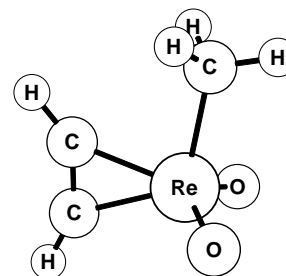


MICROWAVE SPECTRA AND MOLECULAR STRUCTURE OF ACETYLENEMETHYLDIOXORHENIUM, A RHENIUM METALACYCLOPROPENE^a

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The molecular structure for ((η^2 -acetylene)methyl)dioxorhenium (ACMDO) was obtained by measuring and analysing the rotational spectra for 14 isotopomers. This appears to be the first gas-phase measurement for a rhenium metalacetylene, and the first structural data on this compound. This complex is closely related to reaction intermediates in methyltrioxorhenium(MTO) and OsO_4 catalysed oxidation reactions. These reactions are very important in industrial chemical production and for syntheses of chiral products. Only a few alkyne complexes of transition metals in high oxidation states are known and even fewer have been structurally characterized. The microwave spectra were measured in the 4-11 GHz range using a Flygare-Balle-type pulsed-beam microwave spectrometer. Rotational constants and rhenium quadrupole coupling tensors were obtained for all isotopomers. The acetylene ligand structure is modified and exhibits partial sp^2 hybridization. The C-C bond length is increased by 0.08 Å to 1.29 Å. The H-C-C interbond angles are reduced from 180° to 141°, and 152°. The quadrupole splitting patterns and systematic changes in the quadrupole coupling tensors were very helpful in making positive assignments.



^aSupported by THE NATIONAL SCIENCE FOUNDATION