noteworthy are studies concerning the organoaluminum chemistry of oxygen-based macrocyclic ligands, crown ethers. Seminal studies by Atwood et al.[1,2] demonstrated the unique ability of organoaluminum moieties, upon adduct formation, to greatly distort crown ethers, forcing them to assume unusual exodentate conformations. Re-

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