

DIOSMACYCLOALKANES AS MODELS FOR THE FORMATION OF  
HYDROCARBONS FROM SURFACE METHYLENES

Progress Report

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4/1/88 to 3/31/89

In collaboration with Oren Anderson, Phil Vergamini (Los Alamos), and Allen Larson (Los Alamos), we have obtained a neutron diffraction data set for  $\text{Os}_2(\text{CO})_8(\mu\text{-C}_2\text{H}_4)$ . While the structure is still being solved, it is already clear that the hybridization at both of the ethylene carbons is  $\text{sp}^3$ . Our first interpretation of our liquid crystal NMR results had suggested a very acute H-C-H angle. As a result of the neutron diffraction results we are reexamining the structural implications of the liquid crystal data; it appears that the dipolar coupling constants must be averaged over the two equivalent conformations of the diosmacyclobutane ring, whereas we had been treating the molecule system as though it had an averaged flat structure. We have also obtained  $^{13}\text{C}$  liquid crystal data for  $\text{Os}_2(\text{CO})_8(\mu\text{-C}_2\text{H}_4)$ . Liquid crystal NMR ( $^{13}\text{C}$  as well as  $^1\text{H}$ ) spectra have been obtained for  $\text{Os}(\text{CO})_4(\text{C}_2\text{H}_4)$  and its solution structure determined, in order to test our methodology on a molecule with a rigid structure.

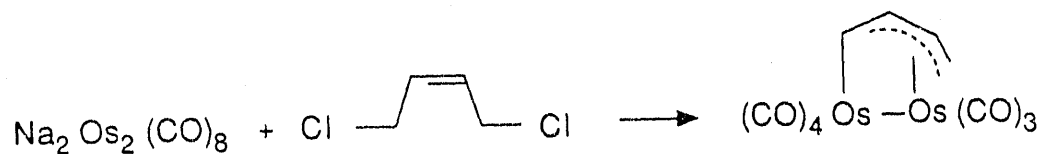
In conjunction with our collaborators Chris Anson (Cambridge) and Norman Sheppard (University of East Anglia), the normal modes of  $\text{Os}(\text{CO})_4(\mu\text{-C}_2\text{H}_4)$  and its deuterated and  $^{13}\text{C}$ -labelled isotopomers have been completely assigned. A partial vibrational analysis of  $\text{Os}_2(\text{CO})_8(\mu\text{-propene})$ ,  $\text{Os}_2(\text{CO})_8(\text{trans-2-butene})$ , and  $\text{Os}_2(\text{CO})_8(1\text{-butene})$  has been completed.

In collaboration Martyn Poliakoff and Jim Turner at Nottingham,  $\text{Os}_2(\text{CO})_8$  has been generated by the photolysis of  $\text{Os}_2(\text{CO})_9$  in inert gas matrices. The three principal carbonyl stretching frequencies of  $\text{Os}_2(\text{CO})_8$  (all terminal) have been assigned.

We have prepared  $\text{Os}(\text{CO})_4(\mu\text{-CH}_2\text{CH}_2\text{CH}_2)$  and its 3,3-dideuterio analog. In the course of this work the reaction of  $\text{Na}_2\text{Os}(\text{CO})_4$  with a number of 1,3-propanediol derivatives has been examined. 1,3-Propanediol ditosylate afforded much better yields of the osmacycle than did either the ditriflate or diiodide. 2,2-Dideutero-1,3-propanediol ditosylate was used to prepare the deuterium-labelled osmacyclobutane.  $\text{Os}_2(\text{CO})_8(\mu\text{-CH}_2\text{CH}_2\text{CH}_2)$  and its dideuterio analog have been

prepared from  $\text{Na}_2\text{Os}_2(\text{CO})_8$  and 1,3-diiodopropane. 1,3-Propanediol ditosylate and ditriflate are inefficient electrophiles for diosmacyclopentane synthesis. These species will allow us to examine the mechanism of metallacycle decomposition.

In the course of trying to prepare a diosmacyclohexene from  $\text{Na}_2\text{Os}_2(\text{CO})_8$  and *cis*-1,4-dichloro-2-butene we have isolated a novel allylosmium species.



In addition to IR,  $^1\text{H}$  NMR and MS analysis, the product has been characterized by 2-D  $^1\text{H}$  COSY and  $^1\text{H}$ - $^{13}\text{C}$  HETCOR NMR techniques.

#### List of Publications

After January 1988

Acknowledging DOE Support

"Synthesis of  $\text{Os}_2(\text{CO})_8(\mu\text{-CHCH}_3)$  from a Geminal Ditriflate and its Reversible Carbonylation to a Ketene-bridged Diosmacycle", R.M. Bullock, R.T. Hembre, J.R. Norton\*, *J. Am. Chem. Soc.*, **1988**, *110*, 7868.

" $[\text{Os}_2(\text{CO})_8(\mu_2\text{-}\eta^2\text{-C}_2\text{H}_4)]$  as a Vibrational Model for 1,2-di- $\sigma$  Chemisorbed Ethylene on Metal Surfaces", C.E. Anson, B.F.G. Johnson, J. Lewis, D.B. Powell, N. Sheppard, A.K. Bhattacharyya, B.R. Bender, R.M. Bullock, R.T. Hembre, and J.R. Norton\*, *J. Chem. Soc. Chem. Commun.*, **1989**, in press.

Outline of Plans for 4/1/89 to 3/31/89  
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We will finish examining the mechanism of olefin loss from substituted and unsubstituted 1,2-diosmacyclobutanes. We hope to be able to distinguish a dissociative mechanism from a mechanism involving associative displacement of an olefin which has "slipped" onto a single osmium from its original bridging position. We will compare the dissociation rate constant for  $\text{Os}_2(\text{CO})_8(\mu\text{-CH}_2\text{CH}_2)$  with that for  $\text{Os}_2(\text{CO})_8(\mu\text{-CD}_2\text{CD}_2)$  and thereby determine the secondary isotope effect for ethylene dissociation. The results will be compared to the values predicted from the vibrational frequencies of various molecules (i.e.,  $\text{Os}(\text{CO})_4\text{C}_2\text{H}_4$ , free  $\text{C}_2\text{H}_4$ ) which model various possible transition states.

We will study the chemistry of  $\text{Os}_2(\text{CO})_9$ , including the mechanism of CO loss and substitution. We will thus be able to make the  $^{13}\text{C}$ -labelled  $\text{Os}_2(\text{CO})_9$  necessary in order for our collaborators (Poliakoff and Turner, Nottingham) to generate various isotopomers of  $\text{Os}_2(\text{CO})_8$  by photolysis in low temperature matrices. The results will enable us to determine the structure of  $\text{Os}_2(\text{CO})_8$ .

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