Microwave Spectra and Gas-Phase Structural Parameters of Bis(η^5-cyclopentadienyl)tungsten Dihydride

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Microwave spectra for 11 isotopomers of bis(η^5-cyclopentadienyl)tungsten dihydride ($(C_5H_5)_2WH_2$) were recorded in the 5−14 GHz region using a Flygare−Balle-type pulsed beam spectrometer. Spectra arising from four tungsten isotopomers of both the $(C_5H_5)_2WH_2$ and $(C_5H_5)_2WHD$ species and three W isotopomers for the $(C_5H_5)_2WD_2$ complex have been measured. The ∼250 *b*-type transition frequencies assigned for these near-prolate asymmetric top molecules were accurately described ($\sigma_{\mathrm{fit}} = 2-4$ kHz) using the rotational parameters *A*, *B*, and *C* and one centrifugal distortion constant, Δ_J. The small value obtained for Δ_J indicates a fairly rigid structure. From a least-squares fit using the resulting 33 rotational constants to obtain the molecular structure, we were able to determine the W−H bond length, $r(\mathrm{W-H}) = 1.703(2)$ Å, the H−W−H bond angle, $\angle(\mathrm{H-W-H}) = 78.0(12)°$, the W−Cp centroid distance, $r(\mathrm{W-Cp}) = 1.940(8)$ Å, the angle made by the Cp centroids with tungsten, $\angle(\mathrm{Cp-W-Cp}) = 155(2)°$, and the average C−C bond length, $r(\mathrm{C-C}) = 1.429(8)$ Å. The hydrogen atom separation is $r(\mathrm{H-H}) = 2.14(2)$ Å, indicating that this is clearly a "classical dihydride" rather than an "η^2-dihydrogen" complex. The WH_2 moiety parameters determined from Kraitchman's equations ($r(\mathrm{W-H}) = 1.682(2)$ Å, $\angle(\mathrm{H-W-H}) = 78.6(2)$, $r(\mathrm{H-H}) = 2.130(2)$ Å) agree well with the least-squares results. Furthermore, the r_e parameters obtained from DFT calculations agree well with the experimental r_0 structural parameters. To our knowledge, this work marks the first microwave study of a bent-metallocene complex. The present measurements were made with a pulsed-beam Fourier transform spectrometer employing a homodyne-type detection system, and this configuration is described. This homodyne system greatly simplifies the microwave circuit, with no apparent loss in sensitivity.

I. Introduction

The preparation of the first organometallic transition-metal hydride ($H_2Fe(CO)_4$) in 1931 by Hieber[1] initiated extensive research into the chemistry, structure, and spectroscopic properties of these complexes. The intrigue and importance of TM hydrides is apparent from the numerous review articles appearing in the recent literature.[2−5] They are important participants in numerous industrial processes, such as catalytic hydrogenation and hydroformylation reactions, and are versatile stoichiometric reagents in organic and organometallic synthesis.[6]

Bis(η^5-cyclopentadienyl)tungsten dihydride was first synthesized[7] in 1961, and subsequently there have been numerous reports of its uses and importance in inorganic and organometallic chemistry.[8−24] The spectroscopic investigation of $(C_5H_5)_2WH_2$ was initiated by Green et al. in 1961.[7] In their initial paper detailing the synthesis of the title complex, the authors performed a high-resolution NMR study of $(C_5H_5)_2WH_3^+$, obtained by dissolving the dihydride in concentrated HCl. The spectrum revealed two equivalent hydridic protons and one nonequivalent hydridic proton, indicating the nonlinearity of the metal-to-ring axes. Then in 1975, Green and co-workers measured the ionization potentials of several bent bis(η^5-

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cyclopentadienyl)metal complexes, including $(C_5H_5)_2WH_2$, using photoelectron spectroscopy and proposed a molecular orbital bonding model to account for the observed spectra.[25] In 1986, solution and matrix-isolated Raman and IR studies of the W−H and W−Cp stretching regions were performed by Girling et al. to identify the skeletal vibrational modes.[26] Finally, in 2002, gas-phase and *n*-pentane solution electronic absorption spectra revealed the lowest lying $5d_{x^2}$ (HOMO) → R6p Rydberg transition of $(C_5H_5)_2WH_2$, having a term value of $T = 16\,600$ cm^{-1}.[27] No previous X-ray or neutron diffraction studies have appeared.

To our knowledge, the present work on bis(η^5-cyclopentadienyl)tungsten dihydride marks the first microwave study of a bent-metallocene complex. We have observed pure rotational transitions of four tungsten isotopomers (^{182}W, 26.5%; ^{183}W, 14.3%; ^{184}W, 30.6%; ^{186}W, 28.4%) in natural abundance, and the mono- and dideuterated isotopomers ($(C_5H_5)_2WHD$ and $(C_5H_5)_2WD_2$) were synthesized and their spectra recorded. The $(C_5H_5)_2WH_2$ and $(C_5H_5)_2WD_2$ isotopomers have C_{2v} symmetry, reducing the number of independent structural parameters needed to specify the structure. The 33 rotational constants measured were used to refine a partial gas-phase structure, which is compared to DFT predictions and bonding parameters of the WH_2 moiety obtained from Kraitchman's equations.

II. Experimental Section

A. Sample Preparation. Bis(η^5-cyclopentadienyl)tungsten dihydride was purchased from Aldrich (No. 510807) and used without further purification to limit handling. The lemon yellow complex darkens quickly with more than brief exposure to air; thus, the sample cell was loaded in a drybox under a nitrogen atmosphere. The mono- and dideuterated complexes $(C_5H_5)_2WDH$ and $(C_5H_5)_2$-WD_2 were synthesized via a method described by Ito and Nakano.[28] A 0.2 g portion of $(C_5H_5)_2WH_2$ was weighed into a three-neck round-bottom flask fitted with a vacuum adapter and cold finger. A 2.0 mL portion of acetic acid-*d* (99 atom % D, Aldrich No. 151777) was added, and the resulting colorless solution was stirred overnight at room temperature under a nitrogen flow. The solvent was removed under vacuum, leaving yellow crystals, which were purified by sublimation. From the resulting sample, rotational transitions corresponding to both the mono- and dideuterated isotopomers, as well as the parent complex, could be observed.

B. Pulsed-Beam Fourier Transform Microwave Spectrometer using a Homodyne Detection System. Microwave spectra were measured in the 5−14 GHz region using a Flygare−Balle-type pulsed-beam Fourier transform spectrometer which is similar to earlier spectrometers[29] but was modified to employ a homodyne detection system. This homodyne system greatly simplifies the microwave circuit, with no apparent loss in sensitivity. The glass sample cell was connected directly to the pulsed valve (General Valve, Series 9, 2 mm orifice), and the enclosure surrounding the solenoid and sample was maintained at ~95 °C to obtain sufficient sample vapor pressure. Research grade neon was employed as carrier gas at a backing pressure of 0.7−0.8 atm. Gas pulses were injected transversely into the microwave cavity (background pressure 10^{-6} Torr) at a rate of 1−2 Hz. The most intense transitions of the main isotopomer could be detected with a single gas pulse, with FWHM line widths of ~30 kHz for the well-resolved lines, giving measurement uncertainties of 1−6 kHz.

The first pulsed-beam Fourier transform (PBFT) microwave spectrometer[30] (Flygare−Balle) and subsequent spectrometers[31−38] (to the best of our knowledge) employed superheterodyne microwave detection systems. This detection scheme offered substantial improvement in signal-to-noise ratio (*S*/*N*) over simple video detectors, as used on early Stark-cell spectrometers, and was probably the best choice available 15−26 years ago. In the early PBFT spectrometers the molecular response signal was passed directly from the Fabry−Perot cavity to the mixer of the superheterodyne receiver using a small antenna in the cavity, connected to semirigid coaxial cable,[29] or through a small coupling hole in one mirror, leading into a wave guide. This type of superheterodyne system was successful because the chosen intermediate frequency (IF) was 20−30 MHz, and this was high enough so that the 1/*f* noise associated with the electronics and nonlinear devices (such as the superheterodyne mixer) was much lower than would be obtained with video detection, or homodyne detection, without preamplification.

The high availability and low cost of low-noise, wide-bandwidth solid-state amplifiers in the past 10−12 years, and more recently lower-noise cryogenic amplifiers, has allowed other design configurations for improved *S*/*N*. For the present work, we have used MITEQ amplifiers AFS3-04000800-10-KCR-4 and AFS3-08001200-10-KCR-4, which have noise figures of nearly 1 dB at 300 K and much lower values at 77 K, where they were operated. These amplifiers are placed between the antenna, which picks up the molecular "free induction decay" (FID) signal, and the input of the mixer for the superheterodyne or homodyne detector system. These amplifiers amplify the molecular FID signal by 20−30 dB, so that the added noise from the mixer and subsequent amplifier becomes insignificant. After this amplification step, there is no longer a significant difference in resulting *S*/*N* whether we use superheterodyne detection with 20 MHz IF or the homodyne system with 0 frequency IF and signal frequencies in the 10−800 kHz range. The real advantage of the homodyne system is that the same microwave source can be used for the stimulating signal going into the microwave cavity and the local oscillator (LO) signal for the homodyne mixer. In the early systems, a separate, phase-locked microwave source was used to provide the LO signal for the superheterodyne detector. In more recent systems,[35,39,40] the offset LO signal was generated from the stimulating signal frequency using a single-sideband mixer. Tests were conducted using both the superheterodyne system with 20 MHz IF and the homodyne system using single substitution ^{13}C transitions for (butadiene)iron tricarbonyl.[41] With the present system these lines could be seen with only a few beam pulses. The improvement in *S*/*N* for the

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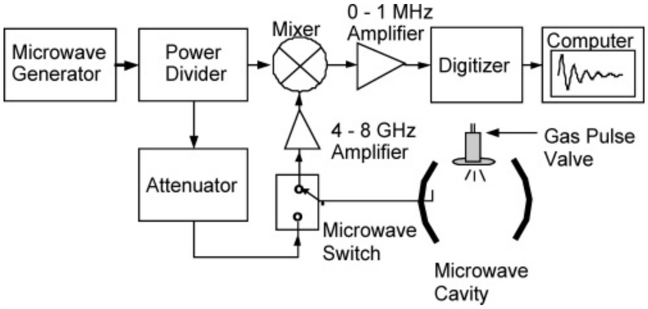

Figure 1. Diagram of the microwave electronics configuration for the HOMODYNE spectrometer system. The microwave generator is an HP Model 8673D. The 4−8 GHz amplifier is a MITEQ Model AFS3-04000800-10-KCR-4, operated at 77 K. A MITEQ Model AFS3-08001200-10-KCR-4 amplifier is used for 8−12 GHz.

cooled 77 K amplifiers was about a factor of 2, which means a factor of 4 reduction in required data collection time. We believe that the reason the improvement is not greater is that the noise from the amplifier is *added* to the thermal noise from the mirrors, which were at 300 K for these experiments. Cooling the mirrors, as recommended by Grabow et al.,[42] would provide further improvement in *S*/*N*. A diagram of the present apparatus configuration is shown in Figure 1. A disadvantage of the present system, relative to some of the SSB-mixer systems, is that molecular emission signals above and below the stimulating frequency become superposed on the mixer output. This requires making measurements with at least two different stimulating frequencies to discriminate “above stimulating frequency” from “below stimulating frequency” signals.

III. Results and Analysis

Before searching for microwave spectra of $(C_5H_5)_2WH_2$, extensive DFT calculations were performed using the *Gaussian 03* program suite[43] to optimize the structure and obtain preliminary rotational constants. Results from our best calculations are reported in Table 5 and in the footnote to Table 4. Becke’s three-parameter hybrid exchange functional[44] with the Perdew−Wang 1991 gradient-corrected correlation functional[45] (B3PW91) was employed, while the carbon and hydrogen atoms were described with Dunning’s correlation-consistent triple-ζ basis sets augmented by diffuse functions (aug-cc-pVTZ),[46] and the Hay−Wadt VDZ (n+1) ECP[47] was chosen for tungsten. Figure 2 illustrates the theoretical minimum-energy geometry for $(C_5H_5)_2WH_2$ in the principal-axis coordinate system. The calculations predict that the complex possesses C_{2v} symmetry with the *b* axis coincident with the 2-fold rotation axis and the *ab* and *bc* planes coincident with the mirror planes. The Cp rings are eclipsed, and the H atoms on C3, C4, C8, and C9 are nearly eclipsed with the hydridic protons H21 and H22. The calculated dipole moment is 1.34 D, lying along the *b* principal axis.

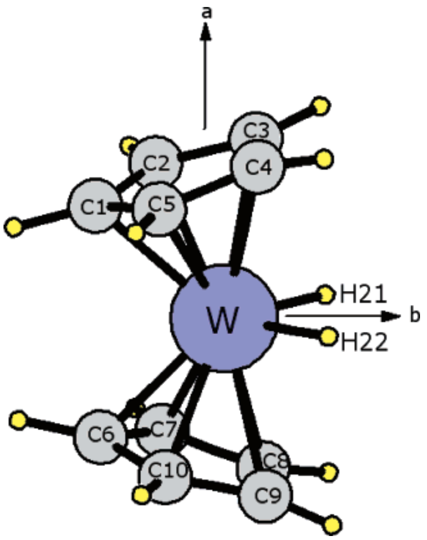

Figure 2. Molecular structure for the $(C_5H_5)_2WH_2$ complex, illustrating the principal axis system and the atom-numbering scheme used in the structural analyses.

Using these preliminary rotational constants (see footnote to Table 4), Pickett’s SPCAT program[48] was used to predict the *b*-type transition frequencies with selection rules $\Delta J = 0, \pm1$, $\Delta K_a = \pm1$, $\Delta K_c = \pm1, \pm3$. Upon searching, the $J'_{K_a'K_c'} \leftarrow J''_{K_a''K_c''} = 4_{14}-3_{03}$ transition was found at 7956.9180(19) MHz, just ~15 MHz below the predicted value. Over 250 *b*-dipole transitions were measured for the $(C_5H_5)_2WH_2$, $(C_5H_5)_2WDH$, and $(C_5H_5)_2WD_2$ complexes. The assignments, transition frequencies, and their observed and calculated values are reported in Tables 1−3. Transitions arising from the four observed W isotopomers were well resolved for the $\Delta K_a = +1$ lines, with typical splittings of 0.5−2.0 MHz between adjacent lines and with the expected frequency ordering $^{186}W < {}^{184}W < {}^{183}W < {}^{182}W$. In the $K_a' \leftarrow K_a'' = 0 \leftarrow 1$ and $2 \leftarrow 3$ stacks, the transition frequency order is reversed ($^{186}W > {}^{184}W > {}^{183}W > {}^{182}W$), while in the $K_a' \leftarrow K_a'' = 1 \leftarrow 2$ stack, the relative ordering changes between the two asymmetry-split components. Spectra predicted from the DFT rotational constants of the various W isotopomers significantly aided the assignments in these cases. The *Q* branches ($\Delta J = 0$) of the $K_a' \leftarrow K_a'' = 3 \leftarrow 2$ and $3 \leftarrow 4$ stacks occur at ~6060 and ~8490 MHz, respectively, and Table 2 reports the assignable *Q*-branch transitions for the various $(C_5H_5)_2WH_2$ species. Nuclear quadrupole splittings due to the ^2H nuclei were unresolvable.

The observed transitions were analyzed using Pickett’s SPFIT[48] least-squares fitting program, and the results are summarized in Table 4. It was found that the ~45 lines measured for each of the $(C_5H_5)_2WH_2$ isotopomers could be accurately described ($\sigma_{fit} = 3-4$ kHz) using only four variable parameters: *A*, *B*, *C*, and Δ_J. The Δ_J centrifugal distortion constant is only ~0.02 kHz; attempts to include more centrifugal distortion parameters gave undetermined values for the additional distortion constants and did not significantly improve the fit. The small values for distortion constants indicate that

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Table 1. Observed $\Delta J = \pm 1$ Transitions of the Various Tungsten Isotopomers of $(C_5H_5)_2WH_2$[a]

$J'_{K_a'K_c'} \leftarrow J''_{K_a''K_c''}$	$^{182}WH_2$	$^{183}WH_2$	$^{184}WH_2$	$^{186}WH_2$
$3_{13} \leftarrow 2_{02}$	6280.1611 (−2.3)	6279.5895 (3.6)	6279.0115 (−2.3)	6277.8766 (−0.9)
$4_{14} \leftarrow 3_{03}$	7958.3643 (−3.7)	7957.6387 (−2.2)	7956.9187 (−2.4)	7955.4877 (−3.8)
$5_{15} \leftarrow 4_{04}$	9631.4242 (1.4)	9630.5244 (1.1)	9629.6319 (−0.5)	9627.8652 (0.4)
$6_{16} \leftarrow 5_{05}$	11299.5266 (−2.1)	11298.4353 (−0.3)	11297.3524 (−0.2)	11295.2049 (−1.0)
$7_{17} \leftarrow 6_{06}$	12962.9466 (4.3)	12961.6377 (0.7)	12960.3424 (−0.4)	12957.7824 (0.9)
$4_{04} \leftarrow 3_{13}$	5616.7933 (−1.9)	5617.0208 (−1.2)	5617.2416 (−6.4)	
$5_{05} \leftarrow 4_{14}$	7336.8438 (−3.6)	7337.1094 (−5.1)	7337.3780 (−1.9)	7337.8956 (−6.0)
$6_{06} \leftarrow 5_{15}$	9061.3896 (−5.7)	9061.7188 (−0.6)	9062.0384 (−1.7)	9062.6738 (0.5)
$7_{07} \leftarrow 6_{16}$	10790.0969 (0.8)	10790.4912 (0.9)	10790.8793 (0.4)	10791.6506 (1.0)
$8_{08} \leftarrow 7_{17}$	12522.5547 (−0.1)	12523.0313 (2.7)	12523.4974 (3.6)	12524.4242 (3.4)
$2_{21} \leftarrow 1_{10}$	7034.4442 (−0.4)	7033.4844 (−0.9)	7032.5326 (−0.5)	7030.6467 (0.2)
$2_{20} \leftarrow 1_{11}$	7045.3445 (2.6)	7044.4336 (−0.5)	7043.5344 (1.3)	7041.7486 (0.8)
$3_{22} \leftarrow 2_{11}$	8723.3320 (2.2)	8722.2744 (3.7)	8721.2217 (1.7)	8719.1387 (1.6)
$3_{21} \leftarrow 2_{12}$	8756.1656 (−0.4)	8755.2691 (5.7)	8754.3707 (3.3)	8752.5938 (2.4)
$4_{23} \leftarrow 3_{12}$	10406.7930 (2.9)	10405.6074 (1.8)	10404.4326 (2.0)	10402.1016 (0.2)
$4_{22} \leftarrow 3_{13}$	10472.8266 (2.4)	10471.9590 (2.9)	10471.0961 (2.0)	10469.3916 (6.1)
$5_{24} \leftarrow 4_{13}$	12084.8359 (4.2)	12083.4974 (1.3)	12082.1738 (2.5)	12079.5443 (−1.4)
$5_{23} \leftarrow 4_{14}$	12195.6128 (2.6)	12194.8164 (7.4)	12194.0169 (4.3)	12192.4414 (6.0)
$6_{25} \leftarrow 5_{14}$	13757.4658 (−1.8)	13755.9500 (−5.3)	13754.4544 (−0.6)	13751.4844 (0.7)
$6_{24} \leftarrow 5_{15}$	13924.9063 (11.8)	13924.1931 (−2.7)	13923.5033 (2.9)	13922.1239 (−1.4)
$6_{15} \leftarrow 5_{24}$	6670.5891 (−3.9)	6671.6571 (−6.2)	6672.7203 (−4.4)	6674.8203 (−3.8)
$7_{17} \leftarrow 6_{24}$	8099.4436 (0.4)	8099.1599 (−0.6)	8098.8821 (−0.6)	8098.3272 (−2.1)
$7_{16} \leftarrow 6_{25}$	8407.5346 (−1.6)	8408.7305 (1.1)	8409.9092 (−1.6)	8412.2522 (0.2)
$8_{18} \leftarrow 7_{25}$	9750.9482 (−0.8)	9750.3704 (4.4)	9749.7910 (2.0)	9748.6484 (1.5)
$8_{17} \leftarrow 7_{26}$	10149.6086 (0.2)	10150.9492 (2.4)	10152.2701 (0)	10154.8945 (−2.8)
$3_{31} \leftarrow 2_{20}$	11166.5039 (7.8)	11164.9641 (8.5)	11163.4359 (9.9)	11160.4063 (9.7)
$3_{30} \leftarrow 2_{21}$	11166.5576 (−11.2)	11165.0219 (−7.0)	11163.4945 (−5.6)	11160.4643 (−7.7)
$4_{32} \leftarrow 3_{21}$	12866.0582 (−0.4)	12864.4618 (−6.0)	12862.8854 (−3.0)	12859.7570 (−3.0)
$4_{31} \leftarrow 3_{22}$	12866.4203 (−2.5)	12864.8359 (0.3)	12863.2614 (1.7)	12860.1392 (0.9)
$8_{27} \leftarrow 7_{34}$	7526.7920 (−1.4)	7527.7529 (−9.2)	7528.7221 (−0.5)	7530.6283 (0.9)
$8_{26} \leftarrow 7_{35}$	7542.0219 (−0.2)	7543.1413 (3.2)	7544.2422 (−2.6)	7546.4408 (−1.0)

[a] The numbers in parentheses are observed minus calculated values in units of kHz.

Table 2. Observed $\Delta J = 0$ Transitions of the Various Tungsten Isotopomers of $(C_5H_5)_2WH_2$[a]

$J'_{K_a'K_c'} \leftarrow J''_{K_a''K_c''}$	$^{182}WH_2$	$^{183}WH_2$	$^{184}WH_2$	$^{186}WH_2$
$9_{36} \leftarrow 9_{27}$	6050.5469 (−3.8)		6047.4466 (−3.2)	
$8_{35} \leftarrow 8_{26}$	6056.5906 (−5.7)	6055.0888 (−9.6)	6053.6089 (−1.2)	6050.6625 (−1.9)
$7_{34} \leftarrow 7_{25}$	6060.8648 (5.0)	6059.4019 (−0.7)	6057.9500 (−4.7)	6055.0888 (−1.2)
$6_{33} \leftarrow 6_{24}$		6062.2913 (0.8)		6058.0601 (0.4)
$5_{32} \leftarrow 5_{23}$	6065.5195 (1.0)	6064.1088 (2.6)	6062.7049 (2.1)	6059.9242 (−2.7)
$4_{31} \leftarrow 4_{22}$	6066.5490 (−3.7)	6065.1484 (−2.0)	6063.7562 (−0.8)	6061.0007 (−0.2)
$3_{30} \leftarrow 3_{21}$	6067.0713 (−3.3)	6065.6726 (−4.8)	6064.2924 (3.4)	6061.5426 (−0.3)
$3_{31} \leftarrow 3_{22}$	6067.4318 (−4.6)	6066.0543 (11.6)	6064.6547 (−3.0)	6061.9203(1.6)
$4_{32} \leftarrow 4_{23}$	6067.6365 (−0.2)	6066.2479 (3.0)	6064.8613 (−0.5)	6062.1250 (−1.6)
$5_{33} \leftarrow 5_{24}$	6068.0463 (2.8)	6066.6549 (−0.6)	6065.2763 (0)	6062.5511 (2.1)
$6_{34} \leftarrow 6_{25}$	6068.7583 (−0.8)		6066.0021 (−3.7)	6063.2917 (−0.3)
$7_{35} \leftarrow 7_{26}$			6067.1726 (−1.4)	6064.4782 (−3.8)
$8_{36} \leftarrow 8_{27}$			6068.9287 (5.7)	
$9_{45} \leftarrow 9_{36}$			8488.7930 (−1.4)	
$9_{46} \leftarrow 9_{37}$			8489.0773 (−3.4)	
$8_{44} \leftarrow 8_{35}$	8493.2974 (−4.5)			
$8_{45} \leftarrow 8_{36}$	8493.4397 (−1.5)		8489.5300 (−3.0)	
$7_{43} \leftarrow 7_{34}$	8493.7090 (8.3)	8491.7409 (−1.4)	8489.8016 (5.1)	
$7_{44} \leftarrow 7_{35}$	8493.7539 (−10.1)			8486.0123 (−2.6)
$5_{41} \leftarrow 5_{32}$	8494.1280 (6.1)	8492.1641 (−3.6)		8486.3864 (0.6)
$4_{41} \leftarrow 4_{32}$		8492.2595 (−2.5)		8486.4814 (−13)

[a] The numbers in parentheses are observed minus calculated values in units of kHz.

the complex is fairly rigid. In fitting the data sets for the $(C_5H_5)_2WDH$ and $(C_5H_5)_2WD_2$ species, which include from 14 to 7 lines, the Δ_J centrifugal distortion constant was fixed to 0.027 kHz, the value obtained for the most abundant $(C_5H_5)_2{}^{184}WH_2$ isotopomer. This gave precisely determined rotational constants with standard errors of 2−3 kHz. We note here the excellent agreement between the B3PW91 and $^{184}WH_2$ experimental rotational constants. The differences between the calculated and experimental rotational constants are 1% or less.

IV. Discussion

A. Kraitchman Analysis. Having measured multiple tungsten isotopomers of the $(C_5H_5)_2WH_2$, $(C_5H_5)_2WDH$, and $(C_5H_5)_2WD_2$ species, we were able to use Kraitchman's equations to locate the principal axis coordinates of the W and H atoms. To locate the tungsten atom, we have chosen the most abundant $(C_5H_5)_2{}^{184}WH_2$ complex as the parent, while using both $(C_5H_5)_2{}^{182}WH_2$ and $(C_5H_5)_2{}^{186}WH_2$ as singly substituted isotopomers. $(C_5H_5)_2{}^{184}WDH$ was paired with the $(C_5H_5)_2{}^{184}WH_2$ parent to determine the hydrogen atom coordinates. For a nonplanar asymmetric top, Kraitchman's equations are best formulated in terms of the planar moments of inertia.[49] Considering the symmetry of the complex, all isotopically substituted atoms lie in the *bc* plane ($|a| = 0$), and the W atom

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(49) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*, 3rd ed.; Wiley: New York, 1984; pp 661−664.

Table 3. Observed Transitions from the Various Mono- and Dideuterated Isotopomers of Bis(η^5-cyclopentadienyl)tungsten Dihydride[a]

$J'_{K_a'K_c'} \leftarrow J''_{K_a''K_c''}$	^{182}WDH	^{184}WDH	^{186}WDH	^{183}WDH	^{182}WD$_2$	^{184}WD$_2$	^{186}WD$_2$
$9_{36} \leftarrow 9_{27}$	6233.0965 (−2.4)	6232.0498 (−3.7)	6231.0169 (−3.2)	6232.5714 (−2.8)			
$4_{14} \leftarrow 3_{03}$	7901.9089(0.1)	7900.6003 (0)	7899.3060 (−0.1)	7901.2526 (0.3)	7854.5417 (−0.3)	7853.2919 (−1.6)	7852.0653 (3.9)
$5_{15} \leftarrow 4_{04}$	9564.5501 (−2.6)	9562.9427 (0)	9561.3516(1.5)		9510.8112 (−0.1)	9509.2630 (−1.3)	9507.7357 (−2.4)
$6_{16} \leftarrow 5_{05}$	11221.3333 (0.1)	11219.3922 (4.7)	11217.4629 (0.1)			11159.1068 (1.6)	
$4_{04} \leftarrow 3_{13}$	5629.2500 (1.5)	5629.6323 (−4.3)	5630.0189 (0.1)	5629.4458 (4.2)			
$5_{05} \leftarrow 4_{14}$	7348.3680 (−2.4)	7348.8156 (−0.3)	7349.2539 (−0.7)	7348.5884 (−3.1)			
$2_{21} \leftarrow 1_{10}$	6946.8424 (−1.7)	6945.0843 (−3.4)	6943.3555 (1.6)	6945.9603 (−1.6)			
$2_{20} \leftarrow 1_{11}$	6960.0729 (−2.5)	6958.4063 (−1.8)	6956.7617 (−0.9)	6959.2370 (−0.6)			
$3_{22} \leftarrow 2_{11}$	8628.5599 (0.4)	8626.6266 (2.2)	8624.7126 (−1.1)	8627.5911 (3.5)	8538.6725 (−3.7)	8536.8854 (−0.4)	8535.1133 (0.9)
$3_{21} \leftarrow 2_{12}$	8668.4681 (−2.4)	8666.8079 (1.8)	8665.1602 (−3.1)		8580.5716 (2.3)	8579.0527 (−2.4)	8577.5553 (0.6)
$4_{23} \leftarrow 3_{12}$	10303.6922 (−2.9)	10301.5313 (−6.2)	10299.4078 (1.4)		10208.0000 (2.6)	10205.9893 (1.0)	10203.9980 (−1.4)
$4_{22} \leftarrow 3_{13}$	10384.0612 (1.2)	10382.4538 (2.8)	10380.8643 (1.2)		10292.3919 (−0.7)	10290.9475 (3.3)	10289.5091 (−0.5)
$5_{24} \leftarrow 4_{13}$	11972.2682 (7.3)	11969.8359 (−0.8)	11967.4414 (−0.2)				
$5_{23} \leftarrow 4_{14}$	12107.2865 (1.9)	12105.7930 (3.4)	12104.3164 (1.5)		12012.3021 (−0.2)	12010.9792 (−1.1)	12009.6719 (−0.1)

[a] The numbers in parentheses are observed minus calculated values in units of kHz.

Table 4. Rotational and Distortion Constants for 11 Measured Isotopomers of Bis(η^5-cyclopentadienyl)tungsten Dihydride[a]

param	^{182}WH$_2$	^{183}WH$_2$	^{184}WH$_2$	^{186}WH$_2$	^{182}WHD	^{183}WHD
A (MHz)	2063.33400(20)	2063.03083(21)	2062.72985(15)	2062.13368(14)	2035.32879(39)	2035.04964(72)
B (MHz)	855.26809(21)	855.26925(22)	855.27056(16)	855.27236(16)	853.98117(19)	853.98009(30)
C (MHz)	844.44337(21)	844.39355(22)	844.34444(15)	844.24627(15)	840.85865(14)	840.81385(36)
Δ_J (kHz)	0.0216(22)	0.0228(23)	0.0272(16)	0.0260(16)	[0.027]	[0.027]
σ_{fit} (kHz)	4.36	4.39	3.25	3.02	2.73	2.71
no. of lines	46	43	48	44	14	7

param	^{184}WHD	^{186}WHD	^{182}WD$_2$	^{184}WD$_2$	^{186}WD$_2$
A (MHz)	2034.77306(45)	2034.22459(22)	2008.11448(75)	2007.60460(65)	2007.09886(72)
B (MHz)	853.97957(22)	853.97795(10)	851.87276(45)	851.87518(39)	851.87805(43)
C (MHz)	840.76937(16)	840.680952(83)	838.11192(27)	838.02499(20)	837.93956(26)
Δ_J (kHz)	[0.027]	[0.027]	[0.027]	[0.027]	[0.027]
σ_{fit} (kHz)	3.13	1.55	1.98	1.84	1.90
no. of lines	14	14	7	8	7

[a] ^{184}WH$_2$ DFT: $A = 2086.6618$ MHz, $B = 852.3157$ MHz, $C = 842.8363$ MHz from B3PW91/aug-cc-pVTZ on C and H and Hay−Wadt VDZ ($n + 1$) ECP on W.

lies on the b axis ($|c| = 0$). In principle, this should simplify the problem, as substitution of a hydrogen atom, from symmetry considerations, should result in no change in the planar moment of inertia as measured from the a axis: $\Delta P_a = {}^1/_2(-\Delta I_a + \Delta I_b + \Delta I_c) = 0$. Substitution of the W atom should maintain both ΔP_a and $\Delta P_c = {}^1/_2(-\Delta I_c + \Delta I_a + \Delta I_b) = 0$. In general, these relationships are only rigorously true for a hypothetical "rigid" structure which does not vibrate, or when the equilibrium moments of inertia are employed. Ground-state vibrational averaging effects can often lead to unreliable results when dealing with substitution of an atom on a symmetry axis or in a symmetry plane, particularly in the case of H-atom substitution. For example, upon ^{182}W substitution of the $(C_5H_5)_2{}^{184}WH_2$ parent, $\Delta P_c \approx 0$ and $\Delta P_b = -0.0718(1)$ amu Å^2, but $\Delta P_a = 0.0017(1)$ amu Å^2. Because the reduced mass, μ, is negative in this case ($\mu = M\Delta m/(M + \Delta m)$, where M is the total mass of the parent molecule and Δm is the mass difference of the substituted atom and parent atom), an imaginary number is obtained for the a coordinate: $|a| = 0.029(1)i$ Å. Single deuterium atom substitution between $(C_5H_5)_2{}^{184}WDH$ and the $(C_5H_5)_2{}^{184}WH_2$ parent results in a translation of the center of mass (COM), a rotation of the principal axes, and a significant change in the W−H$_2$ group vibrational amplitudes projected onto the new principal axes. This substitution results in $\Delta P_a = 0.0361(1)$ amu Å^2 and a corresponding $|a| = 0.1887(3)$ Å, which should, from symmetry considerations, be zero. Similar zero-point vibrational effects have been observed in the dihydrides of the d^8 metal tetracarbonyls ($H_2M(CO)_4$, M = Fe,[50] Ru,[51] Os[52]). Rudolph[53] has shown that, in cases of isotopic substitution on a principal axis or in a symmetry plane, it is preferable to set the appropriate ΔP_i terms to zero, in accord with the molecular symmetry. Thus, the W and H atomic coordinates were obtained from eqs 13.71−13.73 of ref 49 by assuming $\Delta P_a = \Delta P_c = 0$ for the W atom substitution analysis and $\Delta P_a = 0$ for the H atom substitution analysis. In this manner, we obtained an average W atom $|b|$ coordinate of 0.1887(2) Å from ^{182}W and ^{186}W substitution of the $(C_5H_5)_2{}^{184}WH_2$ parent. From the $(C_5H_5)_2{}^{184}WDH$ and $(C_5H_5)_2{}^{184}WH_2$ pair, the H atom substitution coordinates were $|b| = 1.4903(1)$ Å and $|c| = 1.0654(1)$ Å. From these coordinates, we determined r_s(W−H) = 1.682(1) Å, r_s(H−H) = 2.130(1) Å, and ∠(H−W−H) = 78.6(1)°. We also used Kraitchman's procedure for the multiple substitutions of the equivalent hydrogen atoms using ^{184}WH$_2$−^{184}WD$_2$ as the appropriate parent−isotopomer pair, and assumed that the WH$_2$ group lies in the bc plane. This analysis gave the $|b|$ and $|c|$ coordinates of the hydrogen atoms, yielding r_s(H−H) = 2.131(1) Å. This large H···H separation distance clearly indicates that this is a "classical dihyride" rather than a "η^2-dihydrogen" complex. Using the W atom $|b|$ coordinate obtained above in the single substitutions of ^{182}W and ^{186}W for the $(C_5H_5)_2{}^{184}WH_2$ parent, we obtain an average r_s(W−H) = 1.682(1) Å and an average ∠(H−W−H) = 78.6(1)°. The results of the Kraitchman analyses are summarized in Table 5. We note that the "experimental" errors in the substitution (r_s) structural

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Table 5. Comparison of Bis(η^5-cyclopentadienyl)tungsten Dihydride Structure Parameters Obtained from Least-Squares Analyses, Kraitchman Analyses, and DFT Calculations

	r(W−H) (Å)	r(H−H) (Å)	∠(H−W−H) (deg)	r(W−Cp) (Å)	∠(Cp−W−Cp) (deg)	av r(C−C) (Å)
r_0[a] least-squares fit	1.703(2)[c]	2.14(2)[c]	78.0(12)[c]	1.940(8)[d]	155(2)[d]	1.429(8)
Kraitchman						
single substitutions	1.682(2)[d]	2.130(2)[d]	78.6(2)[d]			
multiple substitutions	1.682(2)[d]	2.131(2)[d]	78.6(2)[d]			
DFT[b]	1.696	2.125	77.6	1.941	152.6	1.425(11)

[a] Standard deviation of least-squares fit 77 kHz. [b] B3PW91/ with aug-cc-pVTZ basis on H and C atoms and Hay−Wadt VDZ (n + 1) ECP on W atom. [c] Listed uncertainties are 2σ. [d] Listed uncertainties are 20σ.

parameters depend only upon the errors in the moments of inertia, which are determined very precisely by microwave spectroscopy. Costain[54] has shown that vibrational effects tend to cancel to a large degree; however, when large-amplitude vibrational motions are involved, the experimental error is often smaller than the uncertainty inherent in the Kraitchman model due to residual zero-point vibrational effects. In fact, the uncertainties reported here and given in Table 5 are 20 times those obtained from error propagation of errors in the rotational constants. We feel these errors still do not reflect the total uncertainty arising from the large-amplitude WH_2 group vibrational motion.

B. Least-Squares Structure Fit. A set of the more important r_0 structural parameters for the $(C_5H_5)_2WH_2$ complex has been obtained by a least-squares refinement of five adjustable parameters to obtain a fit to the 33 available rotational constants. Without information from a sufficient number of isotopic species to determine the complete structure, we had to make some assumptions about the complex. We first assumed C_{2v} symmetry for the vibrationally averaged structure. Second, studies of similar complexes have shown that the cyclopentadienyl rings deviate very little from planarity.[55−57] Thus, we have constrained the C_5H_5 rings to be planar in the analysis. Also, the Cp carbon−hydrogen bond distance, r(C−H), was fixed at 1.077 Å, which was the average value from the DFT calculations and was in agreement with the average value from a neutron diffraction study of the $(C_5H_5)_2MoH_2$ complex.[56] Under these constraints, we then fit the structure to the experimental rotational constants employing the following parameters as variables: the tungsten−hydrogen bond distance, r_0(W−H), the H−W−H bond angle, ∠(H−W−H), the distance from the cyclopentadienyl ring center to the tungsten atom, r_0(Cp−W), the Cp-center−W−Cp-center bending angle, ∠(Cp−W−Cp), and a single Cp ring radius variable, r_0(Cp), to describe the size of the cyclopentadienyl rings. Three different strategies for defining this last parameter were explored. During initial attempts to fit the structure, equal C−C bond distances and ∠(C−C−C) bond angles were assumed, while varying the (equal) distance of each carbon atom from the Cp-ring (pentagon) center. This gave a reasonable structure, with a fit standard deviation of 137 kHz; however, both DFT and the $(C_5H_5)_2MoH_2$ neutron diffraction study indicate that the C−C bond distances and ∠(C−C−C) bond angles are not equal. To compensate for this, we first initialized the geometry of the cyclopentadienyl carbon atoms to the DFT geometry and made the distance from the Cp-ring center of mass to C(1) (see Figure 1) a variable parameter. The coordinates of the other carbon atoms were then scaled accordingly to provide Cp-ring dimensions which are proportional to values obtained from the DFT calculations. This was then repeated using the initial geometry and ring dimensions of the cyclopentadienyl rings from the $(C_5H_5)_2MoH_2$ neutron diffraction study.[56] These DFT-scaled and $(C_5H_5)_2MoH_2$-scaled analyses gave fit standard deviations of 88 and 77 kHz, respectively. The results of the best fit, using the above constraints, are given in Table 5. r(H−H) was not a variable parameter in the fit but was determined from r(W−H) and ∠(H−W−H). The average r(C−C) distance was also not a fitted parameter but was determined from the cyclopentadienyl ring radius parameter, r(Cp), and the subsequent scaling of the Cp ring (vide supra). The atomic coordinates in the principal axis system of the $(C_5H_5)_2{}^{184}WH_2$ isotopomer which were obtained from the structure fit results are given in Table 6.

Table 6. Atomic Coordinates of the $(C_5H_5)_2{}^{184}WH_2$ Complex in the Center of Mass (*abc*) System Obtained from the Least-Squares Structure Fit[a]

atom	*a*	*b*	*c*	atom	*a*	*b*	*c*
C1	1.634	−1.437	0.0[b]	C8	−2.106	0.700	−0.707
C2	1.814	−0.617	−1.170	C9	−2.106	0.700	0.707
C3	2.106	0.700	−0.707	C10	−1.814	−0.617	1.170
C4	2.106	0.700	0.707	H16	−1.400	−2.488	0.0[b]
C5	1.814	−0.617	1.170	H17	−1.744	−0.934	−2.196
H11	1.400	−2.488	0.0[b]	H18	−2.293	1.547	−1.341
H12	1.744	−0.934	−2.196	H19	−2.293	1.547	1.341
H13	2.293	1.547	−1.341	H20	−1.744	−0.934	2.196
H14	2.293	1.547	1.341	H21	0.0[b]	1.487	1.071
H15	1.744	−0.934	2.196	H22	0.0[b]	1.487	−1.071
C6	−1.633	−1.437	0.0[b]	W23	0.0[b]	0.163	0.0[b]
C7	−1.814	−0.617	−1.170				

[a] The coordinates are given in angstroms, We estimate the error in these coordinates to be ± 0.002−0.008 Å. [b] Coordinate constrained to zero in fit under symmetry considerations.

Unfortunately, the lack of spectra from ^{13}C-substituted species limits the degree to which some of the parameters for the C_5H_5 ligands can be independently and accurately determined. The main complication is that, without ^{13}C data, the fit parameters associated with the Cp ring geometry (r(W−Cp), ∠(Cp−W−Cp), and the radius r(Cp)) are highly correlated. Attempts were made to fix one or more of these Cp-associated parameters to reasonable values, such as those from DFT calculations or those from the $(C_5H_5)_2MoH_2$ neutron diffraction study. These constraints successfully eliminated the correlations but yielded larger fit standard deviations and gave ∠(H−W−H) values of ~90°, much larger than the values obtained from DFT and Kraitchman results. In order to obtain reasonable results for the WH_2 geometry, all three of the aforementioned Cp parameters were treated as adjustable parameters in the least-squares analysis. This, however, resulted in the ∠(Cp−W−Cp) being correlated with the r(Cp−W) and r(Cp) parameters with coefficients of 0.998 and 0.992, respectively, while the r(Cp−W) and r(Cp) parameters have a correlation coefficient of 0.990. The r(W−H) distance is free from any significant level of correlation, but the H−W−H angle is correlated to each of the three Cp parameters with coefficients of 0.96. While the least-squares results in Table 5 represent our best fit ($\sigma_{\mathrm{fit}} = 77$ kHz), the

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Table 7. Structural Parameters of Various Transition-Metal Hydrides

molecule	method	r(M−H) (Å)	∠(H−W−H) (deg)	r(H−H) (Å)	r(M−Cp) (Å)	av r(C−C) (Å)	∠(Cp−M−Cp) (deg)[b]
$(C_5H_5)_2WH_2$[a]	microwave	1.703(2)	78.0(12)	2.14(2)	1.940(8)	1.429(8)	155(2)
$(C_5H_5)_2MoH_2$[c]	neutron diffraction	1.685(3)	75.5(3)	2.06	1.94	1.421(5)	151.5[d]
$(C_5H_5)_2NbH_3$[e]	X-ray	1.69(4)	63(3)	1.75	2.059(11)	1.394(6)	143[d]
$(C_5H_5)_2TaH_3$[e]	neutron diffraction	1.774(3)	62.9(5)	1.85	2.065	1.421(3)	141[d]
$(C_5H_5)W(CO)_3H$[f]	microwave	1.79(2)			2.03(1)	1.423(4)	
$(C_5H_5)Mo(CO)_3H$[g]	microwave	1.80(1)					

[a] This work. [b] Angle measured from the Cp centroid. [c] Reference 56. [d] The reference reports the angle measured from the normals of the Cp rings to the metal. The value in this table is measured from the Cp centroid and was determined from the crystal structure for direct comparison. [e] Reference 58. [f] Reference 60. [g] Reference 59.

r(Cp−W), ∠(Cp−W−Cp), and r(Cp) parameters cannot be independently and accurately determined from the available data, and consequently, we have made conservative estimates of the uncertainties for these parameters. For the WH_2 moiety parameters (r(W−H), ∠(H−W−H) and r(H−H)), the listed uncertainties (Tables 5 and 7) are 2σ, because these parameters are not highly correlated with other parameters. For the highly correlated parameters r(Cp−W), ∠(Cp−W−Cp), and the average r(C−C), the listed uncertainties are 20σ. Even the 20σ uncertainties may underestimate errors, since there are significant contributions due to correlations and vibrational effects.

It should also be noted here that we have assumed the vector from the tungsten atom to the Cp centroid is normal to the Cp ring plane. The DFT predictions and $(C_5H_5)_2MoH_2$ neutron diffraction study indicate, however, that the rings are very slightly tilted by ∼3.5°, such that the W−Cp centroid−C(1) angle is ∼86.5°. Fixing this "tilt angle" in the least-squares analysis did decrease the σ_{fit} value but resulted in a r(W−H) distance shorter than both the Kraitchman and DFT values. As the Kraitchman analysis has been shown to partially compensate for vibrational effects,[54] both the r_s and DFT r_e values of the W−H bond length should be shorter than the effective (r_0) value. We have chosen to neglect this small Cp tilting in our analysis.

C. Comparisons to Similar Molecules. In Table 7 we compare the present $(C_5H_5)_2WH_2$ structure parameters to those of several relevant transition-metal hydride complexes. Note that the Cp−M−Cp bending angle is smaller in the trihydride complexes $(C_5H_5)_2MH_3$ (M = Nb, Ta; ∠Cp-M-Cp = ∼140°)[58] than in the dihydride complexes $(C_5H_5)_2MH_2$ (M = Mo,[56] W; ∠Cp−M−Cp = ∼150°). Furthermore, in both cases, the r(M−H) distance increases on going from row 4 to 5, but the r(M−Cp) distance is relatively unchanged. When the Mo and W bis(cyclopentadienyl) dihydrides are compared with the cyclopentadienyl tricarbonyl hydrides,[59,60] it is observed that the r(M−H) values are significantly longer for the tricarbonyl hydride complexes, and the r(M−Cp) value for $(C_5H_5)W(CO)_3H$ is significantly longer than that of $(C_5H_5)_2WH_2$, indicating that the bonding is highly dependent upon the oxidation state of the metal.

V. Conclusions

In this work, we have undertaken the first quantitative structure determination of the bis(η^5-cyclopentadienyl)tungsten dihydride complex. Rotational constants from 11 different isotopomers have yielded precise values for the WH_2 structure parameters, with the values from the partial r_0 structure fit in good agreement with those from the Kraitchman analyses. The above data and analyses provide highly accurate and precise structural parameters for the corrdinates and geometry of the $W-H_2$ region of the molecule. We believe that this is the more interesting and important part of the molecule. The coordinates and experimental geometry are less accurate for the Cp rings. Experimental parameters for Cp ring positions and geometry could be improved with further measurements of spectra for ^{13}C substitutions at the three unique carbon atom locations on the Cp ring. These additional data would allow a more accurate determination of the r(Cp−W), ∠(Cp−W−Cp) and r(Cp) ring parameters.

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