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ORGANOMETALLIC AND SURFACE CHEMISTRY OF MIXED-METAL SYSTEMS

Progress Report

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Abstract

Three new SO_2 complexes of metal cluster compounds were prepared: $[PPN][HFe_3(CO)_9SO_2]$, $[PPN]_2[Ru_3CO_9SO_2]$ and $[PPN]_2[Ru_3(CO)_7(SO_2)_3]$. The x-ray structures were determined for two of these and the transformation of bound SO_2 to cluster bound SO and S ligands was investigated.

Progress

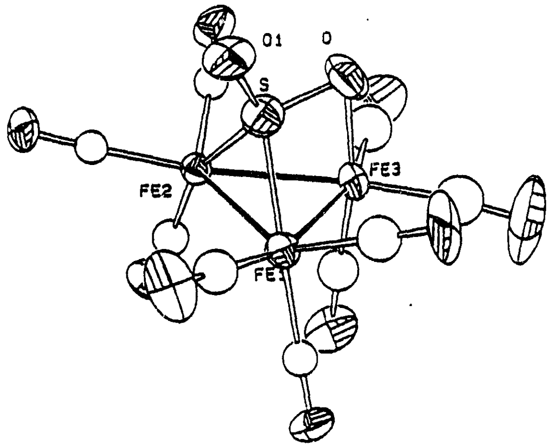
One of our current research goals is to gain basic information about the reaction patterns displayed by SO_2 in clusters. Of special interest is the reductive cleavage of SO_2. By analogy with our findings in CO chemistry one approach is to explore the electrophilic attack at the oxygen of cluster-bound SO_2 and the subsequent reductive cleavage of the S-O bond. Another point under investigation is the modes of bonding of SO_2 to tri and higher nuclearity clusters of group 8 metals.

A graduate student on this DOE-sponsored research, Gail Karet, has found that sulfur dioxide reacts with $[PPN]_2[HFe_3(CO)_{11}]$, to produce the cluster $[PPN][HFe_3(CO)_9SO_2]$, for which the x-ray crystal structure reveals the unusual μ_3,η^2-SO_2 bonding pattern, I. This SO_2 ligand exhibited one very long S-O distance of 1.62(1) Å and one shorter distance (1.434(9)Å) which was nearly the S-O distance found in free SO_2. The cluster $[PPN]_2[Ru_3(CO)_{11}]$ was found to react with SO_2 to produce two different SO_2 clusters, $[PPN]_2[Ru_3(CO)_9SO_2]$ and $[PPN]_2[Ru_3(CO)_7(SO_2)_3]$. The x-ray structure of the former again reveals the presence of the μ_3,η^2-SO_2 ligand. The IR and ^{13}C NMR spectroscopy of the latter indicate the presence of one μ_3,η^2-SO_2 ligand and two more conventionally bonded SO_2 ligands that bridge Ru atoms through sulfur. The only other SO_2 complexes of anionic clusters were prepared several years ago in our laboratory by Paula Bogdan. The attraction of anionic SO_2 clusters is their potential reactivity with nucleophiles on the O atom in a manner analogous to the extensive chemistry of CO.

The cluster $[PPN][HFe_3(CO)_9SO_2]$ reacts with acetyl chloride to form a species, which appears to contain S-O-Ac. Reduction of this species leads to the formation of the known cluster $[PPN]_2[Fe_3(CO)_9S]$ with cleavage of both S-O bonds. The infrared and ^{13}C NMR spectra of the product of the reduction were found to match those in the literature for

$[PPN]_2[Fe_3(CO)_9S]$. Reduction of I without prior acetylation leads to cleavage of only one S-O bond to form the cluster $[PPN][Fe_3(CO)_9SO]$ in moderate yields. This compound, which was characterized by x-ray diffraction, provides a rare example of SO bound to a cluster.

The reactions of anionic metal clusters containing SO_2 is indeed rich with reactions involving the SO_2 ligand. Further studies are under way to explore the scope of this chemistry. Special attention will be paid to role of multimetal binding and O bonding in the transformations of SO_2.



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