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Reorientational Dynamics and the Barrier to Internal Rotation in $\text{Cp}_2\text{Co}_3(\mu_2\text{-CO})(\text{CO})_3(\mu_3\text{-CPh})$

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Received September 26, 1990

NMR spin-lattice relaxation times of the phenyl, cyclopentadienyl, and terminal carbonyl ^{13}C nuclei in $\text{Cp}_2\text{Co}_3(\mu_2\text{-CO})(\text{CO})_3(\mu_3\text{-CPh})$ were measured as a function of temperature in the solvent chloroform. The phenyl carbon T_1 's were used to calculate the diffusion coefficient characterizing the ring's net spinning rate, $D_S(\text{Ph}) = D_{\parallel} + R(\text{Ph})$. The values of $D_S(\text{Ph})$, at all temperatures, are 1 order of magnitude lower than those reported for a similar tricobalt complex with no barrier to internal rotation. The parallel diffusion coefficients of the cluster's framework (D_{\parallel}), determined from $T_1(^{13}\text{C})$ of the terminal carbonyls at two magnetic field strengths, are equal to $D_S(\text{Ph})$, to within experimental error. Thus, the rate of internal phenyl group rotation, $R(\text{Ph})$, is ~ 0 on a nanosecond time scale. From this result, the rotational barrier, V_0 , was estimated to lie in the range $5 \text{ kcal/mol} < V_0 < 9 \text{ kcal/mol}$. Internal rotation rates of the cyclopentadienyl groups, $R(\text{Cp})$, were found to be far greater than $R(\text{Ph})$ at all temperatures, indicating that the barrier to phenyl group rotation is not due to inter-ring steric repulsions. Rather, it can be attributed to an electronic interaction of the bridging carbonyl's π^* orbital with the phenyl π system through the metal 2e and carbonyl 2p orbitals. This is only the second system in which a bridging carbonyl/capping group orbital interaction has been observed and the first for which the barrier to internal rotation has been experimentally determined.

Introduction

The study of homogeneous and heterogeneous transition-metal clusters continues to receive attention due to their potential to function as models for multisite substrate activation^{2,3} and selective catalysts for the synthesis of commodity chemicals.^{4,5} However, one problem commonly encountered is cluster fragmentation to mononuclear species which are invariably responsible for the observed reactivity. Fragmentation reactions can, in principle, be retarded through the use of nonfluxional capping ligands.^{6,7} The capping group, in addition to maintaining the cluster's integrity during catalytic reactions^{6,7} and multielectron redox processes,⁸ can interact electronically with metal and ligand orbital electrons,⁹ thereby affecting bonding properties of these complexes.

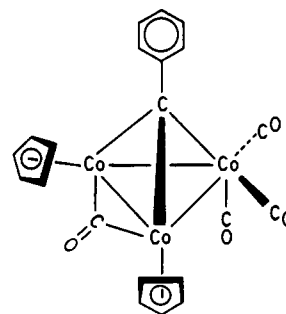
In phenyl group capped (e.g. phosphinidene, benzyldiene) clusters, one expects electronic (or steric) interactions to slow the rate of internal ring rotation. Hence, NMR spin-lattice relaxation times,¹⁰ which are sensitive to molecular motions on a subnanosecond time scale, offer a potentially powerful technique to in-

vestigate reorientation and bonding in these systems.

In recent NMR relaxation investigations,^{11,12} we have demonstrated that internal phenyl group rotational rates span a broad range, varying from total immobility [in $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$]¹¹ to completely free rotation, as rapid as in benzene itself [in $\text{Co}_3(\text{CO})_9(\mu^3\text{-CPh})$].¹²

In the past several years, there have been conflicting data on whether a bridging carbonyl on the cluster's skeleton can interact electronically with the capping phenyl group, slowing its rotation. On the other hand, Stone et al.,¹³ on the basis of observed splittings of the ortho and meta resonances in the ^{13}C NMR spectra, reported that the phenyl ring in $\text{CoFe}_2(\mu_2\text{-CO})(\text{CO})_8(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})$ is locked in a fixed conformation at -80°C in CD_2Cl_2 . They attributed this result to interaction of the $\mu\text{-CO}$'s π^* orbital with the phenyl π system through the metal 2e and carbonyl 2p orbitals. However, it has been suggested that the observed ^{13}C NMR behavior in the Stone cluster derives from the presence of a second isomer as a result of slowed carbonyl exchange.¹⁴ In contrast, McGlinchey and co-workers¹⁴ found no splittings in the low-temperature NMR spectra of a series of clusters with bridging carbonyls, $\text{Cp}_2\text{Co}_3(\mu_2\text{-CO})(\text{CO})_3(\mu_3\text{-CAr})$, where Cp = cyclopentadienyl and Ar = Ph, Tol, Xyl. Therefore, they were able to conclude that there is no hindrance to ring rotation on the NMR chemical shift time scale.

In an effort to establish, on a much shorter time scale, whether there exists a bridging carbonyl/phenyl group interaction sufficiently strong to slow the rate of internal ring rotation, we have undertaken an investigation of carbon-13 NMR relaxation times of the cluster $\text{Cp}_2\text{Co}_3(\mu_2\text{-CO})(\text{CO})_3(\mu_3\text{-CPh})$.



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Table I. ^{13}C NMR Relaxation Times in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\mu_3\text{-CPh})^{a-c}$

T , K	$T_{10}(\text{Ph})$, s	$T_{1M}(\text{Ph})$, s	$T_{1P}(\text{Ph})$, s	$T_1(\text{Cp})$, s	$T_1^A(\text{CO})^d$, s	$T_1^B(\text{CO})^e$, s
211	0.29 (0.01) [0.26]	0.29 (0.01) [0.26]	0.22 (0.01) [0.19]	0.83 (0.03) [0.83]	0.53 (0.03) [0.53]	0.71 (0.02) [0.71]
218	0.33 (0.02) [0.32]	0.32 (0.02) [0.32]	0.23 (0.02) [0.23]	0.96 (0.03) [0.98]	0.59 (0.02) [0.59]	1.03 (0.06) [1.03]
248	0.57 (0.02) [0.66]	0.53 (0.03) [0.63]	0.40 (0.01) [0.47]	1.79 (0.05) [1.84]		
273	0.99 (0.07) [1.08]	0.97 (0.06) [1.01]	0.70 (0.05) [0.76]	3.06 (0.14) [3.06]		
298	1.64 (0.13) [1.62]	1.51 (0.02) [1.48]	1.20 (0.09) [1.12]	4.07 (0.06) [3.94]		
323	2.53 (0.04) [2.27]	2.22 (0.16) [2.05]	1.66 (0.11) [1.55]	4.91 (0.08) [4.91]		

^a All relaxation times represent the average of two measurements.

^b Quantities in parentheses represent the mean deviation of the two runs from the average. ^c Quantities in square brackets were obtained from a least-squares fit of the relaxation times by the Arrhenius equation. These values were used in all further calculations. ^d Measured at $B_0^d = 7.05$ T ($\nu_0 = 75.44$ MHz). ^e Measured at $B_0^e = 4.70$ T ($\nu_0 = 50.29$ MHz).

In order to obtain a complete characterization of overall phenyl ring and cyclopentadienyl rotational dynamics, we have measured $T_1(^{13}\text{C})$ for the cyclopentadienyl and terminal CO carbons, as well as for the protonated phenyl group ^{13}C nuclei, as a function of temperature in the solvent CDCl_3 .

Experimental Section

The tricobalt cluster $\text{Cp}_2\text{Co}_3(\mu_2\text{-CO})(\text{CO})_3(\mu_3\text{-CPh})$ was prepared according to the procedure of Robinson et al.¹⁵ using $\text{Co}_3(\text{CO})_9(\mu_3\text{-CPh})$.¹⁶ CDCl_3 was distilled from P_2O_5 and stored under argon by using Schlenk techniques.¹⁷ The NMR sample was prepared in a 5-mm NMR tube that contained 0.05 g (1.0 mmol) of $\text{Cp}_2\text{Co}_3(\mu_2\text{-CO})(\text{CO})_3(\mu_3\text{-CPh})$ dissolved in ~ 0.5 mL of CDCl_3 (ca. 0.2 M) and was freeze-pump-thaw degassed three times prior to flame sealing. The NMR sample was observed to be stable in CDCl_3 for the duration of the NMR study, as judged by reproducible T_1 's and the line widths associated with the cluster's and solvent's ^{13}C resonances. Thus, we conclude that cluster fragmentation is negligible, contrary to the noted solvent sensitivity reported by Robinson et al.¹⁵

The ^{13}C NMR spectra were acquired at $B_0 = 7.05$ T ($\nu_0 = 75.44$ MHz) on a Varian VXR-300 NMR spectrometer. Measurements on the terminal carbonyl ligands were also performed at $B_0 = 4.70$ T ($\nu_0 = 50.29$ MHz) on a Varian Gemini-200 spectrometer. Chemical shifts were measured relative to CDCl_3 ($\delta = 77.0$ ppm) and reported in ppm downfield from TMS. The phenyl region resonances were observed at $\delta = 128.4$, 127.7, and 127.0 ppm, for the ortho, meta, and para carbons, respectively. The cyclopentadienyl and carbonyl peaks are located at $\delta(\text{Cp}) = 88.0$ ppm and $\delta(\text{CO}) = 199.2$ ppm.

The probe temperature was regulated by cooled or heated gas flow and measured with a thermocouple that was calibrated by using NMR thermometers.^{18,19}

^{13}C spin-lattice relaxation times were measured (at natural abundance) by using the standard IRFT pulse sequence, $(180^\circ - \tau - 90^\circ - A_1)_n$,²⁰ with 10τ values plus $\tau \rightarrow \infty$. T_1 's were calculated via nonlinear regression using a three-parameter magnetization equation.²¹ All measurements were repeated at least twice at each temperature. The results, presented in Table I, represent the average of the two runs.

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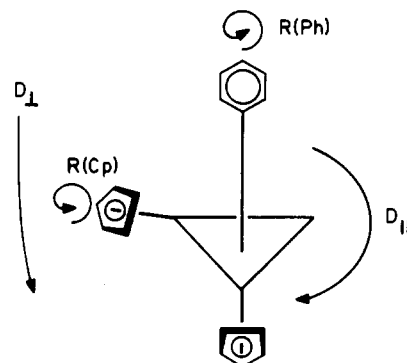
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Nuclear Overhauser enhancements were determined for the phenyl and cyclopentadienyl carbons, by using standard procedures.²⁰ The enhancements were found to be complete, $\eta = \eta_{\text{max}} = 2.00$, to within experimental error, indicating that these carbons are relaxed exclusively via dipolar coupling to the attached protons.²²

As seen in Table I, carbonyl relaxation times were measured only at the lowest temperatures. Measurements at higher temperature were prohibited due to broadening of the resonances by ^{13}C - ^{59}Co scalar coupling.^{23,24} We note that the three terminal carbonyls are exchanging rapidly, as evidenced by the appearance of a single peak in this region of the spectrum.^{25,26} Because of the CO exchange, one obtains an average for the relaxation rate, T_1^{-1} . There is no exchange with the bridging CO at low temperature, since one observes a separate resonance for this carbonyl.

Calculations

$\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})$ is an asymmetric top molecule and, thus, in principle requires three independent diffusion coefficients to characterize its overall rotational motion. However, from its structure,¹⁴ one finds that the two semiaxis lengths in the Co_3 plane are close to equal and are somewhat shorter than the vertical axis length. Therefore, in order to make the calculations tractable, it is assumed that this molecule approximates a prolate pseudosymmetric top, with the unique axis perpendicular to the Co_3 plane and containing the C1 and C4 phenyl carbons. Its overall skeletal rotation is then specified by the "tumbling" and "spinning" diffusion coefficients, D_\perp and D_\parallel , corresponding to rotation perpendicular and parallel to the unique axis. To completely characterize its reorientational dynamics, one must introduce the additional coefficients, $R(\text{Ph})$ and $R(\text{Cp})$, which measure the internal rotation rates of the phenyl and cyclopentadienyl rings, respectively. We note that, qualitatively, one may interpret a diffusion coefficient simply as the rate of rotation (in cps).



As shown in expressions below, the coefficients D_\perp , $R(\text{Ph})$, and $R(\text{Cp})$, exhibit a very nonlinear dependence upon the experimental relaxation times. This tends to exaggerate variations in the experimental data, yielding relatively large fluctuations in the coefficients, which tend to mask trends in their dependence upon temperature. To minimize scatter in the derived coefficients, we have fit the experimental phenyl and cyclopentadienyl T_1 's to the Arrhenius equation and have used the least-squares best fit values (in square brackets in Table I) in the calculations.

Determination of D_\perp and $D_S(\text{Ph})$. It is well-known²⁷ that in symmetric top molecules containing a phenyl group that undergoes internal rotation about the symmetry axis, dipolar relaxation of the para carbon (T_{1P}) is a function solely of the tumbling diffusion constant, D_\perp , whereas relaxation of the ortho and meta carbons (T_{1O} and T_{1M}) depends, in an equivalent fashion, upon both D_\perp and the sum of the parallel and internal

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rotation coefficients, $D_S(\text{Ph}) = D_{\parallel} + R(\text{Ph})$; we have introduced¹¹ $D_S(\text{Ph})$ as the total spinning rate of the phenyl group about its C_2 axis.

We have, in our previous studies,^{11,12} developed expressions which permit the straightforward calculation of D_{\perp} and $D_S(\text{Ph})$ from T_{1P} and the ratio $\chi = T_{1O}/T_{1P}$ ($=T_{1M}/T_{1P}$). The interested reader is referred to the earlier papers^{11,12} for the details of this procedure.

It must be noted that, from Table I, $T_{1O} \approx T_{1M}$ at all but the two highest temperatures, where it is seen that $T_{1O} > T_{1M}$. This indicates a possible breakdown in the assumption that the skeletal rotation is that of a symmetric top, in which case the ortho and meta C-H vectors are no longer equivalent.²⁷ However, there are insufficient data to analyze the system on the basis of completely anisotropic reorientation (requiring three diffusion coefficients) with superposed internal rotation of the phenyl group.

Calculation of D_{\parallel} . The parallel diffusion coefficient for overall spinning of the cluster may be determined if one can measure the rotational correlation time, τ_c , for a vector attached rigidly to the molecular skeleton. This calculation can be performed via $T_1(^{13}\text{C})$ measurements on the three carbonyls attached to the Co not containing the Cp groups. From the crystal structure,¹⁴ the relevant CO bond vectors lie at angles of 69.6, 77.5, and 162.7° from the unique axis.

These carbons are relaxed predominantly by chemical shift anisotropy (CSA), which is magnetic field dependent, with a second contribution from spin rotation, which is independent of B_0 .²⁸ The net relaxation rate, therefore, is given by^{28,29}

$$T_1^{-1}(^{13}\text{C}) = T_{1\text{CSA}}^{-1} + T_{1\text{SR}}^{-1} = (2/15)\gamma^2(\Delta\sigma)^2\tau_c B_0^2 + T_{1\text{SR}}^{-1} \quad (1)$$

Thus, measurement of T_1 at two values of B_0 permits one to obtain the quantity $(2/15)\gamma^2(\Delta\sigma)^2\tau_c$. Calculation of the correlation time, τ_c , then requires that one have a value for the chemical shift anisotropy, $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$, of the carbonyl carbon. $\Delta\sigma$ has not been measured for this system, but may be estimated from the carbonyls' chemical shifts relative to free carbon monoxide³⁰ and the near cylindrical symmetry of terminal CO ligands in metal carbonyls,³¹ which implies that the paramagnetic contribution to σ_{\parallel} is approximately zero. This procedure, which has been outlined elsewhere,³² yields $\Delta\sigma = 416$ ppm for the terminal carbonyls in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})$.

The correlation time of a vector attached rigidly to the molecular skeleton is a function of θ , its angle from the top axis, and of the diffusion coefficients, D_{\perp} and D_{\parallel} .³³

$$\tau_c(\theta) = \frac{A(\theta)}{6D_{\perp}} + \frac{B(\theta)}{5D_{\perp} + D_{\parallel}} + \frac{C(\theta)}{2D_{\perp} + 4D_{\parallel}} \quad (2)$$

The coefficients are given by $A = (1/4)(3 \cos^2 \theta - 1)^2$, $B = 3 \sin^2 \theta \cos^2 \theta$, and $C = (3/4)\sin^4 \theta$.

A slight complicating feature is that the three carbonyls are exchanging between sites at different angles, θ_i , relative to the axis (vide supra). The exchange is rapid relative to T_1 , but much slower than molecular reorientational times. Therefore, one obtains the average relaxation rate and, hence, average correlation time, $\tau_c(\text{avg})$. This quantity is related to the individual correlations times for the three vectors by eq 3, where the $\tau_c(\theta_i)$ are given by eq 2.

$$\tau_c(\text{avg}) = (1/3)[\tau_c(\theta_1) + \tau_c(\theta_2) + \tau_c(\theta_3)] \quad (3)$$

The procedure for the calculation of D_{\parallel} , then, is to measure T_1^A and T_1^B at two field strengths, B_0^A and B_0^B , from which one obtains $\tau_c(\text{avg})$ from eq 1 and $\Delta\sigma$. With the D_{\perp} from phenyl group relaxation times, one then fits eqs 2 and 3 to find the value for the parallel diffusion coefficient, D_{\parallel} , which minimizes the deviation between the experimental and calculated correlation time.³⁴

Calculation of $R(\text{Cp})$. Like the phenyl group, the cyclopentadienyl rings can undergo internal rotation (about their C_5 axes). However, since the internal rotation axis is not coincident with the unique axis, the analysis is somewhat more complex.

Table II. Diffusion Coefficients in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\mu_3\text{-CPh})^a$

T , K	D_{\perp} , ns^{-1}	$D_S(\text{Ph})$, ns^{-1}	$D_S(\text{Bz})$, ns^{-1}	D_{\parallel} , ^b ns^{-1}	$R(\text{Ph})$, ns^{-1}	$R(\text{Cp})$, ns^{-1}
211	0.7	1.5	15	1.6	≈ 0	11
218	0.9	1.9	18	1.9	≈ 0	12
248	1.8	3.8	33	3.9	≈ 0	19
273	2.9	6.2	51	6.3	≈ 0	26
298	4.2	9.2	72	9.3	≈ 0	33
323	5.9	15.8 ^c	97	12.9	$\approx 3^c$	41

^a Values in the table are presented to two significant digits. However all calculations were performed prior to roundoff. ^b $D_{\parallel} = 2.2D_{\perp}$. See text. ^c This point is believed to be in error. See text.

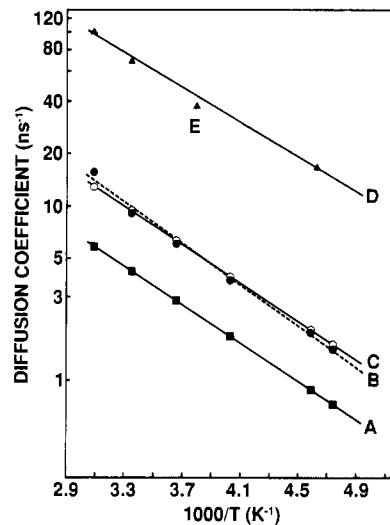


Figure 1. Temperature dependence of rotational diffusion coefficients in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})$ and related systems: (A) D_{\perp} (solid line and filled squares); (B) $D_S(\text{Ph})$ (dashed line and filled circles); (C) D_{\parallel} (solid line and open circles); (D) $D_S(\text{Bz})$ (solid line); (E) $D_S(\text{Ph})$ in $\text{Co}_3(\text{CO})_9(\text{CPh})$ (filled triangles).¹²

The correlation time for rotation of the Cp's C-H vectors may be obtained from their relaxation times by

$$T_1^{-1} = \frac{\gamma_c^2 \gamma_H^2 h^2}{4\pi^2 r_{\text{CH}}^6} \tau_c = 2.269 \times 10^{10} \tau_c \quad (4)$$

where the numerical coefficient was calculated by using standard values for Planck's constant (h) and the magnetogyric ratios, γ_c and γ_H , and $r_{\text{CH}} = 1.08 \text{ \AA}$.³⁵

Woessner et al.³⁶ have developed a general expression for the correlation time undergoing internal rotation in a symmetric top molecule as a function of the overall and internal diffusion coefficients, D_{\perp} , D_{\parallel} , and R , and α and Δ , which signify the angle between the symmetry and internal rotation axis and the angle between the latter axis and the rotating vector, respectively. For the CH vector in the cyclopentadienyl ring, $\Delta = 90^\circ$; the Woessner equation³⁶ then reduces to eq 5. The coefficients, C_i , in this equation are functions of α .³⁷

$$\tau_c = \frac{C_1}{6D_{\perp}} + \frac{C_2}{6D_{\perp} + 4R} + \frac{C_3}{5D_{\perp} + D_{\parallel}} + \frac{C_4}{5D_{\perp} + D_{\parallel} + 4R} + \frac{C_5}{2D_{\perp} + 4R} + \frac{C_6}{2D_{\perp} + 4D_{\parallel} + 4R} \quad (5)$$

With $\alpha = 85^\circ$ (calculated from the crystal structure¹⁴) and the diffusion constants, D_{\perp} and D_{\parallel} , from earlier experiments, it is straightforward to determine the value of R in eq 5, which minimizes the deviation

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 (33) Woessner, D. E. *J. Chem. Phys.* **1962**, *37*, 647.
 (34) The calculations of D_{\parallel} (from eqs 2 and 3) and $R(\text{Cp})$ (from eq 5) were performed by using iterative programs written for an IBM compatible PC in Turbo Basic.

- (35) r_{CH} for Cp is often quoted as 0.95 Å. However, Churchill (Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213) has noted that this value, determined from X-ray diffraction, corresponds to the distance between maxima in the electron density. He points out that for applications requiring the internuclear distance, one should use the spectroscopically determined value, 1.08 Å.
 (36) Woessner, D. E.; Snowden, B. S., Jr.; Meyer, G. H. *J. Chem. Phys.* **1969**, *50*, 719. In the notation of this reference, $R_1 = D_{\parallel}$ and $R_2 = D_{\perp}$.
 (37) $C_1 = (1/16)[3 \cos^2 \alpha - 1]^2$; $C_2 = (9/32) \sin^4 \alpha$; $C_3 = (3/16) \sin^2 2\alpha$; $C_4 = (3/8) [\sin^2 \alpha + (1/4) \sin^2 2\alpha]$; $C_5 = (3/16) \sin^4 \alpha$; $C_6 = (3/32)[(1 + \cos^2 \alpha)^2 + 4 \cos^2 \alpha]$.

between the calculated and experimental correlation times.³⁴ We term this quantity $R(\text{Cp})$ to distinguish it from the phenyl ring internal rotation coefficient.

Results and Discussion

Shown in the second and third columns of Table II and in Figure 1 (lines A and B) are the tumbling and spinning diffusion coefficients, D_{\perp} and $D_S(\text{Ph})$, of the phenyl group in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})$. One finds that their ratio remains approximately constant at $D_S(\text{Ph})/D_{\perp} \approx 2.1$ – 2.2 at all but the highest temperature, where it rises to 2.7. The authors believe that the inconsistency of this point with the other data may arise from the possible breakdown of the assumption of symmetric top behavior at higher temperature (*vide supra*).

It is most informative to compare the spinning rate of the phenyl group with the rate of the equivalent rotation of benzene itself (about its C_2 axis) in the same solvent.³⁸ The latter quantity is displayed as $D_S(\text{Bz})$ in Table II and in Figure 1 (line D). One sees clearly that the rotation of the phenyl group about its C_2 axis in this cluster is markedly below the rate observed for free benzene in chloroform, by approximately 1 order of magnitude. Shown also in Figure 1 (points E) is the phenyl rotation rate that we reported recently for $\text{Co}_3(\text{CO})_9(\mu_3\text{-CPh})$ in CDCl_3 .¹² This latter cluster contains no bridging carbonyls, and Schilling and Hoffmann⁹ have predicted, on the basis of symmetry and EHMO calculations, that the capping group has no preferred orientation in complexes of this type. This is verified experimentally since, from Figure 1, one sees that $D_S(\text{Ph}) \approx D_S(\text{Bz})$ at all temperatures.

From the above comparison, it is quite clear that the rate of phenyl group spinning in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})$ is substantially slowed compared to systems in which there are no electronic or steric barriers to internal ring rotation. As discussed in the Introduction, McGlinchey et al.¹⁴ found in this and related clusters that the aryl group is completely mobile on the NMR chemical shift time scale. We see, therefore, that on the much shorter time scale, measuring by spin–lattice relaxation times offers a far more sensitive probe of internal rotational rates in capped transition-metal clusters.

The Barrier to Internal Phenyl Group Rotation. As discussed in an earlier section, phenyl carbon relaxation times yield only the sum of the parallel and internal rotation diffusion coefficients, $D_S(\text{Ph}) = D_{\parallel} + R(\text{Ph})$. Therefore, the actual rate of internal rotation, $R(\text{Ph})$, depends upon the magnitude of D_{\parallel} . For example, if $D_{\parallel} \approx D_{\perp}$, then $R(\text{Ph})$ is finite on the nanosecond time scale; e.g. at 298 K, $R(\text{Ph}) \approx 5 \text{ ns}^{-1}$ (Table II). Alternatively, if $D_{\parallel} \approx D_S(\text{Ph})$, then $R(\text{Ph}) \approx 0$ (i.e. less than approximately 1 ns^{-1}).

In order to determine D_{\parallel} and, hence, $R(\text{Ph})$ we have performed relaxation time measurements on the terminal CO's at two values of B_0 . Using procedures outlined above, we have obtained the following results: at 211 K, $D_{\parallel} = 1.7 \text{ ns}^{-1}$ and $D_{\parallel}/D_{\perp} = 2.4$; at 218 K, $D_{\parallel} = 1.8 \text{ ns}^{-1}$ and $D_{\parallel}/D_{\perp} = 2.0$. As discussed,^{13C-59Co} scalar coupling prohibits carbonyl relaxation time measurements at higher temperatures. Therefore, we have estimated D_{\parallel} as a function of temperature by assuming the average ratio $D_{\parallel}/D_{\perp} = 2.2$. The results are shown in the fifth column of Table II and in Figure 1 (line C).

At all but the highest temperature, where we suspect the results are not accurate (*vide supra*), one finds that $D_{\parallel} = D_S(\text{Ph})$ to within 0.1 ns^{-1} . Therefore, the internal rotation rate, $R(\text{Ph})$, is ~ 0 on a nanosecond time scale. We must note, however, that this conclusion must be viewed with a degree of caution since the calculation of D_{\parallel} is very sensitive to the value of D_{\perp} , due to the nonlinear relationship between the two diffusion coefficients (eq 2). For example, if D_{\perp} at 211 K is increased or decreased by 5%, the ratio, D_{\parallel}/D_{\perp} , will decrease or increase by approximately 15%. The ratio is also sensitive to the value of the correlation time, τ_c , which itself depends upon the estimated value of $\Delta\sigma$.

It is possible to use the results of this investigation to obtain an estimated range for the barrier to internal rotation, V_0 , through application of the equation³⁹

$$R = R_0 e^{-V_0/R_0 T} \quad (6)$$

R_0 is the gas constant, R_0 is the diffusion coefficient of benzene molecule rotating freely about its C_2 axis (its value may be obtained from $R_0 = (5/3)(k_B T/I)^{1/2}$),⁴⁰ k_B is Boltzmann's constant, and I is the moment of inertia, $I = 1.48 \times 10^{-38} \text{ g cm}^2$.⁴¹

An estimate for the minimum barrier height may be calculated directly from eq 6 by assuming, from the earlier discussion, that $R < 1 \text{ ns}^{-1}$ at 298 K, which leads to $V_0(\text{min}) > 4.7 \text{ kcal/mol}$. One may also obtain a maximum for V_0 from the fact that one does not observe any splitting in the ortho or meta NMR resonances at the lowest temperature studied (211 K). This indicates that, at this temperature, R is greater than the rate required to induce coalescence. This rate may be obtained from the standard relation, $R = 2\pi\delta\nu/\sqrt{2}$,¹⁸ where $\delta\nu$ is the static frequency difference between the two peaks (in s^{-1}). Assuming a static splitting of approximately 2 ppm¹³ corresponds to $\delta\nu = 150 \text{ s}^{-1}$ [for $\nu_0(^{13}\text{C}) = 75 \text{ MHz}$] and $R > 670 \text{ s}^{-1}$. Use of eq 6 then gives $V_0(\text{max}) < 9.2 \text{ kcal/mol}$.

As noted in the Introduction, Stone et al.¹³ found splittings in the ortho and meta aryl resonances in the carbonyl-bridged cluster, $\text{CoFe}_2(\mu_2\text{-CO})(\text{CO})_8(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})$, at $-80 \text{ }^\circ\text{C}$; the resonances were not split in the room-temperature spectrum. One may use these data in eq 6 to obtain approximate barrier limits in this cluster: $9 \text{ kcal/mol} < V_0 < 13 \text{ kcal/mol}$.⁴² It is interesting to note that the experimental range lies reasonably close to the barrier height, $V_0 = 14 \text{ kcal/mol}$, which they predicted by simple extended Hückel MO calculations.¹³ The range in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})$, $5 \text{ kcal/mol} < V_0 < 9 \text{ kcal/mol}$, is somewhat lower. However, the barriers may be of similar magnitude if V_0 in the latter complex is nearer the upper limit.

The Nature of the Barrier. Stone et al.¹³ explained the frozen aryl group rotation in $\text{CoFe}_2(\mu_2\text{-CO})(\text{CO})_8(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})$ at low temperatures in terms of an electronic interaction of the $\mu_2\text{-CO}$'s π^* orbital with the 2e metal orbitals, which splits their degeneracy, leading to an asymmetric interaction with the carbyne's 2p orbital and, thence, to preferred orientation of the ring parallel to the bridging carbonyl. It is tempting to invoke a similar electronic interaction between the bridging carbonyl and the phenyl ring, through the metal 2e and carbyne 2p orbitals, to explain the large barrier to rotation in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})$. However, McGlinchey and co-workers,¹⁴ from their crystal structure of this complex, pointed out that, although they expected no significant steric interaction between the phenyl and cyclopentadienyl groups, the ortho protons of the two rings can approach to within 1.3 \AA of one another for the appropriate orientation of the two groups. Since this is well below the sum of their van der Waals radii ($2r_{\text{H}} = 2.8 \text{ \AA}$),⁴³ one cannot exclude a mutual steric obstruction of the phenyl and cyclopentadienyl rings' rotation via a "gear" type mechanism, similar to that found by Mislow and Norton.⁴⁴

If the two rings do interfere sterically with one another's internal rotation, then one should observe slowed rotation of the cyclopentadienyl group about its C_5 axis. To test this possibility, we have measured the relaxation times of the Cp carbons as a function of temperature. As outlined earlier, this data, together with the overall diffusion coefficients, D_{\perp} and D_{\parallel} , were used to calculate the internal rotation rates of the cyclopentadienyl ring, $R(\text{Cp})$.

(38) (a) Tanabe, K. *Chem. Phys.* **1978**, *31*, 319. (b) Tanabe, K. *Ibid.* **1979**, *38*, 125. These references report a room-temperature diffusion coefficient of 72 ns^{-1} . The temperature dependence of $D_S(\text{Bz})$ was calculated by assuming an activation energy, $E_a(\eta/T) = 2.27 \text{ kcal/mol}$,¹⁰ where η is the viscosity of the solvent chloroform.

(39) (a) Alger, T. D.; Grant, D. M.; Harris, R. K. *Chem. Phys.* **1972**, *76*, 281. (b) Lyster, J. R., Jr.; Grant, D. M. *J. Phys. Chem.* **1972**, *76*, 3213.

(40) Oehme, K.-L.; Rudakoff, G.; Radeaglia, R. *Adv. Mol. Relax. Interact. Processes* **1976**, *8*, 1.

(41) Dais, P. *Magn. Reson. Chem.* **1987**, *25*, 141.

(42) In calculating $V_0(\text{min})$, we have assumed that $R < 100 \text{ s}^{-1}$ at $-80 \text{ }^\circ\text{C}$, since one observes 2 ppm splittings in the phenyl resonances. We have assumed further that the experiments were performed at $\nu_0(^{13}\text{C}) = 75 \text{ MHz}$, since the spectrometer frequency was not given in ref 13; these assumptions have only a small effect on the estimated barrier limits.

(43) Bondi, A. J. *J. Phys. Chem.* **1964**, *68*, 441.

(44) Eddin, R. T.; Norton, J. K.; Mislow, K. *Organometallics* **1982**, *1*, 561 and references therein.

The results are shown in the last column of Table II.

One sees from Table II that $R(\text{Cp}) \gg R(\text{Ph})$ at all temperatures, supporting the independent rotation of the cyclopentadienyl rings relative to the aryl ring. One would expect any steric interaction between the two rings to be reflected by an equivalent reduction in $R(\text{Cp})$. From this result, the authors believe that one may reasonably eliminate steric hindrance as the basis of the observed phenyl rotation barrier in $\text{Cp}_2\text{Co}_2(\text{CO})_4(\text{CPh})$, which may, therefore, be attributed primarily to electronic orbital interactions between the bridging CO and capping phenyl group.^{9,11-13}

Summary and Conclusions

In this investigation, we have utilized ^{13}C NMR spin-lattice relaxation times to obtain a complete characterization of the overall and internal rotation dynamics in $\text{Cp}_2\text{Co}_2(\text{CO})_4(\text{CPh})$ as a function of temperature in the solvent chloroform.

From the phenyl carbon T_1 's, we obtained the molecular tumbling diffusion coefficient, D_{\perp} , and the total phenyl ring spinning rate, $D_S(\text{Ph}) = D_{\parallel} + R(\text{Ph})$. $D_S(\text{Ph})$ in the complex was found to be 1 order of magnitude lower than both (a) the equivalent rotational rate of free benzene in chloroform and (b) the measured values of $D_S(\text{Ph})$ in $\text{Co}_3(\text{CO})_9(\mu_3\text{-CPh})$, a cluster with neither electronic nor steric interactions between the ring and molecular skeleton.

^{13}C relaxation times of the terminal carbonyl ligands, measured at two magnetic field strengths, were used to calculate the parallel diffusion constant, D_{\parallel} , of the cluster's framework. It was observed that, to within experimental error, $D_{\parallel} = D_S(\text{Ph})$, from which it was concluded that the internal phenyl rotational rate, $R(\text{Ph})$, is ~ 0 on a nanosecond time scale. This result permitted the

determination of an estimated range for the barrier, V_0 , to internal rotation: $5 \text{ kcal/mol} < V_0 < 9 \text{ kcal/mol}$.

To determine whether the hindrance to internal rotation of the phenyl group in the cluster might be due to a gear type mutual interaction of the phenyl and cyclopentadienyl rings, ^{13}C T_1 's of the Cp carbons were used to calculate the internal rotation rate of this ring about its C_5 axis. It was found that $R(\text{Cp}) \gg R(\text{Ph})$ at all temperatures, from which one may reasonably conclude that the barrier is not due to inter-ring steric effects. Rather, the rotational barrier can be attributed to electronic interaction of the bridging CO's π^* orbital with the aryl π system through the metal 2e orbitals, as proposed recently by Stone et al.¹³ to explain the slowed ring rotation in $\text{CoFe}_2(\mu_2\text{-CO})(\text{CO})_8(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})$.

The results of this investigation illustrate the powerful utility of the NMR relaxation time technique to probe reorientational and internal rotation dynamics on a nanosecond time scale. In this system, these measurements permitted the observation and estimation of an internal rotation barrier which could not be detected by using conventional temperature-dependent ^{13}C NMR spectroscopy.

To the authors' knowledge, this is only the second metal carbonyl cluster in which an orbital interaction between a bridging CO and capping ligand has been observed experimentally and the first for which the barrier range to internal rotation has been determined. Further experiments on additional homo- and heteronuclear systems will be required to assess the generality and range of magnitudes of this type of electronic interaction.

Acknowledgment. We acknowledge the Robert A. Welch Foundation [Grants B-1039 (M.G.R.) and B-657 (M.S.)] and the UNT Faculty Research Fund for support of this research.

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Spectroscopic and Electrochemical Studies of Monomeric Oxomolybdenum(V) Complexes with Five-Membered Chelate Rings and Alkoxy or Alkanethiolato Ligands

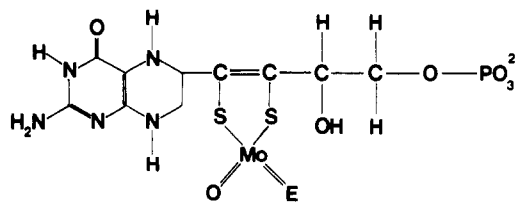
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Received July 12, 1990

A series of monomeric oxomolybdenum(V) complexes of the type $\text{LMoO}[\text{X}-\text{CHR}'-\text{CHR}''-\text{Y}]$ ($\text{L} = \text{hydrotris}(3,5\text{-dimethyl-1-pyrazolyl})\text{borate}$; $\text{X} = \text{O}$, $\text{Y} = \text{S}$, $\text{R}' = \text{Me}$, $\text{R}'' = \text{H}$ or $\text{R}' = \text{R}'' = \text{H}$, Me ; $\text{X} = \text{Y} = \text{O}$, S , $\text{R}' = \text{R}'' = \text{Me}$) have been synthesized. Several monoalkoxy and monoalkanethiolato complexes with the general formula of $\text{LMoO}(\text{Cl})(\text{XR})$ ($\text{X} = \text{O}$, $\text{R} = \text{Me}$, Et , ^nPr ; $\text{X} = \text{S}$, $\text{R} = \text{Et}$, ^nPr , ^iPr) also have been prepared. All of these complexes have been characterized by elemental analyses, mass spectrometry, infrared and UV-visible spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and cyclic voltammetry. The electronic absorption spectra for chelate complexes with $\text{X} = \text{Y} = \text{O}$ or S show two transitions with similar extinction coefficients in the range 400–900 nm. The energy difference between these two bands is approximately 3400 and 3600 cm^{-1} for $\text{X} = \text{Y} = \text{O}$ and S , respectively. In the potential window +2.0 to -2.0 V, all of these complexes exhibit one quasi-reversible reduction wave, corresponding to forming the analogous monooxomolybdenum(IV) species. The reduction potentials shift to the negative direction with an increase in the number of methyl groups on the chelate rings and with an increase in the number of methylene units in the monodentate alkoxy or alkanethiolato ligands.

Introduction

The molybdenum cofactor, Mo-co (I), is proposed to possess pterin and alkyl phosphate ester moieties that attach to a dithiolene group.^{1,2} The actual functions of these groups in the side chains are not yet known, but the pterin group may be involved in electron transfer with the molybdenum center during turnover.³



(E = O, S)

(I)

- (1) (a) Johnson, J. L.; Rajagopalan, K. V. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 6856-6860. (b) Kramer, S. P.; Johnson, J. L.; Riberiro, A. A.; Millington, D. S.; Rajagopalan, K. V. *J. Biol. Chem.* **1987**, *262*, 16357-16363.
- (2) Cramer, S. P.; Stiefel, E. I. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley: New York, 1985; Chapter 8, pp 411-441.
- (3) (a) Burgmayer, S. J. N.; Stiefel, E. I. *J. Chem. Educ.* **1985**, *62*, 943-953. (b) Lehnen, J.; White, B. M.; Kendrick, M. J. *Inorg. Chim. Acta* **1990**, *167*, 257-259.

Recently, we have reported that the variation of the sizes of the chelate rings in a series of monomeric (diolato)- and (dithiolato)oxomolybdenum(V) complexes can have marked effects