

Microwave Measurements and Calculations on Cyclopentadienylrhodium Dicarboxyl, a V_{10} Hindered Rotor

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The microwave rotational spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ was measured in the 5–15 GHz range using a Flygare–Balle type spectrometer system. Attempts to fit the spectrum using a rigid-rotor model resulted in large deviations between measured and calculated frequencies and an unreasonably large A rotational constant. A better fit, including more transitions, was obtained using a V_{10} -barrier hindered rotor Hamiltonian, and a much more reasonable A rotational constant was obtained. The barrier height obtained is $V_{10} = 347(13)$ GHz (0.14 kJ mol⁻¹). The rotational constants are $A = 1613(10)$ MHz, $B = 1046.7(7)$ MHz, and $C = 759.7(10)$ MHz. Quantum-mechanical calculations using the DFT options in Gaussian 94 provided structural parameters in good agreement with measurements and a barrier height $V_{10} = 272$ GHz (0.11 kJ mol⁻¹). The calculated structure showed C_2 -symmetry distortions of the cyclopentadienyl moiety, in agreement with previous X-ray data for Cp* $\text{Rh}(\text{CO})_2$. The calculated rotational constants and V_{10} barrier height are in good agreement with the experimental results. The calculations indicate that there is coupling between the internal rotation and distortions of the Cp ligand, and this could very likely provide the major contribution to deviations between the hindered-rotor calculated frequencies and the measured frequencies.

Introduction

Many small, mononuclear transition-metal complexes have been studied recently using microwave spectroscopy, and very few of these complexes exhibit “fluxional” or hindered rotation effects in the microwave spectra. Even the “ring-whizzer” (cyclooctatetraene)iron tricarbonyl¹ exhibits a rigid-rotor-type microwave spectrum.² Exceptions are cyclopentadienylcobalt dicarbonyl,³ which appears to be a V_{10} -barrier hindered rotor, and cyclopentadienylvanadium tetracarbonyl,⁴ which appears to have low-frequency vibrational modes or distortions which reduce the nominal C_4 symmetry of the CO ligands.

Cyclopentadienylrhodium dicarbonyl, with only three ligands, has a relatively open structure and therefore may react readily with other compounds. It has been observed to catalyze hydroformylation and hydrogenation of alkenes, cyclotrimerization of alkynes,⁵ and activation of C–H bonds.⁶ The small number of ligands and the “open” structure are likely to be responsible for

the low barrier to internal rotation. The spectrum of cyclopentadienylcobalt dicarbonyl³ was difficult to analyze, due to the presence of internal rotation and ⁵⁹Co quadrupole coupling. Although the fits to the spectrum were poor by present microwave standards, approximate values for structural parameters and an internal rotation barrier, $V_{10} = 820(200)$ GHz (0.33 kJ mol⁻¹), were obtained by fitting the spectrum. The present studies of the analogous rhodium complex were initiated with the hope that the spectral analysis would be more straightforward and much better fits would be obtained, since no quadrupole coupling would be present. Deviations of a few megahertz between measured and calculated frequencies are obtained in the present work, indicating that there may be additional interaction terms which are not included in the present analysis. Distortions of the cyclopentadienyl ring due to interaction with the $\text{Rh}(\text{CO})_2$ group are likely to be the primary reason for the difficulties in fitting the microwave spectrum. The structure of (pentamethylcyclopentadienyl)rhodium dicarbonyl has been reported previously.^{7,8} The results of both X-ray structure studies indicate C_2 -symmetry distortions of the Cp ring, with C–C distances of 0.04 Å magnitude; therefore, similar effects

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would be expected for CpRh(CO)₂ and significant distortions are predicted from the present DFT calculations.

Experimental Section

The sample was synthesized from RhCl₃ using published procedures.^{9,10} To a 500 mL Schlenk flask was added 3.9 g (10 mmol) of [RhCl(CO)₂]₂, 8.1 g (30 mmol) of Tl(C₅H₅), a magnetic stirbar, and 200 mL of hexane. After it was purged with nitrogen, the flask was sealed, covered with aluminum foil, and stirred vigorously for 24 h. After filtration, the solvent was removed using a water aspirator vacuum. The oily brown residue that remained was distilled from bulb to bulb using high vacuum and liquid-nitrogen cooling. The yellow-orange oil collected was then redistilled a second time to give 2.8 g (12.5 mmol, 57%) of pure (C₅H₅)Rh(CO)₂ as a bright yellow-orange oil.

[RhCl(CO)₂]₂ was prepared¹¹ from the direct treatment of solid [RhCl₃(H₂O)₂] on a medium-porosity glass frit held at 98 °C with CO gas saturated with CH₃OH.

Microwave transitions were measured using a Flygare-Balle type pulsed-beam Fourier transform spectrometer system.¹² A stream of neon, at 0.7 atm pressure, was passed over the sample and into a General Valve Series 9 solenoid valve to produce the pulsed beam. The sample and pulse valve were held at a temperature of 35 °C to produce sufficient vapor pressure. Many transitions were observed with excellent signal-to-noise ratio in the 5–15 GHz range. The series of transitions with $\Delta J = +1$, $\Delta K = 0$, and $\Delta m = 0$ was readily identified and assigned using a rigid-rotor model. The observed transitions used in the data analysis are listed in Table 1.

Data Analysis

A rigid-rotor model, with centrifugal distortion terms, was used in the first attempts to fit the observed transitions. Seven $K_p = 0$, $\Delta K_p = 0$ transitions could be fit with a standard deviation of 1.7 MHz. Twelve transitions, including $K_p = 0, 1$, or 2, could be fit with a standard deviation of 3.5 MHz. Typical standard deviations for “rigid-rotor” transition-metal complexes are 3–5 kHz, nearly a factor of 1000 better than the above fits. In addition, the best-fit values for the A rotational constant were 2099 MHz ($K = 0$) and 2216 MHz ($K = 0, 1, 2$). These values are much larger than the value of $A = 1700$ MHz calculated from parameters obtained from X-ray work^{7,8} on Cp*Rh(CO)₂ and using typical Cp structural parameters. Furthermore, there were many observed transitions not included in the rigid-rotor fits.

The spectrum for the analogous cobalt complex CpCo(CO)₂ also did not fit a rigid-rotor model very well,³ so attempts were made to fit the spectrum as being due to a hindered rotor. For both complexes, the Cp ring is considered the “top” and the M(CO)₂ moiety the frame. These complexes will have 10-fold and possibly 20-fold, or higher, contributions to the barriers to internal rotation, since the Cp and M(CO)₂ groups have symmetry axes C_5 and C_2 , respectively. With such a high barrier multiplicity, a low barrier height would be

Table 1. Measured and Calculated Transition Frequencies for Cyclopentadienylrhodium Dicarbonyl^a

expt	calcd	(M.–C.)	M	J	K	M	J	K
5269.442	5265.159	4.283	0	3	0	0	2	0
5273.646	5269.070	4.576	1	3	1	1	2	1
5415.393	5416.854	-1.462	0	3	2	0	2	2
5436.848	5441.533	-4.685	2	3	0	2	2	0
5574.230	5572.134	2.096	0	3	-2	0	2	-2
6623.476	6624.636	-1.161	2	4	2	2	3	2
6848.352	6841.396	6.956	1	4	1	1	3	1
6868.786	6867.546	1.240	0	4	0	0	3	0
7141.328	7145.340	-4.011	3	4	3	3	3	3
7280.170	7281.283	-1.113	2	4	0	2	3	0
8211.479	8212.468	-0.989	2	5	2	2	4	2
8356.403	8355.702	0.700	1	5	1	1	4	1
8395.581	8398.847	-3.266	0	5	0	0	4	0
8935.787	8943.414	-7.627	0	5	2	0	4	2
9228.750	9229.179	-0.430	1	5	-1	1	4	-1
9784.099	9780.741	3.358	2	6	2	2	5	2
9858.775	9858.800	-0.025	1	6	1	1	5	1
9896.164	9897.980	-1.816	0	6	0	0	5	0
11040.000	11033.608	6.392	2	6	0	2	5	0
11140.065	11139.263	0.802	1	6	3	1	5	3
11337.144	11336.577	0.567	3	6	3	3	5	3
11363.802	11368.455	-4.653	1	7	1	1	6	1
11395.164	11394.993	0.172	0	7	0	0	6	0
12345.211	12351.455	-6.244	0	7	2	0	6	2
12794.767	12795.213	-0.446	1	7	3	1	6	3
12874.818	12869.756	5.062	2	8	2	2	7	2
12898.953	12901.490	-2.538	0	8	0	0	7	0
14009.246	14004.800	4.446	0	8	2	0	7	2
14418.297	14418.410	-0.113	0	9	0	0	8	0

^a All frequencies are in MHz. (M.–C.) are the differences between measured and calculated frequencies. The calculated values were obtained using the least-squares-fit parameters given in Table 2.

expected, so a $|JKm\rangle$, free rotor basis¹³ or “IAM” method was used. The Hamiltonian matrix elements were given previously,³ based on earlier work.¹⁴ Since the CO ligands are composed of only bosons ($I = 0$), the required symmetry with respect to exchange of the CO groups will place restrictions on the allowed states¹⁵ for CpRh(CO)₂. Only states with even values for $|m - K|$ can exist.

A program¹⁶ based on the $|JKm\rangle$ representation, including the V_{10} barrier terms, was used to fit observed transitions. The measured and calculated transition frequencies are listed in Table 1. The top moment of inertia for the Cp group, I_a , was fixed at 114.4 amu Å², a value based on typical structural parameters for the cyclopentadienyl group. Since the V_{10} term results in matrix elements off-diagonal in m by ± 10 , fairly large m values must be used in the matrix of possible states. Calculations with maximum m values of 48–64 were carried out, and the results were in agreement, within a few kilohertz, indicating a maximum m of 48 was sufficiently high. For calculations with higher barrier heights, higher m values were required. The standard deviation for the fit with 7 adjustable parameters and 29 lines is 4.1 MHz. The parameter values are listed in Table 2. The standard deviation is larger than

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Table 2. Molecular Parameters Obtained from a Least-Squares Fit to the Data Given in Table 1^a

param	value (2 σ)	param	value (2 σ)
A	1613(10)	Δ_{JK}	0.15(8)
B	1046.7(6)	Δ_K	-0.4(6)
C	759.7(10)	V_{10}	346708(6635)
Δ_J	-0.014(5)	$\sigma(\text{fit})$	4.13

^a Values are in MHz. Listed uncertainties are 2 σ .

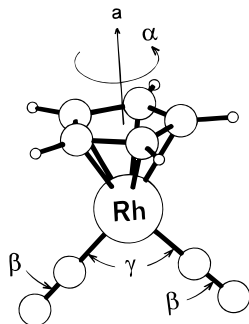


Figure 1. Structure of the $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ complex. The internal rotation angle is α , and the rocking motion occurs along the OC–Rh–CO angle β .

expected or desirable, but the parameter values are still reasonably well-determined. Possible reasons for this large deviation include distortions of the Cp group by the $\text{Rh}(\text{CO})_2$ moiety or other structural relaxation effects¹⁷ not included in the present analysis. The DFT calculations (see below) indicate that interactions between the Cp and $\text{Rh}(\text{CO})_2$ groups may cause the C_2 axis of the $\text{Rh}(\text{CO})_2$ moiety to tilt away from the a axis of the complex and cause distortions of the Cp group. This would decrease the V_{20} term in the hindered-rotor potential. The distortions and tilt angle will depend on the internal rotation angle; therefore, the dynamics of this molecule become quite complex.

Structural Parameters

The basic structure of the $\text{CpRh}(\text{CO})_2$ complex is shown in Figure 1. Data are only available for the normal isotopomer at the present time; therefore, the structural analysis is quite limited. If we fix the structure of the cyclopentadienyl ligand, the Cp–Rh distance at 1.906 Å, and the C–O bond length at 1.12 Å, we can fit the experimental B and C rotational constants to obtain $r(\text{Rh}-\text{C})$, the rhodium–carbonyl carbon bond length and $\angle\text{C}-\text{Rh}-\text{C}$, the carbon–rhodium–carbon angle (γ). Approximate values obtained are $r(\text{Rh}-\text{C}) = 1.88$ Å and $\angle\text{C}-\text{Rh}-\text{C} = \gamma = 88.6^\circ$. These parameters are in good agreement with X-ray values for $\text{Cp}^*\text{Rh}(\text{CO})_2$ determined by Lichtenberger *et al.*⁷ of 1.854 Å and 90.1° and values from Braunstein *et al.*⁸ at 1.845 Å and 88.5° . The basic structure is shown in Figure 1.

Computational Results

Computations were carried out on IBM RISK6000 and SGI Origin 2000 computers at the BPW91 level of density functional theory (DFT); *i.e.*, with the gradient corrections of Becke¹⁸ for exchange and corrections of Perdew and Wang¹⁹ for correlation. Dunning's (4s2p)-

[9s5p] basis sets²⁰ were used for C and O atoms, while the (2s)[4s] basis was used for H atoms. The (6s5p3d)-[8s7p6d] basis set of Stoll and Preuss²¹ was used for Rh along with the corresponding quasi-relativistic core potential.²¹ These methods were particularly useful in previous geometry optimizations of compounds containing a many-electron metal center.²² All calculations employed the Gaussian 94 package.²³

Geometry optimizations of the $\text{CpRh}(\text{CO})_2$ molecule were calculated with different values of the torsional angle α associated with internal rotation of the $\text{Rh}(\text{CO})_2$ fragment of the molecule, allowing relaxation of the $\text{Rh}(\text{CO})_2$ fragment along the "rocking" coordinate β (see Figure 1). Initially, the symmetry of the Cp group was fixed at D_{5h} assuming a regular pentagon (section A below), and optimized geometries and single-point energies were determined for a few values of the dihedral angle (α) of the CO plane measured with respect to a carbon in the Cp ring. The photoelectron study²⁴ indicated that the Cp group, may lose D_{5h} symmetry through interaction with the $\text{Rh}(\text{CO})_2$ group and the X-ray crystal structure of $\text{Cp}^*\text{Rh}(\text{CO})_2$ ^{7,8} indicated a C_1 symmetry ground state; therefore, the calculations were also carried out (section B below) allowing the Cp group to relax to the lower symmetry. In an effort to map out the potential energy surface of the internal rotation, nine separate calculations were performed at intervals of 2.25° torsional angle between the CO plane and a single chosen carbon in the Cp group. Geometries at both 0 and 18° were restricted to C_s symmetry, while all others were optimized in C_1 symmetry. Geometries with the "tilted" $\text{Rh}(\text{CO})_2$ group (section C below) were optimized under the same symmetry constraints at intervals of 3° along the α coordinate.

A. Cp (D_{5h})–Rh(CO)₂ (C_{2v}). Initial geometry optimizations were carried out under the high-symmetry conditions that would be expected for a $\text{CpRh}(\text{CO})_2$ molecule in the gas phase with no interactions between the ligands. The Cp group is fixed with D_{5h} symmetry, and the $\text{Rh}(\text{CO})_2$ group is fixed with C_{2v} symmetry, with the major rotation axes (C_5 and C_2) coinciding with the a axis of the molecule. The staggered and eclipsed rotamers were calculated to have very similar geometries with a small energy barrier of 80 GHz (0.03 kJ mol⁻¹) to internal rotation. The single-point energies are shown in Table 3. Frequency calculations on these structures *both* contained one low-energy imaginary frequency corresponding to internal rotation. The presence of imaginary frequencies gives a reliable indication

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Table 3. Single-Point Energies for the Eclipsed ($\alpha = 0^\circ$) and Staggered ($\alpha = 18^\circ$) Geometries in Which the Cp Group Was Restricted to C_{5v} Symmetry

rotamer (deg)	energy (hartrees)
0	-530.794 180 930
18	-530.794 168 738

Table 4. Single-Point Energies for the Series of Rotamers in Which the Cp Group Was Allowed To Relax to Lower Symmetry

rotamer (deg)	energy (hartrees)	rotamer (deg)	energy (hartrees)
0	-530.794 927 6	11.25	-530.794 928 7
2.25	-530.794 938 8	13.5	-530.794 911 6
4.5	-530.794 954 7	15.75	-530.794 904 6
6.75	-530.794 960 6	18	-530.794 899 8
9	-530.794 949 2		

of the need to include symmetry-lowering distortions to find the minimum-energy structure.

B. Cp (C_1)–Rh(CO)₂ (C_{2v}). The solid-state structure of Cp*₂Rh(CO)₂ shows deviation of the Cp* group from C_{5v} symmetry, where the local symmetry is reduced to C_2 by the adjacent CO ligands. Gas-phase photoelectron data²⁴ on CpRh(CO)₂ also indicate deviations from C_5 symmetry in the Cp group. After considering these issues (and the fact that the barrier height in the symmetrical complex was calculated to be too small), we performed calculations in which the Cp group was allowed to relax to C_2 symmetry in the staggered and eclipsed conformations and to C_1 symmetry in intermediate rotameric states. Optimizations were performed at intervals of 2.25° along the torsional angle α from 0 to 18°. The single-point energies (listed in Table 4) obtained from these calculations were fit to a cosine function with both 10- and 20-fold periodicity (eq 1). The 20-fold potential is necessary because neither 0° nor 18° was a minimum on the surface; in fact, they each represented a local maximum, the minimum was found at $\alpha = 6.75^\circ \pm 36n$ (and $29.25^\circ \pm 36n$). The results of these calculations are shown in Figure 2. The potential function V_B is given in eq 1.

$$V_B = V + V_{10} \cos(10\alpha) + V_{20} \cos(20\alpha) \quad (1)$$

$$V = -530.794\ 960\ 6 \text{ hartrees}, V_{10} = -17.3 \text{ microhartrees}, V_{20} = 20.4 \text{ microhartrees}$$

The barrier to internal rotation that was obtained from a least-squares fit to the calculated single-point energies has an extra V_{20} term but otherwise is in general agreement with that determined from the experimental microwave spectrum. There are two periodic (Fourier) terms in this calculated potential corresponding to 10- and 20-fold barriers of approximately equal value. The two terms combined provide a maximum barrier of 400 GHz (0.16 kJ mol⁻¹), in excellent agreement with the 10-fold barrier height computed from the microwave data. With restriction of the Cp geometry to C_{5v} symmetry the barrier height was considerably smaller (80 GHz).

C. Cp (C_1)–Rh(CO)₂ (C_1). A frequency calculation for the lowest energy state on the calculated $V_{10} + V_{20}$ potential energy curve of the internal rotation coordinate indicated that there is a low-energy imaginary frequency that appears to be due to a rocking or tilting

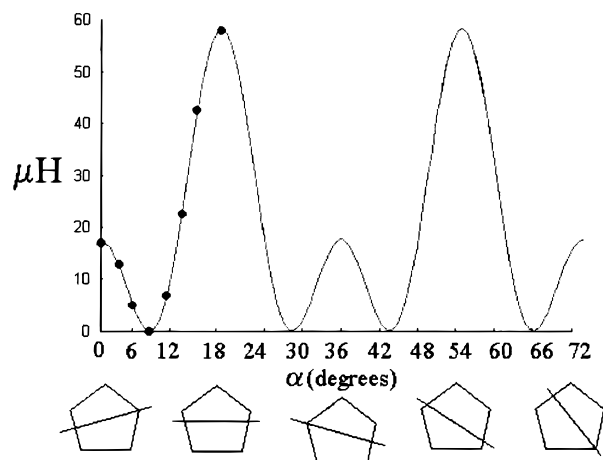


Figure 2. Potential energy surface mapped out by the calculations described in part B. The energy axis is in microhartrees with respect to the minimum energy rotamer at $\alpha = 6.75^\circ$. The single-point energies represented by dots on the graph were fit to the potential function $-20.4 \cos(10\alpha) + 17.4 \cos(20\alpha)$, which is shown as the smooth curve. The single-point energies are listed in Table 4.

motion of the Rh(CO)₂ group with respect to the Cp plane. Further calculations were done to examine the correlation of this motion with the internal rotation. If the rocking motion was in phase with the internal rotation, a drastic change in the potential energy surface would be expected. The rocking would have a maximum amplitude at values of $\alpha = 0^\circ \pm 36n$, as the interactions between ligands are minimized through spatial separation of the atoms. However, it appears that the rocking motion itself can perturb the Cp group and produce further distortions at all values of α . The calculations indicate that the $\alpha = 0^\circ \pm 36n$ rotamers have decreased considerably in potential energy, but the $\alpha = 18^\circ \pm 36n$ rotamers have also decreased in energy. The latter result was unexpected, because in the $\alpha = 18^\circ$ conformation, motion along the rocking coordinate destroys the C_5 symmetry of the molecule and requires further distortion of the Cp group. The results indicate that the $\alpha = 18^\circ$ rotamer showed a further decrease in potential energy than the $\alpha = 0^\circ$ rotamer. This results in a lower total barrier height with the minimum on the potential energy surface occurring at $\alpha = 18^\circ$. The most important result of coupling these two motions is the reduction of the potential energy surface of the internal rotation from a combination of both 10- and 20-fold barriers to primarily a 10-fold barrier. This result is consistent with the experimental data, since no dependence on the V_{20} potential was found in an attempted fitting process including both V_{10} and V_{20} potentials. This potential energy barrier was also determined from single-point energies (listed in Table 5) of a series of rotamers by fitting the energies to a cosine function (eq 2).

$$V_C = V + V_{10} \cos(10\alpha) + V_{50} \cos(50\alpha) \quad (2)$$

$$V = -530.795\ 936\ 1 \text{ hartrees}, V_{10} = 21.5 \text{ microhartrees}, V_{50} = -2.9 \text{ microhartrees}$$

The results of this calculation are shown in Figure 3. The calculated V_{10} barrier height is 272 GHz (0.11 kJ mol⁻¹).

Table 5. Single-Point Energies for the Series of Rotamers in Which the Cp Group's Symmetry Was Relaxed and the Rocking Coordinate β Was Relaxed

rotamer (deg)	energy (hartrees)	rotamer (deg)	energy (hartrees)
0	-530.795 916 0	12	-530.795 940 7
3	-530.795 915 1	15	-530.795 957 3
6	-530.795 930 1	18	-530.795 957 4
9	-530.795 936 4		

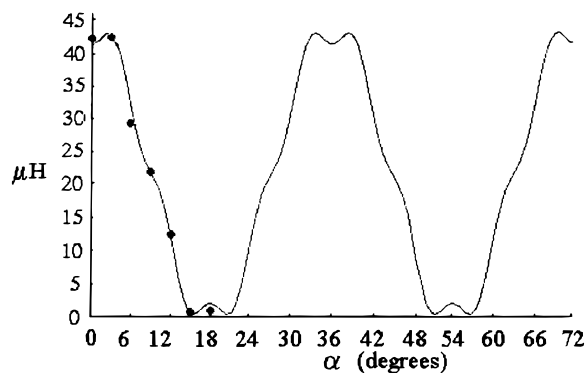


Figure 3. Potential energy surface mapped out by the calculations described in part C. The energy axis is in microhartrees with respect to the minimum energy rotamer at $\alpha = 18^\circ$. The single-point energies represented by dots on the graph were fit to the potential function $21.5 \cos(10\alpha) - 2.9 \cos(50\alpha)$, which is shown as the smooth curve. The single-point energies are listed in Table 5.

Discussion

The calculations were initially undertaken to see if the calculated internal rotation barrier height would be in reasonable agreement with the value determined by fitting the spectrum. The calculated numbers do indeed agree quite well with those determined from the least-squares fit to the microwave data. The experimental and calculated values are given in Table 6. Calculated rotational constants are all within 4% of those determined experimentally with the calculated *A* rotational constant actually lying within 1σ of the experimental

Table 6. Comparison of Experimental (expt) and Calculated (DFT) Parameters (MHz) for Cyclopentadienylrhodium Dicarboxyl

param	expt	DFT
<i>A</i>	1613(5)	1619.3
<i>B</i>	1046.7(4)	1010.5
<i>C</i>	759.7(5)	731.2
V_{10}	347(6)	272

value. A barrier height for the internal rotation of the $\text{Rh}(\text{CO})_2$ fragment can also be determined from the difference in single-point energies of the ground- and transition-state rotamers. For the calculations discussed in part B, the difference of $60 \mu\text{H}$ between the C_s symmetry rotamers at 0° and the 6.75° rotameric ground state yields a barrier height of 400 GHz (0.16 kJ mol^{-1}). This value compares very well with the barrier height of 347 GHz (0.14 kJ mol^{-1}) determined from the microwave spectrum. The calculations described in part C illuminate the possibility of two coupled low-energy internal motions in this molecule. Although the geometry change due to the rocking motion is very slight, it has a large effect on the potential energy surface along the α coordinate. The potential barrier reduces to primarily 10-fold periodicity and results in an eclipsed ground state, in sharp contrast to the results of the calculations in part B. The barrier height is reduced to 272 GHz (0.11 kJ mol^{-1}) but is still in good agreement with the experimental potential (Table 6). The calculations clearly indicate that this complex is not a "simple" hindered rotor with nearly rigid top and frame. The idea of distortions of the Cp group is supported by both the present calculations and earlier solid-state structure studies and is consistent with the present difficulties in fitting the microwave spectrum. The effects of the calculated $\text{Rh}(\text{CO})_2$ rocking motion and interaction of this motion with Cp-group distortions provide further complications in treating the hindered rotation quantitatively.

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