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Microwave Spectroscopy Measurements of the Gas-Phase Structure of Cyclopentadienyltungsten Tricarbonyl Hydride

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High-resolution microwave spectra for ^{13}C isotopomers of cyclopentadienyltungsten tricarbonyl hydride were measured using a pulsed-beam Fourier transform microwave spectrometer system. The new rotational constants for the ^{13}C isotopomers are combined with the previously obtained rotational constants for normal and deuterium isotopomers to obtain the gas-phase structure of cyclopentadienyltungsten tricarbonyl hydride. The new frequencies for the five unique ^{13}C isotopomers were measured in the 5−7 GHz range for $C_5H_5W(CO)_3H$. Kraitchman analysis and least-squares structure-fitting procedures were used to determine the structural parameters. The results from the structural fit yielded the W−H bond length, r_0(W−H) = 1.79(2) Å, which agrees very well with the previously reported value, r_s(W−H) = 1.79(4) Å, obtained with a much smaller data set. The present study also yielded the distance from tungsten to the C_5H_5 ring, r(W−Cp) = 2.03(1) Å, which corresponds to an average W−C (of Cp) bond length of 2.37(2) Å. The experimental ring radius for Cp of r(Cp) = 1.20(2) Å corresponds to an average cyclopentadienyl C−C bond length of 1.423(4) Å. Deviations of near 0.02 Å from C_5 symmetry for the W−C bond lengths for the Cp ligand and smaller deviations for the C−C bond lengths were obtained from the DFT calculations, and incorporating these deviations into the least-squares fit improved the standard deviation by a factor of 5. The average bond length from tungsten to the carbonyl carbons is r(W−CO) = 1.97(2) Å. Results obtained from the structural fit are in very close agreement with the experimental, Kraitchman analysis values. Results from new DFT calculations are given, with heavy-atom coordinates in very good agreement with experimental values, and a slightly shorter calculated W−H bond length, r_e(W−H) = 1.73 Å.

I. Introduction

Transition-metal monohydride complexes play important roles in many chemical and biological processes. One important class of these monohydride complexes is the $C_5H_5M(CO)_3H$ (where M = Cr, Mo, W) complexes. These transition-metal hydride complexes often serve as useful catalysts and metal precursors in acid−base synthetic reactions. For example, a number of molecular derivatives of such complexes have been explored as selective catalysts,[1−3] stoichiometric reactants or reactive intermediates for hydrogenation, hydroformulation reactions,[4−6] and protonation of aldehydes and ketones.[7] Central to these catalytic reactions is the fact that, for these types of complexes, the metal−hydrogen bond can function as a proton, hydrogen, or hydride donor under various reaction conditions. For example, Shafiq and coworkers have investigated the acidity and solubility of $(C_5H_4CO_2H)W(CO)_3H$ and related complexes in water.[8] They have shown that, in a polar solvent such as water, the W−H site of $(C_5H_4CO_2H)W(CO)_3H$ is less likely to deprotonate than in organic solvents. It was found, however, that in organic solvents deprotonation of the W−H site becomes thermodynamically favorable. These results suggest that the acidity of the W−H bond is highly dependent on the structure and intermolecular interactions of the other ligands.

Various interesting applications have been proposed for the cyclopentadienyltungsten tricarbonyl hydride complex, $C_5H_5W(CO)_3H$, in recent years. One example is the study reported by Otten and Lamb, who suggested that this monohydride and related complexes might be of potential use as surface-supported catalysts. They demonstrated that the protonated form of the $C_5H_5W(CO)_3H$ complex could bind firmly on alumina surfaces via the carbonyl ligands, thus leaving the reactive hydrogen atom exposed above the surface.[9]

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Another potentially important and useful application of tungsten-based transition-metal compounds is in the use of tungsten to store or capture hydrogen atoms, potentially providing a new type of hydrogen storage device. Recently, Pyykkö and co-workers have studied the possible existence of stable WH_{12} species, using density functional theory (DFT) and second-order perturbation theory MP2 calculations.[10] Their calculations have shown that the four side-on-bonded H_2 units can be detached more easily than the remaining four classical W−H hydride ligands. We believe that new data for the gas-phase W−H bond length could be useful for evaluating the theoretical methods and finding the basis sets and functionals which provide the most accurate structures.

To increase our experimental understanding of the properties of M−H bonds and other molecular properties for $C_5H_5M(CO)_3H$ and related complexes, we recently reported gas-phase microwave measurements of Mo−H and W−H bond lengths for $C_5H_5Mo(CO)_3H$ and $C_5H_5W(CO)_3H$.[11] Our results, based on Kraitchman analysis of normal and deuterated isotopomers, yielded Mo−H and W−H bond lengths of 1.79(4) and 1.80(1) Å, respectively. The nearly equal M−H bond lengths can be attributed to the lanthanide contraction associated with the f electrons of the tungsten atom. These M−H bond lengths are the only experimental structural information reported in the previous work.[11] Only a few ^{13}C transitions had been obtained in this earlier work for the $C_5H_5W(CO)_3H$ complex and no ^{13}C transitions for the $C_5H_5Mo(CO)_3H$ complex.

In the present study, we report the microwave measurements of rotational constants for many additional isotopomers of the d^4 metal monohydride $C_5H_5W(CO)_3H$, to find the complete gas-phase structure of this molecule. Microwave spectra of ^{13}C isotopomers for the $C_5H_5W(CO)_3H$ complex were successfully measured in the frequency range of 5−7 GHz. By combining the present ^{13}C isotopic data with our previously measured tungsten and deuterium isotopic data,[11] we were able to determine a nearly complete gas-phase structure for $C_5H_5W(CO)_3H$. Although X-ray data for $C_5H_5W(CO)_3H$ were reported about 35 years ago,[12] the H atom coordinates were very poorly determined, and no previous data for the gas-phase structure of this complex were known. Accurate structural information is of fundamental importance for understanding the strength, stability, and reactivity of the metal−hydrogen bond for the $C_5H_5W(CO)_3H$ complex. In addition, the gas-phase structural information can supply some information about how steric interactions affect the stability of the W−H bond. Thus, we believe that these new results will further increase our understanding of the reactivity of M−H bonds in free complexes such as $C_5H_5M(CO)_3H$ and related molecules. Moreover, information on the gas-phase structural results of $C_5H_5W(CO)_3H$ should be useful for testing the validity of the theoretical methods.

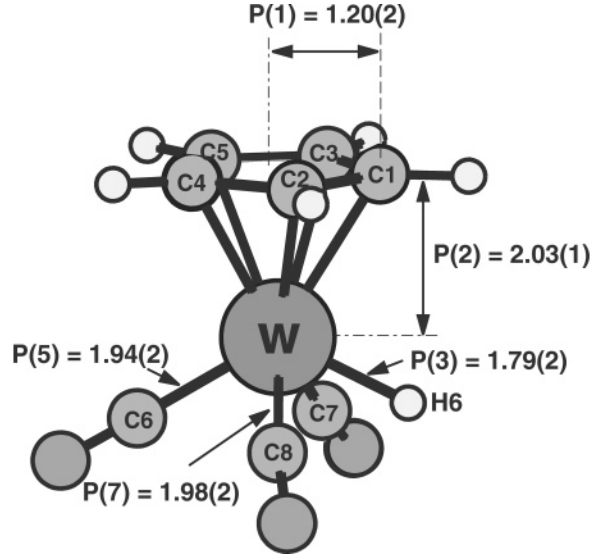

Figure 1. Basic structure of the cyclopentadienyltungsten tricarbonyl hydride complex, identifying the structural parameters along with the fit results. The size of the hydrogen atoms has been increased for illustration purposes. The rest of the structure is nearly to scale. Legend: $P(1)$, the ring radius of Cp; $P(2)$, the distance from W to the centroid of Cp; $P(3)$, $P(5)$, $P(7)$, the distances from W to the respective carbon atoms; $P(4) = 23(2)°$, the W−H_6 angle with the z axis; $P(6) = 45(1)°$, the W−C_6 angle with the x axis.

II. Experimental Section

Cyclopentadienyltungsten tricarbonyl hydride, $C_5H_5W(CO)_3H$, was purchased from Aldrich (No. 511234) and resublimed prior to use for the present measurements. The rotational transitions of ^{13}C isotopomers, in natural abundance, were measured in the 5−7 GHz range using a Flygare−Balle type pulsed-beam Fourier transform spectrometer (PBFTS) system.[13] The resublimed sample was transferred into a glass sample cell in the drybox. The sample cell then was placed and securely anchored into the connector located at the back end of the pulsed valve. The sample cell was evacuated to remove any remaining air and moisture. Neon gas was then admitted into the sample cell; neon pressure was set in the range of 0.7−0.8 atm, and this pressure was maintained throughout the experiment. The sample and pulse valve were heated to about 60−65 °C in order to obtain a sufficient sample vapor pressure. Although the molecular signal could be observed at about 35 °C, for the common isotopomer heating the sample to 65 °C exponentially increased the strength of the molecular FID signal. The instrumental settings were optimized using a strong transition of the parent complex as a test line. We adjusted the cavity mode, time delay, and microwave power until the signal of the parent test line could be obtained within a single beam pulse. Many of the observed ^{13}C frequency transitions were seen with a signal averaging between 500 and 1500 beam pulses. No ^{18}O isotopomers were observed for the $C_5H_5W(CO)_3H$ complex in the present experiments.

III. Results and Data Analysis

Sixty transitions due to five unique ^{13}C isotopomers, with various tungsten isotopes, were observed for the $C_5H_5W(CO)_3H$ complex in the present study. Three unique ^{13}C isotopomers on the C_5H_5 ring were mea-

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Table 1. Measured and Calculated Unique ^{13}C Transitions for Different Sets of Tungsten Isotopomers Obtained from the Measurements and Least-Squares Fits[a]

J	K_a	K_c	J'	K_a'	K_c'	measd	calcd	residual	J	K_a	K_c	J'	K_a'	K_c'	measd	calcd	residual
$^{13}C_2$ $C_5H_5{}^{186}W(CO)_3H$																	
3	2	1	4	2	2	5740.377	5740.377	0.0000	4	3	2	5	3	3	6978.619	6978.620	−0.0007
4	1	4	5	1	5	6537.678	6537.677	0.0013	4	1	3	5	1	4	6988.618	6988.619	−0.0009
4	0	4	5	0	5	6556.209	6556.207	0.0022	4	4	0	5	4	1	6997.130	6997.132	−0.0024
4	2	3	5	2	4	6841.178	6841.182	−0.0042	4	2	2	5	2	3	7191.892	7191.887	0.0046
$^{13}C_2$ $C_5H_5{}^{184}W(CO)_3H$																	
3	2	1	4	2	2	5740.540	5740.540	0.0000	4	3	2	5	3	3	6978.767	6978.766	0.0013
4	1	4	5	1	5	6537.737	6537.737	0.0004	4	1	3	5	1	4	6988.736	6988.736	−0.0002
4	0	4	5	0	5	6556.263	6556.264	−0.0005	4	4	0	5	4	1	6997.289	6997.290	−0.0011
$^{13}C_5$ $C_5H_5{}^{183}W(CO)_3H$																	
4	1	4	5	1	5	6550.903	6550.907	−0.0036	4	1	3	5	1	4	6995.581	6995.586	−0.0047
4	2	3	5	2	4	6849.248	6849.240	0.0076	4	3	1	5	3	2	7091.203	7091.208	−0.0046
4	3	2	5	3	3	6983.439	6983.434	0.0053									
$^{13}C_5$ $C_5H_5{}^{182}W(CO)_3H$																	
4	1	4	5	1	5	6550.959	6550.959	0.0003	4	3	2	5	3	3	6983.520	6983.520	0.0004
4	2	3	5	2	4	6849.358	6849.358	−0.0008	4	1	3	5	1	4	6995.833	6995.833	0.0002
$^{13}C_1$ $C_5H_5{}^{186}W(CO)_3H$																	
4	0	4	5	0	5	6558.828	6558.827	0.0003	4	1	3	5	1	4	6986.075	6986.081	−0.0063
4	2	3	5	2	4	6837.603	6837.598	0.0049	4	3	1	5	3	2	7075.551	7075.557	−0.0062
$^{13}C_7$ $C_5H_5{}^{186}W(CO)_3H$																	
4	2	2	5	2	3	7179.832	7179.824	0.0073	4	1	3	5	1	4	7004.852	7004.849	0.0023
3	2	1	4	2	2	5763.893	5763.887	0.0059	4	2	2	5	2	3	7218.508	7218.514	−0.0062
4	0	4	5	0	5	6570.873	6570.874	−0.0008									
$^{13}C_1$ $C_5H_5{}^{183}W(CO)_3H$																	
4	1	4	5	1	5	6539.350	6539.345	0.0050	4	3	1	5	3	2	7075.734	7075.738	−0.0048
4	2	3	5	2	4	6837.703	6837.709	−0.0063	4	2	2	5	2	3	7180.112	7180.103	0.0089
4	1	3	5	1	4	6986.308	6986.311	−0.0027									
$^{13}C_7$ $C_5H_5{}^{184}W(CO)_3H$																	
4	0	4	5	0	5	6570.808	6570.809	−0.0006	4	3	2	5	3	3	7002.800	7002.803	−0.0030
4	2	3	5	2	4	6860.716	6860.714	0.0020	4	4	0	5	4	1	7023.739	7023.737	0.0015
$^{13}C_7$ $C_5H_5{}^{183}W(CO)_3H$																	
3	2	1	4	2	2	5764.052	5764.053	−0.0011	4	4	0	5	4	1	7024.089	7024.090	−0.0007
4	1	4	5	1	5	6553.752	6553.748	0.0038	4	3	1	5	3	2	7121.356	7121.354	0.0015
4	0	4	5	0	5	6570.920	6570.927	−0.0062	4	2	2	5	2	3	7218.700	7218.707	−0.0065
4	1	3	5	1	4	7004.971	7004.967	0.0042	5	0	5	6	0	6	7838.835	7838.836	−0.0006
4	4	1	5	4	2	7015.016	7015.011	0.0055									
$^{13}C_7$ $C_5H_5{}^{182}W(CO)_3H$																	
3	2	1	4	2	2	5764.212	5764.209	0.0032	4	4	0	5	4	1	7024.254	7024.254	0.0004
4	2	3	5	2	4	6868.912	6860.916	−0.0035	5	1	5	6	1	6	7832.347	7832.346	0.0005
4	1	3	5	1	4	7005.080	7005.079	0.0009	5	0	5	6	0	6	7838.904	7838.903	0.0012
4	4	1	5	4	2	7015.167	7015.170	−0.0026									
$^{13}C_6C_5H_5{}^{184}W(CO)_3H$																	
3	2	1	4	2	2	5750.232	5750.227	0.0057	4	2	2	5	2	3	7204.595	7204.597	−0.0015
4	4	0	5	4	1	7013.157	7013.161	−0.0041	5	0	5	6	0	6	7853.199	7853.198	0.0009

[a] Frequencies are given in MHz. Residual refers to the difference between measured and calculated transition frequencies. The atomic labeling scheme corresponds to the labeling scheme in Figure 1.

sured. Using our atomic labeling scheme, these unique isotopomers are $^{13}C_1$, $^{13}C_2$ (equivalent to $^{13}C_3$), and $^{13}C_4$ (equivalent to $^{13}C_5$), as shown in Figure 1. Two unique ^{13}CO isotopomers were also measured, and these are $^{13}C_6$ and $^{13}C_7$ (equivalent to $^{13}C_8$). Table 1 shows the measured and calculated ^{13}C rotational transition frequencies obtained using the least-squares fitting procedure for the $C_5H_5W(CO)_3H$ complex. Most of the observed a-type transitions were confined to three groups, namely $J = 3 \rightarrow 4$, $4 \rightarrow 5$, and $5 \rightarrow 6$. Since relatively fewer numbers of transitions were measured for the ^{13}C isotopomers compared to the parent complex, these measured transitions were fit using only three variable parameters: the A, B, and C rotational constants. Table 2 shows the measured rotational parameters obtained from the previous study[11] for the normal and deuterated isotopomers of the most abundant isotopomers, $C_5H_5{}^{184}W(CO)_3H$ and $C_5H_5{}^{184}W(CO)_3D$. For these isotopomers, many more transitions were measured so that A, B, C, and the distortion constants (Δ_J and δ_J) were obtained. The measured quartic centrifugal distortion constants are very small, ranging between 0.02 and 0.04 kHz, suggesting a fairly rigid structure. More importantly, they are not expected to vary significantly with isotopic substitution; thus, fixing the values for the distortion constants for ^{13}C isotopomers is not expected to introduce any additional

Table 2. Experimental Rotational Parameters Obtained from the Least-Squares Fits for the Normal and Deuterated Species of the Most Abundant (^{184}W) Tungsten Isotope

param	$C_5H_5{}^{184}W(CO)_3H$	$C_5H_5{}^{184}W(CO)_3D$
A (MHz)	968.6999(12)	963.2217(18)
B (MHz)	752.5415(4)	748.5042(4)
C (MHz)	639.7433(4)	639.5198(4)
Δ_J (MHz)	0.000034(2)	0.000034(2)
δ_J (MHz)	0.000015(2)	0.000023(2)
σ_{fit} (MHz)	0.004	0.003

Table 3. Experimental Rotational Parameters Obtained from the Least-Squares Fit for Unique ^{13}C Isotopes on the C_5H_5 Ring of (η^5-Cyclopentadienyl)tungsten Tricarbonyl Hydride[a]

param	$^{13}C_2$[b]	$^{13}C_2$[c]	$^{13}C_5$[d]	$^{13}C_5$[e]	$^{13}C_1$[f]	$^{13}C_1$[g]
A (MHz)	966.2535(86)	966.2843(30)	964.6513(224)	964.8898(30)	967.1710(248)	967.4019(240)
B (MHz)	747.7477(6)	747.7742(2)	747.3814(26)	747.4011(4)	746.0566(22)	746.1003(22)
C (MHz)	635.2710(6)	635.2778(2)	636.8614(26)	636.8594(3)	635.6467(26)	635.6300(24)
Δ_J (kHz)	0.036[h]	0.10[h]	0.0	0.0	0.0	0.0
$\sigma_{\rm fit}$ (kHz)	3.2	1.1	8.4	1.0	8.8	9.3

[a] The indicated error limits correspond to 2σ. [b] $C_5H_5{}^{186}W(CO)_3H$. [c] $C_5H_5{}^{184}W(CO)_3H$. [d] $C_5H_5{}^{183}W(CO)_3H$. [e] $C_5H_5{}^{182}W(CO)_3H$. [f] $C_5H_5{}^{186}W(CO)_3H$, [g] $C_5H_5{}^{183}W(CO)_3H$. [h] Fixed parameter.

Table 4. Experimental Rotational Parameters Obtained from the Least-Squares Fit for $^{13}C_1$ or $^{13}C_3$ CO Isotopomers of (η^5-Cyclopentadienyl)tungsten Tricarbonyl Hydride[a]

param	$^{13}C_7$[b]	$^{13}C_7$[c]	$^{13}C_7$[d]	$^{13}C_7$[e]	$^{13}C_6$[f]
A (MHz)	963.3498(288)	963.9450(378)	963.3792(108)	963.3985(68)	964.7016(561)
B (MHz)	750.7390(20)	750.7620(28)	750.7649(10)	750.7879(6)	749.0557(28)
C (MHz)	636.8150(30)	636.7799(24)	636.8189(8)	636.8227(4)	638.1326(22)
Δ_J (kHz)	0.0	0.0	0.023[g]	0.020[g]	0.0
$\sigma_{\rm fit}$ (kHz)	8.9	4.0	4.9	2.8	7.2

[a] The indicated error limits correspond to 2σ. [b] $C_5H_5{}^{186}W(CO)_3H$. [c] $C_5H_5{}^{184}W(CO)_3H$. [d] $C_5H_5{}^{183}W(CO)_3H$. [e] $C_5H_5{}^{182}W(CO)_3H$ and $^{13}C_2$ CO isotopomer. [f] $C_5H_5{}^{184}W(CO)_3H$. [g] Fixed parameter.

uncertainty in the resulting fit parameters A, B, and C. Measured rotational parameters for the unique sets of ^{13}C transitions are summarized in Tables 3 and 4. In all these cases, the fit standard deviation is in the range of 1−9 kHz. The measured and "best fit" calculated rotational constants are given in Table 5. The standard deviation of the preferred structural fit is 0.18 MHz.

IV. Structural Analysis

Kraitchman analyses were carried out for the measured ^{13}C rotational constants to obtain the C_5H_5 and CO carbon atom coordinates in the center of mass (COM) system. Results of the Kraitchman analysis for the tungsten and deuterium isotopomers were given in our previous study.[11] From these COM atomic coordinates, we obtained the Kraitchman structural parameters (r_s) for this complex, which are shown in Table 6. Table 6 also includes structural data obtained from the DFT calculations and from the preferred structural fit.

In the present study, 33 rotational constants were measured for various unique ^{13}C isotopomers (Tables 3 and 4) and these were combined with the previously obtained 24 rotational constants for various tungsten and deuterium isotopomers.[11] In all of the measurements, we acquired a total of 57 rotational constants and these were used in the least-squares fits to determine the molecular structure of $C_5H_5W(CO)_3H$. Several different adjustable parameters were employed in the structural fit program, and a list of the parameters we believe could be most accurately determined is as follows: $P(1) = r$(Cp), the ring radius of C_5H_5 (Cp); $P(2) = r$(W−Cp), the distance between the center of the ring and the W atom; $P(3) = r(W{-}H_6)$, the tungsten−hydrogen bond distance; $P(4)$, the $W{-}H_6$ angle with the molecular z axis; $P(5) = r(W{-}C_6)$, the distance from tungsten to the C_6 atom; $P(6)$, the $W{-}C_6$ angle with the z axis; $P(7) = r(W{-}C_7)$, the distance from tungsten to the C_7 atom (equivalent to C_8). The basic structure of this complex and these parameters are shown in Figure 1, with the numbering of the carbon atoms indicated. The fit results for the measured and calculated rotational constants for various isotopomers are illustrated in Table 5. As stated, a total of 57 rotational constants were used in the global structure fit, and this yielded a standard deviation of 0.18 MHz. For this fit many of the structural parameters, such as C−H and C−O bond lengths, and the small deviations from C_5 symmetry of the Cp ligand were fixed at values obtained from the DFT calculations. We also tried fits where the Cp ligand was constrained to C_5 symmetry, but the standard deviation was much larger (~1 MHz), and so these results are not listed. We note that the major deviation from C_5 symmetry relative to the W atom is that $r(W{-}C_1) > r(W{-}C_2) > r(W{-}C_4)$, with differences of 0.02 Å. This can be interpreted as a "tilt" of the Cp group away from being perpendicular to the nominal z axis. Smaller deviations of the C−C bond lengths for the Cp ligand from the equal values expected for C_5 symmetry were also obtained from the calculations and included in calculating the atom coordinates in the least-squares structure fit. For the preferred fit (Table 6, fifth column), the complex was constrained to have a plane of symmetry (C_s symmetry).

The structural parameters obtained from the least-squares fit are in very good agreement with the Kraitchman results (see Table 6) and in reasonably good agreement with the DFT results. We note that in the present DFT calculation the tungsten−hydrogen ($W{-}H_6$) bond distance is still underestimated, and this may be primarily due to the fact that the calculated value is an r_e value, whereas the structural fit results will be much closer to r_0 values. The present W−H bond length from the C_s-symmetry-constrained DFT calculations is closer to the experimental values than that from the previous calculation.[11] The structure fit and the Kraitchman values for the metal−hydrogen bond length agree remarkably well, within the error limits. Except for this metal−hydrogen bond distance, we note that the agreement for Kraitchman, DFT, and structural fit parameters are quite good and agree within the experimental error limits. The Cartesian coordinates obtained from the least-squares fit results are given in Table 7.

V. DFT Calculations

In the present study, we performed density functional theory (DFT) calculations with the constraint of C_s (a−c

Table 5. Results from the Structural Fit Showing Measured and Calculated Rotational Constants (*A*, *B*, *C*) for Various Isotopomers[a]

isotopomer	measd (M)	calcd (C)	M − C
^{184}W	968.6999	968.6834	0.0165
	752.5415	752.5705	−0.029
	639.7433	639.8015	−0.0582
^{186}W	968.6546	968.6489	0.0057
	752.5138	752.5495	−0.0357
	639.7462	639.8014	−0.0552
^{182}W	968.7459	968.7183	0.0276
	752.5679	752.5917	−0.0238
	639.7440	639.8016	−0.0576
^{183}W	968.7242	968.7008	0.0234
	752.5542	752.5810	−0.0268
	639.7439	639.8016	−0.0577
^{184}W and $^{13}C_2$	966.2843	966.2854	−0.0011
	747.7742	747.7271	0.0471
	635.2778	635.2764	0.0014
^{184}W and $^{13}C_6$	964.7016	965.5164	−0.8148
	749.0557	748.6294	0.4263
	638.1326	638.3276	−0.1950
^{184}W and $^{13}C_7$	963.9450	963.3256	0.6194
	750.7620	750.8080	−0.0460
	636.7799	636.8739	−0.0940
^{184}W and D	963.2217	963.1533	0.0684
	748.5042	748.6212	−0.1170
	639.5198	639.3587	0.1611
^{186}W and $^{13}C_2$	966.2535	966.2512	0.0023
	747.7477	747.7063	0.0414
	635.2710	635.2761	−0.0051
^{186}W and $^{13}C_1$	967.1710	967.1431	0.0279
	746.0566	746.0006	0.0560
	635.6467	635.7106	−0.0639
^{186}W and $^{13}C_7$	963.3498	963.2928	0.0570
	750.7390	750.7880	−0.0490
	636.8150	636.8738	−0.0588
^{186}W and D	963.1808	963.1227	0.0581
	748.4790	748.6027	−0.1237
	639.5225	639.3587	0.1638
^{182}W and $^{13}C_5$	964.8898	965.0396	−0.1498
	747.4011	747.3268	0.0743
	636.8594	636.7744	0.0850
^{182}W and $^{13}C_7$	963.3985	963.3589	0.0396
	750.7879	750.8282	−0.0403
	636.8227	636.8739	−0.0512
^{182}W and D	963.2502	963.1842	0.0660
	748.5245	748.6400	−0.1155
	639.5233	639.3588	0.1645
^{183}W and $^{13}C_5$	964.6513	965.0209	−0.3696
	747.3814	747.3154	0.0660
	636.8614	636.7742	0.0872
^{183}W and $^{13}C_1$	967.4019	967.1921	0.2098
	746.1003	746.0303	0.0700
	635.6300	635.7110	−0.0810
^{183}W and $^{13}C_7$	963.3792	963.3422	0.0370
	750.7649	750.8180	−0.0531
	636.8189	636.8739	−0.0550
^{183}W and D	963.2534	963.1686	0.0848
	748.5189	748.6306	−0.1117
	639.5122	639.3588	0.1534

[a] Rotational constants are given in MHz and are given in the order *A*, *B*, and *C* for each isotopomer. The standard deviation for the fit is 0.18 MHz.

Table 6. Comparison of the Internal Structural Parameters Obtained from the Kraitchman Analysis, DFT Calculations, and the Structural Fit (in Å)[a]

param	Kraitchman	DFT[b]	DFT[c]	structural fit
W−H6	1.79(4)	1.716	1.734	1.79(2)
W−C1	2.39[d]	2.387	2.401	2.40(2)
W−C2	2.399(4)	2.368	2.386	2.38(2)
W−C3	2.41(4)	2.368	2.386	2.38(2)
W−C4	2.357(18)	2.340	2.360	2.35(2)
W−C5	2.357(18)	2.340	2.360	2.35(2)
W−C6	1.962(6)	1.990	1.983	1.944(20)
W−C7	1.969(6)	1.981	1.973	1.980(20)
W−C8	1.969(6)	1.981	1.973	1.980(20)
C1−C2	1.42[d]	1.421	1.429	1.420(4)
C1−C3	1.42[d]	1.421	1.429	1.420(4)
C2−C4	1.495(14)	1.423	1.429	1.422(4)
C3−C5	1.49(2)	1.423	1.429	1.422(4)
C4−C5	1.470(14)	1.431	1.438	1.430(4)

[a] The atomic labeling scheme corresponds to the labeling scheme in Figure 1. The indicated error limits correspond to 2σ. [b] From ref 11. [c] This work. [d] *b* axis C_8 coordinates are fixed to the DFT value.

Table 7. Cartesian Coordinates for Cyclopentadienyltungsten Tricarbonyl Hydride (in Å) Obtained from Structural Fit

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
W	0.005	0.000	−0.092	H1	−2.473	0.000	−1.982
C1	−2.249	0.000	−0.916	H2	−2.162	2.184	−0.432
C2	−2.076	1.150	−0.101	H3	−2.162	−2.184	−0.432
C3	−2.076	−1.150	−0.101	H4	−1.665	1.327	2.092
C4	−1.802	0.715	1.224	H5	−1.665	−1.327	2.092
C5	−1.802	−0.715	1.224	H6[a]	0.740	0.000	−1.721
C6	1.337	0.000	1.324	O1	2.126	0.000	2.161
C7	1.065	−1.577	−0.649	O2	1.631	−2.520	−0.998
C8	1.065	1.577	−0.649	O3	1.631	2.520	−0.998

[a] Hydrogen atom directly bound to the tungsten atom.

mirror plane) symmetry for the $C_5H_5W(CO)_3H$ complex, using the B3PW91 functional and basis sets with polarization and diffuse functions. Results obtained from these calculations are shown in Table 6, columns 3 and 4. In column 3 are the results from our previous calculation,[11] and column 4 shows our new theoretical results obtained with the complex constrained to C_s symmetry. We used the Pople basis set 6-311G++(d,p) with diffuse and polarization functions for C, O, and H and the Hay−Wadt VDZ effective core potential for the tungsten atom. Details and references for the methods and basis sets were given earlier.[11]

VI. Discussion

Using the present data, combined with the data obtained from the previous study,[11] we were able to determine both the r_s and r_0 structural parameters for the $C_5H_5W(CO)_3H$ complex. The r_s structural parameters were obtained directly from Kraitchman analyses of the isotopic data, whereas the "near-r_0" structural parameters were determined by adjusting structural parameters to fit calculated rotational constants to the measured rotational constants, using a least-squares structural fitting program available in our laboratory. The present W−H bond length as determined from the structural fit is r_0(W−H) = 1.79(2) Å, in excellent agreement with the Kraitchman value. Since a much larger data set was used in the present work, the effects of correlation in the fit are much smaller and the confidence in the values of the structural parameters obtained is much higher. The DFT-calculated value, r_e(W−H) = 1.734 Å, is significantly shorter than the experimental values; we believe that this discrepancy could be reduced if one were to apply vibrational averaging corrections and use larger basis sets for the W atom. There is previous evidence that third-row transition-metal hydrides exhibit anomalously large anharmonicity in the M−H bond from microwave work on a rhenium hydride.[14] Looking at the Cartesian coordinates obtained from the structural fit (see Table 7), we note that the hydrogen (H_6) lies in the $a-c$ plane (b coordinate is zero) and the sign of a and c coordinates of W and H_6 are consistent with the Kraitchman atomic coordinates. We believe that the r_0 value is more precise. However, because no vibrational corrections were made to the fit results, the r_s and r_0 values obtained do not represent the true r_e equilibrium bond length for $C_5H_5W(CO)_3H$.

The η^5-C_5H_5−W carbon−tungsten bond distances and W−C bond lengths to the carbonyl groups obtained from Kraitchman and structural fit analyses are in agreement, within the experimental uncertainties, and display the same trend in distortions from C_5 symmetry as the least-squares-fit values. The average cyclopentadienyl C−C bond length obtained is 1.423(4) Å, and this agrees well with the DFT-calculated value. The DFT calculations indicated deviations of near 0.02 Å from C_5 symmetry for the W−C bond lengths for the Cp ligand and smaller deviations for the C−C bond lengths. Incorporating these deviations into the least-squares fit improved the standard deviation by a factor of 5.

VII. Conclusion

A nearly complete gas-phase structure of η^5-cyclopentadienyltungsten tricarbonyl hydride has now been obtained from microwave data. The least-squares-fit, DFT-calculated, and Kraitchman results show that the basic structure of the complex is close to the “piano stool” type of structure. The hydrogen atom attached to the metal is located between two of the three carbonyl ligands and is bent away from the C_5H_5 ring. This hydrogen is found to be in the $a-c$ plane of the complex.

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