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Relaxation mechanisms, bonding, and molecular reorientation in $CpRe(CO)_3$

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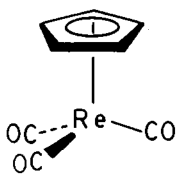
Abstract

Carbonyl ^{13}C and ^{17}O and cyclopentadienyl ^{13}C NMR spin–lattice relaxation times of $CpRe(CO)_3$ were measured as a function of temperature in the solvent $CDCl_3$. Analysis of $T_1(^{13}CO)$ revealed that, unlike in most metal carbonyls, where chemical shift anisotropy is the dominant mechanism, the major contribution to ^{13}C relaxation is via scalar coupling to the directly bonded rhenium. The oxygen-17 quadrupole coupling constant [determined from $T_1(^{17}O)$], and the π^* antibonding orbital population was very close to values reported in several (arene)$Mo(CO)_3$ complexes, indicating similar pi bond strengths. The C–K force constants (k_{CO}), on the other hand, were quite dissimilar, indicating that k_{CO} is not a pure measure of π bonding in metal carbonyls. Comparison of rotational correlation times of the cyclopentadienyl group and $M(CO)_3$ unit revealed substantial internal rotation of the Cp ring. The rate, however, is slower than expected for a free rotor, indicating the presence of a finite barrier to internal rotation.

Introduction

The experimental and theoretical investigation of the magnitude associated with the rotational barrier of polyene-ML_3 complexes continues to receive attention [1–15]. In the absence of mitigating steric constraints, negligible polyene rotational barriers are predicted on the basis of symmetry considerations [8,9]. However, we note that there exists a dearth of information dealing with the polyene rotational barrier in polyene-$M(CO)_3$ complexes as determined by ^{13}C NMR spin–lattice (T_1) relaxation times. To our knowledge, such T_1 measurements have been performed for (arene)$Mo(CO)_3$ [14] and $CpM(CO)_3$ (where M = Mn, Re) [15]. In the former study, although not discussed explicitly [14], the data imply a very high barrier to internal rotation. The latter report does reveal a low polyene rotation barrier about the d^6-ML_3 center; however, we note that the results derive from measurements performed in the solid state, where intermolecular rotational barriers predominate.



As part of our interest in the chemistry associated with organometallic rhenium carbonyls [16,17] and relaxation phenomena in organometallic compounds [18,19], we have investigated the barrier to cyclopentadienyl rotation in $CpRe(CO)_3$ via spin–lattice relaxation measurements in solution.

The earlier investigation of (arene)$Mo(CO)_3$ [14] included measurement of the carbonyls' ^{17}O quadrupole coupling constants (QCCs), which are a measure of M–CO π bond strengths [19]. We have also used ^{17}O relaxation time measurements to determine the QCCs and π orbital populations in $CpRe(CO)_3$. The results are compared with those for the arylmolybdenum complexes and with the predictions based upon Cotton–Kraihanzel force constants [20].

Experimental

$CpRe(CO)_3$ was prepared from $Re_2(CO)_{10}$ and dicyclopentadiene according to the procedure of Gladysz et al. [21]. $CDCl_3$ was distilled from P_2O_5 and stored under argon with Schlenk techniques [22]. The NMR sample was prepared in a 5 mm NMR tube that contained 60 mg (0.18 mmol) of $CpRe(CO)_3$ dissolved in 0.6 ml of $CDCl_3$ (~ 0.3 *M*) and was freeze–pump–thaw degassed three times prior to flame sealing.

The carbonyl carbon-13 and oxygen-17 relaxation times and the methinyl carbon-13 T_1 values and nuclear Overhauser enhancements (NOEs) were measured as a function of temperature at $B_0 = 70.5$ kG [$\nu_0(^{13}C) = 75.4$ MHz and $\nu_0(^{17}O) = 40.7$ MHz] on a Varian VXR-300 FT–NMR spectrometer. ^{13}CO T_1 values were also measured at $B_0 = 47.0$ kG [$\nu_0(^{13}C) = 50.3$ MHz] on a Gemini-200 spectrometer. The details of the relaxation time and NOE experiments, and of temperature regulation and measurement have been presented elsewhere [18,19,23].

All experiments were repeated at least twice; the results in the tables represent the average of the runs.

Results and discussion

$CpRe(CO)_3$ is an asymmetric-top molecule of, at most, C_s symmetry. However, from its crystal structure [24], the three semi-axis lengths of the volume ellipsoid are close to equal [25*], with an average molecular radius, $R = 3.36$ Å. The components of the inertia tensor are also similar in magnitude, with an average value, $I = 774 \times 10^{-40}$ g cm^2. Hence, in the calculations below, we assume (by

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* Reference number with asterisk indicates a note in the list of references.

Table 1

^{13}CO relaxation times in $CpRe(CO)_3$

T (°C)	B_0 (kG)	$T_1(^{13}CO)$ (s) [a]	T_{1SC} (s)	T_{1CSA} (s)	τ_c (ps)	J (Hz)
25	47.0	0.83 (0.03)	0.85	40		
	70.5	1.70 (0.08)	1.90	18	11.2	1150
50	47.0	1.21 (0.09)	1.23	113		
	70.5	2.58 (0.05)	2.77	50	4.0	1590

[a] All measurements were performed at least twice. The quantities in parentheses represent the mean deviation between runs.

necessity) [26*] that the reorientational behavior of the molecular skeleton is isotropic, characterized by a single diffusion coefficient, D.

The magnetogyric ratios of the two isotopes, ^{185}Re (37.1%) and ^{187}Re (62.9%), are close to identical [27]; therefore, in calculations below, we have used the weighted average, $\gamma(\mathrm{Re}) = 6.064 \times 10^3\ \mathrm{s^{-1}\ G^{-1}}$. The reported rhenium quadrupole coupling constants of the two isotopic species of $CpRe(CO)_3$ are also quite similar [28]; again, we have used the weighted average, $\chi(\mathrm{Re}) = 598.9\ \mathrm{MHz} = 3.763 \times 10^9\ \mathrm{s^{-1}}$.

Carbonyl carbon-13 relaxation mechanisms

The carbonyl ^{13}CO relaxation times in $CpRe(CO)_3$ at two temperatures and magnetic field strengths are presented in Table 1 [$T_1(^{13}CO)$].

Owing to the extremely large chemical shift anisotropies ($\Delta\sigma \approx 400$ ppm) [29], this mechanism (CSA) usually dominates the ^{13}C relaxation in transition metal carbonyls [19,30,31]. However, as a result of the near coincidence of the Re and ^{13}C magnetogyric ratios [27,32], scalar coupling (SC) to the directly bonded rhenium nuclei also contributes significantly to the observed relaxation time. Additionally, one expects comparatively minor contributions from spin–rotation (SR) and inter- and intramolecular dipole-dipole (DD) relaxation [33*]. Using standard formulae for CSA and SC relaxation [34–36], the following expression is obtained for the net relaxation rate (T_1^{-1}):

$$\frac{1}{T_1} = \frac{1}{T_{1SC}} + \frac{1}{T_{1CSA}} + \frac{1}{T_{1O}}$$

$$= \frac{2}{15}\omega_0^2\,\Delta\sigma^2\tau_c + \frac{8\pi^2}{3}S(S+1)J^2\frac{T_1(\mathrm{Re})}{1+\Delta\omega^2 T_1(\mathrm{Re})^2} + \frac{1}{T_{1O}} \qquad (1)$$

In this equation, $\omega_0 = \gamma(^{13}C)B_0$ (the carbon-13 resonance frequency); $\Delta\sigma$ is the ^{13}C chemical shift anisotropy; τ_c is the rotational correlation time; $S = 5/2$ (the spin of both ^{185}Re and ^{187}Re); J is the Re–C coupling constant (in Hz); $T_1(\mathrm{Re})$ is the rhenium spin–lattice relaxation; $\Delta\omega = [\gamma(\mathrm{C})\text{-}\gamma(\mathrm{Re})]B_0 = 662.5 \times B_0$ (the difference in resonance frequencies); T_{1O} represents the contribution owing to other relaxation mechanisms (primarily spin–rotation) [33*]. We have calculated an approximate chemical shift anisotropy, $\Delta\sigma \approx 408$ ppm, using the experimental ^{13}CO chemical shift in CpRe(CO)$_3$ (193.1 ppm downfield from TMS), and the common assumption that the paramagnetic contribution to the parallel component of the shielding tensor vanishes (*i.e* $\sigma_{\parallel}^{p} = 0$) [29]. We have also estimated that $T_{1O} \approx 150$ s, which is the average value measured in our recent study of group 6 hexacarbonyls [19].

It would appear from eq. 1 that the relaxation rate is a function of three independent parameters, J, τ_c and T_1(Re). However, rhenium is relaxed exclusively by quadrupolar interactions, which are dependent upon the magnitude of the nuclear quadrupole coupling constant. Therefore, with the assumption (see above) that the reorientation is isotropic, the rhenium relaxation time is governed by the same τ_c, and is given by [34]:

$$\frac{1}{T_1} = \frac{3}{40}\,\frac{2S+3}{S^2(2S-1)}\,\chi^2\tau_c = \frac{3}{125}\,\chi^2\tau_c \qquad (2)$$

where χ is the rhenium QCC (in s^{-1}).

We have utilized an iterative program (written in BASIC) to fit τ_c and J in eqs. 1 and 2 to the experimentally observed relaxation times at two values of B_0 (Table 1). The calculated parameters at 25°C and 50°C are given in the last two columns of the table. The variation in J with temperature is almost certainly a result of experimental error. However, the average coupling constant, $J_{avg} = 1370$ Hz, is of the same magnitude as values reported recently in two rhenium carbonyl clusters ($J \approx 1000$ Hz) [36]. The correlation time at 25°C is also quite similar in magnitude to values reported ($\tau_c = 8$–12 ps) in several mononuclear carbonyls [14,19,30]. We note that, not surprisingly, the choice of T_{1O} has a relatively small effect on the calculated parameters. The assumption that $T_{1O} = 100$ s or 1000 s caused only a 3–5% variation in J and τ_c from values in the table.

We have used these parameters to calculate the individual contributions to relaxation at both field strengths and temperatures (T_{1SC} and T_{1CSA} in Table 1). As expected from the the qualitative dependence of T_1(obs) on B_0, scalar coupling dominates the relaxation. The dependence of T_{1SC} on B_0 (i.e. on $\Delta\omega$) and temperature is consistent with the inequality, $\Delta\omega T_1(\mathrm{Re}) \gg 1$ [37*], in which limit, $T_{1SC}^{-1} \propto \tau_c/(\Delta\omega)^2$ [2,35]. The observed decrease of T_{1CSA} with B_0 and its increase with temperature is consistent with the relation, $T_{CSA}^{-1} \propto \omega_0^2\tau_c$.

Even though $T_{1CSA} \gg T_{1SC}$, to assume that scalar coupling is the sole relaxation mechanism introduces serious errors into the analysis. To illustrate, if the 25°C results are reanalyzed as above except with $\Delta\sigma = T_{1O}^{-1} = 0$, or via the standard straight line plot of T_1 versus $\Delta\omega^2$ [35,36], then the calculated parameters are $\tau_c = 40$ ps and $J = 665$ Hz. This correlation time is four times longer than typical values found in mononuclear complexes [14,19,30], and is, in fact, comparable in magnitude to rotational times reported in tri- and tetranuclear metal carbonyl clusters [18]. It should be stressed that accurate analysis of ^{13}CO relaxation in rhenium carbonyl complexes requires the inclusion of contributions from both the scalar coupling and chemical shift anisotropy in the relaxation equation.

Re–CO π bonding

Approximate Cotton–Kraihanzel (C–K) C≡O force constants [20], k_{CO}, have been widely utilized to study pi bonding in transition metal carbonyls. Unfortunately, there is now an abundance of experimental [38] and theoretical [39] evidence that the σ bond order also affects the force constant; a stronger sigma bond induces an increase in k_{CO} [38,39].

Unlike C–K force constants, the oxygen-17 quadrupole coupling constant, $\chi(^{17}\mathrm{O})$, is a much purer measure of the C≡O π bond order [40]. A number of investigators [14,19,30,31] have utilized ^{17}O and ^{13}C NMR relaxation to measure the ^{17}O QCC and obtain valuable information on the factors affecting the M–CO π bond strength. Most studies have been interpreted qualitatively; a smaller QCC corresponds to a more symmetrical environment surrounding the oxygen nucleus and, hence, a stronger π bond. However, recently, we developed a simple relationship between χ and $[2\pi]$, the population of the antibonding 2π (or π^*) orbital [19]:

$$[2\pi]_\chi = \xi \frac{\chi_{\mathrm{CO}} - \chi}{\chi_0} \tag{3}$$

In this equation, $\chi_{\mathrm{CO}} = 4.43$ MHz (the QCC of free carbon monoxide) [41] and the quantities ξ and χ_0 are constants [42*,43*]. The subscript, χ, on the left hand side of eq. 3 is used to indicate that the antibonding orbital population was determined from the ^{17}O QCC. A stronger π bond will result in a greater value of $[2\pi]_\chi$. Thus, the calculated value of this parameter furnishes a semi-quantitative estimate of the magnitude of $\mathrm{M}(d_\pi) \rightarrow \mathrm{CO}(p_\pi)$ backbonding.

$\chi(^{17}\mathrm{O})$ may be calculated directly from $T_1(^{17}\mathrm{O})$ via eq. 2 ($S = 5/2$ for ^{17}O) if one has measured the correlation time. Using our values of τ_c at 25°C and 50°C (Table 1) and the relaxation times in Table 2, we have determined two values for the QCC, $\chi = 0.70$ MHz (25°C) or $\chi = 1.03$ MHz (50°C), with an average $\chi_{\mathrm{avg}} = 0.87 \approx 0.9 \pm 0.2$ MHz. We note that one does not expect any significant dependence of the QCC on temperature; the discrepancy between the two values almost surely results from uncertainties in the calculated correlation times [44*].

Using the average QCC in eq. 3, we have determined that $[2\pi]_\chi = 0.54 \pm 0.03$ electrons/CO in CpRe(CO)$_3$, which we have displayed in Table 2, along with π orbital populations in other representative metal carbonyls. Note that $\chi(^{17}\mathrm{O})$ and, therefore, $[2\pi]_\chi$, is comparable in magnitude to values in several arenemolybdenum tricarbonyls [14]. The antibonding orbital occupancy in CpRe(CO)$_3$ (per CO) is significantly greater than in Cr(CO)$_6$ [19]. This result is a direct manifesta-

Table 2

QCCs, pi orbital populations and C–K force constants in some metal carbonyls

Complex	$\chi(^{17}\mathrm{O})$ (MHz)	$[2\pi]_\chi$ (e$^-$/CO)	k_{CO} (mdyn/Å)
Cr(CO)$_6$	1.9_5 [a]	0.38	16.5 [b]
V(CO)$_6^-$	1.2 [c]	0.50	14.6 [d]
CpRe(CO)$_3$	0.9 [e]	0.54	15.7 [e]
(tol)Mo(CO)$_3$ [f]	0.9 [g]	0.54	14.8 [h]
(mes)Mo(CO)$_3$ [i]	0.8 [g]	0.56	14.6 [h]

[a] Ref. 19. [b] Ref. 46a. [c] Ref. 14b. [d] From vibrational frequencies in ref. 46b. [e] This work. Force constant calculated from measured frequencies, $\nu(\mathrm{A}_1) = 2030$ cm^{-1} and $\nu(\mathrm{E}) = 1939$ cm^{-1}. [f] tol ≡ toluene. [g] Ref. 14. [h] Refs. 14 and 46c. [i] mes ≡ mesitylene.

tion of the polyene unit functioning as a stronger donor (σ) ligand as compared with the isolobal *fac* tricarbonyl ligand set [45].

Brownlee *et al.* [14] have reported an interesting linear correlation between $\chi(^{17}O)$ and the C–K force constant [20], k_{CO}, which, if generally valid, would provide a simple method for estimating the QCC and 2π orbital population. As shown in the last column of Table 2, k_{CO} for CpRe(CO)$_3$ is much higher than the measured force constants [46] in (arene)Mo(CO)$_3$ complexes and in V(CO)$_6^-$, even though its π bond strength is comparable in magnitude with these latter species. Indeed, based upon a linear correlation established by Cr(CO)$_6$ and V(CO)$_6^-$, one would predict [from the CpRe(CO)$_3$ force constant] that $\chi = 1.6$ MHz and $[2\pi]_\chi =$ 0.43 e$^-$/CO, which would imply a much weaker π bond than that determined experimentally in this study. Unfortunately, therefore, the linear correlation between χ and k_{CO} is not generally applicable. We plan additional experiments on other group 7 (Mn and Re) complexes to determine whether there is a correlation between $[2\pi]_\chi$ and k_{CO} within this series.

Reorientational dynamics and internal rotation

As seen above, determination of χ and $[2\pi]_\chi$ from $T_1(^{17}O)$ requires auxiliary ^{13}C NMR relaxation time measurements (at two field strengths) in order to calculate τ_c for use in eq. 3. It would be extremely useful if the rotational correlation times could, instead, be estimated accurately from currently available models of molecular reorientational diffusion coefficients [47].

We have used the experimental oxygen-17 relaxation times [$T_1(^{17}O)$ in Table 3] and the average QCC [$\chi(^{17}O) = 0.9$ MHz $= 5.65 \times 10^6$ s^{-1}] in eq. 2 to determine the rotational correlation time and, hence, the diffusion coefficient [$D = (6\tau_c)^{-1}$] [47] as a function of temperature. The results are presented in Table 3 and in Fig. 1 (the solid circles and line A). A fit of the data by the Arrhenius equation yields an experimental activation energy, $E_a = 3.0$ kcal/mol.

Shown also in Fig. 1 (line B) are diffusion coefficients calculated by the classic Gierer–Wirtz (GW) microviscosity model of molecular reorientation [48,49*]. Although qualitatively of the same magnitude as the measured diffusion coefficients, the model predicts values that are greater than experiment; *e.g.* at 25°C, D(GW) = 36 ns^{-1} versus D(exp) = 24 ns^{-1}. In addition, the calculated tempera-

Table 3

^{17}O and ^{13}C relaxation times and rotational diffusion coefficients in CpRe(CO)$_3$

T (°C)	$T_1(^{17}O)$ (ms) [a]	$T_1(^{13}C\text{–}H)$ (s) [a]	η	τ_c(C–H) (ps)	D (ns^{-1})	R (ns^{-1})
−25	64 (02)	6.0 (0.3)	2.0	7.35	8.2	70
0	101 (08)	8.2 (0.2)	2.0	5.37	12.9	68
25	190 (20)	9.8 (0.2)	2.0	4.50	24.3	31
50	250 (10)	8.5 (0.1)	1.4	3.67	32.0	31

[a] All measurements were performed at least twice. The quantities in parentheses represent the mean deviation between runs.

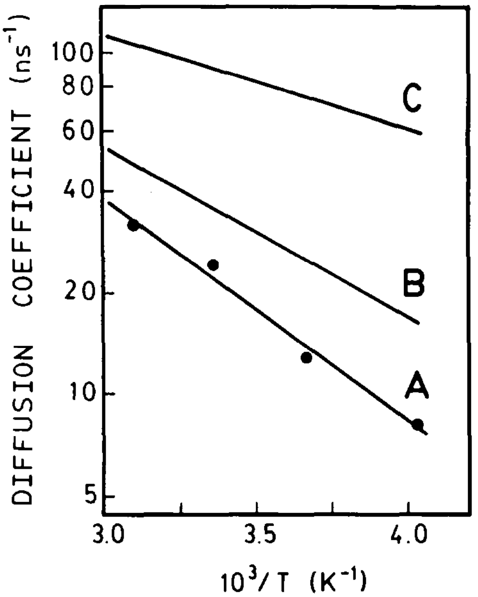

Fig. 1. Temperature dependence of experimental and calculated rotational diffusion coefficients of $CpRe(CO)_3$ in chloroform. (A) D(exp); (B) D(GW); (C) D(HKW).

ture dependence yields a somewhat lower activation energy, E_a(GW) = 2.3 kcal/mol, than that observed experimentally.

It is of interest to calculate the ^{17}O QCC using correlation times determined from the model. Using $\tau_c(GW) = \{6D(GW)\}^{-1}$ with $T_1(^{17}O)$ in eq. 2 (at 25°C and 50°C), we find that $\chi(^{17}O)_{cal} = 1.1$ MHz, which is acceptably close to the experimental QCC [$X(^{17}O) = 0.9$ MHz] [50*]. Thus, in the absence of ^{13}C relaxation measurements of the correlation time, the simple microviscosity model may be used profitably to obtain a qualitative estimate of the ^{17}O QCC.

More recently, Hynes, Kapral and Weinberg (HKW) [51] formulated a model of molecular reorientation for spherical molecules in solution that has proven more accurate than the earlier Gierer–Wirtz theory in a number of systems [47,52]. We have applied the HKW equations [51] to calculate D as a function of temperature (line C in the Fig. 1). Unlike earlier studies, we see that for $CpRe(CO)_3$ in $CDCl_3$, the HKW theory yields calculated diffusion coefficients that are far greater than both experimental values and coefficients from the GW model. For example, at 25°C, $D(HKW) = 90$ ns^{-1}, which is more than three times greater than experiment. The temperature dependence is also markedly lower than found experimentally with E_a(HKW) = 1.2 kcal/mol. Not surprisingly, the ^{17}O QCC calculated from τ_c(HKW) is also in serious error; $\chi(^{17}O)_{cal} = 1.7$ MHz, almost twice the measured value.

The correlation time obtained from $T_1(^{17}O)$ measures the rate of rotation of a vector parallel to the M–C≡O and, hence, characterizes overall molecular reorientational diffusion. In contrast, dipole-dipole carbon-13 relaxation of the methinyl carbons (by the directly attached proton) is governed by the rotational time of the C–H vector. This quantity depends both upon the overall diffusion constant, D, and the coefficient, R, which characterizes the rate of internal rotation of the cyclopentadienyl group. Therefore, one may use these data to obtain an estimate of the internal rotation rate.

The measured ^{13}C–H relaxation times are given in the third column of Table 3. As seen also in the table, the measured NOEs (η) are at a maximum ($\eta_{\max} = 1.987 \approx 2.0$) at all but the highest temperature, indicating that, except at 50°C, relaxation is exclusively by dipolar relaxation [*i.e.* $T_1(^{13}\text{C–H}) = T_1DD$].

We have calculated $T_{1\text{DD}}$ at 50 °C from the standard relation, $T_{1\text{DD}} = [\eta_{\max}/\eta)T_1(^{13}\text{C–H})$. One may then obtain the rotational correlation time from the expression [34]:

$$\frac{1}{T_{1\text{DD}}} = \frac{\gamma_C^2 \gamma_H^2 h^2}{4\pi^2 R_{\text{CH}}^6} \tau_c = 2.269 \times 10^{10} \tau_c(\text{C–H}) \tag{4}$$

where the numerical coefficient was evaluated using $R_{\text{CH}} = 1.08$ Å [53]. The resulting correlation times are given in Table 3.

Woessner [54] has developed a relation for the correlation time of a vector undergoing internal rotation in a symmetric-top molecule, as a function of $D_\perp$, $D_\parallel$ and R. Assuming isotropic overall reorientation ($D_\perp = D_\parallel$), his expression reduces to [55*]:

$$\tau_c(\text{C–H}) = \frac{A}{6D} + \frac{B}{6D+R} + \frac{C}{6D+4R} \tag{5}$$

A, B and C are functions of θ, the angle between the internally rotating vector and the overall rotation axis. For the C–H vector in the Cp ring, $\theta = 90°$ and one has $A = 0.25$, $B = 0$ and $C = 0.75$. We have used the experimental diffusion coefficients [D] and correlation times [τ_c(C–H)] in eq. 5 to determine R at the various temperatures; the results are shown in the last column of Table 3. The apparent decrease in the internal rotation rate with increasing temperature is clearly unrealistic. We believe it probably results from experimental errors in τ_c and D and from the highly non-linear dependence of R upon these quantities. Further, one must be reminded that the required assumption of isotropic reorientation precludes any quantitative interpretation of the results.

Still, one concludes from the magnitude of the coefficient, R, that there is substantial internal rotation of the Cp ring relative to the Re(CO)$_3$ skeleton in this complex. This conclusion is in marked contrast to recent results for several arylmolybdenum tricarbonyls [14], where it was found that the correlation times characterizing rotation of the arenes' C–H vector were equal to or longer than τ_c for overall reorientation of the molecule. This implies that there is no significant internal rotation of the aryl ring in these complexes.

The internal rotation in CpRe(CO)$_3$ is not completely unhindered, however, in which case the values of R would be far higher. One may obtain an order of magnitude estimate of the barrier to internal rotation, V_0, through use of the relation [56], $R = R_0\, e^{-V_0/R_GT}$, where $R_0 = (5/3)[kT/I_{\text{Cp}}]^{1/2}$, R_G is the gas constant and $I_{\text{Cp}} = 190 \times 10^{-40}$ g cm^2 is the moment of inertia of the Cp ring about its C$_5$ axis. With these expressions and the data in Table 3, we obtain estimates of V_0 ranging from 1.7 to 2.6 kcal/mol, which is comparable with the barrier-measured by ^{1}H relaxation time measurements in solid CpRe(CO)$_3$ ($V_0 = 1.7$ kcal/mol) [15], and far higher than the negligible intramolecular electronic barrier (0.002

kcal/mol) predicted by extended Hückel calculations [8,9] on the isolated complex. It is likely that this barrier arises at least in part from intermolecular solvent-solute interactions since, using the above formulae with the experimental spinning diffusion coefficient of free benzene in $CDCl_3$ [57] one finds a barrier of 1.3 kcal/mol. There may well also be a component arising from intramolecular electronic interactions within the complex. However, a quantitative assessment of the relative magnitudes of the inter- and intramolecular contributions would require experimental determination of the intramolecular barrier to rotation in the complex [58*].

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