

MICROWAVE MEASUREMENTS OF STRUCTURE CHANGES FOR LIGAND MOLECULES BOUND TO TRANSITION METALS ^a

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Precise values for structural parameters for transition metal complexes have been obtained from high-resolution PBFT microwave measurements. The changes in structural parameters for the small organic molecule ligands are relatively large and well-determined. Results for $C_2H_4-Os-(CO)_4$, $C_2H_4-Fe-(CO)_4$, $C_2H_2-Re-(O)_2CH_3$, $C_6H_6-Cr-(CO)_3$ and $C_4H_6-Fe-(CO)_3$ will be discussed and compared. For the Ethylene Osmium Tetracarbonyl complex, the experimental ethylene C-C bond length is 1.432 Å, which falls between the free ethylene value of 1.339 Å and the ethane value of 1.534 Å. The angle between the plane of the CH₂ group and the extended ethylene C-C bond (out-of-plane angle) is 26°. Ethylene structural changes are larger for the Os complex than for the similar Fe complex. For Acetylene Methyl dioxoRhenium, 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 146°, and 147°. The planar, D_{6h} structure of free benzene is changed to a C_{3v} structure with alternating C-C bond lengths due to interaction with Cr-(CO)₃ in the complex. The structural changes are small but significant, since the benzene reactivity is changed. For Butadiene Iron Tricarbonyl, the terminal CH₂ groups are rotated by 28° out of the butadiene plane and the CH₂ plane is folded away from the butadiene C1-C2 axis by 27° in a direction away from the iron atom. Free butadiene has a trans planar conformation, much different from the distorted cis conformation in the complex. These structural changes are usually accompanied by significant changes in reactivity, which has proved useful for transition metal catalysts and metal containing enzymes.

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