Diffusional and Internal Rotation in Single and Linked Trinuclear Bis(carbyne) Cluster Complexes Determined by ^{13}C NMR Relaxation Time Measurements

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Received October 15, 1996[⊗]

Carbon-13 NMR relaxation times have been measured as a function of temperature for a family of bis(carbyne) cluster complexes: $(CpCo)_3(\mu_3\text{-CPh})_2$ (**1a**), $(CpCo)_3(\mu_3\text{-CH})(\mu_3\text{-CPh})$ (**1b**), and $X(1,4\text{-}C_6H_4)Y$ with X = Y = $(CpCo)_3(\mu_3\text{-CPh})(\mu_3\text{-C}-)$ (**2**); X = $(CpCo)_3(\mu_3\text{-CPh})(\mu_3\text{-C}-)$, Y = $-C{\equiv}CPh$ (**3**); or X = Y = $-C{\equiv}CPh$ (**4**). These molecules can be regarded as symmetric top molecules in which the phenyl rings are adjacent to zero, one, or two Cp_3Co_3 metal cluster units. Molecular rotational diffusion coefficients about the different axes of the molecules ($D_\perp$and D_s) obtained from the relaxation times indicate that the motions of the molecules are highly anisotropic. Rapid *internal* rotation of the phenyl rings described by the rotation rates R contributes significantly to that anisotropy. Phenyl rings adjacent to an alkyne group rotate at a rate comparable to that of free benzene whereas phenyl rings bound to a $(CpCo)_3$ group through a μ_3-carbyne ligand show significantly reduced rates of rotation. The observed difference in rotation rates is believed to be due primarily to steric interactions between phenyl rings and their substituents.

Introduction

The use of organometallic complexes as precursors to new materials has begun to play an important role in current research in the area of organometallic chemistry.[1,2] The reasons for this are severalfold. The ability of metal centers to exhibit multiple, stable valence states,[3,4a] including ones involving partially filled molecular orbitals, can lead to materials with partially filled electronic bands which are conductive. Additionally, new inorganic materials have recently been described which have both novel and useful magnetic properties such as high magnetic saturation and shielding properties.[5] Although much work remains to be done in the development of such materials, a common theme in their design is the molecular level engineering of specific linking groups which facilitate the desired interactions between metal centers or units. Properties which are known to be important in the interactions between metal units are the distance separating units, the nature of intervening or linking groups between units, and the orientation of one unit relative to another.[6] The distance separating two units determines the magnitude of so-called “through space” interactions which include electrostatic charge interactions and dipolar interactions between unpaired spins. The nature of the linking group encompasses many factors such as the electronic structure of the group, its flexibility and its dynamics. The relative orientation of the MOs of the metal units is of critical importance in determining the magnetic behavior of a material. Understanding the role of each of these factors and developing methodologies to control and tailor each is one of the current goals in molecular materials engineering.

Recently, molecular metal cluster complexes have been used as building blocks for such materials, and dimers and oligomers have been formed as the result of linking several clusters together. The linking groups have involved metal ions[7] or a number of organic functional groups including alkynes,[4b] alkanes,[8] and cyclopentadienone.[4c] We have begun to explore the properties of a family of linked, bis(carbyne) cluster complexes of the form $R-C{\lessdot}(CpCo)_3{\gtrdot}C-X-C{\lessdot}(CpCo)_3{\gtrdot}C-R$ as possible models for conducting organometallic polymers and new liquid crystalline materials. These complexes, which can be prepared from the corresponding alkyne complexes by scission of the C≡C bond,[9,10] are both thermally and chemically quite robust. At the same time, they undergo a number of reversible oxidation reduction reactions which produce a wide range of mixed valence states.

In the studies described here, the linking group is a 1,4-disubstituted phenyl group (Figure 1). Several properties make this group ideal for consideration as a connecting group between metal centers. It is chemically stable, has a well-defined and rigid structure which determines the distance and orientation of the groups bound to it, and has a π-MO system which can be utilized in mediating electronic interactions between different groups. The trinuclear cluster complexes used as monomers are composed of three CpCo fragments in a triangular array

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

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S0020-1669(96)01243-8 CCC: $14.00

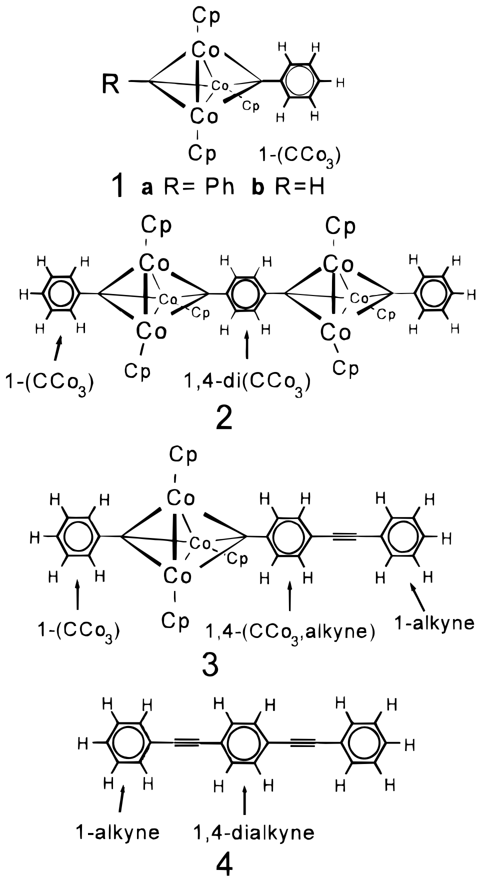

Figure 1. Illustrations of compounds **1**−**4**. Phenyl groups are labeled according to the number, type, and pattern of substituents to which they are bound.

capped on both sides by triply-bridging carbyne ligands. In this study the monomeric bis(carbyne) complexes **1a** and **3** and the linked complex **2** are investigated (Figure 1). The alkyne **4** was also studied for comparison purposes.

In conjunction with our investigations of the electronic properties of these complexes, we became interested in the dynamics of the phenyl groups and whether motions of these groups affect their ability to mediate electronic interactions between the metal units they link together. A study of the crystal structures and electrochemical properties of these complexes will be published elsewhere.[11] Herein we describe the results of a detailed analysis of both the molecular motions and internal rotational dynamics of phenyl-linked bis(carbyne) complexes. Such information is of interest in the design of polymer systems based on these and other organometallic units and linking entities.

Experimental Section

The cluster complexes **1**−**3** were prepared from the corresponding diphenylacetylene and bistolan alkyne adducts via thermally induced alkyne scission reactions in refluxing decahydronaphthalene similar to the procedures described by Vollhardt and coworkers.[10] Bistolan **4** was synthesized following the procedure of Nguyen et al.[12] CD_2Cl_2 was dried over CaH_2 and degassed by several freeze−pump−thaw cycles before use. NMR samples were prepared in flame-sealed tubes after vacuum transfer of the solvent. Concentrations were 76 mM for **1**, 10.4 mM for **2**, 30 mM for **3**, and 93 mM for **4**. Due to its low solubility, samples of **2** were made up in 10 mm tubes, whereas 5 mm tubes were used for all other samples.

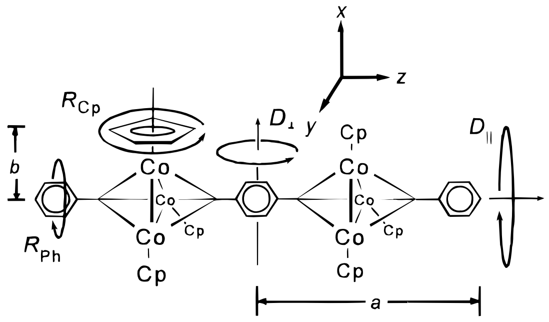

Figure 2. Definitions of axis length *a* and *b* and illustrations of molecular rotational diffusion coefficients, D_i, and internal rotation coefficients R_i. $D_\perp$: motion perpendicular to the primary axis. $D_{||}$ rotation about the primary axis. R_{Ph}: internal rotation of phenyl substituent. R_{Cp}: internal rotation of Cp ring.

Spectra were acquired at 9.4 T using a Bruker AMX400-WB NMR spectrometer operating at a carbon-13 frequency of 100.62 MHz. Assignment of the carbon resonances was made using heteronuclear $^{13}C\{^1H\}$ correlation spectroscopy.[11] Probe temperatures were calibrated using methanol or ethylene glycol according to the procedure described by Van Geet[13] and are believed to be accurate within 1 °C.

^{13}C spin−lattice relaxation times were measured with the fast inversion recovery pulse sequence[14] (180°−τ−90°−acq) using relaxation delays of $2T_1$−$3T_1$ and 12 τ values ranging from 3 μs to $5T_1$. A three-parameter fit was used to obtain the relaxation times from the data. Nuclear Overhauser enhancements (NOE) were measured by comparing the intensities of the carbon-13 signals in regular decoupled and inverse gated decoupled[15] spectra.

Determination of Diffusion Coefficients

The general shape of the compounds investigated in this study can be approximated by a prolate symmetric top with one long semiaxis (*a*) and two shorter semiaxes of equal length (*b*) as illustrated in Figure 2 for the linked cluster system **2**. *b* is defined as the distance from the center of the Co_3 triangle to an average cyclopentadienyl hydrogen position. Estimates for the lengths of *a* and *b* were obtained from crystal structures of complex **1a** and the linked cluster complex **2**.[11] Bond distances obtained from these crystal structures were also used to estimate the axis lengths for the alkyne-substituted cluster **3** and for bistolan **4**.

The diffusional motions in these molecules can then be described by two molecular diffusion coefficients: spinning about the unique axis (*z*), described by $D_{||}$, and tumbling of the molecule perpendicular to the unique axis (*x* or *y*), described by the diffusion coefficient $D_\perp$. In the cases of **2** and **3**, the large difference in molecular dimensions ($a \gg b$) leads to the expectation that molecular tumbling ($D_\perp$) will be significantly slower than rotation about the long axis ($D_{||}$). Furthermore, internal rotation of the phenyl (R_{Ph}) and cyclopentadienyl rings (R_{Cp}) as well as the cobalt cluster fragment (R_{Co_3}) must also be considered as contributing factors to the dynamics of molecular reorientation of these molecules, *vide infra*.

Phenyl Ring Rotation

If both the overall spinning of the entire molecule and the internal rotation of a phenyl group take place about the primary molecular axis (*z*), then the total effective spinning rate experienced by the phenyl group is the sum $D_{s,Ph} = D_{||} + R_{Ph}$. Equations relating the dipolar relaxation times of ellipsoidal

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molecules undergoing internal rotation to the rotational diffusion coefficients have been developed by Woessner and co-workers.[16] Application of this theory to phenyl ring rotation in carbyne ligands of metal cluster complexes has been described by Richmond and Schwartz.[17] If internal rotation occurs about an axis parallel to the main symmetry axis of the ellipsoid, then, in the extreme narrowing limit ($\tau_c\omega \ll 1$), the relationship between diffusion coefficients and relaxation time is given by

$$\frac{1}{T_1} = \frac{\gamma_C^{\,2}\gamma_H^{\,2}\hbar^2}{r_{CH}^{\,6}}\left\{\frac{A}{6D_\perp} + \frac{B}{5D_\perp + D_\| + R} + \frac{C}{2D_\perp + 4(D_\| + R)}\right\} \tag{1}$$

where $A = (3\cos^2\Theta - 1)/4$, $B = 3\sin^2\Theta\cos^2\Theta$, $C = (3\sin^4\Theta)/4$, and Θ is the angle between the C−H bond and the rotational axis.

For the carbons in the para position the angle Θ is equal to 0. In this case the factor A in eq 1 equals 1 and $B = C = 0$. Equation 1 then simplifies to

$$\frac{1}{T_{1,\text{para}-C}} = \frac{\gamma_C^{\,2}\gamma_H^{\,2}\hbar^2}{r_{CH}^{\,6}}\frac{1}{6D_\perp} = \frac{3.781 \times 10^9}{D_\perp} \tag{2}$$

where standard values for γ_H, γ_C, and $\hbar$ and a value of 1.08 Å for the C−H bond length[18] have been used. From eq 2 one can see that the relaxation of the para carbon gives directly the tumbling rate $D_\perp$, for the entire molecule, independent of all other motions.

For the ortho and meta carbons Θ equals 60° and 120°, respectively. In either case the coefficients in eq 1 are $A = {}^1/_{64}$, $B = {}^9/_{16}$, and $C = {}^{27}/_{64}$ and the relaxation time therefore depends on R_{Ph}, $D_\|$, and $D_\perp$. Using eqs 1 and 2 and the definition $D_s = D_\| + R_{Ph}$, the ratio $T_{1,\text{ortho}}/T_{1,\text{para}}$ is given by

$$\frac{T_{1,\text{ortho}}}{T_{1,\text{para}}} = \frac{T_{1,\text{meta}}}{T_{1,\text{para}}} = \frac{64}{1 + \dfrac{216}{5 + \dfrac{D_s}{D_\perp}} + \dfrac{162}{2 + 4\dfrac{D_s}{D_\perp}}} \tag{3}$$

The ratio $D_s/D_\perp$ may then be determined by fitting the ratio $T_{1,\text{ortho}}/T_{1,\text{para}}$ to eq 3 using $D_s/D_\perp$ as an adjustable parameter. D_s can then be obtained using $D_\perp$ calculated from eq 2. It should be noted that this analysis yields only independent values for $D_\perp$ and D_s which is the sum $D_\| + R_{Ph}$. Separation of D_s into $D_\|$ and R_{Ph} is not possible with dipolar relaxation times of the phenyl carbons alone.

Finally, the above equations are valid only if the motion of the molecule is in the fast narrowing limit. As discussed below, this assumption may not be valid for complex **2**.

Cp Ring Rotation

The NOE for the cyclopentadienyl carbon atoms in **1a** is 1.61 at 300 K and is independent of temperature. This suggests that coupling with the quadrupole moment of the cobalt atoms contributes significantly to their overall relaxation. In such cases, dipolar contributions to the carbon relaxation times T_1^{DD}(Cp) may be obtained from the relation[19]

Table 1. ^{13}C T_1 Relaxation Times (s^{-1}) Obtained for **1a**

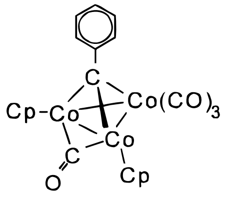
T/K	$T_{1,\text{para}}$	$T_{1,\text{ortho}}$	$T_{1,\text{meta}}$	$T_{1,\text{Cp}}$	$T_{1,\text{Cp}}^{DD}$
300.0	1.3(1)	4.0(2)	4.1(2)	4.3(2)	5.4(2)
290.4	1.1(1)	3.4(2)	3.5(2)	3.7(2)	4.2(2)
280.2	1.0(1)	3.0(2)	3.1(2)	3.2(2)	3.7(2)
269.8	0.83(8)	2.5(2)	2.6(2)	2.7(2)	3.1(2)
259.4	0.69(7)	2.1(1)	2.2(1)	2.3(1)	2.4(1)
248.9	0.56(6)	1.7(1)	1.8(1)	1.9(1)	2.1(1)
238.4	0.46(5)	1.3(1)	1.3(1)	1.5(1)	1.7(1)

$$T_1^{DD}(\text{Cp}) = \frac{1.994}{\text{NOE(exp)}}T_1(\text{exp}) \tag{4}$$

In compounds **1**−**3** the rotational axes of the Cp rings are perpendicular to the main axis of the molecule. Equations relating the relaxation times of the Cp carbons to diffusion coefficients can be obtained from Woessner's general equations describing relaxation in ellipsoidal molecules with internal rotation[16b] and have been presented by Schwartz and Richmond.[20] The correlation time of a carbon on a Cp ring depends on three parameters: the internal rotation rate R_{Cp}, the diffusion coefficient $D_\perp$, and the spinning rate $D_{s,Co_3} = D_\| + R_{Co_3}$ describing the rotation of the Cp_3Co_3 triangle about the main axis. For the bis(carbyne) systems **1a** and **1b** one can approximate D_{s,Co_3} by $D_\|$ since the Cp_3Co_3 moiety accounts for the bulk of the molecule. In the linked cluster systems (**2** and **3**), the two Cp_3Co_3 units are expected to rotate faster than the molecular spinning rate. In this case, $D_\|$ cannot be used to approximate D_{s,Co_3}.

Results and Discussion

Recently Richmond, Schwartz, and co-workers utilized ^{13}C NMR relaxation data to describe the rotational diffusion coefficients for phenyl ring rotation in several trinuclear metal clusters containing capping carbyne ligands[17] such as **5** and **6**.



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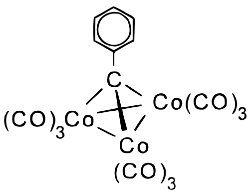

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The studies described here extend these measurements to include a series of linked cluster systems based on the (CpCo)$_3$ fragment. These compounds contain up to three different types of phenyl rings within one molecule allowing us to directly compare the rates of rotation of phenyl rings bound to different numbers of carbyne and/or alkyne carbons.

Carbon-13 T_1 relaxation times were measured over a range of temperatures from 310 to 250 K. Table 1 shows the experimental relaxation times for the bis(carbyne) cluster **1a**. The relaxation times for the ortho and meta carbons of the phenyl ring are the same within the experimental uncertainty of our measurements whereas the relaxation times for the para carbons are significantly shorter. This difference is a strong

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(20) See eq 5 of ref 17c. For the complexes in this study, a value of 90° was used for α describing the angle between the rotational axis of the Cp ligand and the main axis of the molecule.

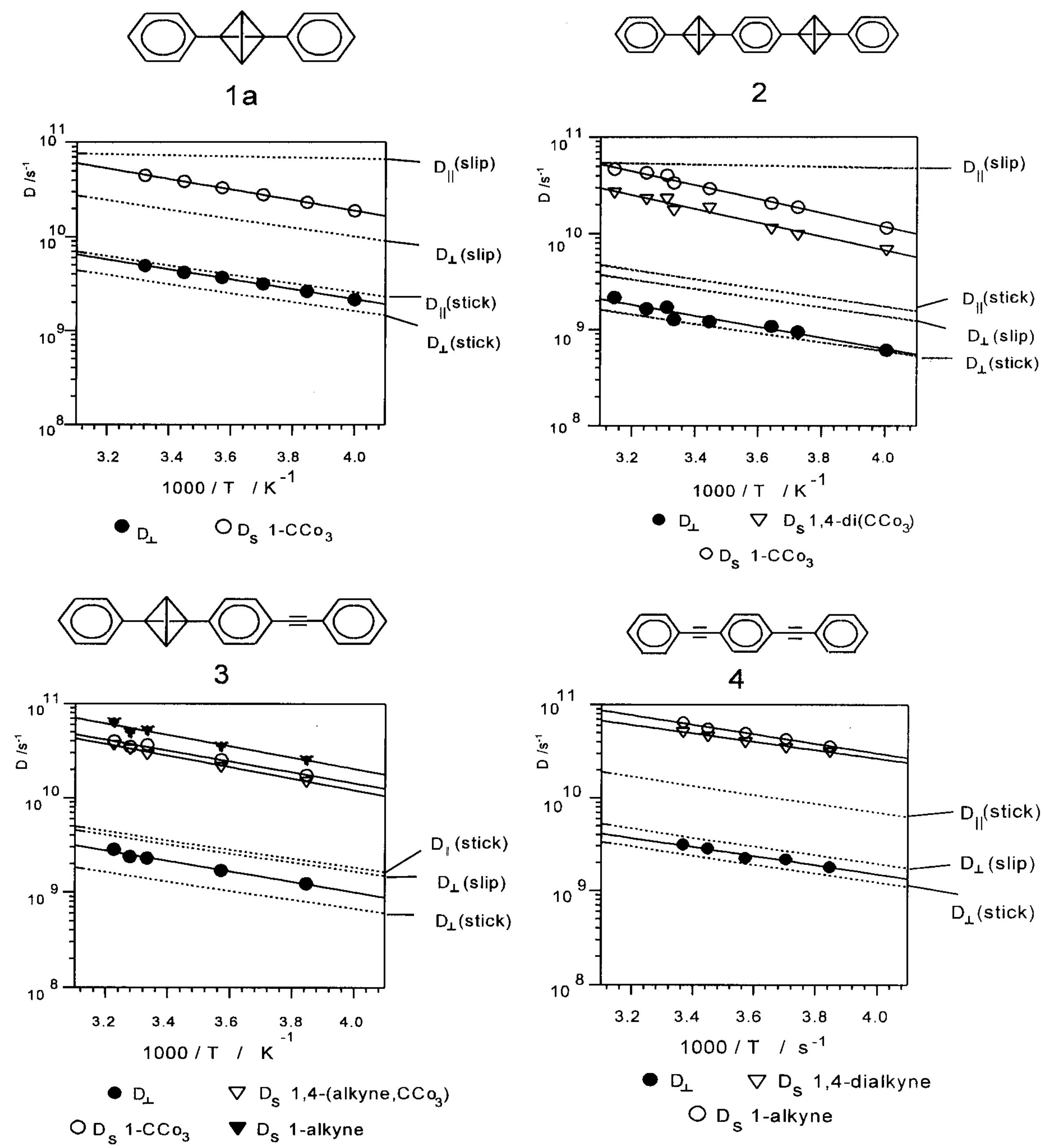

Figure 3. Semilog plots of experimental and calculated diffusion coefficients versus inverse temperature. Symbols represent experimental data; solid lines, regression fits to the data; dotted lines, predictions of hydrodynamic models discussed in the text. See Figure 1 for substituent symbol abbreviations.

indication that the reorientation of the phenyl group is anisotropic. All relaxation times increase with increasing temperature, as expected for rotational motions faster than the ^{13}C Larmor frequency. The relaxation times obtained for complexes **2**−**4** show similar behavior. A complete summary of these data is supplied in the Supporting Information. Nuclear Overhauser enhancements of 200% were found for the phenyl carbons in compounds **1a**, **1b**, **3**, and **4** as expected for molecules whose correlation times are in the extreme narrowing limit ($\tau_c\omega \ll 1$) where relaxation is dominated by dipolar coupling with the protons.

In the case of the linked cluster **2**, however, NOEs smaller than 200% were observed for the phenyl carbons, especially at lower temperatures ($T = 250$ K; C_p, 140%, $C_{o/m}$, 170%). Due to the chemical and structural similarities between **2** and the other molecules it is unlikely that other relaxation mechanisms such as chemical shift anisotropy play a significant role in the relaxation of **2**. Furthermore, spin rotation mechanisms can be ruled out since it is most efficient in small molecules with high rotation rates and its influence is expected to decrease with molecular weight. It is therefore most plausible to assume that we also have exclusively dipolar relaxation in the linked cluster **2** but that the tumbling of a molecule of this size is slow such that the condition for extreme narrowing is no longer satisfied. The more general frequency dependent equations for dipolar relaxation have therefore been used to extract the diffusion coefficients for **2** from the T_1 values.[21] These equations are included in the Supporting Information.

Using eqs 2 and 3, diffusion coefficients were obtained from the relaxation times for **1**−**4**. Semilogarithmic plots of the diffusion coefficients versus inverse temperature are shown in Figure 3. Dotted lines represent values of $D_\perp$ and $D_\parallel$ obtained from hydrodynamic models discussed below. Regression

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Table 2. Internal Rotation Diffusion Constants for **1**−**4** at 298 K[a]

	1a	**1b**	**2**		**3**			**4**	
	1-CCo_3[b]	1-CCo_3[b]	1-CCo_3[b]	1,4-diCCo_3[b]	1-alkyne	1-CCo_3[b]	1,4-(alkyne, CCo_3[b])	1-alkyne	1,4-dialkyne
$D_s/(ns)^{-1}$	45.3(7)	54(1)	36(2)	20(2)	50(4)	34(2)	30(1)	63(1)	50(1)
$R/(ns)^{-1}$	37.5(7)	44	31(2)	16(2)	45(4)	28(2)	24(1)	46(1)	33(1)
$(D_s/D_\perp)_{exp}$	9.2	7.0	23.3	13.1	21.9	14.9	13.2	20.7	16.7
E_a/kJ mol^{-1}	10.7		11.1	10.8	11.4	10.9	11.4	9.34	9.71
V_i/kj mol^{-1}	2.4	2.0	2.9	4.6	2.0	3.1	3.5	1.9	2.7

[a] D_s: overall motion of individual phenyl group ($R_i + D_{||}$); internal rotational diffusional constant, R_i, estimated according to hydrodynamic "stick" model described in text. [b] $Cp_3Co_3(\mu_3\text{-}C)$ substituent abbreviated as CCo_3.

Table 3. Molecular Diffusion Coefficients $D_{||}$ and $D_\perp$ for Complexes **1**−**4** at 298 K

	1a	**1b**	**2**	**3**	**4**
$2a$/Å	1.30	*b*	21.2	20.0	18.3
$D_\perp(exp)/(ns)^{-1}$	4.92(4)	7.7(4)	1.5(1)	2.3(1)	3.0(1)
$D_{||}/(ns)^{-1}$ [a]	7.8	9.8	4.4	6.3	17.1
$D_\perp(stick)/D_\perp(exp)$	0.68	*b*	0.80	0.61	0.82
$D_\perp(slip)/D_\perp(exp)$	4.23	*b*	1.85	1.60	1.30
$(D_{||}/D_\perp)_{stick}$	1.58	1.26	2.93	2.72	5.69

[a] Calculated according to the hydrodynamic models discussed in the text. [b] Not calculated.

analyses through the experimental data are shown as solid lines. Tables 2 and 3 compare the room temperature diffusion coefficients derived from the data over all measured temperatures for all four compounds.

As can be seen in Figure 3, the overall spinning rates of the phenyl substituents D_s are about an order of magnitude larger than the rate of tumbling $D_\perp$ for all of the complexes described here. This anisotropy in the motions of the phenyl groups can be explained by noting that tumbling of a phenyl group also involves tumbling of the entire molecule about its long axis while the spinning motion of a phenyl group involves not only the overall rotation of the molecule but also internal rotation about the single bond connecting the phenyl substituent to a carbyne carbon. Our experimental data yield only the total rotation rate D_s. However, comparing the values of D_s for nonequivalent phenyl groups within one molecule allows one to distinguish between the contributions of internal rotation and molecular shape to the anisotropy in the motions in these molecules. For example, complexes **2**, **3**, and **4** each contain two different types of phenyl groups which rotate at different rates about the main axis of each molecule. Such behavior can only arise if the different phenyl groups show different *internal* rotation rates since the contribution of the overall molecular rotation ($D_{||}$) to D_s is equal for all phenyl groups within one molecule. Differences in D_s within a molecule must arise from different values of R_{Ph} and can be taken as proof of the presence of internal motion.

The observed differences in the spinning rates allow further conclusions to be drawn. In the linked cluster system **2** the total rotation rate for the inner phenyl group ($D_{s,1,4\text{-diCCo}_3}$) is considerably slower than that for the outer phenyl groups ($D_{s,1\text{-CCo}_3}$) (Table 2). On the other hand, rotation rates for the linking phenyl group ($D_{s,1,4\text{-(CCo}_3\text{,alkyne)}}$) and the terminal phenyl substituent on the carbyne ($D_{s,1\text{-CCo}_3}$) in **3** are quite similar while the terminal phenyl substituent on the alkyne group of **3** shows a significantly faster rotation rate. These observations support the assertion that the presence of a $(CpCo)_3$(carbyne) substituent introduces a significantly larger barrier to the rotation of the phenyl group than does an alkyne substituent. Binding to a second carbyne reduces the rate of rotation even further, resulting in the following order for phenyl group rotation rates with regard to number and substituent type: 1-alkyne > 1,4-alkyne > 1-CCo_3 ≈ 1,4-(CCo_3,alkyne) > 1,4-diCCo_3 ($CCo_3 \equiv Cp_3Co_3(\mu_3\text{-}C)$).

From Raman studies the rate of rotation of a benzene molecule in CD_2Cl_2 about its C_2 axis is 100 (±20) ns^{-1} at room temperature.[22] This rate can be regarded as the maximum rotation rate for any phenyl substituent with no barrier to rotation other than interactions with a CD_2Cl_2 solvent cage. None of the phenyl substituents in this series of molecules exhibit this rotation rate.

As can be seen from Table 2, the values of $D_{s,1\text{-CCo}_3}$ in **2** and **3** are identical within their uncertainties whereas both are significantly different from D_s for **1a** and **1b** though all of these rates describe the spinning of a phenyl group carrying a single $(CpCo)_3$(carbyne) substituent. $D_{s,1\text{-alkyne}}$ values for **3** and **4** are also significantly different even though both characterize the rotation of a phenyl ring with one alkyne substituent. These differences are due to the contribution which overall molecular diffusion ($D_{||}$) makes to the total rotation of the phenyl rings. That contribution differs from molecule to molecule. For a comparison of molecular diffusion between different molecules, an independent determination of $D_{||}$ is needed. In other studies, carbon-13 relaxation times of carbonyl ligands rigidly bound to the metal skeleton have been used for this purpose;[17] in the molecules under discussion, however, such a ligand is not available.

An alternative to the direct measurement of $D_{||}$ is the use of hydrodynamic models to calculate theoretical values of $D_\perp$ and $D_{||}$. The simplest theories of anisotropic reorientation of molecules in fluid solution are modifications of the Stokes−Einstein−Debye theory of reorientation of spheres in a viscous medium.[23] In these models, the reorientation of a symmetric top molecule in a solvent with viscosity η is given by

$$D_i = \frac{1}{f_i}\frac{kT}{8\pi\eta ab^2} \tag{5}$$

where a and b are the radii along the long and the short main axes of the solute molecule, D_i stands for either $D_{||}$ or $D_\perp$, and f_i are the friction coefficients for the rotation about either axis relative to a sphere of equal volume.

In the so-called "stick" limit the solute is assumed to be large in size compared to solvent molecules (a, $b \gg r_{solvent}$). The solvent molecules are thought to stick to the solute and cause a viscous drag opposing its rotation. Equations relating the ratio of the length of the two axes of the ellipsoid with $f_\perp$ and $f_{||}$ have been developed by Perrin.[24] Using literature values for solvent viscosity,[25] diffusion coefficients for this model have been calculated and are shown in Table 3. For the molecules under discussion, the stick model gives the correct order of magnitude for $D_\perp$, but slightly underestimates its value. The temperature dependencies of the experimental data are also quite similar to those derived from eq 5. Fitting the data to the Arrhenius

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equation gives a range of 9−11 kJ mol^{-1} for the activation energy associated with molecular tumbling. These values, when compared with the calculated temperature dependence of T/η for CH_2Cl_2 according to eq 5 (9.13 kJ mol^{-1}), indicate that the temperature dependence of the tumbling is determined mainly by the viscosity of the solvent.

When the molecular dimensions of the solute and solvent are similar, the frictional drag on the solute is overestimated by the stick model, resulting in diffusion coefficients which are smaller than observed. Hu and Zwanzig have described a different model for small solute molecules[26] which assumes that the solute "slips" through the solvent molecules without the solvent sticking to the molecule. The friction experienced by the molecules is then described exclusively by the displacement of solvent molecules during rotation. The expression one obtains for $D_\perp$ in the slip limit is analogous to eq 5 except that the friction coefficients $f_\perp$(slip) are different. For $D_\parallel$ in symmetric top molecules, however, the rotation in the slip limit depends only on the moment of inertia of the molecule:

$$D_\parallel(\text{slip}) = \frac{3}{4\pi}\sqrt{\frac{kT}{I_\parallel}} \qquad (6)$$

From Figure 3 one can see that for complexes **1a** and **2**−**4** the slip model overestimates the values of $D_\perp$ to an even larger degree than the "stick" model underestimates them. Furthermore, the predicted temperature dependence of $D_\parallel$(slip) is significantly different than experimentally observed, demonstrating that the motions of these molecules are in the diffusional region governed by solvent viscosity rather than the inertial region.[27] Table 3 summarizes the experimental values for $D_\perp$ at 298 K and compares them to the values calculated from the two models. The observed rate of tumbling decreases in the order **1a** > **4** > **3** > **2** following increasing size of the molecule as measured by the long axis length (2a). The "stick" model better describes the diffusional behavior of our molecules and is therefore the one used to estimate internal rotation rates.

Having calculated values of $D_\parallel$, one is now able to separate D_s into its components and obtain approximate values for the rate of internal rotation. In Table 3 the experimental ratio $D_s/D_\perp$ ($D_s = D_\parallel + R_{Ph}$) is compared to the ratio $D_\parallel/D_\perp$ expected for a rigid molecule based on the "stick" model. One can see that for all investigated molecules D_s is significantly larger than the value of $D_\parallel$, consistent with a significant contribution from internal phenyl rotation R_{Ph} to the total spinning rate D_s. The theoretical ratio $(D_\parallel/D_\perp)_{stick}$, together with the experimental value for $D_\perp$, gives an approximate value for $D_\parallel$ from which internal rotation rates R_{Ph} for individual phenyl groups may be obtained. These values are summarized in Table 3.

Phenyl groups bearing similar substituents in different molecules in this series exhibit identical rotation rates: 46(1) versus 45(4) ns^{-1} for $R_{1\text{-alkyne}}$ for **3** and **4**, respectively, and 31(2) versus 28(2) ns^{-1} for $R_{1\text{-CCo}_3}$ for **2** and **3**. One would also expect the phenyl groups in **1a** to have the same internal rotation rate as the terminal phenyl groups next to a carbyne in **2** and **3**. That this is not observed (R_{Ph}, 37.5(7) ns^{-1} **1a**, 44 ns^{-1} **1b**, versus $R_{1\text{-CCo}_3}$(**2**) ≈ $R_{1\text{-CCo}_3}$(**3**) ≈ 30 ns^{-1}) might reflect the fact that the "stick" model does not describe the anisotropy of the diffusional motion consistently for molecules with widely varying shapes. Self-consistent rotation rates are obtained for the more anisotropic, rod-like molecules **2**−**4** as opposed to **1a** and **1b**, which are more spherical in shape than the others.[28]

We can obtain approximate values for the internal barrier to phenyl group rotation from different substituents V_i, using the relationship[29]

$$V_i = -R_G T \ln\left(\frac{R_{Ph}}{R_{C_6H_6}}\right) \qquad (7)$$

where R_G is the gas constant and $R_{C_6H_6}$ is the rotation rate of free benzene in methylene chloride. The results (Table 2) indicate that the presence of one Cp_3Co_3−carbyne substituent raises the barrier by 3 kJ mol^{-1} while a second cluster fragment adds another 1.7 kJ to the barrier. These substituent effects on the barriers to rotation of phenyl groups originate from a combination of effects which may be broadly divided into those involving steric and those involving electronic interactions between the substituent and the phenyl group. The discussion that follows describes the relative contributions of these interactions.

Previous studies of phenyl rotation rates for the tricobalt carbyne systems $Cp_2Co_3(CO)_3(\mu\text{-}CO)(CPh)$ (**5**) and $Co_3(CO)_9(CPh)$ (**6**)[17] have revealed interesting differences. For complex **5**, phenyl ring rotation was found to be effectively locked on a nanosecond time scale, whereas for complex **6**, the phenyl ring rotation rate was found to be comparable to the rate of rotation for free benzene. Consistent with these observations, frontier orbital theory suggests that in **5** the presence of the bridging CO ligand leads to a preferred orientation of the phenyl substituent with respect to that ligand,[30,31] resulting in a higher barrier to phenyl rotation in **5** than in complex **6**. Even considering the uncertainty of our values of R_{Ph}, the carbyne-bound phenyl substituents in **1**−**3** appear to be somewhere between these two extremes.

In trinuclear clusters with three equivalent vertices such as **6** as well as in the complexes investigated in our study, electronic interactions between the metal fragments and the phenyl groups do not depend on the orientations of the phenyl group and lead to a low barrier of activation for phenyl ring rotation. There are at least two possible causes for the remaining difference in rotation rates of **6** on one hand and **1**−**3** on the other. The first is that the two phenyl rings interact electronically through the Cp_3Co_3 unit, resulting in a preferred orientation of the π-systems relative to each other. The second is that the barrier is derived from steric interactions between Cp ligands and the phenyl ring.

Using the crystal structure of **1a**[11] as a model, we qualitatively examined the steric interactions of the phenyl and cyclopentadienyl groups as illustrated in Figure 4. The hydrogen atoms of the cyclopentadienyl ligands and the phenyl ring may come as close as 1.2 Å in the course of mutual free rotation. This is less than twice the van der Waal radius of a hydrogen atom in benzene (1.0 Å).[32] With the cyclopentadienyl rings kept rigid in the positions obtained from the crystal structure, force field calculations using SYBYL[33] yield a barrier to phenyl group rotation on the order of 1000 kJ mol^{-1}, i. e., orders of magnitude

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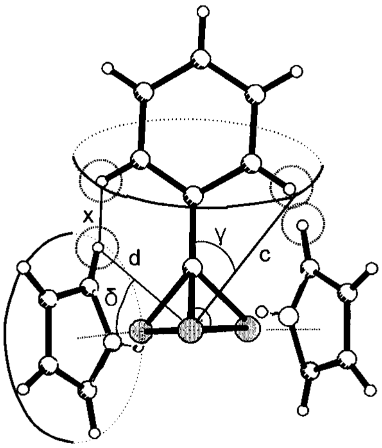

Figure 4. Rotational cones defined by the rotation of the phenyl and Cp rings based on the solid state structure **1a**. Distances *c* and *d* describe the separations of respective hydrogens of each ligand from the center of the metal triangle. γ and δ describe the angles between *c* and *d* and the respective rotation axis of each ligand. With $\gamma \approx \delta \approx 34°$, and $c = 3.6$ Å, and $d = 3.8$ Å, the smallest distance between the hydrogen atoms of the two rings is $x = 1.22$ Å. Dotted circles represent van der Waals radii of the hydrogens.

higher than observed. If one correlates the rotation of the Cp and phenyl groups to minimize steric interactions, the calculated barrier to rotation for the phenyl group drops to 13.8 kJ mol^{-1}. Although this barrier is still higher than what is observed, these force field calculations do not allow for librational motions of the phenyl rings which are expected to lower the barrier to rotation. It therefore appears that steric interactions between the phenyl and Cp rings could explain the magnitude of the barrier to rotation of the phenyl groups with $(CpCo)_3(\mu_3\text{-}C)$ substituents.

Such steric interactions raise the question of whether the motions of the two phenyl and Cp rings are completely correlated resulting in equal rotation rates for both groups. If we assume $D_{s,Co_3} \approx D_{||}$ in **1a** and use the approximate value of $D_{||}$ from the hydrodynamic stick model as described above, one obtains a value of $R_{Cp} = 95$ ns^{-1} for **1a** at 298 K. This value is considerably larger than the internal rotation rate of the phenyl rings and is not consistent with the presence of correlated motion. Although the value obtained for R_{Cp} depends strongly on the estimate made for $D_{||}$, the above conclusion still holds true even if the value of $D_{||}$ was twice as large as that obtained from the "stick" model. At first glance this argument appears to rule out steric interactions as an explanation for the observed barrier of rotation. However, when evaluating the crystal structure and molecular modeling results, one finds that, in its most favored configuration, a phenyl ring bound to a $(CpCo)_3$-(carbyne−) fragment is oriented parallel to one of the three Cp ligands. It therefore sterically interacts with only two of the three Cp rings at a time (Figure 5) whereas the third Cp ring is able to spin freely with a very low barrier (0.8 kJ mol^{-1}). This condition allows the cyclopentadienyl rings to rotate, on average, faster than the phenyl ring even in the presence of steric interaction between the two groups.

It should also be noted that, in the case of a full gear type motion between the phenyl groups and Cp rings, one would also expect the rates of rotation of the two phenyl rings in **2** ($R_{1\text{-}CCo_3}$ and $R_{1,4\text{-}diCCo_3}$) to be equal. The experimental observation of two distinct rotation rates indicates that steric interactions are large enough to slow down the motion of the phenyl groups but too small to engage a full gear type motion of the entire system.

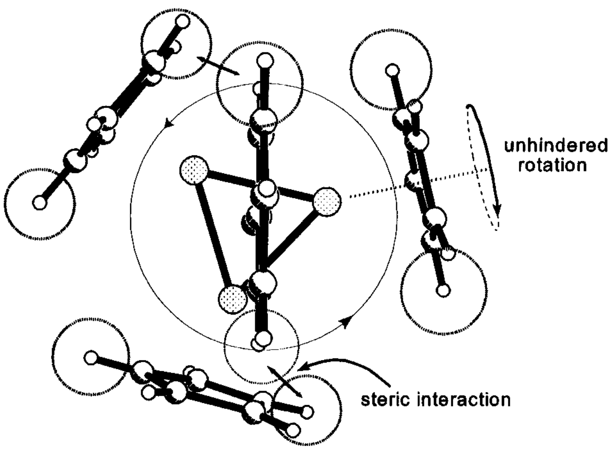

Figure 5. Top view of **1a** in the solid state illustrating the interactions of the phenyl ring with only two of the possible three Cp rings simultaneously.

Although steric interactions appear to be a significant factor in explaining the rotational behavior exhibited by the phenyl rings with Cp_3Co_3 substituents, electronic interactions between the phenyl rings cannot be ruled out. The fact that R_{Ph} is somewhat larger in **1b** than **1a** may be explained by either type of interaction. The absence of a second phenyl ring in **1b** excludes any mutual phenyl ring interactions, but one can also expect the Cp ring centroids in **1b** to move toward the sterically less demanding μ_3-CH group, thus reducing steric interactions between the Cp and phenyl rings.

In the case of the rotation of the alkyne-substituted phenyl rings in the cluster complex **3** and bistolan **4**, steric interactions can be ruled out and consistently lower barriers to rotation are observed. In these cases the barrier is therefore believed to be caused by electronic interaction between the π-systems of the phenyl rings through the C≡C triple bond.

Conclusions

Analysis of the carbon-13 NMR relaxation times of the protonated carbons in the phenyl rings of the bis(carbyne) cluster systems **1**−**3** and in bistolan **4** reveals anisotropic reorientation of the phenyl rings. Tumbling rates perpendicular to the main axis decrease with increasing size within this family of complexes. Internal rotation of the phenyl rings is the main contributor to the observed molecular spinning rate and accounts for the motional anisotropy observed for these complexes. The rate of internal rotation depends on the type of substituent attached to the phenyl ring. Steric interactions between the phenyl group and the Cp ligands of the Cp_3Co_3 fragment appear to be the major factor influencing the barrier to phenyl group rotation.

Acknowledgment is made to the donors of the Petroleum Research Fund (PRF 29106-AC5) for partial funding of this research.

Supporting Information Available: Tables of ^{13}C NMR T_1 relaxation times for compounds **1a**, **2**, **3**, and **4** measured at different temperatures and equations used to calculate diffusion coefficients for complex **2** (3 pages). Ordering information is given on any current masthead page.

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