the spin–orbit interaction. I have found in the case of solid Fe(TPP) that $\Delta = 400\ \mathrm{cm}^{-1}$, and this means the $^3A_{2g}$ state is lowest before the spin–orbit interaction is taken into account. However after the spin–orbit interaction is included, the lowest state is only 74% $^3A_{2g}$ and the next state at 93 cm^{-1} is 73% $^3A_{2g}$. For Fe(PC) with $\Delta = -900\ \mathrm{cm}^{-1}$ the lowest state is 100% ^3E_g, and the next states at 15 and 27 cm^{-1} are 13% and 23% $^3A_{2g}$, respectively.

Conclusion

It has been shown that the theory is adequate to explain the susceptibility and pseudocontact shift for four-coordinate ferrous porphyrin complexes of intermediate spin ($S = 1$) with symmetries less than axial in nature. The theory for the contact shift is less satisfactory, particularly for the β-pyrrole position when the macrocycle is ruffled in conformation.

Acknowledgment. This work was done while I was on sabbatical leave at Colorado State University, and I acknowledge the hospitality shown by the Department of Chemistry at CSU during my stay. I also acknowledge the help of Professor Strauss at CSU, who introduced me to the problem and helped with valuable discussions during the progress of the work. This work was supported in part by an operating grant from the Natural Sciences and Engineering Research Council of Canada.

Registry No. Fe(OEP), 61085-06-1; Fe(OEC), 78319-96-7; Fe(TPP), 16591-56-3; Fe(PC), 132-16-1.

Contribution from the Department of Chemistry and Center for Organometallic Research and Education,
University of North Texas, Denton, Texas 76203, and Department of Medicinal Chemistry,
College of Pharmacy, and Department of Chemistry, University of Houston, University Park, Houston, Texas 77004

Carbon-13 Relaxation and Reorientational Dynamics in a Bicapped Tetracobalt Cluster

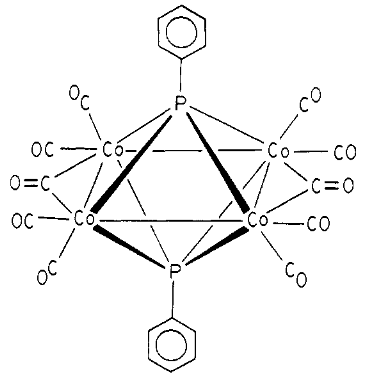
M. Schwartz,[1a] M. G. Richmond,[1a,b] A. F. T. Chen,[1a] G. E. Martin,[1c] and J. K. Kochi*[1d]

Received May 18, 1988

^{13}C spin–lattice (T_1) relaxation times and nuclear Overhauser enhancements of the phenyl (ortho, meta, and para) carbons in the tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ were measured as a function of temperature in CDCl$_3$. Three of the resonances exhibit triplet structure, indicating significant $^{31}P\cdots{}^{31}P$ interaction between the phosphinidene capping ligands. The rotational diffusion constants D_S ($=D_\parallel + R$) and $D_\perp$ derived from the T_1's reveal that the phenyl spinning rate (D_s) is approximately twice as rapid as molecular tumbling ($D_\perp$) at all temperatures. Comparison with the experimental diffusion constants in other systems suggests strongly that the phenyl rings do *not* undergo internal rotation ($R \approx 0$). This immobility is explained only partially by steric factors in the molecule. Comparison of the experimental results with diffusion constants calculated by the Perrin "stick" and Hu–Zwanzig "slip" models shows that the reorientational dynamics of the cluster is not well described by either of these limiting theories. Diffusion constants calculated by the newer Hynes–Kapral–Weinberg model provide the best agreement with the experimental results.

Introduction

The study of transition-metal clusters remains an active field due to their conceptual relationship to metal crystallites and heterogeneous catalysts, with newer interest stemming from the potential of polynuclear clusters to function as building blocks in the development of unusual electronic, magnetic, and optical materials.[2,3] Our previous studies have focused on the redox and ligand-substitution reactions of the tetracobalt cluster I whereas others have reported its catalytic activity.[4,5] While NMR investigations on I and various derivatives have been reported, no ^{13}C NMR data associated with the carbons of the phenylphosphinidene group have been reported. This dearth of data,



I

---

(1) (a) Department of Chemistry, University of North Texas. (b) Center for Organometallic Research and Education, University of North Texas. (c) Department of Medicinal Chemistry, College of Pharmacy, University of Houston. (d) Department of Chemistry, University of Houston.

(2) (a) Moskovits, M., Ed. *Metal Clusters*; Wiley-Interscience: New York, 1986; and references therein. (b) Gates, B. C.; Guczi, L.; Knozinger, H., Eds. *Metal Clusters in Catalysis*; Elsevier: New York, 1986; and references therein. (c) Lewis, J.; Green, M. L. H., Eds. *Metal Clusters in Chemistry*; Cambridge University Press: Cambridge, England, 1982; and references therein. (d) Johnson, B. F. G., Ed. *Transition Metal Clusters*; Wiley: New York, 1980; and references therein.

(3) (a) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (b) Muetterties, E. L. *Science (Washington, D.C.)* **1977**, *196*, 839. (c) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (d) Muetterties, E. L. *J. Organomet. Chem.* **1980**, *200*, 177. (e) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (f) Smith, A. K.; Basset, J. M. *J. Mol. Catal.* **1977**, *2*, 229. (g) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41. (h) Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67. (i) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *32*, 127.

(4) (a) Richmond, M. G.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 656, 1334. (b) Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, *6*, 254.

(5) (a) Pittman, C. U.; Wilemon, G. M.; Wilson, W. D.; Ryan, R. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 478. (b) Ryan, R. C.; Pittman, C. U.; O'Connor, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1980. (c) Pittman, C. U.; Richmond, M. G.; Wilemon, G. M.; Absi-Halabi, M. In *Catalysis of Organic Reactions*; Kosak, J. R., Ed.; Dekker: New York, 1984; Chapter 5. (d) Wang, Y. P.; Zhang, S. M.; Wu, N.; Luo, Y. Z.; Fu, H. X. *J. Organomet. Chem.* **1986**, *307*, 65.

0020-1669/88/1327-4698$01.50/0

coupled with the recent observation of restricted phenyl rotation and atropisomerism in the related cluster $Co_4(CO)_7[P(OMe)_3]_3(PPh)_2$,[6] prompts this NMR study concerning the reorientational dynamics of the aryl group in I. To our knowledge this is the first such relaxation study on a cluster compound possessing capping μ_4-PPh groups.

The measurement of NMR spin–lattice (T_1) relaxation times has proven to be a sensitive probe of the reorientation of molecules in solution and the effects of intermolecular association on the rotational dynamics.[7] Reorientation of the bicapped tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ (I) in solution is of interest for several reasons. The shape of this cluster approximates that of a quasi-symmetric top, since the lengths of two of the three axes are close to equal. This compound, though, is significantly larger than most other symmetric top molecules heretofore studied by NMR relaxation.[7b] Further, the phosphinidenes' phenyl groups potentially may rotate about their C_2 axes (the C–P bond) relative to the molecular frame.

In order to determine (a) whether there is internal rotation of the phenyl rings and (b) the capability of current theories to predict the reorientational parameters of a molecule of this size, we have studied the ^{13}C relaxation times of the aromatic carbons in $Co_4(CO)_{10}(PPh)_2$ as a function of temperature in solution. The results of this investigation should lay the groundwork for future studies of relaxation times and rotational dynamics in reacting mixtures and other polynuclear metal clusters.

Experimental Section

General Data. The tetracobalt cluster $Co_4(CO)_{10}(PPh)_2$ was prepared from sodium tetracarbonylcobaltate and dichlorophenylphosphine.[4] $CDCl_3$ was distilled from P_2O_5 and stored under argon by using Schlenk techniques.[8] Samples for NMR analysis were prepared in 10-mm NMR tubes that contained 0.29 g (4.0 mmol) of $Co_4(CO)_{10}(PPh)_2$ dissolved in 4 mL of $CDCl_3$ (ca. 0.1 M). All NMR samples were degassed by at least three freeze–pump–thaw cycles prior to flame sealing the NMR tube. The NMR spectra were acquired at $B_0 = 7.05$ T (75.5 MHz for ^{13}C) on a Nicolet NT-300 wide-bore spectrometer at the University of Houston (relaxation times) and a Varian VXR-300 spectrometer at the University of North Texas (Overhauser enhancements). Chemical shifts, referenced to $CDCl_3$ (77.0 ppm), are reported in ppm downfield from Me_4Si. The temperatures were measured with a digital thermometer equipped with a copper–constantan thermocouple and are believed accurate to ±2 °C.

Spin–lattice relaxation times were measured by using the inversion recovery pulse sequence $(180°\text{–}\tau\text{–}90°\text{–}A_t)_n$[9] with a delay of at least $5T_1$ between repetitions. Eleven τ values (including $\tau > 5T_1$) were used for each measurement. T_1's were calculated by nonlinear regression using the three-parameter magnetization equation.[10]

Nuclear Overhauser enhancements, η, were obtained by using standard techniques.[9] Enhanced intensities (I_E) were measured as the area under the peaks by using continuous broad-band ^{1}H decoupling. Nonenhanced intensities (I_N) were obtained with gated decoupling (decoupler on only during FID acquistion). Overhauser enhancements were calculated as $\eta = (I_E/I_N) - 1$. The maximum theoretical enhancement is $\eta_{max} = 1.988$, which obtains if ^{13}C relaxation results exclusively from dipolar coupling to ^{1}H.[11]

Results and Discussion

Spectral Assignments and ^{31}P–^{13}C Coupling. Shown in Figure 1 is the ^{1}H-decoupled ^{13}C NMR spectrum of the phenyl carbons in $Co_4(CO)_{10}(PPh)_2$. One observes that the spectrum is composed of three 1:2:1 triplets (at 129.3, 131.5, and 132.4 ppm) and a singlet (at 132.0 ppm). Measured Overhauser enhancements at various temperatures were found to be complete ($\eta = \eta_{max} = 2.0$) for all resonances except the triplet at 131.5 ppm ($\eta = 0.6$). Integrated intensities (nonenhanced) of the peaks at 131.5 and 132.0 ppm were half those of the other resonances.

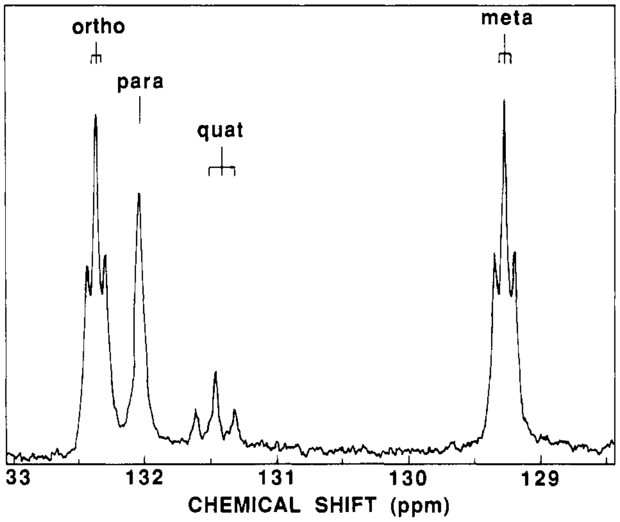


Figure 1. Phenyl region ^{13}C NMR spectrum of $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$.

On the basis of relative intensities and Overhauser enhancements, the triplet at 131.5 ppm is assigned, straightforwardly, to the quaternary carbon, and the singlet at 132.0 ppm to the para carbon.

In the ^{13}C spectra of substituted benzenes with either P^{III} or P^{V} substituents, it has been reported that the ortho resonance invariably is found downfield from the meta peak.[12] On this basis, we assign the triplets at 129.3 and 132.4 ppm to the meta and ortho carbons, respectively.

In the absence of interaction between the phosphinidene groups, one expects the NMR spectrum to consist of simple doublets, with a splitting equal to $J(^{31}P\text{–}^{13}C)$. Therefore, the observed triplets provide clear confirmatory evidence of significant P···P attractions, as has been suggested on the basis of the X-ray structure[13] and MO calculations.[14] Jaeger, Aime, and Vahrenkamp,[15] in a recent investigation of related iron clusters $Fe_4(CO)_{11}(PR)_2$, also report triplets for three of the aromatic carbons and note that this indicates considerable $^{31}P\cdots^{31}P$ coupling.

Indeed, a 1:2:1 triplet is precisely the pattern expected for the X (^{13}C) portion of an AA′X spectrum (in this case, $^{31}P'\cdots^{31}P\text{–}^{13}C$).[16-18] One further expects that the AA′ (i.e. ^{31}P) spectrum will be either an eight-line multiplet, or a doublet, depending on the magnitude of $J_{AA'}$ relative to $J_{AX} - J_{A'X}$.[16] Thus, in principle, analysis of the carbon-13 satellites in the ^{31}P NMR spectrum could permit determination of $J_{PP'}$ or, at the very least, an estimate of its magnitude. Unfortunately, the ^{31}P NMR resonances are severely broadened by scalar coupling to ^{59}Co, precluding the measurement on this cluster.

It is still possible to obtain estimates of ^{31}P–^{13}C coupling constants if one assumes that $^nJ_{PC} \gg {}^{n+1}J_{P'C}$, due to the additional "bond" between P′ and C. In this case, the expected splitting in the ^{13}C spectrum, $(1/2)(^nJ_{PC} + {}^{n+1}J_{P'C})$,[16] reduces to $(1/2)^nJ_{PC}$. From measured splittings in the spectra, we obtain the following: quaternary carbon, $^1J_{PC} = 22.1$ Hz; ortho carbon, $^2J_{PC} = 10.5$

---

(6) Richmond, M. G.; Kochi, J. K. *Inorg. Chim. Acta* **1987**, *126*, 83.

(7) Three reviews on NMR relaxation and reorientational dynamics are: (a) Wright, D. A.; Axelson, D. E.; Levy, G. C. In *Topics in Carbon-13 NMR*; Levy, G. C., Ed.; Wiley: New York, 1979; Vol. 3, p 103. (b) Boere, R. T.; Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1982**, *13*, 319. (c) Versmold, H. *NATO ASI Ser., Ser. C* **1984**, *No. 135*, 309.

(8) Shiver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

(9) Martin, M. L.; Delpuech, J. J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: London, 1980; Chapter 7.

(10) Craik, D. J.; Levy, G. C. In *Topics in Carbon-13 NMR*; Levy, G. C., Ed.; Wiley: New York, 1984; Vol. 4, p 239.

(11) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect: Chemical Applications*; Academic: New York, 1971.

(12) Modro, T. A. *Can. J. Chem.* **1977**, *55*, 3681.

(13) (a) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904. (b) Ryan, R. C. Ph.D. Dissertation, University of Wisconsin, Madison, WI, 1976.

(14) Halet, J. F.; Hoffmann, R.; Saillard, J. Y. *Inorg. Chem.* **1985**, *24*, 1695.

(15) Jaeger, T.; Aime, S.; Vahrenkamp, H. *Organometallics* **1986**, *5*, 245.

(16) Abraham, R. J.; Bernstein, H. J. *Can. J. Chem.* **1961**, *39*, 216.

(17) Schaefer, T. *Can. J. Chem.* **1962**, *40*, 1678.

(18) The AA′X spectrum is the limiting form of an ABX spectrum when $\delta_{AB} = 0$, which will occur if A and B are chemically equivalent (as are the two P's by symmetry) but magnetically nonequivalent (i.e. if $J_{AX} \neq J_{BX}$).

Table I. Temperature Dependence of Relaxation Times and Rotational Diffusion Constants

T, K	T_{1P}, s	T_{1M}, s	T_{1O}, s	χ,[a] s	σ	$D_\perp$,[b,c] ns^{-1}	D_s,[b,c] ns^{-1}
333	0.99	1.41	1.30	1.37	2.13	3.7 (4.1)	8.0 (8.1)
328	1.04	1.39	1.39	1.34	2.02	3.9 (3.9)	8.0 (7.6)
323	0.96	1.26	1.20	1.28	1.83	3.6 (3.6)	6.6 (7.1)
318	1.00	1.19	1.17	1.18	1.51	3.8 (3.4)	5.7 (6.6)
308	0.84	1.09	1.12	1.32	1.96	3.2 (3.0)	6.2 (5.7)
289	0.65	0.85	0.86	1.32	1.96	2.5 (2.3)	4.8 (4.2)
280	0.57	0.70	0.70	1.23	1.67	1.7 (2.0)	3.6 (3.6)
248	0.31	0.36	0.37	1.18	1.51	1.2 (1.1)	1.8 (1.9)

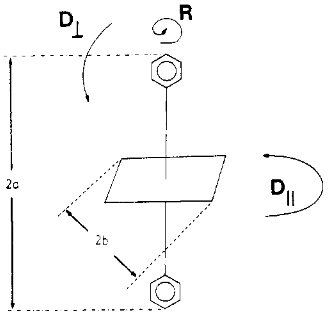
[a] χ was calculated by using the average of T_{1M} and T_{1O}. [b] Values of $D_\perp$ and D_s have been rounded to two digits. However, calculations were performed prior to rounding. [c] Numbers in parentheses are values interpolated from a least-squares fit to the Arrhenius equation.

Hz; meta carbon, $^3J_{PC}$ = 11.4 Hz. It would be of interest to compare these results with those from the iron clusters, but the splittings were not reported.[15] We do, however, find very good agreement with the reported ortho and meta carbon P–C coupling constants in several benzenes with P^V substituents ($-P(O)R_2$ and $-P(S)R_2$),[12] even though the phosphorus hybridization is quite different in these compounds. Unlike P^{III}-substituted benzenes, where $^2J \geq 3^3J$, the pentavalent compounds all show ortho and meta carbon coupling constants of magnitude comparable (8–18 Hz) to ours, with the meta carbon coupling constant being slightly greater (e.g. in $Ph-P(S)Me_2$, ^2J = 10.6 Hz and ^3J = 11.8 Hz),[12] as found here. The para carbon coupling constants vary from 2 to 4 Hz,[12] whereas we observe no splitting. A small coupling, however, would be obscured by the breadth of the para carbon resonance ($\Delta\nu_{1/2}$ = 5.7 Hz (fwhm)).

In contrast to earlier results on P^V-substituted benzenes, where ^1J = 80–190 Hz,[12] our value of 22.1 Hz lies closer to the quaternary carbon P–C coupling constants reported in the trivalent $Ph-PR_2$ compounds.[12]

It will be informative to compare the coupling constants found here with future results for other (μ_4-PPh_2)-bicapped clusters and with coupling constants for tetravalent (μ_3-$PPh)_2$ clusters.

Molecular Structure and Phenyl Group Rotation. $Co_4(CO)_{10}(PPh)_2$ is of D_{2h} symmetry and is, thus, an asymmetric top molecule; i.e., all three axis lengths and moments of inertia are different. However, from the crystal structure,[13b] the two axis lengths (from the molecular center) in the Co_4 plane (b and c) are nearly equal and shorter than the distance from the center to the top of each phenyl (a).



Therefore, the molecule can be well approximated as a prolate[19] symmetric top with axis lengths a = 8.1 Å and $b \approx c$ = 4.7 Å and axial ratio $\rho = b/a = 0.58$.

As a quasi-symmetric top, the cluster's overall reorientational dynamics can be characterized by two rotational diffusion constants, $D_\parallel$ and $D_\perp$, which represent rotation parallel and perpendicular to the unique axis, a, as shown in the diagram. This, however, is not a rigid molecule since, in solution, each phenyl ring may potentially rotate about its C_2 axis (the C–P bond). This motion can be characterized by a third, *internal rotation*, diffusion constant, R (see diagram).

The internal rotation axis coincides with the principal axis, a. Hence, it is intuitively reasonable, and has been proven rigorously,[20] that the *total* "spinning" rate of the phenyl group about its axis, which we denote as D_s, is represented by the sum of the overall ($D_\parallel$) and internal rotation (R) diffusion constants; i.e., $D_s = D_\parallel + R$. The phenyl's rate of "tumbling", though, is equal to that of the molecular skeleton ($D_\perp$).

Analysis of Spin–Lattice Relaxation Times. The overall and internal rotation of molecules containing phenyl groups has been studied extensively by using NMR relaxation times.[21] The C–H bonds of the para, meta, and ortho carbons lie at 0, 60, and 120°, respectively, relative to the principal axis (a). Therefore, measurement of the $^{13}C-^1H$ dipole–dipole relaxation times permits a direct determination of both $D_\parallel$ and D_s.

For relaxation by dipolar interactions between two nuclei (in this case, ^{13}C relaxation by the attached proton), the standard equation for the relaxation rate (T_1^{-1}) is[22]

$$T_1^{-1} = \frac{[\gamma(^{13}C)]^2[\gamma(^1H)]^2\hbar^2}{r_{CH}^6}\tau_c(\theta) \qquad (1)$$

In this equation, $\hbar = h/2\pi$, where h is Planck's constant and $\gamma(^{13}C)$ and $\gamma(^1H)$ are the nuclear magnetogyric ratios. $\tau_c(\theta)$ is the rotational correlation time of the vector connecting the two nuclei, and it represents the time for the vector to rotate by 1 radian. θ is the vector's angle relative to the principal axis.

Woessner[20] has derived the following expression for $\tau_c(\theta)$ for symmetric top molecules with internal rotation parallel to the top axis:

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

$A = (3\cos^2\theta - 1)/4$, $B = 3\sin^2\theta\cos^2\theta$, and $C = (3\sin^4\theta)/4$; as noted above, $D_s = D_\parallel + R$.[23] For the para carbon ($\theta = 0°$), $A = 1$, $B = C = 0$, and eq 2 reduces to $\tau_c(\theta) = 1/(6D_\perp)$. Hence, eq 1 may be rewritten as

$$T_{1P}^{-1} = \frac{[\gamma(^{13}C)]^2[\gamma(^1H)]^2\hbar^2}{r_{CH}^6}\frac{1}{6D_\perp} = \frac{3.781 \times 10^9}{D_\perp} \qquad (3)$$

We have used standard values for $\gamma(^{13}C)$, $\gamma(^1H)$, and $\hbar$ and have used $r_{CH} = 1.08 \times 10^{-8}$ cm to obtain the numerical relation.

One sees that relaxation of the para carbon depends only on the tumbling motion ($D_\perp$) of the molecule and is independent of

---

(19) In a prolate spheroid ($a > b = c$), the unique axis (a) is longer than the other two ($b = c$), and $\rho = b/a < 1$. Conversely, for an oblate spheroid, $a < b = c$, and $\rho > 1$.

(20) Woessner, D. E. *J. Chem. Phys.* **1962**, *37*, 647.

(21) (a) Levy, G. C.; White, D. M.; Anet, F. A. *J. Magn. Reson.* **1972**, *6*, 453. (b) Levy, G. C.; Cargioli, J. D.; Anet, F. A. L. *J. Am. Chem. Soc.* **1973**, *95*, 1527. (c) Imanari, M.; Ohuchi, M.; Ishizu, K. *J. Magn. Reson.* **1974**, *14*, 374. (d) Wilson, N. K. *J. Am. Chem. Soc.* **1975**, *97*, 3573. (e) Harris, R. K.; Kimber, B. J. *Adv. Mol. Relax. Processes* **1975**, *8*, 23. (f) Levy, G. C.; Holak, T.; Steigel, A. *J. Am. Chem. Soc.* **1976**, *98*, 495. (g) Oehme, K. L.; Rudakoff, G.; Radeglia, R. *Adv. Mol. Relax. Processes* **1976**, *8*, 1. (h) Heatley, F.; Cox, M. K.; Jones, A.; Jacques, B. *J. Chem. Soc., Perkin Trans.* **1976**, *2*, 510. (i) Oehme, K. L.; Rudakoff, G.; Radeglia, R. *Adv. Mol. Relax. Interact. Processes* **1978**, *12*, 87. (j) Wasylishen, R. E.; Pettitt, B. A. *Can. J. Chem.* **1979**, *57*, 1274. (k) Dais, P. *Magn. Reson. Chem.* **1987**, *25*, 141.

(22) Becker, E. D. *High Resolution NMR: Theory and Applications*, 2nd ed.; Academic: New York, 1980; Chapter 8.

(23) The notation used here has become conventional in recent years. It corresponds to Woessner's original notation[20] as follows: $D_\perp = R_2$; $D_\parallel = R_1$; $R = R_1'$.

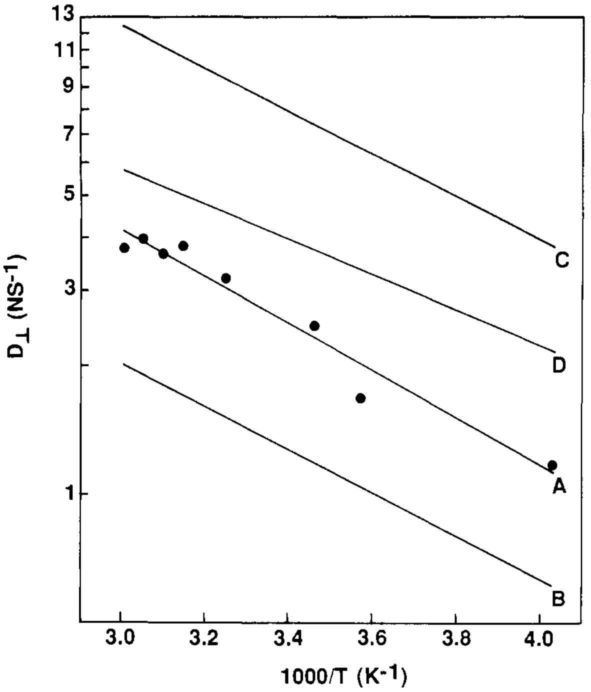


Figure 2. Temperature dependence of experimental and calculated tumbling diffusion constants: (A) experiment; (B) stick model; (C) slip model; (D) HKW model.

phenyl group spinning (D_s). This, of course, is to be expected since rotation of the ring about its C_2 axis does not alter the orientation of the para carbon C–H bond.

Relaxation of the meta ($\theta = 60°$) and ortho ($\theta = 120°$) carbons depends upon both $D_\perp$ and D_s. For either angle, $A = {}^1/_{64}$, $B = {}^9/_{16}$, and $C = {}^{27}/_{64}$. One may use eq 1 and 2 to show that the ratio of T_{1O} (or T_{1M}) to T_{1P} is given by

$$\chi = \frac{T_{1O}}{T_{1P}} = \frac{T_{1M}}{T_{1P}} = \frac{64}{1 + \dfrac{216}{5+\sigma} + \dfrac{162}{2+4\sigma}} \tag{4}$$

where $\sigma = D_s/D_\perp = (D_\parallel + R)/D_\perp$.

It is a straightforward procedure to use T_{1P} in eq 3 to determine the molecular tumbling rate, $D_\perp$. Then, the relaxation time ratio, χ, may be used in eq 4 to calculate σ and, hence, the phenyl spinning rate, D_s.[24]

Reorientational Dynamics in $Co_4(CO)_{10}(PPh)_2$. Presented in Table I are the ^{13}C relaxation times of the para, ortho, and meta carbons of $Co_4(CO)_{10}(PPh)_2$ as a function of temperature. Since, as noted above, measured nuclear Overhauser enhancements are complete ($\eta = 2.0$) for these carbons, the sole contribution to their T_1's is ^{13}C–^1H dipole–dipole relaxation. Therefore, they may be used directly in eq 3 and 4 above.

It is satisfying to note that, in general, T_{1M} and T_{1O} are virtually equal, as they should be since the C–H vectors at 60 and 120° relative to the principal axis depend on the same combination of $D_\perp$ and D_s; i.e., the two angles have the same A, B, and C in eq 2 (vide supra). One observes also that T_{1O} and T_{1M} are invariably longer than T_{1P}, which establishes immediately that the phenyl spinning is faster than its tumbling rotation.

Shown in the last columns of Table I are the rotational diffusion constants, $D_\perp$ and D_s, derived from T_{1P} and χ, as discussed above. One observes that, at all temperatures, $D_s/D_\perp \approx 1.5$–2.2. Thus, the rate of phenyl group spinning is approximately twice as great as the molecular tumbling rate.

It is common in the literature to refer to rotational correlation times, τ_c, which are related simply to the diffusion constants by $(\tau_c)_\perp = (6D_\perp)^{-1}$ and $(\tau_c)_s = (6D_s)^{-1}$. As an example, our interpolated values at 25 °C are $D_\perp = 2.6\ ns^{-1}$ ($2.6 \times 10^9\ s^{-1}$) and $D_s = 4.9\ ns^{-1}$, which correspond to the correlation times $(\tau_c)_\perp$ = 64 ps (6.4×10^{-11} s) and $(\tau_c)_s$ = 34 ps. Therefore, an alternative, but equivalent, statement to the one above is that it takes half the time to spin by 1 radian as to tumble by the same amount.

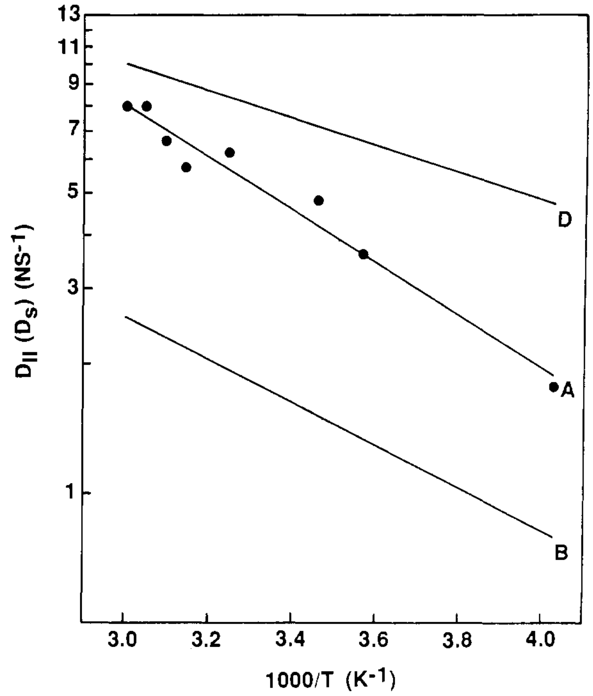


Figure 3. Temperature dependence of experimental and calculated spinning diffusion constants: (A) experiment; (B) stick model; (D) HKW model.

By way of brief comparison, the rotational correlation times in tetracobalt clusters are far longer than in small- to moderate-size molecules (e.g.: CH_2Cl_2, 0.6 ps;[25] CD_3I, 1.5 ps;[26] $Fe(CO)_5$, 5 ps;[27] $Mo(CO)_6$, 9 ps[28]). Not surprisingly, this cluster's correlation times are a bit longer, although of the same magnitude, than the value, τ_c = 23 ps, reported for two triosmium cluster compounds.[29]

We have fit the experimental results for both $D_\perp$ and D_s to the linearized Arrhenius equation: $\ln D = \ln A - E_a/RT$ (line A in Figures 2 and 3). The calculated activation energies, E_a, are 2.5 kcal/mol for $D_\perp$ and 2.8 kcal/mol for D_s. Since the standard deviation in E_a is 0.2 kcal/mol for each line, yielding error limits of ±0.4 kcal/mol (90% confidence limits), the temperature dependencies of the two diffusion constants are approximately the same, to within experimental error.

It would, of course, be very valuable to separate D_s into its two components, $D_\parallel$, which characterizes the spinning of the whole molecule, and R, which measures the rate of *internal* phenyl group rotation. This cannot be accomplished by using ring carbon relaxation times alone. The separation could be performed if we were able to obtain the ^{13}C relaxation times (due to chemical shift anisotropy) of the CO carbons. Since they lie on the rigid molecular frame, their T_1's depend upon $D_\perp$ and $D_\parallel$, rather than $D_\perp$ and D_s. Unfortunately, the carbonyl resonances in this tetracobalt cluster are quite severely broadened by ^{13}C–^{59}Co scalar coupling, precluding any quantitative measurements.

While a rigorous determination of $D_\parallel$ and R is not possible, one can, however, estimate their relative magnitudes through comparison with a theoretical model and experimental results on other systems.

---

[24] The quantity σ in eq 4 was obtained from experimental values of χ by iterative calculation using a simple program written in Applesoft (Extended Basic).

[25] Rodriguez, A. A.; Chen, S. J. H.; Schwartz, M. *J. Magn. Reson.* **1987**, *74*, 114.

[26] Gillen, K. T.; Schwartz, M.; Noggle, J. H. *Mol. Phys.* **1971**, *20*, 899.

[27] Spiess, W. H.; Mahnke, H. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 990.

[28] Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *J. Magn. Reson.* **1985**, *61*, 22.

[29] Aime, S.; Gobetto, R.; Osella, D.; Hawkes, G. E.; Randall, E. W. *J. Chem. Soc., Dalton Trans.* **1984**, 1863.

Table II. Experimental and Calculated Rotational Diffusion Constants in Representative Molecules

molecule	V_{molec},[a] Å^3	ρ	$(D_\perp)_{\mathrm{cal}}$,[b] ns^{-1}	$(D_\perp)_{\mathrm{exp}}$, ns^{-1}	$(D_\parallel)_{\mathrm{exp}}$, ns^{-1}	$(D_\parallel/D_\perp)_{\mathrm{exp}}$	$(D_\parallel/D_\perp)_{\mathrm{cal}}$[b]
CD_3I[c]	55	0.69	22	107	1800	16.8	1.17
$CDCl_3$[d]	72	1.35	16	96	180	1.9	0.94
$VOCl_3$[e]	86	1.25	12	49	70	1.4	0.95
CCl_3CN[f]	91	0.74	9	44	91	2.1	1.12
3-chlorobiphenyl[g]	227	0.53	1.7	6.8	12.5	1.8	1.37
3-aminobiphenyl[h]	244	0.55	2.9	5.1	12.2	2.4	1.34
$Co_4(CO)_{10}(PPh)_2$[i]	750	0.58	1.3	2.6	4.9	1.9	1.29

[a] Molecular volume. [b] Calculated by using the Perrin "stick" model (ref 30). [c] Reference 26; neat liquid at 295 K. [d] Reference 31; neat liquid at 293 K. [e] Reference 31; neat liquid at 303 K. [f] Reference 31; neat liquid at 298 K. [g] Reference 21d; 0.6 M in C_2Cl_4 at 311 K. $(D_\perp)_{\mathrm{exp}}$ and $(D_\parallel)_{\mathrm{exp}}$ calculated from $T_{1\mathrm{P}}$ and $T_{1\mathrm{O,M}}$ on aminated phenyl. [h] Reference 21f; 2 M in C_2Cl_4 at 311 K. $(D_\perp)_{\mathrm{exp}}$ and $(D_\parallel)_{\mathrm{exp}}$ calculated from $T_{1\mathrm{P}}$ and $T_{1\mathrm{O,M}}$ on aminated phenyl. [i] This work; 0.1 M in $CDCl_3$. Interpolated values at 298 K.

Table III. Comparison of Theoretical and Experimental Diffusion Constants

	experiment[a]		stick		slip		HKW	
T, K	$D_\perp$, ns^{-1}	$D_\parallel$, ns^{-1}	$(D_\perp)_{\mathrm{cal}}/(D_\perp)_{\mathrm{exp}}$	$(D_\parallel)_{\mathrm{cal}}/(D_\parallel)_{\mathrm{exp}}$	$(D_\perp)_{\mathrm{cal}}/(D_\perp)_{\mathrm{exp}}$	$(D_\parallel)_{\mathrm{cal}}/(D_\parallel)_{\mathrm{exp}}$	$(D_\perp)_{\mathrm{cal}}/(D_\perp)_{\mathrm{exp}}$	$(D_\parallel)_{\mathrm{cal}}/(D_\parallel)_{\mathrm{exp}}$
333	4.1	8.1	0.5	0.3	3.0	7.1	1.4	1.2
298	2.6	4.9	0.5	0.3	3.1	11.1	1.5	1.5
248	1.1	1.9	0.5	0.4	3.4	26.4	1.9	2.5

[a] Values are interpolated from a least-squares fit to the Arrhenius equation.

The classic early theory of anisotropic reorientation by Perrin[30] (to be discussed in the next section) permits a prediction of the ratio $D_\parallel/D_\perp$ as a function of the axial ratio $\rho = b/a$. For this molecule, with $\rho = 0.58$, the model provides the estimate that $D_\parallel/D_\perp = 1.3$. Using this ratio with the interpolated room-temperature diffusion constants $D_\perp = 2.6$ ns^{-1} and $D_s = 4.9$ ns^{-1} yields the value $R = 1.5$ ns^{-1}. This internal diffusion constant is extremely low, indicating greatly restricted internal rotation of the phenyl rings. By comparison, in molecules with relatively unhindered phenyl group rotation (e.g. Ph_2CH_2,[21k] Ph_2SiH_2,[21e] Ph_2S,[21k] Ph_2Se[21k]), one finds that R = 40–60 ns^{-1}.

However, even as low a value as 1.5 ns^{-1} quite likely overestimates the actual rate of internal rotation. This is seen by comparison with the observed and calculated ratios, $D_\parallel/D_\perp$, in other systems where $D_\perp$ and $D_\parallel$ have been measured experimentally.[6,21,26,31] Shown in Table II are the experimental and calculated diffusion constants in a number of representative molecules. From the last two columns of the table, one sees that, independent of molecular size (V_{molec}) or shape (ρ), the experimental ratio $(D_\parallel/D_\perp)_{\mathrm{exp}}$ is always significantly greater than that calculated from the theoretical model.[30] Of particular interest are the substituted biphenyls, which are moderately large molecules with axial ratios close to that of our cluster. These molecules also exhibit internal rotation (of the unsubstituted phenyl group relative to the ring with the substituent). In these systems, one can determine $D_\perp$ from $T_{1\mathrm{P}}$ (eq 3). Use of eq 4 with $T_{1\mathrm{O}}/T_{1\mathrm{P}}$ or $T_{1\mathrm{M}}/T_{1\mathrm{P}}$ of the substituted ring then gives $D_\parallel$, whereas relaxation times of the unsubstituted phenyl yield D_s. Therefore, $D_\parallel$ and R can be determined independently.

In the biphenyls, $(D_\parallel/D_\perp)_{\mathrm{exp}}$ is equal to or greater than our ratio, $(D_s/D_\perp)_{\mathrm{exp}} = 1.9$, and well above $(D_\parallel/D_\perp)_{\mathrm{cal}}$. Oehme et al.[21g] report similar results in five other substituted biphenyls ($(D_\parallel/D_\perp)_{\mathrm{exp}}$ = 2.5–3.5, whereas $(D_\parallel/D_\perp)_{\mathrm{cal}}$ = 1.3–1.4). From this comparison, we must conclude that it is quite likely in our system that $D_s \approx D_\parallel$ and $R \approx 0$; i.e. the phenyl groups are actually immobile on a molecular rotation time scale (20–100 ns).

The reason for the lack of mobility of the phenyl ring is explained only partially by the structural parameters of the complex. In the crystal, the planes of the phenyls approximately bisect the Co–Co bonds containing the bridging carbonyls.[13b] In the process of rotation about the C–P bond in solution, the ortho protons pass within 1.9 Å of the terminal carbonyls' oxygen nuclei. This is somewhat less than the sum of the hydrogen and oxygen van der Waals radii[32] ($r_H + r_O$ = 2.7 Å). This certainly accounts for the lack of completely free internal phenyl rotation, but does not explain the apparently complete rigidity of the ring. For example, in meta-substituted biphenyls, the ortho protons approach within 1.7 Å during rotation. This is approximately the same amount below the sum of their van der Waals radii ($2r_H$ = 2.4 Å) as in our system. Yet from the T_1 data, one calculates, as outlined above, that R = 7 ns^{-1} in 3-chlorobiphenyl[21d] and R = 10 ns^{-1} in 3-aminobiphenyl.[21f] Even in 2-chlorobiphenyl,[21d] where the closest approach distance (1.5 Å) is 1.45 Å less than the sum of the van der Waals radii ($r_H + r_{Cl}$ = 2.95 Å), one finds that R = 4 ns^{-1} in the solvent dibromoethane and R = 6 ns^{-1} in $CDCl_3$.

One sees from the above comparison that steric factors alone cannot explain the apparently complete immobility of the phenyl rings in the cluster. At this point, one can only speculate on additional factors that may be inhibiting the ring rotation. One possibility could be solvation of the phenyls by the $CDCl_3$ solvent. There is spectroscopic evidence that the acidic proton in chloroform forms a weak hydrogen bond with the π system in benzene.[33] An alternative explanation might be interaction of the benzene π electrons with the d orbitals on phosphorus. T_1 measurements in other solvents and MO calculations would help to determine whether either of these factors can account for the lack of internal phenyl group rotation in $Co_4(CO)_{10}(PPh)_2$.

Theoretical Models of Rotational Diffusion. In addition to measurement of the experimental diffusion constants, $D_\perp$ and $D_\parallel$, in a given molecule, it is valuable to compare these results with those calculated by various theories. Thus, one may assess the utility of the theoretical models to furnish a priori predictions of the reorientational behavior in other, similar systems. This tetranuclear cluster is of particular interest since it is considerably larger than the symmetric top molecules studied in the great majority of previous NMR investigations.[6] In this section, we shall assume as discussed above, that $D_\parallel \approx D_s$.

The earliest theory of anisotropic rotational diffusion was developed by Perrin,[30] as an extension of the classic Stokes–Einstein–Debye[34] (SED) "stick" theory of reorientation of spheres in a viscous, continuous medium. As the word implies, the model assumes that the solvent sticks (or clings) to the surface of the molecule, which creates a viscous drag retarding its rotation. The Perrin modification of the SED relation is given by

$$D_i = \frac{1}{f_i} D_{\mathrm{SED}} = \frac{1}{f_i} \frac{kT}{8\pi\eta r^3} \qquad (5)$$

η and T are the viscosity and temperature, and k is Boltzmann's constant. r is the average molecular radius of the solute, which

---

(30) Perrin, F. *J. Phys. Radium* **1934**, [7] *5*, 497.
(31) Gillen, K. T.; Noggle, J. H. *J. Chem. Phys.* **1970**, *53*, 801.
(32) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 41.
(33) Tanabe, K.; Hiraishi *J. Mol. Phys.* **1980**, *39*, 493 and references contained therein.
(34) Debye, P. *Polar Molecules*; Dover: New York, 1929.

is the geometric mean of the axis lengths; $r = (ab^2)^{1/3} = 5.63$ Å. f_i and D_i represent either $f_\perp$ and $D_\perp$ or $f_\parallel$ and $D_\parallel$. Perrin has developed analytical expressions for $f_\perp$ and $f_\parallel$ of both prolate and oblate spheroids as a function of the axial ratio, ρ. Using eq 96 of his paper,[30] with $\rho = 0.58$, one obtains $f_\perp = 1.322$ and $f_\parallel = 1.025$, which are used in eq 5 to calculate $D_\perp$ and $D_\parallel$ as a function of temperature.[35]

From line B in Figures 2 and 3 and from Table III, we see that $D_\perp$ calculated from the Perrin stick model is about a factor of 2 smaller than $(D_\perp)_{\mathrm{exp}}$, with a factor of 3 separating theory and experiment for $D_\parallel$.

Actually, the diffusion constants calculated by using the stick model are considerably closer to experimental values for the cluster than is usually found in studies of small molecules.[7] From Table II, one sees that $(D_\perp)_{\mathrm{cal}}$ is typically a factor of 4–6 times too small in most systems. Although not shown directly in the table, the discrepancy is even greater for $D_\parallel$, where the calculated diffusion constant is 5–10 times (or more) smaller than the experimental value. It is not surprising that the Perrin stick model is somewhat more successful in the Co_4 cluster, since the presumption that the solute radius is much greater than that of the solvent (inherent in assuming a continuous solvent medium) is more valid in this system.

As a consequence of the invariably low estimates of $D_\perp$ and $D_\parallel$ furnished by the stick model, Hu and Zwanzig[36] more recently developed an opposing "slip" model of rotational diffusion, in which they assume that the surrounding solvent does not stick at all to the rotating molecule. Thus, for spherical molecules, there is no retarding friction and the molecule rotates freely (as in the gas phase) at a rate controlled by its moment of inertia. Similarly, for symmetric top molecules, rotation about the symmetry axis ($D_\parallel$) is that of an inertially controlled free rotor. The tumbling motion ($D_\perp$), on the other hand, does require displacement of solvent molecules and is, therefore, slowed by the medium's viscosity, although to a much lesser degree than in the stick limit. This newer theory has provided much improved predictions of diffusion constants in liquids containing small- to moderate-sized molecules.[7b,37]

The expression for $D_\perp$ using the slip model is the same as eq 5 above, although the $f_i = f_\perp$ is different. For a prolate top with $\rho = 0.58$, one obtains[36,38] $f_\perp = 0.213$. We have calculated $D_\perp$ as a function of temperature using the slip theory, as displayed in Figure 2 (line C) and Table III. We have also used the equation for the rotational correlation time of a free rotor, $(\tau_c)_\parallel = (2\pi/9)(I_\parallel/kT)^{1/2}$ [39] and $D_\parallel = [6(\tau_c)_\parallel]^{-1}$ to calculate the parallel diffusion constant. This result, too, is presented in Table III (it has not been drawn in Figure 3 due to its large magnitude).

One observes that the slip model overestimates the rotational diffusion constants by an even greater amount than that by which the older stick model underestimates the experimental values. Hence, in contrast to most quantitative comparisons on other, smaller molecules, which lie closer to the slip limit,[66,37] the reorientational dynamics in this relatively large cluster compound is not well described by either of the limiting stick or slip theories of rotational diffusion, but lies at a point between the two extremes.

Finally, we wish to compare our experimental results with rotational diffusion constants calculated by the newest model, developed by Hynes, Kapral, and Weinberg (HKW).[40] Noting the failure of either of the two limiting models to provide a general description for the reorientational behavior of molecules in liquids, their theory allows for the fact that rotation, in general, lies somewhere between the stick and slip limits. Although originally formulated for spherical molecules, the HKW model has been extended, in an intuitive fashion, by Tanabe to symmetric top molecules.[41] For brevity, we present only the results and omit extended discussion of the model and the equations used to calculate $D_\perp$ and $D_\parallel$, which may be found in other references.[38,40,41]

As seen both from line D in Figures 2 and 3 and from Table III, the diffusion constants, $D_\perp$ and $D_\parallel$, calculated by the HKW model generally lie closer to the experimental results than do values obtained from either the purely stick or slip models. Although not presented in the table, the newest theory is also superior in that it predicts a range, $(D_\parallel/D_\perp)_{\mathrm{cal}} = 1.7$–$2.3$, that is in far better agreement with the experimental ratio, $(D_\parallel/D_\perp)_{\mathrm{exp}} \approx 2$, than are calculated ratios from either of the earlier models (stick, $(D_\parallel/D_\perp)_{\mathrm{cal}} = 1.3$; slip, $(D_\parallel/D_\perp)_{\mathrm{cal}} = 5$–$13$).

Conclusions

The quaternary, ortho, and meta phenyl carbons of the ^{1}H-decoupled ^{13}C spectra of $Co_4(CO)_{10}(PPh)_2$ exhibit 1:2:1 triplet structure, indicating they are split by both ^{31}P nuclei. This provides additional evidence for earlier suggestions[13-15] that there are significant magnetic interactions between phosphorus atoms in $Co_4(CO)_{10}(PPh)_2$ and other phosphinidene-bicapped clusters. Since the internuclear phosphinidene distance in $Co_4(CO)_{10}(PPh)_2$ exceeds that commonly accepted for a P–P σ bond,[13] P···P interaction most likely arises from a through-space coupling or a P–Co–P through-bond coupling phenomenon.

Analysis of the ^{13}C spin–lattice relaxation times reveals that the spinning motion of the phenyl groups (D_s) is approximately twice as rapid as tumbling of the molecule ($D_\perp$). Comparison with experimental results on other systems strongly suggests that this anisotropy is in the overall rotational rates of the molecular framework and not due to internal ring rotation. Rather, the phenyl groups appear to be immobile on a molecular rotation time scale.

Comparison with the various theories reveals that, unlike that of smaller molecules, the reorientational dynamics of this tetranuclear cluster is not well characterized by the limiting "slip" model of rotational diffusion but actually lies between the "slip" and "stick" limits. The newest Hynes–Kapral–Weinberg (HKW) theory provides the best agreement with the experimental diffusion constants.

Further experiments involving the molecular dynamics of related bridging ligands in other polynuclear systems are planned.

Acknowledgment. We thank the National Science Foundation (J.K.K.), the Robert A. Welch Foundation (J.K.K., G.E.M., M.G.R., and M.S.), and the University of North Texas Faculty Research Fund (M.G.R. and M.S.) for financial support.

Registry No. I, 58092-22-1.

---

[35] The calculated ratios, $(D_\parallel/D_\perp)_{\mathrm{cal}}$, in Table II are obtained simply from the Perrin model since, from eq 5, $(D_\parallel/D_\perp)_{\mathrm{cal}} = f_\perp/f_\parallel$.

[36] Hu, C.-M.; Zwanzig, R. *J. Chem. Phys.* **1974**, *60*, 4354.

[37] (a) Bauer, D. R.; Brauman, J. I.; Pecora, R. *J. Am. Chem. Soc.* **1974**, *96*, 6840. (b) Bauer, D. R.; Alms, G. R.; Brauman, J. I.; Pecora, R. *J. Chem. Phys.* **1974**, *61*, 2255. (c) Fury, M.; Jonas, J. *J. Chem. Phys.* **1976**, *65*, 2206. (d) Vold, R. R.; Sparks, S. W.; Vold, R. L. *J. Magn. Reson.* **1978**, *30*, 497.

[38] Rodriguez, A. A.; Chen, A. F. T.; Schwartz, M. *J. Mol. Liq.* **1988**, *37*, 117.

[39] Bartoli, F. J.; Litovitz, T. A. *J. Chem. Phys.* **1972**, *56*, 413.

[40] Hynes, J. T.; Kapral, R.; Weinberg, M. *J. Chem. Phys.* **1978**, *69*, 2725.

[41] (a) Tanabe, K. *Chem. Phys.* **1978**, *31*, 319. (b) *Chem. Phys.* **1979**, *38*, 125.