

I. Transition Metal Complexes and Radicals – Recent Accomplishments.

The extremely high sensitivity and high resolution of the pulsed-beam, Fourier transform microwave spectrometer (PBFT microwave spectrometer) systems have opened the door for numerous new structural measurements on larger and less stable molecules and complexes. Our research has focused on transition metal complexes, since this class of compounds plays so many important roles in the chemical industry and in biological systems, and hydrogen bonding interactions.

A) PROTON TUNNELING IN THE FORMIC ACID - PROPIOLIC ACID DIMER

We have reported¹ microwave measurements of concerted proton tunneling splittings for the formic acid – propiolic acid dimer, measured in the frequency range 4 to 14 GHz. Both a-dipole rotational transitions and b-dipole ro-vibrational transitions were measured. All of the observed transitions were split into doublets by the effects of the concerted tunneling of the two acid protons. The small splittings of 1 to 1.5 MHz for the a-dipole transitions are due to the differences in rotational constants for the upper and lower tunneling states. The b-dipole transitions are combination transitions with change in rotational state and tunneling state and provide direct information on the tunneling splittings. No similar splittings were observed when deuterium was substituted for either or both of the hydrogen bonding protons. The formic acid-propionic acid and formic acid dimers both have symmetric double well potentials and display double hydrogen bonding and local structure which is very similar to the A-T base pair of DNA (see Fig. 2).

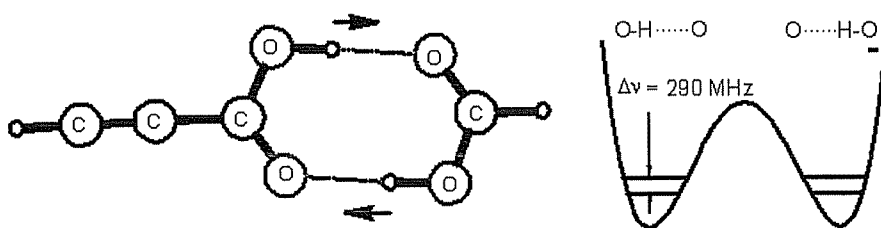


Figure 2 Proton tunneling for the formic acid – propionic acid dimer.

We expect that these simpler hydrogen bonded dimers should be useful models for some of the tunneling effects that influence the dynamics of base-pair interactions. Spectra for six isotomers of the formic acid-propionic acid, doubly hydrogen bonded complex were

measured and used to determine structural parameters for the complex. A least squares fit of the rotational constants reveal that the complex is planar and that the monomer centers of mass are separated by $3.87(2)\text{\AA}$ with O---H hydrogen bond lengths of 1.67\AA . The (corrected) tunneling splitting is 290 MHz.

B) 1,2 AZABORINE

This project has been completed and results published². The first microwave spectra for the unusual and elusive aromatic molecule, 1,2-dihydro-1,2-azaborine (azaborine) have been measured, providing accurate rotational constants, nitrogen and boron quadrupole coupling strengths and important bond lengths and other structural parameters. Azaborine BNC_4H_6 is an interesting case because it is closely related to benzene, the quintessential aromatic molecule. 1,2-Dihydro-1,2-azaborine represents a hybrid structure between the archetypical organic aromatic molecule, benzene, and its inorganic counterpart, borazine. The measured rotational constants were used to accurately determine coordinates for the substituted atoms and provide sufficient data to determine most of the important structural parameters for this molecule. The experimental bond lengths determined are: $R(\text{B-N}) = 1.45(3)\text{\AA}$, $R(\text{B-C}) = 1.51(1)\text{\AA}$, and $R(\text{N-C}) = 1.37(3)\text{\AA}$. The c-axis nitrogen nuclear quadrupole coupling component, the planar structure and nearly equal heavy-atom bond lengths all support the aromatic character of this molecule. perpendicular to the c-axis for nitrogen is consistent with other nitrogen-containing aromatic molecules, supporting the aromatic character of 1, 2-dihydro-1,2-azaborine. this molecule.

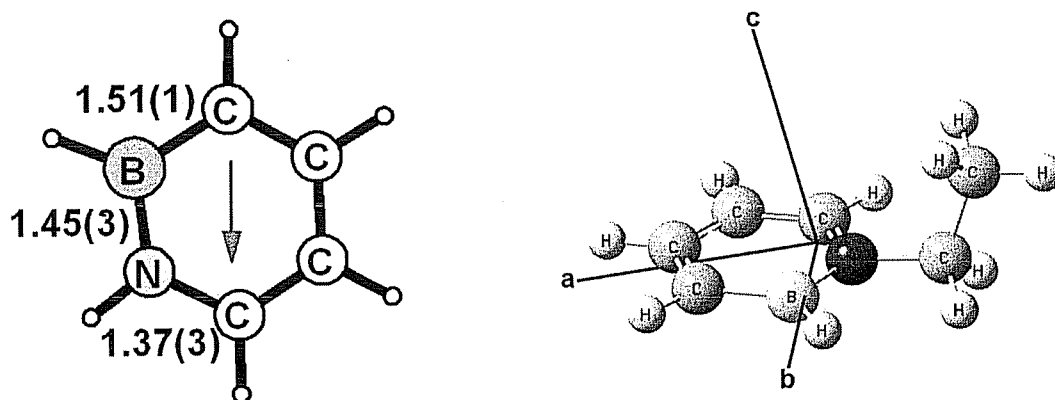


Fig. 3. Structures for 1,2-dihydro-1,2-azaborine and *N*-Et-1,2-azaborine

New microwave spectra and quadrupole coupling constants are also reported³ for 1-ethyl-1,2-dihydro-1,2-azaborine (*N*-Et-1,2-azaborine). *N*-Et-1,2-azaborine is a molecular derivative of 1,2-dihydro-1,2-azaborine, a six-membered aromatic heterocycle in which a single C-C fragment of benzene is replaced by an isoelectronic B-N fragment.^{4,5} Results of the measurements and calculations indicate that the basic molecular structure of *N*-Et-1,2-azaborine is similar to ethylbenzene

C) SPECTRA AND STRUCTURE FOR ETHYLENE OSMIUM TETRACARBONYL

Changes in the structure of ethylene on coordination to $\text{Os}(\text{CO})_4$ were accurately measured and reported recently.⁶ Rotational spectra of seven isotopomers of $\text{Os}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_4)$, were measured in the 4 -12 GHz. Olefin-transition metal complexes of this type occur extensively in recent organic syntheses and serve as important models for transition states in the metal-mediated transformations of alkenes. The changes in the structure of ethylene on

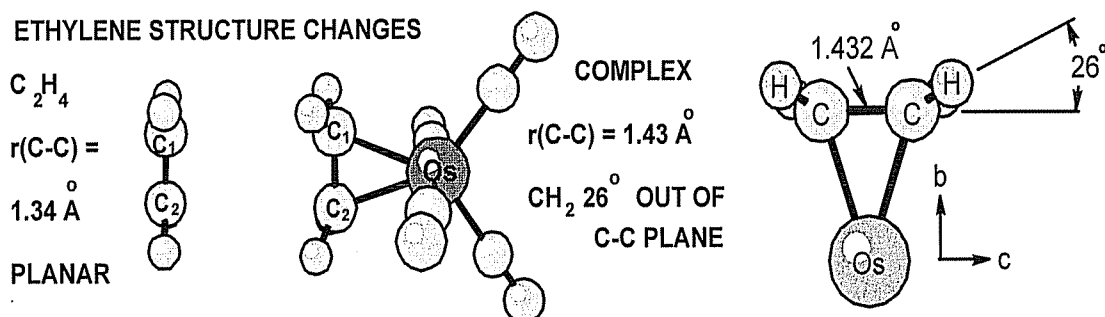


Figure 4. Changes in the structure of ethylene when bonded to osmium

coordination are large and well-determined. 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 CH_2 group and the extended ethylene C—C bond ($\angle_{\text{out-of-plane}}$) is $26.0(3)^\circ$, indicating that this complex is better described as a metallacyclopropane than a π -bonded olefin-metal complex. The new results on this osmium complex were compared with earlier work on the similar complex, tetracarbonyl ethylene iron ($\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_4)$).⁷ The ethylene structural changes upon coordination to the metal were found to be larger for the ethylene-osmium complex than for the analogous ethylene-iron complex, consistent with the expected greater π donation for the osmium atom. It should be noted that our best DFT structure calculations provided quite accurate structure predictions for both the ethylene-osmium⁶, and the ethylene-iron⁷ complexes.

D) Design and Construction of a 1 to 10 GHz Pulsed-beam, Fourier Transform Spectrometer

This research involved the design and construction of a microwave spectrometer system for measurements of rotational transition frequencies for transition metal complexes, hydrogen-bonded complexes, and other molecules in the 1 to 10 GHz region of the microwave spectrum. This type of spectrometer system was first constructed by Balle and Flygare⁸ and many additional spectrometers of this type have been constructed, but nearly all reported measurements have been made at frequencies greater than 4 GHz. In order to maintain uniform sensitivity over a wide tuning range the basic Fabry-Perot TEM₀₀-mode cavity design was retained. Large mirrors are required to obtain high Q values at 1 GHz, and the present system has 1.22 m (4 ft.) mirrors, providing excellent Q-values down to 800 MHz. Q-values range from 15,000 to 40,000. The 5 ft.-dia. vacuum chamber is pumped with a Varian NHS-35 diffusion pump. Labview programs are used to control spectrometer and tune the mirrors. A homodyne-type⁹ microwave system is used for signal detection. Molecular signals were first obtained using this spectrometer in December 2009. The first successful measurement: was the $5_{33} \rightarrow 5_{32}$ transition at 2210.969 MHz of difluorobenzene. After some optimization of parameters, the $0_{00}-1_{01}$ line of difluorobenzene, 3551.755 MHz could be observed with a SINGLE BEAM PULSE (see Fig. 1) and a transition was observed at 904.039 MHz.

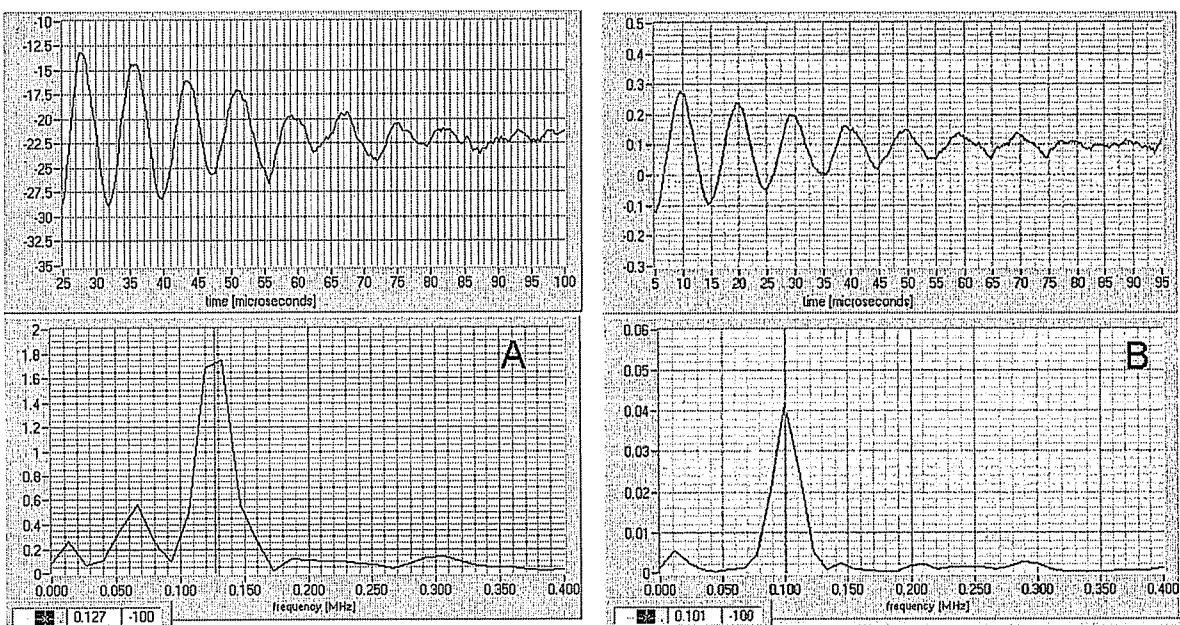


Figure 1. A) Single-shot measurement ($0_{00}-1_{01}$ difluorobenzene, 3551.755 MHz),
B) Low-frequency line, difluorobenzene $1_{10}-1_{11}$ at 904.039 MHz

A summary of low-frequency monomer transitions measured are given in Table 1. "Pulses" is the number of beam pulses required to obtain S/N = 3/1. For these measurements, a single General Valve, Series 9 pulse valve was used, pulsing at 10 Hz. It is clear that substantial improvements in sensitivity and S/N can be obtained by using multiple valves, or a much larger valve and increasing the pulse rate. For the formic acid – propiolic acid dimer, 8 new transitions were measured in the 1.7 to 3.6 GHz range. 25 pulses were required for the strongest transition at 3460.75 MHz.

Table 1. Transitions measured with the low-frequency spectrometer for monomers.

Difluorobenzene			Butadiene-iron-tricarbonyl			Iodobenzene		
	Freq(MHz)	pulses		Freq(MHz)	Pulses		Freq(MHz)	Pulses
$1_{10}-1_{11}$	904.0330	50	$0_{00}-1_{01}$	1891.7255	15	$0_{00}-1_{01}$	1130.5288	700
$5_{33}-5_{32}$	2210.9685	20	$0_{00}-1_{10}$	1963.4607	15	$0_{00}-1_{01}$	1522.7385	250
$2_{12}-2_{11}$	2712.1060	5	$1_{11}-2_{12}$	3759.0951	2	$0_{00}-1_{01}$	1522.7445	25
$0_{00}-1_{01}$	3551.7550	1	$1_{01}-2_{02}$	3776.2009	1			
			$1_{10}-2_{11}$	3807.8065	2			
			$1_{11}-2_{21}$	3974.2981	10			

E) MICROWAVE SPECTRUM OF FORMIC ACID-FORMAMIDE DIMER

The rotational spectrum of 5 isotopomers of the complex formed between formic acid and formamide have been measured and analyzed. The rotational constants and quadrupole coupling strengths were obtained. Using the 15 rotational constants obtained with HC^{13}OOH , HCOOD , DCOOD and $\text{H}_2\text{N}^{15}\text{CHO}$ isotopologes, key structural information was obtained from a least squares fit. The $\text{R}(\text{CO}\cdots\text{HN})$ bond distance of 1.77 Å and $\text{R}(\text{OH}\cdots\text{OC})$ bond distance of 1.81 Å and the $\angle(\text{OCH})$ of formic acid of 121° were obtained. The "best fit" $\angle(\text{OCH})$ of formic acid is quite different from the monomer value of 106.9°. Density functional theory using B3PW91, HCTH407 and TPSS and MP2 calculations were performed using 6-311++G(d,p) and the results are compared to experimentally determined parameters. This work was done in collaboration with a high school teacher, Bryan Sargus. The manuscript is in preparation.

F) ARGON-CYCLOPENTADIENYL THALLIUM – WEAKLY-BOUND COMPLEX

This is the FIRST report¹⁰ of microwave measurements on a weakly-bound complex formed between a noble gas and an organometallic molecule. Accurate structures were obtained from the measurements and MP2 calculations on this complex. A pseudodiatom model, with Lennard-Jones potential yields an approximate experimental binding energy of 339 cm^{-1} . The argon atom is located on the *a*-axis of the $\text{C}_5\text{H}_5\text{Tl}$ monomer, directly opposite from the thallium metal atom. The measured separation distance between argon and the cyclopentadienyl ring is $R = 3.56 \text{ \AA}$. It is interesting to note that the DFT calculations yielded a repulsive potential energy function.

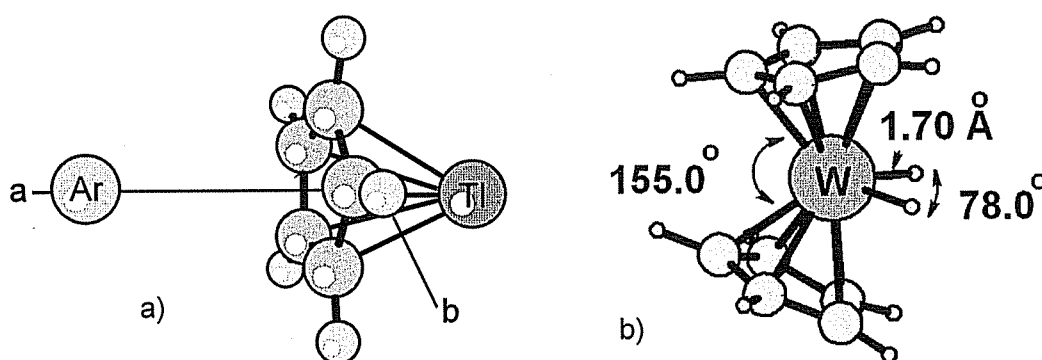
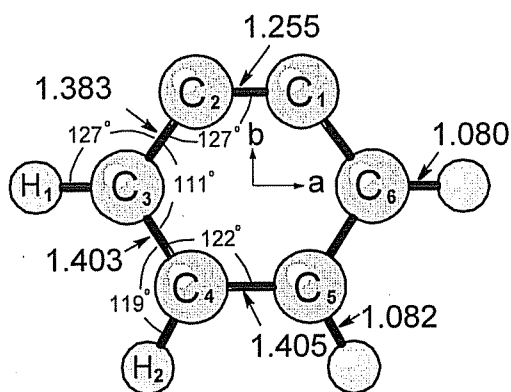


Figure 5. a) The basic structure of the argon-cyclopentadienyl thallium dimer. b) Molecular Structure for the $(\text{C}_5\text{H}_5)_2\text{WH}_2$ complex.

G) BIS(η^5 -CYCLOPENTADIENYL)TUNGSTEN DIHYDRIDE To the best of our knowledge, this work marks the first microwave study of a bent metallocene complex. Microwave spectra for 11 isotopomers of bis(η^5 -cyclopentadienyl)tungsten dihydride $((\text{C}_5\text{H}_5)_2\text{WH}_2)$ were recorded in the 5-14 GHz region and used to obtain a nearly complete 3D structure for this complex.¹¹ Molecular structure parameters obtained are the W-H bond length, $r(\text{W-H}) = 1.70(1) \text{ \AA}$, the H-W-H bond angle, $\angle(\text{H-W-H}) = 78.0(20)^\circ$, the W-Cp centroid distance, $r(\text{W-Cp}) = 1.94(2) \text{ \AA}$, the angle made by the Cp centroids with tungsten, $\angle(\text{Cp-W-Cp}) = 155(5)^\circ$, and the average C—C bond length, $r(\text{C-C}) = 1.43(2) \text{ \AA}$. The hydrogen atom separation is $r(\text{H-H}) = 2.14(1) \text{ \AA}$, indicating that this is clearly a “classical dihydride” rather than an “ η^2 -dihydrogen” complex. Comparing the Mo and W bis(cyclopentadienyl) dihydrides with the cyclopentadienyl tricarbonyl hydrides,^{12,13} it is observed that the $r(\text{M-H})$ are significantly

longer for the tricarbonyl hydride complexes, and the $r(\text{M-Cp})$ for $(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}$ is significantly longer than that of $(\text{C}_5\text{H}_5)_2\text{WH}_2$.

H) ACCURATE STRUCTURE FOR O-BENZYNE A complete, highly accurate and precise near-equilibrium structure for the radical o-benzyne has been obtained by measuring rotational spectra for 7 isotopomers, and including calculated vibrational averaging corrections in the analysis.¹⁴ The *ab initio*-calculated vibrational averaging corrections were applied to the measured A_0 , B_0 and C_0 rotational constants and the resulting experimental, near-equilibrium rotational constants were used in a least squares fit to determine the near-equilibrium structural parameters.



The new value for the "acetylenic" C-C bond, $r(\text{C}_1\text{-C}_2)$ is 1.255 Å, which falls between the value for HCCH (1.203 Å) and H_2CCH_2 (1.332 Å), being a bit closer to the acetylene value. The fit is much improved, with $\sigma < 30$ kHz. The new bond lengths and angles obtained are in very good agreement with most of the recent *ab initio* calculations. The new parameter values are shown in Figure 6.

o-benzyne was identified over 50 years ago as a short-lived reaction intermediate, and has been studied by many methods,¹⁵ but the first detailed structure was obtained from the recent accurate and precise microwave measurements.^{16, 17}

I) CYCLOHEPTATRIENE-TITANIUM-CYCLOPENTADIENE Update

Samples have been prepared and new microwave spectra have been obtained for the Cycloheptatriene-Titanium-Cyclopentadiene complex ($\eta^7\text{-C}_7\text{H}_7\text{Ti } \eta^5\text{-C}_5\text{H}_5$) with a single deuterium substitution on the the cycloheptatriene (CHT), and spectra have also been obtained for ^{13}C isotopomers. The spectra were used to determine structural parameters. The C-H bonds are bent out of the plane of CHT carbon atoms by 8.6°. (work in progress, accepted for publication)