Microwave Molecular Structure Measurements for Tetracarbonyldihydroosmium, a Classical Dihydride

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Abstract: Microwave rotational spectra for six isotopomers of $H_2Os(CO)_4$ were measured in the 4−12 GHz range using a Flygare-Balle-type spectrometer. The 18 rotational constants from these isotopomers were used to determine eight structural parameters describing the gas-phase structure of this complex. This near-octahedral complex has C_{2v} symmetry and the dipole moment lies along the *c*-principal axis for the normal isotopomer. The distance between H atoms, obtained directly from experimental structural parameters, is $r_{HH} = 2.40(2)$ Å. This rather long H−H distance indicates that this is clearly a "dihydride" rather than a "dihydrogen" complex. The Os−H bond lengths are $r_{OsH} = 1.72(1)$ Å. The osmium−carbonyl carbon bond lengths for axial and equatorial carbonyl groups are $r_{OsC1} = 1.96(1)$ Å and $r_{OsC3} = 1.97(2)$ Å. Results for other structural parameters obtained using least-squares fitting and the structural parameters obtained using the Kraitchman method are presented and discussed. No evidence for internal motion was observed for this complex.

Introduction

Metal−hydrogen bonding has recently been a very active research area since transition metal hydrides are involved in many useful and important reactions. They may function as stoichiometric reactants, intermediates, or catalysts in hydrogenation, hydroformulation, or other reactions.[1−4] They show a broad range of patterns of reactivity, some behaving as hydride donors,[5] others active as protonating agents,[6] and some exhibiting hydrogen atom transfer.[7]

Transition metal complexes containing two hydrogen atoms have been the subject of much recent interest and research activity. The unexpected discovery by Kubas *et al.*[8] in 1984 of dihydrogen complexes, where the H−H bond remains intact with the H−H bond length very close to that of a free hydrogen molecule, initiated a very large number of searches for other complexes of this type. These complexes are identified as "dihydrogen" complexes to distinguish them from the classical "dihydrides" where the hydrogen atoms would be independently bound to the metal atom and separated from each other by much larger distances.

Dihydrogen complexes are believed to be of fundamental importance in a wide variety of processes,[9] ranging from hydrogenation of alkenes or alkynes to understanding the functioning of metalloenzymes such as hydrogenases[10] or nitrogenase.[11] The rapid progress in this area and many of the large number of dihydrogen complexes discovered recently are discussed in an extensive review by Jessop and Morris.[12] There are other cases where dihydrogen complexes are believed to be transient intermediates in oxidative addition of dihydrogen or reductive elimination of dihydrogen.[12] The most useful methods[8] for determining the details of hydrogen atom bonding and identifying dihydrogen were discussed by Kubas.[13] The methods include single-crystal neutron diffraction, IR measurements of hydrogen frequencies, or NMR measurements of T_1 values or spin−spin coupling parameters. Many complexes previously thought to be classical dihydrides have been found to be dihydrogen complexes. Theoretical developments regarding various dihydrogen complexes are reviewed in the book by Dediu.[14] Hydrogen atom coordinates are often poorly determined using X-ray diffraction and the X-ray structure alone is not usually considered to give a reliable identification of dihydrogen complexes. The hydrogen atom separation for dihydrogen complexes is typically $r_{HH} \cong 0.8$ Å, very close to the free hydrogen molecule value of $r_{HH} = 0.74$ Å. A suggested criterion for "dihydride" complexes[12] is $r_{HH} \geq 1.8$ Å. Therefore it appears that accurate measurements of r_{HH} can be useful and important in this area.

The hydrogen atom coordinates have been accurately determined for transition metal hydride complexes from microwave measurements on H and D isotopomers.[15,16] The accuracy and precision for the microwave measurements is typically a few hundredths of an angstrom, so this type of measurement should provide helpful information in studies of dihydrogen and dihydride complexes. There does not appear to be published experimental data on the structure of $H_2Os(CO)_4$. Theoretically determined structural parameters for this complex and X-ray structural data for the related complex $C_2H_4Os(CO)_4$, however,

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Table 1. Measured Transition Frequencies and DEV (Deviation = Measured − Calculated) Frequencies for $H_2{}^{192}Os(CO)_4$ and $H_2{}^{190}Os(CO)_4$[a]

						$H_2{}^{192}Os(CO)_4$		$H_2{}^{190}Os(CO)_4$	
J	K_p	K_o	J'	K'_p	K'_o	meas	DEV	meas	DEV
1	0	1	2	1	1	3999.851	0.0002		
1	1	0	2	2	0	4569.405	−0.0003	4570.343	−0.0002
1	1	1	2	2	1	4654.967	−0.0004	4656.012	0.0003
2	0	2	3	1	2	5896.795	0.0004		
2	1	1	3	2	1	6273.900	0.0007	6275.028	−0.0002
2	1	2	3	2	2	6491.101	−0.0003	6492.465	0.0003
2	2	0	3	3	0	7085.414	−0.0011	7086.954	0.0004
2	2	1	3	3	1	7105.051	0.0002	7106.633	0.0000
3	0	3	4	1	3	7870.619	−0.0011	7872.338	-0.0004
3	1	2	4	2	2	8021.670	0.0012	8023.095	0.0000
3	1	3	4	2	3	8376.474	0.0008	8378.223	0.0004
3	2	1	4	3	1	8783.836	0.0017	8785.482	0.0005
3	2	2	4	3	2	8870.580	−0.0002	8872.404	-0.0008
3	3	0	4	4	0	9585.500	0.0004	9587.645	0.0000
3	3	1	4	4	1	9588.212	−0.0003	9590.365	-0.0006
4	1	3	5	2	3	9837.098	−0.0018	9838.944	-0.0013
4	0	4	5	1	4	9922.369	−0.0002	9924.695	0.0021
4	1	4	5	2	4	10308.293	0.0002	10310.484	-0.0021
4	2	2	5	3	2	10454.897	−0.0016	10456.651	0.0012
4	2	3	5	3	3	10667.734	0.0003	10669.863	0.0004
4	3	1	5	4	1	11310.790	0.0007	11313.083	0.0004
4	3	2	5	4	2	11328.592	−0.0006	11330.941	-0.0003
5	1	4	6	2	4	11734.592	0.0010	11736.989	0.0000

[a] The calculated frequencies were obtained from a least-squares fit to measured frequencies with parameters given in Table 4. Values in MHz.

were published recently.[17] The structural parameters for the $Os(CO)_4$ fragment of the ethylene complex[17] were used for preliminary calculations of the microwave spectrum.

Experimental Section

The $H_2Os(CO)_4$ complex was prepared following the general method given by George, Knox, and Stone,[18] with modifications given by Collman *et al.*[19] and Carter *et al.*[20] These methods involve the direct addition of H_3PO_4 to $Na_2[Os(CO)_4]$. In the present work the $NaK_{2.8}$ amalgam was used as the alkali metal to facilitate controlled additions to the reaction mixture. Reactions were carried out in a two-necked 250-mL round-bottom flask with a Teflon-coated magnetic stir bar. NH_3 (50 mL) was distilled under vacuum, first into a trap containing a small piece of metallic sodium, then into the reaction flask. The solid $Os_3(CO)_{12}$ (Strem 76-2000) was added, a small portion at a time, using a cutoff glass syringe with Teflon plunger inserted horizontally into a distillation adapter on top of the reaction flask. The liquid ammonia in the reaction flask was maintained at −77 °C with 1 atm of dry N_2 above it. The $NaK_{2.8}$ was added using a syringe through a septum into the reaction flask. Alternate additions of small amounts of $NaK_{2.8}$ and $Os_3(CO)_{12}$ were made over a 2 h period using the color change to indicate complete reaction. After complete reaction of 1 g of $Os_3(CO)_{12}$, a small excess of $NaK_{2.8}$ was added and the NH_3 pumped off. The tan-colored $Na_2Os(CO)_4$ was pumped on overnight to remove most of the remaining NH_3. An excess of 80% phosphoric acid was added dropwise to the $Na_2Os(CO)_4$ in a 0 °C reaction flask under 1 atm of dry nitrogen. The reaction flask was connected to a liquid nitrogen cooled trap to collect the hydride. The reaction mixture was stirred and then product was collected in the 77 K trap which contained a few grams of P_2O_5 (Fluka 7910) by reducing the pressure at the outlet of the trap. The product was subsequently slowly transferred under vacuum to a sample cell. For the deuterated isotopomers, deuterated phosphoric acid (Aldrich 17,675-3) was used in the second step.

Table 2. Measured Transition Frequencies and DEV (DEV = Measured − Calculated), for $HD^{192}Os(CO)_4$ and $D_2{}^{192}Os(CO)_4$[a]

						HD $^{192}Os(CO)_4$		D_2 $^{192}Os(CO)_4$	
J	K_p	K_o	J'	K'_o	K'_p	meas	DEV	meas	DEV
1	0	1	2	1	1	3978.807	0.0009	3957.718	−0.0010
1	1	0	2	2	0	4534.781	0.0001	4500.823	0.0001
1	1	1	2	2	1	4618.954	−0.0019	4583.511	−0.0001
2	0	2	3	1	2	5868.130	−0.0009	5839.132	−0.0020
2	1	1	3	2	1	6234.910	−0.0012	6196.482	−0.0002
2	1	2	3	2	2	6448.307	−0.0009	6405.911	0.0011
2	2	0	3	3	0	7028.494	−0.0001	6972.690	−0.0009
2	2	1	3	3	1	7047.967	0.0008	6991.929	−0.0005
3	0	3	4	1	3	7833.261	−0.0007	7795.137	0.0009
3	1	2	4	2	2	7978.038	−0.0012	7934.677	−0.0007
3	1	3	4	2	3	8326.150	0.0002	8275.977	0.0017
3	2	1	4	3	1	8722.046	−0.0014	8661.466	0.0004
3	2	2	4	3	2	8807.948	0.0010	8746.244	−0.0024
3	3	0	4	4	0	9506.744	0.0003	9429.512	0.0007
3	3	1	4	4	1	9509.457	0.0020	9432.207	0.0013
4	1	3	5	2	3	9788.035	0.0006	9738.775	0.0011
4	0	4	5	1	4	9874.889	0.0036	9826.161	0.0012
4	1	4	5	2	4	10249.684	−0.0009	10190.923	−0.0023
4	2	2	5	3	2	10388.932	0.0032	10324.212	0.0015
4	2	3	5	3	3	10599.221	0.0003	10531.432	0.0027
4	3	1	5	4	1	11226.777	−0.0023	11144.332	−0.0013
4	3	2	5	4	2	11244.560	0.0003	11161.989	−0.0009
5	1	4	6	2	4	11679.015	−0.0011	11622.605	−0.0011
5	0	5	6	1	5	11964.567	−0.0010		
4	4	0	5	5	0	11977.586	−0.0006		
5	2	3	6	3	3			11991.092	−0.0002

[a] Parameters given in Table 4 and frequencies in MHz.

Table 3. Measured Transition Frequencies for $H_2{}^{192}Os(CO)_4$ with Single ^{13}C Isotopic Substitution in the Axial ($^{13}C1$) and Equatorial ($^{13}C3$) Positions[a]

						$^{13}C1$ (axial)		$^{13}C3$ (equatorial)	
J	K_p	K_o	J'	K'_o	K'_p	meas	DEV	meas	DEV
2	0	2	3	1	2	5861.912	−0.0001	5878.236	−0.0025
2	1	1	3	2	1	6252.627	0.0005	6238.484	−0.0012
2	1	2	3	2	2	6468.946	−0.0001	6454.938	−0.0012
2	2	0	3	3	0	7075.989	0.0000	7031.649	0.0010
2	2	1	3	3	1	7094.842	−0.0009	7051.993	0.0007
3	0	3	4	1	3	7820.039	−0.0007	7850.074	−0.0030
3	1	2	4	2	2	7985.232	0.0009	7985.443	0.0016
3	1	3	4	2	3	8340.492	−0.0020	8336.991	−0.0009
3	2	1	4	3	1	8763.738	0.0016	8724.787	−0.0004
3	2	2	4	3	2	8847.482	−0.0033	8814.117	0.0007
3	3	0	4	4	0	9574.188	−0.0001	9511.517	0.0005
3	3	1	4	4	1	9576.715	0.0021	9514.419	−0.0011
4	1	3	5	2	3	9783.661	0.0000	9801.485	0.0018
4	0	4	5	1	4	9855.968	0.0014	9899.257	0.0023

[a] Fit parameters are given in Table 4. Frequencies in MHz.

Microwave spectra were measured in the 4−12 GHz range using a Flygare-Balle spectrometer system.[21] A 1% mixture of the sample vapor in 0.5−1.0 atm of neon was pulsed into the cavity. Transitions due to the $H_2Os(CO)_4$ complex were readily identified since the four most abundant masses (^{192}Os 41%, ^{190}Os 26%, ^{189}Os 16%, and ^{188}Os 13%) resulted in multiplets with approximately 1 MHz line splittings. These relatively large splittings occurred because the osmium atom is displaced approximately 0.2 Å from the center of mass of the complex due to the large unbalance in mass of the H atoms and CO groups.

The single-substitution ^{13}C isotopomers were observed in the natural abundance sample although it was sometimes difficult to sort all the lines since the osmium isotopes resulted in multiplets for all transitions. The sample synthesized with the deuterated phosphoric acid yielded spectra for both the double-deuterium and single-deuterium isotopomers, since there was some exchange in the synthesis and supply tank for the pulsed nozzle system.

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Table 4. Rotational and Distortion Constants for Six Isotopomers of $H_2Os(CO)_4$ Obtained by Fitting the Data Listed in Tables 1−3[a]

parameter	$H_2{}^{192}Os(CO)_4$	$H_2{}^{190}Os(CO)_4$	$HD^{192}Os(CO)_4$	$D_2{}^{192}Os(CO)_4$	$^{13}C1$ (ax)	$^{13}C3$ (eq)
A (MHz)	1245.6334(4)	1245.9279(4)	1234.7593(6)	1224.1037(7)	1244.8410(3)	1235.3960(3)
B (MHz)	918.0758(4)	918.2357(4)	914.6856(6)	911.2080(6)	911.4833(2)	916.2592(3)
C (MHz)	809.8235(9)	809.8237(9)	807.9836(13)	806.2441(13)	805.0165(9)	806.8891(11)
Δ_J (kHz)	0.109(6)	0.112(8)	0.104(10)	0.106(10)	fixed	fixed
Δ_{JK} (kHz)	0.36(3)	0.37(3)	0.39(4)	0.34(4)	fixed	fixed
Δ_K (kHz)	−0.33(3)	−0.34(3)	−0.36(4)	−0.27(6)	fixed	fixed
δ_K (kHz)	0.69(6)	0.69(6)	0.69(6)	0.64(8)	fixed	fixed
σ_{FIT} (kHz)	1.0	1.0	1.6	1.6	1.6	1.7

[a] Listed errors are 2σ. The "FIXED" values of the distortion constants were fixed at values for the normal isotopomer.

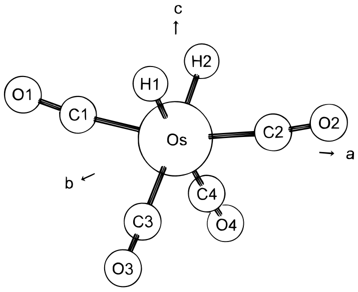

Figure 1. The structure of tetracarbonyldihydroosmium, showing the numbering of atoms and principal inertial axes. The *c*-axis is coincident with the *z*-axis and the C_2 symmetry axis for the normal isotopomer.

Table 5. Results of the Least-Squares Fit To Determine Structural Parameters for Tetracarbonyldihydroosmium from the Experimental Rotational Constants[a]

	Bond Lengths (Å)		
OsC1	1.958(12)	Os−C3	1.968(16)
Os−H	1.720(11)	H1−H2	2.40(2)[b]
	Interbond Angles (deg)		
z−Os−C1	81.6(14)	z−Os−C3	130.6(11)
H1−Os−H2	88.3(7)	C3−Os−C4	99(2)[b]
Os−C1−O1	174(5)		
Os−C3−O3	178(4)	C1−Os−C2	163.(3)[b]
	Fixed Bond Lengths (Å)		
C1−O	1.130	C3−O	1.143

isotopomer	parameter	measd	calcd	DEV
NORMAL	A	1245.6334	1245.6094	0.0240
	B	918.0758	918.1134	−0.0376
	C	809.8235	809.8684	−0.0449
^{190}Os	A	1245.9279	1245.9072	0.0207
	B	918.2358	918.2752	−0.0394
	C	809.8236	809.8684	−0.0448
HD	A	1234.7593	1234.7788	−0.0196
	B	914.6856	914.6621	0.0235
	C	807.9836	807.9500	0.0336
D2	A	1224.1037	1224.1480	−0.0443
	B	911.2080	911.1220	0.0861
	C	806.2441	806.1360	0.1081
$^{13}C1$	A	1244.8410	1244.8431	−0.0022
	B	911.4833	911.4786	0.0046
	C	805.0165	805.0216	−0.0052
$^{13}C3$	A	1235.3960	1235.3762	0.0198
	B	916.2592	916.2949	−0.0357
	C	806.8891	806.9352	−0.0460

[a] Frequencies are in MHz, the standard deviation for the fit is 0.059 MHz. [b] These parameters were not treated as adjustable parameters in the least-squares fit, but are directly obtainable from fit parameters.

Data Analysis and Rotational Constants

The measured rotational transitions for $H_2{}^{192}Os(CO)_4$ and $H_2{}^{190}Os(CO)_4$ are listed in Table 1. The measured frequencies for $HD^{192}Os(CO)_4$ and $D_2{}^{192}Os(CO)_4$ are listed in Table 2 and the single-substitution ^{13}CO data are given in Table 3. Also listed in these tables is the deviation (DEV = measured − calculated) between measured frequencies and those calculated using the least-squares fits. The measured transitions could be fit using an A-reduced, Watson-type Hamiltonian in the I^r representation. Values for the adjustable parameters are listed in Table 4. The parameter δ_J was not independently determinable from the present data sets and was set equal to zero in the calculations. The listed uncertainties on parameters are two standard deviations (2σ). The rotational constants were determined to approximately seven significant figures for six isotopomers of this complex. We note that the C rotational constants for the ^{192}Os and ^{190}Os isotopomers are in excellent agreement, confirming that the Os atom is on the *c*-axis.

Structural Parameters

The eighteen measured rotational constants were used in a least-squares fit to determine eight structural parameters describing the geometry of this complex. The structure and atom numbering for this complex is shown in Figure 1. The results of this structural fit are given in Table 5. The only independent structural parameters which were fixed were the two C−O bond lengths. These could also be determined from the microwave data by treating all of the independent structural parameters, including these C−O bond lengths, as variable parameters in the least-squares fitting procedure. For the results presented in this paper we chose to fix the C−O bond length at the X-ray values because we believe that the precision and accuracy of the X-ray values[17] is higher than we would obtain using the present data set, and previous experience has indicated that C−O bond lengths do not change appreciably from gas-phase microwave to solid-state X-ray data. The listed errors are two standard deviations (2σ) and indicate that bond lengths are determined to ±0.01 Å and three of the interbond angles to ±1°. Since no isotopic substitution data were obtained for the oxygen atoms, the O atom coordinates are not as well determined and the uncertainties on Os−C1−O and Os−C3−O angles are 5° and 4°.

We wish to emphasize that although r_{HH}, the distance between the two hydrogen atoms, was not explicitly a variable parameter in the fit procedure, it is simply and directly related to the fit parameters Os−H (bond length) and H1−Os−H2 (interbond angle). Therefore, the H−H distance r_{HH} = 2.40(2) Å is considered to be an experimental result. The largest deviations between measured and calculated rotational constants (Table 5, "DEV") occur for the D_2 isotopomer. It is likely that this indicates that there are small changes in the Os−H bond lengths or angles on deuterium substitution, due to anharmonicity in the Os−H potential or anharmonicity in the H−Os−H bending potential. Large isotope effects of this type were reported in previous work[15] on $HRe(CO)_5$. The Os−H bond length obtained here, r_{OsH} = 1.72 Å, is significantly shorter than r_{ReH} = 1.80 Å obtained for the rhenium hydride.[15]

The Cartesian coordinates for the atoms in the principal axis system are given in Table 6. These coordinates would be helpful in making comparisons with X-ray or neutron diffraction results,

Table 6. Cartesian Atomic Coordinates (Å) in the Principal Axis System Obtained From the Least-Squares Fit to the Measured Rotational Constants for Tetracarbonyldihydroosmium[a]

atom	*a*	*b*	*c*
C1	1.937	0.0	0.504
C2	−1.937	0.0	0.504
O1	3.033	0.0	0.779
O2	−3.033	0.0	0.779
C3	0.0	1.494	−1.061
C4	0.0	−1.494	−1.061
O3	0.0	2.393	−1.769
O4	0.0	−2.393	−1.769
H1	0.0	−1.198	1.453
H2	0.0	1.198	1.453
Os	0.0	0.0	0.219

[a] Uncertainties in the coordinates range from 0.01 to 0.03 Å.

Table 7. Comparison of Present Microwave Structural Parameters for $H_2Os(CO)_4$ (I) with Calculated Values (ref 17) for this Complex and with X-ray Diffraction Results (ref 17) for $H_4C_2Os(CO)_4$

	I		
parameter	microwave	theory	$H_4C_2Os(CO)_4$
Os−C1 (ax) (Å)	1.96	1.979	1.94
Os−C3 (eq) (Å)	1.97	2.010	2.22
Os−H (Å)	1.72	1.676	
C1−Os−C2 (deg)	163	160.7	171.3
C3−Os−C4 (deg)	99	100.0	106.0
Os−C1−O (deg)	174	174.4	173.7
Os−C3−O (deg)	178	177.9	178.2
H1−Os−H2 (deg)	88	85.1	

or results of new molecular orbital calculations. A comparison of the present results with calculated results[17] for $H_2Os(CO)_4$ and the X-ray results[10] for $C_2H_4Os(CO)_4$ is given in Table 7. We note that the agreement between the microwave data and theoretical calculations for $H_2Os(CO)_4$ is remarkably good, especially considering the large number of electrons and large binding energies for core electrons for this complex.

Kraitchman Analysis

A Kraitchman analysis was carried out using the measured rotational constants for the various isotopomers, with $H_2{}^{192}Os(CO)_4$ as the "unsubstituted" molecule. The equations for single isotopic substitution on a nonplanar asymmetric top[22] were used. This analysis provided the absolute values of the molecular frame *a*, *b*, and *c* coordinates for the hydrogen, carbon, and osmium atoms and the results are listed in Table 8, along with the corresponding values from the least-squares fit structural analysis. The parameters involving deuterium (D−D distance, r_{OsD} and ∠D1−Os−D2) were obtained using $D_2Os(CO)_4$ as the reference molecule and $HDOs(CO)_4$ as the substituted molecule.

Most of the parameters listed in Table 8 show excellent agreement when comparing the Kraitchman results with values from the least-squares fit. The exception is the parameters involving the H1−Os−H2 angle. The Os−H1 and Os−D1 distances are in very good agreement, but the H1−Os−H2 and D1−Os−D2 angles show a significant difference and, consequently, the H1−H2 and D1−D2 distances also differ by amounts greater than the estimated errors. We note that this effect is *underestimated* in the Kraitchman analysis, since we must use combinations of partially deuterated and either D_2 or H_2 isotopomers to carry out the analysis. We interpret these differences as an indication of an anharmonic (asymmetric) contribution to the bending potential for deformation of the H1−Os−H2 angle. This effect is clearly substantially larger than would be expected for smaller molecules not involving transition metals.

Table 8. Comparison of Selected Interatomic Distances and Interbond Angles Obtained Using the Kraitchman Equations with Corresponding Values Obtained from the Structural Least-Squares Fit

	Kraitchman	structural fit
	Interatomic Distances (Å)	
H1−H2	2.39	2.40(2)
D1−D2	2.33	2.40(2)
Os−C1	1.95	1.96(1)
Os−C3	1.97	1.97(2)
Os−H1	1.72	1.72(1)
Os−D1	1.72	1.72(1)
	Interbond Angles (deg)	
H1−Os−H2	87.9	88.3(7)
D1−Os−D2	84.9	88.3(7)
C1−Os−C2	162.8	163(3)
C3−Os−C4	100.8	99(2)

Discussion

Accurate, gas-phase values for structural parameters have been obtained from microwave spectra for six isotopomers of tetracarbonyldihydroosmium. The separation between the hydrogen atoms has been accurately determined from the data and the value $r_{HH} = 2.40$ Å is substantially larger than the value of 0.8 Å expected for a "dihydrogen" complex, so this molecule is clearly a "classical dihydride" complex. The agreement with the calculated structural parameters[17] is remarkably good, and this indicates that careful calculations could be useful for differentiating between dihydrogen and classical dihydride complexes. The observed long H−H distance, and lack of any observed internal rotation, also correlate with the fact that this is not a dihydrogen complex, since internal rotation would be expected for a dihydrogen complex. We note that evidence for internal motion was obtained by Vancea and Graham[23] for the related complex $H_2Fe(CO)_4$, using NMR measurements. So without experimental results, there would still be some question whether the iron-group dihydrides formed dihydrogen-type complexes, or classical dihydrides.

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